

CHAPTER 2

HEAVY METAL AVAILABILITY FROM SLAGS

INTRODUCTION

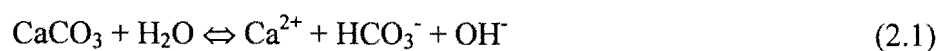
Slags are often used as agricultural limes due to its high CCE when finely ground. The area around Middelburg and Witbank on the Eastern Highveld of South Africa has soils that are prone to natural and man induced acidification and also has two steel producers that produce a large amount of slags. Due to the proximity of the source and the acidity problem this is also the area with the highest probable use of slags.

These slags contain impurities in the form of heavy metals and in some cases these impurities can reach levels of several parts per thousand. Although this is a cause of concern in the environmental field today due to possible pollution of whole ecosystems and subsequently the food chain, very little has been published in South Africa concerning the hazard posed by the heavy metals contained in the slags.

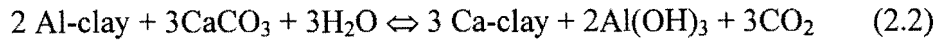
Testing heavy metals for bioavailability is problematic due to a variety of reasons. These include differences in test crops, extraction methods, test conditions, and lack of adequate reference crops or values. A proper understanding of all the factors is a prerequisite to assessing materials for the bioavailability of the metals that it contains.

The Use of Slags as Liming Materials

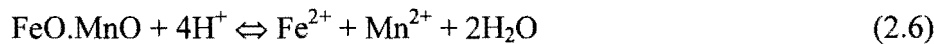
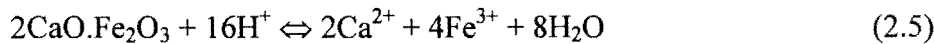
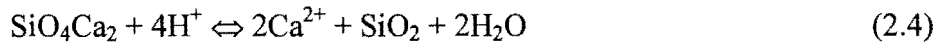
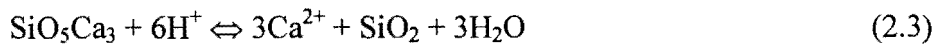
Lime can be applied in different forms of which calcitic and/or dolomitic lime is known best. Other liming materials include different slags derived from the processing of steel. Lime has a rather uniform composition and the neutralising reaction is thus quite simple. In water CaCO_3 dissolves and hydrolyses to form OH^- as follows:



The solubility of lime in water is very low and the neutralising effect is due mainly to a contact exchange reaction on the soil particle surface (Jenny and Overstreet, 1938; Warfvinge and Sverdrup, 1989). The produced OH⁻ ions react with H₃O⁺ ions that are formed by the oxidation of reduced N and with exchangeable Al³⁺. The equation for the complete reaction is:



The slag's composition differs due to different processes used in the processing of steel, therefore the neutralising reaction is not precisely known. It is not a pure carbonate but also contains Ca-silicate and could react (together with other constituents) in the following manner:



(After Balcázar, 1998, as quoted in Vanacker, 1999).

Several types of slags are used as agricultural liming materials, such as blast furnace slag, open-hearth slag, and basic slag. These are all the by-products of steel processing plants and their composition depend on the raw material (ore), the specific process, and the product of the plant. Due to this, Ca and Mg aluminosilicates, Fe, Mn, phosphates, and other elements such as Cr, Ni, Co, Cd, Cu, Zn, Mo, and Ba may occur in differing quantities. Some of the elements can reach concentrations of several parts per thousand, which are then added to the soil.

Two main forms of slags are produced in and distributed from the heart of the Loskop Dam catchment area near Witbank and Middelburg. This is also the area in which soil acidification is reaching critical proportions in parts, and in which many soils are very

sensitive to acidification (Fey & Dodds, 1998). The waste product, if finely ground, has a high Calcium Carbonate Equivalent (CCE) and is relatively cheap in comparison to other mined liming materials. Due to high transport costs and the proximity of the slags, large quantities are used in the area. As mentioned earlier, a source of concern is the fact that slags contain varying amounts of trace elements and heavy metals and that although most of the elements are not plant available at the pH levels in the soil after liming, the build-up of these elements could be detrimental in the long-term. Table 2.1 gives an indication of the average composition of the slags.

TABLE 2.1. Average composition of slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).

Chemical Compound	Columbus Steel %	Highveld Steel %
Al ₂ O ₃	2.3	1.3
CaO	49.5	55.4
Cr ₂ O ₃	3.0	-
FeO	0.6	16.7
MgO	11.4	6.5
MnO	0.9	1.1
P	-	0.4
S	-	0.4
SiO ₂	30.6	17.9
TiO ₂	0.7	-
V ₂ O ₅	-	1.6

Heavy Metals in Soils

In order to better appreciate the effect of added heavy metals to the soil through the application of slags, it is necessary to have an idea how these metals act in soils. It is furthermore necessary to understand how different soils, originating from different parent materials and soil processes, will react to the addition of these slags in terms of the presence and bio-availability of these metals. Although “heavy metals” are by

definition those elements having a density greater than five, here it will refer to the metals generally used and discharged by industry (Jones & Jarvis, 1981). The metals discussed in this study all occupy positions in the first transition series of the periodic table.

In recent years many comprehensive works (Kabata-Pendias & Pendias, 1992; Alloway, 1995) as well as research publications on the bio-availability and contamination of heavy metals in soils have been published, the scope of which is too wide to cover in this study. Many of these concern pollution with heavy metals through the application of sewage sludge (Steyn, 1994; Tsadilas, *et al.*, 1995; Brallier, *et al.*, 1996; Hooda, *et al.*, 1997) but very few touch on pollution through the use of slags (Amaral Sobrinho, *et al.*, 1992; Amaral Sobrinho, *et al.*, 1993). Different researchers and institutions developed many techniques and guidelines to evaluate the data, but due to variation in all the aspects of research, there is still a long way to go in standardising testing procedures and reference levels of these elements in soils (McLaughlin, *et al.*, 2000). The fact remains that the use of materials that contain heavy metals in quantities to pose a threat to the environment leads to the necessity of proper research and guidelines to minimise the material's impact on the environment.

