CHAPTER 5

The Influence of Increasing Lime Rates on Ammonium EDTA (NH$_4$-EDTA) Extractable Metals and Organic Matter from two Acid Long-term Biosolids Disposal Soils

5.1   Abstract

In a previous study it was found that EDTA extractable heavy metals increased after heavy liming of two different sacrificial biosolids disposal soils. A similar result was reported in literature with an inconclusive explanation for the phenomenon. The two soils from the previous trial were subjected to increasing lime additions and incubated over a period of three weeks. On each of the four replicates of the five application rates a pH (CaCl$_2$) determination and an NH$_4$-EDTA extraction was performed. The metals Al, Fe, Mn, Cd, Cr, Cu, Ni, Pb, and Zn were determined in the NH$_4$-EDTA extracting solution and the absorbance of each replicate determined at 465 nm to determine increases in organic matter extracted. The NH$_4$-EDTA extractability of Cd and Pb exhibited the most pronounced increase with increasing pH. The other metals exhibited varying degrees of increased extraction with Ni exhibiting a decrease. Absorbance values indicated that increase quantities of organic matter was extracted at higher pH levels. The increased metal extractability was correlated with increases in organic matter in the extracts. The use of EDTA extraction values in the drawing up of heavy metal guidelines for soils high in organic matter is discouraged due to the variability of metal extractability at altered pH levels. Heavy metal uptake by plants under conditions of increasing pH should be investigated to determine the extent to which metal mobility is influenced by liming of high organic matter containing soils.

5.2   Introduction

One of the main problems related to the prolonged application of biosolids to land is the increase in soil heavy metal content. A further aspect of concern is that soils of sacrificial disposal sites are often acidified, therefore leading to an increased risk of metal mobility in soil. Liming of sacrificial soils is not a simple solution as Van der Waals et al. (2005) reported that several metals increased in extractability (NH$_4$-

EDTA) after intensive liming in a pot trial. Similar results were reported by Bloomfield and Pruden (1975) where the EDTA extractability of Cd, Cu, Cr, Ni, Pb, and Zn increased in "limed sludge samples" and Cr increased in "limed sludge + soil samples". Lake et al. (1984) attributed the increase in Cr levels to the chemistry of the Cr(VI) form in soils but did not elaborate on the behaviour of the other metals.

Lime induced increases in heavy metal mobility (due to the higher solubility of certain organic matter fractions at higher pH) has been given as a concern regarding the amelioration of acid soils with a high organic matter content (Hue, 1995; Moore, 1997). The matter is by no means clear-cut and Welch and Lund (1987) stated that studies on the movement of metals in soils to below the sludge-amended soil layer "show fragmentary and contradictory results". Brown et al. (1997) referred to a number of studies in which heavy metal movement after biosolids addition was predicted or discussed. Only two of these studies (Robertson et al., 1982; Lund et al., 1976) indicated that some metals had indeed moved to layers lower than the biosolids incorporated layer. In most cases, however, metals did not move in soils even under acidic conditions.

The results as reported by Van der Waals et al. (2005) lead to questions regarding the cause of the increased metal extraction with an increase in soil pH. Organic matter extractability with neutral salt and aqueous solutions is known to increase with an increase in pH (Yin et al., 1996; You et al., 1999). Stevenson (1982) reported that the sodium salt of EDTA also appeared to be a good extractant of organic matter. Very little work had been done on the extraction of organic matter with EDTA because "neither the carbon nor nitrogen content of the soil extracts can be used to measure the quantity of organic matter extracted". Thus, the pH dependence of organic matter extractability as well as the ability of EDTA to extract organic matter could have lead to the results obtained by Van der Waals et al. (2005).

As an extractant of heavy metals, EDTA is of particular interest due to the number of studies that have indicated a correlation between extractable metal levels in soils and plant uptake by a range of crops. In this sense Hooda et al. (1997) indicated that EDTA was a reliable test for predicting plant available metals. Some workers (Bruemmer and van der Merwe, 1989) have gone as far as proposing guideline metal

levels in soils with EDTA as extractant. On the other hand, several studies have also failed to find such a correlation.

