Trace element pollution of soils by abandoned gold mine tailings near Potchefstroom, South Africa

by

PAUL-JOHAN AUCAMP

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Co-Supervisor: Prof MC Laker
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ABSTRACT

The extent to which trace elements from reworked tailings have polluted the underlying soils at the abandoned Machavie Gold Mine was investigated. Material from five tailings dams has been reworked by wind and water erosion and deposited over an area of ± 1,1 km^2 downslope from the tailings impoundments. The tailings deposit varies in thickness between 0,01 m to 1,50 m. The influence of this tailings cover on the underlying soils was investigated by means of a series of test pits from which disturbed samples were retrieved. The investigated soils consist of residual dolomitic soils overlain by colluvial and alluvial soils. The tailings is a source of contamination as it produces trace element-rich acidic leachate from the decomposition of sulphide minerals in the tailings. The average pH of the tailings is very acidic at 3,43. Soluble sulphate salts that have precipitated on the reworked tailings, show high water-soluble concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn. All the soils directly underlying the reworked tailings are affected by the acidic, trace element rich-leachate produced in the tailings. The trace element content of the tailings and soils was compared with the guideline concentrations which indicate that the soils and tailings should be further investigated for As, Co, Cr, Cu and Ni contamination. To assess the degree of contamination in the soils, extractable concentrations of As, Co, Cr, Cu, Ni, Pb and Zn were determined by using NH_4NO_3, which is recommended by various authors as an environmental leaching agent. An ammonium nitrate extractable Zn-equivalent was introduced and used to show that the upper clayey alluvial soils pose a greater threat to plant life than the sandy colluvial soils. The mobility of the trace elements was investigated by determining the percentage of the total element concentration which is extractable with NH_4NO_3. Trace element mobilities increase with lower soil pH values once a pH of 5 is reached.

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SAMEVATTING

Die ondersoek handel oor die mate waartoe grond wat oorlê word deur goudmynslik, deur sekere spoorelemente besoedel word. Die studie area is die geslote Machavie goudmyn wat oos van Potchefstroom, in die Noordwes Provinsie geleë is. In die studie area is 'n gebied van ± 1,1 km^2 besoedel deur wind en water verspreide goudmynslik afkomstig van vyf slikdamme. Die dikte van die slik wissel tussen 0,01 m en 1,50 m. Die invloed van die goudmynslik op die onderliggende gronde is ondersoek deur die grawe van 'n aantal toetsgate waaruit versteurde grondmonsters verkry is. Die gronde in die studie area bestaan uit residuele dolomiet wat oorlê word deur kolluviale en alluviale gronde. Die goudmynslik kan as 'n bron van suur en spoorelementbesoedeling beskou word aangesien die slik 'n gemiddelde pH(water) van 3,43 het, en oplosbare soute wat neergeslaan het op die oppervlakte van die herwerkte slik, hoë water oplosbare konsentrasies van As, Cd, Co, Cr, Cu, Ni, Pb en Zn, bevat. Die meerderheid grond wat oorlê word deur die slik, is geaffekteer deur die slik aangesien die gronde lae pH's het. Die spoorelement inhoud van die gronde is vergelyk met internasionale limiet konsentrasies, en daar is bevind dat die konsentrasies van As, Co, Cr, Cu en Ni in die gronde verder ondersoek moet word. Ammoniumnitraat is gebruik as 'n loginsmiddel om die ekstraheerbare konsentrasies van As, Co, Cr, Cu, Ni, Pb en Zn in die gronde te bepaal. 'n NH$_4$NO$_3$ ekstraheerbare Zn-ekwivalent is gebruik om te wys dat die kleierigge alluviale bogrond 'n groter gevaar vir plantlewe inhou as die sanderigge kolluviale bogrond. Die mobiliteit van die spoorelemente is ondersoek deur die persentasie van die totale spoorelement inhoud wat ekstraheerbaar deur NH$_4$NO$_3$ is, te bepaal. Daar is bewys dat spoorlement mobilitiet 'n funksie van die pH van die grond is, aangesien hoër spoorelement mobiliteite onder 'n pH van 5 voorkom.

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CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION

According to the Environmental Data Report of the United Nations Environmental Programme (UNEP, 1993) there is an increasing awareness that the health of populations are at risk from pollution hazards, but also that the interactions between pollution and health are not well understood. It is estimated that the quantity of hazardous waste generated on a global scale is in the order of 350 - 500 x 10^6 tons per annum (UNEP, 1993). According to Fyfe (1998), the population of the world is expected to double in the next fifty years to reach a total of 10 - 12 billion. The greatest increase in population is expected in the 'developing' nations while the majority of these people is expected to live in urban environments (Fyfe, 1998). This will increase the amount and concentrations of waste produced to values in excess of current global estimates. These wastes include domestic, industrial and mining related effluent that must be disposed of or isolated in an environmentally responsible manner. Problems associated with this are evident from the numerous publications and conferences devoted to the subject of environmental contamination.

A need to provide housing and services exists in South Africa. Engineering and environmental geologists are involved with identifying safe sites for housing from a geotechnical and geochemical point of view (Van Rooy, 1996). The land requirement is often greatest in and around cities where redevelopment of previously contaminated industrial or mining land may occur. The British Institute for Civil Engineers (ICE) defines contaminated land as "Land that contains substances which, when present in sufficient quantities or concentrations, are likely to cause harm, directly or indirectly, to man, to the environment, or on occasion to other targets" (Harris & Herbert, 1994). When redevelopment occurs, care should be taken that the new home owners are not exposed to toxic or carcinogenic substances present on the site but not identified during the geotechnical investigation. For this reason, many countries, especially those in the European Union, have instigated soil pollution threshold values for soils (e.g. Interdepartmental

Committee on the Redevelopment of Contaminated Land, 1987). These concentration guidelines can be used to assess whether a site is polluted, before development of an area is allowed.

Mining is one of the activities of man that can have a severe effect on the environment. Nriagu (1996), examined the history of global metal pollution using evidence obtained from peat deposits and arctic ice sections, and showed that metal pollution had started in Roman times where uncontrolled mining and smelting of Pb, Cu, Zn, Hg, Sn and Zn occurred for the first time in an intensive manner. Since then, increased pollution occurred at a rate comparable to the degree of industrialization of the world. By 1990, the global emissions of Cu, Pb and Zn have reached 500, 3500 and 2800 thousand metric tons, respectively (Figure 1.1).

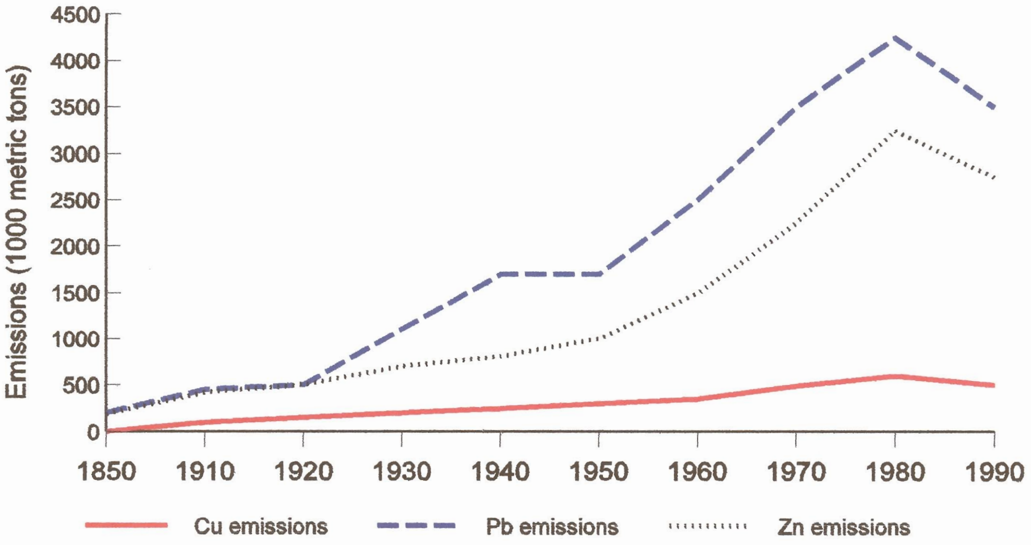


Figure 1.1 Recent historical changes in anthropogenic emissions of Cu, Pb and Zn to the atmosphere, after Nriagu (1996).

In 1998, South Africa produced approximately 533,6 million tons of waste, of which 87,7 per cent was from mining (Lourens, 1999). South Africa has vast economic exploitable mineral reserves with an extensive mining establishment. A literature survey conducted by Rösner, Boer, Reyneke, Aucamp and Vermaak (1998), shows that gold mining activities in the Gauteng Province are polluting the surrounding environment through an increase in acidity, salinization and heavy metal content of soils, sediments and groundwater bodies. The greatest threat posed by mining in the Gauteng Province is the uncontrolled release of acid mine drainage (AMD). According to Gray (1997), acid mine drainage affects the geo-environment and especially aquatic systems in various ways. Soil systems are affected by increased acidity, with a corresponding lowering of soil pH. The natural soil pH buffering system of soils is depleted and salinization of soils increases. An increase in soluble metals occurs with a corresponding increase in metal mobility.

Mining activities are responsible for an increase in certain trace elements in soils, sediments and groundwater reserves that occur within the influence sphere of the mine. Although trace elements such as I, Co, Mo and others are essential to human health, these micro-nutrients can be toxic when present in excessive concentrations. Non essential exogenous metals, for example Hg, are toxic at virtually all concentrations (Crounse, Pories, Bray & Mauger, 1983). It remains difficult to make an objective assessment of the effects of metal pollution on human health and to recommend remediation goals at contaminated sites (Fyfe, 1998). The reason for this is that toxicological predictions of how end receptor groups (e.g. humans, animals, plants or aquatic ecosystems) will be affected by contaminated land, are difficult due to the complexity of physical and chemical interactions that dictate the movement of toxins and carcinogens through the food chain to the end receptor group. The real, and often fatal, danger of trace elements on human health has however been described by case histories e.g. Hg poisoning of the fishing village of Minamata in Japan (Ellis, 1989).

Hatheway (1998) states that the engineering geological profession occupies a niche market in the sense that it can generate predictable site specific data that describes the geology, geohydrology and geotechnical nature of a site. The engineering geologist is therefore the natural candidate of professional field-orientated persons to become more involved in, or conduct, site specific risk assessment investigations where soil and groundwater contamination is involved. This view is supported by Van Rooy (1996), who states that engineering geologists in South Africa should assist in evaluating the effects of waste disposal, and any other polluting practice, and to monitor pollution levels in soils, air and groundwater.

It is against this background that a research project was initiated with the aim to investigate the degree of soil pollution occurring at an abandoned gold mine in the North West Province of South Africa.

1.2 RESEARCH AREA

The research was conducted at the abandoned Machavie gold mine, west of Potchefstroom. Gold from the Black Reef Formation of the Transvaal Supergroup was mined, while the mine was operational until the 1940's. During the life of the mine, five tailings dams were produced. After closure, the tailings were reworked by wind and water erosion to the extent that large areas downslope from the tailings dams are now covered with a layer of tailings, generally less than 0,20 m thick, but up to 1,50 m thick in some places.

1.3 OBJECTIVES OF RESEARCH AND LAYOUT OF DISSERTATION

1.3.1 Objectives of the research

The primary aim of the research, which investigates the degree of soil pollution occurring at an abandoned gold mine, is to contribute towards the understanding of how trace element pollutants behave in soils. To achieve this aim, it was necessary to satisfy the following secondary aims:

(i) the distribution of total element concentrations of As, Co, Cr, Cu, Ni, Pb, and Zn in the tailings as well as in the soils affected by reworked gold mine tailings, and

(ii) the mobility of As, Co, Cr, Cu, Ni, Pb and Zn in the tailings and the affected soils as well as the influences of selected soil properties on the mobility of the trace elements.

Machavie gold mine presents an ideal research locality as the mine is situated far from any industrial or urban activities that could add to the contamination load of the area. Pollution occurring in the study area is therefore only attributed to the abandoned mine.

1.3.2 Layout of dissertation

Chapter 2 is a literature survey of pollution by trace elements and of acid mine drainage from gold mine tailings dams. In Chapter 3 a general description of the geomorphology, climate, vegetation cover, geology and pedology of the study area is presented. Chapter 4 describes the site specific geology, pedology and geotechnical properties of the study area in detail. In Chapter 5 the total trace element concentrations in the gold mine tailings and the affected soils are investigated while in Chapter 6, the NH_4NO_3 extractable trace element concentrations in the tailings and affected soils are investigated. Discussion of the results and conclusions are contained in Chapter 7.

CHAPTER 2 LITERATURE SURVEY

2.1 INTRODUCTION

Over ninety-nine per cent of the element content of the earth's crust is composed of the "major elements" which are O, Si, Al, Fe, Ca, Na, K, Mg, Ti and P. The remainder of the elements in the periodic table are trace elements as their specific concentrations in the earth's crust do not generally exceed 0,1 per cent (1000 mg/kg) (Alloway, 1995). Trace elements can also be referred to as micro-nutrients which are those elements essential for growth and development of organisms (e.g. Zn, Mn, Cu, Fe, Mo and B). However, a micro-nutrient in excessive quantity can be toxic, while non-essential exogenous metals, for example Cd and Hg, are toxic at virtually all concentrations. Heavy metals refer to metallic elements with an atomic weight greater than that of Fe (55,8 g/mol) or to an element with a density greater than 5,0 g/cm^3 (Pierzynski, Sims & Vance, 1994). Although trace elements are ubiquitous in soil parent material, soils are contaminated by trace elements due to anthropogenic inputs. According to Alloway (1995), the major sources of anthropogenic trace element inputs are: metalliferous mining and smelting; agricultural and horticultural materials; sewage sludges; fossil fuel combustion; metallurgical industries (manufacture, use and disposal of metals); electronics (manufacture, use and disposal of electronic equipment); chemical and other manufacturing industries; waste disposal, warfare and military training.

2.2 NATURAL CONCENTRATIONS OF TRACE ELEMENTS IN SOILS

2.2.1 Geochemical origin of trace elements in soils

Trace elements occur in rock forming minerals due to isomorphic substitution or by fixation on free structural sites. Isomorphic substitution refers to the replacement of one of the major elements by a trace element ion in the crystal lattice of the mineral at the time of crystallization.

The substitution is governed by the ionic charge, ionic radius and electronegativity of the major element and the trace element replacing it. Substitution can take place when there is a difference of less than 15 per cent in the radii of the replacing ions and when the charge of the ions do not differ by more than one unit (Bohn, McNeal & O'Conner, 1985). The natural concentration of trace elements in soils is a result of weathering that releases trace elements from their host minerals during soil formation (Kabata-Pendias, 1992).

Soils represent a dynamic chemical system where mineral transformation occurs continuously. Weathering is the basic soil forming process and the degree of weathering that trace element containing primary minerals are subjected to, will therefore influence the lithogenic metal content of soils (Kabata-Pendias & Pendias, 1986). Weathering can be defined as the physical disintegration and chemical decomposition of rocks (Alloway, 1995). Singer & Munns (1992), describes physical weathering as the process which breaks down rocks to smaller particle sizes. Processes such as freezing and thawing, uneven heating, abrasion and shrinking and swelling (due to wetting and drying) break large particles into smaller ones. Plant roots that grow into thin cracks or the formation of salt crystals in cracks, can force joints or cracks open until the rock breaks.

Chemical weathering is the process that changes minerals from their original composition to new minerals and chemical components that are stable and equilibrated in the particular soil environment in the presence of water (Kabata-Pendias & Pendias, 1986). The rates at which these reactions take place are directly related to temperature and water availability, thus chemical weathering is more pronounced in the humid tropics than in cold and dry areas (Alloway, 1995). Water increases the rate of chemical weathering as water contains weathering agents (e.g. CO_2, O_2, organic acids such as humic and fulvic acid, SO_2 (aq), H_2SO_4 and HNO_3) in solution and transports these to chemically active sites on mineral surfaces. Water provides the H^+ ion to enable acid forming gasses to act as acids:

$$CO_2\,(g) + H_2O \rightarrow H^+(aq) + HCO_3^-(aq) \text{ and } SO_2\,(g) + H_2O \rightarrow H^+(aq) + HSO_3^-(aq)$$

Rainwater is usually slightly acidic due to the presence of dissolved CO_2, or more acidic due to acid-rain forming agents. Rainwater also lacks alkalinity and the slightly acidic rainwater is chemically aggressive and promotes weathering (Manahan, 1994). Typical chemical weathering reactions include: Dissolution; hydration; dehydration; hydrolysis; oxidation; acid hydrolysis and complexation. These chemical weathering reactions are responsible for the conversion of rock forming minerals to soils. According to White (1995), the rate at which chemical weathering of silicate minerals in the natural environment takes place, depends on a number of factors, including mineral surface reactivity, the role of hydrologic heterogeneity on fluid residence times in soils, soil pH, vegetation and climate.

2.2.2 Pedogenic processes that translocate trace elements in soils

Pedogenesis is defined by Alloway (1995) as the process by which a thin surface layer of soil develops on weathered rock material, gradually increasing in thickness and undergoing differentiation to form a soil profile. The soil profile contains distinct layers (horizons) which differ, according to Jennings, Brink & Williams (1973), in moisture content, colour, consistency, structure, and texture. Soil formation is a function of climate, biological activity, topography, parent material and time (White, 1995).

Soil is a multicomponent system consisting of solid, liquid and gaseous phases as well as living organisms (Bohn *et al.*, 1985). The solid phase is composed of inorganic matter (primary and secondary soil minerals) and organic matter. The liquid phase or the soil solution is a water solution with a composition and reactivity defined by the properties of the incoming water and affected by fluxes of matter and energy originating from the soil solid phase, biological system and the atmosphere. The gaseous phase or the soil atmosphere is composed of the same gases as the atmosphere (CO_2, N_2 and O_2) as well as gases that arise from biological activity (Yaron, Calvert & Prost, 1996).

Natural translocation and accumulation of trace elements in soils are the result of soil processes which include leaching, gleying, podzolization, surface organic accumulation and ferralitisation (Thornton, 1999).

2.3 BEHAVIOUR OF TRACE ELEMENTS IN SOILS

According to Bourg (1995), the mobility of trace elements in soils depends on a complex network of interactions between aqueous and heterogeneous chemical reactions, as well as physical phenomena such as particle coagulation and flocculation. Bourg (1995), distinguishes between soil chemical reactions that tend to increase trace element mobility in soils (e.g. dissolved inorganic and organic complexation) and reactions that delay trace element availability and transport (e.g. precipitation, adsorption, co-precipitation and sorption).

The soil solution is the medium for these reactions, and the dynamic equilibria reactions which can occur in soils are schematically displayed in Figure. 2.1 after Lindsay (1979) and Sparks (1995). Plants take up ions in the soil solution which can then be redistributed in the food chain (1). These ions are released back to the soil solution when the plants die and decompose (2). Ions in the soil solution can be sorbed on inorganic and organic soil components (3) and these sorbed ions can be desorbed back to the soil solution (4). If the soil solution becomes supersaturated with a certain mineral, this mineral will precipitate (5) and a mineral will dissolve if the soil solution is undersaturated with a mineral, until equilibrium is reached (6). Ions in the soil solution can be transported through the soil to the groundwater or ions can be removed through surface runoff. Upward movement of ions can occur through capillarity, a process driven by evaporation and drying (7 and 8). Micro-organisms can remove ions from the soil solution (9). When these organisms die and organic matter is decomposed, ions are released into the soil solution (10 and 2). Gases may be released to the soil atmosphere in soil pores (11) or become dissolved in the soil solution (12).

while low or negative values indicate the existence of reduced species and the soil is said to be under anaerobic conditions. Oxic soil conditions range between +300 to +800 mV (pE of 5,1 - 13,5) while reducing soil conditions range between +118 to -414 mV (pE of +2 to -7). The Eh of soil can be measured, but soil colour provide a good indication of the redox status of the soil. Red and bright yellow-brown colours indicate oxic conditions while blue-green, dull yellow and grey soil colours indicate anaerobic conditions. These colour differences are related to the oxidation state of iron in the soil.

2.5 NATURAL AND PROVOKED MOBILIZATION OF TRACE ELEMENTS IN SOILS AND SEDIMENTS

According to Kabata-Pendias (1992) the affinity of metals to the various soil components governs their mobility. Metals such as Cd and Zn that are generally more mobile, exist mainly as organically bound, exchangeable and water soluble species, while less mobile elements such as Pb, Ni and Cr are mainly bound in silicates or the residual fraction. Copper and Mo occur predominately in organically bound or exchangeable soil fractions. The water soluble, organically bound and exchangeable soil fractions are the most mobile trace element occurrences in soils. Figure. 2.2 depicts the speciation of heavy metals in soils. The mobility of metals in soils is strongly influenced by changing soil environmental conditions.

According to Förstner & Kersten (1988) the solubility, mobility and bioavailability of particle-bound metals can be increased by four main factors in terrestrial and aquatic environments:

1. Lowering of pH. In general most metal cations are most mobile under acid conditions with the exception of Mo that is more mobile under alkaline soil conditions.
2. Increased occurrence of natural or synthetic complexing agents which can form soluble metal complexes that will increase metal mobility.
3. Increasing salt concentrations result in an increase in competition for sorption sites on solid surfaces which increase the release of metals from sorption sites. In addition, Cl

forms soluble chloro-complexes with some trace metals.

4. Changing redox conditions. Hydrous Mn-, Al- and Fe-oxides will dissolve when placed in a reducing environment, causing the release of co-precipitated metals into the soil solution (Alloway, 1995). According to Bourg (1995) in medium to strong alkaline pH and oxidizing environments, amorphous Fe and Mn oxides in soils are strong adsorbents or co-precipiating matrices. When the environment is only slightly oxidizing, and for medium acidic pH ranges, the surface reactive Fe and Mn oxyhydroxides are solubilized when Fe^{3+} and Mn^{4+} are reduced to soluble species. Thus co-precipitated metals are released. When the pH is slightly alkaline, Fe and Mn may precipitate as carbonates that are less adsorbent than the corresponding oxides.

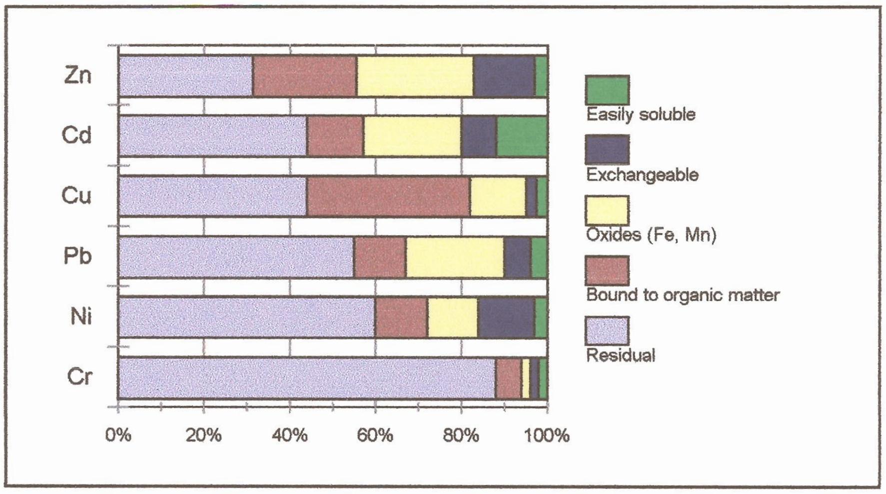


Figure 2.2 Speciation of trace elements in soils as a percentage of total content after Kabata-Pendias (1992)

Förstner & Kersten (1988) summarised the relative mobilities of elements in sediments and soils under changing pH and Eh conditions (Table 2.2). Changes from reducing to oxidizing soil conditions will involve the transformation of sulphide minerals and cause soil pH to decrease. This will increase the mobility of chalcophile elements such as Hg, Zn, Pb, Cu and Cd. The mobility of Mn and Fe on the other hand, is lower under oxidizing conditions.

Table 2.2. Relative mobilities of elements in sediments and soils as function of Eh and pH (after Förstner & Kersten (1988), cf, references therein).

	Electron Activity		**Proton activity**	
Relative mobility	**Reducing**	**Oxidizing**	**Neutral to alkaline**	**Acid**
Very low mobility	Al, Cr, Mo, V, U, Se, S, B	Al, Cr, Fe, Mn	Al, Cr, Hg, Cu, Ni, Co	Si
Low mobility	Si, K, P, Ni	Si, K, P, Pb	Si, K, P, Pb	K, Fe(III)
Medium mobility	Mn	Co, Ni, Hg, Cu, Zn, Cd	Mn	Al, Pb, Cu, Cr, V
High mobility	Ca, Na, Mg, Sr	Ca, Na, Mg, Sr, Mo, V, U, Se	Ca, Na, Mg, Cr	Ca, Na, Mg, Zn, Cd, Hg
Very high mobility	Cl, I, Br	Cl, I, Br, B	Cl, I, Br, S, B, Mo, V, U, Se	Cl, I, Br, B

2.6 TRACE ELEMENT TOXICITY

At least 25 elements are considered essential to life; these include C, H, N, O and macro-nutrients such as Na, K, Mg, S, P, Cl, Si and Fe, of which the majority are metals. This trend also holds for the micro-nutrients that are V, Cr, Mn, Fe, Co, Ni, Ca, Zn, Mo, Se, Fe and I. Trace elements or "heavy metals" refer to micro-nutrients and other non-essential elements that have low natural environmental concentrations. The micro-nutrients are essential to growth but a micro-nutrient in excessive quantity can be toxic, while non-essential exogenous metals, for example Hg, are toxic at virtually all concentrations (Crounse *et al.*, 1983). Any trace element can have an adverse effect on any organism if the dose is high enough. The biological function, phytotoxicity and mammalian toxicity character of some trace elements are presented in Table 2.3.

According to McBride (1994) the elements listed in Table 2.3 that are more toxic to animals than plants (e.g. As and Pb) present the most insidious hazard to human health as these elements may accumulate in plants to concentrations that are toxic to animals or humans while the plants do not display any signs of phytotoxicity. The toxicity rating in Table 2.3 is dependant on the actual likelihood or frequency of toxicity in the natural environment. For example, Mn has a low toxicity to plants but Mn- induced phytotoxicity (commonly occuring as high Mn^{2+}concentrations) can develop in wet soils. In comparison, Cr and Pb have a higher phytotoxicity rating but they are usually very insoluble in soils so that these elements rarely induce toxicity.

Table 2.3 Biological function and toxicity of some trace elements (after McBride 1994)

Element	**Biological Function**	**Phytotoxicity**	**Mammalian Toxicity**
As	None known in animals. Constituent of phospholipid in algae and fungi	Medium - High (5 - 20 ppm)	High
Co	Essential for animals. Co-factor in many enzymes. Plays a role in symbiotic N_2 fixation.	Medium - High (15 - 50 ppm)	Medium
Cr	May be involved in sugar metabolism in mammals	Medium - High (5 - 30 ppm)	Cr^{6+} High while Cr^{3+} Medium
Cu	Essential to all organisms. Co-factor in redox enzymes, O_2 transport	Medium - High (20 - 100 ppm)	Medium
Ni	None known in animals. May be essential to plants. Found in urease enzyme.	Medium - High (10 - 100 ppm)	Medium
Pb	None known	Medium (30 - 300 ppm)	High (cumulative poison)
Zn	Essential to all organisms. Co-factor in numerous enzymes	Low - Medium (100 - 400 ppm)	Low - Medium

Values in parenthesis are concentrations of element in leaf tissue that show toxicity in plants that are neither highly sensitive or tolerant.

2.7 GEOCHEMICAL BEHAVIOUR OF CERTAIN TRACE ELEMENTS

This section is a discussion of the abundance in soils and geochemical behaviour of the trace elements considered in this study. The following discussion borrows heavily form McBride (1994) and Alloway (1995).

2.7.1 Arsenic

Mean arsenic concentrations in soils range from 2,2 - 25 ppm worldwide. Arsenic occurs in soils in the +3 and +5 oxidation state, although -3 and 0 oxidation states are possible in strongly reduced soils and sediments. Arsenate (+5), as AsO_4^{3-}, represents the oxidized state and occurs in aerobic soils, while arsenite (+3), which takes forms such as $As(OH)_3$ and AsO_3^{3-}, is stable in anaerobic soils.

The chemical behaviour of arsenate is similar to that of phosphate in soils as it is likely to be adsorbed by Fe, Mn and Al oxides, noncrystalline aluminosilicates and, to a lesser extent, layer silicates. Arsenate adsorbs most effectively at low pH values and has therefore a low mobility in acid soils with a high clay or oxide content. However, in neutral to alkaline soils, especially if the soils are sodic, As may be mobile in the form of soluble Na arsenate. The oxidation of arsenite to arsenate is promoted by the presence of microbes and Mn oxides.

Arsenite adsorbs less effectively in alkaline soils than arsenate in acid soils, adsorption being most effective in soil pH ranging form 7 to 9. If oxic soils are subjected to anaerobic conditions, both co-precipitated or adsorbed arsenate and arsenite can be released into the soil solution by the dissolution of Fe and Mn oxides. Desorbed arsenate is then reduced to arsenite which is eventually converted to insoluble forms, causing As mobility first to increase and then to decrease if anaerobic conditions are maintained. When soils remain anaerobic for long periods, sulphides, formed under reducing soil conditions, may co-precipitate As in its lower oxidation state. Volatile alkylarsene($(H_3C)_3AsO$) compounds may also form under these conditions causing, a loss of As to the atmosphere or to air-filled soil pores.

2.7.2 Cobalt

Mean cobalt concentrations in soils range from 1,6 - 21,5 ppm worldwide. Cobalt occurs in soils in the +2 and +3 oxidation state. Co^{2+} is the dominant form in the soil solution. Cobalt preferentially associates with Fe and Mn oxides due to sorption and co-precipitation. Cobalt is strongly sorbed on Mn-oxides where Co^{2+} is oxidized to Co^{3+}, which results in a low mobility of Co in oxidized soils. Cobalt is usually found in association with Mn-oxides in soils where Co can replace Mn in the oxide structure. Under neutral soil conditions cobalt is less mobile than under acid soil conditions due to increased sorption of Co on oxides, silicate clays and organic matter, and possibly the precipitation of $Co(OH)_2$. Under strongly reducing conditions, the precipitation of Co-sulphides may inhibit mobility.

2.7.3 Chromium

Mean Cr concentrations in soils range from 7 - 221 ppm worldwide. Chromium occurs in soils in the +3 (chromic) and +6 (chromate) oxidation state. Cr^{3+} is the dominant form in the soil solution. The chromic cation is very immobile in soils as it complexes strongly with soil organic matter and sorbs even at relatively low pH values on oxides and silicate clays. In Fe-oxides, Cr^{3+} can replace Fe in the crystal lattice, and in higher soil pH conditions, $Cr(OH)_3$ precipitates, both processes reducing mobility. If the soil is not exceedingly acidic, the Cr^{3+} form is very immobile in soils and thus the insoluble Cr^{3+} form dominates in most soil types, and it generally occurs as insoluble hydroxides and oxides.

The mobility and bioavailability of the chromate ion (CrO_4^{2-}) in soils is higher, as chromate is less strongly adsorbed by soil constituents. The chromate ion is very toxic and is stable at higher soil pH values, but generally most Cr^{6+} is spontaneously reduced to Cr^{3+} under acid soil conditions in the presence of soil organic matter, as the organic material provides complexing groups which stabilise the chromic form. This reduction occurs more rapidly in acid soils than in alkaline soils.

2.7.4 Copper

Mean Cu concentrations in soils range from 6 - 80 ppm worldwide. Copper mainly occurs in soils as the divalent Cu^{2+} cation, although reduction of Cu^{2+} (cupric) to Cu^{+} (cuprous) and Cu^{0} (metallic copper) can occur in reducing conditions, particularly when stabilizing halide or sulphide ions are present.

Copper has a low mobility in reduced soils as the element is chalcophile, and forms insoluble minerals such as Cu_2S and CuS. In oxic soils, Cu^{2+} is also relatively immobile as copper is easily adsorbed on most colloidal soil material (e.g. Mn-, Fe- and Al-oxides, silicate clays and humus). Adsorption increases with increasing soil pH. Above a pH of 6, precipitation of malachite or azurite may occur in soils with a sufficient Cu concentration. Organically bound Cu^{2+} is the least mobile of all organically bound divalent transition metals. Copper is rated to have a low mobility in near-neutral soils as the high-affinity of soil colloids for Cu^{2+} reduces the concentration of the element in the soil solution. In more alkaline soils, the mobility of copper may become significant due to the formation of soluble complexes of Cu^{2+} (hydroxy, carbonate and organic matter complexes) which are adsorbed to al lesser degree.

2.7.5 Nickel

Mean Ni concentrations in soils range from 4 - 55 ppm worldwide, The Ni^{2+} oxidation state is the only stable form of nickel in the soil environment. The Ni^{2+} cation is comparable in geochemical behaviour with Cu^{2+}, except that it is slightly less electronegative than Cu^{2+}. However, nickel is several times more phytotoxic than Cu. Nickel is the smallest divalent transition metal cation and fits easily into octahedral sites of silicate clays and co-precipitates readily into Mn- and Fe-oxides. Nickel also bonds preferentially with soil organic matter and bio-accumulation of Ni in organic rich soils is pronounced. The mobility of Ni is rated as medium in acid soils but very low in neutral to alkaline soils, as Ni sorption on oxides, noncrystalline aluminosilicates and clay minerals increases above pH 6. Under reducing soil conditions Ni has a restricted mobility since Ni^{2+} is incorporated into sulphides.

2.7.6 Lead

Mean Pb concentrations in soils range from 10 - 84 ppm worldwide. Lead exists principally in the Pb^{2+} oxidation state in soils. Lead is the least mobile heavy metal in soils, particularly under reducing or non-acid soil conditions. Lead is a strongly chalcophile element and is very immobile in reducing soil conditions as lead precipitates as insoluble sulphide compounds. In oxic soils, Pb solubility decreases with increasing pH, since at higher pH levels, complexation of Pb with organic matter, sorption of Pb on oxides and clays and precipitation of Pb-carbonate, -hydroxide or -phosphates, are favoured. Manganese oxides in soils may also oxidize Pb^{2+} to the even less soluble Pb^{4+} ion which will further reduce the mobility of lead in oxic soils. Lead complexes strongly with soil organic matter and when introduced to soils, will bio-accumulate in organic rich topsoil. In alkaline soils however, the mobility of lead may be slightly increased due to formation of Pb-organic or Pb-hydroxy complexes.

2.7.7 Zinc

Mean Zn concentrations in soils range from 17 - 125 ppm worldwide. Zinc exists only in the Zn^{2+} oxidation state in soils. Zinc is the most mobile and soluble trace metal cation under acidic, oxic soil conditions, as Zn^{2+} is held in exchangeable forms on soil organic matter and clays. However, the mobility of zinc in neutral soils is significantly lower, since sorption on oxides and aluminosilicates as well as complexation with soil organic matter, lowers the solubility of zinc. Zinc is not known to co-precipitate into octahedral sites of oxides and silicates. In alkaline soils, the mobility of zinc may increase since soluble Zn-organo and Zn-hydroxy anions may form. But if Zn is present in sufficient concentration, insoluble Zn-oxide, hydroxide or hydroxycarbonate precipitates will restrict the mobility of zinc. In anaerobic soils, the release of Zn^{2+} from dissolved

Fe and Mn oxides may at first increase Zn mobility, but the mobility will finally be restricted by the precipitation of exceedingly insoluble ZnS.

2.8 LEACHING TECHNIQUES

Soils consist of a heterogeneous mixture of different organic substances, quartz, primary and secondary alumino-silicate clay minerals, Fe-, Al- and Mn-oxides and other solid components, as well as variety of soluble substances. The binding mechanisms of trace elements in soils are many, and vary with the composition of the soil, the soil pH and the redox conditions particular to the soil. The complexity of possible reactions, and often unknown reaction kinetics in natural soil systems, restricts studies of trace element distribution in the solid soil phase to operationally defined analytical procedures (Brümmer,Gerth & Williams 1986). To assess the reactivity of the species or binding forms of heavy metals in solid materials, different procedures involving sequential extraction techniques have been developed from the original method proposed by Tessier, Campbell & Bisson (1979). These techniques assume that the following trace element species exist in soils: Water soluble (in the soil solution); exchangeable; organically bound; occluded in iron and manganese oxides; definite compounds (e.g. trace element carbonates, phosphates, sulphides); and structurally bound in silicates (the residual fraction).

According to Coetzee, Gouws, Plüddemann, Yocoby, Howell and Drijver (1995), sequential extraction procedures have received adverse critique and controversy in literature over the last decade. The main reasons being that the techniques are used in a nondiscriminatory way with the assumptions (i) that the procedures are selective, (ii) that phase exchanges do not occur and (iii) that matrix effects can be ignored. However various authors have shown that these assumptions can not generally be made.

The water soluble fraction, together with the exchangeable soil fraction, represents the mobile portion of trace elements in soils (Brümmer *et al.*, 1986). The other fractions are essentially immobile and the mobilisation of these bound species is controlled by reaction kinetics. The mobile fraction of trace elements in soils represents the bioavailable portion and leaching techniques such as the 1M NH_4NO_3 technique used by Schloemann (1994), therefore result in extracted ion concentrations that can be correlated with the amount of ions held on charged soil surfaces (e.g. clays, oxides and humus).

2.9 SOIL STANDARDS

Environmental policies governing air and water quality were developed before soil protection became an important issue in the European Union. One of the reasons for this may be that the effects of poor air and water quality are plainly visible, while the effects of soil pollution can remain unnoticed for a long time. Often the effects of bad or dangerous soil quality become apparent during changes in land use (Vegter, 1995).

According to Ferguson, Darmendrail, Freier, Jensen, Jensen, Kasamas, Urzelai & Vegter (1998), most industrialised countries are currently drawing up or revising policies and procedures that deal with contaminated land. These policies contain screening and guideline values that are used to assess whether a soil is polluted or not. Screening values are defined as generic values intended to screen out those sites (or parts thereof) for which risks are too small to warrant more detailed investigation. These values tend to be based on very pessimistic exposure assumptions and/or very stringent criteria for maximum tolerable risk. Guideline values are designed to provide generic guidance to risk assessors on the significance of contaminant concentration in soils or other media. Debate around the usefulness of both screening and guideline values has centered around the reliability of the calculated values, the treatment of uncertainty and the relationship between generic scenarios and real site conditions. The advantages of using generic values are listed below:

- speed and ease of implementation, and similar sites would be handled in a similar way;
- useful for initial assessment of significance of contamination;
- encourage planners and developers to undertake decontamination/restoration;

- reality of contaminated land made understandable for the lay person;
- facilitate environmental audits for industrial/mine sites;
- facilitate monitoring/permitting of operational industrial/mine sites;
- can be used in performance assessment of soil treatment plants;
- imply non-negotiability and reduce local political influences.

2.9.1 Screening values

Steyn, Van der Watt & Claassens (1996) summarised the screening values which apply to South Africa and some other countries (Table 2.4). These values are used to assess whether a soil is contaminated and represent the total concentration of an element in the < 2 mm fraction of a soil.

Table 2.4 Maximum permissible total soil concentrations of some trace elements used in legislation or in guidelines for various countries as summarized by Steyn *et al.* (1996). All values are in mg/kg dry soil for the < 2 mm soil fraction.

	South Africa	**Australia/ New Zealand**	**Germany**	**United Kingdom**	**Switzerland**
Cd	2	3	1.5	3	8
Co	20	-	-	-	25
Cr	80	50	100	400 (provisional)	75
Cu	100	60	60	135*	50
Hg	5	1	1	1	-
Ni	15	60	50	75*	50
Pb	56	300	100	300	50
Zn	185	200	200	300*	200
As	2	20	-	50	-

** Permissible concentration for soil pH 6,00 - 7,00*

2.9.2 Guideline values

Examples of guideline values which comment on the significance of a contaminant concentration in soil are shown in Table 2.5.

Table 2.5 Recommended maximum NH_4NO_3 extractable threshold concentration (mg/l) that should not be exceeded in the soil (from Schloemann (1996), after Prüeß, Turian & Schweikle 1991).

