Heavy metal extractability and plant bioavailability from two sacrificial biosolids soils as influenced by intensive liming

by

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DECLARATION

I, the undersigned, declare that the thesis, which I hereby submit for the degree of Doctor of Philosophy at the University of Pretoria, is my own work, except where acknowledged in the text, and has not previously been submitted for a degree in any form at this or any other tertiary institution.

Johan Hilgard van der Waals

June 2005

Dedicated to Jacquie.

You complete me!

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Abstract

The influence of pH on metal extractability from two sacrificial soils that received large amounts of biosolids was studied in four separate trials. The soils (Soil 1: gravelly sandy loam; Soil 2: sandy clay loam) were collected from different water treatment plants in Gauteng. Both soils had undergone significant changes in physical (organic carbon content) and chemical characteristics (pH, metal and nutrient content) due to the prolonged disposal of biosolids.

A preliminary pot trial was conducted where large quantities of lime were added to the soils. Results indicated that the soils had high pH buffer capacities due to low pH and high organic matter content. An unexpected increase in the metals extracted with NH_4EDTA after intensive liming lead to the performing of three further trials to shed light on the phenomenon.

In the second trial lime was added to the soils at four rates (0, 12, 24, 36 tons ha^{-1}). An increase in most NH_4EDTA extractable metals was found and this was correlated with increasing absorbance values (at 465 nm) of the extracting solutions (indicating increased extractability of organic matter). In the third trial limed (27 ton ha^{-1}) and unlimed samples were incubated over a period of 20 weeks with regular sampling intervals. The NH_4NO_3 extractable metals decreased significantly in the lime treated soils but the NH_4EDTA extractable metals generally increased.

A fourth trial was conducted due to concern regarding the increased EDTA extractable metals after liming and a possible correlation with plant metal bioavailability. The soils were incubated in pots with four lime rates (0, 12, 24, and 36 ton ha^{-1}) and wheat and spinach grown for two months. Although similar trends as for the previous trials were obtained in terms of metal extractability, plant metal content was best correlated with NH_4NO_3 extraction levels.

The results indicate that liming is a safe option for sacrificial soils and that NH_4NO_3 extractable and plant metal levels decrease with liming. The use of EDTA in metal guidelines or in soil metal content studies is discouraged due to its increased metal extractability with liming and poor correlation with plant metal content.

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CHAPTER 1

General Introduction

1.1 Introduction

The disposal of sewage sludge (or biosolids) is a many faceted problem facing most, if not all, local authorities worldwide. The challenges are generally related to treatment and disposal options of the treated material depending on its nutrient, pathogen, heavy metal, or organic pollutant content. In 2001 the Water Research Commission (WRC) initiated a research program that included the following projects:

- **K5/1209**: An evaluation of dedicated land disposal practices for sewage sludge
- **K5/1210**: Laboratory and field scale evaluation of agricultural use of sewage sludge
- **K5/1240**: A technical and financial review of sludge treatment technologies
- **K5/1283**: A detailed metal content survey of South African sewage sludge and an evaluation of analytical methods for metal determination
- **K5/1339**: Survey and methodology for analysing organic pollutants in South African sewage sludge

As part of the K5/1210 project it was decided to investigate the influence of pH on heavy metal mobility in soil that had received metal containing sludges for prolonged periods under the climatic conditions experienced on the South African Highveld. Finding soils that adhered to the requirements mentioned above proved challenging and in the end it was decided to sample two different sacrificial biosolids disposal soils. Sacrificial disposal of biosolids can take many different forms but the end result is often a soil that is enriched with organic matter, heavy metals, acidity, and nutrients such as phosphorus and nitrogen. Very little management, if any, is practiced on these soils and sludge that has been disposed of on these soils is mostly ploughed into the soils when dry. Sludge metal content as well as its land application is variable and no records exist regarding the total tonnage or volume disposed of on the soils. This aspect poses a problem regarding research on these soils due to unknown metal loading rates.

For a preliminary greenhouse trial bulk samples were collected of the two soils. Soil 1 originally was a dystrophic pale-yellow gravely sandy loam soil from Rooiwal, north of Pretoria, that originated on coarse-grained granite and Soil 2 was a dystrophic red sandy clay loam that originated on dolomite from Hartebeestfontein, southeast of Pretoria. Both of the sampled soils had undergone significant changes in physical and chemical characteristics due to the prolonged disposal of biosolids. During the preliminary pot trial, where large quantities of lime were added to the soils, it was found that the soils had high pH buffer capacities due to low pH and high organic matter content. After a six months aerobic incubation and regular wetting and drying of the soils it was found that the EDTA extractable metal fraction of the soils increased for many of the tested metals. This phenomenon was communicated to the steering committee of the project and discussed at a number of steering committee meetings. From the minutes of the final meeting of the steering committee for project K5/1210, held in Pretoria on 26 May 2003, it was clear that general feeling amongst the committee members was that the phenomenon was contrary to "a wealth of literature indicating the opposite". The minutes contained several suggestions for the "anomaly" and these include:

- "The soils might have been acidic enough to affect the extraction efficiency after liming."
- "The liming could have enhanced the mineralization of organic material."
- "The variability could be due to sampling variability as a result of a small sample size."
- "The sample might have had free lime left as it had been taken out after six months where the liming effect normally takes about two years."

Although the suggestions were not very clear, what was clear is that the phenomenon was considered to be a product of erroneous or inadequate trial set-up. Subsequent to the feedback from the steering committee the phenomenon and its far-reaching implications for the rehabilitation of sacrificial soils in South Africa were discussed at length with a number of colleagues from the University of Pretoria as well as other academic and research institutions (locally and abroad). No one was able to provide an acceptable explanation for the increased metal extractability. Here it should be mentioned that high organic matter soils that are severely polluted with heavy metals are scarce in South Africa and little research has been conducted on the behaviour of the metals and organic matter in these soils. The initial results have subsequently been peer reviewed and published as a short communication (Van der Waals et al., 2005).

1.2 Critical Research Questions

In the light of the initial results as well as the situation as discussed above it was decided to conduct a number of dedicated trials to answer the questions that were implied in the minutes as well as the questions that arose in the mind of this worker. The questions that needed answering were:

1. What is the extent of the increased extractability of the metals with the complexing agent EDTA and how do these values compare to those of a neutral salt extractant such as NH_4NO_3?
2. What is the influence of incubation time on the reactivity of the added lime and the extractability of the metals?
3. Could the increased metal extraction be correlated with mineralising organic material?
4. What is the influence of increasing lime application rates on metal extractability and could the values be correlated with other soil characteristics such as extractable organic matter?
5. What is the influence of increased EDTA extractable metals on plant metal uptake and content, especially in the light of a number of studies that have shown correlations between the two?
6. What are the implications of the results obtained in the different trials for the management and rehabilitation of sacrificial disposal sites as well as agricultural fields where biosolids are used on a continual basis?

1.3 Broad Aim of the Study

The aim of this study is to answer the critical research questions posed regarding the phenomenon of increased EDTA metal extractability from sacrificial sewage disposal site soils after intensive liming under laboratory and glasshouse conditions.

1.4 Communication of Results of the Study

At the time of submission of this study several of its results have been communicated through different publications, conference presentations and formal and informal meetings with colleagues. The outputs include:

1.4.1 Publications in Peer Reviewed Journals

Van der Waals, J.H., Snyman, H.G. & Claassens A.S. 2005. Increase in metal extractability after liming of sacrificial sewage sludge disposal soils. *Water SA* 31(2) p. 271-273.
(Chapter 4 is a style-edited version of the above publication)

1.4.2 Submitted Manuscripts for Peer Review

Van der Waals, J.H. & Claassens, A.S. 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. Submitted to *Water SA* March 2005.

1.4.3 Conference Presentations

a. Snyman, H.G., Van der Waals, J.H. & Van Niekerk, C. Aspects of the beneficial agricultural use of sewage sludge in South African soils. IWA Conference on Environmental Biotechnology: Advancement on Water and Wastewater Applications in the Tropics Kuala Lumpur, Malaysia, 9-10 December 2003.

b. Van der Waals, J.H., & Snyman, H.G. 2004. Selected chemical and physical soil properties of three sacrificial sewage sludge disposal sites. Water Institute of South Africa (WISA) Conference, Cape Town, 2-6 May 2004.

c. Van der Waals, J.H. & Claassens, A.S. 2005. Influence of increasing lime rates on ammonium EDTA (NH_4-EDTA) extractable metals and organic matter from two acid long-term biosolids disposal soils. Combined Congress (Soil Science Society of South Africa, South African Society of Crop Production, South African Weed Science Society, Southern African Society for Horticultural Sciences), Potchefstroom, 11-14 January 2005.

1.4.4 Awards

The presentation at the Combined Congress of the Soil Science Society of South Africa, South African Society of Crop Production, South African Weed Science Society, Southern African Society for Horticultural Sciences, Potchefstroom, 11-14 January 2005, was awarded with the “Best Paper” award by the Soil Science Society of South Africa.

CHAPTER 2

Literature Review on the Effect of Liming on Heavy Metal Mobility in Acid Soils After Long-term Biosolids Disposal – A South African Perspective

2.1. Introduction

Large quantities of biosolids are produced annually by a number of water treatment plants in South Africa. Although an ideal agricultural amendment in terms of especially organic matter, nitrogen, phosphorus, and to a lesser extent other macro and micro nutrients, it could pose a problem in terms of nutrient enrichment if applied in large quantities. The reader is referred to a review of benefits and potential hazards linked to the use of biosolids in agriculture applied to South African conditions by Korentajer (1991).

Current guidelines restrict the use of biosolids in agriculture due to possible leaching of nitrogen as well as heavy metal levels in the material. In many cases biosolids are non-beneficially disposed of in landfill sites or on “sacrificial” land that has been set apart for this purpose. “Sacrificial disposal” entails a number of different practices including accumulation in paddies, flooding, irrigation for the purpose of instant-lawn production, and irrigating onto soil with subsequent ploughing after drying.

Heavy metals and nutrients accumulate in these soils due to the lack of removal processes or procedures (Korentajer, 1991; Alloway, 1995). Records concerning the total added tonnage of biosolids to sacrificial lands are not kept in South Africa. In many cases it is also not clear exactly how much time has transpired since the beginning of the disposal. From a research perspective this leads to problems regarding the accurate assessment of the total metal accumulation in the soils due to highly variable application methods.

Organic carbon also accumulates in these soils due to high application rates and low decomposition or removal rates (Korentajer, 1991). The decomposition rates are retarded by the build-up of acidity in the soils due to the mineralization and nitrification of nitrogen contained in the material. The low pH conditions together with the high metal levels in these soils are a cause for concern regarding its groundwater and environmental pollution potential.

Liming of sacrificial soils would be one of the first options considered but according to some authors it should be approached with caution. Lime induced increases in heavy metal mobility (due to the higher solubility of certain organic matter fractions at higher pH) is often 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 with very few references to cases where the increased mobility of heavy metals has been confirmed. In this light 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 the movement of heavy metals after biosolids addition was reported or predicted.

1. Metal movement in soil profiles due to high biosolids application and increasing pH was reported by Darmody et al. (1983).
2. Emmerich et al. (1982) found that the soil below the incorporation layer of biosolids had become very acid and postulated that this could lead to the mobilisation of metals. The conclusion of the study though was that none of the metals underwent movement to below the layer of incorporation.
3. Kou and Baker (1980) stated that the desorption of organic acids from soil particles at higher pH and the subsequent formation of metal-organic complexes may alter the metal sorptive capabilities of soils. In the study the use of NaOH as titrant lead to the increased extractability of Cu at pH levels above 6 with Zn and Cd showing similar but less pronounced trends. The effect of $Ca(OH)_2$ was less pronounced than NaOH in dispersing organic matter.
4. Legret et al. (1988) indicated that metal mobility in soil was Cd>Ni>Pb>Cr after biosolids addition. They attributed Cd's movement in the soil to its presence in the exchangeable fraction and the lower mobility of the other metals to their presence in less mobile fractions.

5. Robertson et al. (1982) found that the addition of biosolids decreased the pH of the soil and that that Zn, Al, and Fe migrated to a depth of 90cm after heavy applications on three different Ultisols.
6. Welch and Lund (1987) concluded that Ni movement in packed soil columns was not correlated with the pH of the unamended soil but rather with the pH after equilibration as well as the texture of the soil. Unsaturated conditions lead to a greater movement of Ni with less water than saturated conditions.
7. In most studies cited by Dowdy and Volk (1983) the conclusion was that metals did not move below the zone of incorporation. The exception was a study by Lund et al. (1976) where metal movement below sludge disposal ponds was attributed to the formation of soluble metal-organic complexes.

In none of the above-mentioned studies was there any clear evidence of the addition of lime leading to a pronounced mobilization of metals. In two separate studies though it has been reported that EDTA extractable metals increased after the addition of lime to polluted high organic matter content soils or materials. In the first study by Bloomfield and Pruden (1975) an increase in the EDTA extractability of Cd, Cu, Cr, Ni, Pb, and Zn in limed sludge samples and an increased extractability of Cr in limed "sludge + soil samples" was reported. Lake et al. (1984) attributed this increase in Cr levels to the chemistry of the Cr(VI) form in soils. In the Bloomfield and Pruden (1975) study no explanation was given for the increased extractability of metals other than Cr from the limed sludge samples. In the second study by Kobayashi et al. (1974) EDTA was used to recover Cd from a polluted soil with the simultaneous addition of lime.

In a recent preliminary study on the influence of pH on metal extractability from sacrificial soils by Van der Waals et al. (2005) it was found that intensive liming increased especially the EDTA metal extractability. The trial's original aim was to determine the extractability of metals after the addition of lime as a rehabilitation measure and was not designed to provide answers to the questions that arose after the increased extractability was detected. The questions are:

1. Did the lime react completely with the soil at the time of sampling?

2. In what way did the soil pH change after liming due to neutralization or reacidification that followed mineralization of organic material, and could these changes explain the increased extractability?
3. What was the influence of incubation time on the pH of the soil? In other words, could the mineralization have lead to a decrease in pH over time that could account for the increased metal extractability?
4. Although the soil with the lime was mixed thoroughly several times, could the metal extractability be correlated with zones in the pots where lime was not incorporated adequately?
5. In the light of Question 4, what would the influence of different pH values or lime application rates be on the extractability of the metals?
6. Are the increased EDTA extractable metal levels correlated with plant uptake or plant availability?

In the light of the posed questions it was decided to conduct a literature survey with regards to the factors that influence the extractability of metals from soils that receive biosolids. Factors affecting the accumulation and mobility of organic material and heavy metals, and especially, the influence of liming on metal mobility in these soils will be discussed.

2.2 Background

In order to address the aim stated above it is necessary to discuss and elaborate on some of the background aspects that influence metal addition to and mobility in soil. This is important since most discussions on transformations or characteristics of organic matter in soil focus on degrading plant material, not digested biosolids. Extrapolation of organic matter knowledge to biosolids disposal soils is therefore somewhat risky and the deductions suspect. A number of studies during the 70's and 80's have shed light on the characteristics of as well as the mobility of metals in sludges and soil.

2.2.1 Degradation of Biosolids in Soil

The characteristics of sludge after production vary in their stability. In a study by Molina et al. (1971) it was shown that pH, Eh, ammonium-nitrogen content, settleability and odour changed rapidly and significantly after exposure to compressed air bubbled through a slurry of anaerobically digested biosolids. Organic carbon, organic nitrogen and nitrite plus nitrate nitrogen content were not significantly influenced. No solubilisation of metals was observed after a two-week period of rigorous aeration. They concluded that digested sludge is a stabilized material that cannot biodegrade immediately. Aerobically digested sludges are susceptible to microbial decomposition and are considered to not be as stable as anaerobically digested sludges (Sommers, 1977).

After incorporation into the soil, reactions that prevail in soil will dominate and the relatively small unstable component (in soil) will undergo decomposition. Miller (1974) reported that 20% of added organic carbon evolved as CO_2 after sludge addition to a soil during a 6 months incubation in a laboratory, with most of the decomposition occurring during the first month (results in general accordance with those obtained by Boyle and Paul, 1989). Curtin and Smillie (1983) also reported a decrease in soil organic matter content over incubation time. In a study by Sommers et al. (1976 – as cited by Terry et al., 1979) 20 – 25 % of added organic carbon was lost within one year after application to 5 soils of different textures. A significant portion of anaerobically digested sludge resisted microbial degradation and most of the C lost from the soil after biosolids addition was from soil organic matter (through the priming effect) and not from the biosolids (Terry et al., 1979). Chan and Heenan (1999) found that the main losses of organic C due to mineralization was from the light fraction of a specific gravity of less than 1.8 and that were bound to macro aggregates. The mineralization rate of newly applied sludge is not influenced by previously applied sludge though (Lindemann et al., 1988). Terry et al. (1979) concluded that sludge derived organic carbon will increase in soils where high rates of sludge are applied to soils over a number of years – in agreement with the conditions experienced in the sacrificial soils of the present investigation.

A combination of factors influences the rate at which the microbially mediated processes lead to the decomposition of organic material in soil (Smith, 1991). As a general rule soil organic matter decomposition is curvilinearly related to soil moisture and is slow at very wet and very dry conditions (Sikora and Szmidt, 2001). An air filled porosity of 0.6 was found to be optimal for CO_2 respiration and it declined at lower and greater values in a trial by Linn and Doran (1984). Temperature was the main factor influencing the evolution of CO_2 due to the decomposition of sludge in a study by Miller (1974). Mineralization and breakdown rate increases during increases in temperature from 10°C to 35°C ambient temperature (Sikora and Szmidt, 2001). Below and above these temperatures the rates decreased drastically. Clark and Gilmour (1983) found that the effect of temperature was much more pronounced under unsaturated than saturated conditions. In the light of the above trends it is to be expected that high organic matter mineralization rates, due to rapid microbial decomposition, should prevail under the conditions experienced in most soils in South Africa (also discussed by Korentajer, 1991).

Soil pH influences a vast range of processes in soil – including organic matter mineralization. Increasing soil pH from acid to near neutral levels leads to an increase in the C, N and S mineralization rates (Tester et al., 1977; Biederbeck, 1978; Campbell, 1978, Logan, 1992). The mineralization to NH_4^+ from organic material is less sensitive to low pH than is the nitrification phase. At the pH levels prescribed for biosolids enriched soils of 6.5, organic material breakdown is very rapid under favourable climatic and drainage conditions (Tester et al., 1977). After the application of N in an organic or reduced form the nitrification phase could lead to acidification of the soil (Hue, 1995; Brallier et al., 1996; Sikora and Szmidt, 2001), especially if the produced NO_3^- is not utilised by plants and leaches out of the soil. This effect is the main contributor to the acidity in well-aerated sacrificial soils and could lead to leaching losses of nutrients (such as Ca and Mg) as was the case reported by Pal and Broadbent (1981).

Very little is known about the effects of heavy metals in biosolids on soil organic material transformation processes (Smith, 1991). Mineralization processes are less sensitive to heavy metals than is nitrification (Smith, 1991) although soil organisms can adapt to high concentrations of heavy metals (Rother et al., 1982). In incubation studies discussed by Smith (1991) no negative effect of metals was found on the mineralization of organic carbon. On the other hand, a study by Brooks and McGrath (1984) indicated that both biosolids and farmyard manure-applied soils had the same levels of organic material and pH. The microbial activity in the sludge-applied soil, though, was half of the farmyard manure-applied soil due to the presence of metals.

Concluding Remarks: From the research results summarised above it can be concluded that sacrificial soils in South Africa will have undergone rapid mineralization of a small component of the added biosolids due to ideal environmental conditions of temperature and fluctuating moisture content with the bulk persisting long after addition. These soils will also have become acidified due to the rapid mineralization and nitrification of organic N. These conclusions are in agreement with soil conditions experienced in the field and laboratory – as will be discussed in the following chapters.

2.2.2 Organo-metalic Complexes

Soil organic matter consists of two major types of compounds namely: (1) non-humic substances and (2) humic substances formed by secondary synthesis reactions (Stevenson, 1982). Humic substances in the soil environment are polydisperse polyelectrolytes and the charges are pH dependent (Clapp et al., 1993). Predominant sources of charge are carboxyl groups and under acid conditions these functional groups behave like neutral polar molecules. Under normal agricultural conditions these molecules are negatively charged and these charges are balanced by cations (Clapp et al., 1993). Due to the relatively large surface areas associated with small colloidal particles, chemical and physical reactions tend to be greatly enhanced (Stevenson, 1982). The significance of complexation is emphasized by Logan (1992) in that he states that: "Complexation is a more significant mechanism than ion exchange for immobilization of trace metals because of the much higher complexation constants for trace metals relative to macro metals, as opposed to ion exchange in which selectivity for trace metals does not compensate for the higher concentrations of macro metals."

Even though complexation is an important mechanism in the immobilisation of heavy metals humic substances can also form water-soluble complexes with metal ions (such as Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, and others) and hydrous oxides (Schnitzer, 1978; Stevenson, 1982). These metal ions insolubilize humic substances by forming inter- and intra-molecular bridges between charges on humic macromolecules or between these and negatively charged inorganic colloids in soils. When these insolubilizing cations are removed the anions become soluble in water with the most highly charged macromolecules (higher oxygen and lower carbon content) solubilizing first (Clapp et al., 1993). Water-soluble complexes of fulvic acids with toxic metals can increase their concentrations in soil solutions in excess of their normal solubilities and are a major cause for concern (Davies, 1980; Tate, 1987; Bourg, 1995). Stability constants that have been determined by a number of workers vary widely though. These stability constants are usually lower than those formed with synthetic complexing agents such as EDTA (Schnitzer, 1978). Other organic complexing agents may also influence the availability of trace elements to higher plants (Stevenson, 1982). Before application to soil the heavy metals that are present in the biosolids are probably complexed with the organic material or biotic surfaces (Nederlof and Van Riemsdijk, 1995) in different forms or incorporated into the cell structures of dead and living microorganisms.

During organic matter mineralization the unstable sludge component is degraded in soil and the organic component of the organo-metalic complexes is either mineralised or altered into humic compounds by microbial and biochemical processes, thereby releasing the metals into the soil solution. Upon release into the soil solution organic material and mineral surfaces of Fe, Mn, Al, and Si as well as other soil conditions determine the sorption rate onto soil particle surfaces. (The influence of Fe and Mn is discussed in more detail later in the chapter).

Sorption is a collective term for adsorption and precipitation reactions and is used due to the difficulty in distinguishing between the two processes on a macroscopic level (Sparks, 2003; Yin et al., 2000). In soils these two processes are not clearly differentiated but are rather facets of a continuum (Choudhry, 1984). The sorption rate is dependent on a variety of factors including the number of binding sites, metal concentration in the soil solution, dominant type or combination of minerals, soil pH, redox conditions, as well as thermodynamic aspects determining the kinetics of the reactions (reaction rate and direction).