The aim of this study was to determine the extent of the NH_4-EDTA extractability of metals at different lime rates (pH) from the two biosolids disposal soils reported on by Van der Waals et al. (2005). In light of the restrictions on carbon determination in EDTA extracts (Stevenson, 1982), it is postulated that the organic matter (extracted with NH_4-EDTA at the different pH levels) could be determined through the use of the Beer-Lambert law as discussed by Schnitzer (1971). Therefore, a further aim of the trial was to determine the extent of organic matter extraction with NH_4-EDTA through light spectrophotometry, as well as to determine the correlation between extracted metals and organic matter.

5.3   Materials and Methods

The soils used by Van der Waals et al. (2005) were also used for this study. Soil 1 is a sandy loam derived from granite and Soil 2 a sandy clay loam derived from dolomite. Both these soils are acid (Soil 1: $pH_{(water)}$ 4.0 and Soil 2: $pH_{(water)}$ 4.2) and have very high pH-buffering capacities due to relatively high organic carbon levels (Soil 1: 2.9% and Soil 2: 3.7 %). Biosolids had been disposed of on the soils for more than 20 years. Due to the varying nature of the biosolids over time as well as the unknown total quantity of the material added to the soils it was not possible to determine the total loading of metals to the soils.

For the trial a representative sample of 15 kg was collected from bulk soil samples (300 kg) that were collected at the two sites. Increasing amounts of $CaCO_3$ (AR) (equivalents of 9, 18, 27, and 36 ton ha^{-1}) were added to 200 g oven dried soil in plastic containers. The soils were thoroughly mixed using a glass rod and 100 ml de-ionised water added. After addition of the water the soils were left to dry at 35 ºC (approximately 7 days). Afterwards, 70 ml de-ionised water (water to soil ratio of approximately 1:3) was added and the soils left to dry three consecutive times at 35 ºC (approximately 4 days). Each treatment was replicated four times and blank samples were included. A pH ($CaCl_2$) determination was done on each of the samples according to the method described by the Non-Affiliated Soil Analysis Work

Committee (1990). The pH (CaCl$_2$) was chosen due to its frequent use in studies reported on internationally as well its ionic strength that would minimise pH drift.

On each of the samples, plus an internal reference sample, an NH$_4$-EDTA extraction was done by adding 50 ml 0.02 M NH$_4$-EDTA to 5 g oven dry soil in a stoppered glass bottle. The original solution to soil ratio as prescribed by the Non-Affiliated Soil Analysis Work Committee (1990) was adapted to ensure adequate NH$_4$-EDTA in the presence of high metal levels. The solution was shaken on a horizontal shaker at 180 oscillations per minute for one hour and filtered immediately afterwards. The metals Al, Fe, Mn, Cu, Zn, Cd, Cr, Ni, and Pb were determined through Atomic Absorption Spectrophotometry (AAS) and the organic matter through light spectrophotometry at 465 nm.

5.4   Results and Discussion

Figure 5.1 presents the pH results of the different lime incubation rates after a three-week period. From the soils' textures it was expected that Soil 2 (Sa Cl Lm) would have had a higher buffer capacity than Soil 1 (Sa Lm). The data, though, points to the sandy loam soil (Soil 1) having a higher buffer capacity. This buffer capacity could be ascribed to the dominant role of the accumulated organic material in the soil that obscures the role of the soils' texture.
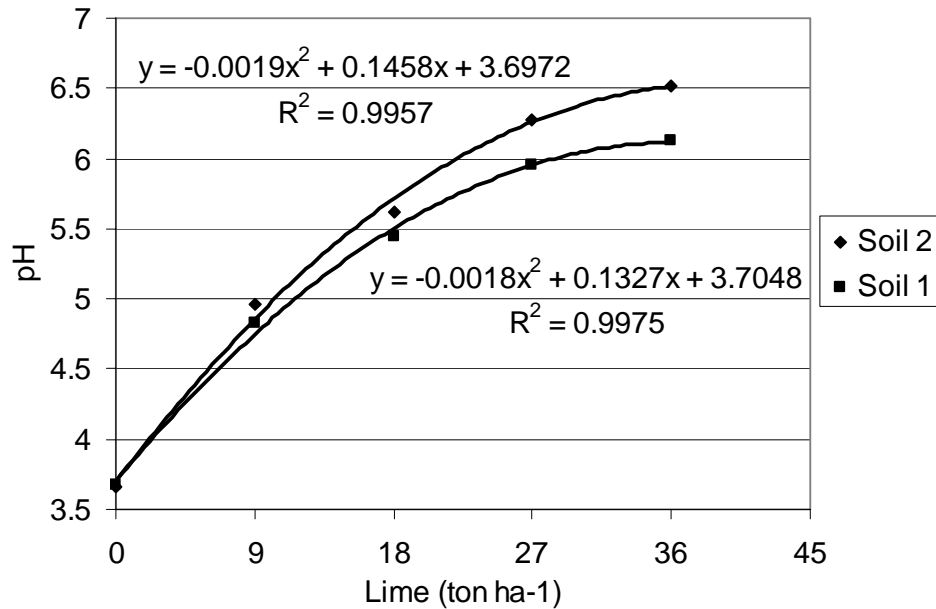
Figure 5.1. Change in pH (CaCl$_2$) at four lime application rates after 3 weeks incubation.

