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.

$$\text{Adjusted result} = \text{ICP-AES result} - \text{Maximum concentration in the blank samples.} \qquad [6.1]$$

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:

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

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).

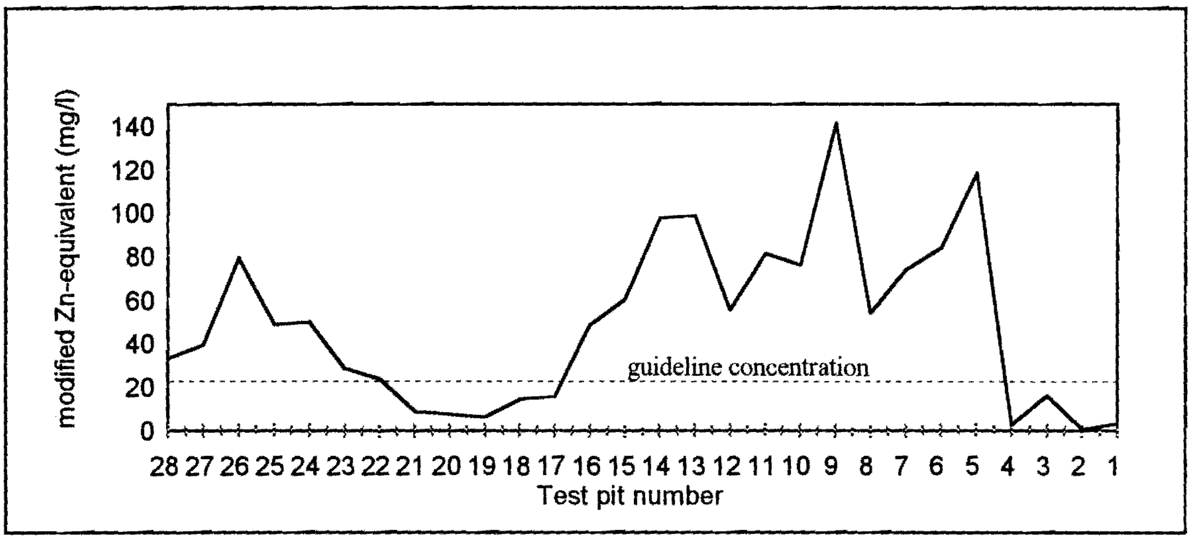

Figure 6.1 Lateral changes in the NH_4NO_3 extractable zinc-equivalent in the topsoil (units AU and CU) along the investigated transect.

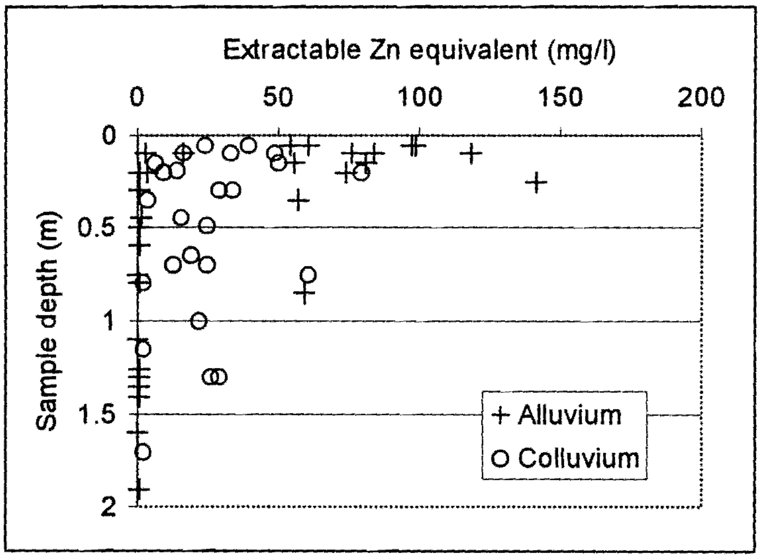

Figure 6.2 Vertical NH_4NO_3 extractable zinc-equivalent concentrations in the colluvial and alluvial soils (soil units CU, CF, AU and AL).

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.

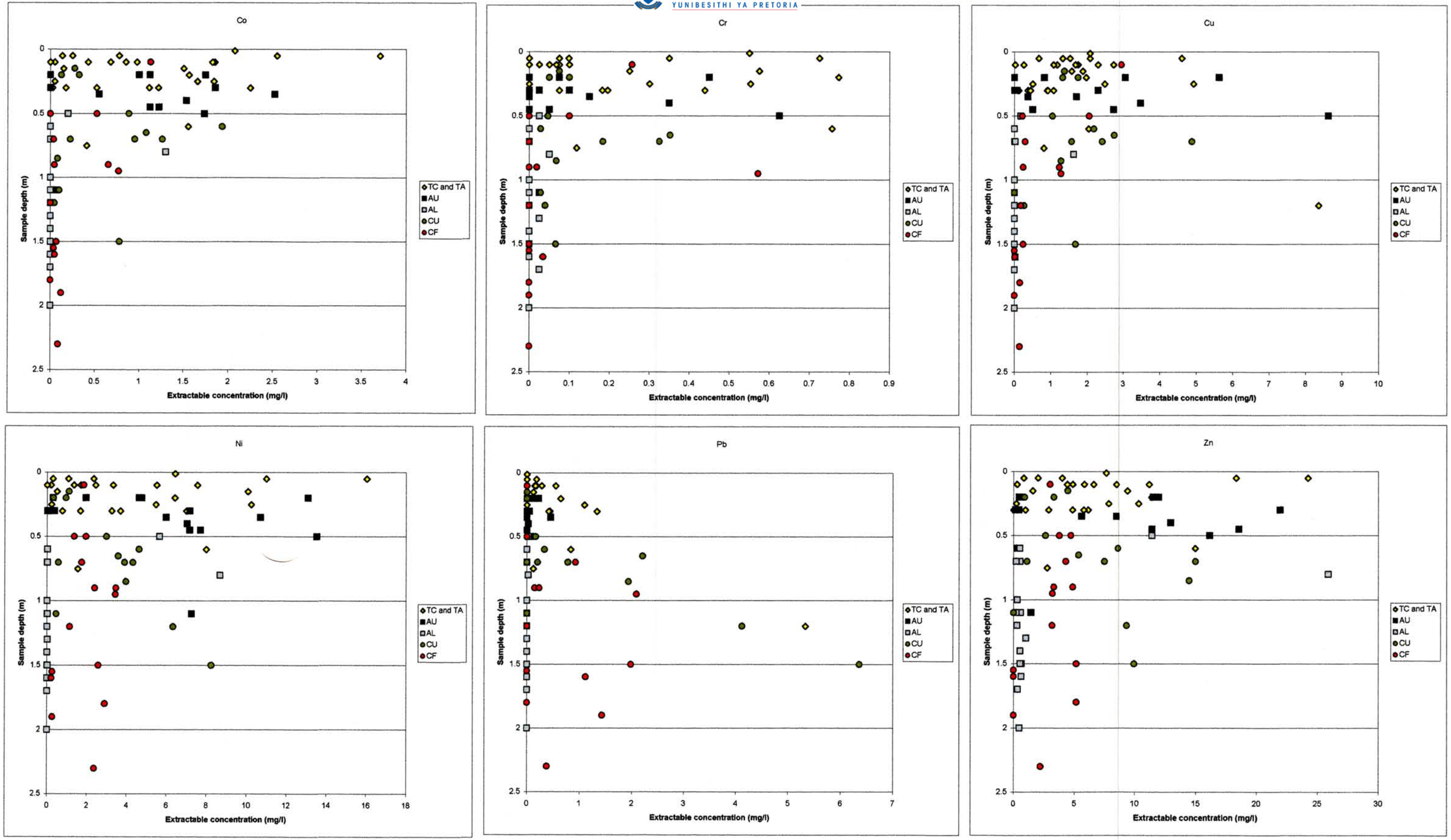

Figure 6.3 Vertical extractable trace element concentration trends

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.