The presence of other elements in the soil could also influence the stability of metal complexes. Divalent cations present in high concentrations in clay mineral soils could lead to a decrease in heavy metal sorption by competing binding (Zachara et al., 1993). In this regard the effect of Ca added through liming could lead to the mobilisation of complexed metals. On the other hand, divalent cations could also lead to the decreased solubility of organic matter in acid soil, therefore leading to increased heavy metal sorption or immobilisation (Yin et al., 2000). Organic complexes of heavy metals can significantly decrease the sorption of metals onto inorganic soil particles, even in the presence of lime (Tate, 1987).

2.2.3 Fulvic and Humic Material and its Influences on Metal Mobility

Low molecular weight fulvic compounds are the chemically most active fractions in biosolids and will complex metal cations more strongly than high molecular weight fractions (Tan et al., 1971; Sposito et al., 1976). They are also water soluble in the pH ranges found in soils (Sposito et al., 1976). An increase in pH leads to an increase in complexation and therefore stability of the metal complexes (Tan et al., 1971, Logan, 1992).

The characteristics of fulvic acid in biosolids amended soils cannot be inferred from the characteristics determined in normal soils due to the definition of fulvic acids being based upon extraction procedures and solubility characteristics rather than particular chemical composition (Sposito et al., 1976). Biosolids fulvic acid, although variable in composition compared to fulvic acid from normal soils, was found to contain much higher levels of S (and therefore sulfone groups) than fulvic acid extracted from soil organic matter (Sposito et al., 1976; Sposito et al., 1982). These sulfonic groups are very strongly acidic (Sposito and Holtzclaw, 1977).

Sposito and Holtzclaw (1977) came to the conclusion that the behaviour of fulvic acid derived from biosolids in soil will be complex and therefore not easy to predict. In a subsequent study Sposito et al. (1977) stated that “there appear to be four separate classes of dissociable functional groups that range in acidity from very strong (ionised at pH < 2) to very week (ionised at pH > 10)”. In this study the functional groups were classed into 4 groups that titrate approximately in the pH ranges < 3, 3-5, 5-8, and > 8. The fulvic acid was found to be of variable shape that influenced the density of the negative charge and the titration curve of the fulvic acid was found to be dependent on concentration of the fulvic acid in solution, implying that it is a polynuclear polyacid (Sposito and Holtzclaw, 1977). Although it is probable that no two functional groups are chemically the same, the fulvic acid has “average” properties that are “classifiable and describable in terms of a few macroscopic parameters” (Sposito et al., 1977). Association of fulvic acids through hydrogen bonding decreased the number of titratable protons where increases in fulvic acid concentration and solutions ionic strength promoted molecular association and coagulation (Sposito et al., 1977).

According to Sposito and Holtzclaw (1977) fulvic acid polyanions have a gross structure of the flexible rod type. Under low pH and high salt concentration conditions these polyanions are found in a state of close association brought together with a bond energy similar to the H-bond. As the pH increases or the salt concentration decreases, significant mutual repulsion of the ionisable sites on the molecular units sets in and the assembly becomes more disperse. Dispersion affects not only the distance between the polyanions but also the geometric configuration and acidity of functional groups – exposing acidic groups that had previously not been exposed to the soil solution.

Sposito et al. (1977) indicated that the complexes formed between Ca^{2+} and fulvic acid extracted from biosolids-soil mixtures were of two types namely: (1) a relatively strong ion pair that is formed between Ca and the most acidic groups in the fulvic acid, and (2) a weaker ion pair that is formed between Ca and the more weakly acidic functional groups. Similar results were reported for Cu^{2+} (Sposito et al., 1979) and Cd^{2+} and Pb^{2+} (Sposito et al., 1981). The weaker complexes depend on the pH of the solution as well as the concentration of the fulvic acid. It was also shown that the Ca^{2+} ion has a “modest” ability to displace protons from undissociated acidic functional groups in fulvic acids extracted from biosolids-soil mixtures.

Concluding Remarks: The phenomena discussed above account for the increased solubility of fulvic acids after liming as well as the buffering effect experienced after the liming of acid organic soils. The increased solubility with increasing pH could be analogous to the results obtained by Van der Waals et al. (2005). This increase in solubility is one of the main concerns when high organic material soils with high heavy metal levels are limed (Hue, 1995).

2.2.4 Iron and Manganese in Biosolids

Iron and manganese can influence the mobility of metals in soils and they often make up a significant and very soluble and plant available component of the metals present in sludges and composts (Logan, 1992; Chaney et al., 2001; He et al., 2001). Upon release, at pH levels close to neutral (6.5 – as required by the guidelines), the Fe and Mn precipitate due to its low solubility at these pH levels and aerobic (oxidising) conditions. Most of the metals released from the mineralising organic material could undergo co-precipitation with Fe and Mn and therefore their solubility is largely determined by the solubility of the Fe and Mn minerals (Bourg, 1995; Chaney et al., 2001).

2.3 Soil Characteristics Determining Metal Mobility

A wide range of soil characteristics determines the mobility or extractability of metals. Mineral (and metal) stabilities in soils under different conditions are determined by factors such as the pH, reduction and oxidation potentials, clay content and type, presence of elements such as phosphorus (Laperche, 2000), organic material content and type (Yin et al., 2000), as well as microorganism activity in soil. Many of these processes are interrelated and could influence the other such as the effect of pH on microorganisms.

2.3.1 Soil pH and Cation Exchange Capacity (CEC)

Organic material exhibits buffering over a wide pH range and although the exact contribution is unknown it is believed to be appreciable (Stevenson, 1982). It can also contribute up to 80% of the CEC of a soil but this contribution is pH dependent (Stevenson, 1982).

The capacity of the soil to adsorb or precipitate metals generally increases with increasing pH (Davies, 1980; Logan, 1992) and a maximum is reached at neutral or slightly alkaline conditions, with As, Mo, and Se being exceptions. Cr^{6+} is also an exception, being more mobile under alkaline conditions (Adriano, 1986; McLaughlin et al., 2000). As the pH decreases there is a strong increase in the solubility of heavy metal complexes, which leads to higher bioavailability and consequently a possible higher uptake by plants (Mayer, 1991). Different metals act differently and Schwarz et al. (1999) found that, in a trial on the heavy metal release from soils during acidification, Cd was the most and Cr the least mobile.

The effect pH has on the heavy metal bio-availability has been confirmed in many different studies that range from metal availability after biosolids application (Sauerbeck, 1991; Smith, 1994; Hooda et al., 1997) to the adsorption of metals on clay fraction minerals (Jinadasa et al., 1995; Kaupenjohann and Wilcke, 1995; Straalen and Bergema, 1995; Schwarz et al., 1999, Yin et al., 2000). The reasons vary from its influence on the dominant species in solution at different pH levels (McLaughlin et al., 2000) to the altered stability (or solubility) of minerals containing the metals during the addition or removal of H^+ (Schwarz et al., 1999). For most metals plant content is positively correlated with soil solution concentration, which in turn, is directly related to soil pH (Kabata-Pendias, 2001).

The CEC of a soil, the magnitude of which is often also linked to pH, influences metal mobility in that it determines the number of binding sites available to metals. The CEC of soil to which a Cd salt was added had a significant effect on the uptake of Cd by maize, with the lower CEC soils leading to a higher Cd uptake (Hinesly et al., 1982). In the same study it was found that the addition of biosolids lead to an insignificant difference between the soils in terms of Cd uptake. This effect could possibly be ascribed to the CEC of the added organic material, increasing the CEC of the soils to the point where differences between the mineral phases were negligible.

The inhibitory effect of metals on soil microorganisms is to a large extent determined by the CEC and pH of a soil. An increased CEC (Doelman and Haanstra, 1979) and pH (Doelman and Haanstra, 1984) leads to lower metal availability and subsequent increase in microorganism activity. Nitrogen transformations (nitrification and mineralization) are also influenced by CEC (Wilson, 1977; Smith, 1991) and pH (Quraishi and Cornfield, 1973; Smith, 1991). Raising of the soil pH or CEC reduces metal toxicity to nodulation process in legumes (McIlveen and Cole, 1974).

2.3.2 Clay Content and Type

The clay content and clay type of a soil can often be positively correlated with the amount of metals taken up by plants (Hooda et al., 1997; Kabata-Pendias, 2001). In many cases the horizon in which an increased content of metals is found, the metal is associated with certain clay minerals (illuvial horizon) or organic material in the A-horizon (Aubert and Pinta, 1977). Structural aspects of soils also play a role in that lithogenic metals such as Al, Fe, or Cr show lower total concentrations on aggregate surfaces than in aggregate cores, whereas ubiquitously deposited metals such as Cd, Pb, or Zn show higher total concentrations on aggregate surfaces (Wilcke and Amelung, 1996).

Different clay minerals in the soil have different affinities for metals. This effect is mainly attributed to the effects of pH on variable-charged sorption sites, which also leads to the increased mobility of Cr^{6+} at higher pH mainly due to the form of the oxyanions (CrO_4^{2-}) in solution (McLaughlin et al., 2000). Jinadasa et al. (1995) found that the metal ion adsorption on synthetically prepared goethite was strongly pH-dependent and that Cr was more strongly adsorbed than Cd and Pb. Fendorf et al. (1996) found that Cr^{3+} was more stable when precipitated on goethite than on silica. When a soil system buffers the addition of acid, heavy metals (e.g. Cr) bound in silicates are released into the soil solution due to the silicate's destruction during the buffering process (Kaupenjohann and Wilcke, 1995).

2.3.3 Time Elapsed After Metal Application

The time elapsed after application of heavy metals to the soils also plays a role in metal mobility. Extractability of Co decreased with increased sorption time in a study by Bibak et al. (1995). Grove and Ellis (1980) found that all extractable Cr fractions, except amorphous and crystalline forms, decreased considerably after a few days to weeks after application. This was especially so for Cr^{3+} in moderately acid to neutral soils and Cr^{6+} in acid soils. Water extractable Cr^{6+} decreased only over several weeks in moderately acidic to alkaline (pH 7.5) soils.

2.3.4 Partition Coefficient

All these factors, and especially pH, determine the extent of the partition coefficient (≈ distribution coefficient) of a metal in soil (Merrington and Alloway, 1997; Impellitteri et al., 2001). This coefficient is defined as the total concentration of the metal in the soil solution divided by the total concentration of the metal in the soil. Soil-water partitioning of organic material as well as the affinity of particulate and dissolved organic matter also determine the partitioning of metals (Yin et al., 2000).

2.3.5 Crop Used and Total Soil Metal Content

Hooda et al. (1997) conducted a trial to determine the heavy metal availability from soils treated previously with biosolids and in which the sludge had time to equilibrate with the soil. The results indicated that the crop used and type of metal influenced the amount that was taken up. A further factor was the total metal content in the soil. Cd, Ni, and Zn levels showed the greatest increases over background levels and Cu and Pb less so, with spinach accumulating the most, carrot intermediate levels and wheat the least.

The variation described above is caused by many differences that exist in plants with respect to plant genetic variation in metal uptake or tolerance, variation within cultivars, the soils on which these plants evolved, and the complexity involved with the plant-rhizosphere-soil interaction (McLaughlin et al., 2000). Steyn (1994) stresses the point that simplified assumptions concerning which plants absorb the most trace elements cannot be made and that it depends on the species of plant and the metal concerned.

2.4 The Effect of Liming and Increased pH on Organic Material Solubility and Metal Mobility

Many remedies for toxic levels of metals in soils have been proposed and tested but in most cases metal toxicity is alleviated through the addition of lime (Hooda et al., 1997; Kabata-Pendias, 2001). Liming increases the soil pH and lowers the activities of the metals in solution. In soils with high organic material contents this trend is sometimes not as clear and could seem to be reversed (Hue, 1995). It is especially true in the short-term, due to the increased solubility of organic material and organo-metallic complexes with increased pH (Allen and Yin, 1996; Moore, 1997; You et al., 1999).

Yin et al. (1996) found that dissolved organic matter increased with an increase in solution pH leading to a decrease in Hg adsorption mineral surfaces due to complexation with dissolved organic matter. You et al. (1999) found similar results with increases in pH resulting in the increased dissolution of organic matter. They proposed two possible reasons namely: (1) increases in pH leads to an increase in negative charges in organic matter and inorganic soil surfaces with consequent repulsion between soil surfaces and organic matter, and (2) increased dispersion of soil particles at higher pH with higher levels of organic matter in the "operationally defined soluble portion" (this is in accordance with the interpretation of data by Sposito et al., 1976, as discussed earlier). They also found that in terms of solubility fulvic acid dominated at low pH and that humic acid increase at a greater rate than fulvic acid with an increase in pH, eventually dominating.

Curtin and Smillie (1983) found a significant increase in organic matter solubility after liming and this was ascribed to desorption or dispersion of the organic material with an increase in soil pH. From their data they concluded that metal-organic complexes were underestimated in soil solutions with higher pH values. Albasel and Cottenie (1985) found a significant decrease in plant heavy metal uptake after liming.

They stated further that plant uptake of heavy metals from limed soils high in organic matter would not necessarily be similar to mineral soils that were limed due to complex complexation reactions of the metals with the soil organic matter. Addition of complexing agents (EDTA and DTPA) to polluted soils increased metal uptake by barley and Italian ryegrass but also decreased the toxicity of the metals at low application rates. They concluded that the addition of metal containing wastes to soils with a high pH would counteract the possible toxic effects of such wastes. Shuman (1986) found that liming decreased the extractable fraction of Zn but increased the organic fraction of Zn and Mn and concluded that liming does not always influence the fractions of metals in soils as it does plant-uptake.

Kedziorek and Bourg (1996) found that the dissolved concentration of heavy metals from artificially contaminated humic acid increased with increasing pH and that this increase was identical to the dissolution of the of the humic acid during increasing pH. A maximum of dissolution of 21% of the humic acid was found and this was accompanied with 100% dissolution of the added metals, indicating that the metals were associated with the more soluble humic acid fraction. In mixtures of humic acid and kaolinite it was found that heavy metal solubility was dominated by the humic acid behaviour. In a mixture of humic acid and amorphous $Fe(OH)_3$ it was found that metal solubility was dominated by the hydroxide at low pH and the humic acid at neutral pH. The influence of the hydroxide at low pH was ascribed to its solubilisation and subsequent release of heavy metals into solution.

Concluding remarks: From the above it is clear that liming (or an increase in pH) of high organic matter soils could lead to the increased extractability of heavy metals. This trend is usually correlated with an increase in organic matter extractability. It is not clear though what the influence is of different extracting solutions on the organic matter or the complexed metals.

2.5 EDTA Extractability of Metals and Organic Matter After Liming

Ethylenediaminetetraaceticacid (EDTA) is often used in heavy metal studies as extracting agent for heavy metals in soils with pH levels below 7. Above a pH of 7 Ca-EDTA complexes are more stable than those of many of the heavy metals of concern and Ca therefore interferes if present in high concentrations in such soils. Although EDTA was found or proposed by many researchers to give a very good indication of the pollution hazard of heavy metals in soils (Hooda et al., 1997) other researchers have found that other complexing agents such as DTPA performed better. In metal studies EDTA is often used as an indication of the potentially bioavailable reservoir whereas KNO_3 and H_2O represent the immediately bioavailable fraction and HNO_3 the non-bioavailable fraction (LeClaire et al., 1984). Immediate plant-uptake of metals is best predicted by using the concentration of the metals in the soil solution (water soluble and exchangeable) though (Mullins et al., 1986).

The use of EDTA in high organic matter metal polluted soils could be problematic due to the fact that chelating agents are known to solubilize part of the organic material while extracting metals (Stevenson, 1982). EDTA is a mild extractant that can also be used to extract organic matter from soils (Dubach and Mehta, 1963). The problem is that neither the carbon nor the nitrogen of the soil extracts can be used to measure the quantity of organic matter extracted and it has therefore never been widely used as extractant for such purposes (Stevenson, 1982).

Mortensen (1963) already mentioned the ability of EDTA to extract organic material from podzol B-horizons and attributed the extraction of the organic matter as reported in Scheffer et al. (1958) to its complexation with Fe and Al. Martin and Reeve (1957) concluded that soil organic material had to be immobilized by ions of one of the transition metals in order for it to be extracted by solutions of organic chelates such as EDTA.

2.6 Concluding Remarks

As mentioned at the beginning of the chapter, there are limited and sporadic references to increased metal extractability with EDTA and simultaneous lime addition (Kobayashi, et al., 1974; Bloomfield and Pruden, 1975). Neither of these studies elaborates on an explanation for the link between increased EDTA extractability and liming. The answer is also not clear when considering the available literature on the characterization of organic matter derived from biosolids, factors determining heavy metal mobility in soils, or the effect of liming on heavy metal extractability. What is clear is that several workers have found or predicted a correlation between soil or solution pH and organic matter extractability and this correlation is expected to influence metal mobility in limed soils. In this regard, the results obtained by Van der Waals et al. (2005) have lead to a number of questions relating to the reason for the phenomenon as well as the implications thereof in terms of plant metal uptake and bioavailability in sacrificial soils.

2.7 Aim of the Study

In the light of the above the aim of this study was, therefore, to determine the following aspects related to the increased EDTA extractability of metals from two sacrificial soils.

1. Lime reactivity with the soil and resultant soil pH over an extended incubation and sampling time and its influence on metal extractability.
2. Mineralization of organic material over an extended incubation and sampling time after liming and its influence on metal extractability.
3. The influence of different pH levels on metal and organic matter extractability.
4. The influence of different pH levels on the metal content of plants and correlation of this data with metal extraction values from the soils.

It is expected that the answers to these questions could contribute significantly to the improved management of sacrificial soils as well as the rehabilitation of presently degraded soils.

CHAPTER 3

Soil Description

3.1 Introduction

As discussed in the preceding chapters the disposal of biosolids is problematic and in South Africa it is often disposed of sacrificially on land. Although sacrificial disposal includes a wide range of practices the two soils that were used for this study have undergone broadly similar ways of biosolids disposal. Soil 1 was a dystrophic pale-yellow gravelly sandy loam soil from Rooiwal, north of Pretoria, that originated on coarse-grained granite and Soil 2 was a dystrophic red sandy clay loam that originated on dolomite from Hartebeestfontein, southeast of Pretoria. The Rooiwal sludge is aerobically digested and is distributed on the land by means of a centre pivot irrigation system (Figure 3.1). The sludge from the Hartebeestfontein works is anaerobically digested and it is disposed through flood irrigation (Figure 3.2). In both cases the dried sludge is incorporated into the soil through ploughing before the following sludge addition. Both sludges vary between 1.5 and 4 % solids and the metal and nutrient contents also vary significantly over time (data not presented here).

Prolonged addition of the sludge to soil leads to a build-up of nutrients, heavy metals, acidity and organic matter (refer to analysis data discussed later in the chapter). The organic matter accumulation is especially pronounced in the Rooiwal soil, which originally very hard in the dry state, becomes spongy due to the accumulation of organic matter as well as regular ploughing (Figure 3.3). After ploughing the soils are left for weeds to grow before further additions take place (Figures 3.4 and 3.5). In some cases trials have been conducted by the local staff to investigate the possibility of growing crops on the land such as at Hartebeestfontein (Figure 3.6) and in others parts of the land is used for informal production of maize, probably without the consent or knowledge of the authorities, such as at Rooiwal (Figure 3.7).

Figure 3.1. Disposal of an aerobically digested biosolids on land by means of a centre pivot irrigation system at Rooiwal.

Figure 3.2. Flood irrigation of an anaerobically digested sludge at the Hartebeestfontein water works.

Figure 3.3. Accumulated organic matter in the Rooiwal soil with shoeprints of up to 5 cm deep due to the spongy nature of the altered soils.

Figure 3.4. Weeds growing at the Rooiwal site (with the Rooiwal power station in the background).

Figure 3.5. Weeds growing at the Hartebeestfontein site with a tractor ploughing a commercial farming land in the background.

Figure 3.6. Maize plants in a field irrigated with biosolids at Hartebeestfontein.

Figure 3.7. Informal production of maize on the edge of a centre pivot field at the Rooiwal site.

The maximum permissible or extractable heavy metal contents in soils is a subject of broad debate in South Africa and guideline levels are currently being reviewed. To illustrate the heavy metal data presented in this chapter one set of data from guidelines of the Water Research Commission (1997) and another suggested by Bruemmer and van der Merwe (1989) are listed in Table 3.1. The merits of the guidelines and guideline levels will only be alluded to briefly in this study.

3.2 Materials and Methods

Bulk topsoil samples from the two soils were collected and from each of these samples a representative sample was collected for chemical and physical analysis Samples were also collected from non-polluted soils in the vicinity of the sacrificial soils to serve as reference samples. It is important to note that biosolids composition varies widely and that those applied to Soils 1 and 2 were from different water treatment plants.

Table 3.1. Maximum metal content in soil (Water Research Commission, 1997), and suggested preliminary threshold values for NH_4-EDTA (pH 4.5) extractable heavy metals for the soils of South Africa (Bruemmer and van der Merwe, 1989)

Element	Maximum permissible metal and inorganic content in soil (mg kg^{-1} soil)	Suggested threshold values (NH_4-EDTA extractable) (mg kg^{-1} soil)
Cd	2	1
Cr	80	50
Cu	6.6	60
Ni	50	20
Pb	6.6	100
Zn	46.5	100

3.2.1 Soil pH and Organic Carbon

The pH of the soils was determined through the method described by the Non-Affiliated Soil Analysis Work Committee (1990) in water, 1 *M* KCl and 0.01 *M* $CaCl_2$, with four repetitions each. Organic carbon was determined according to the Walkley-Black method as described by The Non-Affiliated Soil Analysis Work Committee (1990), also with four repetitions.

3.2.2 Extractable Heavy Metals

An EPA 3050 digestion was done on all the soils (including a reference soil - Canadian Certified Reference Materials, Reference Soil No SO-4, Canada Centre for Mineral and Energy Technology) to determine the “total” Mn, Fe, Cu, Zn, Pb, Ni, Cd, and Cr. Each digestion was repeated four times and blank samples were included. All metals were determined through Atomic Absorption Spectrophotometry. Iron was included in all further trials due to its influence on the mobility of many of the heavy metals of interest.