	Recommended maximum extractable concentrations (mg/l in soil fraction < 2mm)	Impacted soil functions and ranking of concerns				
		Pollutant buffer with regard to plants for human consumption	Pollutant buffer with regard to plants for animal consumption	Habitat for plants	Habitat for soil organisms	Pollutant filter with regard to groundwater
As	1	PC	X	C	X	C
Be	2	X	X	X	X	INV
Bi	1	X	INV	X	X	X
Cd	2	PC	C	X	C	C
Co	5	X	C	C	X	X
Cr	1	X	X	X	PC	C
Cu	2	X	C	C	PC	C
Ni	1	X	X	C	X	X
Pb	2	PC	C	X	C	C
U	4	X	X	X	X	INV
V	1	X	X	INV	X	X
Zn	10	X	X	C	X	X

PC = primary concern, C = concern, INV = further investigations needed to assess risk. X = limited soil functioning only if the maximum concentration is excessively exceeded

2.10 RISK ASSESSMENT OF METAL POLLUTION IN SOILS

Pierzynski *et al.*(1994) define risk as the probability or chance of injury, loss or damage and can be applied to contaminated soils which represent a risk to humans and other organisms as a result of the concentration of pollutants in soils. According to Ferguson *et al.* (1998) risk assessment is an objective way of assessing the impact of polluted soil on human health, ecosystems and the general environment. Risk assessment usually involves a detailed investigation of all sources, pathways and receptors of concern at a site. This process is lengthy and costly, and therefore a tiered approach in investigating a site is followed. The risk assessment procedure is a systematic approach for estimating the probability that site-specific hazards are realized. Firstly, the assimilated data and information obtained from site investigations are used to conduct a baseline risk assessment whereby contaminants of potential concern are detected and the significance of their presence is established in terms of human health and environmental risk. This process requires an assessment of the site by modelling site specific exposure routes through source-path-target substantiation and analysis. The results of a base line risk assessment can be used to decide on the requirements for monitoring, further investigations or remediation measures, if required.

2.10.1 Exposure assessment

Pierzynski *et al.* (1994) define exposure assessment as the procedures by which the identity of the organisms exposed to a soil contaminant is determined. The relative contribution of each route of exposure to the dose of the recipient is also determined. The dose refers to the amount of contaminant ingested or inhaled by the receptor organism. Various organisms can receive a dose in different ways, for example, humans and animals can be dosed via inhalation, by ingestion or by dermal contact with harmful soil contaminants. Plants on the other hand are dosed by extracting contaminated soil water, by respiration with contaminated air or by adsorbing particulate pollutants on the waxy surfaces of leaves. Ferguson *et al.* (1998) list some of the routes by which contaminants may be transported as soil, groundwater, surface water, dust, uptake or adsorption by plants and aerosols. Contaminants may undergo transformation through biological, chemical or physical means when *en route* to the receptor which may affect its toxicity, availability or mobility. Various models may be used to model the ultimate dose to a receptor group and this concentration is used to perform a dose - response analyses in order to characterise the risk to a receptor. The complexity of exposure routes that needs to be considered when performing a risk assessment investigation on a contaminated site, is indicated in Figure.2.3.

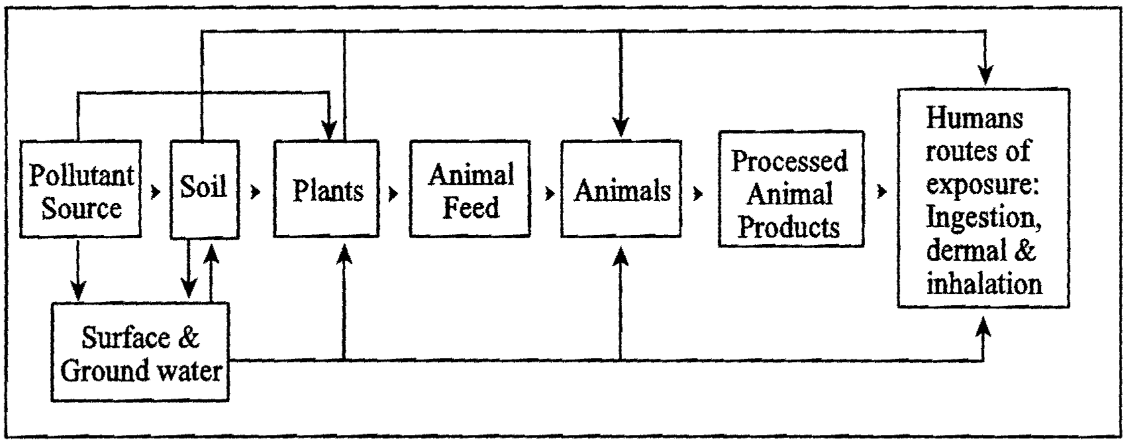


Figure. 2.3 Some human exposure pathways to be considered when performing a risk assessment investigation of a heavy metal contaminated site (after Pierzynski *et al.*, 1994).

2.11 ACID MINE DRAINAGE

The uncontrolled release of acid mine drainage (AMD) is perhaps the most serious impact that mining can have on the environment (Ferguson & Erickson, 1988). In addition to low pH (i.e. high acidity) acid mine drainage often contains dissolved trace elements in toxic concentrations. The high acidity of mine drainage arises from the rapid oxidation of sulphide minerals. AMD may occur anywhere where sulphide minerals are exposed at the earth's surface (e.g. road cuts or quarries), but metal mines where economically recoverable metals often occur in orebodies of concentrated metal sulphides (e.g. pyrite, FeS_2; chalcopyrite, $CuFeS_2$ or sphalerite, ZnS) are the primary source of AMD.

The generation of AMD is controlled by a series of factors that may be categorized as primary, secondary, tertiary and downstream factors (Ferguson & Erickson, 1988). Primary factors are those directly involved in the acid production process. Secondary factors control the consumption or alteration of the products of the acid generation reactions. The tertiary factors are the physical aspects of the waste material or mine site that influence the acid production, AMD migration and consumption. Downstream factors control the precipitation of Fe and other metals in rivers and streams into which AMD is discharged. These factors control the quality (including trace element content) of AMD affected water that emanate from a site.

2.11.1 Primary Factors

The reactions of acid generation from sulphide minerals are discussed according to the three-stage stoichiometric example of pyrite oxidation after James (1997) and Ferguson & Erickson (1988) in which one mole of pyrite oxidises to form two moles of sulphate and two moles of H^+:

Reaction 2.1, represents the oxidation of pyrite to form dissolved ferrous iron, sulphate and hydrogen. This reaction can occur abiotically or can be bacterially catalysed by the bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (2.1)$$

The ferrous iron, (Fe^{2+}) may be oxidised to ferric iron, (Fe^{3+}) if the conditions are sufficiently oxidising, as illustrated by reaction 2.2. Hydrolysis and precipitation of Fe^{3+} may also occur, shown by reaction 2.3. Reactions 2.1, 2.2 and 2.3 predominate at pH > 4,5.

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad (2.2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\,(s) + 3H^+ \qquad (2.3)$$

Reactions 2.1 to 2.3 are relatively slow and represent the initial stage in the three-stage AMD-formation process. Stage 1 will persist as long as the pH surrounding the waste particles is only moderately acidic ($pH > 4,5$). A transitional stage 2 occurs as the pH declines and the rate of Fe hydrolysis (reaction 2.3) slows, providing ferric iron oxidant. Stage 3 consists of rapid acid production by the ferric iron oxidant pathway and becomes dominant at low pH, where the Fe^{2+} (ferric iron) is more soluble (reaction 4):

$$FeS_2 + 14\,Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2.4)$$

Without the catalytic influence of bacteria, the rate of ferrous iron oxidation in an acid medium would be too slow to provide significant AMD generation. As such, the final stage in the AMD generation process occurs when the catalytic bacteria has become established. Reactions 2.2 and 2.4 then combine to form the cyclic, rapid oxidation pathway chiefly responsible for the high contamination loads observed in mining environments.

2.11.2 Limiting factors

Oxygen is an essential reactant in the formation of AMD and determines the oxidation of sulphide minerals as well as the activity of aerobic autotrophic bacteria. The replenishment of oxygen within a mining waste from the atmosphere is required to sustain the rapid bacteriologically catalysed oxidation processes. Significant oxidation may not occur if the oxygen concentration around the sulphide mineral drops to below 1 to 2 per cent (Ferguson & Erickson, 1988).

Water acts as a reactant, a reaction medium and as a product transport medium in the AMD generation and transport process (Ferguson & Erickson, 1988). Bacterial activity may also be limited by the availability of water. The different forms of pyrite present different activities that then affect the rate of the oxidation reaction. Isometric pyrite may not be as reactive as orthorombic marcasite or hexagonal pyrrhotite.

the world's acidic drainage. During AMD, Fe-sulphide minerals generate acid which leads to the further dissolution of other Fe-sulphides and their associated mineral assemblages. Examples of chalcophile trace elements associated with common sulphide minerals are presented in Table 2.6. The various metals released to solution are important contributors to environmental degradation. Among the elements that are most widely encountered as potentially toxic pollutants occurring in mine wastes, are Zn, Pb, Cu, Ni, Cd, Hg, Mo, As and occasionally Cr, Co and Se. The potential threat to the environment by elements is evident in countries like Canada where effluent discharged from metal mine tailings must comply with regulatory standards: The maximum monthly mean concentrations (in mg/l) are as follows: As < 0,5; Cu < 0,3; Pb < 0,2; Ni, < 0,5 and Zn < 0,5. The total soluble metal concentration in the effluent must be less than 25 mg/l.

Table 2.6 Common ore minerals of non-ferrous metals and their associated trace elements, compiled by Alloway (1995).

Metal	**Ore minerals**	**Associated trace elements**
As	FeAsS, AsS Cu ores	Au, Ag, Sb, Hg, U, Bi, Mo, Sn, Cu
Cr	$FeCr_2O_4$	Ni, Co
Cu	Native Cu, $CuFeS_2$, Cu_5FeS_4, Cu_2S, Cu_3AsS_4, CuS	Zn, Cd, Pb, As, Se, Sb, Ni, Pt, Mo, Au, Te
Ni	$(Ni,Fe)_9S_8$, NiAs, $(Co, Ni)_3S_4$	Co, Cr, As, Pt, Se, Te
Pb	PbS	Ag, Zn, Cu, Cd, Sb, Tl, Se, Te
Zn	ZnS	Cd, Cu, Pb, As, Se, Sb, Ag, Au, In

2.11.7 Environmental affects of gold mine tailings in South Africa

In a study of a number of gold mine tailings dams in the Gauteng province, Marsden (1986) concluded that tailings dams of 20 years and older, have an oxidised zone where leachable sulphate (and associated low pH water and other toxic substances) are virtually absent. He supports this conclusion by the fact that grass and other vegetation grows on many discard dumps. Through hand auger and test pitting, the thickness of this zone has been established to be ± 10 m in sand dumps and 2 - 3 m in slimes dams (Marsden 1986).

Blight & du Preez (1997) studied the escape of acid and soluble salt pollution from decommissioned gold mine tailings dams and confirmed the presence of the oxidised tailings zone on the surface of slimes dams. The rate of formation of this zone is greater than the rate of erosion from the dam, and consequently they predict that little pollution enters the environment as a result of physical redistribution of tailings. However, when erosion gulleys, that cut through the oxidised zone, develop on the sides of some tailings dams, acid leachate can escape much easier from the tailings impoundments. Marsden (1986) found that sulphate concentrations in soils surrounding gold mine tailings deposits, where tailings had been allowed to wash onto adjacent land, were on average 0,05 per cent (maximum of 0,25 per cent) up to a depth of 2,00 m.

Rösner *et al.* (1998) summarised the results of research on the environmental effects of South African gold mine tailings. Trace element concentrations in water and sediments were analyzed in the 1970's and it was found that elevated concentrations of Co, Cu, Fe, Mn, Ni and Zn are present in stream systems affected by AMD (Förstner & Wittmann, 1976). Funke (1985) concluded that slimes dams contributed approximately 2 per cent of the total salt load entering the Vaal Barrage system. Marsden (1986) concluded that mine dumps older than 20 years make no significant contribution to the current pollution load on aquatic systems, as these tailings dams are often depleted in sulphur bearing minerals in the oxidised zone. Funke (1990) concluded that the amount of sulphur in mine dumps that still oxidizes at present, is low, particularly when compared with the pollution load deriving from mine pumpage and metallurgical plant operation. Evans (1990) found trace element pollution caused by AMD generation in a wetland adjacent to a tailings dam. Walton, Verhagen & Taussig-Duthe (1993) attributed elevated sulphate and metals (Ni, Cu, Fe) concentrations in both, surface and groundwater systems in the Gauteng region to AMD from tailings dams. Znatowicz (1993) found high concentrations of toxic metal (e.g. As, Cd, Ti, V and U) in water and sediment samples downstream from a gold tailings dam.

Coetzee (1995) detected significant radiometric anomalies in selected drainage systems of the Gauteng Province and attributed these to AMD from tailings dams. Pulles, Heath & Howard (1996) stated that seepage released from various waste deposits such as mine dumps was identified as the most significant pollution source with regard to the deterioration of water quality in Gauteng. Rösner (1996) found significant concentrations of As, Cr, Ni, Pb, V and Zn in the oxidized zone of a number of gold mine tailings dams in Gauteng.

CHAPTER 3 DESCRIPTION OF THE STUDY AREA

3.1 INTRODUCTION

The aim of this chapter is to describe the study area in terms of its locality, history, topography, drainage, regional climate, geology and soils.

3.1.1 Locality and site history

The study area is located in the North West Province, approximately 22 km west of Potchefstroom (Figure 3.1). The Machavie Gold Mine was proclaimed in the 1930's after which mining proceeded actively until the early 1940's when the mine was closed. During this time, five tailings dams were established. After closure of the mine, water and wind erosion dispersed the tailings down slope, towards and on to the floodplain of the Kromdraai Spruit. This has resulted in an area of approximately 1,10 km^2 being covered with a layer of sheetwash and aeolian deposited tailings and the development of some tailings dunes (up to 1,50 m high).

3.1.2 Available information

The following information was used during the course of the study

- The 1:50 000 topographic sheet 2626 DB Eleazar.
- The published 1:250 000 Geological sheet 2626 BC West Rand.
- The 1:10 000 orthophotograph 2626 DB 14 Eleazar.
- The 1:50 000 aerial photographs 208 -210 and 247 -249 of job number 670.
- The 1:250 000 Land Type Series 2626 West Rand.

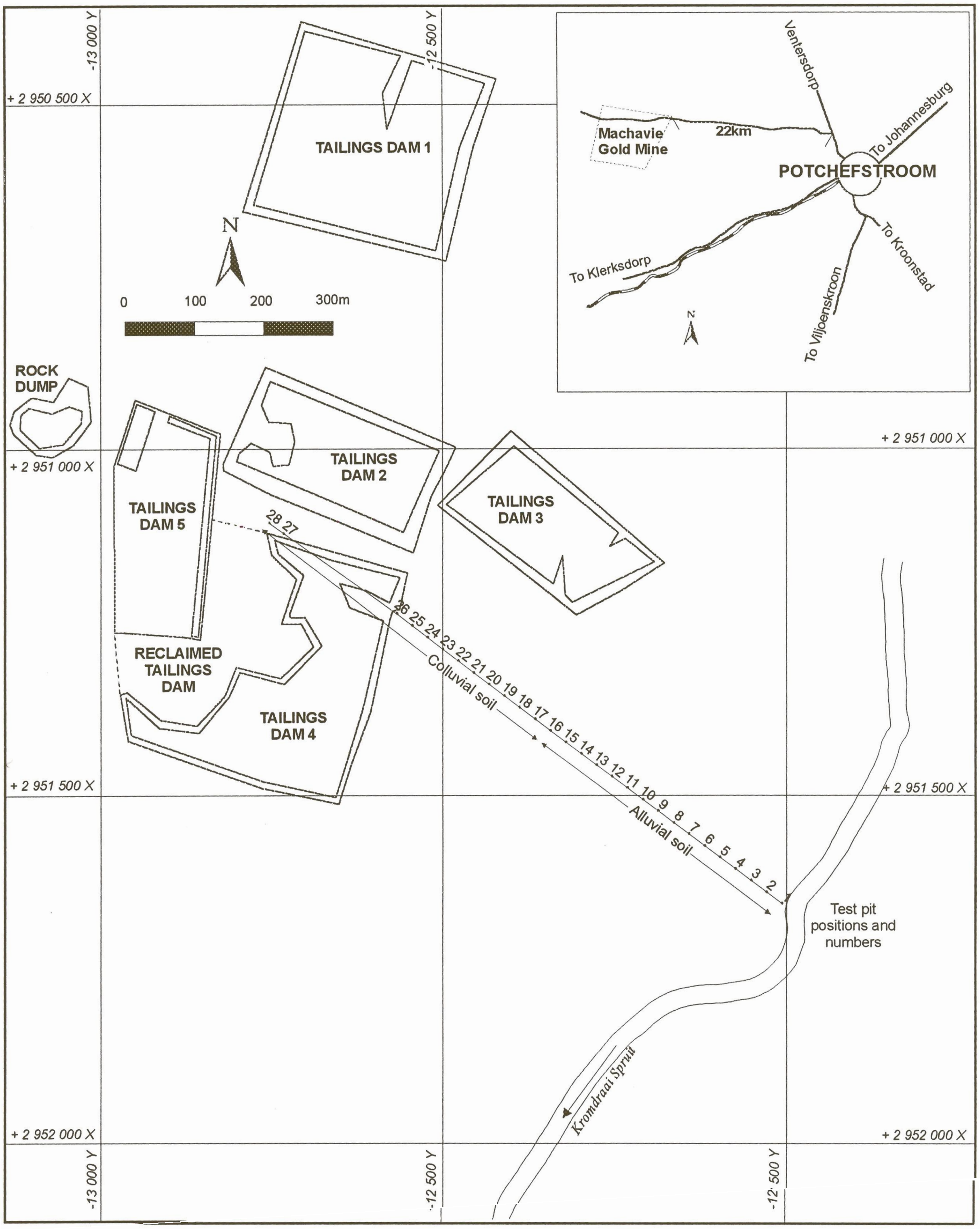


Figure 3.1 Locality of the investigated transect indicating test pit positions relative to the tailings dams and the Kromdraai Spruit.

3.2 CLIMATE

3.2.1 Regional climate of the Potchefstroom - Klerksdorp area.

No site specific climatic data are available for the study area, and therefore the statistics for the Potchefstroom weather station (located at 26° 44' S and 27° 04' E) were used to describe the climate of the area.

3.2.2 Mean monthly and annual rainfall of the Potchefstroom area

Potchefstroom occurs in the summer rainfall region with a long-term average annual rainfall of 613 mm occurring mainly between September and April (Table 3.1). The high evaporation rates of the area imply a water deficit during the whole year (Table 3.1).

Table 3.1 Averaged monthly rainfall and maximum 24 hour rainfall for the Potchefstroom area as well as average monthly A-pan equivalent evaporation data (Weather Bureau, 1995).

MONTH	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**
Average (mm)	119	83	78	61	15	7	4	10	20	55	85	94
Max 24hr rainfall(mm)	95	79	83	83	27	24	23	52	49	53	75	78
Evaporation (mm)	235	195	175	137	115	93	110	156	204	239	233	250

3.2.3 Mean monthly maximum and minimum temperatures

The average minimum and maximum temperatures for the study area are given in Table 3.2. On average, the maximum summer temperature in the area varies between 27,2 °C and 29,2 °C while in winter the average minimum temperature varies between 0,5 °C to 0,7 °C.

Table 3.2 Mean monthly maximum and minimum temperatures (°C) from the Potchefstroom area (Weather Bureau, 1995).

MONTH	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**
Maximum (°C)	22	28	27	24	22	19	19	22	25	27	28	29
Minimum (°C)	16	15	14	10	4	7	5	4	8	12	14	15

3.2.4 Mean monthly wind direction and speed

The area is characterized by the highest frequency of (in decreasing order) NW, N, NE and SW winds, especially during the warmer months of August to January. The wind speeds recorded over a 30 year period are generally low, 0 - 8 m/s with wind speeds of higher than 14 m/s having a frequency of less than 13 % and occurring only in August and September. The latter are very important in respect of wind erosion because they concide with the end of the dry season, i.e. with the period when the soils and tailings are at their driest, making them very vulnerable to wind eroison.

3.3 SITE DESCRIPTION

3.3.1 Topography and drainage

The study area is at an average elevation of 1379 m above mean sea level and has a gentle sloping topography towards the south. The highest part of the area is a hill located to the immediate west of the mine boundary, at 1560 m above mean sea level. The southern section of the mine boundary is the Kromdraai Spruit at an altitude of 1373 m above mean sea level. Sheetwash, in a southerly direction, is the predominant drainage mechanism of the site. This has resulted in the floodplain of the Kromdraai Spruit being covered by eroded tailings. Concentrated surface flow occurs in a donga that runs through a portion of the site, towards the Kromdraai Spruit.

3.3.2 Vegetation

According to Acocks (1988), the vegetation cover of the area is pure grassveld, comprising of *Cymbopogon-Themeda* veld types. Indigenous trees (e.g. *Rhus* species) are present as thickets. According to Erasmus (1997), the vegetated eroded tailings deposits are covered by *Cynodon dactylon* grass.

3.3.3 Geology

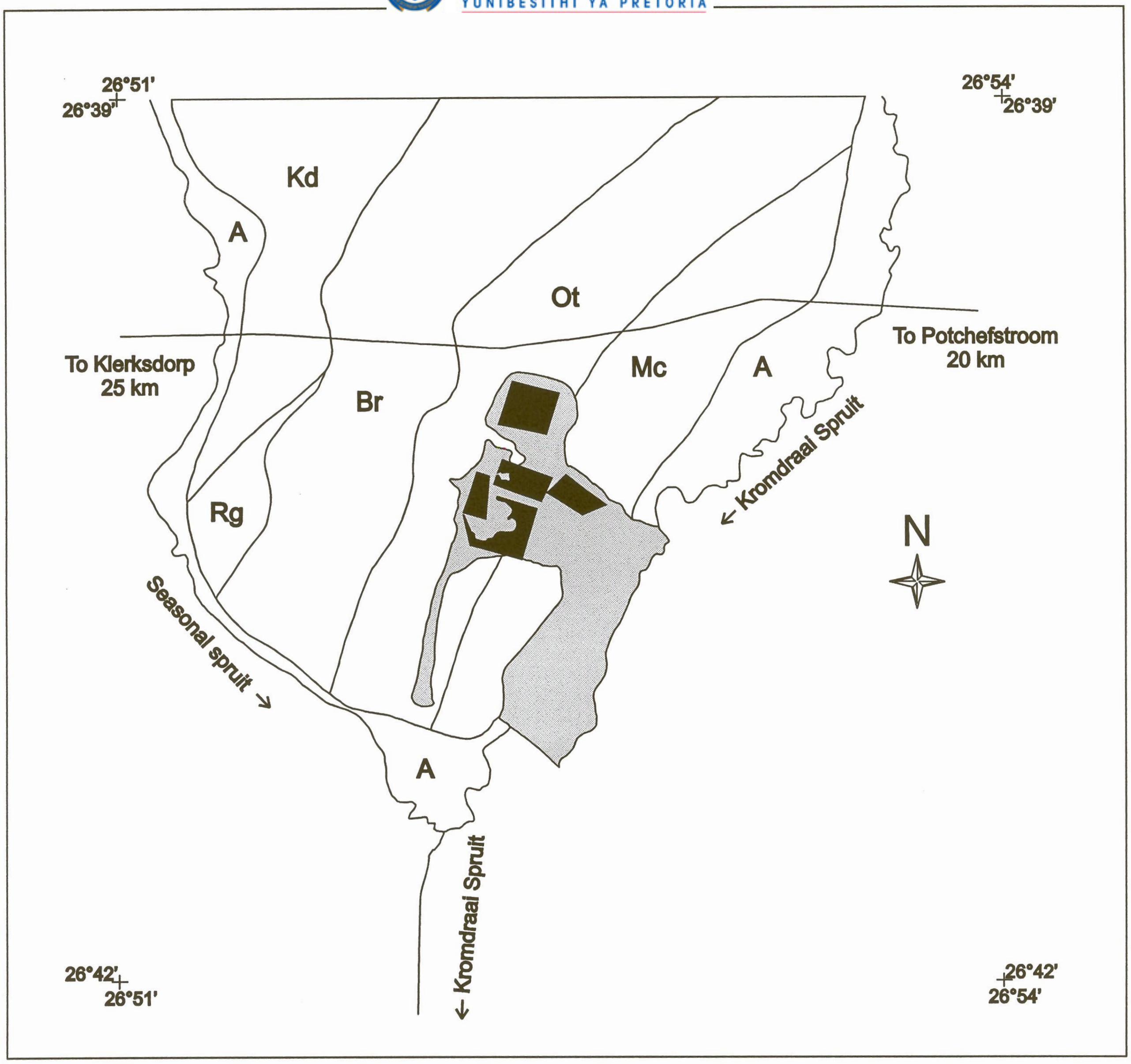
According to the published 1:250 000 Geological Map Series 2626 Wes-Rand, the major part of the study area is underlain by sedimentary rocks of the Transvaal Supergroup while a small portion on the west is underlain by volcanic rocks of the Ventersdorp Supergroup (Figure 3.2) The stratigraphy of the area is shown in Table 3.3.

The Transvaal Supergroup in the study area is represented by the Monte Christo and Oaktree Formations (which belong to the Malmani Subgroup of the Chuniespoort Group) and the Black Reef Formation. The composition of each formation is described after Brink (1979). The Monte Christo Formation consists of light coloured chert-rich recrystallised dolomite with stromatolites and basal oolitic bands. The formation is generally 740 m thick in the West Rand area. The Oaktree Formation consists of dark coloured chert-poor dolomite, sometimes with wad and carbonaceous shale towards the base. According to Eriksson & Truswell (1979) the Oaktree Formation consists of six stratigraphic units which include zones of domical stromatolites, thin shale units as well as the convoluted chert marker. Occasional chert partings occur at the top of the formation. The formation is generally 330 m thick in the West Rand area. The Black Reef Formation consists of a basal conglomerate unit overlain by quartzite, wad and carbonaceous shale. The formation is generally 25 m thick in the West Rand area.

The Platberg Group of the Ventersdorp Supergroup occurs in the western portion of the study area. Two formations of the Platberg Group, the Rietgat and the Kameeldoorns Formations occur in the study area. The Rietgat Formation is composed mainly of greenish-grey amygdaloidal and porphyritic lava, with interbedded shale, tuff, greywacke, conglomerate and impure limestone with algal structures. The Kameeldoorns Formation forms the base of the Platberg Group and is confined mainly to fault troughs. The formation is composed mainly of coarse basal conglomerate and greywacke, agglomerate and tuff, calcareous shale and pure limestone with subordinate greenish-grey lava (Visser, 1989).

Table 3.3 The stratigraphy of the investigated area

Transvaal Supergroup	Chuniespoort Group	Malmani Subgroup	Monte Christo Formation	Chert-rich dolomite
			Oaktree Formation	Chert-free dolomite
			Black Reef Formation	Feldspathic quartzite, shale and conglomerate
Ventersdorp Supergroup	Platberg Group		Rietgat Formation	Greenish-grey amygdaloidal and porphyritic lava, with interbedded shale, tuff, greywacke, conglomerate and impure limestone
			Kameeldoorns Formation	Coarse basal conglomerate and greywacke, agglomerate and tuff, calcareous shale and pure limestone with subordinate greenish-grey lava



LEGEND

■ Tailings dams
▨ Surficial tailings
A Alluvium

FORMATION	SUBGROUP	GROUP	SUPERGROUP
Mc Monte Christo Formation Ot Oaktree Formation Br Black Reef Formation	Malmani Subgroup	Chunies Poort Group	Transvaal Supergroup
Rg Rietgat Formation Kd Kameeldoorns Formation		Platberg Group	Ventersdorp Supergroup

Figure 3.2 Regional geology of the study area.

3.3.4 Pedology

According to the 1:250 000 Land Type Series 2626 Wes-Rand the soils occurring on the 1:10 000 orthophoto 2626 DB 18 Eleazar comprise Land Types Fa14a and Ba42b (Land Type Survey Staff, 1984). Land Type Fa14a underlies the majority of the area and is characterized by a pedologically young landscape of mixed origin. The dominant soil forming process in this area is by rock weathering, and thus orthic A horizons underlain by lithocutanic b horizons are common. Land Type Fa specifically refers to land in which lime is not encountered regularly in any portion of the landscape. Hillcrest areas in this land type are characterized by rock, Mispah and occasionally shallow Hutton form soils. The upper sideslopes are mainly composed of rock and Mispah soils while the lower sideslopes have more Mispah soils. The valley bottom soils are mainly of the Hutton and Westleigh form soils (Land Type Survey Staff, 1984).

Land Type Ba24b occurs in the western portion of the area. Land type Ba indicates land in which red and / or yellow brown apedal soils (Hutton, Bainsvlei, Avalon, Glencoe and Pinedene soil forms) that are dystrophic and / or mesotrophic, dominate over red and / or yellow brown eutrophic soils. In unit Ba24b more than 10 per cent of the area contains plinthic soils, while red soils occupy more than a third of the total area. Hillcrest areas contain mainly rock and Hutton soil forms, while upper slope areas are dominated my Hutton, Mispah and Avalon soil forms. Lower slopes are dominated by Westleigh, Valsrivier and Glencoe soil forms, while valley bottom areas mainly contain Rensburg soil forms (Land Type Survey Staff, 1984).

CHAPTER 4 DESCRIPTION OF SOILS

4.1 INTRODUCTION

The aim of this chapter is to present the physical, mineralogical and geotechnical properties of the soils in the study area, as determined during field work and subsequent laboratory investigations. Chemical properties of the soils are discussed in Chapters 5 and 6. The soil sequence along the investigated transect is described and the variations in grading, geotechnical and mineralogical properties within and between the different soil units are shown.

4.2 METHODOLOGY

4.2.1 Field work

Fieldwork was carried out intermittently between January 1998 and June 1998. Twenty-eight test pits along a transect were excavated by means of a truck-mounted backactor (the positions of the test pits are shown in Figure 3.1). The test pits were excavated to a maximum depth of 2,40 m to determine depth to bedrock, pedological conditions and the possible presence of perched ground water bodies. All test pits were logged according to the MCCSSO (moisture, colour, consistency, structure, soil type and origin) method proposed by Jennings, Brink & Williams (1973). Eighty-eight disturbed samples were taken from individual horizons from the test pits for geotechnical, mineralogical and geochemical testing. Seven shallow holes were excavated to a depth not exceeding 0,60 m to take soil samples from the upper soil profile.

4.2.2 Laboratory work

Eighty-eight samples were tested for their geotechnical properties. Thirty samples are from the tailings and the remaining fifty-eight are from the underlying soils. A schedule of the routine soils testing and the methods used appears in Table 4.1.

Table 4.1 Schedule of the routine soils testing and test methods.

Soil property	**Standard / Method / Equipment**
Grain size distribution	ASTM, D 422 & D4318-95 (1996)
Atterberg limits	TMH 1 (1990)
Soil classification	Unified Soil Classification System (ASTM, D2487 - 1969, (1970))
Degree of expansiveness	Van der Merwe (1964)
Mineralogical analyses	Quantitative XRD analyses with Philips XRD unit and Ziemans difrac 80 software

A summary of the grain size distribution analyses, Atterberg test results, soil classification and degree of expansiveness is presented in Table A.1 in Appendix A.

4.3 SOILS

Twenty-eight test pits were excavated along a transect as shown in Figure 3.1. The soils along the transect comprise sandy colluvial material between Test Pits 28 to 16, and clayey alluvial material between Test Pits 15 to 1. The alluvial soils were deposited by the Kromdraai Spruit, a seasonal stream which forms the south-eastern boundary of the study area.

4.3.1 Colluvial soil descriptions and geotechnical properties

The colluvial portion of the transect starts ±75 m north west of the remnants of tailings dam number 4 and extends for ± 480 m towards the south east (Figures 3.1 and 4.1). Forty-two representative samples (sample numbers MT 16/1 to MT 28/3) were taken, of which twenty-seven are soil samples and the remaining fifteen are tailings.

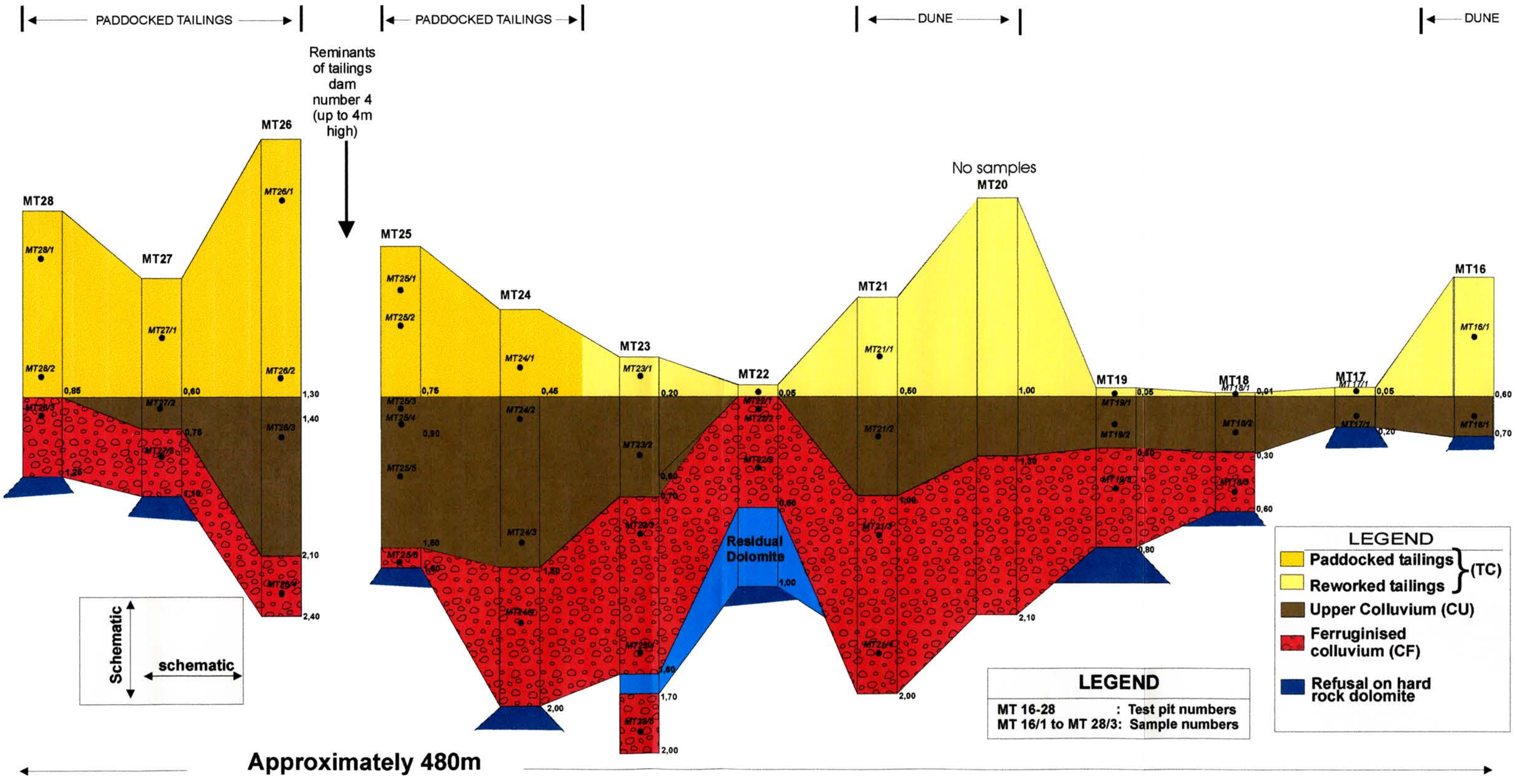


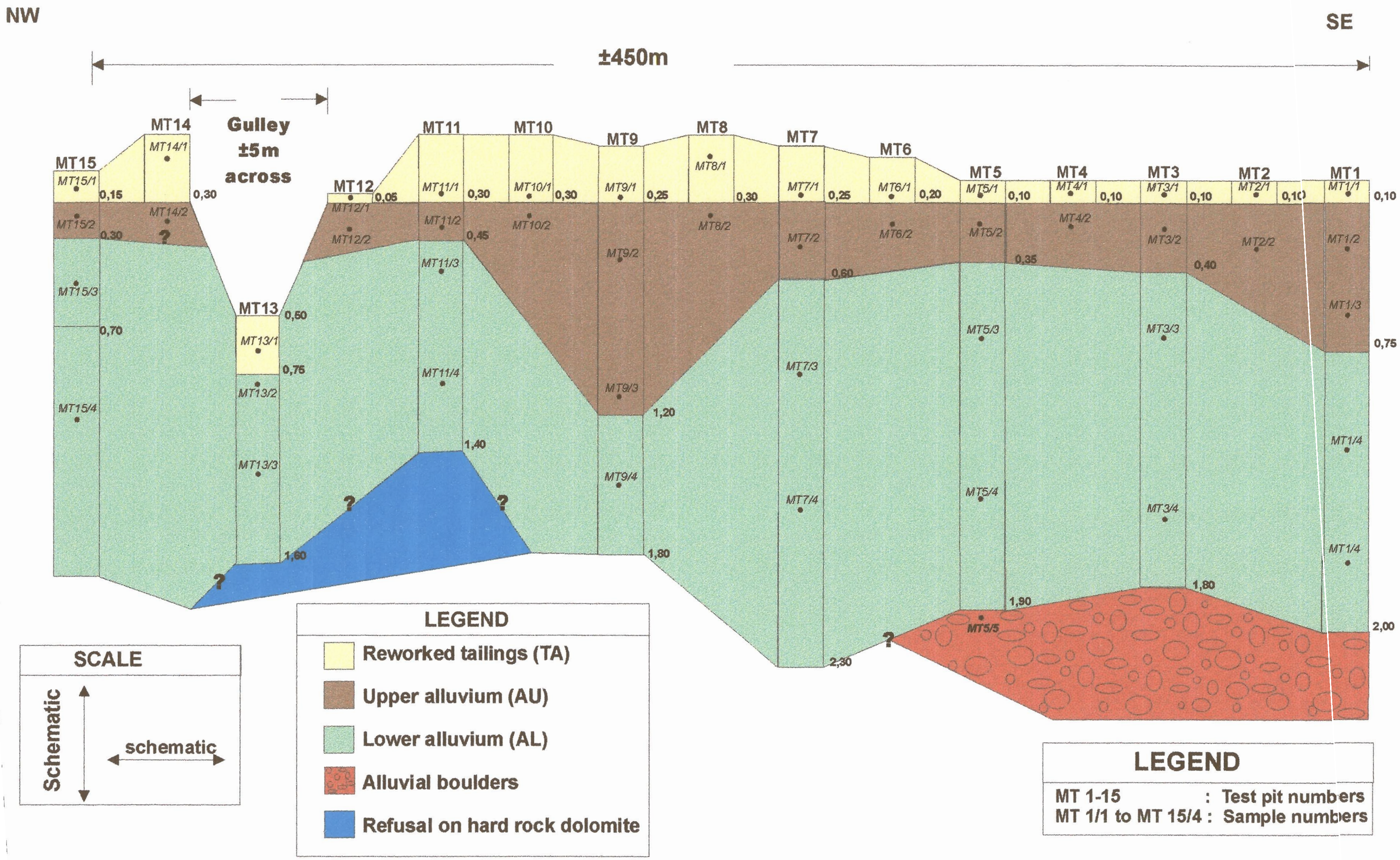
Figure 4.1 Schematic cross section of the colluvial soils and sampling positions

Two distinct soil units occur in the transect underneath the tailings (Figure 4.1). Between Test Pit 28 and 24 the tailings occur as *in situ* paddocked material. Towards Test Pit 16, the tailings occur as eaolian and sheetwash redistributed material. The two tailings units are discussed together as unit TC. Unit CU is a sandy colluvial topsoil unit which is normally underlain by a nodular ferruginised colluvial unit (CF). Unit CF is sometimes underlain by residual dolomite or hard rock dolomite of the Monte Christo Formation. Soil descriptions (after Jennings *et. al.*1979) and Unified Soil Classes of each unit are shown in Table 4.2

The sheetwash / aeolian reworked tailings is mainly composed of sand-sized particles, having on average 67 per cent sand, while the paddocked tailings is mainly composed of silt-sized particles, with silt constituting on average 58 per cent of the samples. Units CU and CF are mainly composed of sandy material with only the nodular ferrugenized unit (CF) having a considerable gravel component (19 per cent on average) consisting of iron / manganese concretions (nodules). All the soil units have a low expansiveness index, indicating that the soils are not prone to swelling.