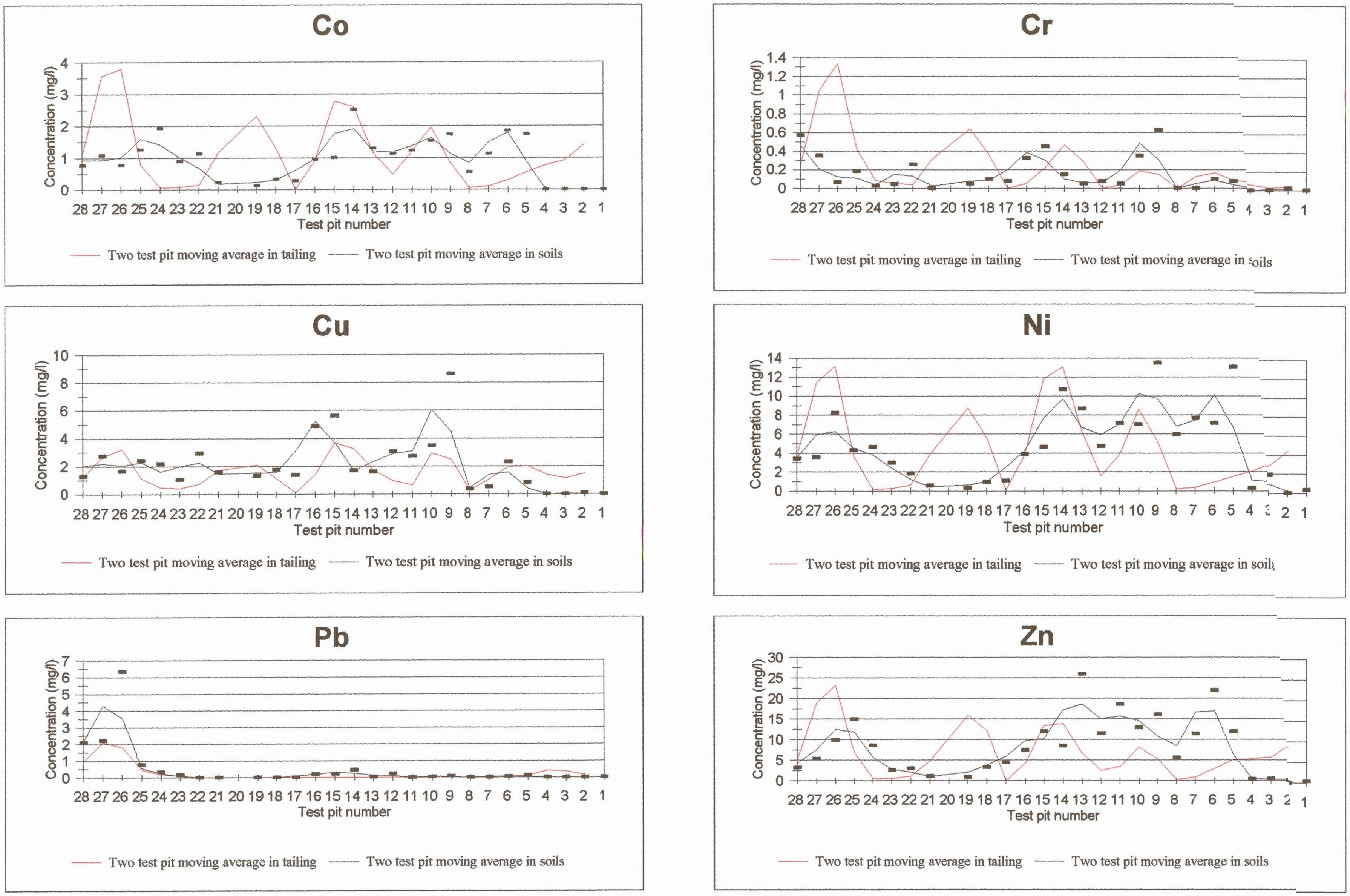

Figure 6.5 Lateral extractable trace element concentration trends in the tailings and the first underlying soil unit, between test pits MT1 and MT28.

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.