An NH_4-EDTA and NH_4NO_3 extraction were done separately to determine potentially plant-available and exchangeable metals respectively. The volumes were adapted from the original 45 cm^3 0.02 *M* NH_4-EDTA and 15 g soil stipulated by the Non-Affiliated Soil Analysis Work Committee (1990) to 50 cm^3 0.02 *M* NH_4-EDTA and 5 g soil to ensure adequate EDTA in the presence of high metal levels. The NH_4NO_3 extraction was as follows: 5 g of oven dry soil was shaken with 50 cm^3 0.2 *M* NH_4NO_3 in a stoppered bottle on a horizontal shaker for 1 hour and then filtered. In both cases Mn, Fe, Cu, Zn, Pb, Ni, Cd, and Cr were determined through Atomic Absorption Spectrophotometry.

3.2.3 Effective Cation Exchange Capacity (ECEC) and Extractable Cations

The Effective Cation Exchange Capacity (ECEC) and extractable cations of the soil, at current pH levels, were determined through a $BaCl_2$ extraction (Hendershot and Duquette, 1986). The method was adapted as follows: 5 g of soil was shaken with 50 ml 0.1 M $BaCl_2$ in a glass bottle on a horizontal shaker for 1 hour and filtered afterwards. The metals Ca, Mg, K, Na, Al, Mn, Fe, Cu, Zn, Pb, and Cd were determined through Atomic Absorption Spectrophotometry and Ni and V through ICP-MS. Due to Cl interference in the determination of Cr by ICP-MS a 0.2 M NH_4NO_3 solution was used, with the same procedure and quantities as stated for the $BaCl_2$ extraction, to determine the exchangeable Cr levels in the soils.

The water-soluble metals were determined through a saturated paste extract according to the method described by The Non-affiliated Soil Analysis Work Committee (1990). Again the metals Ca, Mg, K, Na, Al, Mn, Fe, Cu, Zn, Pb, and Cd were determined through Atomic Absorption Spectrophotometry and Ni, Cr and V through ICP-MS. Extractable acidity and Al were determined through a 1 N KCl extraction and organic carbon according to the Walkley-Black method as described by the Non-affiliated Soil Analysis Work Committee (1990).

3.3 Results and Discussion

3.3.1 Organic Carbon and pH

The organic carbon and pH values for the two sacrificial soils and two reference soils are listed in Table 3.2. From the data it is clear that both soils experienced a highly significant increase in organic material. As a consequence of the biosolids addition, the pH values of these two soils are significantly lower than the reference soils. The pH of Soil 1 is lower and the organic carbon content higher than Soil 2. This could be attributed to several factors namely: the higher pH buffer capacity of high clay content soils (Soil 2) on dolomite compared to that of sandy soils (Soil 1) on granite; a longer period of application; or greater total application on Soil 1 than Soil 2.

Table 3.2. Organic carbon and pH values for the two soils (standard deviation indicated in brackets)

		Org C	pH		
Soil	Type	%	H_2O	$CaCl_2$	KCl
1	Reference	0.59 (0.03)	7.02 (0.12)	6.52 (0.08)	4.88 (0.05)
	Sacrificial	3.70 (0.04)	4.16 (0.01)	3.76 (0.01)	3.25 (0.00)
2	Reference	0.97 (0.04)	6.34 (0.11)	5.86 (0.02)	5.07 (0.03)
	Sacrificial	2.91 (0.11)	4.00 (0.01)	3.66 (0.01)	3.50 (0.01)

3.3.2 Extractable Heavy Metals

The EPA 3050 extractable metal levels for the two soils are presented in Table 3.3 with the values in bold denoting those exceeding the values listed in Table 3.1 (Column 2). Most of the metal levels in the two sacrificial soils exceeded those in Table 3.1. In the case of Cd, Cr, Cu, Ni (except Soil 2), Pb (except Soil 2), and Zn there was a significant increase in metal content due to biosolids application. Some of the values listed in Table 3.1 (Column 2) could be excessively conservative, especially since the reference values for Cu (Soil 2), Ni (Soil 2), and Pb (Soils 1 and 2) exceed the Table 3.1 values. Possible reasons for this could include the fact that the values in Table 3.1 (Column 2) do not indicate an extraction method and the fact that many South African soils have high background metal levels, as discussed by Herselman and Steyn (2001).

Table 3.3. EPA 3050 extractable metal levels (mg kg^{-1}) for Soils 1 and 2 (values in brackets indicate the standard deviation – n = 4)[†]

	Soil 1		Soil 2	
Metal	Reference	Sacrificial	Reference	Sacrificial
Cd	[¶]0.00 (0.00)	**2.05 (1.18)**	[¶]0.00 (0.00)	**2.75 (0.71)**
Cr	10.9 (1.63)	**145 (16)**	44.7 (1.7)	**361 (26)**
Cu	4.97 (0.39)	**141 (21)**	**39.0 (3.5)**	**291 (10)**
Fe	>5000	>5000	>5000	>5000
Mn	122 (2)	60.4 (7.2)	1407 (80)	534 (61)
Ni	2.89 (2.30)	25.8 (3.8)	**58.9 (7.3)**	**68.7 (2.9)**
Pb	**9.29 (4.88)**	**188 (56)**	**24.2 (10.1)**	**46.8 (13.3)**
Zn	25.9 (2.8)	**338 (37)**	44.7 (2.3)	**97.4 (2.2)**

[†] Bold values denote those exceeding the values stipulated in Table 3.1 (Column 2)

[¶] Reference soil values for Cd were below detection limits during determination due to the dilution factor in the EPA 3050 procedure

The Fe levels were in excess of 5 000 mg kg^{-1} in both soils. The Mn levels decreased in both soils after biosolids addition with a significant decrease in Soil 2. From the values it is also clear that some soils derived from dolomite in the Gauteng area have high Mn levels. The decrease in Mn levels is attributed to the lowered pH and altered redox conditions in the soils after biosolids application as well as possible low levels in the sludge. Manganese is highly mobile under low pH and reduced conditions, especially in the presence of ligands (organic material), and therefore readily leaches out of the profile during the application of large volumes of water and reducing agents (organic material and N compounds that can readily undergo oxidization).

Table 3.4 indicates the NH_4-EDTA extractable metals for the two soils. Cadmium, Cr, Cu, Ni, Pb, and Zn exhibited a significant increase in extractability and this is attributed to the high levels applied. Only the sacrificial soil values for Cu (Soil 2) and Zn (Soil 1) exceeded the values suggested by Bruemmer and van der Merwe (1989) even though Cu (Soils 1 and 2 sacrificial, and 2 reference), Pb (Soils 1 and 2 sacrificial and 2 reference) and Zn (Soil 1 sacrificial) exceeded the values given in Column 2 of Table 3.1. Zinc also exceeded the Table 3.1 (Column 2) values in the NH_4NO_3 extraction (Table 3.5). Most of the metals (except Mn in both soils and Zn in Soil 1) were sparingly extractable with NH_4NO_3 but exhibited a significant increase in the sacrificial soils.

Considering that high levels have accumulated in the soils (Table 3.3) and are extractable with EDTA (Table 3.4), the values suggested by Bruemmer and van der Merwe (1989) seem high and not conservative enough, whereas the values in Column 2 (Table 3.1) seem overly conservative.

Table 3.4. NH_4-EDTA extractable metal levels (mg kg^{-1}) for Soils 1 and 2 (values in brackets indicate the standard deviation – n = 4)†

	Soil 1		Soil 2	
Metal	Reference	Sacrificial	Reference	Sacrificial
Cd	0.09 (0.05)	0.45 (0.04)	0.08 (0.07)	0.71 (0.05)
Cr	0.17 (0.21)	0.58 (0.25)	0.08 (0.10)	0.71 (0.10)
Cu	1.02 (0.22)	41.6 (1.42)	7.72 (0.77)	**69.2 (1.46)**
Fe	55.5 (4.65)	454 (22)	160 (13)	293 (13)
Mn	72.6 (4.1)	17.1 (0.4)	1026 (30)	45.7 (3.3)
Ni	0 (0)	4.45 (1.10)	0.31 (0.40)	2.95 (0.53)
Pb	2.69 (0.82)	10.2 (0.5)	7.25 (1.46)	9.10 (1.11)
Zn	2.64 (0.57)	**101 (6)**	10.9 (0.6)	30.9 (2.5)

† Bold values denote those exceeding the values stipulated in Table 3.1 (Column 3)

Table 3.5. NH_4NO_3 extractable metal levels (mg kg^{-1}) for Soils 1 and 2 (values in brackets indicate the standard deviation – n = 4)[†]

	Soil 1		Soil 2	
Metal	Reference	Sacrificial	Reference	Sacrificial
Cd	0.01 (0.01)	0.13 (0.01)	0.01 (0.01)	0.44 (0.04)
Cr	0.01 (0.02)	0.02 (0.02)	0.01 (0.01)	0.09 (0.01)
Cu	0.04 (0.02)	1.70 (0.06)	0.06 (0.06)	10.1 (0.3)
Fe	0.10 (0.20)	6.80 (0.49)	0.65 (0.54)	8.62 (0.38)
Mn	12.7 (1.9)	16.2 (0.2)	3.29 (1.48)	40.6 (1.2)
Ni	0.00 (0.03)	4.71 (0.16)	0.30 (0.03)	3.78 (0.08)
Pb	0.06 (0.02)	0.03 (0.01)	0.02 (0.01)	0.13 (0.01)
Zn	0.00 (0.00)	**65.6 (4.1)**	0.00 (0.00)	17.0 (0.9)

[†] Bold values denote those exceeding the values stipulated in Table 3.1 (Column 2)

3.4 Conclusions and Recommendations

The long-term application of biosolids to the two soils resulted in a significant accumulation of organic carbon and heavy metals, as well as a significant decrease in pH. The extractable metal levels varied considerably between the different extracting procedures, as expected. The guideline or suggested levels in soil mentioned in this paper are not realistic and should be further investigated. When maximum permissible soil metal contents are stipulated in guidelines, a clear distinction should be made with regards to total versus bio-available metal concentrations.

The fact that monitoring of loading rates and the variation in metal content of the biosolids over the application period was not done, although complicating research, should serve as a motivation for the further study into, and monitoring and rehabilitation of sacrificial lands.

CHAPTER 4

Increase in Metal Extractability After Liming of Sacrificial Sewage Sludge Disposal Soils

4.1 Abstract

A sandy and a sandy clay-loam soil from two dedicated (sacrificial) sewage sludge disposal sites were incubated with a total lime equivalent of 45 $Mg \cdot ha^{-1}$. Both these soils were acidified (pH 4.0 to 4.2) and had a significant accumulation of organic material (organic C of 2.9 to 3.7 %) compared to non-polluted soils (organic C of 0.6 to 1.0 %). The limed soils did not attain the desired pH of 6.5 after 6 months' incubation due to a high buffer capacity. After incubation soil samples were taken from the incubated pots and the levels of Al, Fe, Mn, Cu, Zn, Pb and Cd were determined by atomic absorption spectrophotometry (AAS) after extraction with NH_4-EDTA and $BaCl_2$. Most of the metals extracted with $BaCl_2$ (except Mn in the sandy soil and Cd in both soils) decreased after liming. The EDTA-extractable Mn, Fe, and Cd in both soils and Cu and Pb in the sandy clay-loam soil increased after liming, whereas Al and Zn decreased in extractability. (Statistically significant differences could not be determined for the trial due the trial not having been designed for the results that were obtained.) Similar results were reported in literature for EDTA metal extraction but the phenomenon was not elaborated upon, except for Cr. The increased extractability of some of the metals after liming could negatively influence the use of EDTA as an extracting agent in proposed heavy-metal guidelines for similar sacrificial soils. Should liming be considered as a strategy to decrease metal mobility in sacrificial soils, the observed increase in extractability becomes a cause for concern and should receive attention in further research.

4.2 Introduction

In recent years the trend has been to express heavy-metal levels in soils as plant- or potentially plant-available metal levels (Beckett, 1989; McLaughlin et al., 2000) rather than "total" concentrations. This implies that "weaker" extractants or chelating agents be used in heavy-metal studies. Ethylenediaminetetraaceticacid (EDTA), in either the di-sodium or di-ammonium salt form, has been used extensively in a host of studies as an extractant of potentially plant-available heavy metals.

In some trials, EDTA was found to give a very good indication of the pollution hazard of heavy metals in soils as well as being a reliable test for predicting plant-available metals (Hooda et al., 1997; Cajuste and Laird, 2000). Earlier, Bruemmer and Van der Merwe (1989) stated that the NH_4-EDTA-extractable heavy metal concentration gives a good estimate of those potentially plant-available, and therefore suggested it to be used in the establishment of preliminary threshold values for heavy metals in South African soils. Currently, however, there are no guidelines stipulating the maximum EDTA-extractable metal levels in South African soils.

Neutral salt extractants are generally weaker extractants than EDTA and give an indication of the immediately exchangeable (therefore immediately plant-available) metals (Beckett, 1989; McLaughlin et al., 2000). Examples of such extractants are $BaCl_2$, NH_4NO_3, NH_4OAc buffered at pH 7, and more. The $BaCl_2$ method (Hendershot and Duquette, 1986) gives an indication of the effective cation exchange capacity (ECEC) of the soil at unbuffered pH levels. This is particularly relevant in studies where the pH dependence of metal extractability is one of the parameters of investigation.

In a preliminary study it was found that soils from some sacrificial sewage sludge disposal sites can be acidified (pH 4.0 to 4.2) and also have very high pH-buffering capacities due to relatively high organic carbon levels (organic C of 2.9 to 3.7 %). Coupled to this is a significant increase in total heavy metal content of the soil. The aim of this study was to determine the $BaCl_2$ and NH_4-EDTA extractability of a range of metals in two acid soils after liming to near-neutral pH levels and incubation in pots.

4.3 Materials and Methods

The buffer capacity of the two acid soils (here referred to as Soils 1 and 2) was determined with a $Ca(OH)_2$ buffer (as discussed by Van der Waals and Claassens, 2002). The required amount of a commercial dolomitic lime (according to the buffer determination) for a pH of 6.5 was added to each soil in 7.5kg pots (with 4 repetitions) and the soil incubated for 3 months with regular watering and mixing. After sampling the soil and finding only a slight change in pH it was decided to add an equal amount of lime and incubate the soil again for the same period of time. The total amount of lime added amounted to the equivalent of 45 $Mg \cdot ha^{-1}$.

After the second incubation period a representative sample was taken from each pot and the pH determined according to the method described by the The Non-Affiliated Soil Analysis Work Committee (1990). On the limed soil and a sample from the original soil a $BaCl_2$ extraction was done. The method was adapted from Hendershot and Duquette (1986) by shaking 5 g of soil with 50 mℓ 0.1 M $BaCl_2$ in a glass bottle on a horizontal shaker for 1 h. After filtering the solution, the Al, Mn, Fe, Cu, Zn, Pb, and Cd contents were determined through AAS. Further, an EDTA extraction (The Non-Affiliated Soil Analysis Work Committee, 1990) was done on the same samples and Al, Fe, Mn, Cu, Zn, Pb and Cd again determined by AAS. The samples were tested at the same time to minimise experimental error differences. The metals Cr and Ni were not determined due to the termination of the testing after the first results had yielded unexpected increases upon liming, as discussed below.

4.4 Results and Discussion

Table 4.1 gives the pH results of the two soils before and after liming. The pH values increased by 1.4 pH units for Soil 1 and by 1.8 pH units for Soil 2 after the addition of the equivalent of 45 $Mg \cdot ha^{-1}$ lime. This indicates a massive buffering capacity brought about by organic material and complexes stable at pH 4.2 and 4.0 for Soil 1 and 2 respectively. The buffer determination as described by Van der Waals and Claassens (2002) is therefore considered inadequate for soils with high buffer capacities such as these.

Table 4.1. Soil 1 and 2 pH values before and after liming (n = 4)

Method	Soil 1		Soil 2	
	Before	After	Before	After
Water	4.2	5.6	4.0	5.8
$CaCl_2$	3.8	5.3	3.7	5.7
KCl	3.3	5.0	3.5	5.4

Table 4.2 indicates the influence of the lime addition and incubation on the $BaCl_2$ extractable metals from the two soils. The metals Mn and Cd in Soil 1 and Cd in Soil 2 did not decrease in extractability after liming as was expected. The expected decrease was found for Al, Cu, Fe, and Zn. The large coefficients of variation for the limed soils are indicative of the low values determined for some of the metals that approached their detection limit with AAS.

Table 4.3 indicates the EDTA-extractable metals for the two soils before and after liming. Here most of the tested metals (Cu, Mn, Fe, and Cd in both soils and Pb in Soil 2) did not decrease in extractability and in some cases even increased. Aluminium, Zn, and to a lesser extent Pb in Soil 1, indicated the expected decrease in extractability.

In a study by Bloomfield and Pruden (1975) an increase in the EDTA extractability of Cd, Cu, Cr, Ni, Pb, and Zn in limed sludge samples and an increased extractability of Cr in limed "sludge + soil samples" was reported. Lake et al. (1984) attributed this increase in Cr levels to the chemistry of the Cr(VI) form in soils. In the Bloomfield and Pruden (1975) study no explanation was given for the increased extractability of metals other than Cr from the limed sludge samples. Although Zn decreased in extractability in the present study, the effect of increased extraction was still observed for Cu, Mn, Fe, Pb, and Cd, even though the samples are not exactly of the same type as those in the Bloomfield and Pruden (1975) study.

Table 4.2. The effect of liming on $BaCl_2$ extractable metals ($mg \cdot kg^{-1}$ soil; n = 4; values in brackets denote the standard deviation)

Metal ($mg \cdot kg^{-1}$)	Soil 1		Soil 2	
	Before	After	Before	After
Al	35.0 (1.3)	0.2 (0.3)	154.7 (6.7)	0.2 (0.1)
Cu	3.3 (0.2)	0.2 (0.1)	14.1 (0.2)	0.8 (0.1)
Mn	17.5 (0.5)	21.2 (4.0)	29.7 (2.0)	12.4 (3.0)
Fe	6.0 (1.0)	0.5 (0.5)	0.8 (0.8)	0.3 (0.2)
Zn	151.6 (6.4)	11.5 (3.2)	18.5 (0.3)	3.0 (0.4)
Pb	1.8 (2.7)	1.3 (0.7)	1.6 (1.9)	0.3 (0.3)
Cd	0.3 (0.2)	0.3 (0.1)	0.3 (0.2)	0.6 (0.1)
Coefficient of Variation	5.7	25.4	5.6	24.4

Table 4.3. Effect of liming on NH_4-EDTA-extractable metals ($mg \cdot kg^{-1}$ soil; n = 4; values in brackets denote the standard deviation)

Metal ($mg \cdot kg^{-1}$)	Soil 1		Soil 2	
	Before	After	Before	After
Al	113.9 (10.4)	33.2 (3.8)	337.7 (16.5)	222.2 (55.6)
Cu	41.1 (1.8)	37.1 (2.2)	80.8 (1.4)	104.6 (2.9)
Mn	17.2 (0.6)	49.6 (3.8)	37.1 (5.9)	71.3 (6.9)
Fe	242.7 (2.7)	383.5 (11.9)	170.7 (5.6)	271.7 (23.9)
Zn	117.0 (8.2)	49.1 (2.0)	28.8 (1.5)	15.6 (0.8)
Pb	9.8 (0.7)	6.5 (0.3)	8.4 (2.6)	8.1 (1.0)
Cd	0.3 (0.02)	0.8 (0.2)	0.5 (0.01)	1.3 (0.1)
Coefficient of Variation	4.5	4.3	5.1	13.1

4.5 Conclusions and recommendations

The results in this trial lead to a number of questions concerning the extractability of the metals and the conditions in the pots. Firstly, although the lime used was a commercially available lime, the metals listed here did not occur at sufficiently high levels to lead to the resultant increase in extractability (data not presented here). It is also not clear whether the lime had reacted completely with the soil. Secondly, the possible fluctuation in pH during the incubation time is not known and it is therefore impossible to comment on its influence on the metal extractability. Thirdly, the possible mineralization of organic material after liming could not be quantified due to the set-up of the trial (aerobic conditions in a greenhouse) and it is therefore not possible to comment on its influence on the increased extractability.

Although results similar to these have not been widely reported, the phenomenon warrants further investigation. These authors agree with the conclusions of Lake et al. (1984) concerning the increased Cr extractability in the Bloomfield and Pruden (1975) study, but consider the phenomenon of the increased extractability of the metals other than Cr as similar to those reported here. The metals that exhibited an increase in extractability do not occur in soil in the same state as Cr(VI) and therefore require a different explanation.

The trial, having generated a number of questions, was not designed to supply the required answers. It is therefore suggested that a dedicated trial be conducted to determine:

- The change in pH over an extended incubation period with and without the addition of lime with regular sampling intervals.
- The change in metal extractability (complexed and exchangeable) over an adequate incubation period with and without the addition of lime with regular sampling intervals.
- The EDTA metal extractability as influenced by increasing pH (lime application rates).

The increased extractability of the metals after the application of lime has a profound influence on the establishment of metal guidelines when EDTA is used. Before the use of EDTA as an extractant in guideline levels is advocated, this phenomenon has to be investigated further to determine the restrictions of the procedure – especially under the conditions experienced in this trial.

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.

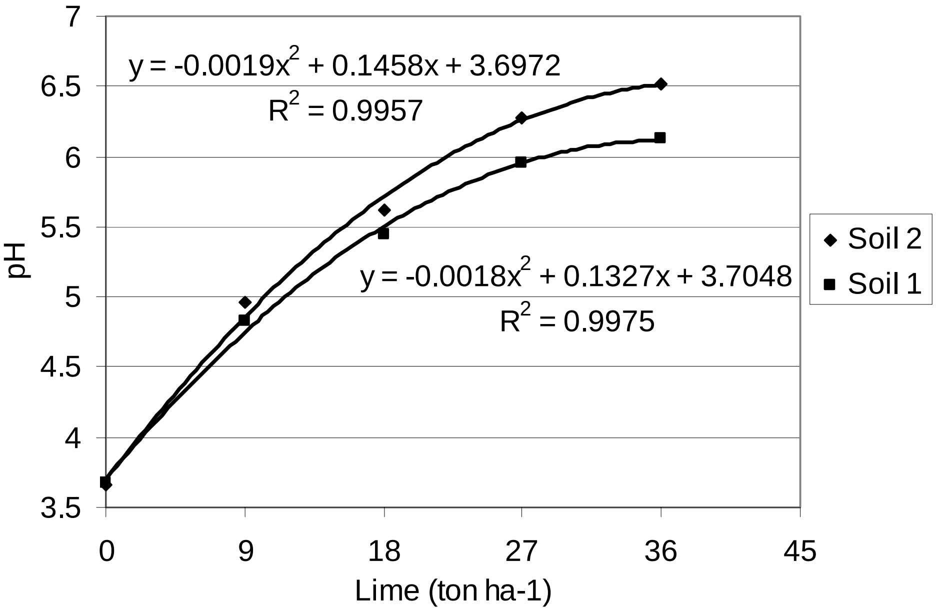

Figure 5.1. Change in pH ($CaCl_2$) at four lime application rates after 3 weeks incubation.