McLaughlin, *et al.*, (2000) discuss several influences on concentration, activity and speciation of metals in soil solutions that affect the phyto- or bioavailability of metals in the soil. It is stated that the above mentioned, as well as plant genotypic variation in metal uptake or tolerance, and the complexity involved with the plant-rhizosphere-soil interaction all contribute to making soil testing for heavy metal phyto-availability inherently difficult. They do a review on literature on the correlation of extraction techniques with the bioavailability of heavy metals and their conclusion is that “no single soil test will outperform others in all situations...” A five points set of quality screening criteria is outlined and the option of the partitioning of calibration data in regions, or according to an environmental endpoint (plant toxicity, microbial toxicity, crop metal uptake) is urged. Furthermore, pathways and test methodologies are suggested to focus and improve research efforts in the soil testing for metals and metalloids.

Several factors may influence the bioavailability of heavy metals in the soil. According to Løbersli, *et al.*, (1991), one of these – soil acidity – is a major factor. Although heavy metals occur in soils as rare elements, the human mediated addition of these to soils could increase their uptake by plants, thereby increasing the toxic effect it has on plants and plant consumers. The capacity of the soil to adsorb or precipitate metals generally increases with increasing pH 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).

Soil pH

The effect pH has on the heavy metal bio-availability has been confirmed in many different studies that range from metal availability after sewage application (Hooda, *et al.*, 1997) to the adsorption of metals on clay fraction minerals (Jinadasa, Dissanayake, & Weerasooriya, 1995; Kaupenjohann and Wilcke, 1995; Schwarz, *et al.*, 1999). 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 & Pendias, 1992).

Cr^{3+} is considered very stable in soils and at a pH of 5.5 and higher is almost completely precipitated (Kabata-Pendias & Pendias, 1992) whereas Cr^{6+} is more stable at low pH than in neutral to alkaline (pH 7.5) soils (Grove and Ellis, 1980). Jinadasa, *et al.*, (1995) found that Cr was more strongly adsorbed on synthetically prepared goethite than Cd and Pb, and sorption strength was strongly pH-dependent.

Both the Co (Steyn, 1994) and Ni (Gupta and Gupta, 1998) availabilities are also strongly influenced by pH with increased availability at low pH.

In soils the available Mn fraction is very low (traces) but increases with decreasing pH and reduced conditions. It is less available in alkaline soils and there are not many reports of toxicity in plants (Kabata-Pendias & Kabata, 1992).

Many remedies for toxic levels of metals in soils have been proposed and tested but in most cases metal toxicities are alleviated through the addition of lime (Hooda, *et al.*, 1997; Kabata-Pendias & Pendias, 1992), thereby increasing the soil pH and lowering the activities of the metals in solution.

Speciation and Valency

Chromium's valency ranges from +2 to +6, but its natural occurrence is restricted to +3 (chromic) and +6 (chromate), with Cr^{6+} being more soluble than Cr^{3+} . Cr can form different complex ionic species e.g. $\text{Cr}(\text{OH})^{2+}$, CrO_4^{2-} , CrO_3^{3-} . Chromite (the mineral) is the most common due to its resistance to weathering, but with continued oxidation Cr forms the more mobile chromate ion (CrO_4^{2-}) (Grove and Ellis, 1980; Kabata-Pendias & Pendias, 1992). Biological reduction of Cr^{6+} to Cr^{3+} is common in soils but biological oxidation of Cr^{3+} to Cr^{6+} has not been reported (Bartlett and Kimble, 1976; Cifuentes, Lindemann, & Barton, 1996).

Ni^+ , Ni^{2+} and Ni^{3+} are the possible valencies of Nickel (Stoeppler & Ostapczuk, 1992) but in soils it is mainly found as Ni^{2+} and very rarely as Ni^+ (Pais & Benton-Jones, 1997). Ni is most mobile in sewage sludge where it forms organic chelates.

Co^{2+} and Co^{3+} are the oxidation states in which Co can occur in nature. Although organic chelates of Co are relatively mobile, Co is generally unavailable to plants in high organic content soils even though the Co content may be high. (Kabata-Pendias & Kabata, 1992).

Mn is found in soils in three oxidation states with the Mn^{2+} state being soluble, mobile and easily available to plants. Mn^{4+} is practically insoluble, non-mobile and unavailable, while Mn^{3+} is relatively scarce (Aubert and Pinta, 1977).

Adsorption of Heavy Metals on Different Soil Surfaces and Soil Structural Aspects

The clay particles in the soil can adsorb heavy metals when added; thereafter the risk of contamination depends on the stability of the sorbed phase. For this reason it is necessary to have an accurate and thorough knowledge of the factors that influence the stability of the sorbed species (Fendorf & Gunter, 1996).

The clay content and clay type of a soil can often positively be correlated with the amount of metals taken up by plants (Kabata-Pendias & Kabata, 1992; Hooda, *et al.*, 1997) 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 instability 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 on it. Fendorf and Gunter (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).

The time elapsed after application of heavy metals to the soils also plays a role. 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.

Co is relatively mobile in oxidising acid environments but does not migrate in a soluble phase due to highly selective adsorption by Fe and Mn oxides (especially if the pH increases) (Kabata-Pendias & Kabata, 1992).

Due to the different minerals and conditions in soils, the metals exhibit different stabilities according to the results of different authors. Paz-González, Taboada-Castro, & Taboada-Castro (2000) found, confirming the results of other studies, that the mobility of certain metals decreased in the order $\text{Zn} > \text{Cu} > \text{Ni} > \text{Co} > \text{Cr}$. Jinadasa, *et al.*, (1995) found that the metal ion adsorption capacity order on goethite was $\text{Cr}^{3+} > \text{Pb}^{2+} > \text{Cd}^{2+}$. In a study on sewage amended soil the sequence of metal concentration was found to be $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cd} > \text{Pb}$ (Hooda, *et al.*, 1997). In another study in Australia (Phillips and Chapple, 1995) the mobility decrease was $\text{Zn} > \text{Cr} \approx \text{Cu} \approx \text{Pb}$. 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.

From the above it is clear that different soil conditions and minerals lead to different metal availabilities – an aspect discussed in detail by McBride (1989).