4.3.2 Alluvial soils description and geotechnical properties

The alluvial soils overlain by reworked gold mine tailings were investigated by means of eight deep test pits and seven shallow test pits (Figure 4.2). The deeper test pits (Test Pits 1, 3, 5, 7, 9, 11, 13 and 15) serve to identify the underlying soils and accommodate sampling, while the remaining shallow test pits were excavated to a depth not exceeding 0,60 m for sampling the upper soil units. This portion starts ±230 m south east of the remnants of tailings dam number 4, progressing ± 480 m south east and terminating on the bank of the Kromdraai Spruit (Figure 3.1). Three characteristic soil units were identified (Figure 4.2) from which thirty-one soil samples and fifteen tailings samples (sample numbers MT1/1 to MT15/4) were taken. Unit TA represents the reworked tailings while AU is an alluvial topsoil unit. Unit AL represents alluvial subsoil which occurs underneath unit AU. Profile descriptions and Unified Soil Classes of each unit are shown in Table 4.3.



igure 4.2 Schematic cross section of the alluvial soils and sampling positions

Table 4.2 Colluvial soil unit description and percentage of Unified Soil Classification classes for each soil unit

Soil unit	**Soil Description**	**Number of samples**	**(percentage) U.S.C.S. class**
Colluvial soils			
TC	Slightly moist, pale yellow brown to light grey, very soft, intact silt; Paddocked or sheetwash and aeolian deposited tailings.	15	(60 %) SM (40 %) ML
CU	Slightly moist, red brown to dark red brown, loose to occasionally medium dense, voided, silty to clayey sand; Colluvium. Unit CU is absent from test pits 22 and 28 indicating these to be disturbed soils.	12	(75 %) SC - SM (17 %) SM (8 %) SC
CF	Abundant coarse-, medium- and fine-grained, sub-rounded to rounded iron / manganese nodules in slightly moist to moist, pale yellow brown or red brown, clayey sand; Nodular ferruginised colluvium. The overall consistency is loose.	14	(50 %) SC - SM (36 %) SM (14 %) SC

SC = Clayey sand, SM = Silty sand, SC - SM = Silty clayey sand, ML = Silt

Table 4.3 Alluvial soil unit description and percentage of Unified Soil Classification classes for each soil unit

Soil unit	**Soil Description**	**Number of samples**	**(percentage) U.S.C.S. class**
Alluvial soils			
TA	This unit is composed of sheetwash and aeolian deposited tailings, consisting of slightly moist, pale yellow brown to light grey, very soft, intact silt.	15	(73 %) ML (13.5 %) CL (13.5 %) SM
AU	Moist, dark grey or dark brown mottled yellow brown, soft to stiff, slightly to distinctly shattered, clay or sandy clay; Alluvium. Monoclinic gypsum crystals (up to 2 cm in length) occur in test pits 9 and 11.	16	(75 %) CL (25 %) CH
AL	Moist, dark grey to dark olive grey, mottled light yellow brown and white, soft to firm with depth, intact or slightly shattered to shattered with depth (slickensided in test pit 11), clay or sandy clay with occasional medium- and fine-grained calcrete and scattered ferricrete nodules with depth. Small sand lenses were observed in test pit 5. Gypsum crystals occur in test pits 9, 13 and 15.	16	(50 %) CL (44 %) CH (6 %) SC

CL = low plastic clay, CH = highly plastic clay, SC = Clayey sand, SM = Silty sand, ML = Silt

The tailings unit (TA) is mainly composed of silt-sized particles, having on average 17,35 per cent clay, 53,89 per cent silt and 28,67 per cent sand. The alluvial topsoil unit AU is composed of approximately equal parts of clay, silt and sand, having on average 36,02 per cent clay, 29,67 per cent silt and 33,49 per cent sand. The alluvial subsoil (unit AU) has however a higher clay content, being on average 43,87 per cent. All the soil units usually have medium to high expansiveness indices, showing the material to be prone to swelling and shrinkage as soil moisture content varies.

4.4 TAXONOMIC CLASSIFICATION AND GENERAL DESCRIPTION OF THE SOILS

According to the South African soil classification system (Soil Classification Working Group, 1991) the colluvial soils are classified in either the Bainsvlei form (profiles MT21, 23, 24 and 25) or the Westleigh form (profiles MT18, 19 and 27)). The diagnostic horizon sequence for the Bainsvlei form is Orthic A / Red apedal B / Soft plinthic B. The Orthic A horizon is just an ordinary topsoil with no special features. The Red apedal B horizon is a structureless to weakly structured well aerated horizon. The Soft plinthic B horizon is a horizon with abundant high chroma (bright red and / or yellow) mottles and / or iron or iron / manganese concretions (nodules) in a soil matrix having at least some grey colours. The Soft plinthic B horizon indicates a layer in which a fluctuating water table, and consequently alternating reducing and oxidizing conditions, is found. In the South African Highveld it has been observed that very intensive lateral movement of water occurs in this layer and that large quantities of dissolved ions are also transported laterally in the process (MC Laker, personal communication). The latter is especially the case for elements which become more soluble in the reduced state. According to the USDA's Soil Taxonomy (Soil Survey Staff, 1975), one of the two international reference soil classification systems, the Bainsvlei and Westleigh soils are both classified as Plintustalfs.

The soils on the alluvial terrace of the Kromdraai Spruit are classified as Rensburg soils according to the South African soil classification system (Soil Classification Working Group, 1991). The diagnostic horizon sequence for the Rensburg form is Vertic A horizon / G horizon.

A Vertic A horizon is a topsoil which has a high content of swelling clays. A G horizon is a sticky clay horizon with dull colours reflecting permanent waterlogging, i.e. a permanent condition of poor aeration (reducing conditions). In the USDA's Soil Taxonomy it is classified as a Vertic Haplaquept.

4.5 MINERALOGICAL COMPOSITION

The mineralogical compositions of the some tailings as well as alluvial and colluvial samples are contained in Table B.1 in Appendix B. Sixty one samples were analysed for their mineralogical composition. These samples include all the alluvial soils and a portion of the colluvial and tailings samples. The averaged mineralogical compositions of the tailings, alluvial and colluvial soils are shown in Table 4.4.

Table 4.4 Average mineralogical compositions of the some tailings, colluvial and alluvial soil samples.

Soil unit	**n**	**Ca**	**D**	**Sid**	**H/G**	**J**	**G**	**T**	**M**	**P**	**Q**	**Mi**	**C**	**S**	**I/S**
TC, TA	20	0,1	0,1	0	0	3,6	0,1	0	0	0,1	84,9	4,3	0,8	1,2	4,7
CU	5	0	0	0	1,2	0	0	1,2	1,2	0	89,4	0,6	0	0	6,8
CF	4	0	0	0	5,3	0	0	14	0	0	70,3	0	0	0	13,7
AU	16	0	0,2	0	0	0	3,4	0	0,9	0,4	78,8	0,3	0	13,4	2,6
AL	16	0,9	0	0,2	0	0	0,1	0	0	0,1	80,8	0,1	0	16,4	1,4

n = number of samples, Ca = calcite, D = dolomite, S = siderite, H/G = haematite / goethite, J = jarosite, G = gypsum, T = todorokite, M = microcline, P = plagioclase, Q = quartz, Mi = mica, C = chlorite, S = smectite, I/S = Illite / smectite interstratification

The tailings material, units TC and TA, is mainly composed of quartz, mica, jarosite and illite / smectite interstratification with calcite, dolomite, gypsum, plagioclase, chlorite and smectite present in trace quantities. The presence of jarosite ($3[KFe^{3+}(OH)_6(SO_4)_2]$ indicates that the tailings produce sulphate, as would be expected during acid mine drainage.

The colluvial topsoil, unit CU (representing Orthic A and Red Apedal B horizons), consists mostly of quartz with lesser amounts of haematite / goethite, todorokite, microcline, mica and clay minerals reported as illite / smectite interstratification. The underlying nodular concretionary layer, unit CF (represents Soft plinthic B horizons), shows higher haematite / goethite, todorokite and clay mineral content in the form of illite / smectite interstratifications, as could be expected from a Soft plinthic horizon. Haematite and goethite are Fe-oxide minerals (Fe_2O_3 and α-FeOOH respectively) while todorokite is a Mn-oxide mineral ($NaMn_6O_{12}\cdot 3H_2O$). The Mn-oxide mineral content in the concretions / nodular ferricrete exceeds the Fe-oxide mineral content. The latter is not unexpected in view of the Mn rich dolomite underlying the study area.

The alluvial topsoil, unit AU (representing the Vertic A horizon), is mostly composed of quartz and smectite with lesser quantities of gypsum. Dolomite, microcline, plagioclase and mica occur in trace concentrations. The presence of gypsum,($4[CaSO_4\cdot 2H_2O]$), in excess of 20 per cent in the alluvial topsoil samples MT11/2 and MT13/2, indicates that sufficient sulphate is produced in the tailings to enable the crystallization of gypsum in the topsoil. The underlying alluvial subsoils (unit AL) has less gypsum but increased concentrations of quartz and smectite as well as increased trace quantities of calcite. The presence of calcite ($CaCO_3$) indicates an increase in Ca^{2+} with depth in the alluvial soils. Siderite ($Fe^{2+}CO_3$) occurs in MT3/4, showing that reducing conditions occur with depth in Test Pit MT3. Unit AL represents G-horizons (i.e gleyed soil material). A G-horizon indicates practically permanent wetness and consequently poor aeration. The typical G-colours indicate that iron is in the ferrous (reduced) condition, which facilitates the formation of siderite. It is also logical to have less gypsum, which is relatively soluble, under such wet conditions.

4.6 SUMMARY

SOIL PROPERTIES

- The colluvial soils classify as Westleigh and Bainsvlei soil forms while the alluvium classifies as a Rensburg soil form according to the South African taxonomic soil classification system. According to the USDA's Soil Taxonomy the Bainsvlei and Westleigh soils are both classified as Plintustalfs while the Rensburg soil is classified as a Vertic Haplaquept.

GEOTECHNICAL PROPERTIES

- The tailings deposited on the colluvial soils show a higher sand fraction (50 - 74 per cent) when compared to the paddocked tailings (13 - 60 per cent) and the tailings deposited on the alluvial soils (4 - 60 per cent). This may indicate that the tailings deposited nearest to the remnants of tailings dam 4 has a greater aeolian component than the tailings deposited on the floodplain of the Kromdraai Spruit. The tailings on the floodplain shows a decrease in sand content towards the Kromdraai Spruit which is consistent with the aeolian and sheetwash depositioning processes where finer material are deposited farthest away from the source (Reading, 1996).

- The colluvial soils are sandy, having an average clay content of 10 per cent and an average sand component of 59 per cent. The alluvial soils are however clayey with an average clay content of 37 per cent and an average sand content of 33 per cent.

- The soil profiles at Test Pits MT22 and MT28 are disturbed as the colluvial topsoil unit (CT) is not present. The colluvial topsoil is characterized by a lateral increase in clay content towards the alluvial soils (Test Pit MT15). There is also a decrease in sand content and an increase in gravel content with depth as the nodular ferruginised unit (CF) is encountered. Unit CF usually exhibits a slightly increased clay content when compared with the overlying soils.

- The alluvial soils usually show an increase in clay content with depth with a corresponding decrease in sand-sized particles. Unit AU (alluvial topsoil) shows a lateral increase in clay content towards the Kromdraai Spruit.

MINERALOGICAL COMPOSITION

- The tailings is mainly composed of quartz, mica, jarosite and illite / smectite interstratification while calcite, dolomite, gypsum, plagioclase, chlorite and smectite are present in trace quantities.

- Unit CU consists mostly of quartz with lesser amounts of haematite / goethite, todorokite, microcline, mica and undifferentiated clay minerals. Unit CF has a higher haematite / goethite, todorokite and clay mineral content than unit CU. The Mn - oxide content (todorokite) exceeds the Fe-oxide mineral content in unit CF.

- Unit AU is mostly composed of quartz and smectite, while it contains lesser quantities of gypsum and dolomite, microcline, plagioclase and trace concentration of mica. The underlying unit AL has less gypsum, but increased concentrations of quartz and smectite as well as increased trace quantities of calcite .

CHAPTER 5 GOLD MINE TAILINGS AS A SOURCE OF CONTAMINATION

5.1 INTRODUCTION

The purpose of this chapter is to show that the gold mine tailings at Machavie gold mine is a source of trace element contamination. Trace element concentrations in the sulphates of the ore were determined, as well as the concentrations of certain water soluble trace elements in salts that precipitated on the surface of the reworked tailings, down-slope of tailings dam number 4. The pH and electrical conductivity (EC) of tailings covering the investigated soils were determined. Soils underlying the derived tailings were also tested for pH and EC to establish if acidic leachate, originating from the tailings, has affected the underlying soils.

The extent of contamination in the investigated areas is characterized by comparing total trace element concentrations in the tailings and soils with the Dutch soil standards after Moen, Cornet & Evers (1986).

5.2 METHODOLOGY

For geochemical analyses, all soil samples were dried at 40°C and disaggregated by using a mortar and pestle. Visible organic matter was removed. The samples were sieved to obtain the finer than 2 mm soil fraction which was milled to be finer than 75 micron. Powder briquettes were pressed from the < 75 micron fraction, using a PVA binder. The samples were analysed for their trace element content with a Philips PW 1606 Simultaneous X-ray Fluorescence Spectrometer (SXRF) (Appendix C). The finer than 2 mm soil fraction is recommended for environmental studies by various authors (e.g. Schloemann (1994) and Alloway (1995)).

The paste pH (water) of all the samples was determined according to the TMH method

(THM1,1990). Electrical conductivity (EC) of the soil and tailings samples was determined according to the soil paste method (TMH1, 1990). The EC of a soil is an indirect measure of the total dissolved solids (TDS) present in a soil. TDS has a negative impact on plant growth due to increased osmotic pressure of the soil solution which inhibit water and nutrient uptake by plants. According to Deuel & Holliday (1994) most crops will be affected at an EC of greater than 400 mS/m, and this value is usually prescribed as a soil cleanup guideline.

5.2.1 Analyzed elements

The Philips PW 1606 Simultaneous X-ray Fluorescence Spectrometer analyses were done for the following elements: TiO_2%, MnO%, Fe_2O_3 t %, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Ba, W, Pb, Th, U. For this study, the elements As, Co, Cr, Cu, Ni, Pb and Zn were selected as they have adverse effects on human and livestock health, aquatic ecosystems as well as crop yield and soil sustainability, when present in elevated concentrations (Department of Water Affairs and Forestry[1,2,3,4],1996). In addition, all these elements (except Co) appear on the priority pollutants list of the United States Environmental Protection Agency (Deutsch, 1997).

Table 5.1 Detection limits for the Philips PW 1606 Simultaneous X-ray Fluorescence Spectrometer (after Elsenbroek, 1996). All values in mg/kg.

	As	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Udl	412	210	2900	1230	2380	636	680
Lld	10	10	4	9	10	4	3

Udl = Upper detection limit and Lld = lower limit of detection.

5.3 TAILINGS AS A SOURCE OF TRACE ELEMENT CONTAMINATION

Trace elements that are geochemically associated with sulphide minerals (e.g. pyrite) are termed chalcophile and include (amongst others) Cd, Cu, Ag, Au, Zn, Hg, Pb, As, Sb, Se, Tl and Mo

(Alloway, 1995). Barton & Hallbauer (1996), ascribe the gold/sulphide mineralisation present in the Black Reef Formation to sedimentological deposition of gold bearing sulphate minerals at ~ 2500 Ma. Table 5.2 contains some maximum average trace element concentrations of pyrite of the Black Reef formation.

Table 5.2. The average maximum trace element content (AMTEC) of pyrite of the Black Reef Formation in mg/kg (after Barton & Hallbauer, 1996).

Element	**Cu**	**Co**	**Ni**	**Ba**	**Cd**	**Cr**	**Mn**	**Ag**	**Au**	**Bi**	**Sr**
AMTEC (ppm)	346	1006	1930	12	0,5	33	16	21	1,5	201	3
Element	**Ti**	**Pb**	**As**	**Zn**	**Na**	**Ca**	**Al**	**Mo**	**Te**	**Se**	**Sb**
AMTEC (ppm)	98	844	1394	90	224	1020	1317	14	21	<0,02	137

Ore samples from the Machavie waste rock dump were collected and crushed. The resulting material was sieved and the fraction finer than 0,150 mm and coarser than 0,075 mm was used to extract the sulphide minerals by means of a gravimetric procedure. Tetrabromoethane with a specific gravity of 2,96 was used to separate the sulphide minerals in the sample from the host rock minerals. The resulting material was analysed on a Philips X-ray diffraction unit which uses Ziemans diffrac 80 software. The sample is composed of 99 per cent pyrite and 1 per cent quartz. The trace element composition of these collected pyrite samples, as measured by the Philips PW 1606 Simultaneous X-ray Fluorescence Spectrometers, is presented in Table 5.3.

Table 5.3 Trace element composition (in mg/kg except Fe_2O_3 t and MnO) of pyrite of the Black Reef Formation from the discard ore dump at Machavie gold mine.

Fe*	**Mn****	**As**	**Ba**	**Co**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Sn**	**Th**	**U**	**V**	**Zn**
0 %	0,12 %	585	1151	2873	9502	420	0	561	0	0	0	0	99	266

**Fe as* Fe_2O_3 *(t) and* ***Mn as MnO*

It is evident from Tables 5.2 and 5.3 that the pyrite in the Black Reef Formation contains high concentrations of some trace elements, particularly As, Ba, Co, Cr, Cu, Ni and Zn. Since gold is associated with the pyrite in the ore of the Black Reef Formation (Barton & Hallbauer, 1996), pyrite rich material would have been mined at Machavie Gold mine. After processing the pyrite rich slimes, the resulting waste stream was then discarded as tailings dams. Tables 5.2 and 5.3 show that high concentrations of certain trace elements can be expected in the tailings dams. The tailings can therefore be regarded as a potential source of trace element contamination.

5.3.1 Salts precipitated on the tailings dams.

According to Lloyd (1997), salts precipitate on the surface of tailings dams as a result of upward capillary movement of salt-rich liquids. In times of water deficit (e.g. winter months in the North-West Province of South Africa) the salt-rich solutions evaporate and cause the deposition of salts. These salt deposits are usually soluble and rich in trace elements (Spotts, Schafer, Luckay, & Mitchell, 1997). Predominantly whitish and some yellowish salt precipitations were observed on the surface of reworked tailings as well as on the sides of the tailings dams. Plate 5.1 shows the extent of salt precipitation on the paddocked tailings adjacent to tailings dam number 4. Plate 5.2 shows a close-up of the precipitations.

Plate5.1

The extent of soluble salts deposited on the paddocked tailings adjacent to tailings dam number 4.

Plate5.2

Close-up of the yellowish and white soluble salts deposited on the paddocked tailings adjacent to tailings dam number 4.

Samples of both the yellowish and whitish precipitates were taken from paddocked tailings adjacent to tailings dam number 4. Mineralogical analyses showed that the whitish precipitate is composed of Halotrichite $Al_2Fe(SO_4)_4{\cdot}22H_2O$; Hexahydrite $MgSO_4{\cdot}6H_2O$; Alunogen $Al_2(SO_4)_3{\cdot}17H_2O$; Melanterite $FeSO_4{\cdot}7H_2O$ and Thenardite Na_2SO_4. The yellowish precipitate is mostly composed of Fe-sulphates, including compounds such as Coquimbite $Fe_2(SO_4)_3{\cdot}9H_2O$; Metavoltine $Na_6K_2Fe_7(SO_4)_{12}O_2{\cdot}18H_2O$ and Copiapite $Fe_{14}O_3(SO_4)_{18}{\cdot}63H_2O$.

The water soluble trace element content of the salts was determined by adding equal weights of each precipitate to de-ionised pure water (having a conductivity of 18 MΩ). Equal weights of precipitate and water were shaken for two hours and filtered through a Watmann number 40 filter paper. The resulting liquid was analysed for As, Cd, Co, Cr, Cu, Ni, Pb and Zn using the ICP-AES technique and the results are shown in Table 5.4.

Table 5.4 Water soluble concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn (mg/l) in the white and yellow precipitate occurring on the paddocked tailings.

Precipitate	**As**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
White	*bdl*	109,09	14,97	63,74	939,75	4,35	369,58
Yellow	303,26	30,37	15,01	40,78	93,79	34,13	113,81

bdl: Concentration below the detection limit of the ICP-AES instrument.

It is evident from the soluble trace element concentrations present in the sulphate precipitates that these sulphate salts, originating from the tailings dams, are a potential source of trace element contamination. In addition, these results also prove that leachate, rich in trace elements, is produced within the tailings.

5.4 THE INFLUENCE OF THE TAILINGS ON THE pH AND EC OF THE UNDERLYING SOILS

The gold mine tailings produces acidic leachate as discussed in Chapter 2, due to the oxidation of pyrite and other sulphide minerals. The acidity and associated trace elements will leach into the underlying soils under normal soil drainage conditions. There are a number of natural buffering reactions that occur in soils that can partially or completely neutralize the acidity. Cations and anions are released by these neutralization reactions and increase the total dissolved solids content (TDS) and the electrical conductivity of the soil solution (James, 1997). The production of sulphate during sulphide mineral oxidation will further increase the salt content of the soil. By examining the pH and conductivity of the soils of the study area, it can be established if the soils are affected by the overlying reworked tailings.

5.4.1 Tailings

Statistical analyses of all the tailings samples (n = 30) show the material to be strongly acidic with an average pH of 3,43. A minimum pH of 2,50 was measured in sample MT 25/1 and a maximum of 4,63 was measured in sample MT 16/1. These results confirm that the tailings produce acidic leachate. The acidity and associated trace elements will leach into the underlying soils under normal soil drainage conditions and adversely affect the pH of the underlying soils. The corrosiveness of the acidic leachate is shown in Plate 5.3 showing metal drums embedded in the tailings that are disintegrating.

Conductivity analyses of the tailings showed the material to have a conductivity ranging between 1,15 mS/m to 171,10 mS/m. These values are well below the threshold level of 400 mS/m.

Plate 5.3

Metal drums in tailings dam number 4, corroded due to the acid nature of the tailings.

5.4.2 Colluvial soils

Colluvial soil unit CU is very strongly acidic with a pH range of 3,26 - 4,70. The underlying nodular ferruginised unit CF is strongly to slightly acidic with pH values ranging from 3,13 - 6,30. The pH ranges of units CU and CF indicate that the colluvial soils underlying the reworked tailings have been acidified. There is generally an increase in soil pH with depth as shown in Figure 5.1, whereas the pH of the tailings showed an opposite trend with increasing depth.

The EC of unit CU ranges from 10,55 - 125,13 mS/m and in unit CF the EC range is 0,88 - 94,87 mS/m. The EC of all the colluvial soil samples is below the threshold value of 400 mS/m

5.4.3 Alluvial soils

The alluvial topsoil unit AU has a pH ranging from strongly acidic to neutral (3,17 - 7,73), but is usually less than 4,50. The alluvial subsoil unit (AL) has a pH ranging from 3,85 - 8,00 but is generally above 7,00. The pH ranges of both the alluvial topsoil and subsoil indicate that the soils have been acidified by the leachate generated in the tailings. The alluvial topsoils, however, are affected to a higher degree, usually displaying lower pH values. There seems to be an increase in soil pH with increasing soil depth (Figure 5.2).

The EC of unit AU ranges from 1,03 - 149,03 mS/m. The EC of the alluvial subsoil (unit AL) ranges from 2,89 mS/m - 200,61 mS/m. All the alluvial soils have EC values below the threshold of 400 mS/m.

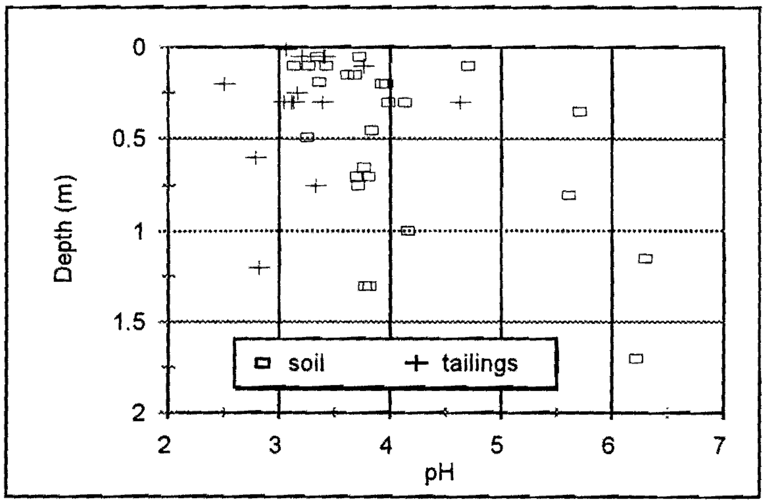


Figure 5.1 Relationship between soil and tailings depth and pH in the colluvial soils.

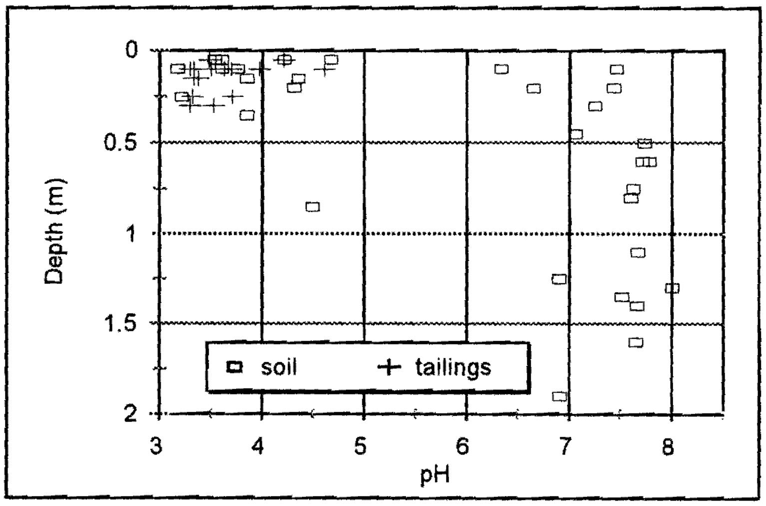


Figure 5.2 Relationship between soil and tailings depth and pH in the alluvial soils

5.5 TRACE ELEMENT SOIL CONTAMINATION

The majority of the soil samples overlain by reworked gold mine tailings show lower pH and higher EC values than found under natural soil conditions. These soils are therefore affected by the overlying tailings. The tailings produces acidic leachate that contains salts and trace elements in solution. The changes in pH will also affect the solubility and bio-availability of elements originally present in the soil. The aim of this portion of Chapter 5 is to investigate if the affected soils show trace element concentrations which are higher than would be expected under natural pedogenic conditions. This would indicate that the soils are contaminated by trace elements originating from the gold mine tailings. This aim is achieved by comparing the total trace element concentrations in the soils to the Dutch ABC threshold concentration values.

5.5.1 Trace element concentrations in the affected soils compared with guideline values

The Dutch ABC system uses a three tier approach to identify if soils or water are contaminated. The first tier concentrations (A-values) are those concentrations below which the soils or water are probably not contaminated. The second tier (B-values) indicate concentrations above which there is a need for further investigation. The last tier (C-values) are those concentration levels above which site clean-up is required, (Moen *et al.*, 1986). Table 5.5 shows the Dutch ABC concentration standards as well as the South African soil quality standards (after Steyn *et al.*, 1996) of the trace elements applicable to the study.

Table 5.5 Dutch ABC guideline concentrations and South African soil standards (mg/kg)

	As	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
SA standards	2	20	80	100	50	56	185
A - values	20	20	100	50	50	50	200
B - values	30	50	250	100	100	150	500
C - values	50	300	800	500	500	600	3000

The South African soil quality standards are generally lower or equal to the first tier concentration values of the Dutch system. For the purpose of this study the Dutch system is employed to assess the pollution status of the soils, as this tiered system can be used to determine both the degree of pollution and when soil cleanup is considered necessary. The South African system however, can only be used to determine if threshold concentrations are exceeded or not.

5.5.1.1 Tier one analyses (Dutch A - value screening)

The percentage and range of samples in the different soil groups that exceed the first tier Dutch concentrations (DATC values) are shown in Table 5.6. The total concentration of each element in samples from the different soil units was compared with the DATC value. The ratio by which each element exceeds the DATC value was determined by dividing the total element concentration in the sample with the DATC-standard (Table 5.5).

Table 5.6 Frequency (percentage of samples) and range of ratio's by which concentrations of selected elements exceed the Dutch A values (DATC) in the soils and tailings.

ELEMENT		**As**	**Co**	**Cr**	**Cu**	**Ni**	**Zn**
DATC VALUE (mg/kg)		**20**	**20**	**100**	**50**	**50**	**200**
SOIL UNIT	**NUMBER OF SAMPLES**	**FREQUENCY (PERCENTAGE OF SAMPLES THAT EXCEED DATC VALUES) AND RANGE OF RATIO'S BY WHICH DATC VALUES ARE EXCEEDED**					
TC & TA	30	(97%) 1,1 - 16,5	(37%) 1,2 - 4	(100 %) 1 - 5,2	(23%) 1 - 1,4	(53 %) (1 - 4)	(3%) 1,03
CU	11	(82 %) 0 - 4,6	(64%) 0 - 3,5	(91%) 1,5 - 4,1	(55%) 0 - 1,7	(73%) 0 - 3,1	(0 %) -
CF	14	(60 %) 1,1 - 1,5	(47%) 1,1 - 5,3	(100%) 1,3 - 7	(27%) 2,1 - 2,6	(100%) 1 - 6	(0 %) -
AU	16	(81 %) 1,1 - 2	(63 %) 1,1 - 6	(100 %) 1,4 - 2,1	(31 %) 1,1 - 1,7	(100 %) 0 - 4,5	(13 %) 1,3 - 1,5
AL	16	(63 %) 0 - 1,5	(38 %) 0 - 3,5	(100 %) 0 - 2,7	(0 %) -	(100 %) 0 - 4	(13 %) 0 - 1,2

It is evident from Table 5.6 that in unit CU, As, Co, Cr, Cu and Ni usually exceed the screening concentrations. Unit CF has excessive concentrations of As, Cr and Ni. Unit AU has excessive concentrations of As, Co, Cr and Ni, while in unit AL, As, Cr and Ni occur at excessive concentration levels in the majority of samples.

According to the Dutch tiered approach the soils underlying the tailings are most probably contaminated by the elements discussed with each soil unit. Lead concentrations in the affected soils never exceed the screening concentrations while zinc concentrations rarely exceed the screening concentrations in the study area.

5.5.1.2 Tier two screening (Dutch B concentrations)

The Dutch B threshold concentration values (DBTC) were used to establish which elements identified during the tier one analyses should be subjected to further study. The same approach was followed as with the tier one analyses, but the B-value concentrations were used. Lead and Zn concentrations did not exceed the DBTC values of 150 mg/kg and 500 mg/kg respectively, in any of the soil samples and are therefore not shown in Table 5.7.

None of the investigated trace element concentrations exceeded the DBTC values in the alluvial subsoil (unit AL). Arsenic exceeds the threshold concentration of 30 mg/kg in 83 per cent of the tailings samples (units TC and TA) while Cr and Ni occasionally exceed their guideline concentrations. This indicates that the tailings is a source of As and possibly Cr and Ni which should be further investigated. The alluvial topsoil (unit AU) shows occasional concentrations of As, Co and Ni which exceed the DBTC standards. In the colluvial topsoil (unit CU) chromium often exceeds the threshold value and As, Co and Ni occasionally exceed their respective guideline values. In unit CF chromium usually exceeds the DBTC value, while Co, Cu and Ni are occasionally present in elevated concentrations. According to the Dutch A B C system, the tailings and soils should be subjected to further investigation in regard to As, Co, Cr, Cu and Ni.

Table 5.7 Frequency (percentage of samples) and range of ratio's by which concentrations of selected elements exceed the Dutch B (DBTC) values in the soils and tailings.

ELEMENT		**As**	**Co**	**Cr**	**Cu**	**Ni**
DBTC VALUE (mg/kg)		**30**	**50**	**250**	**100**	**100**
SOIL UNIT	**NUMBER OF SAMPLES**	**FREQUENCY (PERCENTAGE OF SAMPLES THAT EXCEED DBTC VALUES) AND RANGE OF RATIO'S BY WHICH DBTC VALUES ARE EXCEEDED**				
TC & TA	30	(83%) 0 - 11	(0 %) -	(20 %) 0 - 2	(0 %) -	7 % (0 - 2)
CU	11	(33 %) 0 - 3	(8%) 1,4	(58%) 0 - 1,6	(0 %) -	(25%) 0 - 1,5
CF	14	(0 %) -	(7%) 2,1	(50%) 0 - 2,8	(28%) 0 - 1,3	(28%) 0 - 3
AU	16	(19%) 0 - 1,3	(19%) 0 - 2,3	(0 %) -	(0 %) -	(12%) 0 - 2,3
AL	16	(0 %) -	(0 %) -	(0 %) -	(0 %) -	(0 %) -

5.5.1.3 Tier three screening (Dutch C concentrations)

If the concentration of a particular element exceeds the Dutch - C value concentration screening levels, it indicates that cleanup of such an element is required at the site. The same approach was followed as with the tier one analyses but the C-value concentrations were used.

Arsenic exceeds the DCTC concentration level of 50 mg/kg in 73 per cent of the tailings samples (units TC and TA) by a range of 0 - 6,6 times the screening concentration. This threshold concentration was also exceeded in sample MT24/2 of unit CU. The other elements all occurred in concentrations below the DCTC screening levels.

5.6 VERTICAL AND LATERAL TRACE ELEMENT CONCENTRATION TRENDS

5.6.1 Vertical concentration trends

Trends in vertical trace element concentrations were investigated by plotting the concentrations of As, Co, Cr, Cu, Ni, Pb and Zn as a function of sample depth and the soil unit from which the sample was obtained (Figure 5.3). Vertical concentration trends for each element are discussed below:

Arsenic

From Figure 5.3 it is clear that there is a distinct pattern in As concentration with depth. The highest As concentrations occur in the tailings units (TC and TA) which overlie the transect. Arsenic concentrations are usually higher than 50 mg/kg in the tailings units. In the underlying soils, As is usually present in concentrations less than 50 mg/kg. There is no distinct difference between As concentrations in the upper alluvial soil (unit AU) and the lower alluvial soils (unit AL). Although the distribution pattern is not distinct, it can be seen that As concentrations in the upper colluvial soils (unit CU) is usually higher than in the underlying unit CF. The lowest As concentrations were measured in the alluvial and colluvial subsoil units AL and CF.

Cobalt

Cobalt concentrations are usually less than 35 mg/kg in the overlying tailings units. The highest Co concentrations occur in the upper alluvial soils (unit AU). Although the distribution patterns are not distinct, it seems that Co concentrations are generally higher in unit AU than in unit AL and that unit AU generally has higher Co concentrations than the upper colluvial soils, unit CU. Somewhat higher Co concentrations occur in unit CU compared with the underlying unit CF, although an anomalously high Co concentration of 106 mg/kg occurs in sample MT18/3.

Chromium

The chromium concentrations in the overlying tailings units vary between 112 and 516 mg/kg and is not distinctly higher than the underlying soils. Somewhat higher Cr concentrations sometimes occur in the underlying alluvial subsoil unit AL compared with the overlying alluvial unit AU. The highest Cr concentrations occur in the colluvial subsoil, unit CF (133 - 700 mg/kg) and Cr concentrations are usually higher in unit CF than in the overlying unit CU. Higher Cr concentrations usually occur in units CU and CF when compared with units AU and AL.

Copper

The Cu concentrations in the tailings vary between 11 - 72 mg/kg and is usually not higher than in the underlying soils. In addition the lowest Cu concentrations in the transect were measured in some of the tailings samples. The upper alluvial soils (unit AU) usually has higher Cu concentrations than the underlying unit AL. Although the highest Cu concentrations were measured in some colluvial subsoils, unit CF does not always have higher Cu concentrations than the overlying unit CU.

Nickel

The Ni concentrations in the overlying tailings are usually lower than in the underlying soils. The Ni concentrations of the overlying alluvial soils (unit AU) are usually higher than the underlying unit AL (except for samples MT13/2 and MT15/3). Similar to Cr and Cu, the highest Ni concentrations were measured in the colluvial subsoils, but from Figure 5.3 it is evident that unit CF does not always have higher Ni concentrations than the overlying unit CU.

Lead

There is generally less Pb in the tailings than in the underlying soils. From Figure 5.3 it can be seen that the Pb concentration in the lower alluvial soils (unit AL) is usually higher than the upper alluvial soils (unit AU). Similar to Cr, Cu and Ni concentrations, the highest Pb concentrations were measured in the colluvial subsoils, but unit CF does not always have higher Pb concentrations than the overlying unit CU.

Zinc

The Zn concentration of the upper alluvial unit (AU) is usually higher than the Zn concentration of the overlying tailings as well as the underlying alluvial subsoil (unit AL). No clear concentration distribution pattern can be observed in the colluvial soils as Zn concentrations in units CU and CF are comparable.

5.6.1.1 Discussion of vertical trace element concentration trends

The vertical concentration trends are summarised below and some of the trends are followed by a short discussion which aims to give reasons for the trends that will be further explored in Chapter 6.

- **Arsenic concentrations in the tailings are usually higher than in the underlying soils.** This indicates that the tailings are a source of As contamination. The As could be insoluble and as a result not be able to leach into the underlying soils.
- **The Cr concentration of unit CF is in general higher than the Cr concentration of the overlying unit CU.** Dissolved chromium present in the soil moisture may be preferentially adsorbed on the Fe and Mn oxides which occur in CF.
- **Concentrations of Co, Cu, Ni and Zn is in general higher in the overlying alluvial unit AU than in the underlying unit AL.**
- **Lead and to a lesser extent Cr have higher concentrations in the underlying unit AL than in the overlying AU.**

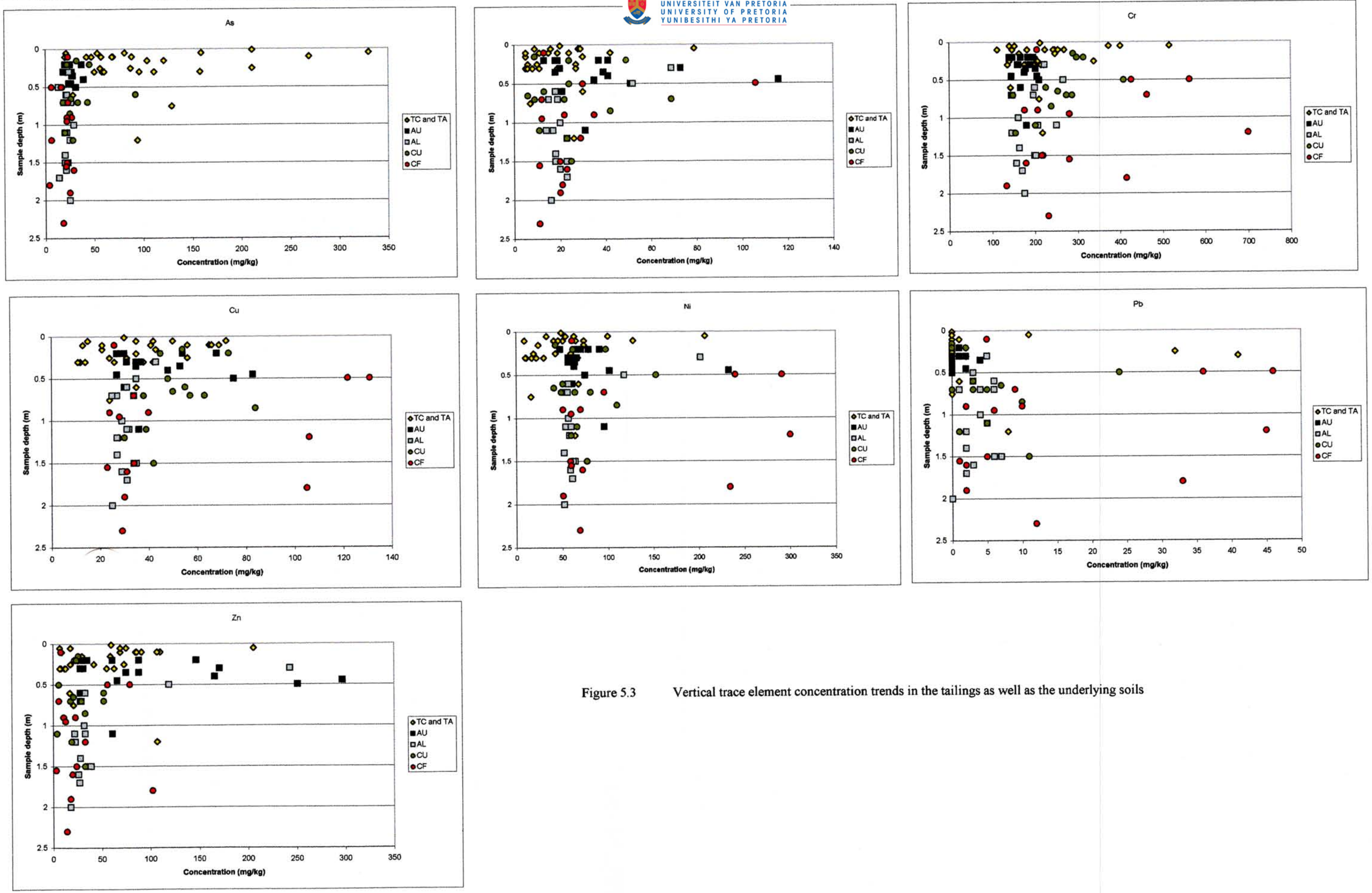


Figure 5.3 Vertical trace element concentration trends in the tailings as well as the underlying soils

5.6.2 Lateral concentration trends

Lateral trends in trace element concentrations were investigated for the transect from test pit MT28, closest to the tailings dams in the north west, to test pit MT1 farthest from the dams and closest to the Kromdraai Spruit in the south east. The lateral trace element concentration trends in the transect are discussed by comparing the trace element concentration in the tailings (units TC and TA) with the trace element concentrations in the soil unit directly underlying the tailings (usually units AU and CU except in test pit MT13 where AL underlies the tailings and MT22 and MT28 where unit CF underlies the tailings) (Refer to Figures 4.1 and 4.2). The vertical dotted lines in Figure 5.4 indicate the area between test pits MT24 and MT23, where the paddocked tailings stop, and pit MT15, at the transition between the colluvial and alluvial soils, respectively. A two test pit moving average was used to decrease scattering and to emphasise any trends. Lateral geochemical trends are discussed separately for each element:

Arsenic

Arsenic concentrations are always higher in the tailings than in the underlying soil. The highest As concentration in the tailings occurs between test pits MT15 and MT16, where the colluvium grades into the alluvium. The highest arsenic concentrations occur in the soils underlying the paddocked tailings (between MT28 and MT25). A slight increase in As concentration, similar to the tailings, occurs between test pits MT15 and MT16, at the contact of the colluvial and alluvial soils.