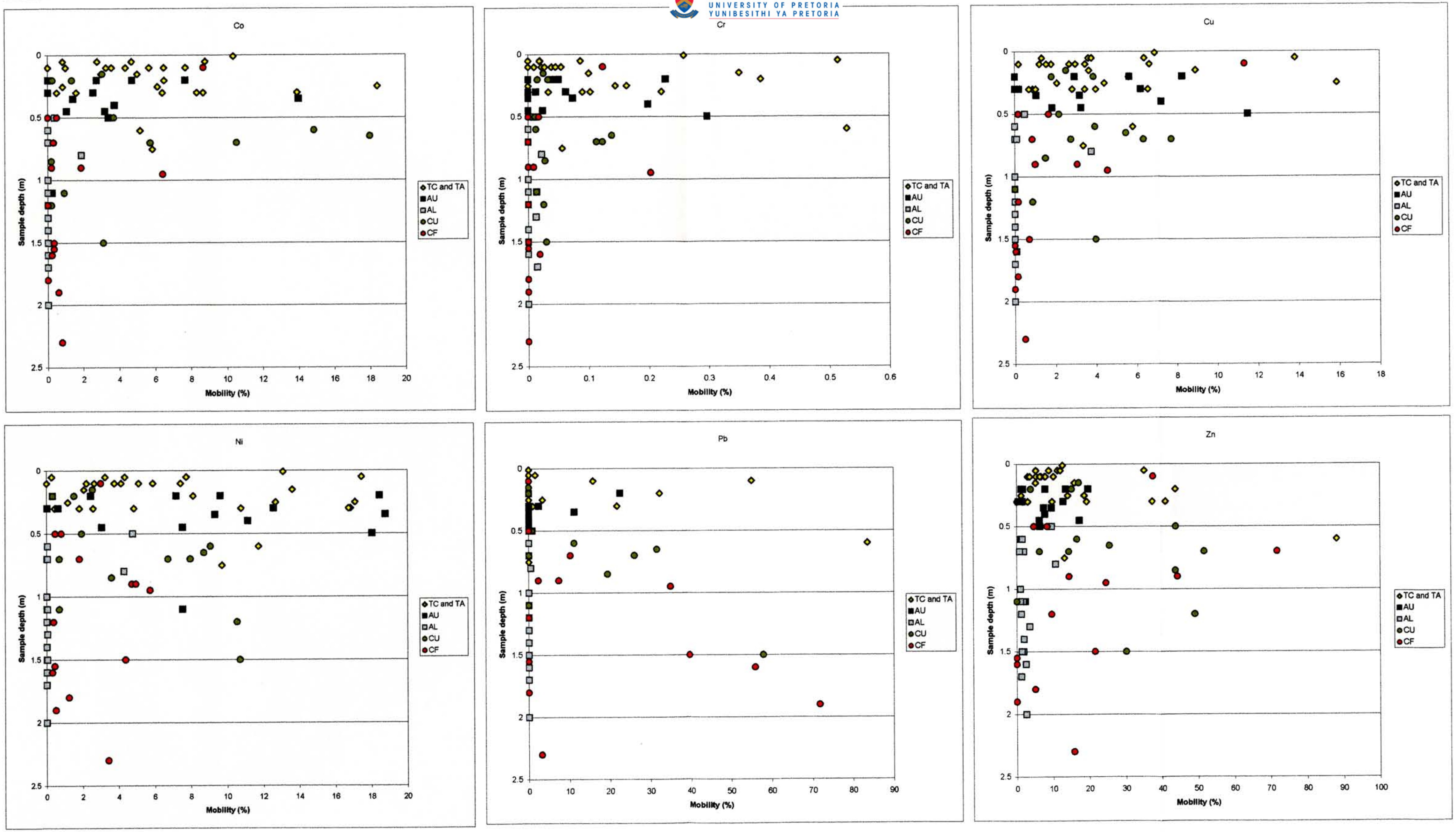

Figure 6.5 Vertical trace element mobility trends

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.

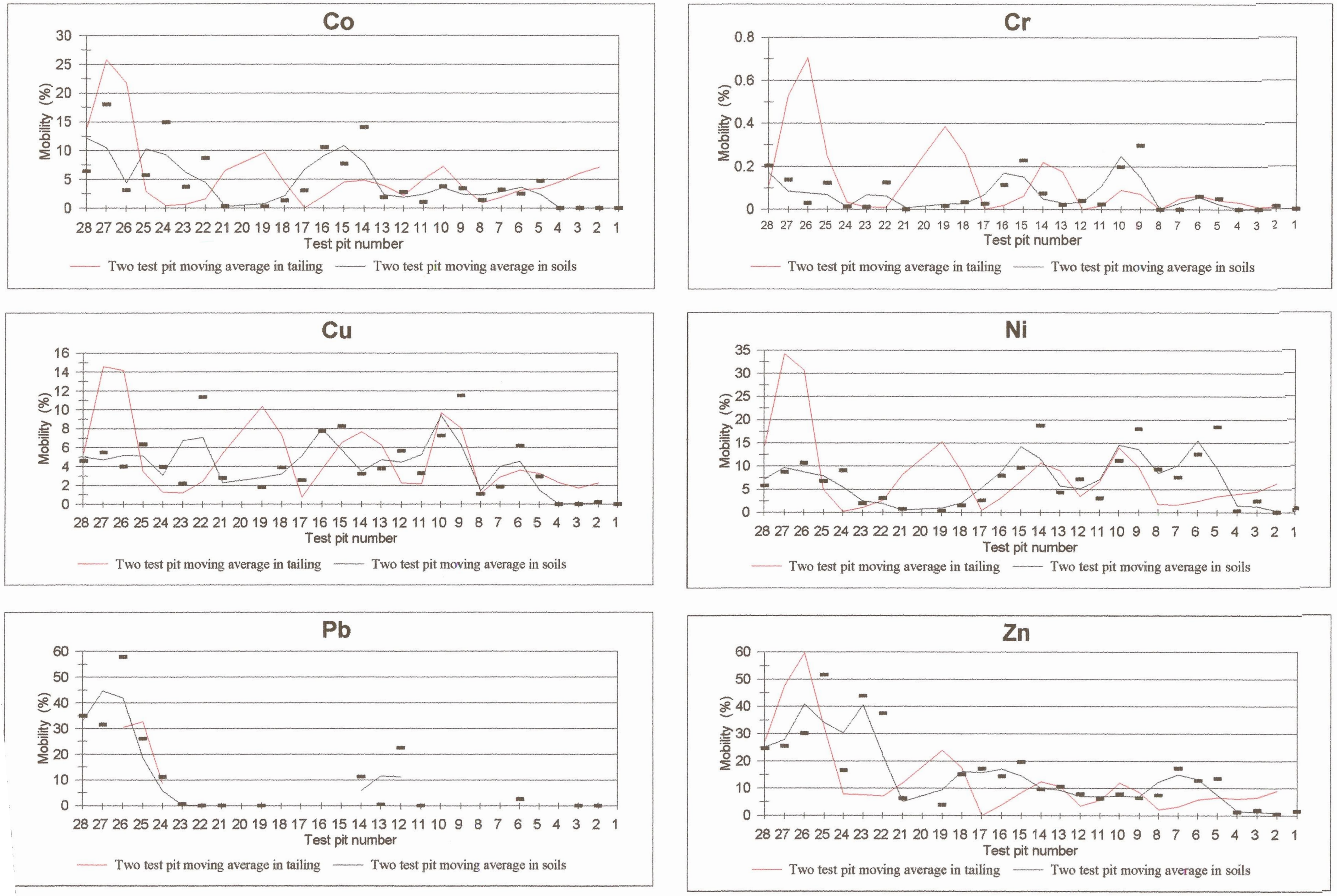

Figure 6.7 Lateral trace element mobility trends in the tailings and the first underlying soil unit, between test pits MT1 and MT28.

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.

