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.