Natural Occurrence

The natural Cr content in soil varies due to texture (high in clay, low in sand), organic C content, iron oxide content and parent material (Aubert and Pinta, 1977). Ultramafic and mafic rocks contain levels of a few parts per thousand and acid igneous and sedimentary rocks ranges between 5 to 120 mg.kg^{-1} (Kabata-Pendias & Pendias, 1992).

Total Cr levels in SA soils are generally higher than the maximum values stipulated by law (Steyn, personal communication). Paz-González, *et al.*, (2000) also indicated that soils formed on ultramafic rocks had total Cr and Ni levels higher than acceptable, but this was due to its lithogenic origin. A site in Brisbane, Australia, was

concluded to pose no environmental and health risk although the total concentration of some metals was up to 40 times the acceptable values adopted for Australia. This was due to the metals (including Cr) being only slightly leachable and very immobile (Phillips and Chapple, 1995).

Total Ni content in soils varies from traces to more than 5000 mg.kg⁻¹ in ultrabasic rocks. Generally older soils, peaty and sandy soils contain the lowest levels, and clayey and high organic content soils contain higher levels. Total Co levels vary from 0.05 to 300 mg.kg⁻¹. (Aubert and Pinta, 1977). Ni and Co is closely associated with Fe and Mn oxides and organic material (chelates) and Ni is similar to Co but is less strongly fixed to soil components (Kabata Pendias & Pendias, 1992), therefore more mobile.

Total Mn levels in soils vary from traces to 10 000 mg.kg⁻¹ (Aubert and Pinta, 1977) but pose no threat due to the prevalent pH levels and redox conditions in most soils.

Extraction and Metal Interaction

Ethylenediaminetetraacetic acid (EDTA) extraction was found or proposed by many researchers to give a very good indication of the pollution hazard of heavy metals. Paz-González, *et al.*, (2000) found, in a study in Northwest Spain, that the EDTA-extractable heavy metal levels were generally low (no indication was given as to the type of EDTA salt used). EDTA was also found to be a reliable test for predicting plant available metals (Hooda, *et al.*, 1997) and Brummer and van der Merwe (1989) indicated that the NH₄-EDTA-extractable heavy metals concentration gives a better estimate of those potentially available, and therefore suggested it to be used in the establishing of preliminary threshold values for heavy metals for South African soils. Canet, *et al.*, (1998) found that only small amounts of Cr could be extracted with Na₂EDTA after sludge application increased soil heavy metals contents.

Steyn (1994) emphasises the influence pH has on the extractant used. In many cases the buffer capacity of NH₄-EDTA had been exceeded by the application of lime to the test soil. Some of the other extractants (Ammonium Bicarbonate-Diethylenetriamine-pentaacetic Acid - AB-DTPA) did not have the same problem due to it having been

developed to prevent competition with Ca^{2+} . The extracting agents used generally gave a good indication of the bio-available metals and indicated a decrease with increased CaCO_3 applications. The EPA method 3050, though, did not predict the bioavailability of metals well at all. De Abreu, *et al.*, (1995) however, state that several extractants were ineffective in evaluating metal availability in wheat and beans.

Many strong extracting agents exist and can be used to extract metals like Cr after it has been strongly sorbed by the solid phase of the soil. Grove and Ellis (1980) found that extractable Cr fractions were low in all but the strongest extracting agents and that water extractable Cr was insignificant compared to the stronger extracting agents.

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 sewage sludge and in which the sludge had time to equilibrate with the soil. The results indicated that the crop used and type of metal analysed 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 (known for its hyper-accumulating tendencies) accumulating the most, carrot intermediate levels and wheat the least. Bhattacharjee, *et al.*, (1998) found relatively wide variation in the metal contents of spinach in a study on natural soils.

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.

Sampling and Testing

Cr occurs ubiquitously in nature; therefore care must be taken to avoid sample contamination during collection, preparation and analysis. It is very valuable to use standard reference materials to aid in the accurate determination thereof (Miller-Ihli, 1992). Miller-Ihli (1992) goes on to extensively describe sample collection, handling, and preparation strategies to avoid sample contamination.

Sampling and testing for Ni and Co levels above 0.2 mg.kg^{-1} poses no problem. For lower levels there are many pollutants in a laboratory i.e. stainless steel instruments and dust, and care should be taken in sample preparation and handling (Stoeppler & Ostapczuk, 1992).

The preferred method of testing for most heavy metals is with inductively coupled plasma-mass spectrometry (ICP-MS) although it is still a relatively new technique (Steyn, 1994). It is a relatively simple technique but it is very sensitive and can detect elements at levels below $\mu\text{g.dm}^{-3}$. Steyn (1994) stipulates the capabilities of ICP-MS and discusses the requirements for sample preparation when determining heavy metals by ICP-MS.

Testing for Cr speciation can be problematic and several researchers have developed or attempted to develop ways to do this (Fodor and Fischer, 1995). Prokisch, *et al.*, (1995) describes a simple and inexpensive method for determining the speciation of Cr in soil extracts by using acidic-activated aluminium oxide to separate Cr^{3+} and Cr^{6+} during testing.

Essentiality, Toxicity and Plant Uptake

Many of the heavy metals added to the soil are also essential elements for plants and or man. The levels needed by either differ but excessive amounts can lead to health complications and even death in man. An example is Cr^{3+} that is essential to animals and man at low levels to maintain normal glucose metabolism (Recommended Daily Allowance (RDA) levels of 50 to $200 \mu\text{g.day}^{-1}$), but at high levels as Cr^{6+} it is toxic to

plants and carcinogenic in animals and man (Miller-Ihli, 1992). Table 2.2 summarises the main aspects concerning the elements of interest in this study.

TABLE 2.2. Heavy metal content, essentiality and toxicity in plants, animals, and man (After Pais and Benton Jones, 1997).