Figure 5.2 indicates the NH$_4$-EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn and Figure 5.3 that of Al, Mn, and Ni as a function of pH (or lime rate). Note that the R^2 value is a function of both the slope of the regression line as well as the closeness of fit of the data. As the slope of the regression curve nears 0 the R^2 nears 0 as well even though there may be a close fit of the data points. The most important parameter therefore is the slope of the regression line and high R^2 values indicate data with both significant slopes and closeness of fit.

The metals exhibited varying degrees of increased extractability upon liming with Cd and Pb exhibiting the most pronounced increases over unlimed values. The Cr values also increased even though they were very variable with a consequent low R^2 value. The Cd and Cr values were very low and were close to the detection limits of AAS. Copper extractability correlated well with pH in Soil 2 and Zn with pH in Soil 1. This difference could possibly indicate that the organic matter determined the Cu extractability and the clay minerals the Zn extractability in Soil 2. It is not clear why this trend is reversed in Soil 1. To a certain extent the same trend applies to Fe and Mn with Fe extractability correlated with pH in soil 2 and Mn with pH in Soil 1. The

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extractability of Al was not correlated with pH whereas the extractability of Nickel decreased with increasing lime rate.

These results support those obtained by Van der Waals et al. (2005) where the NH_4-EDTA extractable levels of a number of metals increased after intensive liming in a pot trial. It is also a confirmation that the results as reported by Van der Waals et al. (2005) were not an artefact of the method used but rather a phenomenon that deserved further investigation.