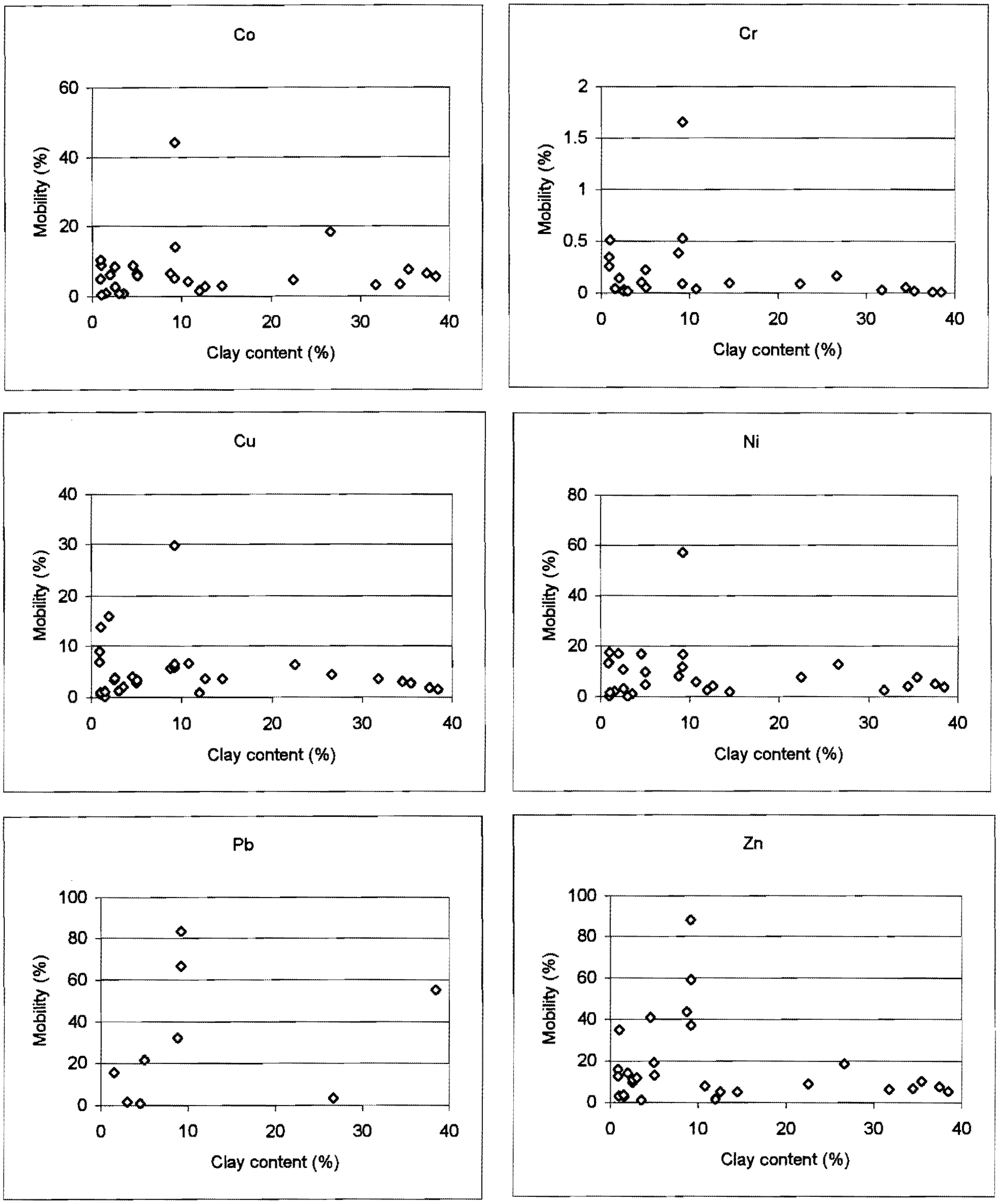

Figure 6.7 Relationship between the clay content of the tailings and the trace element mobilities (Note that the scales differ).

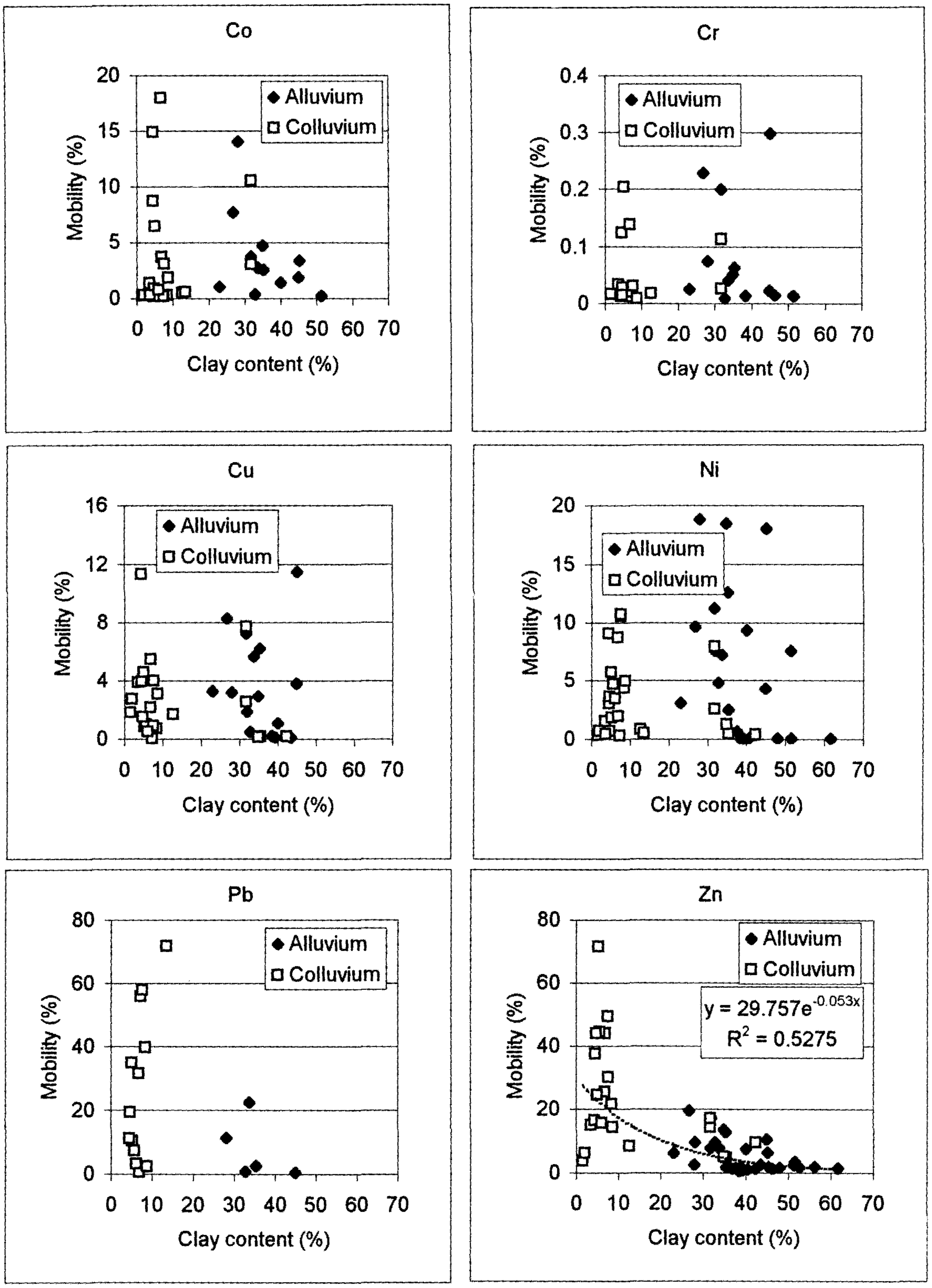

Figure 6.8 Relationship between the clay content of the soil and the trace element mobilities. (Note that the scales differ).

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.