Element	Content in plants (mg.kg ⁻¹)	Reference plant (mg.kg ⁻¹)	Phyto-toxicity (mg.kg ⁻¹)	Essential for plants	Essential in animals/man	RDA in man mg.day ⁻¹
Cobalt (Co)	Legumes 0.10-0.57 Grass 0.03-0.27	0.2	-	No (Suggested for legumes)	Yes	-
Chromium (Cr)	0.02-0.2	1.5	>10	No	Yes	0.05-0.2
Manganese (Mn)	10-500	200	Varies largely	Yes	Yes	0.4-10
Nickel (Ni)	0.3-3.5 (pasture plants)	1.5	Varies largely	Suggested	Yes	0.3-0.5

* Recommended Daily Allowance

Although available Cr⁶⁺ is toxic to plants and animals (Miller-Ihli, 1992), the uptake of Cr from soils by crops is generally insignificant (Gupta & Gupta, 1998) due to the strong adsorption thereof on the clay fraction in soils, therefore posing a minimal hazard to plants and soil organisms (McLaughlin, *et al.*, 2000).

Some plants act as hyperaccumulators of certain elements. An example is Ni where concentrations of more than 6000 mg.kg⁻¹ were found in plants grown on soils with elevated Ni levels. The Co content of foodstuffs (e.g. cabbage) may be as high as 100 mg.kg⁻¹ (Kabata-Pendias & Kabata, 1992).

Mn is readily taken up by plants, therefore the plant Mn concentration should be a direct function of the soluble Mn pool in soils (Kabata-Pendias & Kabata, 1992) with deficiencies generally experienced on alkaline soils and toxicities in acid soils with pH levels much below 5 (Aubert and Pinta, 1977).

Acceptable Levels – Legislation and Suggested Levels

Existing guidelines (Table 2.3) set the maximum permissible levels of contaminants that can be added to the soil in South Africa. These guidelines are for sewage sludge but could also be used for liming materials. When the levels of these elements are considered in the soil, the practice in the past was to use total concentration values. McLaughlin, *et al.*, (2000) indicates that during recent years the trend has shifted more to “mobile” concentration. Brummer and van der Merwe (1989) indicated that the NH₄-EDTA-extractable heavy metals concentration gives a better estimate of its potential availability and therefore suggested the levels in Table 2.3 as the preliminary threshold values. Threshold values for application of metals at certain soil pH levels were also given but these are not necessarily applicable in the case of slags due to the rise in pH it brings about.

TABLE 2.3. Maximum permissible contaminant concentration (mg.kg⁻¹, dry basis) in ameliorants (Department of National Health and Population Development, 1991) and suggested preliminary threshold value for NH₄-EDTA (pH 4.5) extractable heavy metals for the soils of South Africa. (Brummer and van der Merwe, 1989)

Element	Maximum permissible concentration (mg.kg ⁻¹)	Suggested threshold values (NH ₄ -EDTA extractable) (mg.kg ⁻¹) soil
Cd	20	1
Co	100	10
Cr	1750	50
Cu	750	60
Hg	10	1
Mo	25	-
Ni	200	20
Pb	400	100
Zn	2750	100
As	15	-
Se	15	-
B	80	-
F	400	-

MATERIALS AND METHODS

Introduction

Considering all the variables involved in the testing for heavy metal availability it was decided to test the liming materials on a “worst case scenario” with spinach as a test crop. The trial had to discriminate between the limes in terms of metal availability, therefore a suitable control treatment was needed that could equal the neutralising capability of the slags but without the metal content. A normal blank treatment would not suffice due to the major pH difference between the blank and the slag treatments. The ideal control treatment would be pure lime, which could be tested at similar pH levels in the soil, therefore removing the influence of the background metal concentration in the soil. In this trial lime that contains no metals or very low concentrations of heavy metals was used as a control.

Liming Materials

Twenty-four different lime samples were collected from different sources with the aid and under the supervision of representatives from the Registrar of Fertilisers. The lime samples were put through a splitter to ensure homogeneity and sealed on site in tins. From the 24 limes only 12 were selected due to their origin and heavy metal content. Of the 12 selected samples five were slags, two from paper mills and five were natural limes.

Soil

The soil was chosen from the Eastern Highveld – an area where there is an increased probability of farmers using slags as agricultural limes due to the proximity of the source. Some chemical and physical properties of the soils are listed in Table 2.4.

TABLE 2.4: Selected chemical and physical properties of the soil used in the study.

Parameter	
Texture	Sandy Clay Loam
pH _(Water)	5.1
pH _(KCl)	3.9
Ammonium acetate extractable: (mg.kg ⁻¹)	
Ca	622
Mg	151
K	217
Na	0
P – Bray 1 (mg.kg ⁻¹)	21.93

Heavy Metal Content of Limes

To determine the identity and approximate concentration of the heavy metals that could pose a danger after the application of slags, a semi-quantitative scan (ICP-MS) was done on the twenty-four liming materials by the Institute for Soil, Climate and Water (ISCW). From the scan certain limes were selected that contain high levels of: Co, Cr, Mn, and Ni. On the grounds of the scan results, eight of the liming materials were further digested with HClO₄/HNO₃. The procedure followed was the same as a wet digestion for plant materials as prescribed by ALASA (1998) with the exception that a lime sample of 10g was digested in 100cm³ of the acid. The resultant solution was tested quantitatively Cr, Co, and Ni with ICP-MS, and Mn by Atomic Adsorption Spectrophotometry.

The liming materials that contained no heavy metals were used as reference materials (controls). No known reference values or plant materials were available and this was exacerbated by the fact that plants in pots do not perform like plants in the field (Steyn, 1994), therefore leading to the generation of results that will not correlate well with values from reference plants from the field. The main motivation therefore was to minimise the variability by subjecting each plant to the same set of variables except for the type of lime and therefore also the respective heavy metals.

Crops

Two crops were used namely wheat (*Triticum aestivum* ssp. *vulgare* McKey) and spinach (*Spinacia oleracea* L) Spinach was chosen due to its hyper-accumulating properties (Hooda, *et al.*, 1997), and wheat to verify heavy metal levels if excessive levels were found in the spinach. The crops were grown in the soil for a period of eight weeks, after which it was harvested. A follow-up trial with eight weeks of growth (wheat) was also done although the data is not presented here.

Treatments

The twelve liming materials were added to the soil at three different rates to attain pH target values of 5.8, 6.8, and 7.8. Each treatment was replicated four times. For a detail exposition of the reaction of the liming materials in terms of pH see Chapters 3 and 4. The follow up trial made use of the same soil and pots with a new growth of spinach and wheat.