The absorbance at 465 nm, as determined in the NH_4-EDTA extracts, increased as a function of pH, albeit with an average coefficient of determination (Fig. 5.4). The absorbance values are very low and experimental error, large with respect to the values obtained, could possibly account for the variability as expressed in the R^2 values. From the data it is clear though that increased organic matter fractions were extracted at higher pH values with Soil 2 exhibiting a marginally better correlation. This phenomenon confirms the concerns expressed by Hue (1995) and Moore (1997) regarding the influence of lime additions to high organic matter content soils.
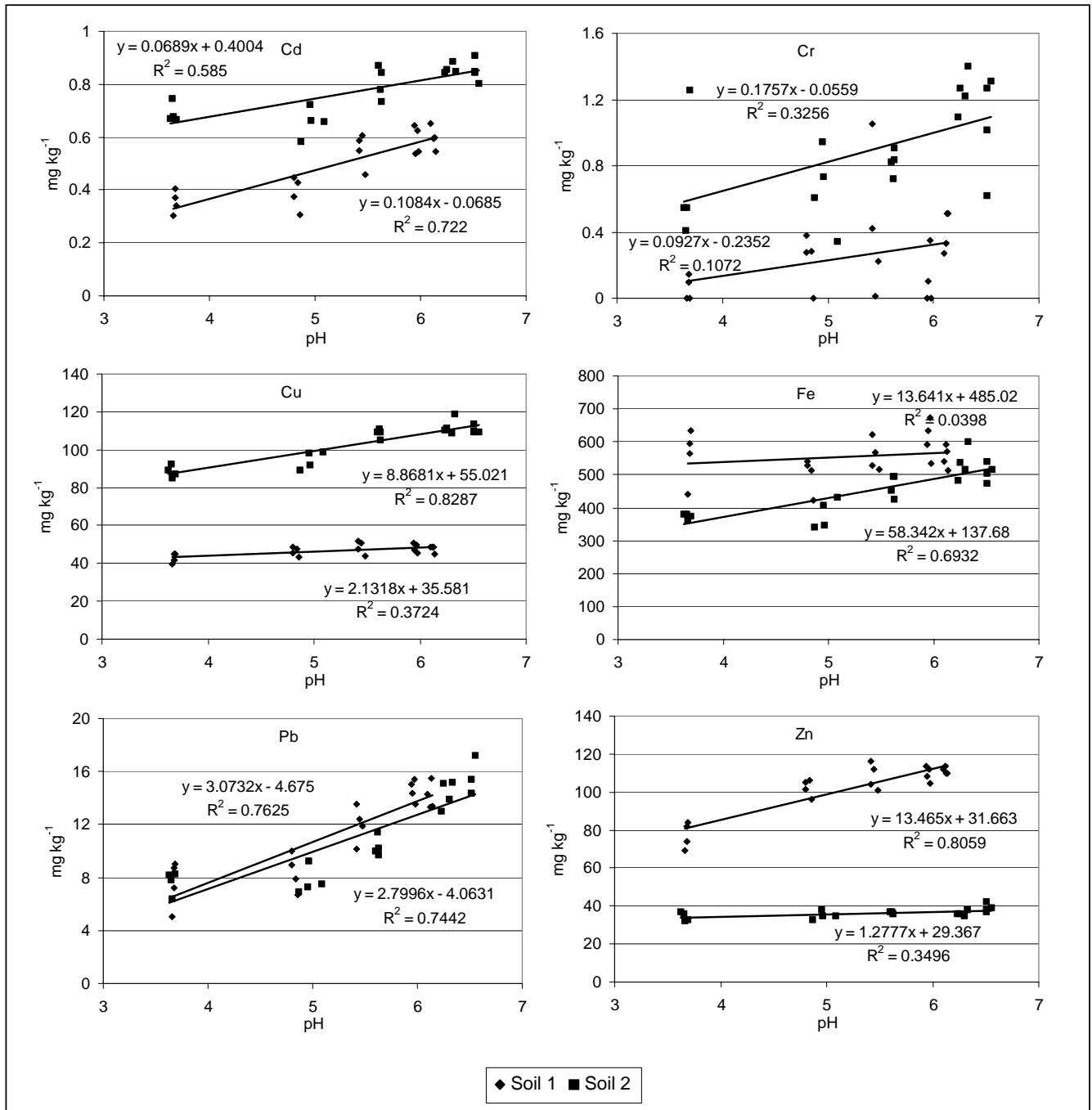
Figure 5.2. The NH$_4$-EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn as a function of pH (CaCl$_2$).
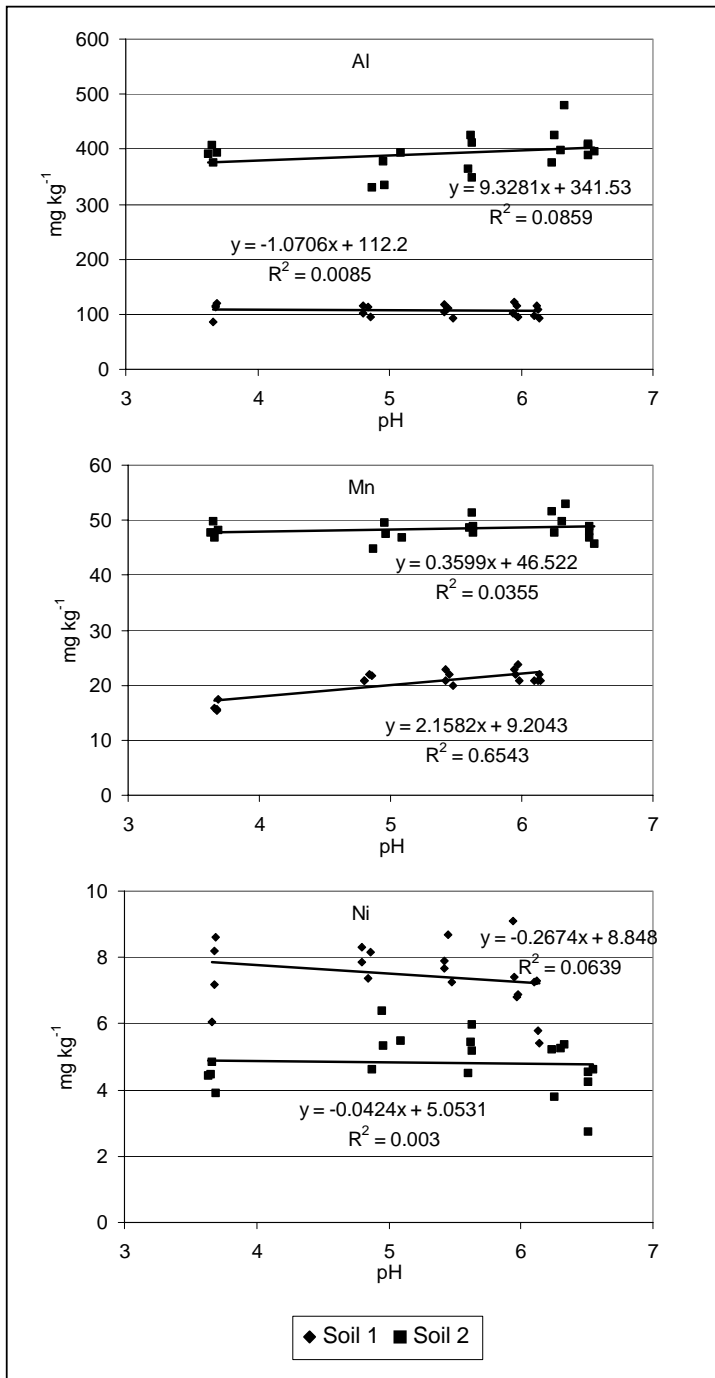
Figure 5.3. The NH$_4$-EDTA extractability of Al, Mn, and Ni as a function of pH (CaCl$_2$).
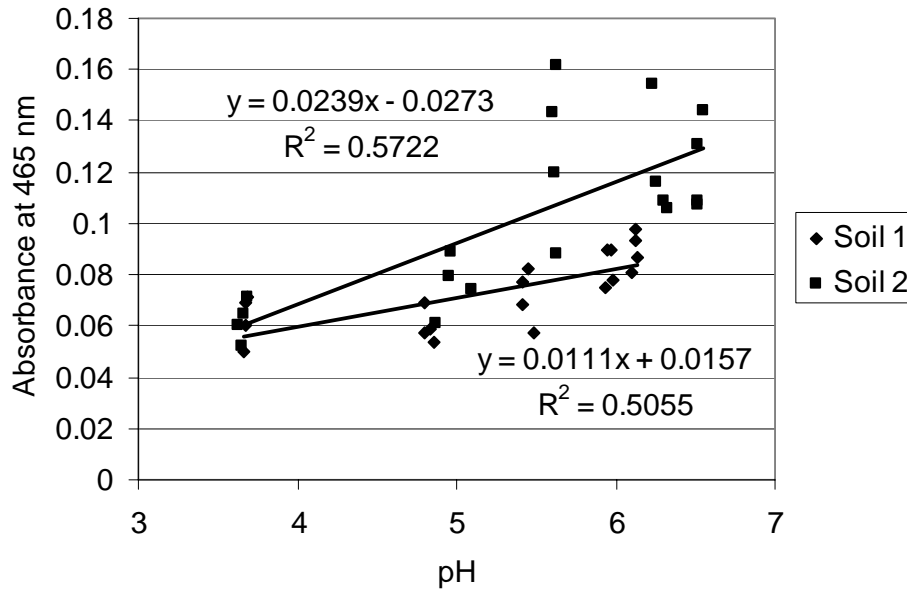
Figure 5.4. Soil 1 and 2 absorbance values as a function of pH ($CaCl_2$) in NH_4-EDTA extracts at four lime application rates after 3 weeks incubation.