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 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.

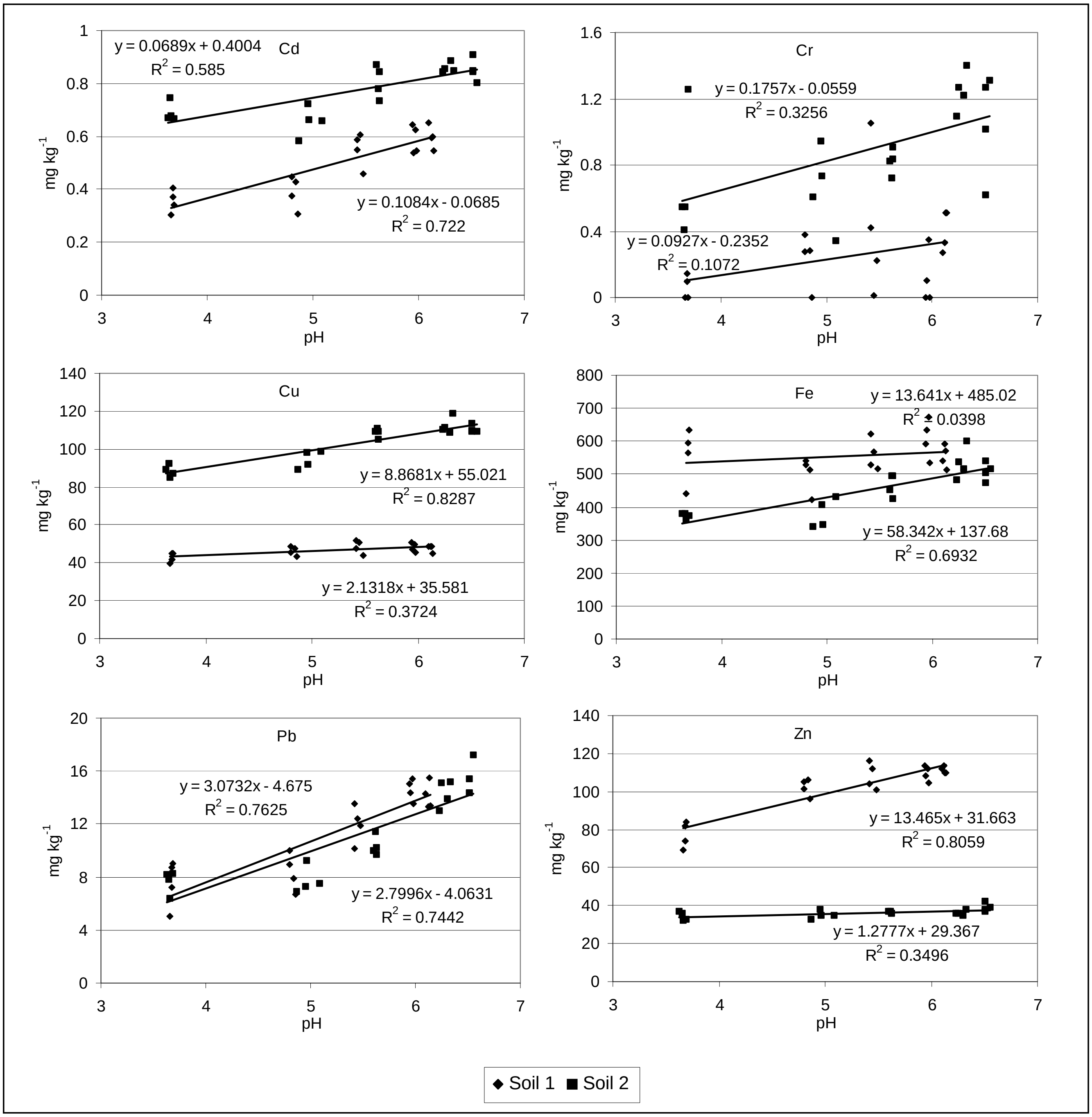

Figure 5.2. The NH_4-EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn as a function of pH ($CaCl_2$).

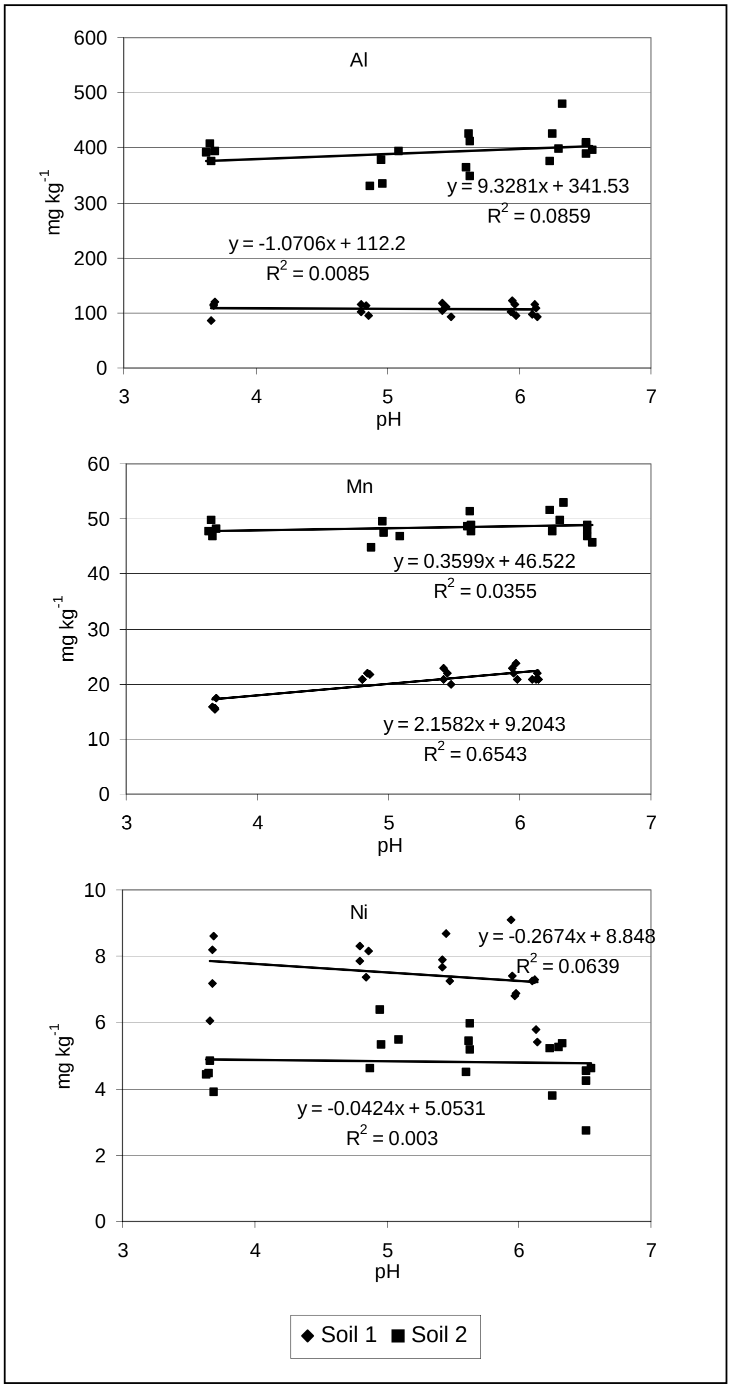

Figure 5.3. The NH_4-EDTA extractability of Al, Mn, and Ni as a function of pH ($CaCl_2$).

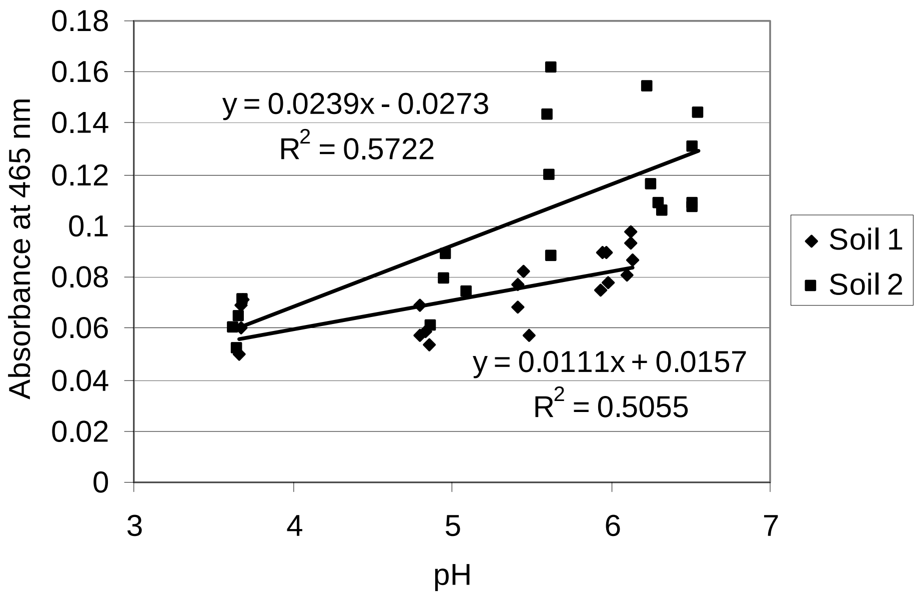

Figure 5.4. Soil 1 and 2 absorbance values as a function of pH ($CaCl_2$) in NH_4-EDTA extracts at four lime application rates after 3 weeks incubation.

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.

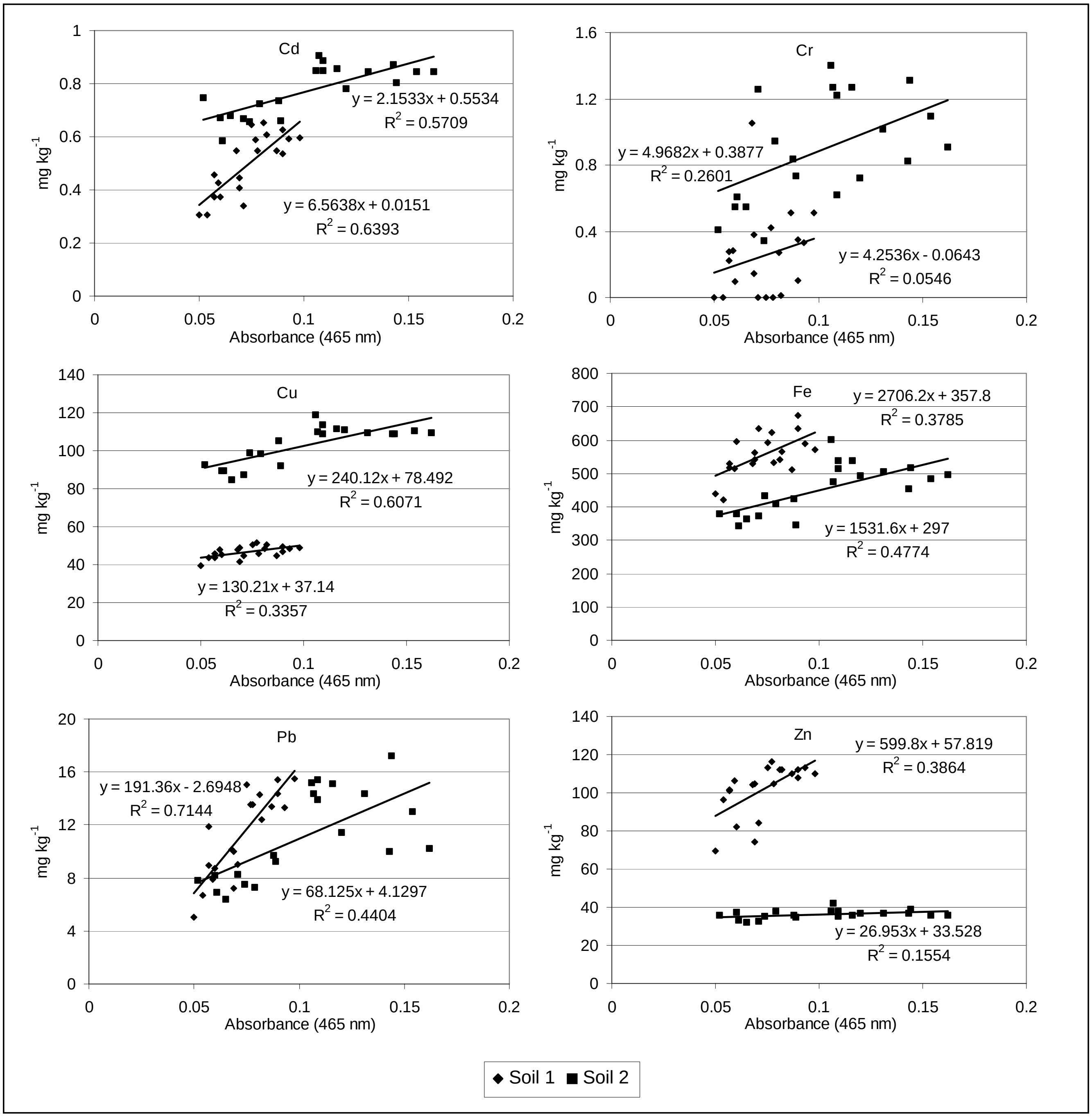

Figure 5.5. The NH_4-EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn as a function of the NH_4-EDTA solution absorbance at 465 nm.

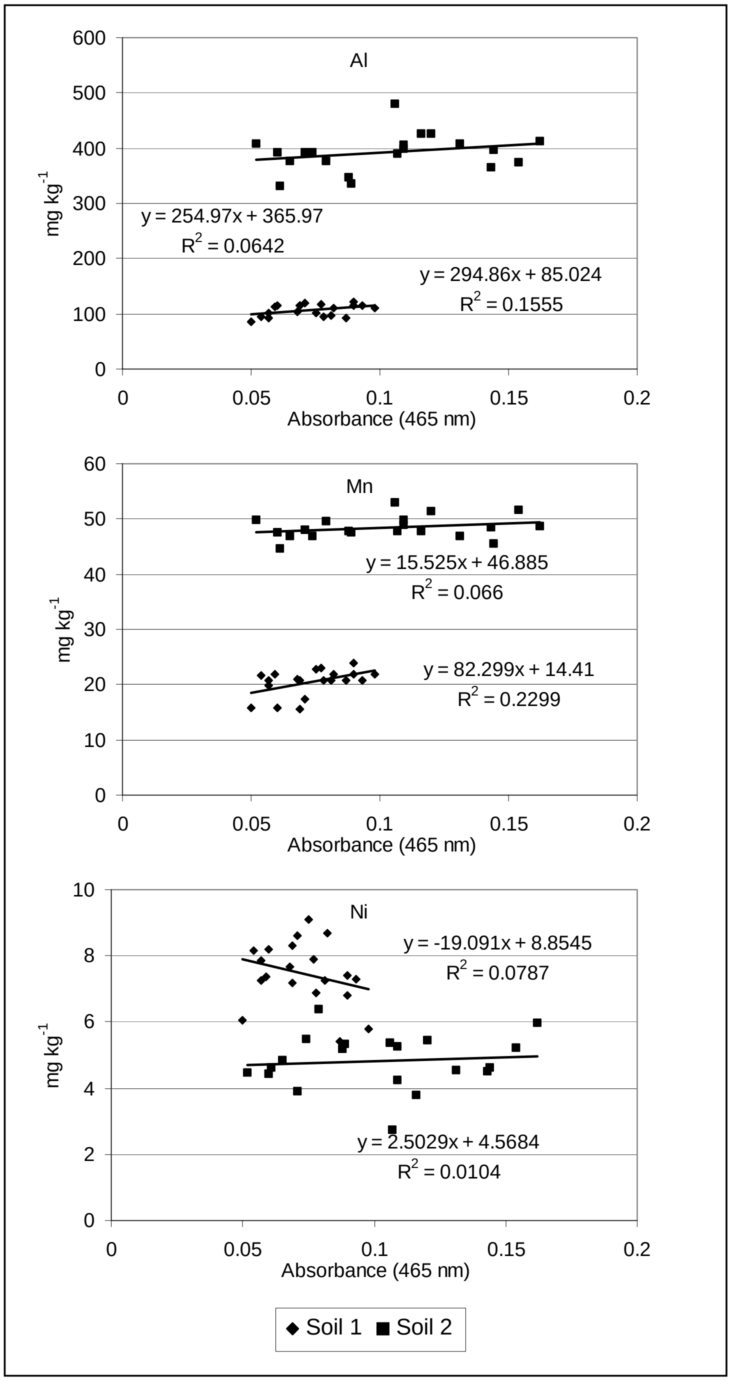

Figure 5.6. The NH_4-EDTA extractability of Al, Mn, and Ni as a function of the NH_4-EDTA solution absorbance at 465 nm.

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.

CHAPTER 6

Changes in Ammonium Nitrate (NH_4NO_3) and Ammonium EDTA (NH_4EDTA) Extractable Metals from Two Long-Term Biosolids Disposal Soils due to Intensive Liming and Incubation

6.1 Abstract

Sacrificial disposal of metal containing biosolids leads to a build-up of organic material, acidity and metals in soils. Preliminary investigations have indicated that intensive liming of these soils could lead to an increase in metal extractability. Two acid soils ($pH_{(water)}$ 4) were collected from different sacrificial sites and incubated in open containers with regular wetting and drying cycles over periods of 0, 1, 2, 4, 6, 8, 12, 16, and 20 weeks. One set of treatments for each soil received the equivalent of 27 tons ha^{-1} $CaCO_3$ (AR) while another was incubated without lime. On the samples a pH ($CaCl_2$) determination and NH_4NO_3 and NH_4EDTA extractions were performed and the metals Al, Fe, Mn, Cd, Cr, Cu, Ni, Pb, and Zn determined in the extracts. The lime reaction was complete within three days after application. Most of the metals indicated a slight increase in NH_4NO_3 extractability over the incubation period in the unlimed treatments and this was positively correlated with a decrease in pH. All the metals showed a significant decrease in NH_4NO_3 extractability after liming. The EDTA extractability of the metals did not correlate with the slight decrease in pH over the incubation period. The EDTA extractability of all the metals (except Ni), however, indicated varying degrees of increase after liming. Liming of sacrificial soils is considered a sound practice due to the significant decrease in extractability of the metals by NH_4NO_3, or exchangeable metal fraction, even though the EDTA extractability of the metals increased after liming. The correlation between the NH_4NO_3 and EDTA extractable metals and plant metal uptake is not known and should be investigated.

6.2 Introduction

Sacrificial biosolid soils are often polluted with high levels of metals that could pose a threat to the environment due to their low pH and high pH buffer capacity. One of the possible approaches to decrease the mobility of the heavy metals in these soils is liming, as it is often used as a rehabilitation strategy in metal polluted soils (Logan, 1992). The most important factor controlling the mobility of metals in soils is pH (Sauerbeck, 1991; Smith, 1994; Hooda et al., 1997) mainly due to its influence on the adsorption of metals on clay minerals (Jinadasa et al., 1995; Kaupenjohann and Wilcke, 1995; Straalen and Bergema, 1995; Schwarz et al., 1999, Yin et al., 2000) as well as the pH stability of organo-metalic complexes (Schnitzer, 1978; Stevenson, 1982; Clapp et al., 1993). Several workers (Hue, 1995; Moore, 1997), though, have cautioned against this strategy in soils that are polluted with metals and that also contain elevated levels of organic matter. The reason for the cautionary approach is the increase in solubility of organic matter (and therefore organo-metalic complexes) upon lime addition and the fear of the migration of these complexes into lower soil horizons or even groundwater.

In this context Van der Waals et al. (2005) have indicated in a previous study that the intense liming of two sacrificial biosolids disposal soils lead to a decrease in most of the $BaCl_2$ extractable metals. However, the EDTA extractability of several of the metals increased when compared to unlimed treatments. In a subsequent study (Chapter 5) it was found that the increased metal extractability in EDTA showed a good correlation with organic matter extracted from the soils. This was due to the characteristics of the EDTA (known as an organic matter extractant) as well as the influence of pH on the solubility of organic matter in soil.

The trials reported on by Van der Waals et al. (2005) and in Chapter 5 represent a once-off sampling of the soils with no further indication as to the influence of incubation time on extractability. Other studies have shown that metal mobility or extractability decreases with time after application due to the precipitation or adsorption of the metals on soil mineral surfaces in increasingly stable complexes or forms (Grove and Ellis, 1980; Bibak et al., 1995).

In order for longer-term data to be applicable to conditions experienced in the field, it is necessary that the effect of liming on the mobility of the metals be investigated under controlled conditions that closely resemble field conditions. The rainfall in the Gauteng province varies between 650 and 750 mm per year and is mainly in the form of thunderstorms that vary in intensity. Topsoil horizons often dry out completely before the follow-up rainfall events due to low relative humidity and high average maximum temperatures (ranging from 28 º – 34 ºC). The soils therefore experience numerous and intense wetting and drying cycles during a season that lead to a rapid mineralization of unstable organic matter. The aim of this study, therefore, was to determine the changes in extractability of metals in the two acid sacrificial soils reported on by Van der Waals et al. (2005) and in Chapter 5 as a function of lime addition and incubation time with repeated wetting and drying cycles.

Under wetting and drying cycle conditions with exposure of the soil and drying to the atmosphere it would not be possible to determine the products of organic matter mineralization, such as gaseous CO_2 emissions, and therefore also impossible to determine its influence on metal extractability. Terry et al. (1979) indicated that mineralization of the unstable organic matter fraction was mostly complete within 28 days after sludge application to soil and that a major component (55 to 80 %) was resistant to decomposition. Due to the "aged" nature of the biosolids in the experimental soils it was concluded that organic matter mineralization would not be significant in the soils and its omission from the study was therefore considered justified.