Fertilisers

The plants in the pots were top dressed through the growing season with NH_4NO_3 and KCl to ensure adequate growth.

Harvest, Sample Preparation and Plant Analysis

After the specified growth period the plants were harvested, washed, and dried in an oven at 65°C overnight. The dried plant material was weighed and the spinach and wheat ground in a mill with tungsten blades to avoid Cr contamination.

An H_2SO_4 digestion (ALASA, 1998) was used to determine the P and N content and an $\text{HClO}_4\text{:}2\text{HNO}_3$ digestion (ALASA, 1998) to determine the heavy metal and trace element content of the spinach. Co, Cr, and Ni were determined by ICP-MS, and Mn by Atomic Adsorption Spectrophotometry.

Due to cost constraints only the spinach of the first harvest was analysed for heavy metals. Only the limes with high heavy metal contents and ones with low contents were used during analysis of plant material. This served a two-fold purpose namely to amplify the differences between the limes without cluttering the graphs with additional data, and to be able to do more of the relevant determinations without wasting funds.

Variation in the Cr values prompted a further Cr analysis as described above.

Statistical Analysis

Due to the cost involved the replicates of the plant samples were pooled before chemical analysis. No statistical evaluation could therefore be done on the results of the heavy metal analysis results due the fact that there was only one determination per sample. The R-squared value (coefficient of determination) in the figures indicates the variation of the values on the Y-axis that is “accounted for” by linear (or other) regression of the Y values on the X values (Samuels, 1991). A value of 1 indicates a very good correlation between the data sets. Note that if the regression line nears horizontal the R-squared value nears 0.

Soil Sampling and Sample Preparation

Soil samples were taken after the first harvest of the spinach and wheat from each pot. After the second harvest of wheat the soil was removed from the pots and a representative sample was taken from each pot. The samples were dried in an oven at 65°C overnight and stored until further determinations had to be done.

EDTA Extractions

Due to cost implications only some of the soils treated with slags were selected to test for NH₄-EDTA extractable metals (two to three soils per metal). This was done to compare metal levels in the soils with those found in the plants (after Brummer and van der Merwe (1989)) and was done after the completion of the follow up trial. The

method as described by The Non-affiliated Soil Analysis Work Committee (1990) was used.

NH₄-EDTA was chosen as general extracting agent due to its regular use in other studies and the fact that Brummer and van der Merwe (1989) proposed it as the standard for heavy metal testing in terms of potentially plant available metals in SA. Furthermore, the data produced could be compared with data from numerous other studies.

RESULTS AND DISCUSSION

Chromium

Table 2.5 indicates the amounts of lime added to the pots to attain the desired pH, the Cr content of the limes as well as the increase in Cr concentration per pot. In Table 2.6 the concentration of Cr in the leaves of the spinach and the increased uptake compared to the control are indicated.

Figures 2.1 and 2.2 indicate the Cr concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively. There is no clear pH trend in the Cr uptake discernable from Fig. 2.2.

An aspect that influenced the results is the interference of chlorine compounds with Cr in ICP-MS determination when perchloric acid is used. Cr is known for its difficulty in determination due to its ubiquitous nature. Wet digestion in nitric acid alone did not prove satisfactory in a study by Blincoe, *et al.*, (1987). Due to the digestion procedures used in this trial (HClO₄/HNO₃) the data was most probably influenced by interferences caused by ³⁵ClOH⁺ and ⁴⁰Ar¹²C⁺ during the determination of ⁵²Cr (Steyn, personal communication). Perchloric acid is not normally used when determining Cr by ICP-MS. Therefore the values presented in the two tables and figures are not reliable and the data of very little value.

TABLE 2.5. Chromium content of limes and amounts of lime and Cr added per pot.

Lime no	Rate	Cr Content of Lime (mg.kg ⁻¹)	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg ⁻¹)
2	1	514.82* (1263.90)**	6.89	4.10	1.16
	2		17.59	10.60	2.96
	3		28.30	17.00	4.77
3	1	510.18 (1077.80)	5.41	3.20	0.78
	2		13.81	8.30	1.98
	3		22.22	13.30	3.19
4	1	192.81	3.60	2.20	0.09
	2		9.20	5.50	0.24
	3		14.80	8.90	0.38
6	1	518.26 (1180.10)	5.91	3.50	0.93
	2		15.09	9.10	2.37
	3		24.26	14.60	3.82
7 (Control)	1	8.64	3.79	2.30	0.00
	2		9.68	5.80	0.01
	3		15.56	9.30	0.02
9	1	10.09 (20.81)	5.47	3.30	0.02
	2		13.97	8.40	0.04
	3		22.47	13.50	0.06
10	1	4.74 (15.04)	7.30	4.40	0.01
	2		18.65	11.20	0.04
	3		30.00	18.00	0.06
11	1	264.28 (257.07)	3.70	2.20	0.13
	2		9.45	5.70	0.32
	3		15.21	9.10	0.52
12	1	336.45	8.70	5.20	0.39
	2		22.21	13.30	1.00
	3		35.73	21.50	1.60

* Semi-quantitative determination by ICP MS-scan

** Quantitative determination by ICP MS

TABLE 2.6. Chromium content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	First Cr Analysis (mg.kg^{-1})	Second Cr Analysis (mg.kg^{-1})	pH
2	1	5.2	21.8	10.7	6.05
	2	8.86	21.9	10.4	7.27
	3	10.67	23.6	9.5	7.88
3	1	5.93	26.0	10.5	6.33
	2	6.42	24.7	11.4	7.42
	3	9.26	21.8	10.8	7.61
4	1	5.68	23.2	-	6.05
	2	9.16	20.9	-	6.55
	3	9.38	19.6	-	7.34
6	1	5.19	19.9	8.9	6.22
	2	7.35	20.3	8.3	7.18
	3	7.2	21.9	10.4	7.60
7 (Control)	1	8.33	21.8	7.2	6.19
	2	12.84	19.5	7.4	7.02
	3	14.66	21.8	7.5	7.86
9	1	5.98	20.8	6.9	6.37
	2	9.32	20.7	9.2	6.95
	3	9.94	20.0	7.3	7.43
10	1	5.5	22.5	-	6.25
	2	7.44	21.6	-	6.79
	3	11.04	21.8	-	7.21
11	1	5.51	19.9	-	5.91
	2	8.03	24.3	-	6.78
	3	9.79	18.4	-	7.27
12	1	3.19	18.8	-	6.12
	2	8.75	20.5	-	6.78
	3	9.66	21.5	-	7.60