Cobalt and Nickel

Cobalt and Nickel display similar geochemical trends and are discussed together. Cobalt and Ni concentrations are generally lower in the tailings than in the underlying soil, except in the vicinity of MT15, at the contact of the colluvial and alluvial soils. For both elements an increase in concentration occurs from test pit MT7 towards the Kromdraai Spruit. The lowest Co concentrations in the colluvial soil occur underneath the paddocked tailings, at the contact of the colluvial and alluvial soils and between test pit MT4 and the Kromdraai Spruit. This relationship is not as distinct for Ni. A localised Ni high occurs in the colluvial soil at test pit MT23, adjacent to the paddocked tailings. A similar localised Co high occurs in the colluvial soils at test pit MT21. In general, the highest Co and Ni concentrations in the soil occur in the alluvial topsoil, with a maximum at test pit MT11. A general decrease in Co and Ni concentration is observed along the alluvial transect as the Kromdraai Spruit is approached.

Chromium

Chromium concentrations in the paddocked tailings are usually lower than in the reworked tailings overlying the colluvial soil. The reworked tailings overlying the alluvial soils show an increased Cr concentration between test pit MT7 and the Kromdraai Spruit. The highest Cr concentration in the tailings occurs at the transition of the colluvial soils into the alluvial soils. In the colluvial topsoils the lowest Cr concentration occurs underneath the paddocked tailings while the highest Cr concentration occurs at MT23, underneath the transition between the paddocked and the reworked tailings. The alluvial topsoils usually contain less Cr than the upper colluvial soils and a general decrease in Cr concentration occurs between MT15 and the Kromdraai Spruit.

Copper

The copper concentration in the tailings is usually less than in the underlying soils, except between test pit MT7 and the Kromdraai Spruit. A peak in Cu concentration is present in the tailings at the transition of the colluvial soils into the alluvial soils. In the colluvial soils Cu is usually less (except at MT25) where the upper soils are underlain by paddocked tailings. In the upper alluvial soils there is a general decrease in Cu concentration towards the Kromdraai Spruit. The highest Cu concentration occurs in the alluvial soil at MT11.

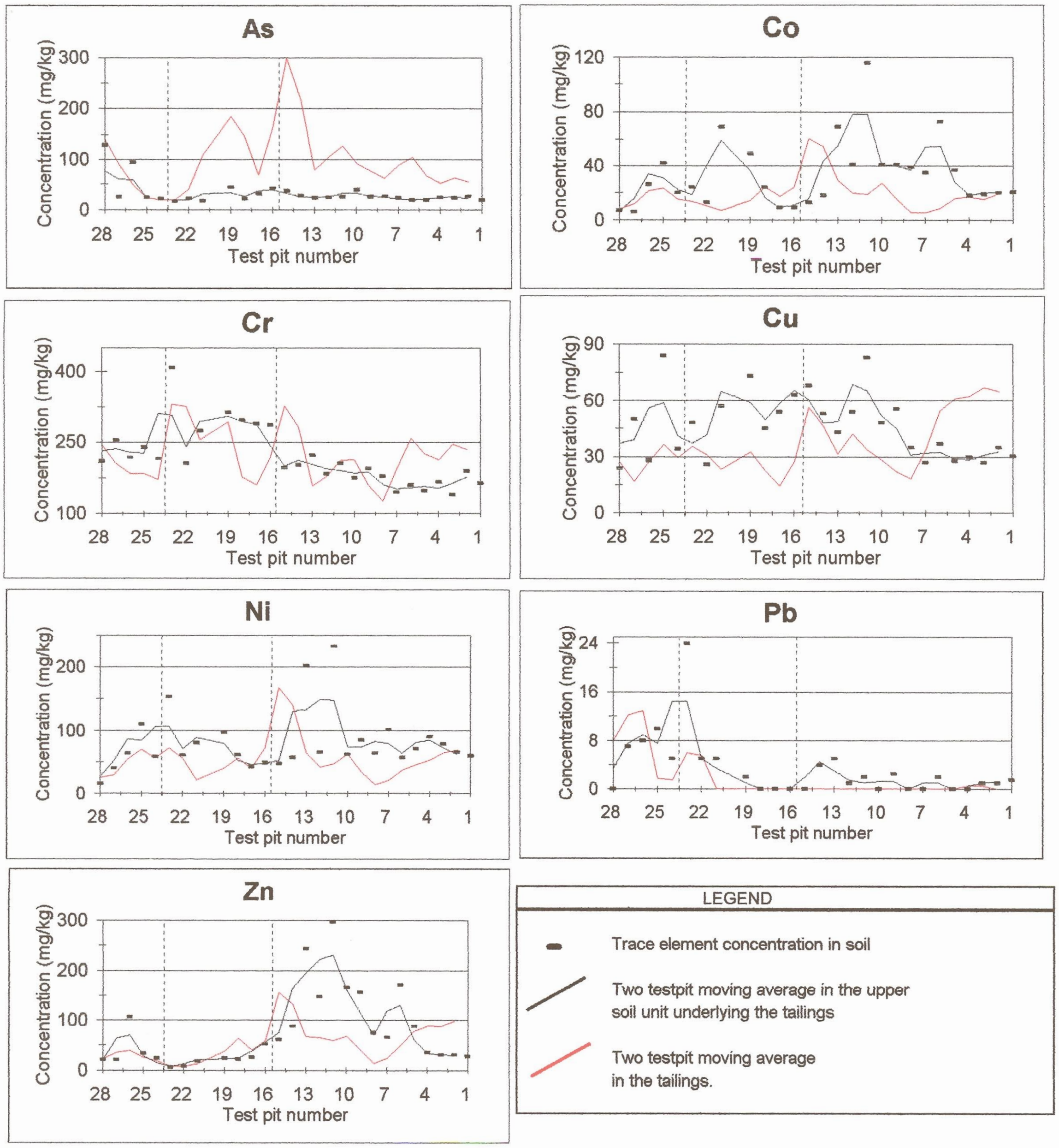


Figure 5.4 Lateral trace element concentration trends in the upper soils and overlying tailings of the investigated transect

Lead

The highest Pb concentrations in the tailings and the soils, occur above the colluvial portion of the transect. In the tailings overlying the colluvial portion of the transect, higher Pb concentrations occur in the paddocked material (MT24 to MT28), while lower Pb concentrations occur in the reworked tailings (MT23 to MT16). In the colluvial soils, a localised Pb high (similar to Cr and Ni) occurs at MT23. The Pb concentration of the upper colluvial soils is in general more than in the alluvial portion of the transect and a general decrease in Pb content is evident in the upper alluvial soils as the Kromdraai Spruit is approached.

Zinc

There is in general less Zn in the tailings than in the underlying soils. Similar to Co, Cu and Ni the highest Zn concentration in the tailings occurs at MT15 where the colluvial soils grade into the alluvial soils. The same increase in element concentration in the tailings is also evident from MT7 towards the Kromdraai Spruit. Zinc concentrations in the colluvial soils are lower than in the alluvial portion of the transect (between MT15 and MT5). Similar to Co, Cu and Ni a localised Zn high occur at MT11.

5.6.2.1 Discussion of lateral trace element concentration trends

The purpose of this section is to summarise lateral trace element concentration trends as observed along the transect in the tailings and the upper portions of the soils underlying the tailings. Some of the trends are followed by a short discussion which aims to give a reasons for the trends that will be further explored in Chapter 6 of this document:

- **In the tailings all the investigated element concentrations except Pb, show a localised high concentration at MT15**. It is at this portion of the transect where the sandy colluvial soils grade into the clayey alluvial soils. Lateral soil moisture movement will reduce as the clayey soils are reached, which may cause soil moisture flow lines to reach the surface. This is an example of the "seepage line" effect that is found in some soil toposequences. Trace elements in solution may then be deposited due to evaporation, causing a localised enrichment in trace element content.

- **In the tailings Co, Cr, Cu, Ni, and Zn show an increase in concentration from MT7 towards the Kromdraai Spruit**. This trend is significant as it shows that higher trace element concentrations occur near the stream, indicating that these elements can enter and affect the surface water environment. This indicates a potential water pollution hazard.
- **In the colluvial portion of the transect Ni, Pb and Cr show high concentrations at MT23, adjacent to the paddocked tailings**.
- **In the alluvial portion of the transect Co, Cu, Ni and Zn show high concentrations at MT11**. This portion of the alluvial transect has a thin vertic A horizon overlying the G-horizon. As the G-horizon has a diagnostically high water content, the observed high element concentrations may be due to evaporation forces which draw water to the A horizon through capillary action. The evaporating water will concentrate dissolved elements in salts which precipitate as the water evaporates, thus enriching the trace element content of the upper soils.

5.7 SUMMARY

INVESTIGATED ELEMENTS

- Of the group of elements determined by the Philips PW 1606 Simultaneous X-ray Fluorescence Spectrometer, only concentrations of As, Co, Cr, Cu, Ni, Pb and Zn were used in the study. These elements, when present in elevated concentrations, have adverse effects on human and livestock health, aquatic ecosystems, crop yield and soil sustainability,.

GOLD MINE TAILINGS AS A SOURCE OF TRACE ELEMENT CONTAMINATION

- The tailings dams of the study area were constructed with slimes produced by milling of ore from the Black Reef Formation. Pyrite was shown to be the principal sulphide mineral in the ore of that formation. Laboratory analyses as well as literature studies show the pyrite to contain high concentrations of As, Ba, Co, Cr, Cu, Ni and Zn. Salts composed of iron-, sodium potassium iron-, aluminum iron-, magnesium-, aluminum- and sodium sulphates precipitate on the tailings due to capillary rise and subsequent evaporation of salt-rich liquids. These salts were demonstrated to have very high water soluble concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn. The tailings are therefore a potential source of trace element pollution.

GOLD MINE TAILINGS IS A SOURCE OF ACIDITY

- It is well known that sulphide-rich gold mine tailings produces acidic leachate due to the oxidation of sulphide minerals in the presence of oxygen and water. The tailings covering the soils in the study area has an average pH of 3,43 indicating that this material produces acidic leachate. These acidic solutions have affected the underlying soils as the pH of the topsoils underlying the tailings are all significantly lower than what would be expected under natural pedological conditions.

SOIL POLLUTION ASSESSMENT

- The acidic leachate produced in the tailings cover, contains dissolved trace elements which will contaminate the soil through which the leachate permeates. In order to assess the extent to which the soils are contaminated by trace elements, the concentrations of As, Co, Cr, Cu, Ni, Pb and Zn in the soil and tailings samples were compared with the Dutch soil quality guidelines.

- According to the Dutch soil quality guidelines the tailings is a potential source of As, Cr and Ni. Unit CU is contaminated with As, Co, Cr and Ni while unit CF has elevated concentrations of Cr, Co, Cu and Ni. Unit AU is contaminated with As, Co and Ni. The alluvial subsoil (unit AL) has no trace elements exceeding guideline concentrations.

- Arsenic was identified as a priority pollutant according to the Dutch-C screening values.

VERTICAL TRACE ELEMENT CONCENTRATION TRENDS

Tailings

Arsenic concentrations in the tailings samples are distinctly higher than in the underlying soils whereas Ni, Pb and to a lesser extent Co and Cu concentrations are usually less in the tailings than in the underlying soils.

Colluvial soils

The Cr concentration of unit CF is in general higher than the Cr concentration of the overlying unit CU. For As and Co there seems to be a general decrease in concentration with depth from unit CU to unit CF. Chromium, Cu, Ni and Pb show the highest concentrations in unit CF, but there is no clear concentration trend regarding unit CU and the underlying CF. The Zn concentrations of units CU and CF are comparable and also show no clear concentration with depth trends.

Alluvial soils

Arsenic concentrations show no clear trends as As concentrations in unit AU are comparable with those in unit AL. Concentrations of Co, Cu, Ni and Zn are in general higher in the overlying unit AU than in the underlying AL. Lead and to a lesser extent Cr have higher concentrations in the underlying unit AL than in the overlying AU.

LATERAL TRACE ELEMENT CONCENTRATION TRENDS

- In the tailings all the investigated element concentrations except Pb, show a localised high concentration at MT15, i.e. at the contact between the sandy colluvial and clayey alluvial soils.
- In the tailings Co, Cr, Cu, Ni, and Zn show an increase in concentration from MT7 towards the Kromdraai Spruit.
- In the colluvial portion of the transect Ni, Pb and Cr show high concentrations at MT23, adjacent to the paddocked tailings.
- In the alluvial portion of the transect Co, Cu, Ni and Zn show high concentrations at MT11, where a thin Vertic A horizon overlies the waterlogged G horizon.

CHAPTER 6 TRACE ELEMENT MOBILITIES

6.1 INTRODUCTION

The vertical and lateral distributions of NH_4NO_3 extractable concentrations of As, Co, Cr, Cu, Ni, Pb and Zn were investigated in the study area. The 1M NH_4NO_3 batch leaching extraction method was used to extract the trace elements from the tailings and soil samples. The extractable soil concentrations were compared with 1M NH_4NO_3 extractable trace element threshold guidelines for soils to determine the degree of trace element pollution in the affected soils. The zinc-equivalent technique was used to investigate the potential effect of phytotoxic trace elements (Zn, Cu and Ni) on plant growth in the affected soils. The mobility of the elements was investigated by comparing the extractable trace element concentration with the total trace element concentration. The influence of various soil properties (e.g. clay content, cation exchange capacity, electrical conductivity and pH) on the mobility of the selected trace elements in the tailings as well as the soils, were investigated. Lastly some explanations for the vertical and lateral extractable concentration and mobility trends, are presented.

The use of a mild extractant has one or both of the following purposes:

1. To determine the potential of a pollutant to be transported to off-site areas (land or water bodies) where it can impact on the receiving environment and / or
2. To determine the bio-availability of a pollutant. If a pollutant does not have a high bio-availability it can not enter the food chain and consequently will not pose a problem (This does not apply to radio-active elements). Total element concentration does not indicate bio-availability because the element may be totally precipitated or incorporated in non -labile forms (e.g. present within the unweathered minerals or specifically absorbed within soil matrix constituents).

6.2 METHODOLOGY

6.2.1 Laboratory analyses

The cation exchange capacities of the finer than 2 mm soil fraction of seventeen tailings and soil samples were determined according to method 11 of the Soil Analysis Work Committee (1990).

The finer than 2 mm fraction of thirty tailings and fifty-eight soil samples were subjected to the 1M NH_4NO_3 extraction technique. The extracted concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn were determined using inductively coupled plasma - atomic emission spectrometry (ICP-AES). The instrument used was a Varion Liberty 200 ICP-AES. The 1M NH_4NO_3 extraction technique according to the method of Schloemann (1994), which comprises the following steps (procedures in brackets were used in this study):

Sieving: The air-dried soil sample is sieved through a 2 mm nylon or stainless steel sieve and the coarse fraction is discarded.
Weighing: 20 gram air-dried and finer than 2 mm sieved soil is weighed in an acid-cleaned 100 ml polypropylene centrifuge beaker (250 ml acid-cleaned Erlen-meyer flask).
Addition: 50 ml 1M NH_4NO_3 AR solution to the soil.
Agitation: Agitate end-over-end for 2 hours at 20°C (closed Erlenmeyer flask containing soil and salt solution was shaken for two hours on a horizontal shaking table).
Filtration: Supernatant is filtered through a folded filter paper into acid-cleaned 100 ml polyethylene bottle (150 mm diameter Whatmann no 40 ash-less filter paper and 100 ml acid-cleaned glass containers)
Stabilizing: The extract is stabilized by adding 0,5 ml conc. HNO_3 (65 %).

6.2.2 Selection of the NH_4NO_3 extraction method

Several soil leaching techniques are available to establish the extractable trace element concentrations of soils. These methods include the US EPA toxicity characteristic leaching procedure, HNO_3 leaching, leaching with citric acid, 1M NH_4NO_3 and water extraction. Schloemann (1994) considers the 1M NH_4NO_3 leaching procedure to be the best suited for environmental purposes for the following reasons:

- The HNO_3 extraction matrix usually results in concentrations which are close to or below the lower detection limits of the ICP-AAS, i.e. baseline (blank) levels are negligible.
- The 1M NH_4NO_3 leaching method is an established method in Germany, probably the strictest country in the world in regard to pollution standards, and is proposed to become an international recognised soil leaching method for environmental purposes.
- In contrast to some of the other methods, the pH of the 1M NH_4NO_3 solution stabilizes in the acid range, ensuring that the leached elements remain in solution.
- The 1M NH_4NO_3 leaching method is relatively simple and rapid to perform.
- Some authors have published acceptable maximum concentration guidelines using NH_4NO_3 leachates for the assessment of polluted soils (e.g. Balingen (1993) and Prüeß *et al.* (1991))

In addition Davies (1983) recommends NH_4NO_3 as one of the salt solutions with which soils can be extracted to determine extractable trace element concentrations. Klein (1998) states that the NH_4NO_3 extraction technique is one of the techniques which has been standardized and is one of the more frequently used test methods to assess trace element associated soil contamination.

6.2.3 Detection limits, reliability of results and adjustment of results

The detection limits for As, Co, Cr, Cu, Ni, Pb and Zn using the 1M NH_4NO_3 solution in the Varion Liberty 200 ICP-AES are contained in Table 6.1.

Table 6.1 Detection limits of As, Co, Cr, Cu, Ni, Pb and Zn in a solution of 1 M NH_4NO_3 on the Liberty 200 ICP-AES in mgl. The wavelength at which each element was analysed as well as the power used during ionization is given. Element concentrations in the blank samples are reported in mg/l.

	As	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Detection limits	0,0572	0,0111	0,0054	0,0093	0,0033	0,0230	0,0092
Wavelength measured (nm)	193,696	228,616	206,149	324,754	341,476	283,306	213,856
Power used for ionization (kW)	1,30	1,20	1,30	1,30	1,30	1,20	1,30
Results of blank analyses B1	0,000	0,000	0,000	0,063	0,188	0,313	0,063
Results of blank analyses B2	0,000	0,000	0,000	0,125	0,000	0,188	0,063
Results of blank analyses B3	0,000	0,000	0,000	0,000	0,020	0,093	0,085
Results of blank analyses B4	0,035	0,015	0,012	0,000	0,000	0,066	0,132

Reliability of analyses was ensured by setting the Varion Liberty 200 ICP-AES to report the average concentration obtained from triplicate concentration readings of the same sample. In addition the standards were analysed again, each time after an experimental run, to ensure that instrumental drift did not occur.

The results of the analyses were adjusted according to equation 6.1.

Adjusted result = ICP-AES result - Maximum concentration in the blank samples. [6.1]

To further ensure conservative results, the adjusted result was only used if it was in excess of three times the detection limit obtained with the 1M concentration of NH_4NO_3. The adjusted results are contained in Table D.1 in Appendix D.

6.2.4 1M NH_4NO_3 extractable guideline concentrations and exceedance ratios

The degree to which the soils of the study area are contaminated by the selected trace elements, was determined by comparing the 1M NH_4NO_3 extractable trace element concentrations in the affected soils with the guideline values for 1M NH_4NO_3 leachable trace elements in soils, as compiled by Prüeß *et al.* (1991). Ammonium nitrate extractable trace element concentrations in excess of these guideline values are known to decrease soil productivity and soil quality.

Table 6.2 Guideline 1M NH_4NO_3 threshold values for soils (mg/l) after Prüeß *et al.* (1991)

As	**Co**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**U**	**V**	**Zn**
1	5	1	2	1	1	2	4	1	10

The exceedance ratio for each element is used to describe the degree to which each element exceeds the guideline values contained in Table 6.2. The exceedance ratio is defined as:

$$\textit{Exceedance ratio} = \frac{\textit{Extractable concentration}}{\textit{Guideline concentration}} \qquad [6.2]$$

Extractable concentration refers to the 1M NH_4NO_3 extractable trace element concentration while *Guideline concentration* refers to the guideline 1M NH_4NO_3 extractable trace element concentrations as compiled by Prüeß *et al.* (1991). The exceedance ratios of the trace elements in the analysed samples are contained in Table D.2 in Appendix D.

6.2.5 Calculation of zinc-equivalents

According to Rowell (1994) potentially toxic elements such as Zn, Ni, Cu and B can have direct effects on crop growth if the concentrations are high enough. Rowell (1994) recommended limits for concentrations of these elements that are based on their effects on crop health. Other elements such as Cd, Pb, Hg, Mo, As, Se, Cr, and F are not normally toxic to crops but can bioaccumulate in crops. In that way animals and humans utilizing such crops can be adversely affected, before crop health is affected.

Toxicities of trace elements to plants depend on various complex factors (e.g. physico-chemical form of trace element in the soil solution, physical plant root properties and biochemical interactions between plant and absorbed trace elements) (Alloway, 1995). Since such a complex evaluation of the possible effects of the polluted soils on plant life is beyond the scope of this project, an attempt was made to evaluate the possible impact on plant life by establishing a screening concentration level in the form of an extractable NH_4NO_3 zinc equivalent. According to Rowell (1994) the zinc equivalent of Zn, Cu and Ni can be calculated as follows: zinc equivalent = $Zn^{2+} + 2Cu^{2+} + 8Ni^{2+}$ (with 560 mg/kg the upper threshold). This equation is based on the assumption that copper is in general twice as toxic to plants than zinc, while nickel is generally eight times as toxic to plants.

To evaluate the hazard posed to crops by the contaminated soils, the 1M NH_4NO_3 extractable concentration guidelines for Cu, Ni and Zn (after Prüeß *et al.*, 1991, as contained in Table 6.2) were used to calculate a NH_4NO_3 extractable zinc-equivalent (10 mg/l + 2(2) mg/l + 8(1) mg/l = 22 mg/l).

6.2.6 Calculation of trace element mobilities

The mobility of Co, Cr, Cu, Ni, Pb and Zn is described using Equation 6.3:

$$Mobility = \frac{Extractable\ concentration}{Total\ concentration} \times 100 \qquad [6.3]$$

Extractable concentration refers to the 1M NH_4NO_3 extractable trace element concentration (in mg/l) while *Total concentration* refers to the total element concentration of the sample (in mg/kg) as determined by the XRF technique. The mobilities of Co, Cr, Cu, Ni, Pb and Zn are shown in Table D.3 in Appendix D. Arsenic is not investigated as the extractable As concentration was always (except sample MT23/3) below the detection limit of the analytical technique.

6.3 RESULTS AND DISCUSSION OF EXTRACTABLE TRACE ELEMENT CONCENTRATIONS

6.3.1 Exceedance ratios

The ratio's by which the extractable concentrations of As, Co, Cr, Cu, Ni, Pb and Zn exceed the 1M NH_4NO_3 extractable concentration guidelines for soils (Table 6.2, after Prüeß *et al.* 1991) were calculated by dividing the extracted trace element concentration by the guideline concentration (Equation 6.2). Arsenic concentrations were below the detection limit of the analytical technique in all the samples (except sample MT23/3) and could therefore not be considered in this section.

The frequencies (percentages of samples) in which Co, Cr, Cu, Ni, Pb and Zn exceed the guideline extractable concentrations are shown in Table 6.3. The tailings (units TC and TA) in particular, are a source of Ni and Co contamination while Cr, Cu and Zn contamination is also present in the tailings. Only three per cent of the extractable Pb concentrations in the tailings exceed the gudeline concentration of 2 mg/l, indicating that the tailings is not a source of Pb contamination.

In the colluvial topsoil (unit CU), Ni and Co exceed the guideline concentrations in more than half the samples. Only Ni exceeds the guideline concentration frequently (i.e. in more than 50 per cent of the samples) in the nodular ferricrete (unit CF). For all the elements a decrease in the frequency of exceedance occurs from unit CU to the underlying unit CF.

The alluvial topsoil (unit AU) has elevated concentrations of Ni and Zn that frequently (in more than 50 per cent of the samples) exceed the guideline concentrations. Extractable Cr and Cu concentrations exceed the guideline concentrations in more than 30 per cent of the sample population. No significant contamination is present in the alluvial subsoil (unit AL).

Table 6.3 Frequency (percentage of samples) and range of ratio's by which concentrations of selected elements from tailings and soils underlying the site exceed guidelines (refer to Table 6.2)

TRACE ELEMENT		**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
GUIDELINE (mg/l)		**5**	**1**	**2**	**1**	**2**	**10**
SOIL UNIT	**NUMBER OF SAMPLES**	**FREQUENCY (PERCENTAGE OF SAMPLES THAT EXCEED GUIDELINE CONCENTRATIONS) AND RANGE OF RATIO'S BY WHICH GUIDELINE CONCENTRATIONS ARE EXCEEDED**					
TC & TA	30	(63%) 1-23	(47%) 1-36	(33%) 1-4	(70%) 1-37	(3%) 3	(20%) 1-6
CU	12	(50%) 2-4	(33%) 1-4	(25%) 1-2	(75%) 1-8	(17%) 1-3	(17%) 1-2
CF	14	(28%) 1-2	(14%) 1-6	(7%) 1	(64%) 1-3	(6%) 1	-
AU	16	(6%) 1-5	(31%) 1-6	(37%) 1-4	(75%) 2-14	-	(50%) 1-2
AL	16	(6%) 3	-	-	(13%) 6-9	-	(13%) 1-3

6.3.2 Zinc equivalents (implications of contamination for plant life)

The NH_4NO_3 extractable zinc-equivalent threshold of 22 mg/l is exceeded by the majority (60 per cent) of the tailings samples, being on average almost 4 times the threshold value. This indicates that the tailings is toxic to most plants.

The lateral changes in NH_4NO_3 extractable Zn-equivalent data along the transect of alluvial and colluvial topsoil are shown in Figure 6.1. It is evident that the clayey alluvial topsoil is more contaminated by Cu, Ni and Zn than the sandy colluvial topsoil. The colluvial topsoil (unit CT) overlain by paddocked tailings (i.e. test pits MT28 to MT24) is more contaminated by Cu, Ni and Zn than the colluvial topsoil overlain by sheetwash / aeolian deposited tailings (MT23 to MT16).

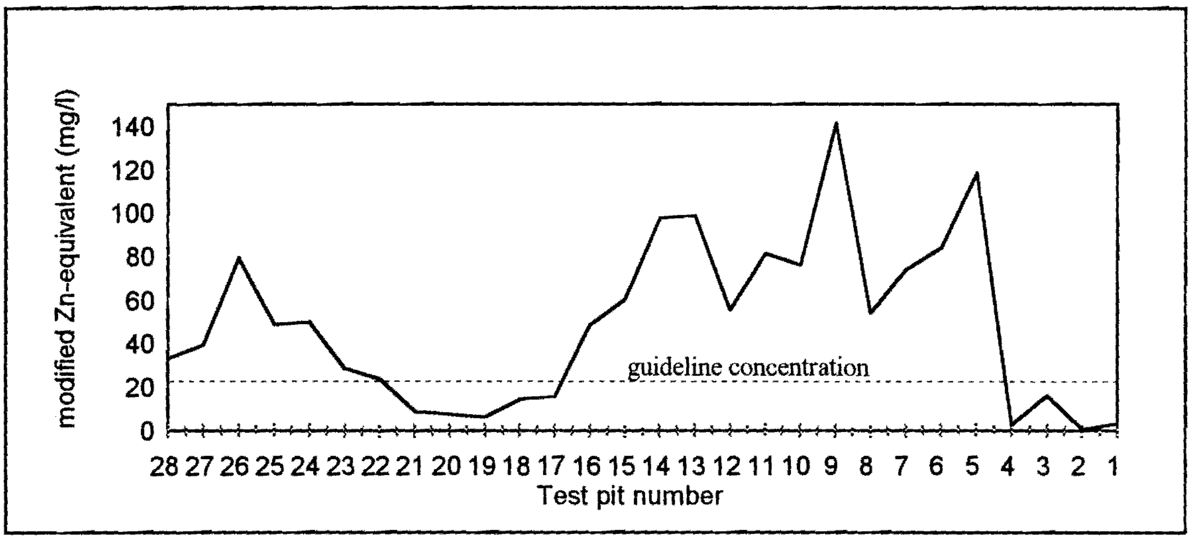


Figure 6.1 Lateral changes in the NH_4NO_3 extractable zinc-equivalent in the topsoil (units AU and CU) along the investigated transect.

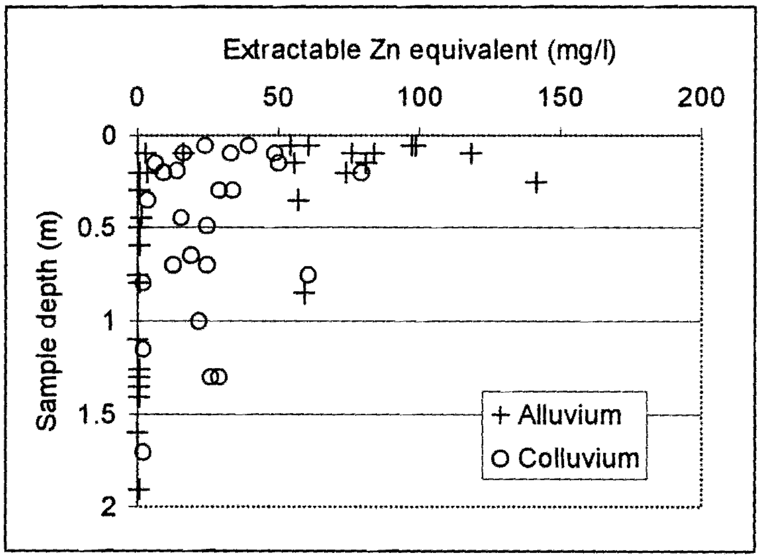


Figure 6.2 Vertical NH_4NO_3 extractable zinc-equivalent concentrations in the colluvial and alluvial soils (soil units CU, CF, AU and AL).

Vertical changes in NH_4NO_3 extractable Zn-equivalent data are shown in Figure 6.2. It is evident that in the alluvial soils Cu, Ni and Zn contamination are generally confined to the upper 0,50 m, while in the colluvial soils some contamination occurs below 0,50 m and down to 1,50 m.

6.3.3 Vertical and lateral extractable trace element concentration trends

6.3.3.1 Vertical extractable trace element concentration trends

Trends in vertical trace element concentrations were investigated by plotting the concentrations of Co, Cr, Cu, Ni, Pb and Zn as a function of sample depth and the soil unit from which the sample was obtained (Figure 6.3). To indicate trends more distinctly, the anomalously high extractable concentrations of Co, Cr, Ni and Zn in sample MT26/2 (being 11,52; 3,62; 36,58 and 63,33 mg/l respectively) were removed. Similar vertical concentration trends for the investigated elements are discussed below:

Cobalt, Chromium, Nickel and Zinc

The highest 1M NH_4NO_3 extractable concentrations of Co, Cr, Ni and Zn occur in the tailings (TC & TA), alluvial topsoil (AU) and colluvial topsoil (CU). Comparing units AU and AL, a distinct decrease in extractable concentration occurs with depth. The trend is not as distinct in the colluvial soils with occasional high extractable concentration occurring in unit CF.

Copper

The vertical extractable trace element concentration trends of Cu is similar to Co, Cr, Ni and Zn, the only difference being that the extractable concentrations in the tailings is generally not as high in relation to the underlying topsoils.

Lead

The highest extractable Pb concentrations occur in the colluvial soils. There is however no distinct difference between extractable Pb in units CU and CF, with high extractable Pb concentrations observed in both.

6.3.3.2 Lateral extractable trace element concentration trends

The lateral 1M NH_4NO_3 extractable concentrations trends of Co, Cr, Cu, Ni, Pb and Zn in the transect are discussed by comparing the extractable concentrations in the tailings (units TC and TA) with the extractable concentrations in the soil unit directly underlying the tailings (usually units AU and CU except in test pits MT13 and MT22 and MT28 where units AU or CF underlies the tailings) along the transect (Figure 6.4). A two test pit moving average was used to decrease scattering and to emphasise trends. Possible explanations for the observed trends will be discussed at the end of Chapter 6.

Tailings

The highest 1M NH_4NO_3 extractable concentrations of Co, Cr, Ni, Pb and Zn occur in the paddocked tailings at test pit MT26. The lowest extractable concentrations in the tailings overlying the colluvial soils occur for all the elements (except Pb) between test pits MT24 to MT22 where the reworked tailings start.

For virtually all the elements (except Pb) a localised high in extractable concentration occurs in the tailings at test pit MT19, between MT15 to MT14 and again at MT10 to MT9. There is also an increase in the extractable trace element concentrations of Co, Cu, Ni and Zn from MT4 to MT1, at the Kromdraai Spruit.

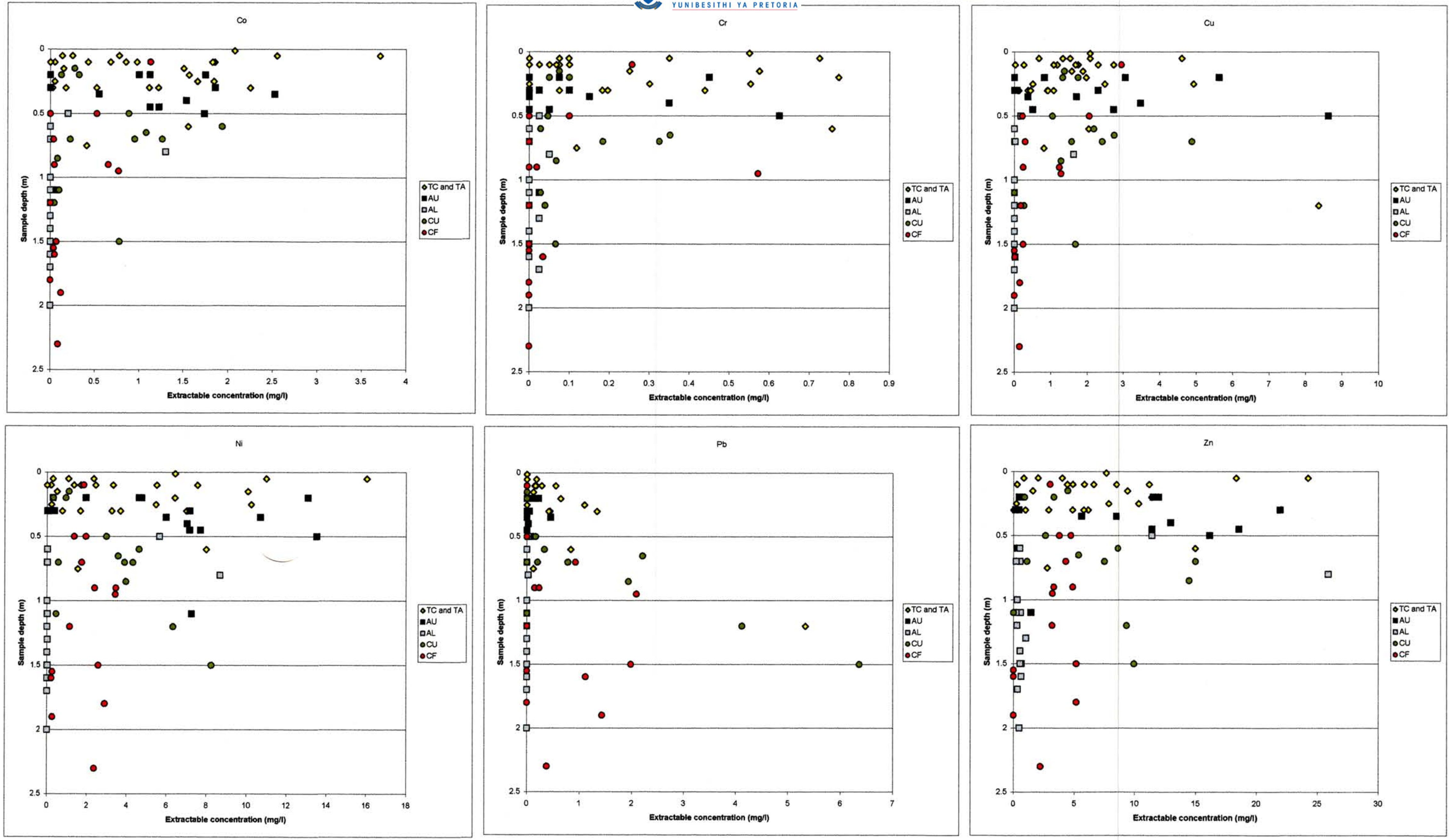


Figure 6.3 Vertical extractable trace element concentration trends

Upper colluvial and alluvial soils

The extractable concentrations of Co, Ni, Pb and Zn are usually higher in the colluvial soils underlying the paddocked tailings (MT28 to MT24) than in the remaining colluvial soils. All the elements in the upper colluvial soils show an increase in extractable concentration as MT16 is approached, where the colluvial soils grade into the alluvial soils.

The extractable concentrations of Co, Ni and Zn are usually higher in the upper alluvial portion of the transect than in the upper colluvial portion of the transect. In the upper alluvial portion of the transect distinct localised highs in extractable concentrations occurs at MT15 to MT14, MT 10 to MT9 and at MT6 to MT5 for all the elements except Pb and Zn. All the elements show low extractable concentrations between MT4 and MT1, on the bank of the Kromdraai Spruit.

6.4 RESULTS AND DISCUSSION OF TRACE ELEMENT MOBILITY

The purpose of this section is to determine the percentage of the total element concentration (determined with the SXRF technique and discussed in Chapter 5) that is extractable by the NH_4NO_3 leaching technique (i.e. the mobility of the trace element in question). Additional aims are to investigate if any vertical and lateral mobility trends exist in the investigated areas.

6.4.1 Vertical trace element mobility trends

Trends in vertical trace element mobilities were investigated by plotting the mobilities of Co, Cr, Cu, Ni, Pb and Zn as a function of sample depth and the soil unit from which the sample was obtained (Figure 6.5). To indicate trends more distinctly, the anomalously high mobilities obtained for Co, Cr, Cu, Ni, Pb and Zn in sample MT26/2 (being 44,30 %, 1,66 %, 29,84 %, 57,15 %, 66,63 % and 59,18 %) were removed. Similarly, the extractable NH_4NO_3 concentration of Pb exceeded the total element concentration in sample MT24/3, and was therefore not used.