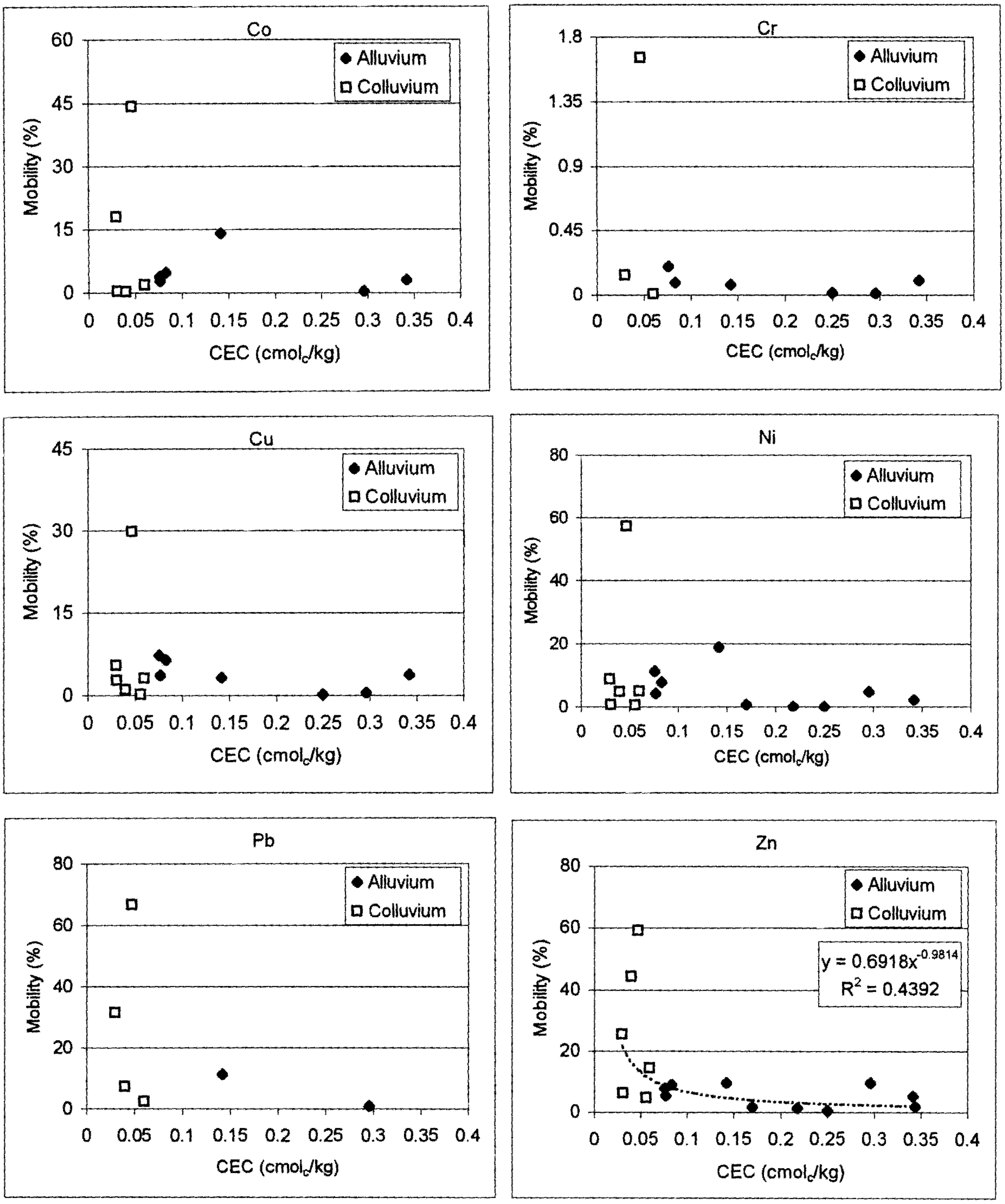

Figure 6.9 Relationship between the cation exchange capacity of the soil and the trace element mobilities. (Note that the scales differ).

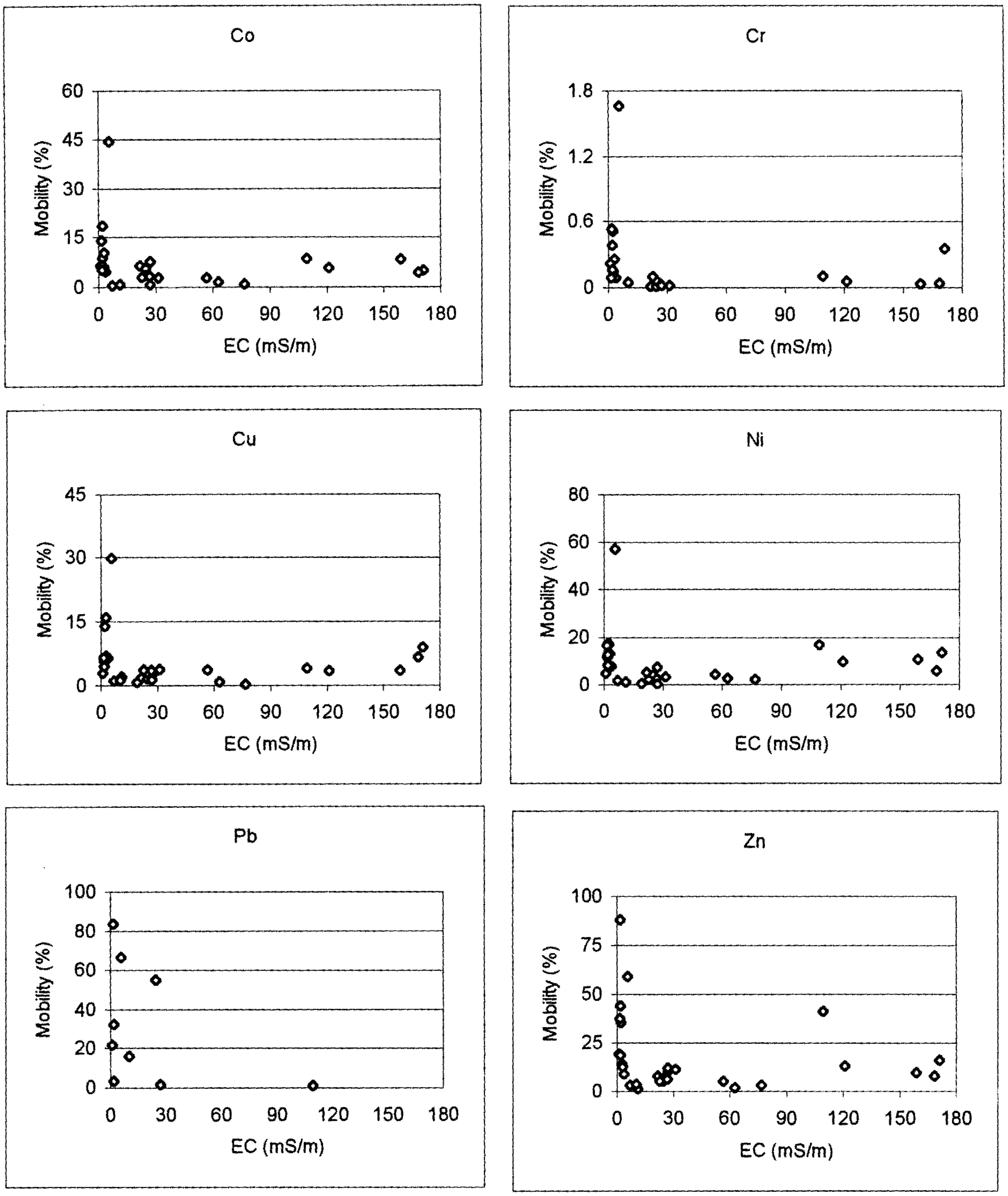

Figure 6.10 Relationship between the electrical conductivity of the tailings and the trace element mobilities (Note that the scales differ).