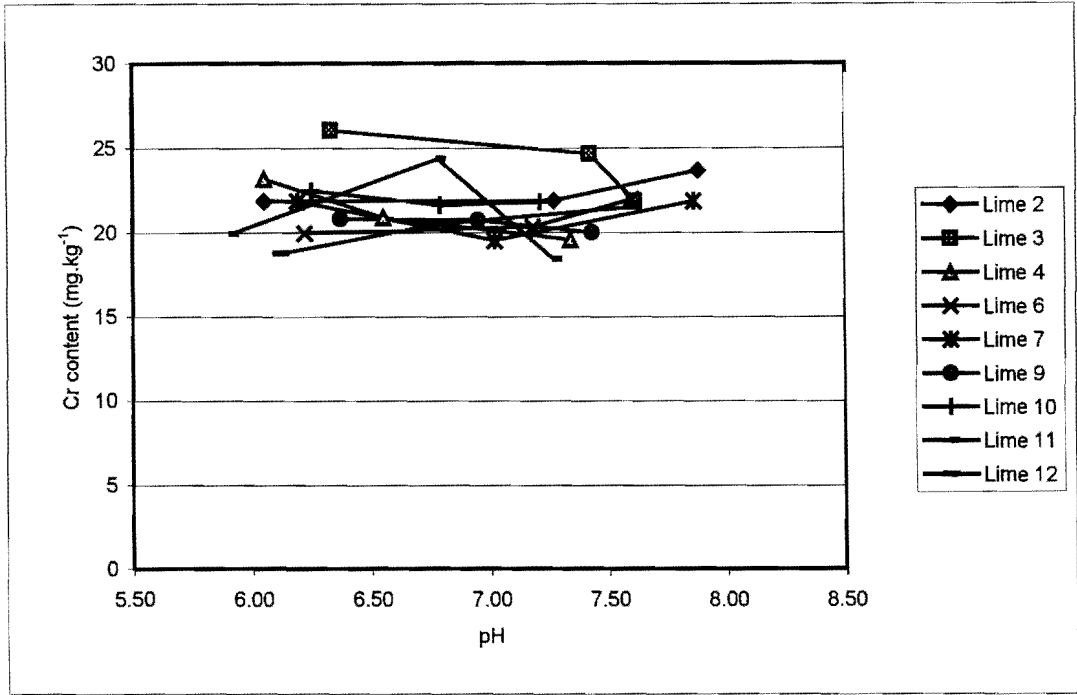


Figure 2.1. Cr content of spinach leaves for each lime at the average pH value.

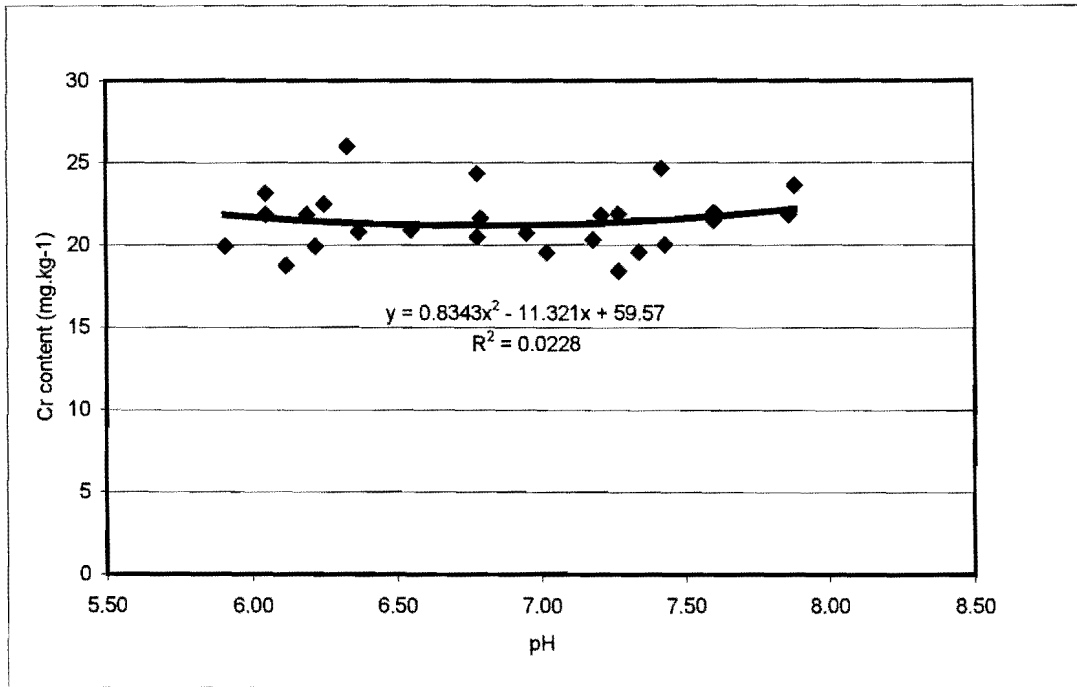


Figure 2.2. Trend in Cr uptake across nine limes at the average pH value.

The NH₄-EDTA extraction results on some of the soils (Table 2.7) indicate very low levels. These levels are far below the level suggested in Table 2.3 and therefore pose very little risk.

TABLE 2.7. NH₄-EDTA extraction (Cr) on soils ameliorated with Limes 2, 3, and 6, seven months after lime application.