6.3 Materials and Methods

6.3.1 Incubation With and Without Lime

The soils that were used for the trials reported on in Chapters 4 and 5 were also used for this trial. The reaction of the two soils on incubation with and without lime was determined by incubating 150 g of each soil in plastic containers for a period of 20 weeks. For the lime treatment 1 g $CaCO_3$ (AR) was added to the 150 g soil (equivalent to 27 tons ha^{-1} if incorporation to a depth of 0.3 m is assumed in a soil with a bulk density of 1.5 g cm^{-3}). The samples were thoroughly mixed with a glass rod and four replicates were prepared for each soil (limed and not limed) for every sampling period of 0, 1, 2, 4, 6, 8, 12, 16 and 20 weeks. At the beginning of the trial all the samples received de-ionised water (100 ml – in excess of saturation) and were thoroughly mixed. The Week 0 samples were removed immediately after the addition of the water and dried at 65 ºC. The remaining samples were left to dry to the atmosphere in a constant temperature room at 27 ºC (approximately 5 – 6 days). These remaining samples received 50 ml de-ionised water (water to soil ratio of 1:3 – roughly equivalent to field capacity) every week, were stirred with a glass rod and left to dry. This was repeated weakly up to Week 20 to simulate repeated wetting and drying cycles in the field. At every interval the assigned samples were removed and dried at 65 ºC. After drying, the samples were stored in sealed polyethylene bags until analysis.

6.3.2 Soil Analysis

Each of the soil samples was analysed for pH ($CaCl_2$) according to the method described by the Non-Affiliated Soil Analysis Work Committee (1990) with a 0.01 M $CaCl_2$ solution. The metals Al, Fe, Mn, Cu, Zn, Cd, Cr, Ni, and Pb were determined through NH_4NO_3 and NH_4EDTA extractions. Ammonium nitrate and NH_4EDTA were chosen due to their frequency of use in studies on exchangeable and "potentially plant-available" metals in soils. The NH_4NO_3 extraction was as follows: 5 g of soil was shaken with 50 ml 0.2 M NH_4NO_3 in a stoppered glass bottle on a horizontal shaker for 1 hour and filtered afterwards. Aluminium, Fe, Mn, Cu, and Zn were determined through Atomic Absorption Spectrophotometry (AAS) and Cd, Cr, Ni, and Pb by ICP-AES due to levels being below the detection limits of AAS. For the EDTA extraction the volumes were adapted from the original 45 ml 0.02 M NH_4EDTA and 15 g soil stipulated by the Non-Affiliated Soil Analysis Work Committee (1990) to 50 ml 0.02 M NH_4EDTA and 5 g soil. This was done to ensure adequate EDTA in the presence of high metal levels. With this extraction all the metals were determined through AAS. In both cases an internal reference soil was included as every 9th determination. All the samples were analysed at the same time to reduce experimental error differences.

6.4 Results and Discussion

6.4.1 Change in pH Upon Incubation

Figure 6.1 presents the change in pH for the limed and unlimed soils upon incubation. In both the unlimed treatments there was a 0.3 to 0.4 pH unit decrease over the incubation period indicating that the processes driving the acidification of the soils (organic matter mineralization, nitrification) had not stabilised yet. In the limed treatments this trend was not as pronounced with an overall slight decrease over the incubation period.

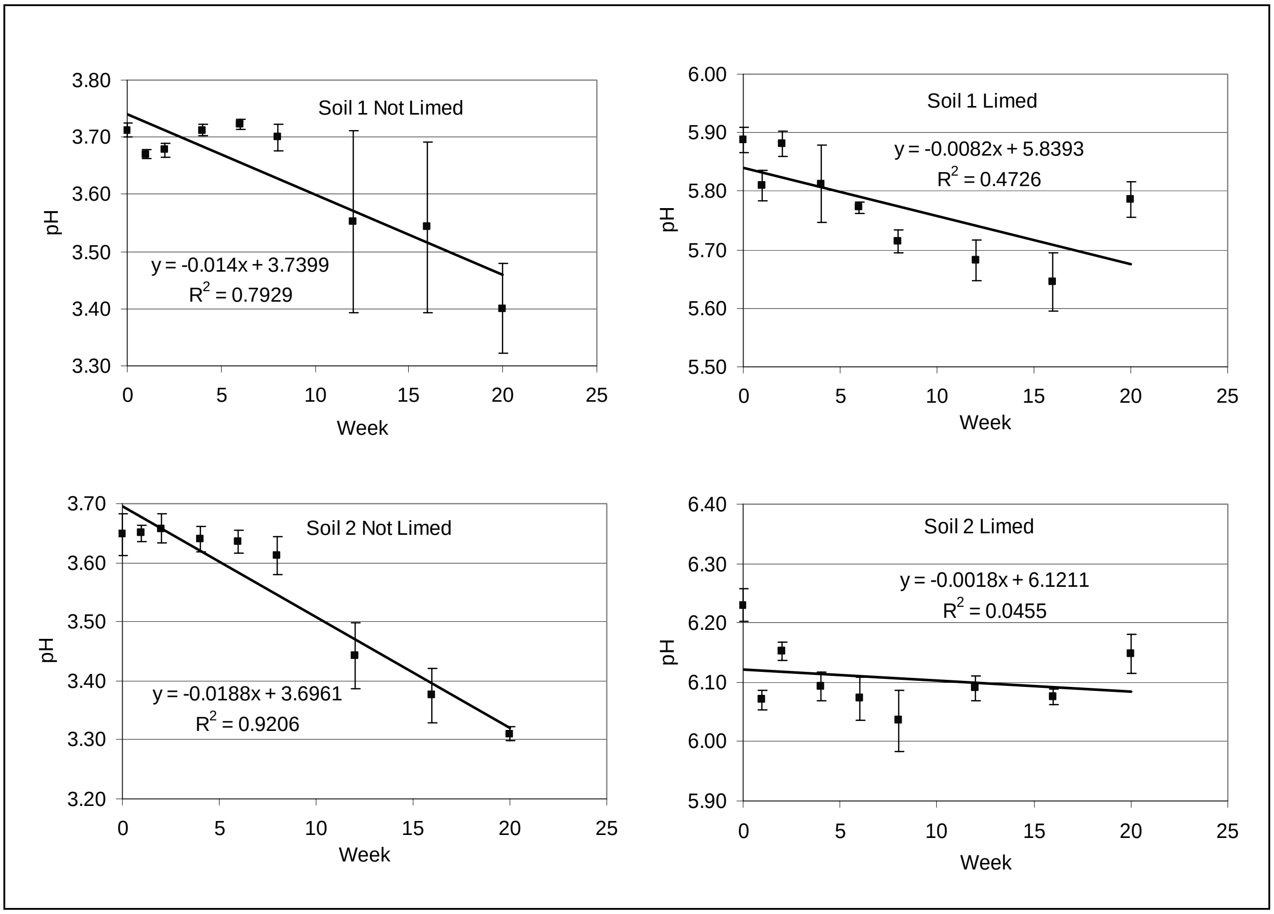

Figure 6.1. Change in pH ($CaCl_2$) over the 20 weeks incubation period for the limed and unlimed treatments. Vertical bars indicate + and – standard deviation.

6.4.2 NH_4NO_3 Extractable Metals

The NH_4NO_3 extractability of Al and Mn (Figure 6.2a), Cd and Zn (Figure 6.3a), and Cu and Ni (Figure 6.4a) increased slightly over the twenty weeks of incubation in the unlimed treatments – mainly due to a slight decrease in pH. Aluminium exhibited a significant increase in Soil 2 to the end of the incubation period. Aluminium and Mn (Figure 6.2b), Cd and Zn (Figure 6.3b), and Cu and Ni (Figure 6.4b) also exhibited a very good correlation with pH, with the trend line in Soil 2 having a steeper slope than the trend line in Soil 1 for most of these metals. The pH trend was very pronounced in Soil 2 (higher clay content than Soil 1) for Cd, Cu, and Zn where the R^2 values exceeded 0.8. The R^2 value that approaches 0 for Mn in Soil 1 is considered an artefact due to the near horizontal trend of the values while the data points had a very good linear fit.

The variability in the Cr and Pb values for both the limed and unlimed treatments in Soil 1 was very high (Figure 6.5a). This trend is not repeated in Soil 2 however. It is postulated that the higher clay content of Soil 2 influenced the extractability of the metals and led to a more clearly defined difference between the limed and unlimed treatments. The presence of more clay in Soil 2 than Soil 1 led to a larger stable surface area for adsorption during the increase in pH after liming, whereas the liming had little influence on the stability of Cr and Pb organic complexes in both soils. Both metals exhibited a clear higher extractability with decreasing pH in the unlimed Soil 2 treatments (Figure 6.5b) whereas the Soil 1 values had the opposite trend.

The extractability of Fe in the unlimed treatments (Figure 6.6a) was variable with a peak at 16 weeks of incubation and a poor correlation with pH in both soils (Figure 6.6b). If the Week 16 values were to be removed the data would indicate a slight decrease over the incubation period. The anomalous Week 16 values are ascribed to a humid climatic spell that could have influenced the water's rate of evaporation during the drying cycle. The Fe extractability probably influenced that of Cr and Pb in that the same trend is evident in the Cr and Pb values.

In most of the lime treated samples there was a very significant decrease in extractability compared to the unlimed treatments. It is also clear that the lime had an immediate effect on the pH of the soils in that the metal extractability decreased already from Week 0. The variability in the limed treatments was significantly lower than the unlimed treatments, except for Cr and Pb in Soil 1. This could be ascribed to the coarser nature of Soil 1 and the difficulty in obtaining a homogenous sample. There wasn't a significant correlation between the metal extractability and pH in the limed samples, with all R^2 values approaching 0 (a function of the slope approaching 0). The limed and unlimed values for Cr and Pb were very variable though for Soil 1 and are, as discussed earlier, attributed to the low clay content of the soil and the low extractability of the metals. All the other metals (except Ni) exhibited a larger decrease in Soil 2 than Soil 1 and this is also attributed to the higher clay content of Soil 2.

6.4.3 NH_4EDTA Extractable Metals

The EDTA extractability of Al and Fe (Fig. 6.7), Cd, Cr and Cu (Fig. 6.8), and Pb (Fig. 6.9) increased with liming and is consistent with the data reported by Van der Waals et al. (2005). Again the Cr values were very variable in Soil 1. The extractability of Mn increased in Soil 2 (Fig. 6.7) and that of Ni and Zn in Soil 1 (Fig. 6.9). Although the increases appear relatively small, they are significant in most cases. There wasn't a correlation between the pH of the soil samples and the EDTA extractability of the metals and the data will therefore not be presented here. The increased extraction of metals after liming in this trial is due to the increased extractability of organic matter as reported in Chapter 5.

6.5 Conclusions and Recommendations

The pH dependence of metal extraction is a well-known phenomenon – especially for neutral salt extractants. From the NH_4NO_3 data it is clear that liming had a significant influence on the extractability of most of the tested metals. Whereas the unlimed soils exhibited a systematic increase in extractability over the incubation period (in most cases linked to a decrease in pH), the limed soils exhibited no clear increases. This indicates that the liming of these soils would decrease the extractability of most metals and that this extractability will remain low after repeated wetting and drying cycles – such as field conditions.

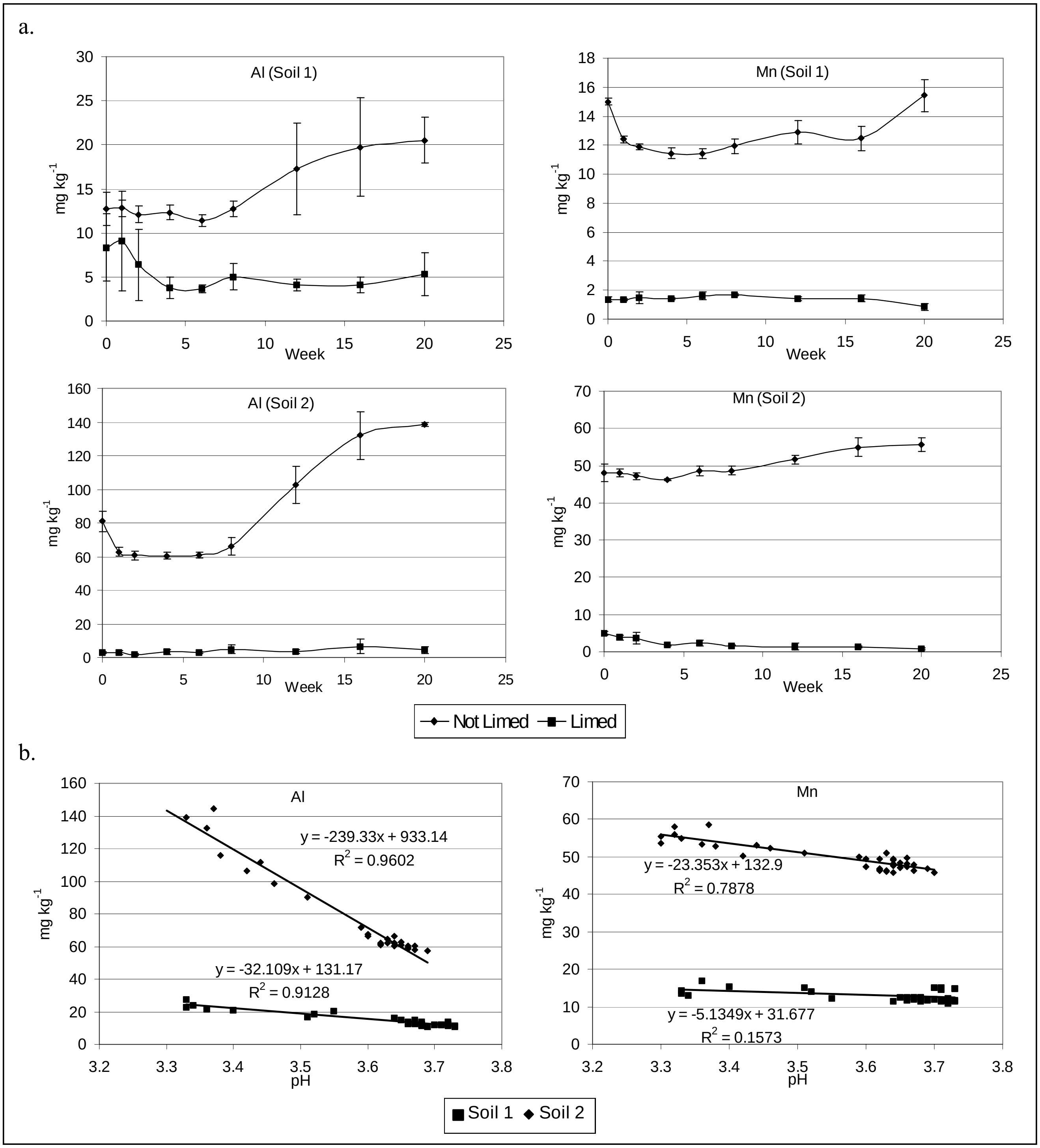

Figure 6.2. Aluminium and manganese levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

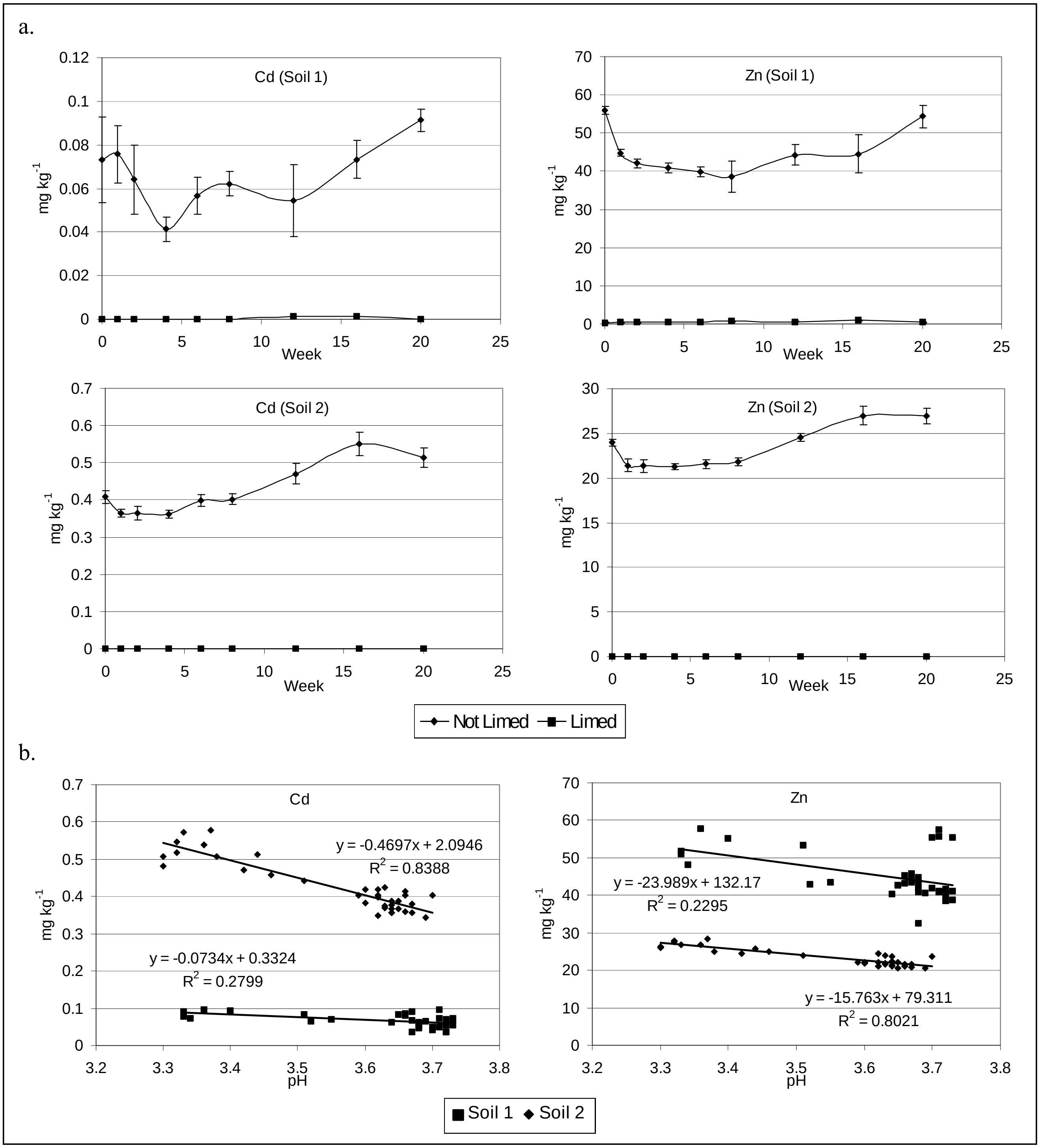

Figure 6.3. Cadmium and zinc levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

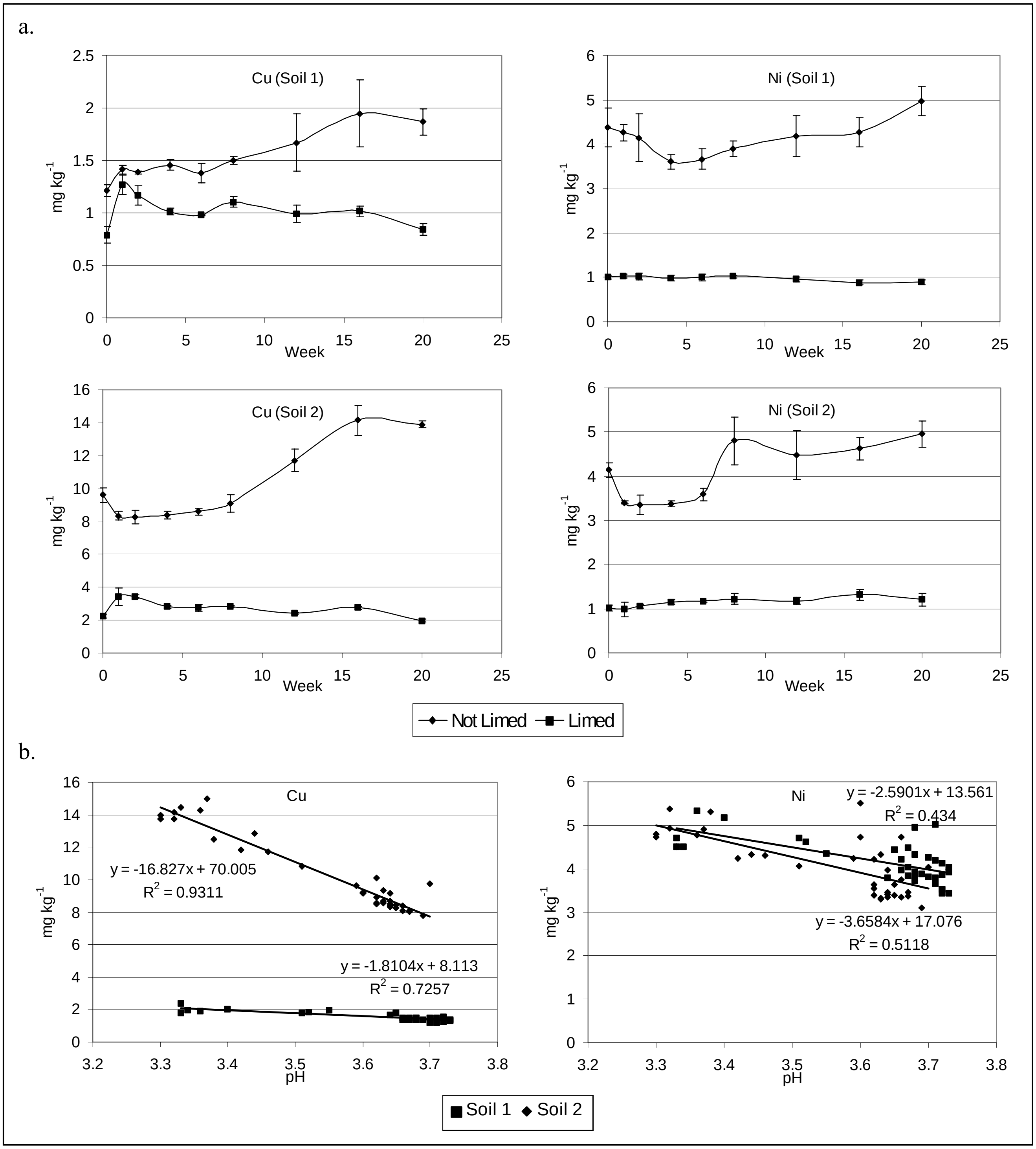

Figure 6.4. Copper and nickel levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