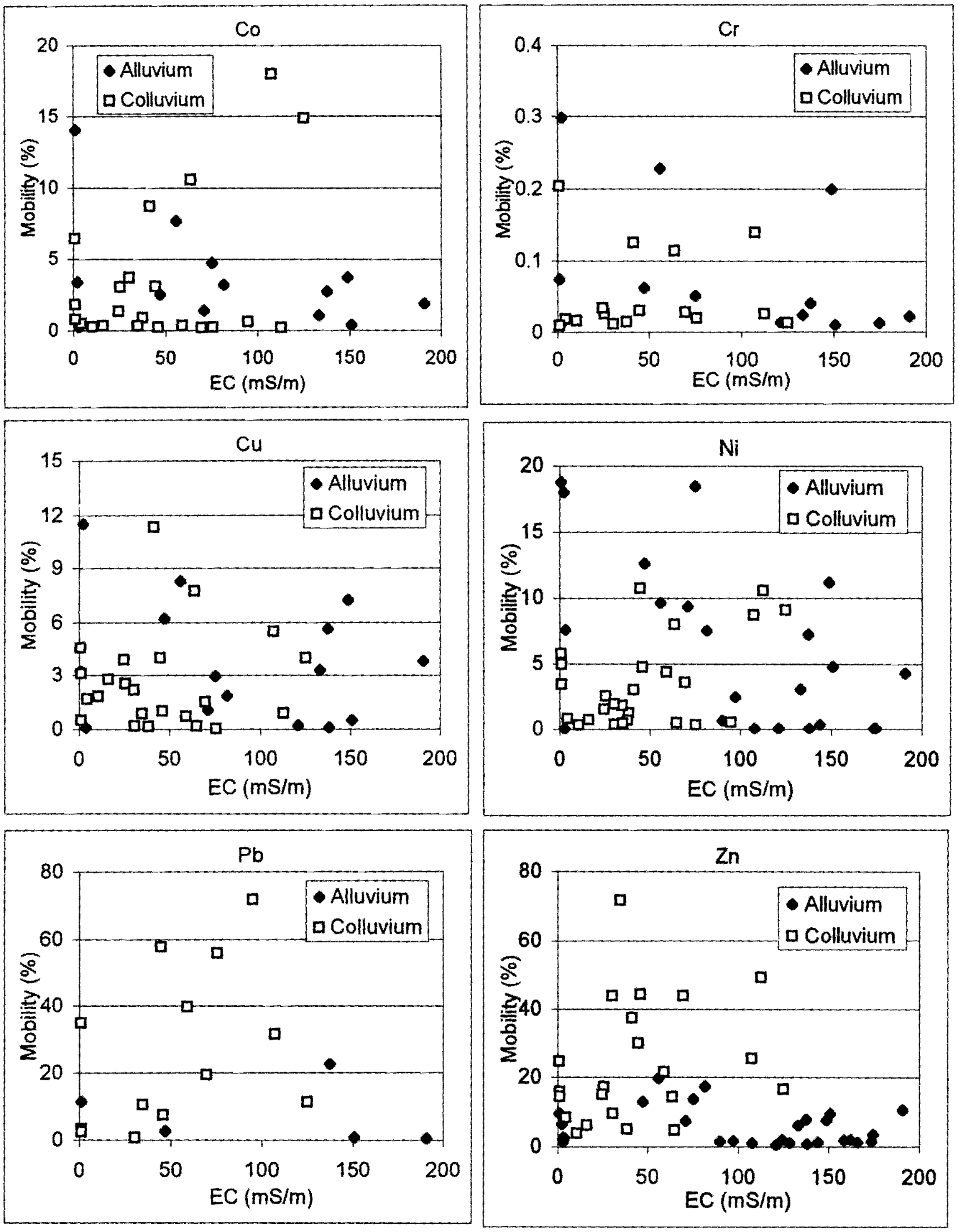

Figure 6.11 Relationship between the electrical conductivity of the soil and the trace element mobilities. (Note that the scales differ).

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.

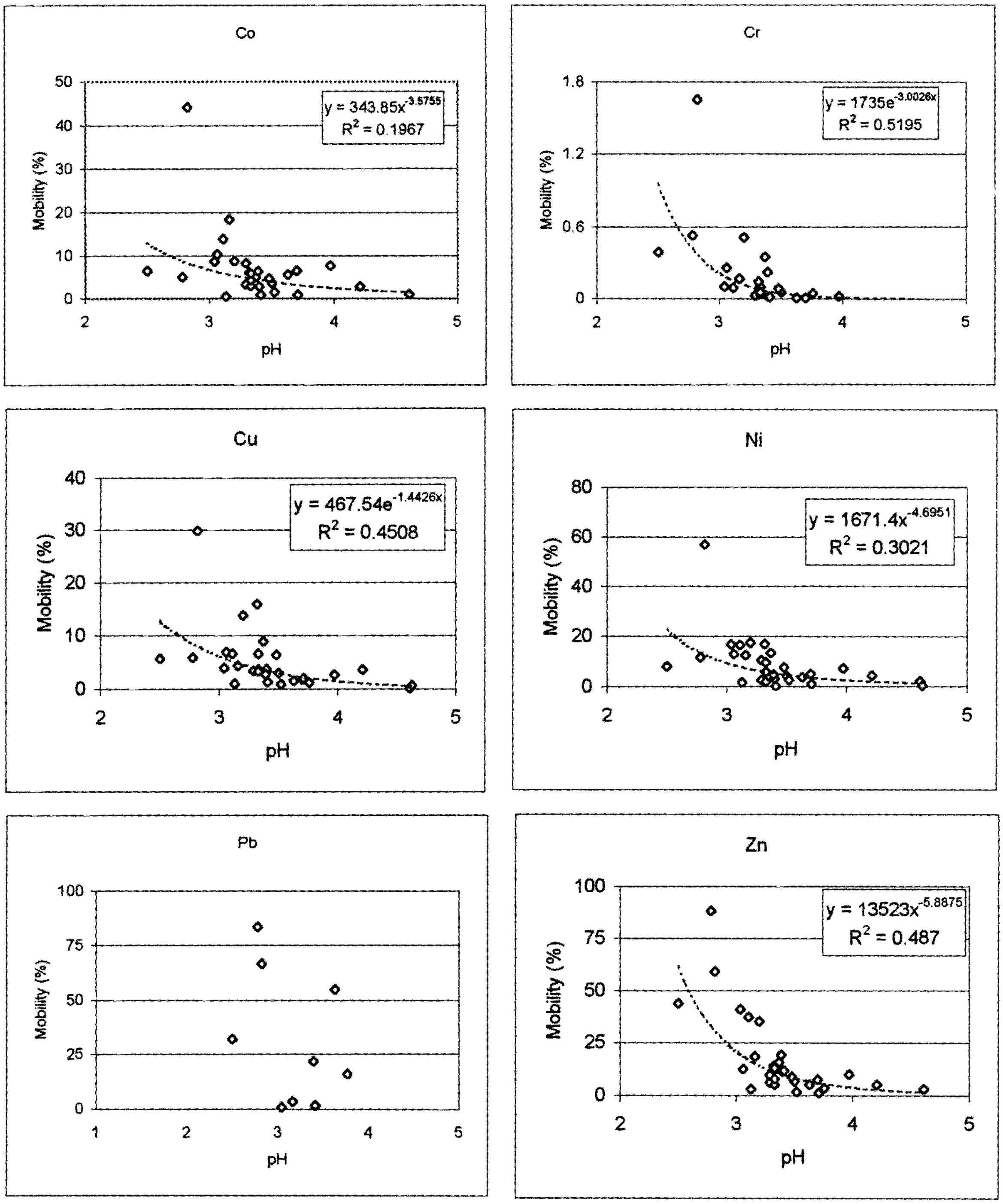

Figure 6.12 Relationship between the pH of the tailings and the trace element mobilities (Note that the scales differ).