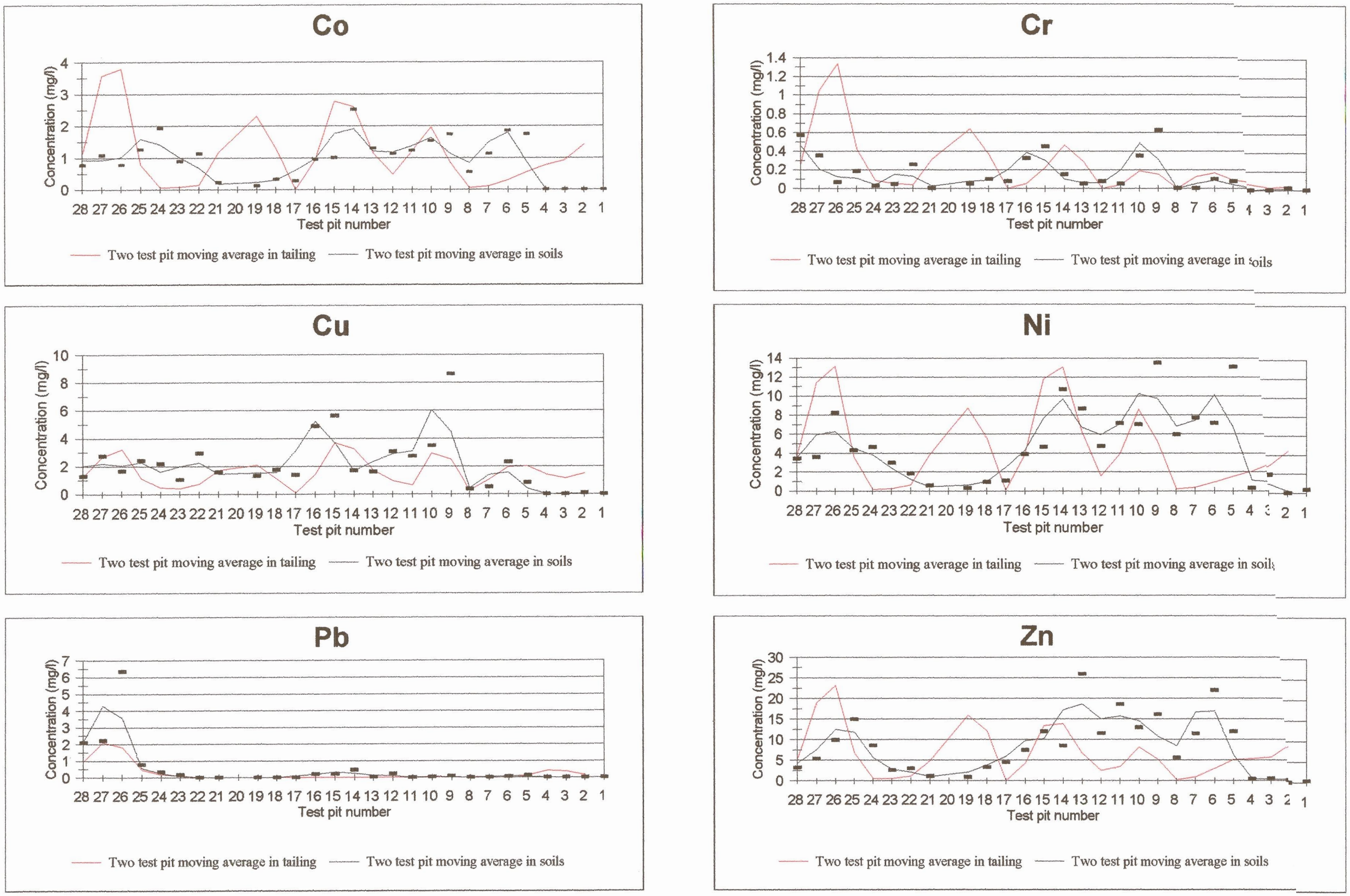


Figure 6.5 Lateral extractable trace element concentration trends in the tailings and the first underlying soil unit, between test pits MT1 and MT28.

As is evident from Figures 6.3 and 6.5 the vertical trace element mobility trends are very similar to the vertical extractable trace element concentration trends.

Cobalt, Chromium, Copper, Nickel and Zinc

The highest mobility percentages of Co, Cr, Cu, Ni and Zn occurs in the tailings (TC & TA), alluvial topsoil (AU) and colluvial topsoil (CU). Comparing unit AU and AL, a distinct decrease in mobility occurs with depth. The trend is not as distinct in the colluvial soils with occasional high mobilities occurring in unit CF (especially for Cu, Ni and Zn).

Lead

The highest Pb mobilities occur in the tailings (TC & TA) and in the colluvial soils (CU and CF). There is however no distinct difference between the mobility of Pb in any of the units as high Pb mobilities occur in units TC & TA, CU and CF.

6.4.2 Lateral trace element mobility trends

The lateral trends in the mobilities of Co, Cr, Cu, Ni, Pb and Zn were investigated by comparing the mobility of the elements in the tailings (units TC and TA) with the mobility of the elements in the soil unit directly underlying the tailings (usually units AU and CU except in test pits MT13 and MT22 and MT28 where units AU or CF underlies the tailings) along the transect (Figure 6.6). A two test pit moving average was used to decrease scattering and to emphasise trend. Possible explanations for the observed trends will be discussed at the end of Chapter 6.

As is evident from Figures 6.4 and 6.6, the lateral trace element mobility trends are also very similar to the lateral NH_4NO_3 extractable concentration trends.

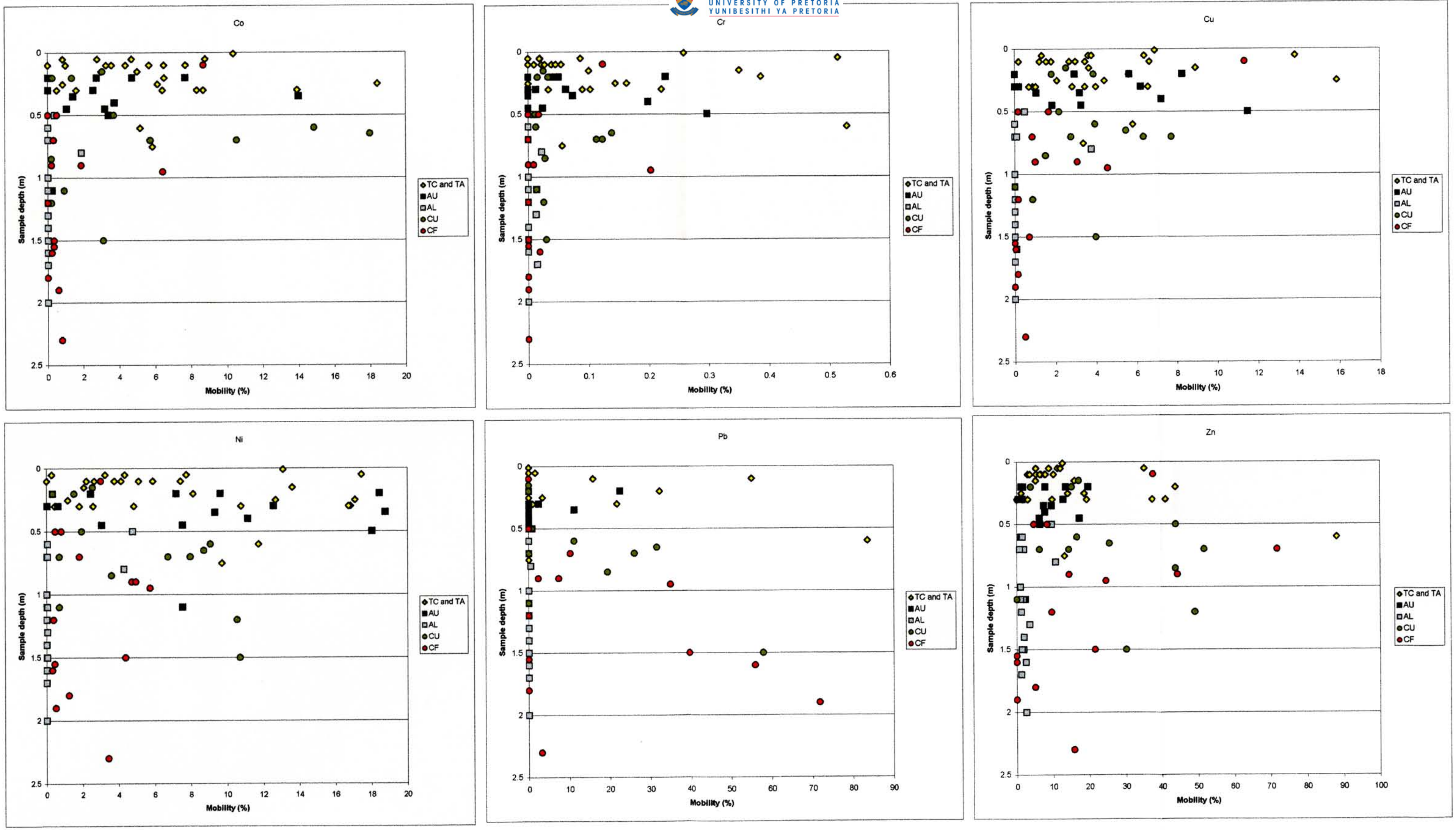


Figure 6.5 Vertical trace element mobility trends

Tailings

The highest trace element mobilities occur in the paddocked tailings (MT28 to MT24). A localised low in trace element mobility in the tailings (excluding Pb) is also evident between MT24 to MT22 where the reworked tailings start. Similar to the extractable concentrations of Co, Cr, Cu, Ni and Zn, a localised high in extractable concentration occurs in the tailings at test pits MT19, between MT15 to MT14 and again at MT10 to MT9. There is also an increase in the mobility of Co, Ni and Zn from MT4 towards MT1,on the bank of the Kromdraai Spruit.

Upper colluvial and alluvial soils

The mobilities of all the elements are usually higher between MT28 and MT22, than in the remaining portion of the upper colluvial soils. There is also a general increase in mobility in the upper colluvial soils from MT22 towards MT16, where the colluvial soils grade into the alluvial soils.

The mobilities of Cu and Ni are usually higher in the upper alluvial portion of the transect than in the upper colluvial portion of the transect. In the upper alluvial portion of the transect, distinct localised highs in mobilities of Cr, Cu and Ni also occur at MT15 to MT14, MT 10 to MT9 and at MT6 to MT5. Similar localised high mobilities occur for Co and Zn at MT15 to MT14 and at MT6 to MT5. All the elements(except Pb) show low mobilities between MT4 and MT1, on the bank of the Kromdraai Spruit.

6.5 RESULTS AND DISCUSSION OF TRACE ELEMENT MOBILITY AS A FUNCTION OF SOIL PROPERTIES.

The mobility of heavy metals in soils is a function of the physical and chemical properties of the soil. Among the physico-chemical properties, the clay mineralogy and organic matter contents are the most important factors as these parameters govern the number of exchange sites in a soil.

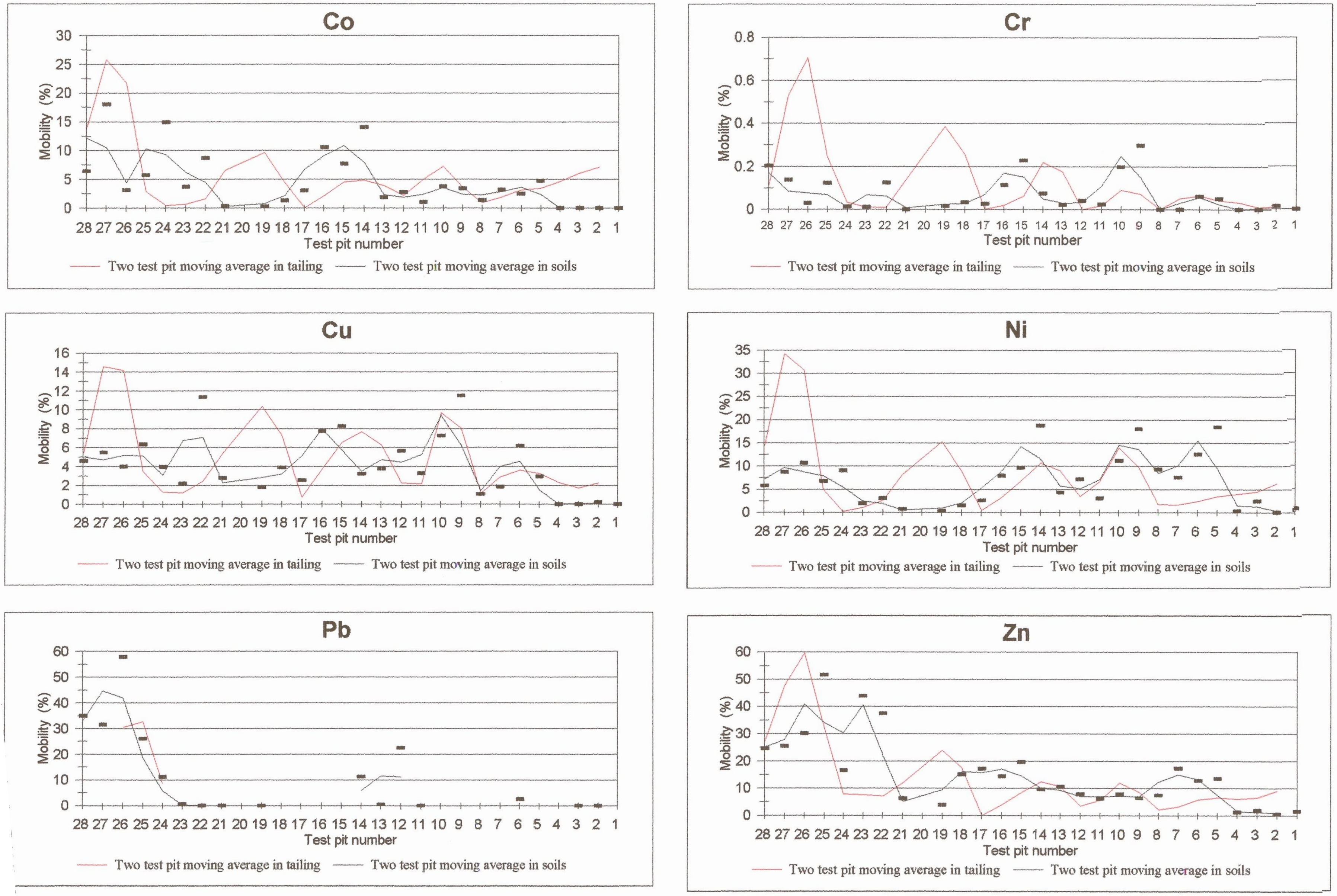


Figure 6.7 Lateral trace element mobility trends in the tailings and the first underlying soil unit, between test pits MT1 and MT28.

Important chemical parameters include the pH and EC as well as the cation exchange capacity of soils (Alloway, 1995). The purpose of this section is to determine if statistically significant relationships exist between trace element mobility and the clay content, cation exchange capacity, electrical conductivity and pH of the investigated tailings and soils.

6.5.1 Clay content

The relationships between the clay content and the individual trace element mobilities for both the tailings and the soils are shown in Figures 6.7 and 6.8.

Tailings

No statistically significant relationships could be established between the clay content of the tailings samples and the mobilities of Co, Cr, Cu, Ni, Pb and Zn (Figure 6.7). At low clay contents the data is scattered, giving both high and low mobilities. At clay contents above 10 per cent the mobilities of the elements are invariably low, with the exception of Pb in one high clay content sample.

Soils

In Figure 6.8 the mobilities of Co, Cr, Cu, Ni, Pb and Zn in the alluvial and colluvial soils are shown separately as a function of the clay content of the soil sample.

The clay contents of the colluvial soils are generally less than 15 per cent with only some soils from unit CF and samples MT16/2 and MT17/2 from unit CU having clay contents of higher than 30 per cent. Although the data scatters, there is an indication that the highest mobilities in the colluvial soils generally occurs below a clay content of 10 per cent. This relationship is more evident for Zn than for the other elements.

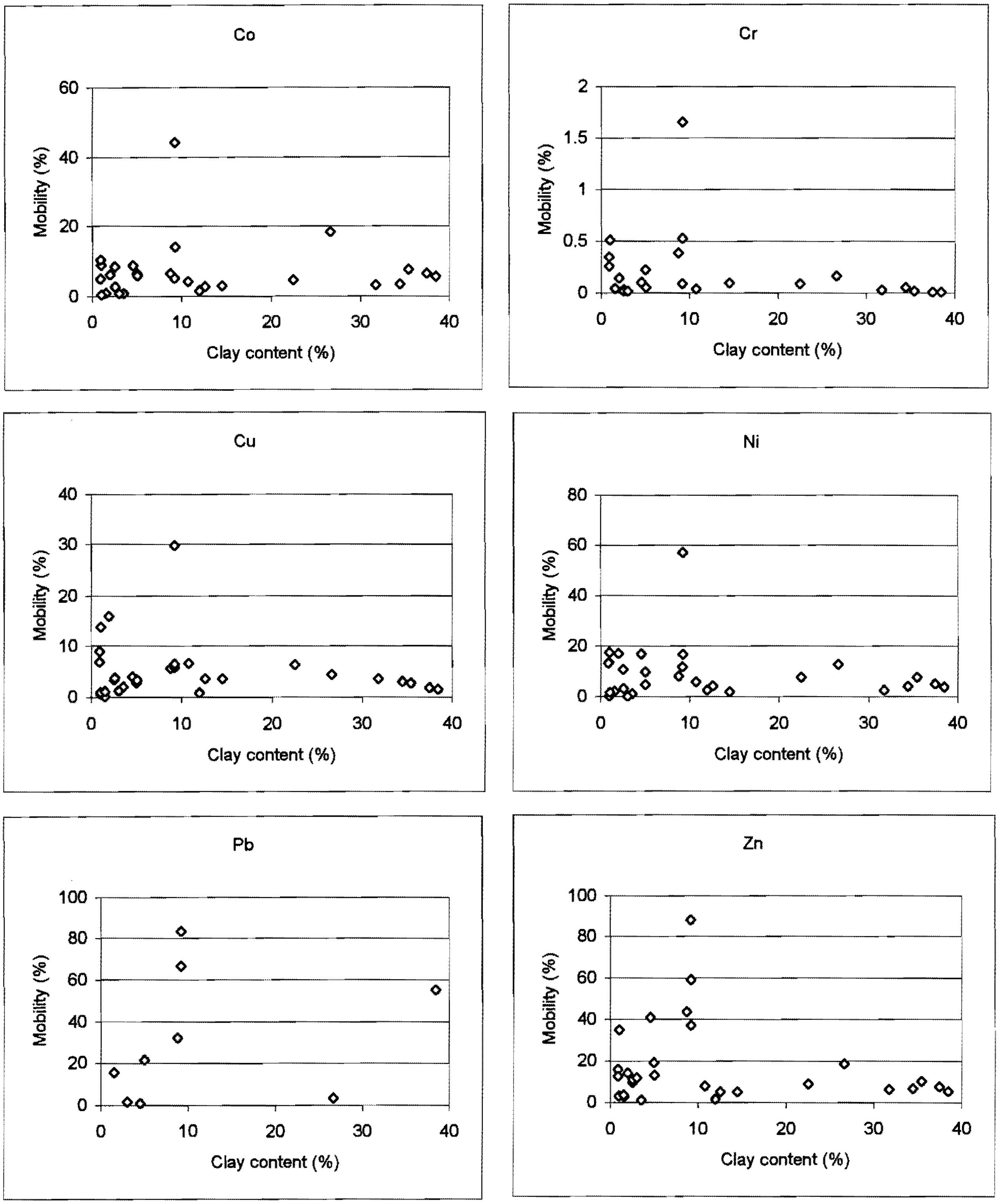


Figure 6.7 Relationship between the clay content of the tailings and the trace element mobilities (Note that the scales differ).

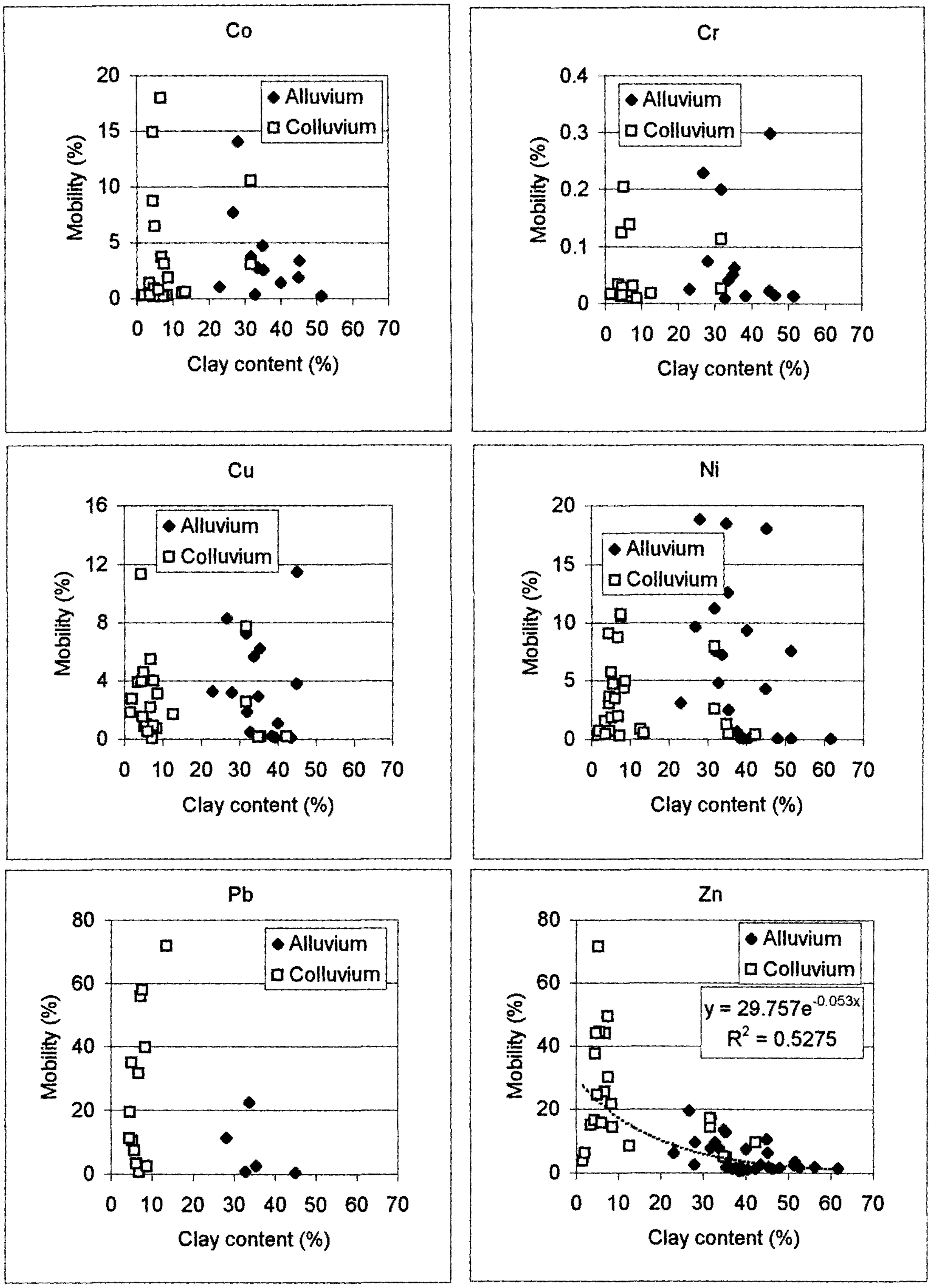


Figure 6.8 Relationship between the clay content of the soil and the trace element mobilities. (Note that the scales differ).

The clay content of the alluvial soils is higher than 20 per cent. Cobalt and especially Zn, show a general increase in trace element mobility with a lower clay content. Chromium, Cu, Ni and Pb mobilities show no clear trend in this regard.

For Zn a coefficient of determination (R^2), of 0,526 (i.e. 52,6 per cent) was obtained when an exponential function is fitted to the combined colluvial and alluvial data. This indicates that a statistical significant relationship exists between the clay content of the soil and the mobility of Zn, to the extent that at least 52,6 per cent of the variability in the mobility of Zn can be accounted for in the differences in the clay content of the soils.

6.5.2 Cation exchange capacity

The cation exchange capacity is a measure of the ability of clay, organic matter and other colloidal soil constituents to adsorb cations from the soil solution. Cation exchange capacities of some soil samples are shown in Table E.1 in Appendix E.

The relationships between cation exchange capacity and the mobilities of Co, Cr, Cu, Ni, Pb and Zn in the soils are shown in Figure 6.9. The data for all the trace elements suggest that slightly higher mobilities of Co, Cr, Cu, Ni, Pb and Zn can be expected at lower cation exchange capacities. The only statistically significant correlation between soil CEC and trace element mobility was established for Zn. A coefficient of determination (R^2), of 44 per cent was obtained when a power function is fitted to the combined colluvial and alluvial soil data. This indicates that a statistical significant relationship exists between the cation exchange capacity of the soil and the mobility of Zn, to the extent that at least 44 per cent of the variability in the mobility of Zn can be accounted for in the differences in the cation exchange capacity of the soils.

The method for determining the cation exchange capacity of samples, buffers the test solution at a pH of 7. This may cause higher than actual CEC to be measured at low soil pH. For the purpose of this study the this tendency was however not further investigated.

6.5.3 Electrical conductivity

The electrical conductivity of a soil is an indication of the amount of dissolved salts present in the soil sample. The relationships between the mobilities of Co, Cr, Cu, Ni, Pb and Zn and the electrical conductivity of the tailings and soils are shown in Figures 6.10 and 6.11 respectively.

Tailings

A slight increase in the mobilities of Co, Cu, Ni and Zn is evident when the EC of the tailings is greater than 100 mS/m (Figure 6.10). However, there is a distinct increase in the mobilities of Co, Cr, Cu, Ni, Pb and Zn in the tailings when the EC is less than approximately 10 mS/m. This indicates that higher trace element mobilities occur in the tailings when the electrical conductivity of the material is very low.

Soils

In Figure 6.11 the mobilities of Co, Cr, Cu, Ni, Pb and Zn are shown separately as a function of the electrical conductivity of the soils. No statistically significant relationships could be defined between the trace element mobilities and the soil EC. There are however two vague opposing trends which are indicated by the data:

- In the colluvial soils, the mobilities of Co, Cr, Cu, Ni, Pb and Zn show a slight increase with increasing conductivity.
- In the alluvial soils, the mobilities of Co and to a lesser extent Cr and Ni, increase with decreasing conductivity.

6.5.4 Trace element mobility as a function of pH

The mobilities of Co, Cr, Cu, Ni, Pb and Zn as a function of pH in the tailings are shown in Figure 6.12, while in Figure 6.13 the mobilities of these elements in the colluvial and alluvial soils are shown as a function of pH. Anomalous data (mobilities > 100 %) are not shown.

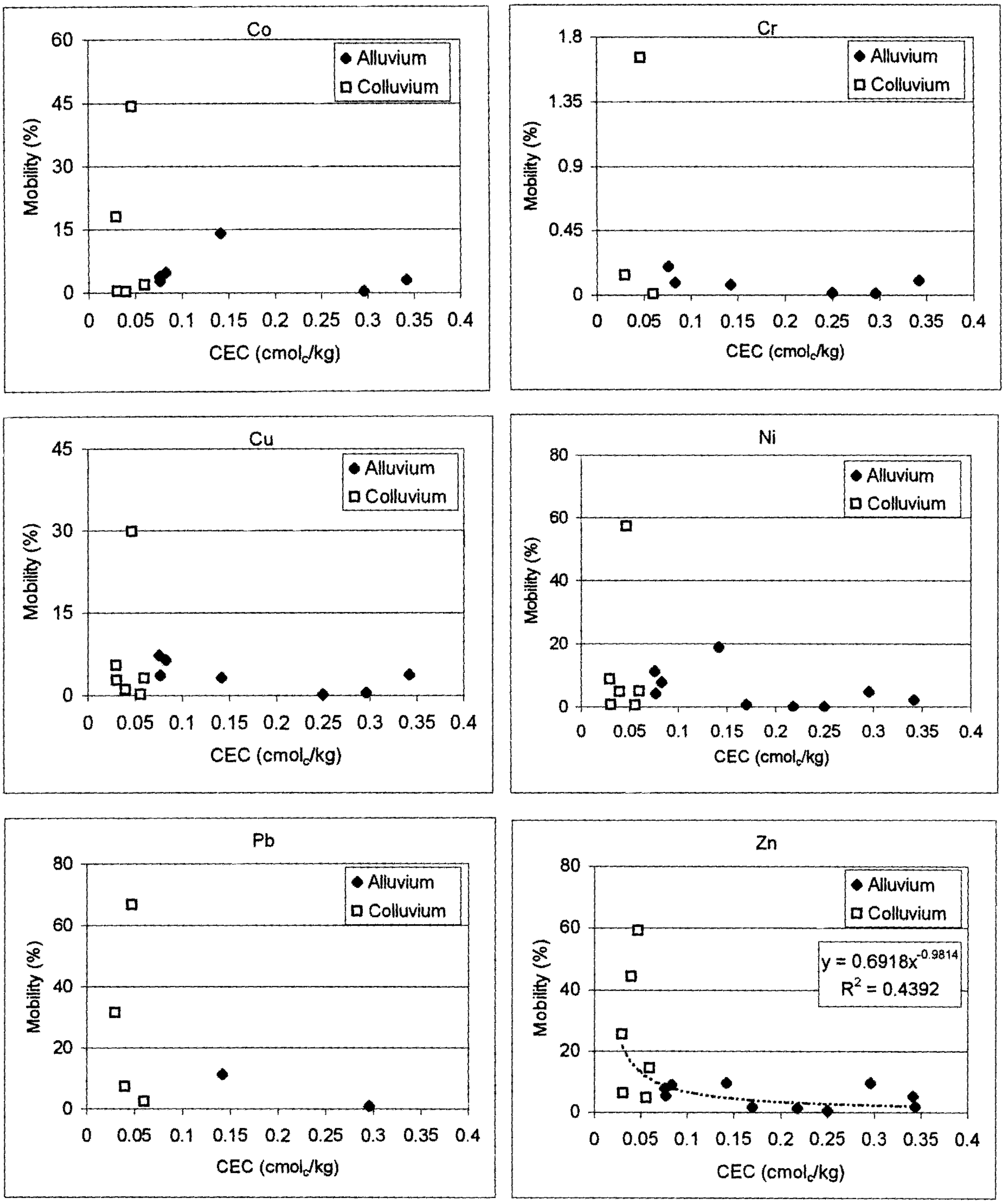


Figure 6.9 Relationship between the cation exchange capacity of the soil and the trace element mobilities. (Note that the scales differ).

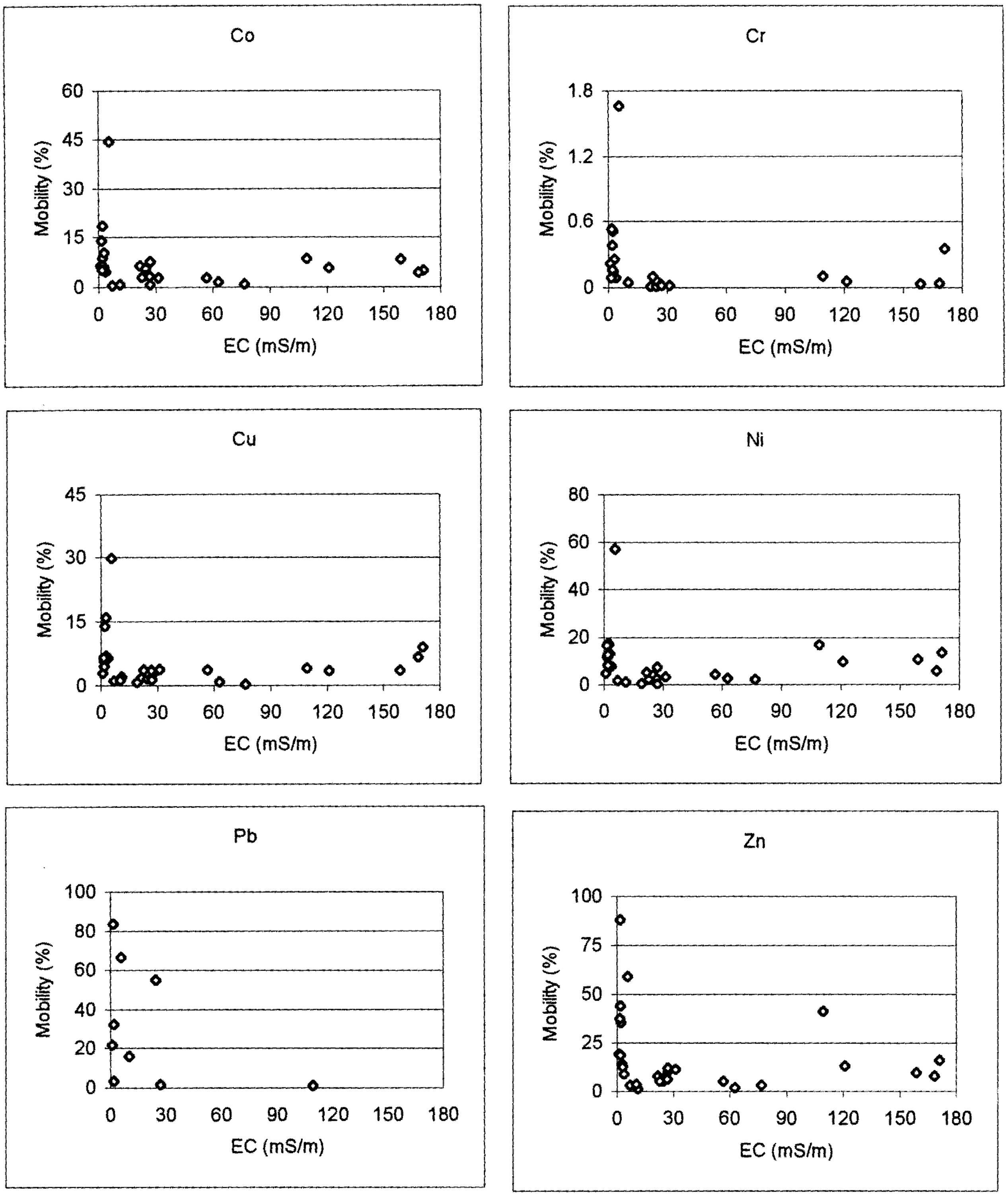


Figure 6.10 Relationship between the electrical conductivity of the tailings and the trace element mobilities (Note that the scales differ).

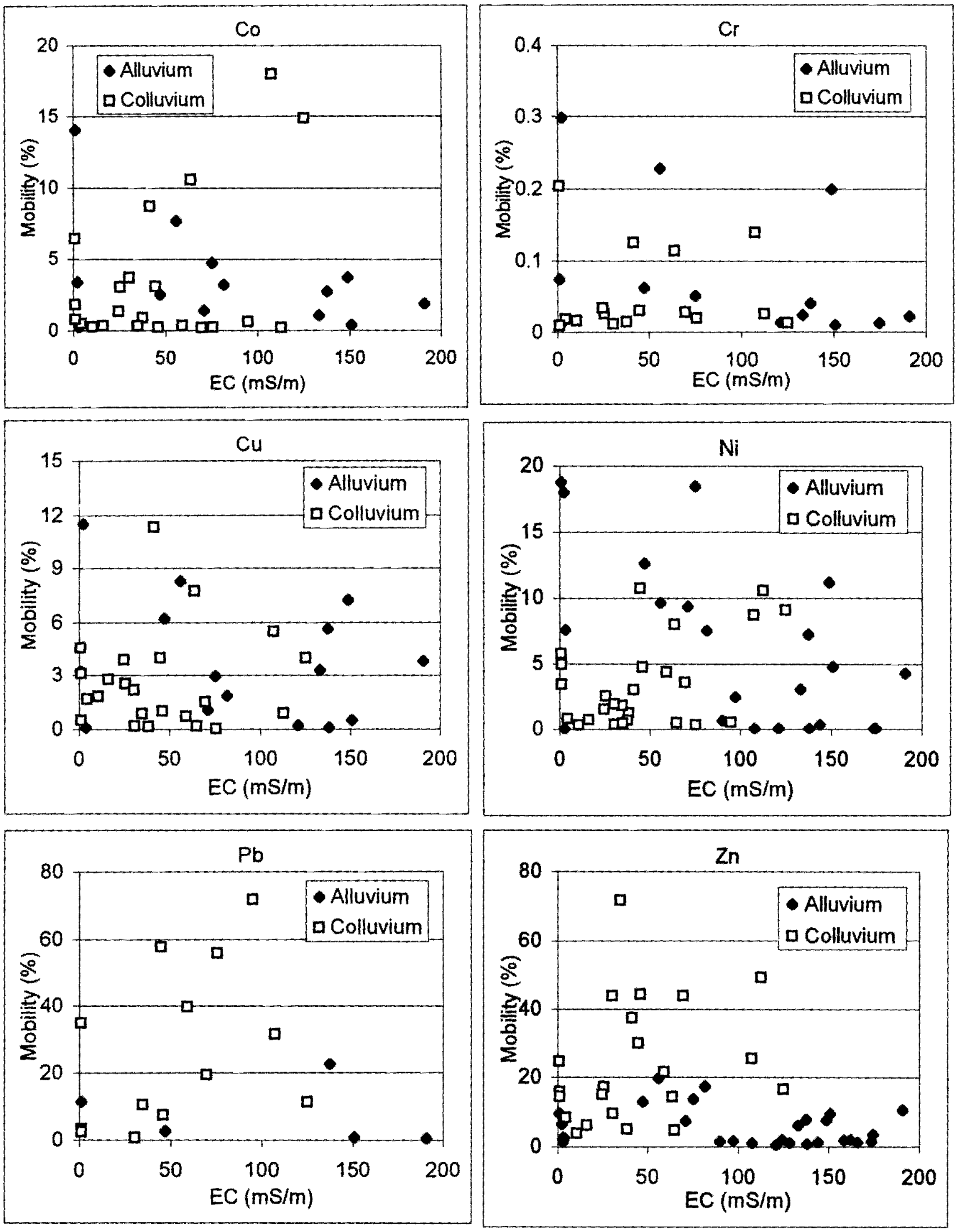


Figure 6.11 Relationship between the electrical conductivity of the soil and the trace element mobilities. (Note that the scales differ).

6.5.4.1 Tailings

From Figure 6.12 it is evident that the mobilities of Co, Cr, Cu, Ni and Zn in the tailings are a function of the pH of the tailings. In all instances there is a sharp increase in mobility below a pH of 3,5 but even at very low pH levels, some samples had low element mobilities.

For Cr, Cu and Zn, coefficients of determination of more than 45 per cent were obtained when an exponential function (for Cr and Cu) and a power function (for Zn) were fitted to the data. This indicates that a statistical significant relationship exists between the pH of the tailings and the mobilities of Cr, Cu and Zn to the extent that at least 45 per cent of the variability in Cr, Cu and Zn mobility can be accounted for in the differences in the pH of the tailings.

6.5.4.2 Soils

From Figure 6.13 it is evident that the mobility of Co, Cr, Cu, Ni, Pb and Zn is in each instance a function of the pH of the soil samples. The colluvial and alluvial soils are plotted separately for each element in Figure 6.13. The mobility of Ni is generally greater in the alluvial soils than in the colluvial soils for similar soil pH values, while in the colluvial soils the mobilities of Pb and Zn are generally greater than in the alluvial soils, for similar soil pH values. The mobilities of Co, Cr and Cu are generally similar in the colluvial and alluvial soils at comparable pH values.

The statical significance of these pH - mobility relationship was investigated by fitting curves to the combined colluvial and alluvial data. This gave larger sample populations and any statistical correlations will therefore be more meaningful than if the colluvial and alluvial soils were treated separately. For Cu, Ni, Pb and Zn coefficients of determination (R^2), of more than 45 per cent were obtained when a power function (for Cu), an exponential function (Ni and Zn) or a quadratic function (for Pb) was fitted to the data. These indicate that a statistical significant relationship exists between soil pH and the mobility of Cu, Ni, Pb and Zn to the extent that at least 45 per cent of the variability in Cu, Ni, Pb and Zn mobility can be accounted for in the differences in soil pH.