Rate	NH ₄ -EDTA extractable Cr (mg.kg ⁻¹)		
Control	0.1754		
	Lime 2	Lime 3	Lime 6
1	0.1609	0.0771	0.0376
2	0.1832	0.0801	0.0793
3	0.3117	0.1243	0.1125

Nickel

Table 2.8 indicates the amounts of lime added to the pots to attain the desired pH, the Ni content of the limes as well as the increase in Ni concentration per pot. The values from the ICP-MS semi-quantitative scan were in some cases very close to the values of the subsequent determination (in brackets). Widely differing amounts of Ni (as calculated) was added to the soil with lime 2 the highest and lime 8 the lowest. Lime 8 therefore served as the control.

In Table 2.9 the concentration of Ni in the leaves of the spinach and deviation from the control are indicated. Figures 2.3 and 2.4 indicate the Ni concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively. Again the values are very high compared to levels of 0.3-3.5 mg.kg⁻¹ in unpolluted plants and the “reference plant” levels from Table 2.2 of 1.5 mg.kg⁻¹. Phytotoxic levels for Ni vary greatly with plant species. The levels from this study fall into the range of the values for Ni found in spinach grown on soils in India (Bhattacharjee, *et al.*, 1998) which ranged from 1 to 21 mg.kg⁻¹, but are generally above the levels found in spinach grown on sludge contaminated soil (mean of 9.46 mg.kg⁻¹) as reported by Hooda, *et al.*, (1997).

TABLE 2.8. Nickel content of limes and amounts of lime and Ni added per pot.

Lime no	Rate	Ni Content of Lime (mg.kg ⁻¹)	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg ⁻¹)
2	1	555.28* (565.63)**	6.89	4.10	0.51
	2		17.59	10.60	1.30
	3		28.30	17.00	2.10
3	1	69.37 (63.97)	5.41	3.20	0.05
	2		13.81	8.30	0.13
	3		22.22	13.30	0.21
5	1	15.05 (6.98)	6.95	4.20	0.01
	2		17.74	10.70	0.04
	3		28.54	17.10	0.06
6	1	72.19 (70.83)	5.91	3.50	0.06
	2		15.09	9.10	0.15
	3		24.26	14.60	0.23
8 (Control)	1	13.81 (1.62)	7.43	4.50	0.01
	2		18.98	11.40	0.03
	3		30.52	18.30	0.06
11	1	47.79	3.70	2.20	0.02
	2		9.45	5.70	0.06
	3		15.21	9.10	0.10
12	1	69.34	8.70	5.20	0.08
	2		22.21	13.30	0.21
	3		35.73	21.50	0.33

* Semi-quantitative determination by ICP MS-scan

** Quantitative determination by ICP MS

TABLE 2.9. Nickel content (mg.kg⁻¹) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Ni (mg.kg ⁻¹)	Minus control (mg.kg ⁻¹)	pH
2	1	5.2	10.95	-2.18	6.05
	2	8.86	10.23	-1.13	7.27
	3	10.67	10.61	0.41	7.88
3	1	5.93	14.24	1.11	6.33
	2	6.42	12.81	1.45	7.42
	3	9.26	10.97	0.77	7.61
5	1	6.16	12.23	-0.90	6.15
	2	6.89	12.47	1.11	7.11
	3	8.49	10.10	-0.10	7.54
6	1	5.19	13.05	-0.08	6.22
	2	7.35	11.65	0.29	7.18
	3	7.2	11.72	1.52	7.60
8 (Control)	1	3.26	13.13	0	6.58
	2	6.85	11.36	0	7.18
	3	7.94	10.20	0	7.53
11	1	5.51	13.00	-0.13	5.91
	2	8.03	13.33	1.97	6.78
	3	9.79	8.21	-1.99	7.27
12	1	3.19	12.18	-0.95	6.12
	2	8.75	13.09	1.73	6.78
	3	9.66	9.76	-0.44	7.60

The relatively high levels could be ascribed to the fact that the spinach did not perform well in the pots (unlike the wheat) (Appendix 6). This could have contributed to elevated levels in the plants and could confirm the statement by Jones and Jarvis (1981) citing many studies that uptake of heavy metals in pots is often exaggerated.

The variation in the values for the Ni-content of spinach indicates that all the values are rather close and that there is no discernable trend with respect to a specific lime leading to a higher uptake. Rather, all the limes seemed to perform similarly with the Ni uptake being a function of the pH.

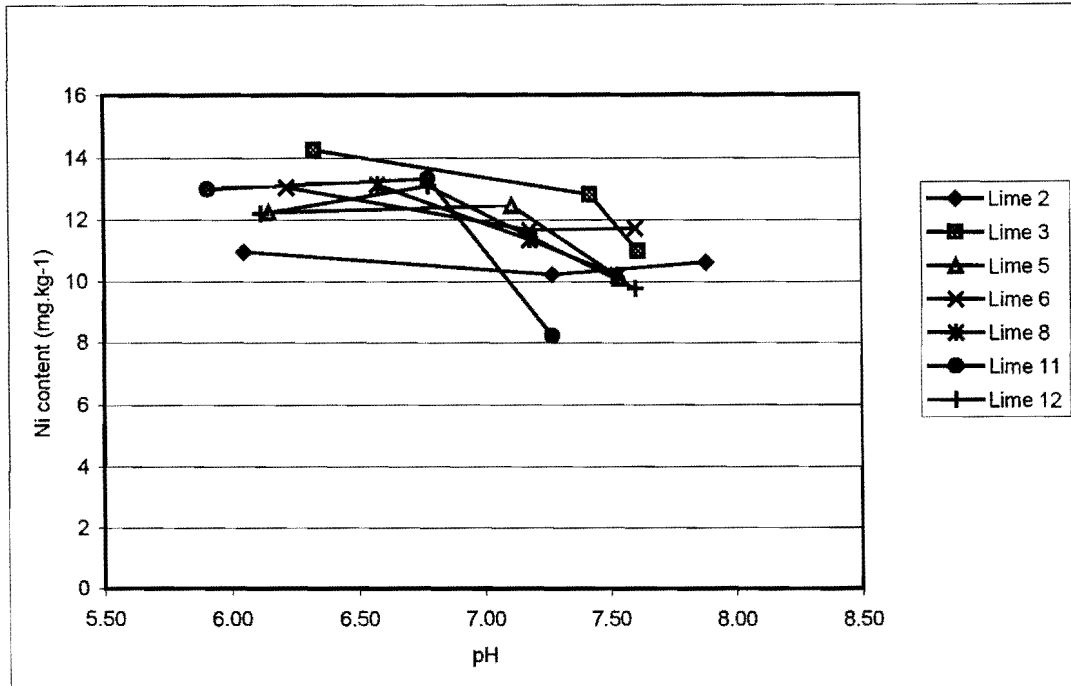


Figure 2.3. Ni content of spinach leaves for each lime at the average pH value.