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)

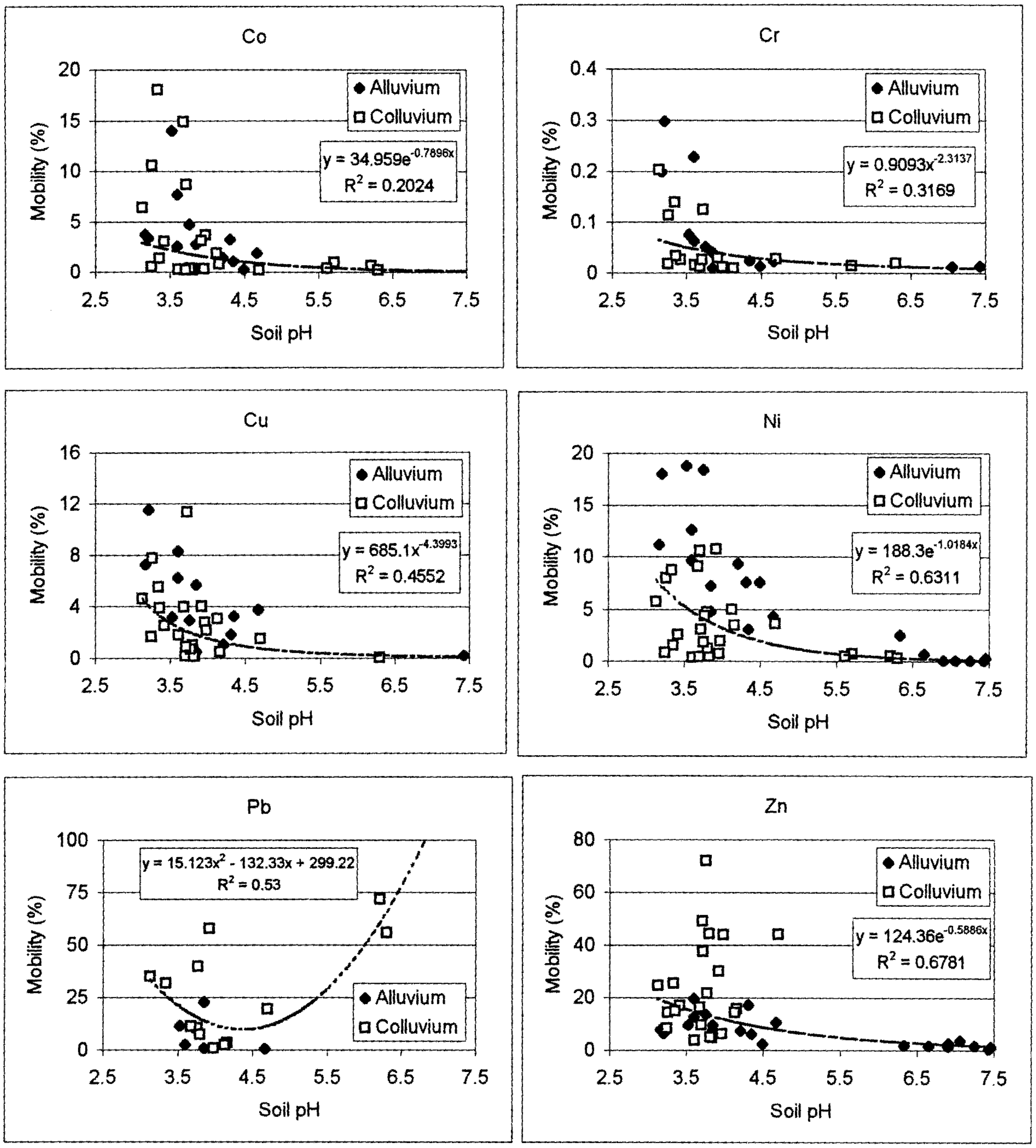

Figure 6.13 Relationship between the pH of the soils and the trace element mobilities (Note that the scales differ).

(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.

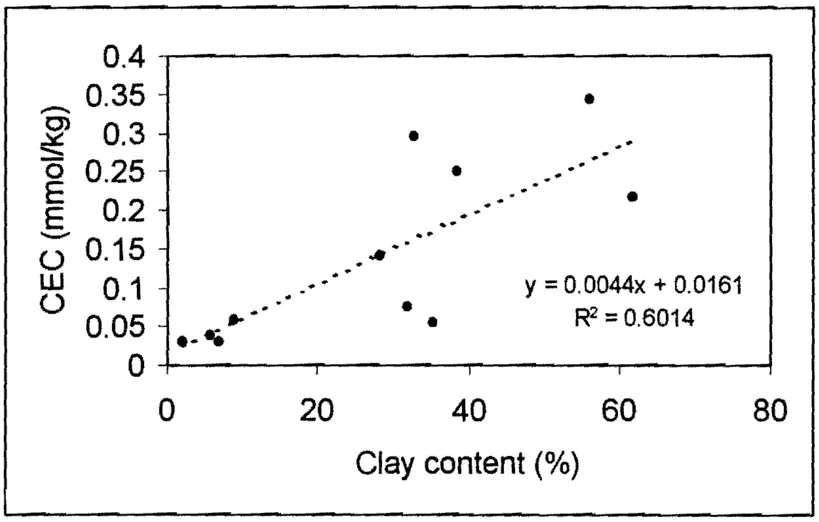

Figure 6.14 Relationship between the clay content of the soil and the CEC of the soil.

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 $\text{cmol}_c\text{/kg}$ 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.

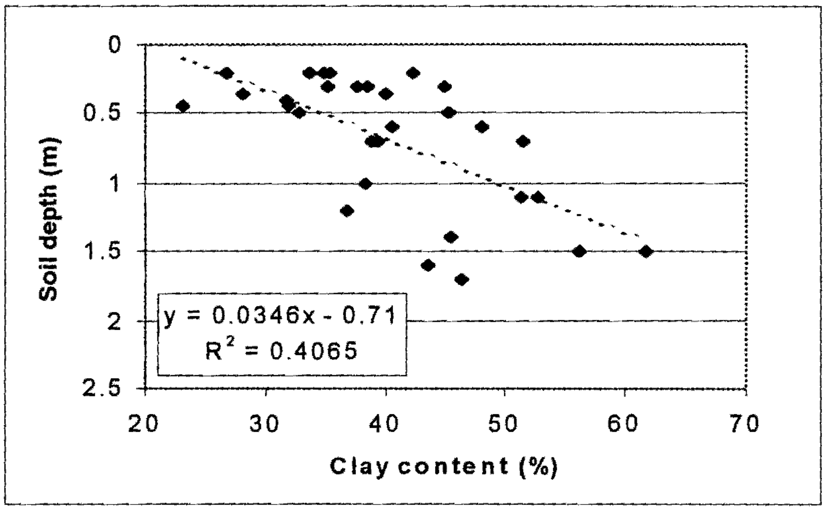

Figure 6.15 Relationship between clay content and soil depth in the alluvial soils (sample MT5/5 not considered)

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.