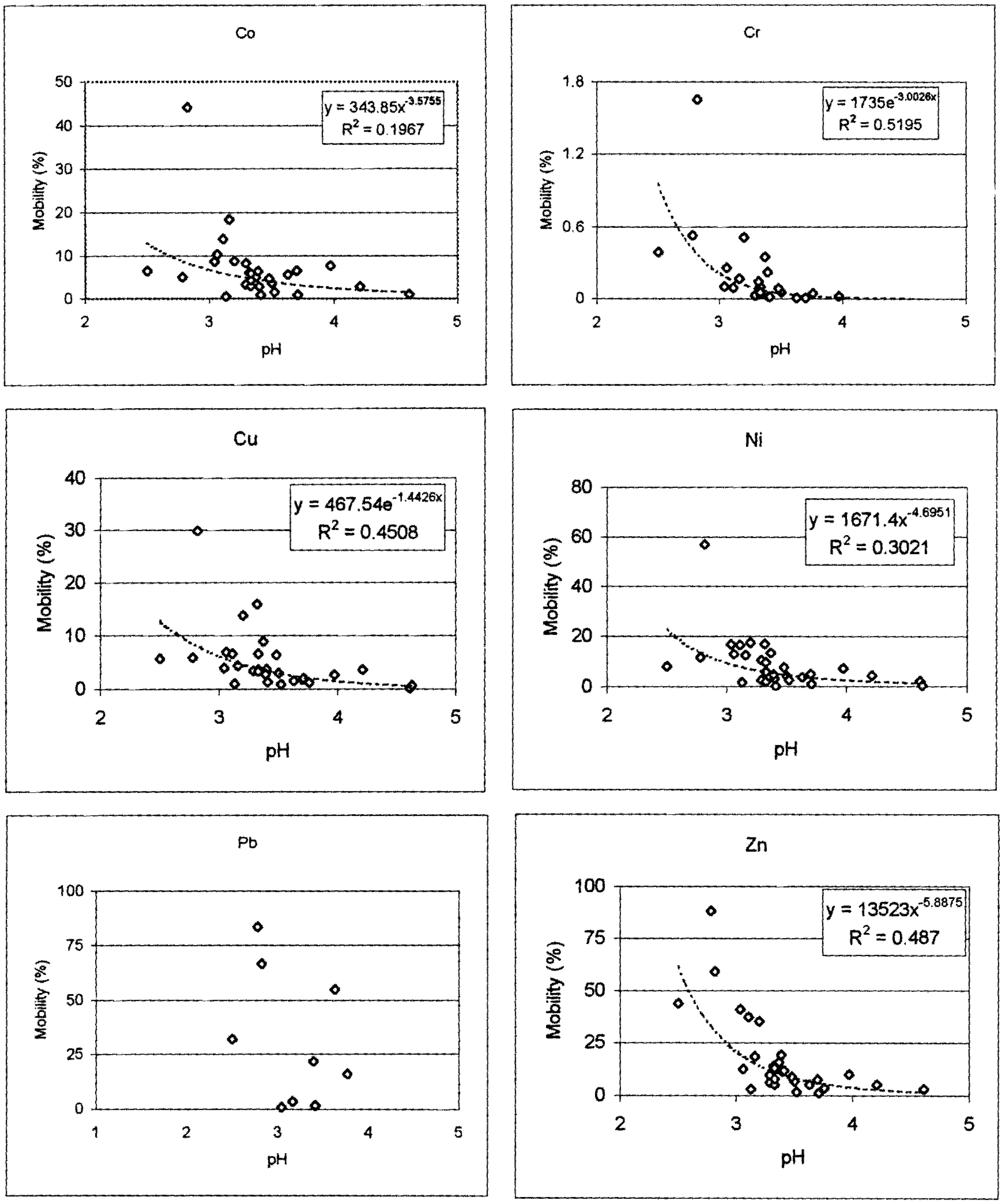


Figure 6.12 Relationship between the pH of the tailings and the trace element mobilities (Note that the scales differ).

Below a pH of 5,0 the mobility of Zn increases dramatically. For Ni and Cu there are definite increases below a pH of 5,0, but below a pH of 4,0, sharp increases in the mobilities of these elements occur. Co really only shows a dramatic increase in mobility below a pH of 4.

These results conform to the well published fact (e.g. Alloway, 1995) that soil pH plays an important role in determining the mobility of certain trace elements in soils. In addition Rösner *et al.* (1998) reported similar increases in the NH_4NO_3 mobilities of Co, Cu, Ni and Zn below a pH of 5 in soils that have been polluted with leachate from gold mine tailings dumps. Szakova, Tlustos, Balik, Pavlikova & Balikova (1999) showed that the NH_4NO_3 mobility of Cd, in soils of the Czech Republic, has the same type of pH dependant relationship as obtained for Co, Cr, Cu, Ni and Zn in this study.

If the mobility of Pb is fitted to a quadratic function, a statistically significant coefficient of determination of 53 per cent is obtained. The data suggest that the mobility of Pb is a minimum at a pH of ~ 4,4 and increases drastically when the pH increases or decreases above or below this value.

6.6 DISCUSSION OF THE MAIN MOBILITY TRENDS

The purpose of this section is to serve as a summary of the main findings regarding trace element mobility trends reported in this chapter. Each trend is given a number and possible explanations for each trend are presented according to the corresponding number in Section 6.6.1.

(1) **General** 1M NH_4NO_3 extractable As concentrations are below the detection limit of the analytical technique. Extractable chromium concentrations are low compared with total Cr concentrations.

(2) **Vertical mobility** A distinct decrease in the mobilities of Co, Cr, Cu, Ni and Zn occurs with depth in the alluvial soils (mobility in unit AU > AL)

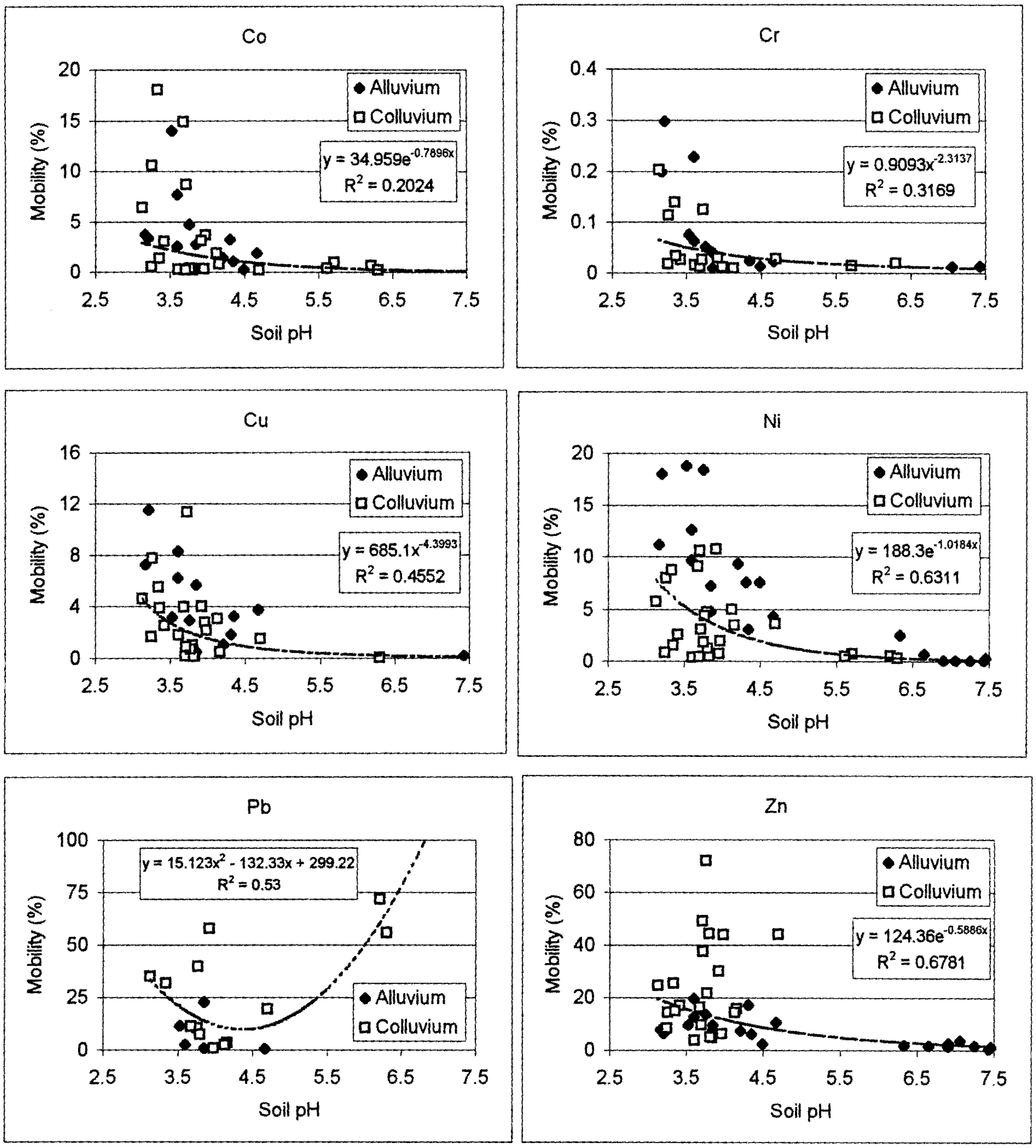


Figure 6.13 *Relationship between the pH of the soils and the trace element mobilities (Note that the scales differ).*

(3) **Lateral mobility** Tailings: The highest mobilities occur in the paddocked material. Localised high mobilities of Co, Cr, Cu, Ni and Zn occur at test pits MT19, MT15-14 and at MT10-9. An increase in the mobilities of Co, Cr, Cu, Ni and Zn occurs from MT4 towards the Kromdraai Spruit.

Upper soil units: The mobilities of all the elements are high between MT28 - 22. A general increase in mobility occurs from MT22-16. Localised high mobilities occur between MT15 - 14, MT10 - 9 and MT 6 - 5. Very low trace element mobilities occur between MT4 - 1.

(4) **Clay content** In both the soils and the tailings, there are weak indications that higher trace element mobilities occur at low clay content.

(5) **Cation exchange capacity** There are weak indications that slightly higher trace element mobilities occur at low CEC.

(6) **Electrical conductivity** In both the tailings and soils the data points were so scattered that no actual trends could be indentified.

(7) **pH** Tailings: Co, Cr, Cu, Ni, Pb and Zn mobilities in tailings increase dramatically below a pH of approximately 3,5.

Soils: Generally a significant sharp increase in the mobilities of Co, Cr, Cu, Ni and Zn occurs below a pH of approximately 4,5 - 5.

6.6.1 Explanations of main mobility trends

In this section an attempt is made to explain the main trace element mobility trends, as summarised above, according to reports in the literature and the findings of this study. The number assigned to each mobility trend is used below to distinguish between explanations:

(1) *The inability of the 1M NH_4NO_3 technique to extract As and low extractable Cr concentrations compared with high total element Cr concentrations.*

The results for the 1M NH_4NO_3 extractable As are in sharp contrast to those for the total element concentration (Chapter 5), where As gave by far the highest indications as pollutant. Two aspects should be kept in mind here:

- Unlike the other elements in the study, As is not usually present in the soil as a cation, but as the arsenate (+5) (AsO_4^{3-}), anion in oxic soils, while the arsenite (+3) anion (which takes forms such as $As(OH)_3$ and AsO_3^{3-}), is stable in anaerobic soils. It is well known that under strongly acidic conditions, such as those prevailing in the study area, anionic species like phosphate and molibdate are fixed strongly to soil constituents and are not extractable and not available for plant uptake. The same principle is likely to hold for As in soils, as the chemistry of As and P has apparent similarities, both commonly form oxyanions of the +5 oxidation state and being located in the same column of the periodic table (Thornton, 1996).
- The 1M NH_4NO_3 extraction technique is essentially an extractant for easily exchangeable cations and anions. As arsenic was not extractable in large concentrations this implies that the extractable As concentrations in the samples are very small. Strongly bound anionic species (e.g. phosphate-, molibdate- and arsenic-compounds) are usually extracted from the soil matrix with other extractants.

(2, 4 and 5) Clay content and cation exchange capacity and vertical mobility trends.

The relationships between trace element mobility, clay content and the cation exchange capacity (CEC) of the soil, suggest that somewhat higher mobilities occur at low clay contents and at low cation exchange capacities. The majority of these trends are not statistically proven, but are suggested by the data in Figures 6.8 and 6.9.

A statistically significant relationship exists between the clay contents and the cation exchange capacities of the soils in the present study, to the extent that 60 per cent of the variance in the CEC of the soil can be explained by the clay content (Figure 6.14). This is the normal situation where the clay mineralogies and the pH levels of soils do not differ much.

The conclusion that can be drawn from these relationships is that lower element mobilities can be expected at higher clay content due to the higher cation exchange capacities of the soils. According to Bohn *et al.* (1985), polyvalent trace elements (e.g. Co^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) are usually more tightly bound to clay minerals than the major soil cations (e.g. Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}). The result is therefore that at higher cation exchange capacities, the trace elements under investigation will be less mobile. This explains why an increase in trace element mobility occurs at low cation exchange capacities and low clay contents.

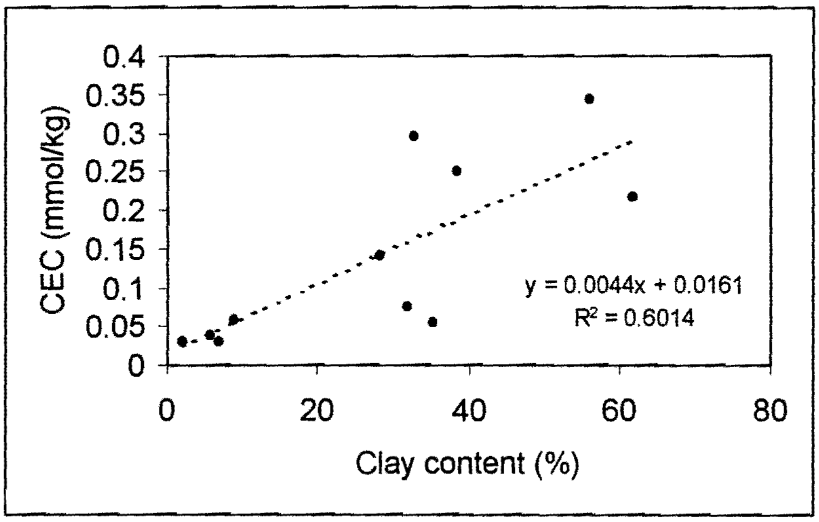


Figure 6.14 Relationship between the clay content of the soil and the CEC of the soil.

In the alluvial soils a decrease in trace element mobility occurs with increasing soil depth. This is not prevalent in the colluvial soils. The sandy soils have a higher permeability and therefore trace element-rich leachate can permeate easier to the underlying soils (unit CF). As these soils have low average CEC (0,03 and 0,05 $cmol_c/kg$ for units CU and CF respectively) trace element contaminants are not bound very strongly to the soil matrix and can therefore migrate to greater depths.

The alluvial soils however, show contamination to be mostly present in the upper soils (unit AU). This is the result of the higher average CEC of the clayey alluvial soils (0,16 and 0,29 cmol_c/kg for units AU and AL respectively) as well as the low hydraulic conductivity of the clay-rich soils. Trace element-rich leachate will migrate more slowly in the alluvial soils, causing higher contact time between contaminants and sorption sites. This will cause greater retardation in unit AU as fewer trace elements migrate downward with the permeating soil solution to unit AL, causing the upper alluvial soils to be more contaminated than the lower alluvial soils. An increase in clay content occurs with depth in the alluvial soils (Figure 6.15) indicating that a decrease in permeability and therefore trace element migration rates can be expected with increasing soil depth in the alluvium.

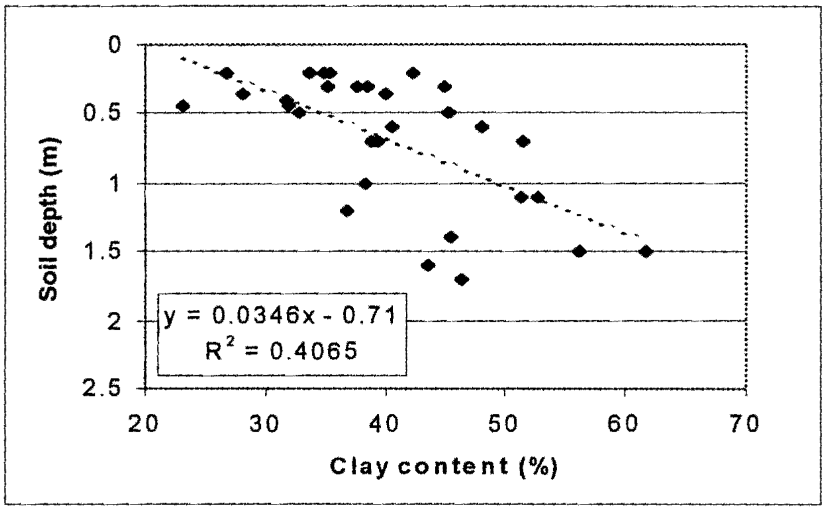


Figure 6.15 Relationship between clay content and soil depth in the alluvial soils (sample MT5/5 not considered)

In addition, the alluvial subsoils show signs of permanent excessive wetness in the form of a G-horizon, i.e. a "gleyed" horizon indicating anoxic (reduced) conditions. Since evapotranspiration exceeds precipitation in the study area, it means that much water will move by capillarity from the free water table in the G-horizon into the topsoil. Dissolved ions move upwards in this water. In the topsoil the water evaporates, leaving ions behind. This is another contributing factor to the creation of higher pollution loads in the alluvial topsoils (unit AU) than in the subsoil (unit AL).

(7) The pH of both the soils and the tailings determine the mobility of the trace elements in the study area.

The following discussion is after Sparks (1995), Alloway (1995) and Bohn et. al. (1985).

The pH is one of the main soil variables which determines the mobility of trace elements. A soil pH measurement gives an indication of the density distribution of hydrogen ions (H^+) (i.e. activity) adsorbed on colloid particles or dissolved in the soil water. As pH is expressed as the negative logarithm of the hydrogen activity of the soil/water, it means that the lower the pH, the higher the H^+ activity in the matrix.

Soil pH, and especially very low pH levels caused by acid mine tailings such as those studied here, affect the mobility and / or plant-availability of mineral elements in various ways. Firstly, most compounds of these elements are simply more soluble in acid environments (i.e. at low pH) than at higher pH. At low pH there is less possibility that these elements can be precipitated into forms with low solubility and therefore low mobility, or low plant-availability.

Secondly, pH affects the charge characteristics and consequently the ion exchange characteristics of soil colloids (alumino-silicate clay minerals, sesquioxides and organic matter). In most soils the colloids have nett negative charges. Two types of negative charges are found: The first are the so-called permanent negative charges, which originate from isomorphous substitution in clay mineral lattices during the formation of secondary alumino-silicate clay minerals in soils. Examples are the substitution of Al^{3+} for Si^{4+} in the tetrahedral layer of illite and the substitution of Mg^{2+} for Al^{3+} in the octahedral layer of montmorillonite. These charges are called "permanent" because they are not affected by factors such as soil pH. The second are the so-called pH dependant negative charges. These are formed due to the dissociation of H^+ from clay minerals and the functional groups of organic matter. The lower the pH of a soil, the less of these pH dependant charges are formed. The result is a lower ability to adsorb cations and a higher cation mobility in the soil at low pH. At very low pH levels, positive charges can develop, which will repel cations and thus sharply increase their mobility. In soils with abundant sesquioxides (even as thin coatings around other minerals) a nett positive charge can develop at very low pH, i.e. below the so-called iso-electric point. Below this pH, mobility of cations will increase dramatically.

Thirdly, the role of H^+ as an exchangeable cation itself is very important. The small H^+ ion is adsorbed more strongly than other cations to negative sites on soil colloids, i.e. it is at the top of the lyotrophic series. The abundance of H^+ ions in strongly acidic soils, strongly replace other cations from the exchange sites, pushing them into the soil solution and thus increasing their mobility.

Anionic trace element species (e.g. important major elements: Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, H_2PO^{4-}, OH^- and F^-, important trace elements: H_2BO^{3-}, MoO_4^{2-} or trace element pollutants: CrO_4^{2-} and $HAsO_4^{2-}$) are attracted by positively charged soil colloids (e.g. Al and Fe hydroxyoxides) or undergo ligand exchange in them. As a consequence these anions may be adsorbed or exchanged and fixed into non-mobile forms on such colloids.

(3) Lateral trace element mobility trends

In the preceding paragraphs it was established that the clay content, cation exchange capacity and the pH of the tailings and soil samples play important roles in determining the mobility of individual trace elements. In an attempt to explain some of the lateral trace element mobility trends, the lateral variations in clay content and pH for selected soil units were plotted in the same manner as in paragraph 6.4.2 (Figures 6.16 and 6.17). As only limited cation exchange capacity samples were taken, the lateral changes in cation exchange capacity could not be plotted. Lateral geochemical trends discussed in Chapter 5 and preceding sections in this chapter, are also further explored in this section.

Trace element mobility and 1M NH_4NO_3 *extractable highs occur in the paddocked tailings.*

Referring to Figure 6.17 it is evident that very low pH values occur in the paddocked tailings.

This explains the high mobility of the majority of elements in the paddocked tailings as opposed to the reworked tailings.

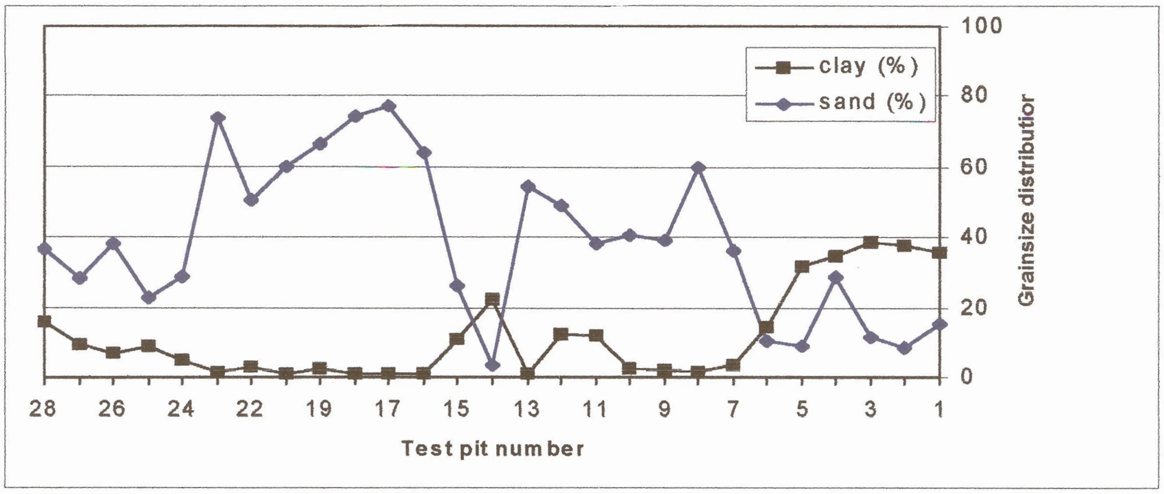


Figure 6.16 Lateral variation in the grainsize distribution of the tailings (units TC and TA) between test pits MT28 to MT1

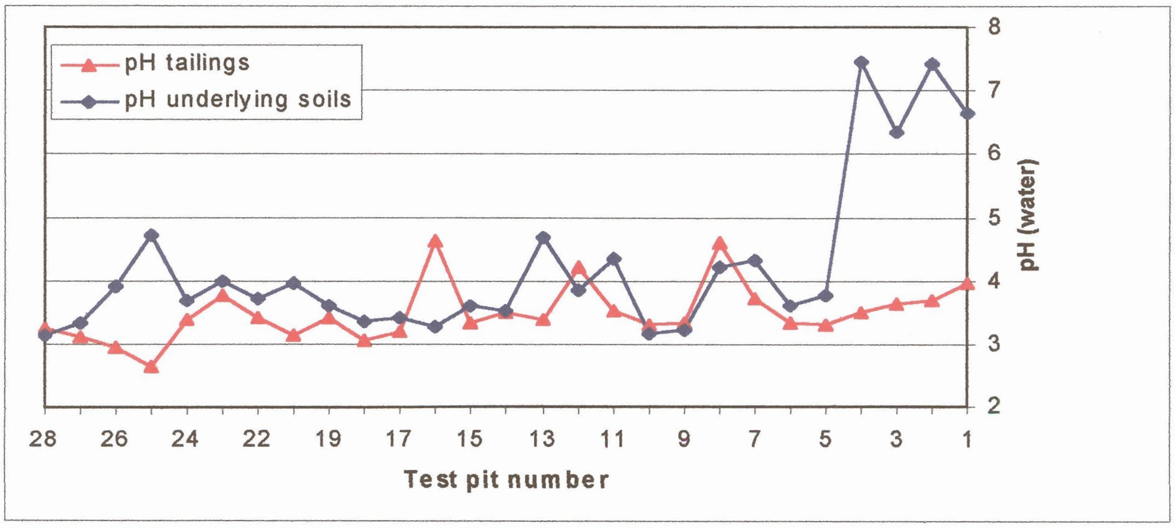


Figure 6.17 Lateral changes in the pH of the tailings and upper soil units between test pits MT28 and MT1.

Localised highs in trace element mobility and 1M NH_4NO_3 extractable concentrations occur in the tailings at MT19, between MT15 - 14 and MT10 - 9, for the majority of elements.

From Figures 6.16 and 6.17 it can be seen that no distinct clay content or pH maxima or minima occur at these test pits. Possible explanations could include enrichment of the tailings at MT19 from lateral seepage from the dunes occurring between MT21 - 20.

A localised high in total trace element concentration in the tailings occurs at MT15. This high corresponds to high extractable concentrations (and therefore to high mobilities). The lateral seepage line effect (as mentioned in Chapter 5) is thought to be responsible here. It is in this portion of the transect where the colluvial soils grade into the clayey alluvial soils. Lateral soil moisture movement will be reduced as the clayey soils is reached, which may cause soil moisture flow lines to reach the surface. Trace elements in solution can then be deposited as soluble salts (due to evaporation) causing enrichment within the tailings.

The localised highs in the majority of total element concentrations, 1M NH_4NO_3 extractable concentrations and mobilities in the tailings in the region of MT11 - 9 can possibly be explained by soil processes. This portion of the alluvial transect has a vertic A horizon overlying the G-horizon. As the G-horizon has a diagnostically high water content, the observed high element concentrations may be due to evaporation forces which draw water to the A horizon through capillary action. The evaporating water will concentrate dissolved elements in salts which precipitate as water evaporates, thus enriching the trace element content of the upper soils and tailings.

There is an increase in total element concentrations in the tailings from MT7 - 1 and in extractable concentrations as well as mobilities from MT4 - 1.

The lateral changes in EC and pH in the tailings do not present an explanation for this trend. Figure 6.16 is used to investigate this trend. The tailings from the tailings dams and paddocks are being redistributed towards the Kromdraai Spruit (test pit MT1) by wind and water erosion (sheetwash processes). In both these sedimentary processes the heavier fraction carried within the sedimentary load (i.e. sand fraction) will be deposited first while the lightest fraction (e.g. clay fraction) will be deposited last. This principle is confirmed by Figure 6.16 which shows the sand fraction decreasing and the clay fraction increasing as the Kromdraai Spruit is approached.

Between MT5 and MT1 the tailings are therefore relatively enriched in fines due to sedimentary processes. In Figures 6.18 and 6.19 the total trace element concentrations are shown as a function of the clay and silt as well as the sand and gravel content of each sample. Although no statistical significant correlations were obtained, there are strong indications that the total element concentrations increase with increasing fines content and decrease with increasing coarse material content. It is therefore proposed that the high total and extractable concentrations in the tailings in the latter portion of the transect are a result of sedimentary enrichment processes.

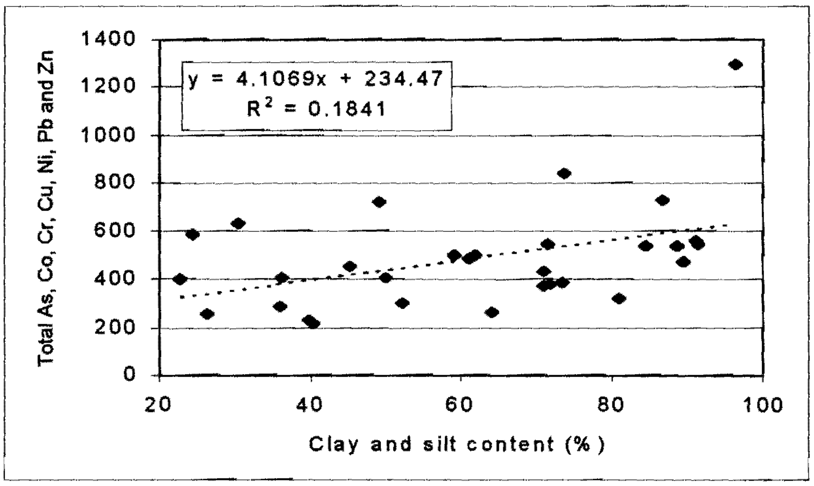


Figure 6.18 Total trace element concentration in the tailings (units TC and TA) as a function of the clay and silt fractions of each sample.

High mobilities, extractable concentrations and certain total element concentrations occur in the colluvial soils underlying the paddocked tailings.

These soils have been exposed to leachate from the tailings dams for the longest period of time, as the paddocks is part of the original construction of the tailings dam. These soils have therefore been exposed to pollutants for a longer period of time than the other soils, resulting in these soils adsorbing higher concentrations of trace element pollutants. In addition, the paddocks are generally thicker than the other tailings, resulting in a greater volume of tailings overlying the soils. There are thus more tailings which produce more trace element rich leachate to contaminate the underlying soils.

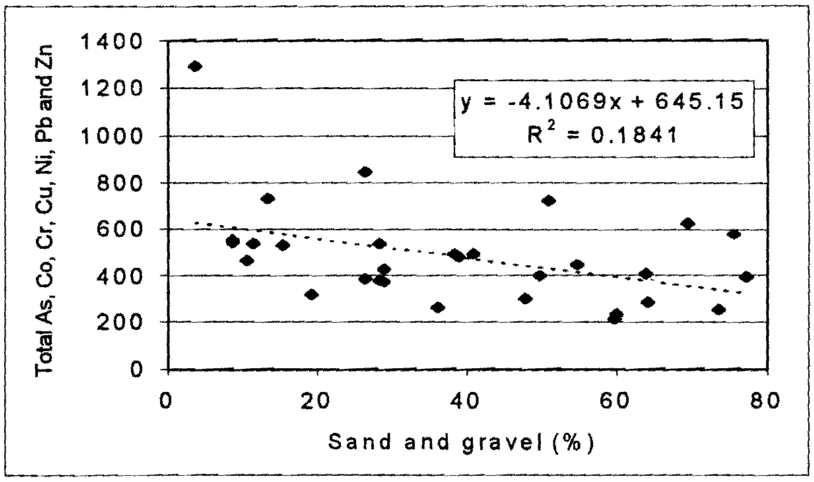


Figure 6.19 Total trace element concentration in the tailings (units TC and TA) as a function of the sand and gravel fractions of each sample.

In the colluvial soils there is a general increase in extractable concentration and mobility from test pit MT22 towards MT16.

This general increase corresponds to a general decrease in soil pH towards MT16. Both these soil variables have been indicated to have an enhancing effect on the mobility of trace elements in the colluvial soils.

The general decrease in soil pH and increase in electrical conductivity towards MT16 can be ascribed to lateral leaching. It is in this portion of the transect where the colluvial soils grade into the clayey alluvial soils. Lateral soil moisture movement will be reduced as the clayey soils is reached, which may cause soil moisture flow lines to reach the surface, acidifying the soils and depositing soluble salts and trace elements in the process.

Localised highs in trace element mobility and 1M NH_4NO_3 extractable concentrations occur in the upper alluvial soils at between MT15 - 14, MT10 - 9 and MT6 - 5, for the majority of elements.

These positions correspond to localised lows in pH of the upper alluvial soils (Figure 6.19). In addition, these positions are also areas of low electrical conductivity. Both pH and electrical conductivity in the alluvial soils have been shown to cause higher trace element mobilities. Similar artificial enrichment processes due to evaporation, as discussed for the tailings between MT15 - 14 and MT10 - 9, are thought to cause the pH lows.

There is a distinct decrease in extractable element concentration as well as mobility from MT4 towards MT1 in the alluvial soils.

The pH of the alluvial soils between MT4 - 1 is the highest of the upper soils of the transect (Figure 6.17). The electrical conductivity of this portion is also relatively high (Figure 6.18). The overlying tailings, however, has a pH of less than 4 and high trace element mobility ratios. As these soils are located the farthest away from the source, it follows that these soils have been exposed to contaminants for the shortest period of time. This indicates that these soils have not yet been acidified and polluted by the overlying tailings.

6.7 SUMMARY

SAMPLE PREPARATION AND ANALYTICAL TECHNIQUE

The finer than 2 mm fraction of 119 samples was extracted with a 1M NH_4NO_3 solution by a slightly modified method of Schloemann (1994). Ammonium nitrate was chosen as the extracting liquid as the method is considered suitable for environmental purposes by a number of authors (e.g. Davies (1983), Prüeß *et al.* (1991), Balingen (1993), Schloemann (1994), Klein (1998) and Szakova *et al.* (1999)).

A Varion Liberty 2000 inductively coupled plasma - atomic emission spectrometer (ICP-AES) was used to analyse the extracted liquid for concentrations of As, Co, Cr, Cu, Ni, Pb and Zn. The results are considered accurate as the technique reports an average value for three measured results and element standards were analysed again after each analytical run to correct for instrument drift. Each result was adjusted by subtracting the highest concentration of an element determined in four blank samples and this adjusted result was only used when it was greater than three times the detection limit for the 1M NH_4NO_3 matrix used during analyses.

EXCEEDANCE RATIOS OF As, Co, Cr, Cu, Ni, Pb and Zn

An exceedance ratio of an element was defined as the NH_4NO_3 extractable trace element concentration divided by the guideline value, as compiled by Prüeß *et al.*(1991). The exceedance ratio of each element was used to describe the degree to which an element exceeds the guideline concentration

In Chapter 5 it was shown that As is a priority pollutant. None of the investigated samples (except MT23/3) has an extractable concentration of As that is above the detection limit of the analytical technique (0,06 mg/l). Arsenic does therefore not exceed the guideline concentration of 0,1 mg/l in any of the soil or tailings samples in the study area, and therefore does not present a significant hazard under current soil physico-chemical conditions.

The alluvial topsoil (unit AU) is polluted with Ni, Co and Zn, while the alluvial subsoil (unit AL) shows no extractable trace elements which occur in excessive concentrations. In the colluvial topsoil unit (unit CU), Ni and Co are present in significant concentrations, while only Ni exceeds the threshold concentration to a significant degree in the underlying nodular ferricrete unit CF.

As a first estimation of the effect that the contaminated soils will have on plant life, the NH_4NO_3 extractable Zn-equivalent is defined. Using this method, it is shown that the clayey alluvial topsoil (unit AU) holds a higher potential danger to plant life than the colluvial soils. However, contamination occurs to a greater depth in the colluvial soils than the alluvial soils.

MAIN NH_4NO_3 EXTRACTABLE AND TRACE ELEMENT MOBILITY TRENDS

Arsenic was not extractable by 1M NH_4NO_3 leaching technique. Extractable chromium concentrations are low compared with total Cr concentrations.

Vertical trends

A distinct decrease in the 1M NH_4NO_3 extractable concentrations as well as mobilities of Co, Cr, Cu, Ni and Zn occurs with depth in the alluvial soils (mobility in unit AU > AL). A similar decrease does not occur in the colluvial soils.

Lateral trends

In the tailings the highest extractable concentrations and mobilities occur in the paddocked material. Localised high extractable concentrations and mobilities of Co, Cr, Cu, Ni and Zn occur at test pits MT19, MT15-14 and at MT10-9. An increase in the extractable concentrations and mobilities of Co, Cr, Cu, Ni and Zn occurs from MT4 towards the Kromdraai Spruit.

In the upper soil units the extractable concentrations and mobilities of all the elements are high between MT28 - 22. A general increase in extractable concentrations and mobility occurs from MT22-16. Localised high extractable concentrations and mobilities occur between MT15 - 14, MT10 - 9, MT 6 - 5. Very low extractable trace element concentrations and mobilities occur between MT4 - 1.

TRACE ELEMENT MOBILITIES AS A FUNCTION OF SOIL PROPERTIES

In both the soils and the tailings, there are weak indications that higher trace element mobilities occur at low clay content. There are also weak indications that slightly higher trace element mobilities can be expected at low cation exchange capacities.

There is a vague, general increase in trace element mobility in the tailings where the EC is below 10 mS/m. Trace element mobilities in the colluvial soils show a general increase with increasing EC. Some trace element mobilities in the alluvial soils, increase with decreasing EC.

Co, Cr, Cu, Ni, Pb and Zn mobilities in the tailings increase drastically below a pH of approximately 3,5. In the soils a drastic increase in the mobilities of Co, Cr, Cu, Ni and Zn occurs below a pH of approximately 4,5 - 5.

A statistically significant correlation exists between the mobilities of Cu, Ni, Pb and Zn and the pH (water) of the soil. A power function relationship exists between Cu, Ni and Zn mobility and soil pH, while a quadratic function relationship exists between Pb mobility and soil pH. This data support the well published fact that the pH of the soil plays an important role in the mobility of trace elements.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

In conclusion it can be stated that this study has shown that both the sandy colluvial soils and the clayey alluvial soils occurring in the study area have been polluted by gold mine tailings derived from poorly stabilised tailings dams occurring up-slope from the study area. The main findings of the study are summarised below:

GOLD MINE TAILINGS AS A SOURCE OF TRACE ELEMENT POLLUTION AND ACIDITY

- Gold ore mined at Machavie is sulphide rich (Barton & Hallbauer 1996) and an amalgamated sample obtained from a number of sulphide bearing rocks from the rock discard dump at the site showed the sulphide mineral to be pyrite. Trace element analyses of the pyrite, as well as literature data on the composition of pyrite of the Black Reef Formation (Barton & Hallbauer 1996) showed the mineral to be rich in trace elements such as As, Ba, Co, Cr, Cu, Ni and Zn.

- The climate of the area is such that evaporation exceeds precipitation. Acidic leachate produced in the near-surface tailings will therefore tend to move towards the surface due to evaporation. The acidic leachate is rich in trace elements originating from the decomposition of sulphides and other minerals present in the tailings. Secondary minerals such as jarosite ($3KFe(OH)_6(SO_4)_2$) present in the tailings, show that sulphate-rich leachate from the decomposition of sulphide minerals is present in the tailings. The acidic leachate evaporates and a salt residue crystallizes which is composed of iron sulphates, sodium potassium iron sulphates, aluminum iron sulphates, magnesium sulphates, aluminum sulphates and sodium sulphates. These salts have high water soluble concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn. Tailings present as sheetwash or aeolian deposited residue, and tailings within the tailings dams are therefore a potential source of trace element contamination.

- The tailings covering the soils in the study area has an average pH of 3,43, indicating that this material produces acidic leachate from the oxidation of sulphide minerals in the presence of oxygen and water. These acidic solutions have affected the underlying soils as the pH of the topsoils underlying the tailings are all significantly lower than what would be expected under the natural pedological conditions of the area. It can therefore be concluded that the tailings has affected the quality of the underlying soils due to an increase in the acidity of the soils.

CHARACTERIZATION OF THE DEGREE OF TRACE ELEMENT SOIL POLLUTION

- Two techniques were employed to characterise the trace element pollution status of the soils underlying the gold mine tailings. Trace element concentrations which, according to the Dutch-B concentration guidelines warrant further investigation, were identified (Chapter 5) and the NH_4NO_3 extractable concentrations of these elements were determined (Chapter 6). The results of the two methods are compared in Table 7.1.

  In Table 7.1 the trace elements are ranked according to the percentage of samples in which a particular trace element exceeds the applicable guideline value. From Table 7.1 it is clear that the Dutch-B concentration screening value system fails to identify the pollutants of concern as identified by the NH_4NO_3 extractable concentration screening values. Nickel and chromium are the only elements that are identified by both screening systems to be contaminants of concern. The Dutch - B value system however, failed to identify Co which, according to the NH_4NO_3 system is a priority pollutant in soil units CU and CF. In the same manner, Zn contamination of unit AU was also not predicted by the Dutch-B value system.

According to literature (e.g. Schloemann, 1994; Davies, 1983) soil leaching systems are more suited for determining the trace element pollution status of soils than for comparing the total element concentrations of soils with screening values. The results of this study confirm this statement.