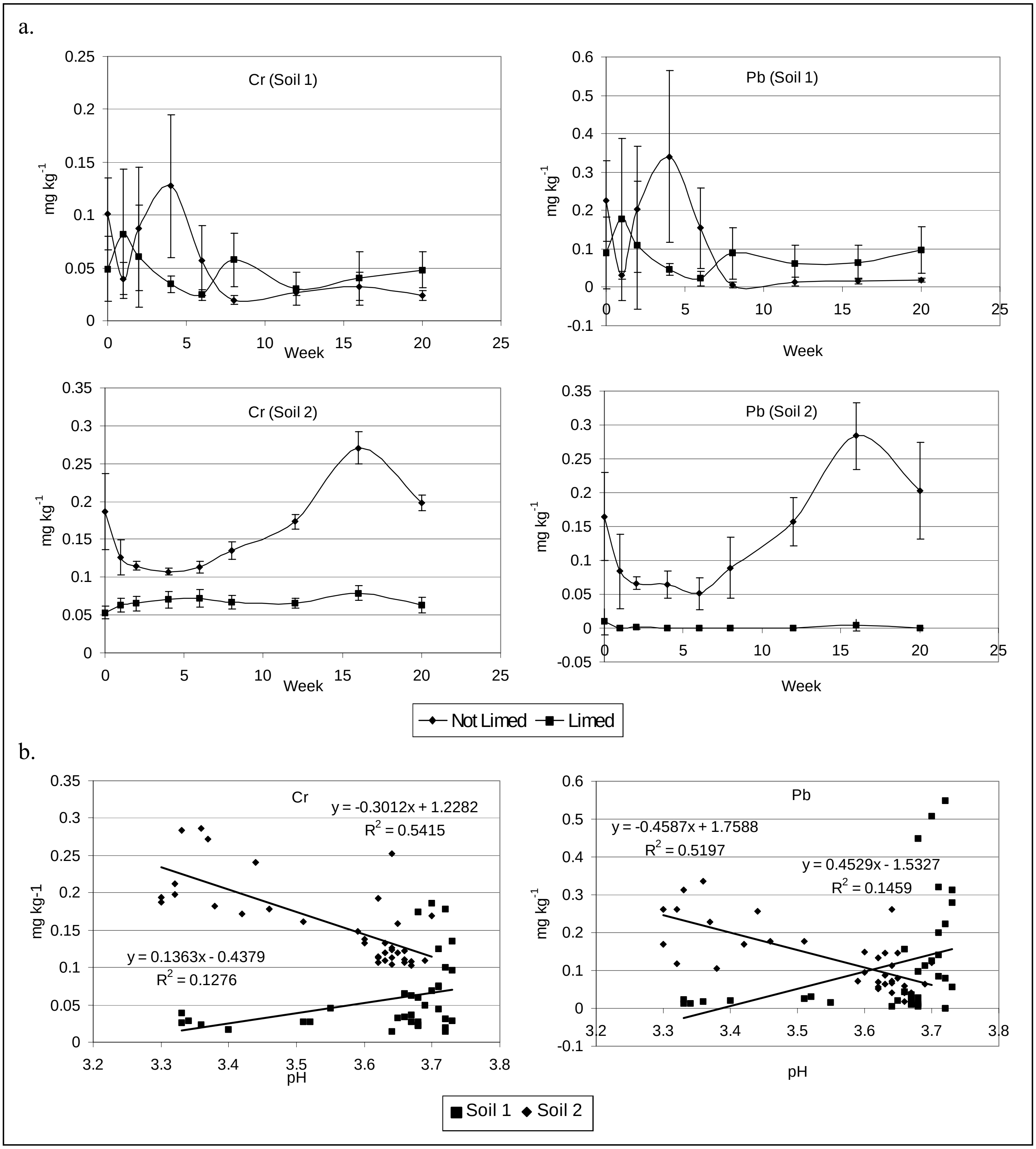

Figure 6.5. Chromium and lead (NH_4NO_3) levels for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

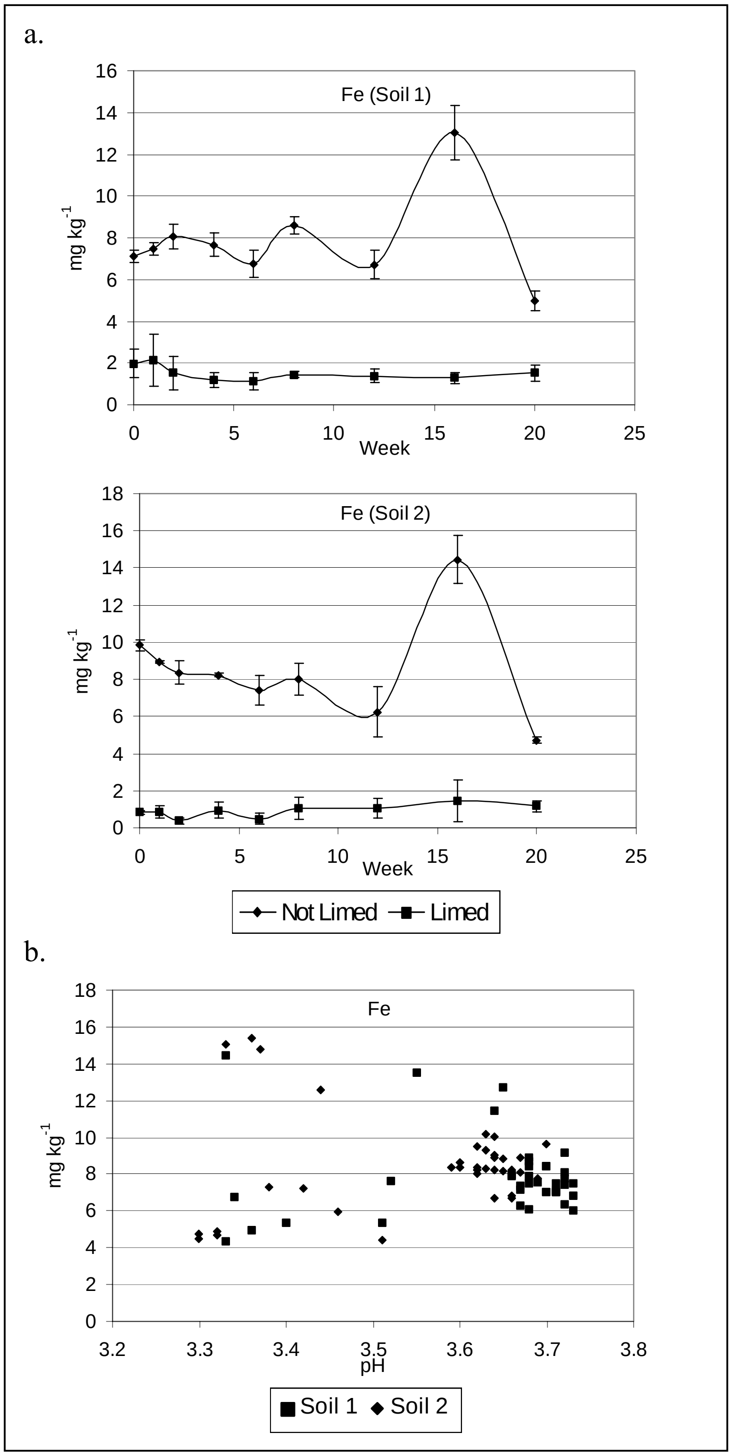

Figure 6.6. Iron levels (NH_4NO_3) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ($CaCl_2$) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.

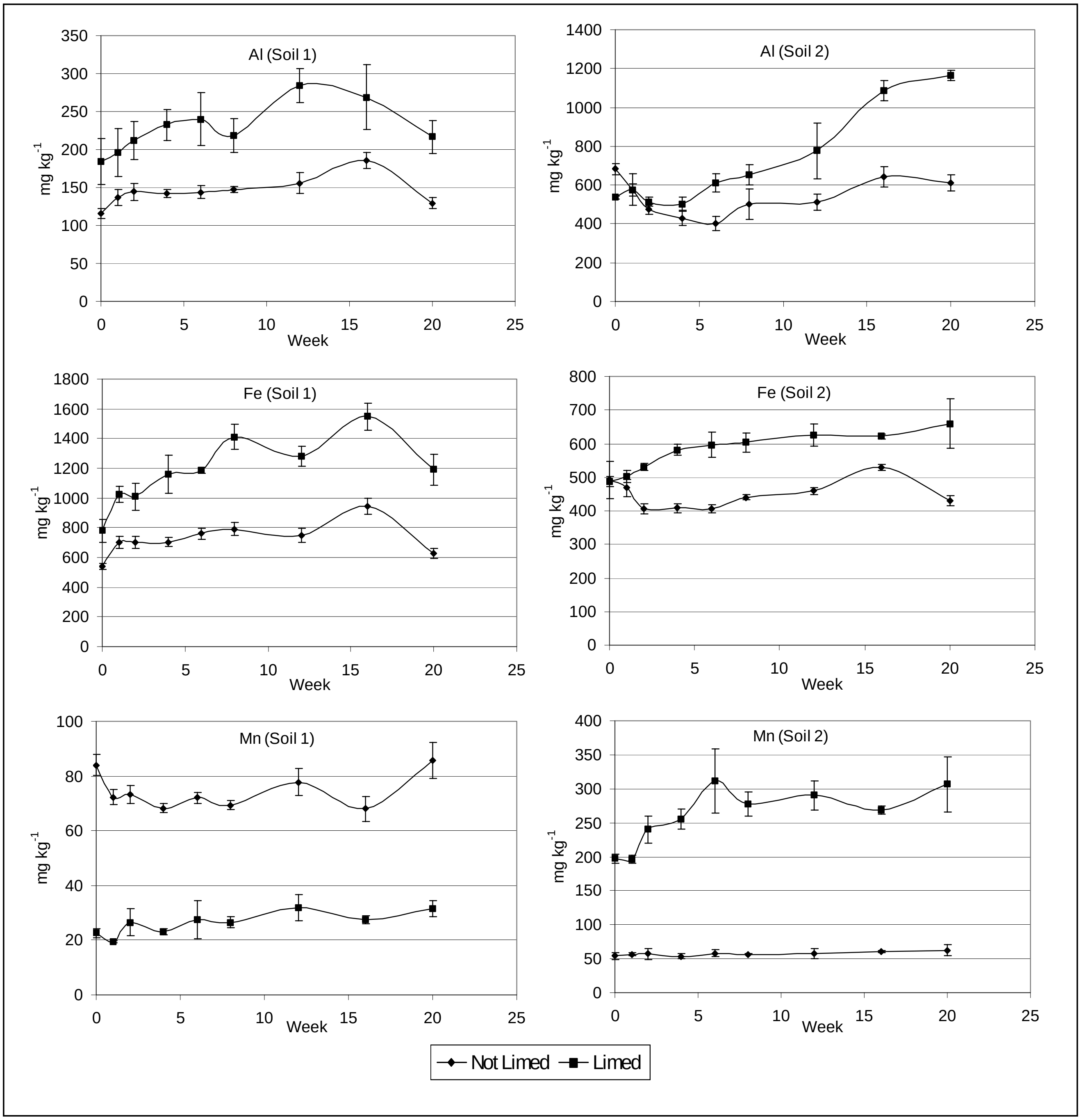

Figure 6.7. The EDTA extractability of Al, Fe, and Mn from two soils with and without liming over a 20-week incubation period. Vertical bars indicate + and – standard deviation.

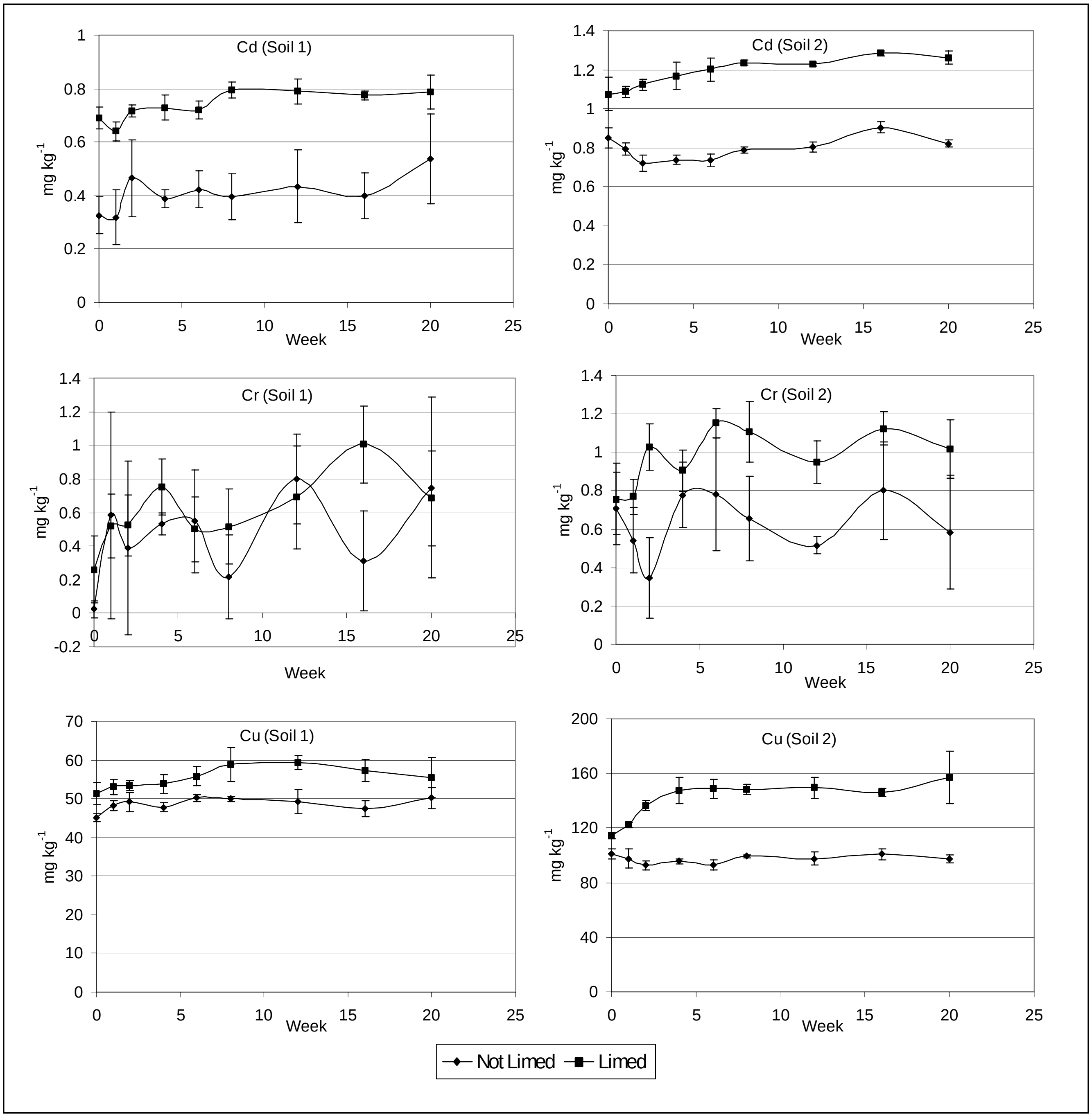

Figure 6.8. The EDTA extractability of Cd, Cr, and Cu from two soils with and without liming over a 20-week incubation period. Vertical bars indicate + and – standard deviation.

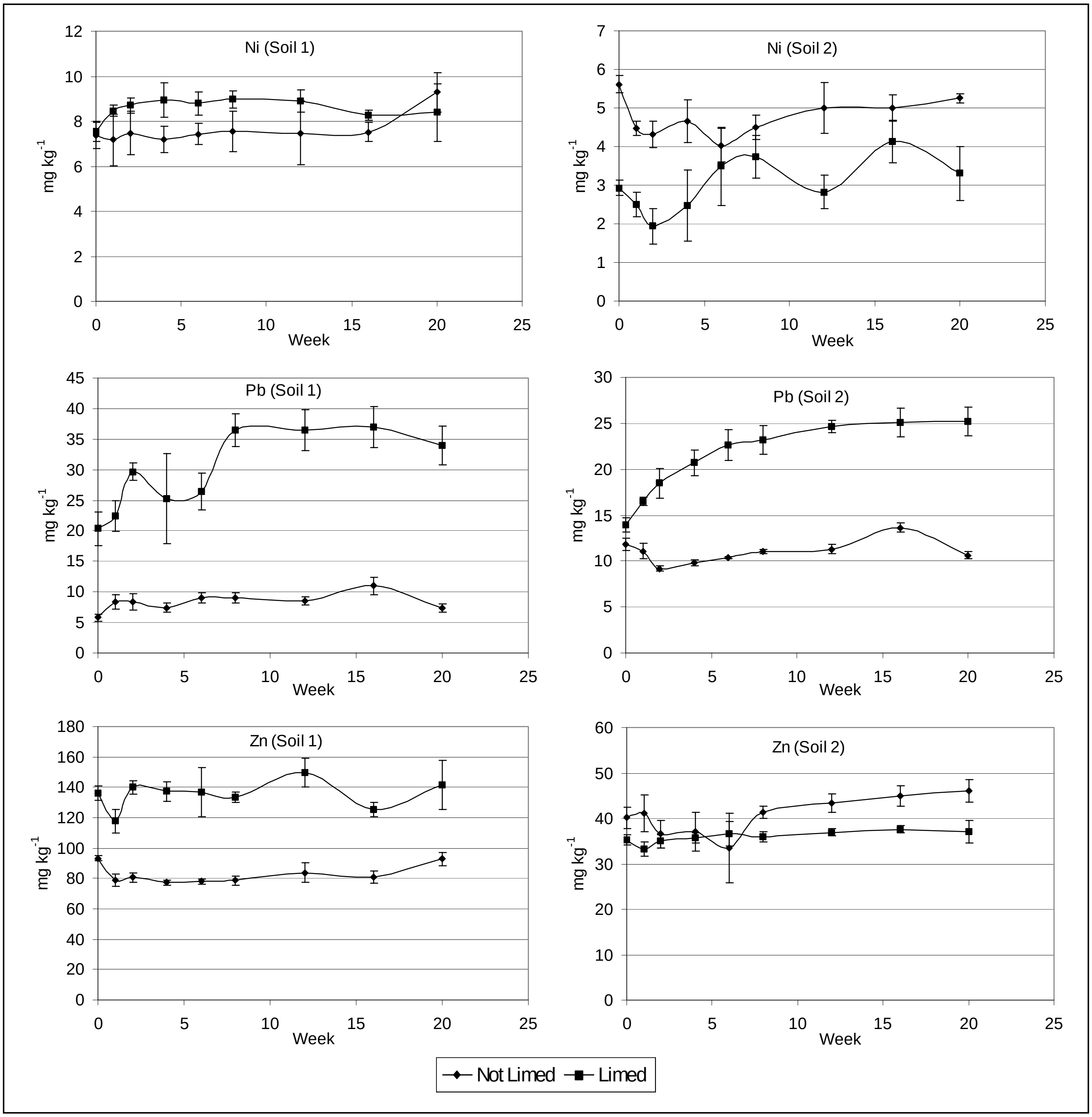

Figure 6.9. The EDTA extractability of Ni, Pb, and Zn from two soils with and without liming over a 20-week incubation period. Vertical bars indicate + and – standard deviation.

The lime reacted immediately after application and the increased EDTA extractability was observed just as rapidly. If decomposition of organic material had played a role in metal release, a slower increase in metal extractability would have been expected. As discussed earlier, significant organic material degradation was not expected due to the "age" and stability of the biosolids derived organic material.

The extracting agent EDTA is often used in heavy metal studies to determine the "potential plant-available" metal levels in soils. The motivation for its use is the correlation that is sometimes found between plant metal levels and extractable soil metal levels (Hooda et al., 1997). In the light of the increased EDTA extractability of certain metals from the two sacrificial soils after liming in this trial it might sound wise to discourage liming as a rehabilitation strategy for such soils. The NH_4NO_3 data, though, point to a very significant decrease in metal extractability after liming. The fraction extracted by the NH_4NO_3 is the immediately exchangeable fraction and therefore also the immediately plant-available fraction. In the light of these results liming can be strongly recommended as a rehabilitation strategy to decrease the immediate plant-availability as well as leachability of metals in these soils. The number of studies that have found a correlation between EDTA extractable metals and plant-uptake prompt the need for further trials to determine plant-uptake from the sacrificial soils after liming.

The incubation of the soil over 20 weeks indicates that unlimed soils have the potential to further acidify and that the metals could become more exchangeable. After liming the metals did not show an increase in NH_4NO_3 extractability over the incubation period indicating that this fraction is not likely to increase in the short-term. This aspect serves as a further motivation for the liming of sacrificial soils.

CHAPTER 7

Heavy Metal Uptake by Wheat from Two Sacrificial Biosolids Disposal Soils at Differential Liming Rates

7.1 Abstract

In previous studies it has been shown that intensive liming of sacrificial biosolids disposal soils leads to an increase in many EDTA extractable metals. This aspect is a cause for concern in that many studies have indicated that plant metal levels could be correlated with EDTA extractable metal levels in soil. To determine the influence of intensive liming of sacrificial soils on plant metal content a dedicated trial was conducted. A new bulk sample of the two soils used in the previous studies was collected and incubated with $CaCO_3$ (AR) in pots at lime application rates equivalent to 0, 12, 24, and 36 tons ha^{-1}. Spinach and wheat were planted and harvested before flowering. The spinach plants did not grow in the 0 lime application treatment and grew poorly in the lime treatments and the wheat plants were therefore the only ones analysed for their metal content. The soils from the pots were sampled and analysed for NH_4NO_3 and NH_4EDTA extractable metals. The NH_4NO_3 extractable metals decreased with increasing lime rate whereas the NH_4EDTA extractable metals generally increased, especially in the one soil. Plant metal levels were better correlated with NH_4NO_3 than with NH_4EDTA metal levels. This indicates that liming leads to a decreased risk of plant metal uptake from sacrificial soils and that it should be introduced into the management of these soils. The use of EDTA in guideline metal levels as well as to determine "potentially plant available" metals is discouraged.

7.2 Introduction

In previous chapters it has been shown that intensive liming influenced the extractability of metals in two sacrificial biosolids disposal soils. The NH_4NO_3 extractable fraction decreased after liming during incubation as expected. However, the EDTA extractable metal fraction increased after intensive liming as well as with increasing lime rates of two sacrificial biosolids disposal soils during incubation. The increased extractability was correlated with an increase in extractability of organic matter at increasing lime rates.

This increase leads to concern regarding the desirability of liming of acid sacrificial soils, especially in the light of a number of studies that have reported a correlation between EDTA extractable metals in soils and plant metal content. In this regard Hooda et al. (1997) and Cajuste and Laird (2000) have indicated that EDTA is a reliable test for predicting plant-available metals. Earlier Bruemmer and Van der Merwe (1989) stated that the NH_4-EDTA-extractable heavy metal concentration gives a good estimate of those potentially plant-available, and even suggested it to be used in the establishment of preliminary threshold values for heavy metals in South African soils. Weaker extractants such as neutral salts extract exchangeable metals (Beckett, 1989; McLaughlin et al., 2000) and is considered to give a good indication of the immediately bioavailable fraction (LeClaire et al., 1984; Mullins et al., 1986).