The extractability of Cd, Cr, Cu, Fe, Pb, and Zn and Al, Mn, and Ni are presented in Figures 5.5 and 5.6 respectively as a function of the absorbance of the NH_4-EDTA solutions at 465 nm. The R^2 values are generally higher than those plotted as a function of pH indicating that the extracted organic material played a significant role in contributing to the increased concentration of especially Cd and Pb in the solutions. For most of the other metals there were a clear increase in extractability as exhibited by the slope of the regression line, but with lower R^2 values. The high variability could be ascribed to the low values of the absorbance readings as discussed earlier.

The addition of large quantities of lime could explain the increased organic matter extraction through a process where the Ca and increased pH leads to the deprotonation of humic and fulvic acids and the formation of Ca-organic salts (Sposito et al., 1977). After the Ca-organic salt formation the organic material becomes more soluble due to the polar nature of the ionic Ca-organic matter bonds. In the presence of NH_4-EDTA and higher pH values the Ca could act as a "bridge" between the soluble chelating agent and the organic matter in the soil (Stevenson, 1982), thereby increasing the solubility of the latter even further.
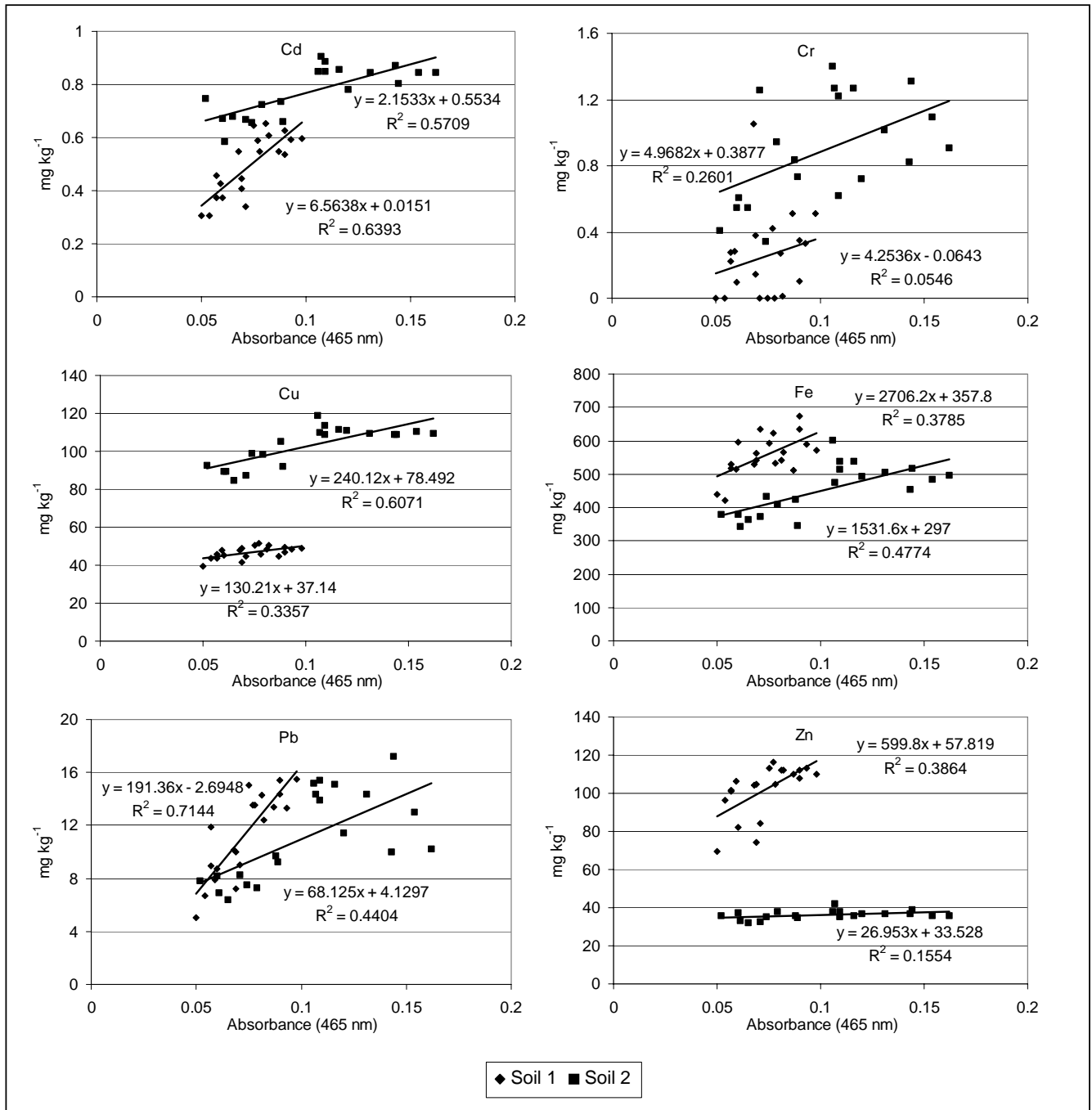
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Figure 5.5. The NH₄-EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn as a function of the NH₄-EDTA solution absorbance at 465 nm.