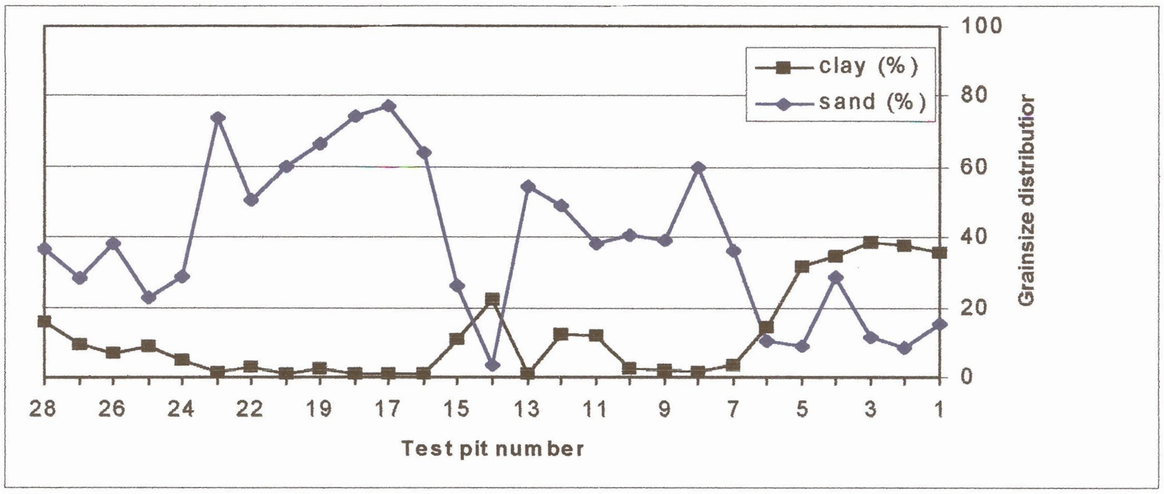

Figure 6.16 Lateral variation in the grainsize distribution of the tailings (units TC and TA) between test pits MT28 to MT1

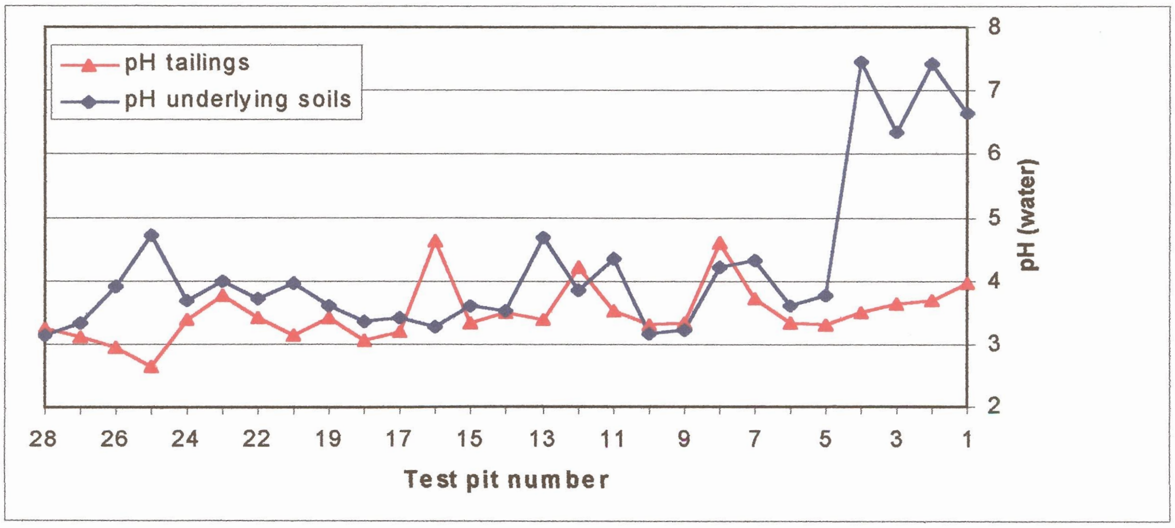

Figure 6.17 Lateral changes in the pH of the tailings and upper soil units between test pits MT28 and MT1.

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.

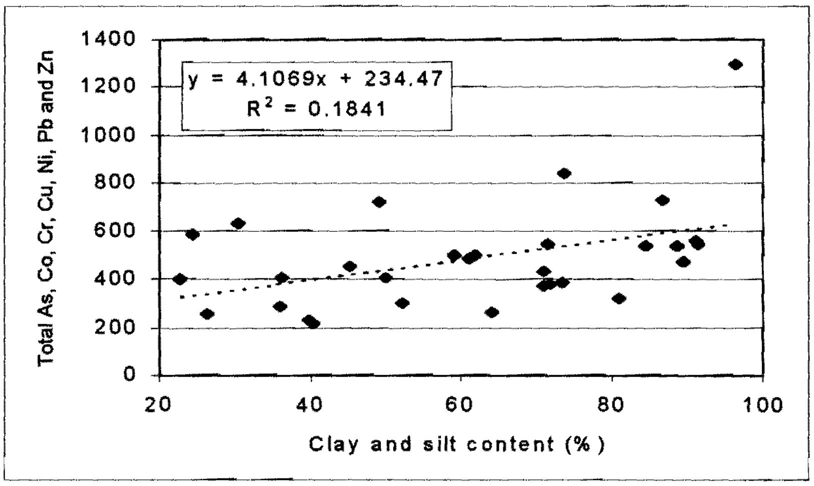

Figure 6.18 Total trace element concentration in the tailings (units TC and TA) as a function of the clay and silt fractions of each sample.

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.

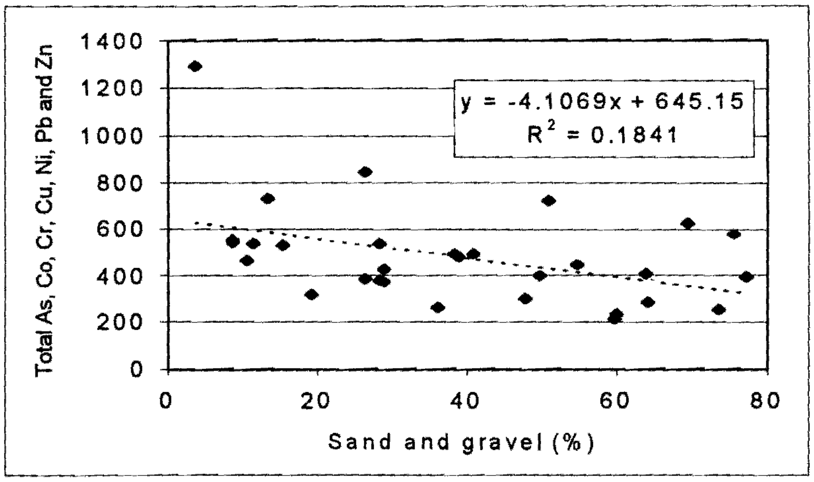

Figure 6.19 Total trace element concentration in the tailings (units TC and TA) as a function of the sand and gravel fractions of each sample.

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.