In light of the above the question arose regarding the plant availability of the metals in the soils after intensive liming. It was therefore decided to conduct a dedicated trial to determine the extent of plant metal uptake from the two sacrificial soils at four increasing lime application rates.

7.3 Materials and Methods

For this trial a new bulk sample of 300 kg per soil was collected. The sample of Soil 1 was collected in the same area as the bulk sample for the previous trials. The Soil 2 sample had to be collected from within the vicinity due to a fresh application of biosolids on the original site. The alternative site was the driest that could be found but still had visible undecomposed or decomposing biosolids mixed into it. The bulk samples were dried, sieved and weighed off into 4 kg nursery pots. For each pot the specified amount of AR $CaCO_3$ for an equivalent lime application rate of 0, 12, 24, and 36 ton ha^{-1} was weighed and thoroughly mixed with the soil. Each treatment was replicated four times. Deionised water was added to the pots and the soils were left to dry to the atmosphere. After drying, the soil of each pot was mixed again to ensure an even distribution of limed soil and it was watered again afterwards. This was deemed necessary due to previous incomplete mixing as well as possible precipitation of Ca-salts at the surface of the soil upon drying.

Four wheat and four spinach seeds were planted per pot and the soils kept moist during the growing season to ensure adequate growth. Spinach was chosen as test crop due to its known ability to accumulate metals to higher levels than many other crops (also reported by Hooda et al., 1997). The wheat cultivar (Tugela DN) is known for its Al and acid tolerance and was included to be certain of harvestable plant material at the zero lime application rate. The plants were harvested before the flowering stage (approximately 2 months of growth) and dried at 65 ºC for 48 hours. The dry matter was milled and analysed for heavy metals through the dry ashing procedure described by Soon (1998). Copper, Fe, Mn and Zn were determined in the digest solutions through AAS and Cd, Cr, Ni, and Pb determined by ICP-MS.

After harvesting the pots were left to dry to the atmosphere and afterwards a representative soil sample was collected from each pot. The pH ($CaCl_2$) and NH_4NO_3 and NH_4EDTA extractable metals were determined according to the same methods as described in Chapter 6. Due to the set-up of the trial the calculation of standard deviation and regression analysis of the data was considered to be adequate statistical analysis.

7.4 Results and Discussion

7.4.1 Soil pH and Dry Matter Yield

The pH results of the four liming rates in the two soils are presented in Table 7.1. The results for Soil 1 compare favourably with those reported in Chapter 5 but those for Soil 2 do not. It is postulated that the reason for the difference is the decomposing organic matter in the bulk sample from Soil 2 and that this could indicate more recent biosolids additions than for the sample used previously. The higher pH value for the zero lime rate confirms this postulation as it is expected that fresh anaerobically digested material will have a pH in excess of 7 and that the pH will decline after prolonged exposure to the atmosphere due to mineralization, nitrification and leaching of N.

Table 7.1. The pH ($CaCl_2$) of the two soils at four liming rates (n = 4; values in brackets denote the standard deviation)

Soil	Lime application rate (ton ha^{-1})			
	0	12	24	36
1	4.06 (0.02)	4.40 (0.02)	5.42 (0.04)	5.91 (0.01)
2	4.73 (0.04)	5.24 (0.03)	5.71 (0.03)	5.90 (0.03)

The dry matter yield per plant of the spinach and wheat is presented in Figures 7.1 and 7.2 respectively. The yield of the spinach was erratic with no yields at the zero lime application rate due to the low pH in the soils. For this reason the spinach dry matter was not analysed further due to the lack of a zero lime rate "control". The wheat yield was also erratic but the general trend indicated an increase in yield with pH. Growth at the zero lime rate was significantly inhibited compared to the lime treatments.

7.4.2 Wheat Metal Content

The metal content of the wheat plants (Table 7.2) shows a decrease with increasing lime rate. The values for the zero lime rate are often significantly higher than those of the different lime rates and could be due to a concentration effect related to the low yield at the low pH treatments. This effect is often more pronounced in Soil 2 and lead to R^2 values that are generally lower than those of Soil 1. In Soil 1 the increasing lime rates lead to a consistent decrease in plant metal content. In Soil 2, though, the 36 ton ha^{-1} lime rate exhibited an increase in plant metal content compared to the 24 ton ha^{-1} rate for Cd, Cr, Fe, Ni, and Pb, albeit not significantly in most cases.

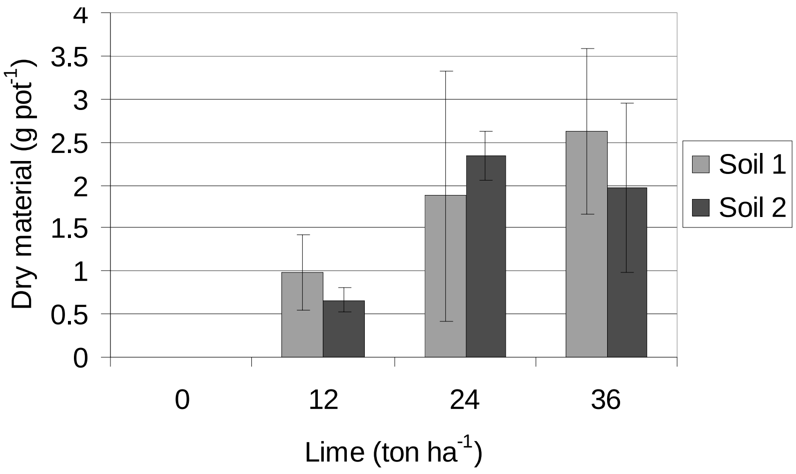

Figure 7.1. Spinach dry matter yield per pot (vertical bars indicate the standard deviation).

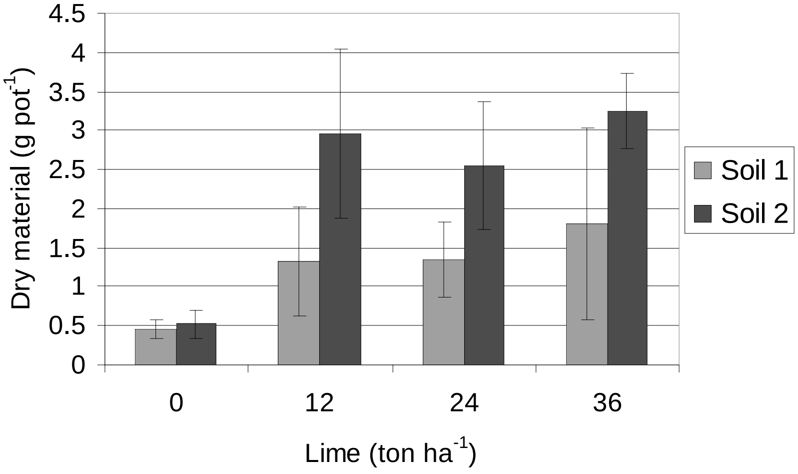

Figure 7.2. Wheat dry matter yield per pot (vertical bars indicate the standard deviation).

Table 7.2. Plant metal content (mg kg^{-1} wheat dry matter) and regression equations for the lime treatments and soils

Metal	Soil	Lime rate (ton ha^{-1})				Regression Equation (plant metal content vs. lime rate	R^2 Value
		0	12	24	36		
Cd	1	1.31 (0.14)	1.07 (0.32)	0.49 (0.12)	0.46 (0.21)	y = -0.3132x + 1.6172	0.91
	2	3.19 (0.90)	0.94 (0.43)	0.91 (0.11)	0.92 (0.10)	y = -0.6844x + 3.2017	0.61
Cr	1	23.1 (2.3)	5.45 (0.59)	5.37 (1.47)	3.22 (0.96)	y = -5.972x + 24.216	0.69
	2	6.65 (0.97)	1.76 (1.20)	0.86 (0.36)	1.01 (0.31)	y = -1.7847x + 7.032	0.70
Cu	1	71.2 (20.6)	49.6 (23.7)	34.6 (7.2)	28.4 (7.1)	y = -14.326x + 81.756	0.94
	2	72.9 (55.9)	49.8 (14.0)	47.7 (13.1)	46.2 (7.7)	y = -8.2197x + 74.696	0.71
Fe	1	218 (61)	200 (82)	148 (78)	138 (69)	y = -29.449x + 249.55	0.93
	2	293 (52)	162 (24)	125 (28)	149 (23)	y = -47.017x + 299.76	0.65
Mn	1	65.5 (12.4)	51.0 (3.6)	39.7 (8.7)	30.6 (6.9)	y = -11.611x + 75.717	0.99
	2	243 (27)	37.9 (10.0)	24.8 (18.6)	17.7 (2.7)	y = -68.971x + 253.31	0.67
Ni	1	7.54 (1.49)	5.91 (1.37)	6.03 (0.65)	3.40 (0.91)	y = -1.2298x + 8.7956	0.86
	2	67.7 (20.0)	13.4 (6.0)	7.55 (4.17)	12.2 (3.7)	y = -17.245x + 68.346	0.61
Pb	1	3.35 (0.99)	2.47 (0.60)	2.86 (0.55)	0.99 (0.30)	y = -0.6699x + 4.0907	0.72
	2	6.75 (2.26)	3.12 (1.70)	1.29 (0.86)	2.64 (0.63)	y = -1.4148x + 6.9893	0.61
Zn	1	171 (27)	103 (13)	55.6 (12.1)	45.0 (9.8)	y = -42.368x + 199.39	0.92
	2	400 (19)	170 (11)	112 (14)	99.0 (11.7)	y = -96.272x + 436.12	0.79

7.4.3 Soil Metal Levels

The NH_4NO_3 and NH_4EDTA extractable metal levels for the two soils are presented in Tables 7.3 and 7.4 respectively. Included in the tables are the regression equations and R^2 values obtained from graphs of the metal extraction values versus soil pH. With the NH_4NO_3 extraction most of the metals decreased significantly in extractability (except Cr and Pb in both soils, Cu in Soil 1, and Fe in Soil 2) with increasing lime rate. The non-significant decrease in Cr and Pb extractability is due to a high variability in the data as was the case in Chapters 5 and 6. In most cases the decrease in extractability was more pronounced in Soil 2 than Soil 1 with steeper slopes of the regression equations and could be the result of Soil 2 originally containing more undecomposed material than Soil 1. Upon liming the material would have undergone accelerated decomposition with a consequent large influence of the lime on metal extractability.

Table 7.3. NH_4NO_3 extractable metal levels and regression equations for the two soils (mg kg^{-1}, n = 4, the values in brackets denote the standard deviation)

Metal	Soil	Lime rate (ton ha^{-1})				Regression Equation ([Metal] vs. pH)	R^2 Value
		0	12	24	36		
Cd	1	0.87 (0.05)	0.53 (0.06)	0.22 (0.04)	0.16 (0.07)	y = -0.3584x + 2.2179	0.88
	2	1.91 (0.23)	0.93 (0.10)	0.42 (0.10)	0.37 (0.04)	y = -1.3249x + 8.0573	0.92
Cr	1	0.15 (0.02)	0.13 (0.08)	0.10 (0.05)	0.14 (0.08)	y = -0.011x + 0.1841	0.02
	2	0.30 (0.08)	0.20 (0.06)	0.18 (0.03)	0.20 (0.08)	y = -0.0815x + 0.6583	0.25
Cu	1	0.81 (0.16)	0.62 (0.06)	0.71 (0.04)	0.74 (0.10)	y = -0.0046x + 0.7396	0.001
	2	2.93 (0.09)	2.57 (0.14)	2.48 (0.06)	2.46 (0.11)	y = -0.3921x + 4.7268	0.72
Fe	1	4.53 (0.48)	3.08 (0.41)	2.65 (0.79)	2.08 (0.41)	y = -1.0995x + 8.5234	0.65
	2	0.77 (0.47)	0.85 (0.12)	1.09 (0.50)	1.17 (0.24)	y = 0.3573x - 0.9573	0.21
Mn	1	2.81 (0.09)	2.11 (0.06)	0.73 (0.05)	0.17 (0.07)	y = -1.4027x + 8.3925	0.99
	2	32.3 (5.4)	10.4 (0.6)	3.56 (0.36)	2.80 (0.64)	y = -25.002x + 147.16	0.87
Ni	1	1.17 (0.08)	0.68 (0.05)	0.51 (0.09)	0.32 (0.04)	y = -0.3854x + 2.5759	0.81
	2	18.8 (2.2)	9.6 (0.4)	4.6 (0.4)	4.0 (0.3)	y = -12.763x + 78.114	0.93
Pb	1	0.23 (0.17)	0.15 (0.12)	0.08 (0.03)	0.09 (0.06)	y = -0.0736x + 0.4999	0.24
	2	0.09 (0.08)	0	0	0	y = -0.07x + 0.3988	0.38
Zn	1	13.7 (0.3)	6.86 (0.22)	1.12 (0.31)	0.13 (0.05)	y = -6.8326x + 39.261	0.89
	2	15.8 (2.58)	8.67 (0.42)	1.21 (0.35)	0.82 (0.21)	y = -13.362x + 78.704	0.95

The EDTA extractable Cd, Cu, Fe, Mn, Pb, and Zn in Soil 1 increased significantly in most cases whereas Cu, Fe, and Pb increased non-significantly in Soil 2 after liming. The extractability of Ni was opposite between the soils but the trends were non-significant for both as was the case for the previous trials reported in Chapters 5 and 6. As reported in these chapters the variability in Cr levels was too large to determine any significant trends. The overall trend was reversed in Soil 2 with a limited decrease in extractability of Cd and Mn and a non-significant decrease in Zn. The reversed trend in the Soil 2 EDTA extractable metal levels could possibly be ascribed to the same factors that lead to the somewhat unexpected pH results. It would appear that the undecomposed biosolids acted differently to material that had undergone changes in the soils after prolonged exposure to the climatic and atmospheric factors.

Table 7.4. NH_4EDTA extractable metal levels and regression equations for the two soils (mg kg^{-1}, n = 4, the values in brackets denote the standard deviation)

Metal	Soil	Lime rate (ton ha^{-1})				Regression Equation ([Metal] vs. pH)	R^2 Value
		0	12	24	36		
Cd	1	0.46 (0.03)	0.61 (0.06)	0.72 (0.04)	0.72 (0.04)	y = 0.1329x - 0.031	0.73
	2	5.23 (0.23)	5.00 (0.14)	4.84 (0.14)	4.63 (0.17)	y = -0.4669x + 7.445	0.65
Cr	1	0.21 (0.19)	0.19 (0.09)	0.20 (0.15)	0.22 (0.13)	y = 0.0086x + 0.1641	0.003
	2	1.04 (0.25)	0.76 (0.07)	0.80 (0.09)	0.64 (0.14)	y = -0.2866x + 2.3553	0.43
Cu	1	23.4 (1.0)	27.3 (2.9)	31.7 (2.0)	32.7 (1.7)	y = 4.742x + 5.3206	0.76
	2	306 (11)	317 (9)	325 (7)	318 (14)	y = 11.721x + 253.29	0.23
Fe	1	147 (25)	208 (32)	304 (15)	359 (33)	y = 109.31x - 286.3	0.91
	2	592 (35)	635 (18)	668 (68)	606 (48)	y = 29.493x + 466.1	0.07
Mn	1	3.79 (0.17)	3.72 (0.35)	4.27 (0.23)	4.32 (0.21)	y = 0.3448x + 2.3197	0.55
	2	316 (12)	313 (13)	297 (5)	282 (12)	y = -28.07x + 453.47	0.59
Ni	1	2.97 (0.71)	4.24 (0.36)	4.52 (0.50)	3.95 (0.65)	y = 0.4479x + 1.7055	0.19
	2	57.1 (3.2)	57.5 (9.0)	47.1 (1.7)	53.2 (4.5)	y = -6.0736x + 86.468	0.20
Pb	1	4.92 (0.69)	7.06 (0.84)	11.6 (0.8)	12.8 (0.3)	y = 4.267x - 12.006	0.95
	2	107 (11)	115 (14)	113 (9)	123 (8)	y = 10.241x + 59.316	0.18
Zn	1	32.4 (1.2)	34.8 (3.5)	42.2 (3.0)	46.9 (3.0)	y = 7.6558x + 1.2286	0.84
	2	380 (13)	371 (7)	373 (7)	368 (19)	y = -8.3823x + 418.18	0.11

7.4.4 Correlation Between Plant and Soil Metal Levels

The plant-uptake metal levels correlated with the NH_4NO_3 and NH_4EDTA extraction values are presented in Table 7.5. From the R^2 values it is clear that the NH_4NO_3 extraction data correlated better with the plant metal levels than the NH_4EDTA data for all the metals except Cu, Fe, and Pb where both extractants performed equally poor. For all the metals except Fe in Soil 2 there was a direct relationship between the amounts taken up by the plants and the amounts extracted from the soil with NH_4NO_3. This was not the case for NH_4EDTA where there was an inverse relationship (indicating a very poor correlation) between the plant content and that extracted from the soil. This inverse relationship diminishes the fear concerning the increased extractability of metals with EDTA at increasing lime rates.

Table 7.5. Regression equations of plant metal content (mg kg^{-1} dry matter) versus NH_4NO_3 and NH_4EDTA extractable metal levels (mg kg^{-1} soil) respectively

Metal	Soil	NH_4NO_3 extractable metals		NH_4EDTA extractable metals	
		Regression Equation (plant vs. soil metal content)	R^2 Value	Regression Equation (plant vs. soil metal content)	R^2 Value
Cd	1	y = 1.2645x + 0.2715	0.77	y = -2.705x + 2.5285	0.58
	2	y = 1.3642x + 0.2443	0.68	y = 1.9215x - 7.9807	0.24
Cr	1	y = 28.769x + 5.5477	0.04	y = 3.6672x + 8.5275	0.003
	2	y = 20.638x - 1.9775	0.41	y = 7.2404x - 3.3301	0.35
Cu	1	y = 72.572x - 6.0811	0.14	y = -3.4446x + 145.07	0.42
	2	y = 24.618x - 10.944	0.05	y = -1.2063x + 435.18	0.32
Fe	1	y = 27.418x + 91.356	0.15	y = -0.2683x + 244.19	0.10
	2	y = -52.509x + 231.74	0.07	y = -0.5173x + 504.21	0.14
Mn	1	y = 12.291x + 28.827	0.75	y = -20.255x + 128.22	0.22
	2	y = 7.2817x - 8.7041	0.88	y = 3.0583x – 843	0.29
Ni	1	y = 3.67x + 3.2637	0.43	y = -0.9261x + 9.3525	0.16
	2	y = 3.6695x - 8.9181	0.74	y = 1.3697x - 48.49	0.11
Pb	1	y = 4.6099x + 1.789	0.25	y = -0.1902x + 4.147	0.35
	2	y = 29.584x + 2.8702	0.40	y = -0.1195x + 17.188	0.29
Zn	1	y = 9.0652x + 43.964	0.91	y = -6.6132x + 352.05	0.64
	2	y = 18.045x + 76.062	0.85	y = 3.4358x – 1086	0.11

7.5 Conclusions and Recommendations

From the data it is clear that liming at increasing rates decreased the NH_4NO_3 extractable metals but lead to an increase in many of the NH_4EDTA extractable metals, especially in Soil 1. The data confirms the data generated through separate studies that have been reported in Chapters 5 and 6.

The increasing lime rates generally lead to a decrease in the metal content of wheat plants grown in the soils. The plant metal data was better correlated with the NH_4NO_3 extractable metal levels than those of NH_4EDTA as is reflected in the slopes and R^2 values of the regression equations.

The fact that the plant metal content was better correlated with the NH_4NO_3 extractable metals and that both of these sets of data indicated a decrease with increasing lime rate indicates a decreased risk of metal mobilisation through liming. The first implication of the data is that sacrificial soils can be limed to increase pH levels and thereby decrease threats posed by the metals to the environment.

The second implication of the data is that the widely held notion that EDTA is a good predictor of plant metal availability is not valid for sacrificial soils. The setting of guideline EDTA extractable metal levels is therefore discouraged unless it involves extensive testing in different soils under a wide range of conditions and the linking of these conditions to the guideline levels. EDTA extract values are imperical and are restricted in the sense that it is influenced by factors other than those determining metal plant availability. The use of NH_4NO_3, on the other hand, is encouraged due its better correlation with plant metal content.

CHAPTER 8

Concluding Remarks and Recommendations

The lack of management of sacrificial soils (especially pH management) is a source of grave concern. The potential risk include metal leaching into groundwater, removal of metals by plants that are in turn consumed by animals or humans, distribution of metals through wind blown particles to neighbouring fields and human settlements, as well as leaching of acid water percolating through the soils into groundwater. The last aspect mentioned here could cause the accelerated formation of sinkholes in underlying dolomite and is a very real threat in the case of Soil 2.

The most obvious pH management approach is the addition of lime to the acidified soils. The increased NH_4EDTA extractability of metals from sacrificial soils due to intensive liming as reported by Van der Waals et al. (2005) lead to concerns regarding the rehabilitation and management of these soils. The results also lead to a number of questions regarding the cause of the increased extractability and the implications thereof on the proposed management of sacrificial soils.

Several trials were conducted to quantify the increased extractability as well as to determine the influence of liming application rate and incubation of the soil with lime on metal extractability and plant metal availability. The following conclusions were reached from the different trials:

1. The addition of lime at increasing rates to sacrificial soils to increase the pH to acceptable levels leads to increased NH_4EDTA extractable metals but decreased NH_4NO_3 metal levels.
2. The increased extractability of metals with NH_4EDTA is ascribed to the ability of EDTA to extract organic matter from the soil. This ability seems to be correlated also with increasing soil pH.
3. Incubation of soils with and without lime over a 20-week period with regular wet and dry cycles lead only to a small influence on metal extractability. This was mainly due to a small change in pH over the incubation period. Liming had the same effect on NH_4EDTA extractable metal levels as in two previous trials.

4. Plant metal levels after a pot trial were better correlated with NH_4NO_3 extractable metal levels that with NH_4EDTA metal levels. This indicates that the NH_4NO_3 extractable metal level is a more realistic indication of plant metal availability than NH_4EDTA metal levels.

From the data it can safely be advised that sacrificial soils should be limed to decrease the risk of metal leaching and uptake by plants. The management of future sacrificial (or rehabilitated) sites should as a matter of principle include the regular addition of lime to prevent excessive build-up of acidity.