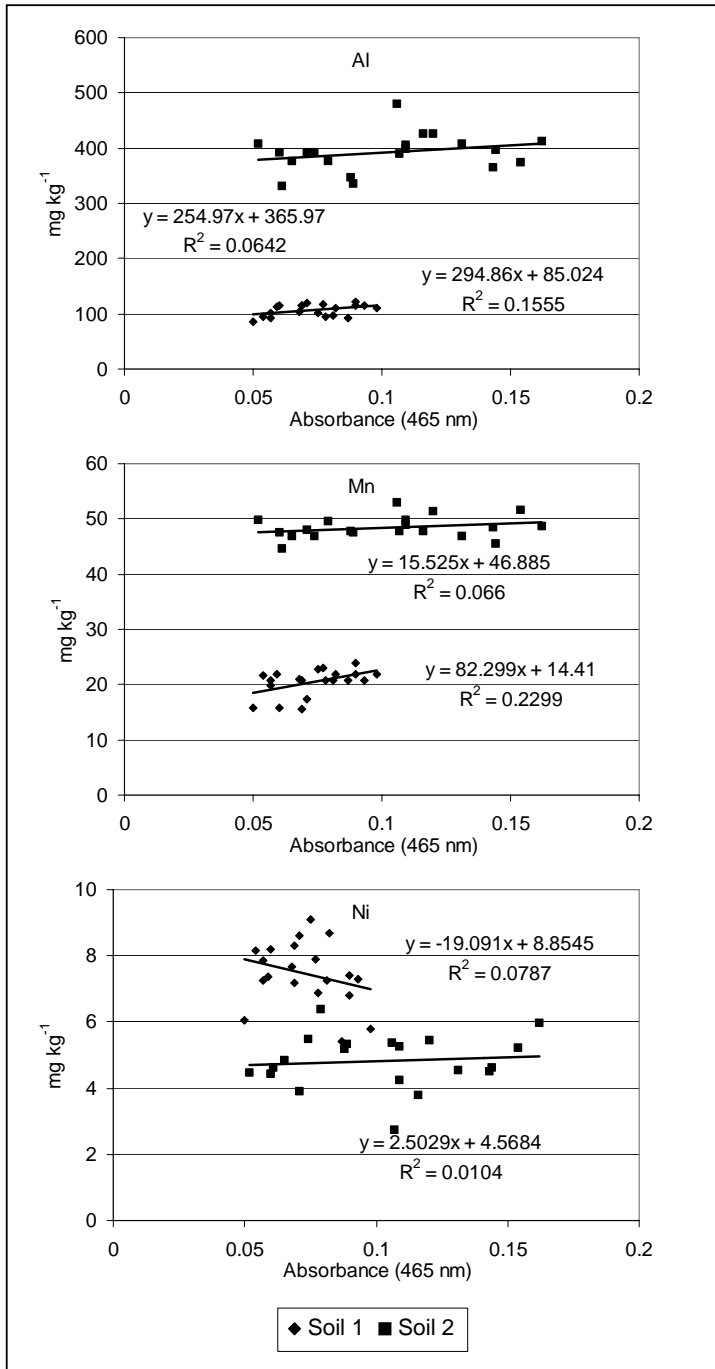
Figure 5.6. The NH$_4$-EDTA extractability of Al, Mn, and Ni as a function of the NH$_4$-EDTA solution absorbance at 465 nm.

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5.5   Conclusions and Recommendations

The NH_4-EDTA extractability of a number of metals was positively correlated with increasing pH for the two soils studied. From the data it is clear that NH_4-EDTA also extracted increasing amounts of organic matter at increasing pH levels. The link between these two observations leads to the conclusion that organo-metalic complexes were extracted and that this is the likely cause of the determination of the increased metal levels.

Caution should be exercised in basing guideline heavy metal levels in soil using NH_4-EDTA as an extracting agent. Studies on correlations between extractable metal levels and plant metal uptake are inconclusive and the ideal extracting agent still has to be found. In the light of increased organic matter extractability with NH_4-EDTA at increasing pH levels, the use thereof is questioned in highly contaminated soils that also have high levels of organic material – natural or anthropogenic.

The question remains as to the plant availability of metals that are complexed with humic and fulvic acids should there be a pH change in the soil. It is recommended that this aspect be elucidated through further trials.