Table 7.1 Comparison between the results of the Dutch-B concentrations screening and the NH_4NO_3 extractable concentrations screening for the investigated area.

Soil unit	**Trace elements of concern according to Dutch-B value screening**	**Trace elements of concern according to NH_4NO_3 extractable concentrations screening**
TC & TA	As >> Cr >> Ni	Ni > Co >> Cr > Cu > Zn > Pb
CU	Cr >> As > Ni	Ni >> Co >> Cr > Cu > Pb > Zn
CF	Cr >> Cu = Ni	Ni >> Co >> Cr > Cu > Pb
AU	As > Co > Ni	Ni >> Zn >> Cu > Cr > Co
AL	-	Ni ≈ Zn ≈ Co

- The inability of the 1M NH_4NO_3 leaching technique to liberate As from the soil and tailings matrix is thought to be a result of the chemical form of As in the soil. Arsenic is usually present as an anion (e.g. AsO_4^{3-}) in the soil. The NH_4NO_3 leaching technique preferentially desorbs easily exchangeable cationic and anionic species from the soil and tailings matrix. Arsenic is not present in significant easily exchangeable fractions and the NH_4NO_3 leaching method therefore obtained extractable As concentrations which are mostly below the detection limit of the analytical technique.

TRACE ELEMENT MOBILITY AS A FUNCTION OF SOIL PROPERTIES

- The mobility of Co, Cr, Cu, Ni, Pb and Zn were investigated by determining the percentage of the total element concentration which is extractable by the 1M NH_4NO_3

leaching technique. It was determined that both soil properties (clay content, cation exchange capacity, electrical conductivity and pH) and the pedological properties of the investigated transect determine trace element mobility.

- There are weak indications that higher mobilities of the majority of trace elements in the soils and tailings occur at low clay contents and at low cation exchange capacities (CEC). High cation exchange capacities are associated with high clay contents. This means that at a high clay content a high colloidal surface area is available and trace elements in solution are easily adsorbed. At a low clay content (and associated low CEC) less colloid surface areas are available for cation adsorption. As the soil water usually contains more major cation species (e.g. Ca^{2+} and Mg^{2+} in natural soils and NH_4^+ in the 1M NH_4NO_3 leaching technique) than trace elements, these trace elements will be easily replaced by the major species when adsorption sites are limited. This causes the trace elements to be mobile when adsorption sites are limited.

  In the alluvial soil, higher trace element mobilities occur in the upper soil unit AU than in the underlying unit AL. This is the result of an increase in the clay content (and therefore the CEC) of the alluvial soils with increased soil depth, causing trace elements to be adsorbed to a higher degree. In addition the low hydraulic conductivity of the alluvial soils means that trace element rich leachate has a slow vertical migration rate, increasing the contact time with colloidal surfaces, which promotes adsorption.

- No statistical correlations were obtained between the electrical conductivity of both the tailings and the investigated soils and trace element mobility. In the tailings and alluvial soils however, there is a tendency for higher trace element mobilities to occur at low electrical conductivities. In the colluvial soils there are indications that higher mobilities occur at higher electrical conductivities.

- The pH of both the tailings and the investigated soils was shown to be a main variable in controlling the mobilities of the investigated trace elements. In the tailings, the mobilities of Co, Cr, Cu, Ni, Pb and Zn increase sharply below a pH of 3,5. In the alluvial and colluvial soils a sharp increase in trace element mobilities occurs below a pH of 5 to 4,5.

- Lateral soil moisture seepage and evaporation are the two main pedological processes which are thought to control some of the main vertical and lateral trace element mobility trends observed in the investigated transect. Lateral movement of soil moisture in the colluvial soils is impeded when the clayey alluvial soils are reached. Flow lines are forced to the surface resulting in the deposition of trace elements through evaporation at the so-called seepage line. This process is thought to cause the localised high extractable concentrations and mobilities of certain trace elements in the tailings and soils in the region of test pit MT15.

  Soil moisture in the G-horizon of the alluvial soils is drawn upwards thorough capillary forces. Trace elements dissolved in the upward moving soil moisture precipitate as soluble salts in the upper soil unit AU and in the tailings cover (unit TA) due to evaporation. This enrichment process contributes to the higher extractable concentrations and mobilities of trace elements in unit AU compared with the underlying unit AL.

7.2 RECOMMENDATIONS

Based on the findings of this study, the following recommendations for further action and further studies are made:

- This study has shown that redistribution of the gold mine tailings from the existing tailings dams is degrading and polluting the receiving soil environment. It is therefore important that tailings dams be stabilised by establishing a grass cover on the surface of the dams. This will inhibit wind and water erosion of the tailings dams.

- It has been shown that low extractable trace element concentrations and low trace element mobilities occur in the alluvial soils between test pit MT4 and MT1, on the bank of the Kromdraai Spruit. This portion is approximately 90 m long. There is however high extractable trace element concentrations and trace element mobilities in the tailings cover overlying the soils. As these soils have not yet been degraded it is important that the tailings cover overlaying these soils be removed. It is proposed that the tailings cover be removed (with a bulldozer) and stockpiled in a berm approximately 100 meters away from the Kromdraai Spruit. A grass cover should be established on the berm as well as in the exposed alluvial soils to inhibit erosion. This should decrease the movement of tailings polluted sheetwash towards the river which will cause degradation of the unpolluted soils.

- The study has determined that the pH of the tailings and the soils plays an important role in determining the mobilities of the investigated trace elements, with all the elements (except Pb) being most mobile under low pH conditions. This suggests that liming of the tailings and soils could be an effective rehabilitation measure to minimize trace element mobility. It is however known that certain trace elements (e.g. As) are more mobile under high pH conditions and liming could therefore be detrimental as certain trace elements may be mobilized while others will become less mobile. Batch experiments could be conducted on the affected soils and tailings by determining the trace element concentration of leachate obtained from the affected soils under various soil pH values. Such a study will determine the effectiveness of liming as a rehabilitation option.

- Total arsenic concentrations in the tailings and soils suggest that As is a priority pollutant. Extractable As concentrations were however mostly below the detection limit of the analytical technique (i.e. the easily exchangeable arsenic fraction in the samples are very small). The risk that As poses on the receiving environment could therefore not be investigated. It is proposed that the chemical nature of the As in the soils and tailings be further investigated to establish if As is indeed a pollutant of concern. Total chromium concentrations in the tailings and soils was also high, but the element has a low mobility. Chromium should also be further investigated to determine the risk posed by the element. The influence of the high sulphate concentrations in the soil solution on trace element mobility should also be considered in any further studies.

- The current landuse of the study area is grazing land for cattle. The ability of the existing grass cover of the polluted tailings and soils to bio-accumulate trace elements which are hazardous to animal life should be investigated. Certain plants can bio-accumulate certain trace elements (e.g. Cd) to levels which are detrimental to the health of grazing animals and subsequent individuals higher up in the food chain.

- Groundwater in the study area are used for both agricultural and domestic purposes. The study area is underlain by a dolomitic aquifer which is usually highly sensitive to pollution due to groundwater compartmentilation. A detailed groundwater study of the area should be conducted to establish the extent to which the regional groundwater quality of the area has been affected. This will determine if human and livestock health is being negatively affected.

REFERENCES

ACOCKS.J.P.H. 1988. *Veld types of South Africa.* Memoirs of the Botanical Survey of South Africa, No. 57.

ALLOWAY, B.J. 1995. *Heavy metals in soils.* Editor B.J. Alloway. Second edition. Blackie, Glasgow. 368 p.

ASTM 1996. *Annual Book of ASTM Standards.* Section 4, Volume 04.08. Soil and Rock (1): D 422 & D4318-95. American Society for Testing and Materials.

ASTM 1970. *Standard test method for classification of soils for engineering purposes.* D2487-1969. American Society for Testing and Materials.

BALINGEN, H.D. 1993. *Umweltschutz in Baden-Württemburg.* Umweltministerium Baden-Württemburg. Fed. Rep. Of Germany. Government Gazette 29 September, 30, 1031 - 1035.

BARTON, E.S. & HALLBAUER, D.K. 1996. Trace-element and U-Pb isotope compositions of pyrite types in the Proterozoic Black Reef, Transvaal Sequence, South Africa: Implications on genesis and age. Chemical Geology, 133, 173 - 199.

BLIGHT, G. & DU PREEZ, J. 1997. The escape of salt pollution from decommissioned gold residue deposits. Journal of The South African Institute of Mining and Metallurgy, July/August 1997, pp 201 - 204.

BOHN, H.L. MCNEAL, B.L. & O'CONNOR, G.A. 1985. *Soil Chemistry* (2nd Ed.). Wiley, New York, 339 p.

BOURG, A.C.M. 1995. Speciation of heavy metals and implications for their mobility. (In:: Salomons, W. Förstner U. & Mader P. eds. Heavy Metals, 19 -31, Springer-Verlag, New York.

BRINK, A.B.A. 1979. *Engineering geology of Southern Africa. Volume 1.* Building Publications, Pretoria, 319 p.

BRÜMMER, G.W. GERTH, J. & HERMS, U. 1986. Heavy metal species, mobility and availability in soils. Zeitschrift feur Pflanzenernaehrung und Bodenkunde. 149 (4): 382-398.

COETZEE, H. 1995. Radioactivity and the leakage of radioactive waste associated with Witwatersrand gold and uranium mining. (In: Proceedings of the conference on Uranium-Mining and Hydrogeology, 90-99, Freiberg, Sachsen).

COETZEE, P.P. GOUWS, K. PLÜDDEMANN, S. YOCOBY, M. HOWELL, S. & DRIJVER, L. 1995. Evaluation of sequential extraction procedures for metal speciation in model sediments. Water SA. 21(1): 51-60.

CROUNSE, R.G. PORIES, W.J. BRAY, J.T. & MAUGER, R.L.1983. Geochemistry and Man: Health and Disease. (2) Elements possibly essential, those toxic and others. (In: Thornton, I. ed Applied Environmental Geochemistry, 309-330, Academic Press Geology Series, Academic Press, London).

DAVIES, B.E. 1983. Heavy metal contamination from base metal mining and smelting; Implications for man and his environment. (In: Thornton, I. ed Applied Environmental Geochemistry, 425-462, Academic Press Geology Series, Academic Press, London).

DEPARTMENT OF AGRICULTURAL 1991. *A binominal soil classification system for South Africa* (2nd Edition). Memoirs of the natural agricultural resources of South Africa, (15), Department of Agriculture, 262p.

[1]DEPARTMENT OF WATER AFFAIRS AND FORESTRY 1996. *South African Water Quality Guidelines* (second edition.) Volume1: Domestic Use. Published by the Department of Water Affairs and Forestry.

[2]DEPARTMENT OF WATER AFFAIRS AND FORESTRY 1996. *South African Water Quality Guidelines* (second edition.) Volume 4: Agricultural Water Use: Irrigation. Published by the Department of Water Affairs and Forestry.

[3]DEPARTMENT OF WATER AFFAIRS AND FORESTRY 1996.. *South African Water Quality Guidelines* (second edition.) Volume 5: Agricultural Water Use: Livestock watering. Published by the Department of Water Affairs and Forestry.

[4]DEPARTMENT OF WATER AFFAIRS AND FORESTRY 1996. *South African Water Quality Guidelines* (second edition.) Volume7: Aquatic Ecosystems. Published by the Department of Water Affairs and Forestry.

DEUEL, L.E. & HOLLIDAY, G.H. 1994. *Soil remediation for the petroleum extraction industry*. PennWell Books, Oklahoma, 287 p.

DEUTSCH, W.J. 1997. *Groundwater geochemistry: Fundamentals and applications to contamination.* Lewis, New York, 221 p.

ELSENBROEK, J.H. 1996. *An analytical report of the calibration on the Philips PW 1606 Simultaneous dispersive X-ray Fluorescence Spectrometer*. Council for Geoscience open file report No. 1996-0236, Pretoria.

ELLIS, D.E. 1989. *Environments at risk - Case Histories of impact assessment*. Springer-Verlag, Berlin.

ERASMUS, F.J. 1997. *Inleidende ondersoek na die Machavie-myn en sy omgewing*. Unpublished report, Department of Mineral and Energy Affairs, Pretoria.

ERIKSSON, K.A. & TRUSWELL. J.F. 1979. Stratotypes from the Malmani Subgroup north-west of Johannesburg, South Africa. Transactions of the Geological Society of South Africa. 77: 211-222.

EVANS, G.H. 1990. *The geochemistry and environmental study of a reed-bed adjacent to a gold slimes dump, with aspects on acid mine water and heavy metal pollution*. B.Sc. thesis Univ. Witwatersrand, Johannesburg, 97 p.

FERGUSON, K.D. & ERICKSON, P.M. 1988. Pre-Mine Prediction of Acid Mine Drainage. (In: Salomons W. & Förstner U. eds. Environmental Management of Solid Waste, Dredged Materials and Mine Tailings. 24-43, Springer-Verlag, New York).

FERGUSON, C. DARMENDRAIL, D. FREIER, K. JENSEN, B.K. JENSEN, J. KASAMAS, H. URZELAI, A & VEGTER, J. (eds). 1998. *Risk Assessment for Contaminated Sites in Europe. Volume 1. Scientific Basis*. LQM Press, Nottingham, 165 p.

FÖRSTNER, U. & WITTMANN, G.T.W. 1976. Metal accumulations in acidic waters from gold mines in South Africa. Geoforum, 7: 44-49.

FÖRSTNER, U. & KERSTEN, M. 1988. Assessment of metal mobility in dredged material and mine waste by pore water chemistry and solid speciation. (In: Salomons W. & Förstner U. eds. Chemistry and Biology of Solid Waste, Dredged Materials and Mine Tailings. 214-237, Springer-Verlag, New York).

FUNKE, J.W. 1985. *Contribution of mining wastes to the mineral pollution of the Vaal catchment area and of the Vaal Barrage*. Water Research Commission, Pretoria, 13 p.

FUNKE, J.W. 1990. *The water requirements and pollution potential of South African gold and uranium mines*. Water Research Commission (Rep. No. KV9/90), Pretoria, 172 p.

FYFE, W.S. 1998. Towards 2050; the past is not the key to the future - challenges for the science of geochemistry. Environmental Geology, 30: 92-95.

GRAY, N.F. 1997. Environmental impact and remediation of acid mine drainage: a management problem. Environmental Geology, 30: 62-71.

HARRIS, M. & HERBERT, S. 1994. *Contaminated land, Investigation, assessment and remediation. British Institute of Civil Engineers design and practice guide*. The Lavenham Press, Sudbury, Suffolk, 77p.

HATHEWAY, A.W. 1998. Engineering geology and the environment. (In: Proceedings of the Eight International Congress of the International Association for Engineering Geology and the Environment. (4) 2269 - 2277).

INTERDEPARTMENTAL COMMITTEE ON THE REDEVELOPMENT OF CONTAMINATED LAND 1987. *Guidance on the assessment and redevelopment of contaminated land*. ICRCL 59/83. ICRCL, 2nd edn. British Department of the Environment. Eastcote.

JAMBOR, J.L. & BLOWES, D.W. 1998. Theory and applications of mineralogy in environmental studies of sulfide-bearing mine wastes. (In: Cabri, L.J & Vaughan, D.J. eds. Modern Approaches to Ore and Environmental Mineralogy. 367 - 402. Short course no. 27 of the Mineralogical Association of Canada, Ottawa, Ontario).

JAMES, A.R. 1997. *The prediction of pollution loads from coarse sulphide-containing waste materials*. Water Research Commission Report No. 559/1/97, Pretoria.

JENNINGS, J.E.B. BRINK, A.B.A. & WILLIAMS, A.A.B. 1973. Revised guide to soil profiling for civil engineering purposes in South Africa. Transactions of the South African Institute of Civil Engineers. 15: 3 - 13.

KABATA-PENDIAS, A. 1992. Behavioural properties of trace metals in soils. Applied Geochemistry, Suppl. Issue No. 2: 3-9.

KABATA-PENDIAS, A. & PENDIAS, H. 1986. *Trace elements in soils and plants.* C.R.C. Press, Florida, 315p.

KLEIN, W. 1998. Remediation of hazardous waste sites. South African Journal of Science. 94: 426-429.

LAMBE, T.W. & WHITMAN, R.V. 1969. *Soil Mechanics.* John Wiley & Sons Inc, New York, 553 p.

LAND TYPE SURVEY STAFF 1984. *Land types of the maps 2626 Wes-Rand, 2726 Kroonstad.* Mem. Agric. Nat. Resour. S.Afr. No.4.

LINDSAY, W.L. 1979. *Chemical equilibria in soils.* New York: Wiley-Interscience.

LLOYD, P.J.D. 1997. *Comment on paper*: The escape of salt pollution from decommissioned gold residue deposits by G.E. Blight & J du Preez. Journal of The South African Institute of Mining and Metallurgy, November/December 1997.

LOURENS, C. 1999. Net closing on illegal waste dumping. Martin Creamer's Engineering News. 19(15): April 23 - 29, 13.

MANAHAN, S.E. 1994. *Environmental chemistry*. 6th edition, Lewis publishers, CRC press, Florida, USA. 811p.

MARSDEN, D.D. 1986. The current limited impact of Witwatersrand gold-mine residues on water pollution in the Vaal River system. Journal of The South African Institute of Mining and Metallurgy. 86 (12): 481 - 504.

MCBRIDE, M.B. 1994. *Environmental chemistry of soils*. Oxford University Press, Oxford.

MOEN J.E.T. CORNET J.P. & EVERS C.W.A. 1986. Soil protection and remedial action: Criteria for decision making and standardisation requirements.(In: Assink J.W. and Vanderbrink W.J eds. Contaminated soil. Martinus Nijhoff Publishers, Dordrecht).

NRIAGU, J.O. 1996. A history of global metal pollution. Science, 272: 223 - 224.

PIERZYNSKI, G.M. SIMS, T.J. & VANCE, G.F. 1994. *Soils and environmental quality*. Lewis, London, 313p.

PRÜEß, A. TURIAN, G. & SCHWEIKLE, V. 1991. Ableitung kritischer gehalte an NH_4NO_3 extrehierbaren ökotoxikologisch relevanten spurenelementen in böden SW-Deutschlands. Mitt. Dtsch. Bodenkundl. Gesellsch., 66(I): 385-388.

PULLES, W. HEATH, R. & HOWARD, M. 1996. A Manual to Assess and Manage the Impact of Gold Mining Operations on the Surface Water Environment. Water Research Commission Report No. TT/79/96, Pretoria.

READING, H.G. 1996. *Sedimentary environments, Processes, Facies and Stratigraphy*. Blackwell Science. United Kingdom, 688p.

RÖSNER, T. BOER, R. REYNEKE, J.L. AUCAMP, P. & VERMAAK, J. 1998. A preliminary assessment of pollution contained in the unsaturated and saturated zone underneath tailings dams. Water Research Commission report number K5/797/0/1, Pretoria.

ROWELL, D.L. 1994. *Soil science, methods and applications.* Addison Wesley Longman Limited, Essex England, 350p.

SCHLOEMANN, H. 1994. The geochemistry of some common Western Cape soils (South Africa) with emphasis on toxic and essential elements. Unpublished PhD thesis, University of Cape Town.

SINGER, M.J. & MUNNS, D.N. 1992. *Soils, introduction.* Second edition. Macmillan, New York, 473p.

SOIL ANALYSES WORK COMMITTEE 1990. *Handbook of standard soil testing methods for advisory purposes.* Soil Science Society of South Africa, Pretoria.

SOIL CLASSIFICATION WORKING GROUP 1991. *Soil classification, a taxonomic system for South Africa.* Memoirs concerning the natural agricultural resources of South Africa. No 15: 262 p.

SOIL SURVEY STAFF 1975. *Soil taxonomy - a basic system of sol classification for making and interpreting soil surveys.* U.S. Dept. Agric. Washington, Handbook No 436: US Govt. Printing Office.

SPARKS, D.L. 1995. *Environmental soil chemistry.* Academic Press, New York, 267p.

SPOTTS, E. SCHAFER, W.M. LUCKAY, C.F. & MITCHELL, T.S. 1997. Determination of runoff metal loading from reclaimed and unreclaimed tailings. (In: Proceedings of the Fourth International Conference on Acid Rock Drainage, Vancouver, 1567 - 1577).

STEYN, C.E. VAN DER WATT, H.V.H. & CLAASSENS, A.S. 1996. On the permissible nickel concentration for South African soils. South African Journal of Science, 92: 359-363.

SZAKOVA, J. TLUSTOS, P. BALIK, J. PAVLIKOVA, D. & BALIKOVA, M. 1999. Extractability and plant -availability of soil As and Cd as influenced by soil properties. (In: Wenzel, W.W. Adriano, D.C. Alloway, B. Doner, H.E. Keller, C. Lepp, N.W. Mench, M. Naidu, R. & Pierzynski, G.M. eds. Proceedings of the 5th Interntional Conference on the Biogeochemistry of Trace Elements, Vienna, Austria).

TESSIER, A. CAMPBELL, P.G.C. & BISSON, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51: 844 - 851.

THORNTON, I 1996. Sources and pathways of arsenic in the geochemical environment: health implications. (In Environmental geochemistry and health. Appleton, J.D.; Fuge, R. & McCall, G.J.H. (eds). Geological Society Special Publication, 113: 153-161.

THORNTON, I. 1999. Bioavailability of trace elements in the foodchain. (In: Wenzel, W.W. Adriano, D.C. Alloway, B. Doner, H.E. Keller, C. Lepp, N.W. Mench, M. Naidu, R. & Pierzynski, G.M. eds. Proceedings of the 5th Interntional Conference on the Biogeochemistry of Trace Elements, Vienna, Austria).

TMH 1 1990. *Standard Test Methods for Road Construction Materials*, Committee for State Road Authorities. Department of Transport, Pretoria.

UNEP 1993. *United Nations Environment Programme. Environmental Data Report. 1993-94*. Blackwell.

VAN ROOY, J.L. 1996. The role of engineering geology and environmental geology in the reconstruction and development programme for South Africa. Bulletin of the International Association of Engineering Geology.53: 115 - 120.

VAN DER MERWE, D.H. 1964. The prediction of heave from the plasticity index and percentage clay fraction of soils. The Civil Engineer in South Africa. Vol 6, No 6: 103 - 107.

VEGTER, J.J. 1995. Soil protection in the Netherlands.(In: Allen, R. Förstner, U. &. Salomons, W. eds Heavy Metals 79-100. Springer-Verlag, New York).

VISSER, D.J.L. 1989. Explanation of the 1: 1 000 000 geological map of the Republic of South Afrika. Council for Geoscience, Pretoria, South Africa, 491p.

WALTON, D. VERHAGEN, B. TH. & TAUSSIG-DUTHE, D.M. 1993. The practical applications of environmental isotopes in pollution studies. (In: Proc. Conf.: South Africa needs Groundwater. Univ. Witwatersrand. (Vol 1), Johannesburg).

WARD, R.C. 1975. *Principles of Hydrology*. Second Edition. McGraw-Hill. Berkshire, Great Britain, 367 p.

WEATHER BUREAU 1995. *Climate of South Africa*. Editor B. R., Schulze. Weather Bureau Publication No. WB28, Pretoria.

WHITE, A.F. 1995. Chemical weathering rates of silicate minerals in soils. (In: White, A.F. & Brantley, S.L. eds. Reviews in Mineralogy, Vol 31, 407 - 458. Chemical Weathering Rates of Silicate Minerals, Editors Mineralogical Society of America,Washington, D.C).

YARON, B. CALVERT, R. & PROST, R. 1996. *Soil Pollution, Processes and Dynamics*. Springer- Verlag, Berlin, Heidelberg, 313p.

ZNATOWICZ, K.P.S. 1993. Radioactive and heavy metal pollution associated with a gold tailings dam on the East Rand. Unpublished B.Sc. Thesis Univ. Witwatersrand, Johannesburg, 113 p.

APPENDIX A

GEOTECHNICAL PROPERTIES

Table A1 **Summary of geotechnical properties**

SAMPLE DESCRIPTION			**GRADING ANALYSES**						**ATTERBERG LIMITS**					***IN SITU* PROPERTIES**	
TEST PIT and Sample No.	**DEPTH (m)**	**UNIFIED SOIL CLASSIFICATION**	**% Clay**	**% Silt**	**% Sand**	**% Gravel**	**GM**	**FM**	**LL**	**LS**	**PI**	**PI ws**	**Exp**	**pH**	**Conductivity (mS/m)**
ALLUVIAL SOILS															
Soil unit TA (redistributed tailings overlying alluvial soils)															
MT1/1	0.10	ML Silt with sand	35.42	49.18	15.40	0.00	0.18	0.21	35.19	7.16	10.90	10.66	low	3.97	27.25
MT2/1	0.10	ML Silt	37.45	53.95	8.60	0.00	0.10	0.12	37.54	7.23	9.65	9.50	low	3.70	21.70
MT3/1	0.10	ML Silt	38.44	50.16	11.40	0.00	0.13	0.15	38.23	7.81	11.85	11.65	low	3.63	24.60
MT4/1	0.10	CL Lean clay with sand	34.42	36.68	28.90	0.00	0.34	0.45	34.42	7.61	11.45	10.90	low	3.50	25.05
MT5/1	0.10	CL Lean clay	31.74	59.56	8.70	0.00	0.10	0.07	31.11	4.77	8.34	8.27	low	3.29	26.94
MT6/1	0.15	ML Silt	14.49	75.01	10.50	0.00	0.11	0.03	-	-	-	-	-	3.33	22.76
MT7/1	0.25	ML Silt with sand	3.54	60.46	36.00	0.00	0.36	0.07	-	-	-	-	-	3.71	11.22
MT8/1	0.10	SM Silty sand	1.54	38.76	59.70	0.00	0.60	0.12	-	-	-	-	-	4.61	76.70
MT9/1	0.25	ML Silt with sand	1.99	59.11	38.90	0.00	0.40	0.15	-	-	-	-	-	3.32	2.60
MT10/1	0.30	ML Silt with sand	2.52	56.68	40.80	0.00	0.42	0.20	-	-	-	-	-	3.29	158.93
MT11/1	0.30	ML Silt with sand	11.97	49.83	38.20	0.00	0.41	0.28	-	-	-	-	-	3.52	62.77
MT12/1	0.05	ML Sandy silt	12.57	37.63	48.80	1.00	0.56	0.47	21.69	1.30	3.10	2.94	low	4.21	56.60
MT13/1	0.15	SM Silty sand	0.89	44.51	54.30	0.30	0.67	0.72	-	-	-	-	-	3.37	171.10
MT14/1	0.05	ML Silt	22.49	73.91	3.60	0.00	0.04	0.03	41.58	3.88	11.61	11.58	low	3.48	3.88
MT15/1	0.10	ML Silt with sand	10.74	62.96	26.30	0.00	0.26	0.05	-	-	-	-	-	3.33	168.50
Soil unit AU (upper alluvial soil)															
MT1/2	0.30	CL Sandy clay of low plasticity	37.66	26.84	35.50	0.00	0.41	0.58	46.00	12.78	24.19	22.95	med	6.65	90.25
MT1/3	0.60	CL Sandy clay of low plasticity	40.57	24.03	35.40	0.00	0.42	0.66	47.41	13.21	22.90	21.45	med	7.73	107.94
MT2/2	0.30	CH Sandy clay of high plasticity	38.45	18.95	30.00	12.60	0.80	0.85	53.02	14.57	26.79	20.71	med	7.43	121.24
MT3/2	0.20	CL Sandy clay of low plasticity	35.38	27.92	36.70	0.00	0.46	0.77	43.86	12.59	19.83	18.12	med	6.33	97.40
MT4/2	0.20	CH Sandy clay of high plasticity	42.28	25.92	31.70	0.10	0.39	0.62	50.88	14.92	27.17	25.43	high	7.46	144.02
MT5/2	0.20	CL Sandy clay of low plasticity	34.88	33.12	32.00	0.00	0.38	0.51	43.93	11.91	17.58	16.62	low	3.76	75.29
MT6/2	0.30	CL Sandy clay of low plasticity	35.28	33.92	30.80	0.00	0.38	0.57	42.02	12.48	19.03	17.71	med	3.60	47.17
MT7/2	0.45	CL Sandy clay of low plasticity	31.92	27.78	40.30	0.00	0.52	0.89	37.86	11.70	15.88	14.01	low	4.31	81.80
MT8/2	0.35	CL Low plastic clay with sand	40.05	32.55	27.40	0.00	0.34	0.55	48.40	14.57	23.70	22.13	med	4.21	71.10
MT9/2	0.50	CH High plastic clay with sand	45.19	30.21	24.60	0.00	0.28	0.37	54.72	15.20	27.04	26.25	med	3.21	2.38
MT9/3	1.10	CH High plastic clay with sand	51.35	26.95	21.70	0.00	0.25	0.35	64.01	13.84	35.73	34.47	high	4.49	3.28
MT10/2	0.40	CL Sandy clay of low plasticity	31.75	32.85	35.20	0.20	0.41	0.55	45.20	11.67	21.22	20.20	med	3.17	149.03
MT11/2	0.45	CL Sandy clay of low plasticity	23.06	36.94	39.80	0.20	0.51	0.74	42.85	11.93	17.88	16.40	med	4.35	133.30
MT12/2	0.20	CL Sandy clay of low plasticity	33.70	29.60	36.70	0.00	0.44	0.69	42.87	10.59	18.81	17.52	med	3.85	137.66
MT14/2	0.35	CL Sandy clay of low plasticity	28.09	35.71	36.20	0.00	0.43	0.67	36.39	8.77	15.75	14.62	med	3.53	1.03
MT15/2	0.20	CL Sandy clay of low plasticity	26.75	31.35	41.90	0.00	0.54	0.89	30.28	8.16	12.18	10.76	low	3.60	56.00

GM:Grading Modulus, FM:Fineness Modulus, LL:Liquid limit, LS:Linear shrinkage, PI:Plasticity Index, PI ws: Plasticity index of whole sample, Exp: Expansiveness

Table A1 **Summary of geotechnical properties**

SAMPLE DESCRIPTION			GRADING ANALYSES						ATTERBERG LIMITS					*IN SITU* PROPERTIES	
TEST PIT and Sample No.	**DEPTH (m)**	**UNIFIED SOIL CLASSIFICATION**	**% Clay**	**% Silt**	**% Sand**	**% Gravel**	**GM**	**FM**	**LL**	**LS**	**PI**	**PI ws**	**Exp**	**pH**	**Conductivity (mS/m)**
ALLUVIAL SOILS (CONTINUED)															
Soil unit AL (Lower alluvial soil)															
MT1/4	1.20	CL Sandy clay of low plasticity	36.83	23.87	38.20	1.10	0.52	0.85	44.85	12.72	23.39	21.30	med	7.67	165.99
MT3/3	0.70	CH Sandy clay of high plasticity	38.81	24.49	34.80	1.90	0.54	0.93	52.99	11.19	26.69	23.33	med	7.78	124.50
MT3/4	1.50	CH High plastic clay with sand	56.16	17.84	25.50	0.50	0.34	0.59	72.50	15.74	39.10	36.59	high	7.66	2.90
MT5/3	0.70	CL Sandy clay of low plasticity	39.32	27.38	32.60	0.70	0.45	0.79	49.64	12.28	26.31	23.80	med	7.71	138.11
MT7/3	1.00	CH Sandy clay of high plasticity	38.28	24.82	36.30	0.60	0.51	0.95	54.50	14.07	29.12	25.64	high	7.62	128.60
MT1/5	1.70	CL Sandy clay of low plasticity	46.35	20.85	32.70	0.10	0.38	0.54	49.09	11.38	27.35	26.05	med	7.65	200.61
MT5/4	1.40	CH High plastic clay with sand	45.38	24.92	28.40	1.30	0.46	0.82	58.45	13.52	31.61	28.10	high	8.00	162.08
MT7/4	1.60	CH Sandy clay of high plasticity	43.47	26.23	29.50	0.80	0.41	0.67	55.33	14.07	31.50	28.73	high	7.51	3.82
MT9/4	1.50	CH High plastic clay with sand	61.73	14.97	19.90	3.40	0.38	0.57	65.21	14.19	35.64	32.53	med	6.90	2.86
MT11/3	0.60	CL Sandy clay of low plasticity	48.07	8.63	38.50	4.80	0.55	0.82	-	-	-	-	-	7.25	173.63
MT11/4	1.10	CL Sandy clay of low plasticity	52.69	17.71	26.60	3.00	0.43	0.62	-	-	-	-	-	7.60	158.68
MT13/2	0.30	CL Sandy clay of low plasticity	44.90	20.50	33.40	1.20	0.52	0.89	47.79	13.70	21.62	19.02	low	4.67	190.94
MT13/3	0.70	CH Sandy clay of high plasticity	51.54	17.96	30.40	0.10	0.36	0.51	53.45	13.64	28.03	26.59	med	7.06	174.73
MT15/3	0.50	CL Sandy clay of low plasticity	32.77	25.33	41.60	0.30	0.62	1.20	44.70	8.52	23.77	19.66	med	3.85	150.99
MT15/4	1.10	CL Sandy clay of low plasticity	31.73	25.07	39.60	3.60	0.71	1.25	43.39	12.20	22.63	18.13	med	7.68	133.79
MT5/5	2.00	SC Clayey sand with gravel	27.95	12.65	35.80	23.60	1.20	0.96	42.46	13.21	21.94	14.36	med	6.91	3.02
COLLUVIAL SOILS															
Soil unit TC (Paddocked and redistributed tailings)															
MT16/1	0.30	SM Silty sand	0.99	34.91	64.10	0.00	0.65	0.33	-	-	-	-	-	4.63	19.29
MT17/1	0.05	SM Silty sand	0.99	21.71	77.30	0.00	0.79	0.46	-	-	-	-	-	3.20	2.27
MT18/1	0.01	SM Silty sand with gravel	0.88	23.62	74.10	1.40	2.95	1.05	-	-	-	-	-	3.06	3.06
MT19/1	0.05	SM Silty sand with gravel	2.56	28.04	66.40	3.00	1.05	1.77	-	-	-	-	-	3.40	31.30
MT21/1	0.30	SM Silty sand	1.01	38.89	60.10	0.00	0.61	0.18	-	-	-	-	-	3.13	7.13
MT22/1	0.05	SM Silty sand	3.01	46.19	50.30	0.50	0.54	0.30	-	-	-	-	-	3.41	27.13
MT23/1	0.10	SM Silty sand	1.53	24.77	73.70	0.00	0.75	0.25	-	-	-	-	-	3.76	10.24
MT24/1	0.30	ML Silt with sand	4.99	66.11	28.90	0.00	0.29	0.06	-	-	-	-	-	3.39	1.15
MT25/1	0.20	ML Silt with sand	8.75	64.85	26.40	0.00	0.27	0.05	-	-	-	-	-	2.50	2.01
MT25/2	0.60	ML Silt with sand	9.20	71.70	19.10	0.00	0.20	0.04	-	-	-	-	-	2.78	1.78
MT26/1	0.30	SM Silty sand	4.55	47.65	47.80	0.00	0.48	0.07	-	-	-	-	-	3.04	109.28
MT26/2	1.20	ML Silt with sand	9.21	62.39	28.40	0.00	0.29	0.06	-	-	-	-	-	2.82	5.69

GM:Grading Modulus, FM:Fineness Modulus, LL:Liquid limit, LS:Linear shrinkage, PI:Plasticity Index, PI ws: Plasticity index of whole sample, Exp: Expansiveness

Table A1 **Summary of geotechnical properties**

SAMPLE DESCRIPTION			GRADING ANALYSES						ATTERBERG LIMITS					*IN SITU* PROPERTIES	
TEST PIT and Sample No.	DEPTH (m)	UNIFIED SOIL CLASSIFICATION	% Clay	% Silt	% Sand	% Gravel	GM	FM	LL	LS	PI	PI ws	Exp	pH	Conductivity (mS/m)
COLLUVIAL SOILS (CONTINUED)															
Soil unit CT (Paddocked and redistributed tailings) (continued)															
MT27/1	0.30	ML Silt with sand	9.22	62.58	28.20	0.00	0.29	0.04	-	-	-	-	-	3.11	1.50
MT28/1	0.25	ML Silt	26.61	60.09	13.30	0.00	0.14	0.11	30.80	3.36	7.76	7.69	low	3.16	2.03
MT28/2	0.75	SM Silty sand	5.04	31.16	60.10	3.70	0.89	1.16	-	-	-	-	-	3.33	121.22
Soil unit CU (Upper colluvial soil)															
MT16/2	0.70	SC Clayey sand	22.45	26.55	51.00	0.00	0.69	1.24	25.49	5.86	9.23	7.62	low	3.26	63.73
MT17/2	0.15	SC-SM Silty, clayey sand	10.43	23.07	61.00	5.50	1.03	1.70	19.55	2.72	5.24	3.81	low	3.42	25.65
MT18/2	0.20	SM Silty sand	8.86	24.04	61.20	5.90	1.07	1.71	17.62	1.90	3.46	2.41	low	3.36	24.70
MT19/2	0.20	SM Silty sand	7.19	21.31	67.00	4.50	1.19	2.24	17.70	1.50	2.53	1.64	low	3.61	10.55
MT21/2	0.70	SM Silty sand	6.28	22.42	69.40	1.90	1.09	2.05	17.27	1.37	2.17	1.50	low	3.96	16.34
MT23/2	0.50	SM Silty sand	6.89	25.41	63.60	4.10	1.05	1.89	17.22	1.21	3.13	2.23	low	3.98	30.46
MT24/2	0.60	SM Silty sand	4.45	23.05	71.70	0.80	1.61	2.03	15.47	1.62	2.24	1.61	low	3.68	125.13
MT24/3	1.20	SM Silty sand	7.49	24.91	65.70	1.90	1.01	1.83	16.83	1.71	3.16	2.22	low	3.71	112.77
MT25/4	0.85	SM Silty sand	4.73	24.47	70.50	0.30	1.03	2.01	-	-	-	-	-	4.70	69.69
MT25/5	1.10	SM Silty sand	4.73	24.47	70.50	0.30	0.99	1.85	-	-	-	-	-	5.71	37.74
MT26/3	1.50	SM Silty sand	7.61	28.19	63.60	0.60	0.89	1.60	17.79	2.33	3.57	2.81	low	3.92	44.78
MT27/2	0.65	SC-SM Silty, clayey sand	6.79	30.91	62.20	0.10	0.86	1.54	17.76	2.33	4.14	3.24	low	3.34	107.41
Soil unit CF (Ferruginised colluvium)															
MT18/3	0.50	SM Silty sand with gravel	4.82	11.98	54.80	28.40	1.94	3.07	18.27	2.01	3.19	1.21	low	3.25	4.49
MT19/3	0.50	SC-SM Silty, clayey sand with gravel	4.32	10.18	52.90	32.60	2.09	3.38	19.82	1.71	5.13	1.69	low	3.83	64.90
MT21/3	1.20	SM Silty sand with gravel	3.90	10.00	60.30	25.80	2.08	3.75	-	-	-	-	-	3.70	30.60
MT21/4	1.80	SM Silty sand with gravel	5.18	12.02	61.90	20.90	2.02	3.95	-	-	-	-	-	3.81	38.30
MT22/2	0.10	SM Silty sand with gravel	4.53	15.77	42.00	37.70	1.79	1.52	17.73	1.38	3.06	1.35	low	3.72	41.41
MT22/3	0.70	SC-SM Silty, clayey sand with gravel	5.22	10.68	66.70	17.40	1.98	4.17	23.25	3.09	5.59	1.83	low	3.76	34.78
MT23/3	0.90	SC-SM Silty, clayey sand with gravel	5.61	11.89	61.90	20.60	1.92	3.68	19.86	1.91	4.25	1.56	low	3.80	45.97
MT23/4	1.50	SC Clayey sand with gravel	8.40	12.70	61.40	17.50	1.88	3.80	24.34	4.57	7.93	2.88	low	3.77	59.20
MT23/5	1.90	SC Clayey sand	13.50	23.50	54.30	8.70	1.16	2.00	19.63	4.36	7.74	5.06	low	6.21	94.87
MT24/4	1.60	SC-SM Silty, clayey sand	7.23	18.97	73.00	0.80	1.35	3.06	18.58	1.71	4.10	2.16	low	6.30	75.65
MT25/6	1.55	SM Silty sand	3.69	11.71	72.50	12.10	1.96	4.39	17.30	1.33	2.55	0.93	low	5.61	35.19
MT26/4	2.30	SC-SM Silty, clayey sand with gravel	6.09	11.91	62.70	19.30	1.91	3.74	19.01	2.58	4.13	1.59	low	4.16	1.13
MT27/3	0.90	SC-SM Silty, clayey sand	8.69	23.41	67.70	0.20	0.92	1.70	17.35	2.20	4.24	3.32	low	4.13	1.12
MT28/3	0.95	SC-SM Silty, clayey sand with gravel	5.04	12.36	55.40	27.20	1.96	3.24	18.21	1.77	4.09	1.50	low	3.13	0.88