The use of EDTA as extracting agent in guidelines should be discouraged unless extensive investigations under different conditions have been conducted. These conditions should include a wide range of polluted soils that are enriched with organic matter. The fact that EDTA also extracts organic matter from soils means that factors influencing organic matter extractability will determine metal extraction levels instead on factors controlling the mobility of the metals. Furthermore, EDTA extract values are imperical and are restricted in the sense that it is influenced by factors other than those determining metal plant availability. This is especially so in the case of high organic matter soils where and increase in pH has opposite effects on plant metal uptake and EDTA metal extractability.

It is suggested that NH_4NO_3 be used as extracting agent to determine the risk of plant metal uptake in polluted soils. The fact that it is a neutral salt implies that it also gives an indication of the metal fraction that poses a risk of leaching in soils.

References

Adriano, D. C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York, pp 533.

Albasel, A. & Cottenie, N. 1985. Heavy metals uptake form contaminated soils as affected by peat, lime, and chelates. *Soil Sci. Soc. Amer. J.* **49**: 386-390.

Allen, H.E. & Yin, Y. 1996. The importance of organic matter on the sorption of cadmium and mercury to soil. The 6th International Conference on Preservation of Our World in the Wake of Change, Jerusalem, Israel.

Alloway, B.J. 1995. Heavy Metals in Soils. Blackie Academic and Professional, Glasgow, pp 368.

Aubert, H. & Pinta, M. 1977. Trace elements in soils (Translated from French). Elsevier, Amsterdam, pp 395.

Beckett, P.H.T., 1989. The use of extractants in studies on trace metals in soils, sewage sludges, and sludge treated soils. In Stewart, B.A. (Ed.), Advances in soil science, vol. 9. Springer-Verlag, New York, pp 143-176.

Bibak, A., Gerth, J. & Borggaard, O.K. 1995. Retention of cobalt by an oxisol in relation to the content of iron and manganese oxides. *Commun. Soil Sci. Plant Anal.* **26**(5&6): 785-798.

Biederbeck, V.O. 1978. Soil organic sulfur and fertility. *In* Schnitzer, M. & Khan, S.U., (Eds.), Soil organic matter. Developments in Soil Science Vol. 8. Elsevier Scientific Publishing Company, Amsterdam, pp 273-310.

Bloomfield, C. & Pruden, G. 1975. The effects of aerobic and anaerobic incubation on the extractabilities of heavy metals in digested sewage sludge. *Environ. Pollut.* **8**:217-232.

Bourg, A.C.M. 1995. Speciation of heavy metals in soils and groundwater and implications for their natural and provoked mobility. *In* Salomons, W., Förstner, U., and Mader, P., (Eds.), Heavy metals. Springer-Verlag, Berlin. pp 19-31.

Boyle, M. & Paul, E.A. 1989. Carbon and nitrogen mineralization kinetics in soil previously amended with sewage sludge. *Soil Sci. Soc. Amer. J.* **53**: 99-103.

Brallier, S., Harrison, R.B., Henry, C.L. & Dongsen, X. 1996. Liming effects on availability of Cd, Cu, Ni, and Zn, in a soil amended with sewage sludge 16 years previously. *Water Air Soil Poll.* **86**: 195-206.

Brooks, P.C. & McGrath, S.P. 1984. Effects of metal toxicity on the size of the soil microbial biomass. *J. Soil Sci.* **35**: 341-346.

Brown, S., Chaney, R. & Angle, J.S. 1997. Subsurface liming and metal movement in soils amended with lime-stabilized biosolids. *J. Environ. Qual.* **26**: 724-732.

Bruemmer, G.W. & Van der Merwe, D., 1989. Report on a visit to the Soil and Irrigation Research Institute, Pretoria: In connection with soil pollution in the R.S.A. and future research requirements. Unpublished report, ISCW, Pretoria.

Cajuste, L.J. & Laird, R.J., 2000. The relationship between phytoavailability and the extractability of heavy metals in contaminated soils. *In* Iskandar, I.K. (Ed.), Environmental restoration of metals-contaminated soils. Lewis Publishers, Boca Raton, Florida, pp 189-198.

Campbell, C.A. 1978. Soil organic carbon, nitrogen and fertility. *In* Schnitzer, M., & Khan, S.U., (Eds.), Soil organic matter. Developments in Soil Science Vol. 8. Elsevier Scientific Publishing Company, Amsterdam, pp 173-271.

Chan, K.Y. & Heenan, D.P. 1999. Lime-induced loss of soil organic carbon and effect on aggregate stability. *Soil Sci. Soc. Amer. J.* **63**: 1841-1844.

Chaney, R.L., Ryan, J.A., Kukier, U., Brown, S.L., Siebielec, G., Malik, M. & Angle, J.S. 2001. Heavy metal aspects of compost use. *In:* Stoffella, P.J. & Kahn, B.A. (Eds.), Compost utilization in horticultural cropping systems. CRC Press, Boca Raton, Florida, pp 323-359.

Choudhry, G.G. 1984. Humic substances: Structural, photophysical, photochemical and free radical aspects and interactions with environmental chemicals. Current topics in environmental and toxicological chemistry, Vol. 7. Gordon and Breach Science Publishers, pp 185.

Clapp, C.E., Hayes, M.H.B. & Swift R.S., 1993. Isolation, fractionation, functionalities, and concepts of structures of soil organic macromolecules. *In* Beck, A.J., Jones, K.C., Hayes, M.H.B. & Mingelgrin, U., (Eds.), Organic substances in soil and water: natural constituents and their influences on contaminant behaviour. The Royal Society of Chemistry, Cambridge, pp 31-69.

Clark, M.D. & Gilmour, J.T. 1983. The effect of temperature on decomposition at optimum and saturated soil water contents. *Soil Sci. Soc. Amer. J.* **47**: 927-929.

Curtin, D. & Smillie, G.W. 1983. Soil solution composition as affected by liming and incubation. *Soil Sci. Soc. Amer. J.* **47**: 701-707.

Darmody, R.G., Foss, J.E., McIntosh M.S. & Wolf, D.C. 1983. Municipal sewage sludge compost-amended soils: Some spatiotemporal treatment effects. *J. Environ. Qual.* **12**: 231-236.

Davies, B.E., 1980. Trace element pollution. *In* Davies, B.E. (Ed.), Applied soil trace elements. Wiley, New York, pp 287-351.

Doelman, P. and Haanstra, L. 1979. Effect of lead on soil respiration and dehydrogenase activity. *Soil Biol. Biochem.* **11**: 475-479.

Doelman, P. & Haanstra, L. 1984. Short-term and long-term effects of cadmium, chromium, copper, lead, and zinc on soil microbial respiration in relation to abiotic soil factors. *Plant and Soil* **79**: 317-327.

Dowdy, R.H. & Volk, V.V. 1983. Movement of heavy metals in soils. *In* Nelson, D.W., et al. (Eds.), Chemical mobility and reactivity in soil systems. SSSA Special Publication Number 11. Madison, WI. pp 229-240.

Dubach, P. & Mehta, N.C. 1963. The chemistry of soil humic substances. *Soils and Fertilizers* **16**(5): 293-300.

Emmerich, W.E., Lund, L.J., Page, A.L. & Chang, A.C. 1982. Movement of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.* **11**: 174-178.

Fendorf, S.E., Li, G. & Gunter, M.E. 1996. Micromorphologies and stabilities of chromium (III) surface precipitates elucidated by scanning force microscopy. *Soil Sci. Soc. Amer. J.* **60**: 99-106.

Grove, J.H. & Ellis, B.G. 1980. Extractable iron and manganese as related to soil pH and applied chromium. *Soil Sci. Soc. Amer. J.* **44**: 243-246.

He, Z., Yang, X., Kahn, B.A., Stoffella, P.J. & Calvert, D.V. 2001. Plant nutrition benefits of phosphorus, potassium, calcium, magnesium, and micronutrients from compost utilization. *In* Stofella, P.J. & Kahn, B.A. (Eds.), Compost utilization in horticultural cropping systems. Lewis Publishers, Boca Raton, Florida, pp 307-320.

Hendershot, W.H. & Duquette, M. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Amer. J.* **50**: 605-608.

Herselman, J.E. & Steyn, C.E., 2001. Predicted concentration of trace elements in South African soils. Report no. GW/A/2001/14, ISCW, Pretoria.

Hinesly, T.D., Redborg, K.E., Ziegler, E.L. & Alexander, J.D. 1982. Effect of soil cation exchange capacity on the uptake of Cd by corn. *Soil Sci. Soc. Amer. J.* **46**: 490-497.

Hooda, P.S., McNulty, D., Alloway, B.J. & Aitken, M.N. 1997. Plant availability of heavy metals in soils previously amended with heavy applications of sewage sludge. *J. Sci. Food Agric.* **73**: 446-454.

Hue, N.V. 1995. Sewage sludge. *In* Soil amendments and environmental quality. Rechcigl, J.E. (Ed.), Lewis Publishers, Boca Raton, Florida, pp 199-247.

Impellitteri, C.A., Allen, H.E., Yin, Y., You, S.J. & Saxe, J.K. 2001. Soil properties controlling metal partitioning. *In* Selim, H.M. & Sparks, D.L. (Eds.), Heavy metals release in soils. CRC Press, Boca Raton, Florida, pp 149-165.

Jinadasa, K.B.P.N., Dissanayake, C.B. & Weerasooriya, S.V.R. 1995. Sorption of toxic metals on goethite: Study of cadmium, lead and chromium. *Int. J. Environ. Studies* **48**(1): 7-16.

Kabata-Pendias, A. 2001. Trace Elements in Soils and Plants. 3rd ed. CRC Press, Boca Raton, Florida, pp 413.

Kaupenjohann, M. & Wilcke, W. 1995. Heavy metal release from serpentine soil using a pH-stat technique. *Soil Sci. Soc. Amer. J.* **59**: 1027-1031.

Kedziorek, M.A.M. & Bourg, A.C.M. 1996. Acidification and mobilization of heavy metals from single and dual-component model solids. *Applied Geochemistry*, **11**: 299-304.

Kobayashi, J., Morii, F. & Muramoto, S. 1974. Removal of cadmium from polluted soil with the chelating agent, EDTA. *In* Hemphill, D. (Ed.), Trace Substances in Environmental Health, Vol. 8. Missouri. pp179-192

Korentajer, L. 1991. A review of the agricultural use of sewage sludge: Benefits and potential hazards. *Water SA* **17**(3): 189-196.

Kuo, S. & Baker A.S. 1980. Sorption of copper, zinc, and cadmium by some acid soils. *Soil Sci. Soc. Amer. J.* **44**: 969-974.

Lake, D.L., Kirk, P.W.W. & Lester, J.N. 1984. Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils: a review. *J. Environ. Qual*. **13**: 175-183.

Laperche, V. 2000. Immobilization of lead by in situ formation of lead phosphates in soils. *In* Iskandar, I.K. (Ed.), Environmental restoration of metals-contaminated soils. Lewis Publishers, Boca Raton, Florida, pp 61-76.

LeClaire, J.P., Chang, A.C., LeVesque, C.S. & Sposito, G. 1984. Trace metal chemistry in arid-zone field soils amended with sewage sludge: IV. Correlations between zinc uptake and extracted soil zinc fractions. *Soil Sci. Soc. Amer. J.* **48**: 509-513.

Legret, M., Divet, L. & Juste, C. 1988. Movement and speciation of heavy metals in a soil amended with sewage sludge containing large amounts of Cd and Ni. *Water Res.* **22**: 953-959.

Lindemann, W.C., Connell, G. & Urquhart, N.S. 1988. Previous sludge addition effects on nitrogen mineralization in freshly amended soil. *Soil Sci. Soc. Amer. J.* **52**: 109-112.

Linn, D.M. & Doran, J.W. 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Sci. Soc. Amer. J.* **48**: 1267-1272.

Logan, T.J. 1992. Reclamation of chemically degraded soils. *In* Advances in Soil Science, Vol. 17. Springer-Verlag, New York. pp 13-35.

Lund, L.J., Page, A.L. & Nelson, C.O. 1976. Movement of heavy metals below sewage disposal ponds. *J. Environ. Qual.* **5**: 330-334.

Martin, A.E. & Reeve, R. 1957. Chemical studies on podzolic illuvial horizons. I. The extraction of organic matter by organic chelating agents. *J. Soil Sci.* **8**(2): 268-278.

Mayer, R. 1991. The impact of atmospheric acid deposition on soil and vegetation. *In* Vernet, J.P. (Ed), Heavy metals in the environment. Elsevier, Amsterdam, pp 21-36.

McIlveen, W.D. & Cole, H., Jr. 1974. Influence of heavy metals on nodulation of red clover. *Phytopathology* **64**: 583.

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P. & Cook, N. 2000. Soil testing for heavy metals. *Commun. Soil Sci. Plant Anal.* **31**(11-14): 1661-1700.

Merrington, G. & Alloway, B.J. 1997. Determination of the residual metal binding characteristics of soils polluted by Cd and Pb. *Water Air Soil Poll.* **100**: 49-62.

Miller, R.H. 1974. Factors affecting the decomposition of an anaerobically digested sewage sludge in soil. *J. Environ. Qual.* **3**: 376-380

Molina, J.A.E., Braids, O.C., Hinesly, T.D. & Cropper, J.B. 1971. Aeration-induced changes in liquid digested sewage sludge. *Soil Sci. Soc. Amer. Proc.* **35**: 60-63.

Moore, T.R. 1997. Dissolved organic carbon: sources, sinks, and fluxes and role in the soil carbon cycle. *In* Lal, R., Kimble, J.M., Follet, R.F. & Stewart, B.A. (Eds.), Soil processes and the carbon cycle. CRC Press, Boca Raton, Florida, pp 281-292.

Mortensen, J.L. 1963. Complexing of metals by soil organic matter. *Soil Sci. Soc. Amer. Proc.* **27**: 179-186.

Mullins, G.L., Sommers, L.E. & Barber, S.A. 1986. Modelling the plant uptake of cadmium and zinc from soils treated with sewage sludge. *Soil Sci. Soc. Amer. J.* **50**: 1245-1250.

Nederlof, M.M. & van Riemsdijk, W.H. 1995. Effect of natural organic matter and pH on the bioavailability of metal ions in soils. *In* Huang, P.M., Berthelin, J., Bollag, J.M., McGill, W.B. & Page, A.L., (Eds.), Environmental impact of soil component interactions: metals, other inorganics, and microbial activities. Lewis Publishers, Boca Raton, Florida, pp 75-86.

The Non-Affiliated Soil Analysis Work Committee, 1990. Handbook of standard soil testing methods for advisory purposes. Soil Science Society of South Africa, Pretoria.

Pal, D. & Broadbent, F. E. 1981. Leaching of calcium and magnesium from soil columns as affected by form of nitrogen in applied sewage. *Soil Sci. Soc. Amer. J.* **45**: 56-60.

Quraishi, M.S.I. & Cornfield, A.H. 1973. Incubation study of nitrogen mineralisation and nitrification in relation to soil pH and level of copper(II) addition. *Environ. Poll.* **4**: 159-163.

Robertson, W.K., Lutrick, M.C. & Yuan, T.L. 1982. Heavy applications of liquid-digested sludge on three Ultisols: I. Effects on soil chemistry. *J. Environ. Qual.* **11**: 278-282.

Rother, J.A., Millbank, J.W. & Thornton, I. 1982. Effects of heavy-metal additions on ammonification and nitrification in soils contaminated with cadmium, lead, and zinc. *Plant and Soil* **69**: 239-258.

Sauerbeck, D.R. 1991. Plant element and soil properties governing uptake and availability of heavy metals derived from sewage sludge. *Water Air Soil Poll.* **57-58**: 227-237.

Scheffer, F., Wright, J.R. & Desjardins, J.G.A. 1958. Comparison of the effectiveness of various extractants of organic matter from two horizons of a Podzol profile. *Can. J. Soil Sci.* **38**: 49-53

Schnitzer, M. 1971. Characterization of humic constituents by spectroscopy. *In* McLaren, A.D. & Skujiņš, J. (Eds.), Soil biochemistry, Vol. 2. Marcel Dekker, Inc., New York, pp 60-95.

Schnitzer, M. 1978. Humic substances: chemistry and reactions. *In* Schnitzer, M., & Khan, S.U., (Eds.), Soil organic matter. Developments in Soil Science Vol. 8. Elsevier Scientific Publishing Company, Amsterdam, pp 1-64.

Schwarz, A., Wilcke, W., Stýk, J. & Zech, W. 1999. Heavy metal release from soils in batch pH_{stat} experiments. *Soil Sci. Soc. Amer. J.* **63**: 290-296.

Shuman, L.M. 1986. Effect of liming on the distribution of manganese, copper, iron, and zinc among soil fractions. *Soil Sci. Soc. Amer. J.* **50**: 1236-1240

Sikora, L.J. & Szmidt, R.A.K. 2001. Nitrogen sources, mineralization rates, and nitrogen nutrition benefits to plants from composts. *In* Stoffella, P.J. & Kahn, B.A. (Eds), Compost utilization in horticultural cropping systems. Lewis Publishers, Boca Raton, Florida, pp 287-305.

Smith, S.R. 1991. Effects of sewage sludge application on soil microbial processes and soil fertility. *In* Advances in Soil Science, Vol. 16. Springer-Verlag, New York, pp 191-212.

Smith, S.R. 1994. Effect of soil pH on availability of metals in sewage sludge-treated soils. II. Cadmium uptake by crops and implications for human dietary intake. *Environ. Poll.* **86**: 5-13.

Sommers, L.E. 1977. Chemical composition of sewage sludges and analysis of their potential use as fertilizers. *J. Environ. Qual.* **6**(2): 225-232.

Soon, Y.K. 1998. Determination of cadmium, chromium, cobalt, lead, and nickel in plant tissue. *In* Kalra, P. Yash (Ed.), Reference methods for plant analysis. Boca Raton, CRC Press, pp 193-198.

Sparks, D.L. 2003. Environmental soil chemistry (2^{nd} Ed.). Academic Press, San Diego, California, pp 352.

Sposito, G., Holtzclaw, K.M. & Baham, J. 1976. Analytical properties of the soluble, metal-complexing fractions in sludge-soil mixtures: II. Comparative structural chemistry of fulvic acid. *Soil Sci. Soc. Amer. J.* **40**: 691-697.

Sposito, G. & Holtzclaw, K.M. 1977. Titration studies on the polynuclear, polyacidic nature of fulvic acid extracted from sewage sludge-soil mixtures. *Soil Sci. Soc. Amer. J.* **41**: 330-336.

Sposito, G., Holtzclaw, K.M. & Keech, D.A. 1977. Proton binding in fulvic acid extracted from sewage sludge-soil mixtures. *Soil Sci. Soc. Amer. J.* **41**: 1119-1125.

Sposito, G., Holtzclaw, K.M. & Le Vesque-Madore, C.S. 1979. Cupric ion complexation by fulvic acid extracted from sewage sludge-soil mixtures. *Soil Sci. Soc. Amer. J.* **43**: 1148-1155

Sposito, G., Holtzclaw, K.M. & Le Vesque-Madore, C.S. 1981. Trace metal complexation by fulvic acid extracted from sewage sludge. I. Determination of stability constants and linear correlation analysis. *Soil Sci. Soc. Amer. J.* **45**: 465-468

Sposito, G., Holtzclaw, K.M., Le Vesque, C.S. & Johnston, C.T. 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge: II. Comparative study of the fulvic acid fraction. *Soil Sci. Soc. Amer. J.* **46**: 265-270.

Stevenson, F.J. 1982. Humus chemistry: genesis, composition, reactions. John Wiley & Sons, Inc., New York, pp443.

Steyn, C.E. 1994. The bioavailability of certain heavy metals in selected organic products. MSc (Agric) dissertation. University of Pretoria, Pretoria.

Straalen, N.M. & Bergema, W.F. 1995. Ecological risks of increased bioavailability of metals under soil acidification. *Pedobiologia* **39**(1): 1-9.

Tan, K.H., King, L.D. & Morris, H.D. 1971. Complex reactions of Zn with organic matter extracted from sewage sludge. *Soil Sci. Soc. Amer. Proc.* **35**: 748-752.

Tate, R.L. 1987. Soil organic matter: biological and ecological effects. John Wiley & Sons, Inc., New York, pp 291.

Terry, R.E., Nelson, D.W. & Sommers, L.E. 1979. Carbon cycling during sewage sludge decomposition in soils. *Soil Sci. Soc. Amer. J.* **43**: 494-499.

Tester, C.F., Sikora, L.J., Taylor, J.M. & Parr, J.F. 1977. Decomposition of sewage sludge compost in soil. I. Carbon and nitrogen transformations. *J. Environ. Qual.* **6**: 459-463.

Van der Waals, J.H. & Claassens, A.S. 2002 Accurate lime recommendations under South African conditions. *Commun. Soil Sci. Plant Anal.* **33**(15-18) 3059-3074.

Van der Waals, J.H., Snyman H.G. & Claassens, A.S. 2005. Increase in metal extractability after liming of sacrificial sewage sludge disposal soils. *Water SA* **31**(2): 271-273.

Water Research Commission, 1997. Permissible utilisation and disposal of sewage sludge. Edition 1. Pretoria. ISBN 1-86845-281-6.

Welch, J.E. & Lund, L.J. 1987. Soil properties, irrigation water quality and moisture level influences on the movement of nickel in sewage sludge-treated soils. *J. Environ. Qual.* **16**: 403-410.

Wilcke, W. & Amelung, W. 1996. Small-scale heterogeneity of aluminum and heavy metals in aggregates along a climatic transect. *Soil Sci. Soc. Amer. J.* **60:** 1490-1495.

Wilson, D.O. 1977. Nitrification in three soils amended with zinc sulphate. *Soil Biol. Biochem.* **9**: 177-180.

Yin, Y., Allen, H.E., Huang, C.P., Sparks, D.L. & Sanders, P.F. 1996. Adsorption of mercury(II) by soil: effects of pH, chloride, and organic matter. *J. Environ. Qual.* **25**: 837-844.

Yin, Y., Lee, S.Z., You, S.J. & Allen, H.E. 2000. Determinants of metal retention to and release from soils. *In* Iskandar, I.K. (Ed), Environmental restoration of metals-contaminated soils. Lewis Publishers, Boca Raton, Florida, pp 77-91.

You, S.J., Yin, Y. & Allen, H.E. 1999. Partitioning of organic matter in soils: effects of pH and water/soil ratio. *Sci. Tot. Env.* **227**: 155-160.

Zachara, J.M., Smith, S.C., McKinley, J.P. & Resch, C.T. 1993. Cadmium sorption on specimen and soil smectites in sodium and calcium electrolytes. *Soil Sci. Soc. Amer. J.* **57**: 1491.