GM:Grading Modulus, FM:Fineness Modulus, LL:Liquid limit, LS:Linear shrinkage, PI:Plasticity Index, PI ws: Plasticity index of whole sample, Exp: Expansiveness

APPENDIX B

MINERALOGY OF THE TAILINGS AND SOILS

Table B.1 Mineralogical composition of some colluvial and alluvial soils (all results reported as percentages)

Sample number	Calcite	Dolomite	Siderite	Hematite / Goethite	Jarosite	Gypsum	Todorokite	Microcline	Plagioclase	Quartz	Mica	Chlorite	Smectite	Il/Sm Inter stratifications
MT1/1								2		79	2		8	9
MT1/2		3							2	84			11	
MT1/3									2	75			22	
MT1/4									2	82	2		14	
MT1/5										73			27	
MT2/1										85	3		3	9
MT2/2								3		79			18	
MT3/1										78		5	5	12
MT3/2										89			11	
MT3/3										77			23	
MT3/4			3							81			16	
MT4/1										90	1		4	5
MT4/2										73			27	
MT5/1					6					77	6	3	3	6
MT5/2										89			11	
MT5/3										77			23	
MT5/4										72			28	
MT5/5										84			16	
MT6/1					13				1	68	6	3		9
MT6/2									2	80			17	
MT7/1		2			2					87	2			7
MT7/2										82			16	2
MT7/3										82			15	3
MT7/4	5									77			18	
MT8/1										96	4		-	
MT8/2										87			6	7
MT9/1					5			1		90	4			
MT9/2						2		1		83	2		10	3
MT9/3						3				76	2		17	2
MT9/4	4					2				76			18	
MT10/1					6					85	4			5
MT10/2						2				84			10	3
MT11/1					7	2				80	5			7
MT11/2						22				64			12	2
MT11/3	3									83			14	
MT11/4	3									79			18	
MT12/1								2		89	2			6
MT12/2						4		2		79			10	5
MT13/1					3					91	3			4
MT13/2						21		3		57			18	
MT13/3										83			17	
MT14/1					7					70	14	2		7
MT14/2								3		85				12
MT15/1					15			2		69	13	2		
MT15/2								2		83			10	5
MT15/3										87				13
MT15/4										91			4	6
MT16/1								1		94	3			1
MT16/2								3		84	3			10
MT17/1					3					93	5			
MT17/2								2		92				6
MT18/1	1				3			2		89	3			1
MT18/2				2				1		90				7
MT18/3							6			82				12
MT19/1					2					94	3			1
MT19/2				3			3			90				5
MT19/3				7			20			55				18
MT21/1										93	3			4
MT21/2				1			3			91				6
MT21/3				5			17			66				11
MT21/4				9			13			78				

APPENDIX C

TOTAL ELEMENT XRF ANALYSES

Table C.1 **XRF analyses of tailings and the alluvial soils (all results reported in mg/kg unless indicated).**

	TiO_2%	MnO%	Fe_2O_3t%	Sc	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	W	Pb	Th	U
MT1/1	0.67	0.06	6.26	15	97	224	24	74	65	110	42	62	26	18	229	13	2	0	0	190	7	0	8	16
MT1/2	0.54	0.19	4.85	11	76	162	20	59	31	28	18	38	40	15	232	15	11	0	0	195	9	0	12	0
MT1/3	0.57	0.25	4.99	12	83	167	21	61	30	28	21	37	59	16	224	15	10	1	0	261	8	3	13	0
MT1/4	0.56	0.26	4.42	13	84	146	23	58	27	23	25	31	82	19	212	15	9	2	4	262	10	2	13	0
MT1/5	0.62	0.26	5.01	11	92	170	23	61	31	27	14	34	43	19	214	16	10	2	0	298	9	2	12	0
MT2/1	0.64	0.04	6.78	15	95	247	15	65	65	85	69	66	19	11	202	7	0	0	0	182	6	0	0	0
MT2/2	0.60	0.20	5.54	14	96	190	20	66	35	31	27	37	47	18	205	15	9	3	0	218	8	1	12	0
MT3/1	0.69	0.03	6.75	15	103	244	15	65	69	91	57	68	20	14	207	10	0	0	0	185	8	1	2	8
MT3/2	0.51	0.20	4.23	9	69	140	19	79	27	31	24	36	33	16	224	15	10	4	0	162	11	1	12	0
MT3/3	0.56	0.21	4.36	13	80	145	19	52	27	28	19	37	65	19	217	15	10	0	0	216	8	1	13	0
MT3/4	0.68	0.22	5.68	14	86	199	23	64	35	36	23	41	42	20	215	17	10	4	0	277	10	7	14	0
MT4/1	0.57	0.05	4.90	11	76	182	19	41	56	86	47	43	21	9	252	11	4	3	0	148	9	0	6	8
MT4/2	0.58	0.19	4.81	11	81	167	18	91	30	35	25	39	42	17	230	15	11	4	0	185	8	0	12	0
MT5/1	0.57	0.03	6.44	13	87	269	13	51	66	69	88	64	14	2	218	3	0	0	0	177	7	0	0	0
MT5/2	0.53	0.19	4.09	10	69	148	37	71	28	88	20	36	26	21	269	16	14	2	0	137	9	0	12	0
MT5/3	0.57	0.20	4.25	13	79	147	19	54	25	28	26	35	64	18	227	16	11	2	0	196	9	4	14	0
MT5/4	0.61	0.19	4.65	12	77	164	18	52	27	28	20	36	58	19	215	15	9	6	6	192	7	2	13	0
MT5/5	0.47	0.13	5.55	11	95	175	16	52	25	18	25	23	29	13	144	14	7	7	16	125	10	0	10	0
MT6/1	0.39	0.02	5.51	8	65	248	5	24	43	30	121	51	7	0	192	0	0	0	0	118	7	0	0	0
MT6/2	0.59	0.22	4.64	10	73	160	73	57	37	171	20	43	26	20	223	16	11	2	0	170	10	2	12	8
MT7/1	0.33	0.01	2.63	3	48	140	6	19	24	18	56	39	18	4	148	8	0	3	0	25	10	0	1	0
MT7/2	0.54	0.25	4.05	9	72	145	35	102	27	66	24	39	29	18	213	15	10	5	4	149	11	0	12	0
MT7/3	0.59	0.26	4.56	12	85	161	20	57	29	32	29	46	64	19	202	15	9	2	0	229	10	4	13	0
MT7/4	0.58	0.18	4.38	12	88	157	20	59	29	26	21	32	46	18	216	16	11	2	0	197	8	3	14	0
MT8/1	0.22	0.01	1.42	1	33	112	5	9	13	9	68	30	19	3	129	8	0	0	0	0	12	0	2	0
MT8/2	0.60	0.29	4.88	12	74	179	39	64	35	75	27	46	29	17	226	15	10	0	0	225	10	0	11	1
MT9/1	0.32	0.03	3.27	4	48	207	27	60	31	73	87	47	10	5	213	5	0	0	0	53	11	0	0	0
MT9/2	0.67	0.07	5.81	13	81	210	51	75	75	251	31	58	24	14	228	16	10	5	3	153	9	0	16	37
MT9/3	0.66	0.29	5.20	12	78	180	31	96	36	61	22	53	34	23	217	16	8	0	0	213	8	5	13	1
MT9/4	0.74	0.27	5.71	16	85	202	18	62	34	39	20	50	40	24	216	17	9	5	0	236	8	6	14	0
MT10/1	0.34	0.05	4.13	5	57	221	27	65	26	63	96	52	8	0	210	0	0	1	0	89	9	0	0	0
MT10/2	0.61	0.11	4.66	11	80	176	41	63	48	166	39	42	23	15	249	15	10	6	8	156	12	0	12	46
MT11/1	0.37	0.03	4.68	7	59	203	11	30	42	55	158	31	9	0	170	0	0	4	3	93	10	0	0	0
MT11/2	0.62	0.31	4.97	15	83	206	116	233	83	297	26	40	39	24	222	18	11	0	0	132	9	2	17	91
MT11/3	0.65	0.17	5.04	15	89	200	18	57	31	33	22	39	63	22	228	16	9	1	0	154	8	6	13	0
MT11/4	0.65	0.10	5.17	13	92	207	17	54	32	33	22	37	42	22	228	17	10	0	0	146	10	5	13	0
MT12/1	0.41	0.09	3.07	7	64	153	28	54	42	75	53	32	20	9	196	12	3	5	4	83	14	0	6	23
MT12/2	0.60	0.19	4.96	11	94	184	41	66	54	147	25	40	26	17	233	17	12	0	0	176	9	1	14	59
MT13/1	0.23	0.28	2.68	2	44	164	30	74	21	59	104	28	14	0	130	2	0	0	0	137	13	0	0	0
MT13/2	0.70	0.42	5.73	15	110	223	69	202	43	243	24	39	38	31	208	18	11	0	0	286	10	5	13	79
MT13/3	0.63	0.14	5.01	11	84	197	15	56	34	29	20	37	28	19	239	17	12	1	0	127	10	6	14	0
MT14/1	0.43	0.44	4.77	9	87	401	79	207	72	206	330	45	0	0	153	0	0	0	0	265	0	0	0	49
MT14/2	0.65	0.08	4.11	9	78	202	18	57	53	88	28	56	23	21	223	16	10	1	0	137	10	4	12	25
MT15/1	0.30	0.16	7.38	11	62	255	42	128	41	107	269	28	0	0	116	0	0	0	0	130	8	0	0	0
MT15/2	0.52	0.06	4.14	9	72	197	13	48	68	61	37	50	19	12	236	15	10	1	0	92	11	0	9	64
MT15/3	0.60	1.02	6.63	14	137	266	52	118	35	119	13	50	32	23	203	14	7	0	0	588	11	3	11	0
MT15/4	0.64	0.31	4.85	13	112	251	14	60	31	22	20	42	47	20	208	15	8	3	0	249	11	5	13	0

Table C.2 **XRF analyses of tailings and the colluvial soils (all results reported in mg/kg unless indicated).**

	TiO_2%	MnO%	Fe_2O_3t%	Sc	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	W	Pb	Th	U
MT16/1	0.27	0.05	1.99	2	44	179	6	17	14	12	58	39	16	5	169	8	0	5	0	41	12	0	0	0
MT16/2	0.55	0.04	4.72	11	80	287	9	49	63	52	43	55	17	8	204	14	8	4	0	137	10	0	9	50
MT17/1	0.22	0.08	2.07	2	40	141	29	63	15	69	81	31	16	3	137	6	0	2	0	14	13	0	0	0
MT17/2	0.41	0.47	6.45	10	90	290	9	43	54	26	32	39	19	5	183	12	5	3	2	730	11	0	15	22
MT18/1	0.25	0.21	4.60	6	55	213	20	49	30	60	211	15	0	0	149	0	0	4	11	173	12	0	0	0
MT18/2	0.50	1.38	6.45	11	105	298	24	62	45	22	22	39	24	7	201	13	8	0	5	1253	11	0	21	14
MT18/3	0.73	6.23	13.02	26	318	563	106	240	122	56	16	43	47	13	198	11	3	0	0	3881	12	36	24	7
MT19/1	0.31	0.83	4.91	6	83	374	9	33	35	18	159	22	12	0	161	0	0	0	0	671	11	0	0	0
MT19/2	0.54	3.32	7.71	17	148	314	49	98	73	24	45	37	37	7	182	11	4	0	0	1743	13	2	23	24
MT19/3	0.88	10.51	14.04	36	333	427	30	291	131	79	6	50	98	30	222	13	4	0	0	3549	13	46	5	19
MT21/1	0.22	0.03	1.40	1	38	136	5	11	12	8	60	31	19	4	145	8	0	0	0	13	13	0	2	0
MT21/2	0.45	1.90	5.29	10	102	274	69	81	57	18	18	35	25	8	197	13	9	0	11	1080	13	5	8	21
MT21/3	0.74	7.31	13.40	29	331	700	29	300	106	33	6	38	44	15	221	11	3	0	0	5123	14	45	1	14
MT21/4	0.86	9.07	12.97	35	275	415	21	234	105	102	4	51	84	38	242	12	4	0	0	3418	14	33	6	0
MT22/1	0.74	1.40	9.33	20	165	516	16	100	50	7	21	65	46	19	269	15	10	0	0	701	9	11	11	0
MT22/2	0.59	0.76	4.97	12	87	206	13	61	26	8	23	55	23	15	256	14	13	1	0	400	8	5	12	0
MT22/3	0.77	0.84	8.64	19	153	463	12	96	34	6	23	56	25	17	307	15	14	0	0	653	7	9	11	0
MT23/1	0.54	0.53	4.33	8	73	147	11	46	21	8	20	51	20	15	261	14	14	0	0	188	6	1	13	0
MT23/2	0.76	1.84	10.50	22	205	409	24	153	48	6	17	60	35	24	263	14	8	0	0	949	8	24	8	0
MT23/3	0.47	0.34	3.94	8	84	176	22	51	24	11	27	31	33	14	212	13	12	0	0	351	6	2	12	0
MT23/4	0.65	0.27	5.75	13	73	216	20	59	34	24	22	55	41	19	214	15	10	0	0	339	6	5	13	0
MT23/5	0.57	0.18	4.14	9	74	133	20	51	30	18	25	41	48	18	207	15	11	0	0	165	6	2	13	0
MT24/1	0.68	0.16	5.59	14	79	198	19	67	38	30	21	71	63	20	219	16	10	0	0	169	5	2	13	0
MT24/2	0.58	0.03	6.42	13	89	226	13	51	55	52	92	59	17	4	169	1	0	0	0	160	5	3	0	0
MT24/3	0.56	0.22	4.87	12	80	155	23	60	30	19	28	35	73	16	192	14	9	0	0	185	6	1	13	0
MT24/4	0.54	0.29	5.53	14	94	179	23	72	31	20	29	45	60	18	182	15	8	0	0	295	6	2	13	0
MT25/1	0.63	0.27	5.91	13	88	200	24	79	35	26	25	49	51	21	198	15	8	0	0	280	6	2	12	0
MT25/2	0.56	0.21	5.05	13	115	143	30	68	35	17	28	29	66	16	173	14	8	0	0	221	6	1	12	0
MT25/3	0.62	0.15	5.34	16	69	149	22	64	38	29	33	47	122	17	185	15	8	0	0	189	3	3	14	0
MT25/4	1.02	0.22	9.87	21	152	239	42	110	84	33	25	72	58	23	177	16	8	0	0	417	5	10	13	0
MT25/5	0.44	1.08	4.02	8	73	201	11	66	39	4	20	36	22	11	232	13	11	2	2	599	9	5	10	0
MT25/6	0.44	0.94	3.80	7	71	280	11	60	23	3	21	34	22	12	245	13	12	0	0	691	8	1	10	0
MT26/1	0.26	0.01	1.08	0	40	176	6	10	11	7	50	44	19	4	188	6	0	6	9	6	7	41	0	0
MT26/2	0.30	0.09	2.96	3	51	218	26	64	28	107	94	49	14	0	166	0	0	0	0	64	6	8	0	0
MT26/3	0.47	1.47	4.72	9	83	219	25	77	42	33	23	44	24	11	226	14	11	0	0	664	9	11	10	12
MT26/4	0.51	1.48	5.09	11	89	231	11	69	29	14	18	45	25	14	237	14	11	0	0	731	8	12	10	0
MT27/1	0.29	0.03	3.62	5	55	215	8	22	14	13	111	44	12	0	167	0	0	0	0	55	6	0	0	0
MT27/2	0.43	0.40	5.81	10	76	254	6	41	50	21	26	42	24	8	207	13	9	0	0	695	8	7	20	28
MT27/3	0.48	1.25	4.44	9	85	207	35	70	40	23	22	42	23	10	231	14	11	0	0	682	8	10	10	18
MT28/1	0.40	0.05	9.14	13	88	338	10	43	56	42	211	55	0	0	157	0	0	0	0	260	1	32	0	0
MT28/2	0.27	0.02	3.77	7	47	210	7	16	24	21	129	27	6	0	172	0	0	0	0	91	4	0	0	0
MT28/3	0.49	0.76	5.40	8	86	281	12	60	28	13	22	42	23	8	239	14	11	0	0	715	7	6	10	0

APPENDIX D

NH_4NO_3 EXTRACTABLE TRACE ELEMENT CONCENTRATIONS, EXCEEDANCE RATIOS AND TRACE ELEMENT MOBILITIES

Table D.1 NH_4NO_3 extractable trace element concentrations of the tailings and soils of the investigated transect (results reported in mg/l)

ALLUVIAL SOILS							
Sample no.	As	Co	Cr	Cu	Ni	Pb	Zn
MT1/1	0.00	1.85	0.05	1.75	5.50	0.15	11.20
MT1/2	0.00	0.00	0.00	0.00	0.38	0.00	0.45
MT1/3	0.00	0.00	0.00	0.00	0.03	0.00	0.30
MT1/4	0.00	0.00	0.00	0.00	0.00	0.00	0.30
MT1/5	0.00	0.00	0.03	0.00	0.00	0.00	0.35
MT2/1	0.00	0.98	0.03	1.18	3.33	0.18	6.58
MT2/2	0.00	0.00	0.03	0.08	0.03	0.00	0.15
MT3/1	0.00	0.85	0.03	1.08	2.45	0.55	4.87
MT3/2	0.00	0.00	0.00	0.00	1.95	0.00	0.55
MT3/3	0.00	0.00	0.00	0.00	0.00	0.00	0.55
MT3/4	0.00	0.00	0.00	0.00	0.00	0.00	0.68
MT4/1	0.00	0.68	0.10	1.68	1.70	0.28	5.82
MT4/2	0.00	0.00	0.00	0.00	0.30	0.00	0.45
MT5/1	0.00	0.43	0.08	2.30	1.35	0.00	4.42
MT5/2	0.00	1.75	0.08	0.83	13.10	0.13	11.95
MT5/3	0.00	0.00	0.00	0.03	0.03	0.00	0.23
MT5/4	0.00	0.00	0.00	0.00	0.00	0.00	0.55
MT5/5	0.00	0.00	0.00	0.00	0.00	0.00	0.48
MT6/1	0.00	0.15	0.25	1.58	0.50	0.13	1.58
MT6/2	0.00	1.86	0.10	2.30	7.18	0.05	21.94
MT7/1	0.00	0.05	0.00	0.50	0.23	0.00	0.23
MT7/2	0.00	1.13	0.00	0.50	7.70	0.00	11.43
MT7/3	0.00	0.00	0.00	0.00	0.00	0.00	0.33
MT7/4	0.00	0.00	0.00	0.03	0.00	0.00	0.65
MT8/1	0.00	0.05	0.00	0.03	0.20	0.00	0.28
MT8/2	0.00	0.55	0.00	0.38	5.98	0.00	5.60
MT9/1	0.00	1.66	0.30	4.93	10.25	0.00	10.32
MT9/2	0.00	1.73	0.63	8.63	13.53	0.08	16.15
MT9/3	0.00	0.08	0.03	0.00	7.25	0.00	1.45
MT9/4	0.00	0.00	0.00	0.00	0.03	0.00	0.55
MT10/1	0.00	2.25	0.08	0.90	7.00	0.00	6.13
MT10/2	0.00	1.53	0.35	3.48	7.04	0.03	12.95
MT11/1	0.00	0.18	0.00	0.38	0.78	0.00	0.98
MT11/2	0.00	1.23	0.05	2.73	7.15	0.00	18.56
MT11/3	0.00	0.00	0.00	0.00	0.03	0.00	0.53
MT11/4	0.00	0.00	0.00	0.00	0.00	0.00	0.60
MT12/1	0.00	0.78	0.00	1.53	2.35	0.00	4.00
MT12/2	0.00	1.13	0.08	3.05	4.75	0.23	11.52
MT13/1	0.00	1.50	0.58	1.88	10.08	0.00	9.41
MT13/2	0.00	1.30	0.05	1.63	8.67	0.03	25.90
MT13/3	0.00	0.00	0.03	0.00	0.03	0.00	1.03
MT14/1	0.00	3.71	0.35	4.60	16.04	0.00	18.33
MT14/2	0.00	2.53	0.15	1.70	10.70	0.45	8.47
MT15/1	0.00	1.83	0.10	2.73	7.55	0.00	8.47
MT15/2	0.00	1.00	0.45	5.63	4.63	0.20	11.98
MT15/3	0.00	0.20	0.03	0.18	5.64	0.03	11.43
MT15/4	0.00	0.00	0.00	0.00	0.03	0.00	0.23

COLLUVIAL SOILS							
Sample no.	As	Co	Cr	Cu	Ni	Pb	Zn
MT16/1	0.00	0.00	0.00	0.10	0.08	0.00	0.00
MT16/2	0.00	0.95	0.33	4.88	3.90	0.20	7.48
MT17/1	0.00	2.55	0.73	2.08	11.00	0.00	24.23
MT17/2	0.00	0.28	0.08	1.38	1.10	0.00	4.46
MT18/1	0.00	2.08	0.55	2.08	6.43	0.00	7.61
MT18/2	0.00	0.33	0.10	1.75	0.95	0.00	3.32
MT18/3	0.00	0.53	0.10	2.05	1.95	0.00	4.73
MT19/1	0.00	0.25	0.08	1.33	1.08	0.00	2.03
MT19/2	0.00	0.13	0.05	1.33	0.33	0.00	0.93
MT19/3	0.00	0.00	0.00	0.23	1.38	0.00	3.78
MT21/1	0.00	0.03	0.00	0.13	0.20	0.00	0.25
MT21/2	0.00	0.23	0.00	1.58	0.58	0.00	1.13
MT21/3	0.00	0.00	0.00	0.18	1.15	0.00	3.18
MT21/4	0.00	0.00	0.00	0.15	2.90	0.00	5.18
MT 22/1	0.00	0.13	0.10	0.67	0.29	0.18	0.84
MT 22/2	0.00	1.13	0.26	2.95	1.85	0.00	3.00
MT 22/3	0.00	0.04	0.00	0.29	1.75	0.92	4.30
MT 23/1	0.00	0.00	0.07	0.26	0.00	0.16	0.29
MT 23/2	0.00	0.89	0.05	1.05	2.99	0.16	2.64
MT 23/3	0.60	0.05	0.00	0.24	2.41	0.15	4.88
MT 23/4	0.00	0.07	0.00	0.24	2.58	1.98	5.18
MT 23/5	0.00	0.12	0.00	0.00	0.26	1.43	0.00
MT 24/1	0.00	1.22	0.44	1.08	3.25	0.44	5.77
MT 24/2	0.00	1.93	0.03	2.18	4.63	0.34	8.60
MT 24/3	0.00	0.05	0.04	0.26	6.33	4.12	9.34
MT 24/4	0.00	0.05	0.03	0.01	0.23	1.12	0.00
MT 25/1	0.00	1.56	0.77	1.97	6.42	0.65	11.39
MT 25/2	0.00	1.55	0.76	2.04	7.99	0.84	14.96
MT 25/3	0.00	1.26	0.18	2.41	4.31	0.78	14.98
MT 25/4	0.00	0.08	0.07	1.28	3.97	1.94	14.47
MT 25/5	0.00	0.10	0.03	0.00	0.46	0.00	0.00
MT 25/6	0.00	0.04	0.00	0.00	0.27	0.00	0.00
MT 26/1	0.00	0.52	0.18	0.44	1.68	0.42	2.87
MT 26/2	0.00	11.52	3.62	8.36	36.58	5.33	63.33
MT 26/3	0.00	0.78	0.07	1.68	8.25	6.36	9.95
MT 26/4	0.00	0.09	0.00	0.15	2.38	0.38	2.21
MT 27/1	0.00	1.12	0.19	0.92	3.68	1.34	4.86
MT 27/2	0.00	1.08	0.35	2.74	3.57	2.21	5.35
MT 27/3	0.00	0.65	0.02	1.23	3.47	0.23	3.32
MT 28/1	0.00	1.84	0.55	2.48	5.46	1.10	7.82
MT 28/2	0.00	0.41	0.12	0.81	1.56	0.12	2.76
MT 28/3	0.00	0.77	0.57	1.28	3.44	2.09	3.20

Table D.2 Trace element exceedance ratios in the tailings and soils of the investigated transect

ALLUVIAL SOILS							
Sample no.	As	Co	Cr	Cu	Ni	Pb	Zn
MT1/1	0.00	3.70	0.50	0.88	5.50	0.08	1.12
MT1/2	0.00	0.00	0.00	0.00	0.38	0.00	0.05
MT1/3	0.00	0.00	0.00	0.00	0.03	0.00	0.03
MT1/4	0.00	0.00	0.00	0.00	0.00	0.00	0.03
MT1/5	0.00	0.00	0.25	0.00	0.00	0.00	0.04
MT2/1	0.00	1.95	0.25	0.59	3.33	0.09	0.66
MT2/2	0.00	0.00	0.25	0.04	0.03	0.00	0.02
MT3/1	0.00	1.70	0.25	0.54	2.45	0.28	0.49
MT3/2	0.00	0.00	0.00	0.00	1.95	0.00	0.06
MT3/3	0.00	0.00	0.00	0.00	0.00	0.00	0.06
MT3/4	0.00	0.00	0.00	0.00	0.00	0.00	0.07
MT4/1	0.00	1.36	1.00	0.84	1.70	0.14	0.58
MT4/2	0.00	0.00	0.00	0.00	0.30	0.00	0.05
MT5/1	0.00	0.85	0.75	1.15	1.35	0.00	0.44
MT5/2	0.00	3.49	0.75	0.41	13.10	0.06	1.20
MT5/3	0.00	0.00	0.00	0.01	0.03	0.00	0.02
MT5/4	0.00	0.00	0.00	0.00	0.00	0.00	0.06
MT5/5	0.00	0.00	0.00	0.00	0.00	0.00	0.05
MT6/1	0.00	0.30	2.50	0.79	0.50	0.06	0.16
MT6/2	0.00	3.71	1.00	1.15	7.18	0.03	2.19
MT7/1	0.00	0.10	0.00	0.25	0.23	0.00	0.02
MT7/2	0.00	2.25	0.00	0.25	7.70	0.00	1.14
MT7/3	0.00	0.00	0.00	0.00	0.00	0.00	0.03
MT7/4	0.00	0.00	0.00	0.01	0.00	0.00	0.07
MT8/1	0.00	0.10	0.00	0.01	0.20	0.00	0.03
MT8/2	0.00	1.10	0.00	0.19	5.98	0.00	0.56
MT9/1	0.00	3.31	3.00	2.46	10.25	0.00	1.03
MT9/2	0.00	3.47	6.25	4.31	13.53	0.04	1.62
MT9/3	0.00	0.15	0.25	0.00	7.25	0.00	0.15
MT9/4	0.00	0.00	0.00	0.00	0.03	0.00	0.06
MT10/1	0.00	4.50	0.75	0.45	7.00	0.00	0.61
MT10/2	0.00	3.06	3.50	1.74	7.04	0.01	1.30
MT11/1	0.00	0.35	0.00	0.19	0.78	0.00	0.10
MT11/2	0.00	2.45	0.50	1.36	7.15	0.00	1.86
MT11/3	0.00	0.00	0.00	0.00	0.03	0.00	0.05
MT11/4	0.00	0.00	0.00	0.00	0.00	0.00	0.06
MT12/1	0.00	1.55	0.00	0.76	2.35	0.00	0.40
MT12/2	0.00	2.25	0.75	1.53	4.75	0.11	1.15
MT13/1	0.00	3.01	5.75	0.94	10.08	0.00	0.94
MT13/2	0.00	2.60	0.50	0.81	8.67	0.01	2.59
MT13/3	0.00	0.00	0.25	0.00	0.03	0.00	0.10
MT14/1	0.00	7.42	3.50	2.30	16.04	0.00	1.83
MT14/2	0.00	5.05	1.50	0.85	10.70	0.23	0.85
MT15/1	0.00	3.65	1.00	1.36	7.55	0.00	0.85
MT15/2	0.00	2.00	4.50	2.81	4.63	0.10	1.20
MT15/3	0.00	0.40	0.25	0.09	5.64	0.01	1.14
MT15/4	0.00	0.00	0.00	0.00	0.03	0.00	0.02

COLLUVIAL SOILS							
Sample no.	As	Co	Cr	Cu	Ni	Pb	Zn
MT16/1	0.00	0.00	0.00	0.05	0.08	0.00	0.00
MT16/2	0.00	1.90	3.25	2.44	3.90	0.10	0.75
MT17/1	0.00	5.10	7.25	1.04	11.00	0.00	2.42
MT17/2	0.00	0.55	0.75	0.69	1.10	0.00	0.45
MT18/1	0.00	4.15	5.50	1.04	6.43	0.00	0.76
MT18/2	0.00	0.65	1.00	0.88	0.95	0.00	0.33
MT18/3	0.00	1.05	1.00	1.03	1.95	0.00	0.47
MT19/1	0.00	0.50	0.75	0.66	1.08	0.00	0.20
MT19/2	0.00	0.25	0.50	0.66	0.33	0.00	0.09
MT19/3	0.00	0.00	0.00	0.11	1.38	0.00	0.38
MT21/1	0.00	0.05	0.00	0.06	0.20	0.00	0.03
MT21/2	0.00	0.45	0.00	0.79	0.58	0.00	0.11
MT21/3	0.00	0.00	0.00	0.09	1.15	0.00	0.32
MT21/4	0.00	0.00	0.00	0.08	2.90	0.00	0.52
MT 22/1	0.00	0.27	0.99	0.33	0.29	0.09	0.08
MT 22/2	0.00	2.26	2.56	1.48	1.85	0.00	0.30
MT 22/3	0.00	0.07	0.00	0.15	1.75	0.46	0.43
MT 23/1	0.00	0.00	0.68	0.13	0.00	0.08	0.03
MT 23/2	0.00	1.77	0.46	0.52	2.99	0.08	0.26
MT 23/3	0.60	0.09	0.00	0.12	2.41	0.07	0.49
MT 23/4	0.00	0.14	0.00	0.12	2.58	0.99	0.52
MT 23/5	0.00	0.24	0.00	0.00	0.26	0.72	0.00
MT 24/1	0.00	2.44	4.39	0.54	3.25	0.22	0.58
MT 24/2	0.00	3.87	0.29	1.09	4.63	0.17	0.86
MT 24/3	0.00	0.09	0.40	0.13	6.33	2.06	0.93
MT 24/4	0.00	0.10	0.35	0.01	0.23	0.56	0.00
MT 25/1	0.00	3.13	7.73	0.98	6.42	0.32	1.14
MT 25/2	0.00	3.10	7.57	1.02	7.99	0.42	1.50
MT 25/3	0.00	2.52	1.84	1.21	4.31	0.39	1.50
MT 25/4	0.00	0.16	0.67	0.64	3.97	0.97	1.45
MT 25/5	0.00	0.20	0.28	0.00	0.46	0.00	0.00
MT 25/6	0.00	0.07	0.00	0.00	0.27	0.00	0.00
MT 26/1	0.00	1.04	1.82	0.22	1.68	0.21	0.29
MT 26/2	0.00	23.04	36.15	4.18	36.58	2.67	6.33
MT 26/3	0.00	1.56	0.66	0.84	8.25	3.18	0.99
MT 26/4	0.00	0.17	0.00	0.07	2.38	0.19	0.22
MT 27/1	0.00	2.23	1.95	0.46	3.68	0.67	0.49
MT 27/2	0.00	2.16	3.52	1.37	3.57	1.10	0.54
MT 27/3	0.00	1.31	0.19	0.62	3.47	0.12	0.33
MT 28/1	0.00	3.68	5.53	1.24	5.46	0.55	0.78
MT 28/2	0.00	0.82	1.18	0.41	1.56	0.06	0.28
MT 28/3	0.00	1.54	5.71	0.64	3.44	1.05	0.32

Table D.3 Trace element mobility (%) in the tailings and soils of the investigated transect

ALLUVIAL SOILS							
Sample no.	As	Co	Cr	Cu	Ni	Pb	Zn
MT1/1	0.00	7.71	0.02	2.69	7.43	0.00	10.18
MT1/2	0.00	0.00	0.00	0.00	0.64	0.00	1.61
MT1/3	0.00	0.00	0.00	0.00	0.04	0.00	1.07
MT1/4	0.00	0.00	0.00	0.00	0.00	0.00	1.30
MT1/5	0.00	0.00	0.01	0.00	0.00	0.00	1.30
MT2/1	0.00	6.50	0.01	1.81	5.12	0.00	7.75
MT2/2	0.00	0.00	0.01	0.21	0.04	0.00	0.48
MT3/1	0.00	5.67	0.01	1.56	3.77	55.00	5.35
MT3/2	0.00	0.00	0.00	0.00	2.47	0.00	1.77
MT3/3	0.00	0.00	0.00	0.00	0.00	0.00	1.96
MT3/4	0.00	0.00	0.00	0.00	0.00	0.00	1.88
MT4/1	0.00	3.55	0.05	2.99	4.15	0.00	6.76
MT4/2	0.00	0.00	0.00	0.00	0.33	0.00	1.29
MT5/1	0.00	3.27	0.03	3.48	2.65	0.00	6.41
MT5/2	0.00	4.72	0.05	2.95	18.45	0.00	13.58
MT5/3	0.00	0.00	0.00	0.10	0.05	0.00	0.80
MT5/4	0.00	0.00	0.00	0.00	0.00	0.00	1.96
MT5/5	0.00	0.00	0.00	0.00	0.00	0.00	2.64
MT6/1	0.00	3.00	0.10	3.66	2.08	0.00	5.25
MT6/2	0.00	2.54	0.06	6.22	12.59	2.50	12.83
MT7/1	0.00	0.83	0.00	2.08	1.18	0.00	1.25
MT7/2	0.00	3.21	0.00	1.85	7.55	0.00	17.31
MT7/3	0.00	0.00	0.00	0.00	0.00	0.00	1.02
MT7/4	0.00	0.00	0.00	0.09	0.00	0.00	2.50
MT8/1	0.00	1.00	0.00	0.19	2.22	0.00	3.06
MT8/2	0.00	1.41	0.00	1.07	9.34	0.00	7.47
MT9/1	0.00	6.13	0.14	15.89	17.08	0.00	14.13
MT9/2	0.00	3.40	0.30	11.50	18.03	0.00	6.43
MT9/3	0.00	0.24	0.01	0.00	7.55	0.00	2.38
MT9/4	0.00	0.00	0.00	0.00	0.04	0.00	1.41
MT10/1	0.00	8.33	0.03	3.46	10.77	0.00	9.72
MT10/2	0.00	3.73	0.20	7.24	11.17	0.00	7.80
MT11/1	0.00	1.59	0.00	0.89	2.58	0.00	1.77
MT11/2	0.00	1.06	0.02	3.28	3.07	0.00	6.25
MT11/3	0.00	0.00	0.00	0.00	0.04	0.00	1.59
MT11/4	0.00	0.00	0.00	0.00	0.00	0.00	1.82
MT12/1	0.00	2.77	0.00	3.63	4.35	0.00	5.33
MT12/2	0.00	2.74	0.04	5.65	7.20	22.50	7.84
MT13/1	0.00	5.01	0.35	8.93	13.61	0.00	15.95
MT13/2	0.00	1.88	0.02	3.78	4.29	0.50	10.66
MT13/3	0.00	0.00	0.01	0.00	0.04	0.00	3.53
MT14/1	0.00	4.69	0.09	6.39	7.75	0.00	8.90
MT14/2	0.00	14.03	0.07	3.21	18.77	11.25	9.62
MT15/1	0.00	4.35	0.04	6.65	5.90	0.00	7.91
MT15/2	0.00	7.69	0.23	8.27	9.64	0.00	19.63
MT15/3	0.00	0.38	0.01	0.50	4.78	0.83	9.60
MT15/4	0.00	0.00	0.00	0.00	0.00	0.00	0.01

COLLUVIAL SOILS							
Sample no.	As	Co	Cr	Cu	Ni	Pb	Zn
MT16/1	0.00	0.00	0.00	0.71	0.44	0.00	0.00
MT16/2	0.00	10.56	0.11	7.74	7.96	0.00	14.38
MT17/1	0.00	8.79	0.51	13.83	17.45	0.00	35.12
MT17/2	0.00	3.06	0.03	2.55	2.56	0.00	17.14
MT18/1	0.00	10.38	0.26	6.92	13.11	0.00	12.68
MT18/2	0.00	1.35	0.03	3.89	1.53	0.00	15.10
MT18/3	0.00	0.50	0.02	1.68	0.81	0.00	8.44
MT19/1	0.00	2.78	0.02	3.79	3.26	0.00	11.25
MT19/2	0.00	0.26	0.02	1.82	0.33	0.00	3.85
MT19/3	0.00	0.00	0.00	0.17	0.47	0.00	4.78
MT21/1	0.00	0.50	0.00	1.04	1.82	0.00	3.13
MT21/2	0.00	0.33	0.00	2.76	0.71	0.00	6.25
MT21/3	0.00	0.00	0.00	0.17	0.38	0.00	9.62
MT21/4	0.00	0.00	0.00	0.14	1.24	0.00	5.07
MT 22/1	0.00	0.84	0.02	1.34	0.29	1.67	12.04
MT 22/2	0.00	8.70	0.12	11.35	3.03	0.00	37.53
MT 22/3	0.00	0.31	0.00	0.87	1.82	10.27	71.71
MT 23/1	0.00	0.00	0.05	1.22	0.00	15.89	3.62
MT 23/2	0.00	3.69	0.01	2.18	1.95	0.68	43.92
MT 23/3	0.00	0.21	0.00	1.01	4.72	7.36	44.39
MT 23/4	0.00	0.34	0.00	0.71	4.38	39.67	21.57
MT 23/5	0.00	0.60	0.00	0.00	0.51	71.71	0.00
MT 24/1	0.00	6.42	0.22	2.84	4.85	21.75	19.22
MT 24/2	0.00	14.88	0.01	3.96	9.07	11.18	16.54
MT 24/3	0.00	0.21	0.03	0.88	10.55	412.25	49.16
MT 24/4	0.00	0.22	0.02	0.04	0.32	55.86	0.00
MT 25/1	0.00	6.51	0.39	5.62	8.12	32.26	43.82
MT 25/2	0.00	5.17	0.53	5.82	11.75	83.50	88.01
MT 25/3	0.00	125.87	73.04	96.64	69.11	38.64	49.78
MT 25/4	0.00	0.20	0.03	1.52	3.61	19.40	43.86
MT 25/5	0.00	0.92	0.01	0.00	0.70	0.00	0.00
MT 25/6	0.00	0.34	0.00	0.00	0.45	0.00	0.00
MT 26/1	0.00	8.69	0.10	4.00	16.83	1.01	41.04
MT 26/2	0.00	44.30	1.66	29.84	57.15	66.63	59.18
MT 26/3	0.00	3.12	0.03	3.99	10.71	57.84	30.14
MT 26/4	0.00	0.79	0.00	0.50	3.44	3.17	15.78
MT 27/1	0.00	13.95	0.09	6.57	16.74	0.00	37.35
MT 27/2	0.00	18.01	0.14	5.48	8.71	31.56	25.48
MT 27/3	0.00	1.87	0.01	3.09	4.96	2.32	14.43
MT 28/1	0.00	18.42	0.16	4.42	12.70	3.43	18.62
MT 28/2	0.00	5.85	0.06	3.38	9.72	0.00	13.15
MT 28/3	0.00	6.42	0.20	4.58	5.74	34.90	24.60

APPENDIX E

CATION EXCHANGE CAPACITIES OF SOME SOIL AND TAILINGS SAMPLES

Table E.1 Cation exchange capacities of some of the soil and tailings samples in the investigated transect

Soil unit	**Sample number**	**CEC (cmol_c/kg)**
TC & TA	MT2/1	0.17
	MT6/1	0.342
	MT12/1	0.077
	MT14/1	0.083
	MT 26/2	0.047
AU	MT2/2	0.25
	MT10/2	0.076
	MT14/2	0.142
AL	MT3/4	0.344
	MT9/4	0.218
	MT15/3	0.296
CU	MT21/2	0.031
	MT 27/2	0.03
	MT 25/3	0.026
CF	MT19/3	0.056
	MT 27/3	0.06
	MT 23/3	0.04