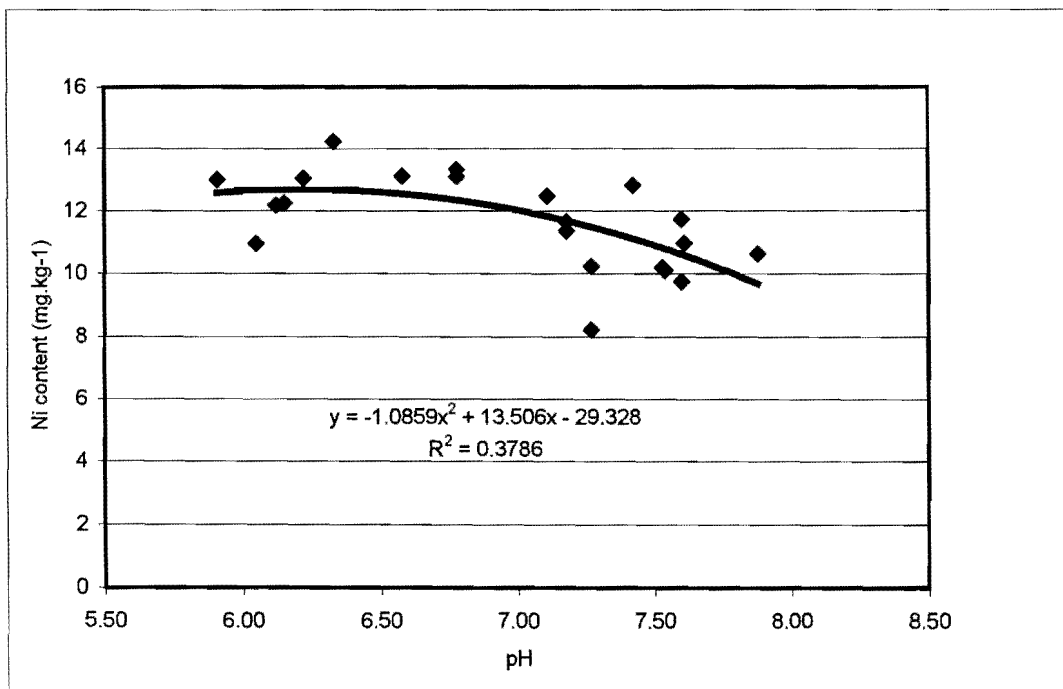


Figure 2.4. Trend in Ni uptake across nine limes at the average pH value.

No Ni was detected in the NH₄-EDTA extraction. According to Steyn (personal communication) this is uncommon and factors other than those discussed here could have contributed to the inability to detect Ni.

Cobalt

Table 2.10 indicates the amounts of lime added to the pots to attain the desired pH, the Co content of the limes as well as the increase in Co concentration per pot. Widely differing amounts of Co was added to the soil with lime 3 the highest and lime 8 the lowest. Lime 8 therefore served as the control treatment.

TABLE 2.10. Cobalt content of limes and amounts of lime and Co added per pot.

Lime no	Rate	Co Content of Lime (mg.kg ⁻¹)	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg ⁻¹)
1	1	9.56*	5.94	3.60	0.008
	2		15.16	9.10	0.019
	3		24.38	14.60	0.031
2	1	8.56 (7.12)**	6.89	4.10	0.008
	2		17.59	10.60	0.020
	3		28.30	17.00	0.032
3	1	20.95 (18.64)	5.41	3.20	0.015
	2		13.81	8.30	0.039
	3		22.22	13.30	0.062
5	1	3.38 (3.80)	6.95	4.20	0.003
	2		17.74	10.70	0.008
	3		28.54	17.10	0.013
6	1	19.11 (19.87)	5.91	3.50	0.015
	2		15.09	9.10	0.038
	3		24.26	14.60	0.062
8 (Control)	1	3.10 (3.16)	7.43	4.50	0.003
	2		18.98	11.40	0.008
	3		30.52	18.30	0.013

* Semi-quantitative determination by ICP MS-scan

** Quantitative determination by ICP MS

The calculated concentration increase in the soil is very low, indicating a very insignificant hazard. In Table 2.11 the concentration of Co in the leaves of the spinach and deviation from the control are indicated. The levels in the leaves are very high when compared to the concentration increase due to the addition of the limes (or slags), but moderately high when compared to natural levels of 0.1-0.57 mg.kg⁻¹ and the “reference plant” levels from Table 2.2 of 0.2 mg.kg⁻¹. Values for Co compare favourably with those found in spinach grown on soils in India (Bhattacharjee, *et al.*, 1998), which ranged from 1 to 7 mg.kg⁻¹.

Figures 2.5 and 2.6 indicate the Co concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively.

TABLE 2.11. Cobalt content (mg.kg⁻¹) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Co (mg.kg ⁻¹)	Minus control (mg.kg ⁻¹)	pH
1	1	4.33	2.60	0.17	6.35
	2	4.71	1.63	0.11	6.91
	3	8.96	1.40	-0.01	7.29
2	1	5.2	2.36	-0.07	6.05
	2	8.86	1.81	0.29	7.27
	3	10.67	1.14	-0.27	7.88
3	1	5.93	2.74	0.31	6.33
	2	6.42	2.31	0.79	7.42
	3	9.26	2.34	0.93	7.61
5	1	6.16	2.60	0.17	6.15
	2	6.89	1.56	0.04	7.11
	3	8.49	1.52	0.11	7.54
6	1	5.19	2.14	-0.29	6.22
	2	7.35	1.34	-0.18	7.18
	3	7.2	1.74	0.33	7.60
8 (Control)	1	3.26	2.43	0	6.58
	2	6.85	1.52	0	7.18
	3	7.94	1.41	0	7.53

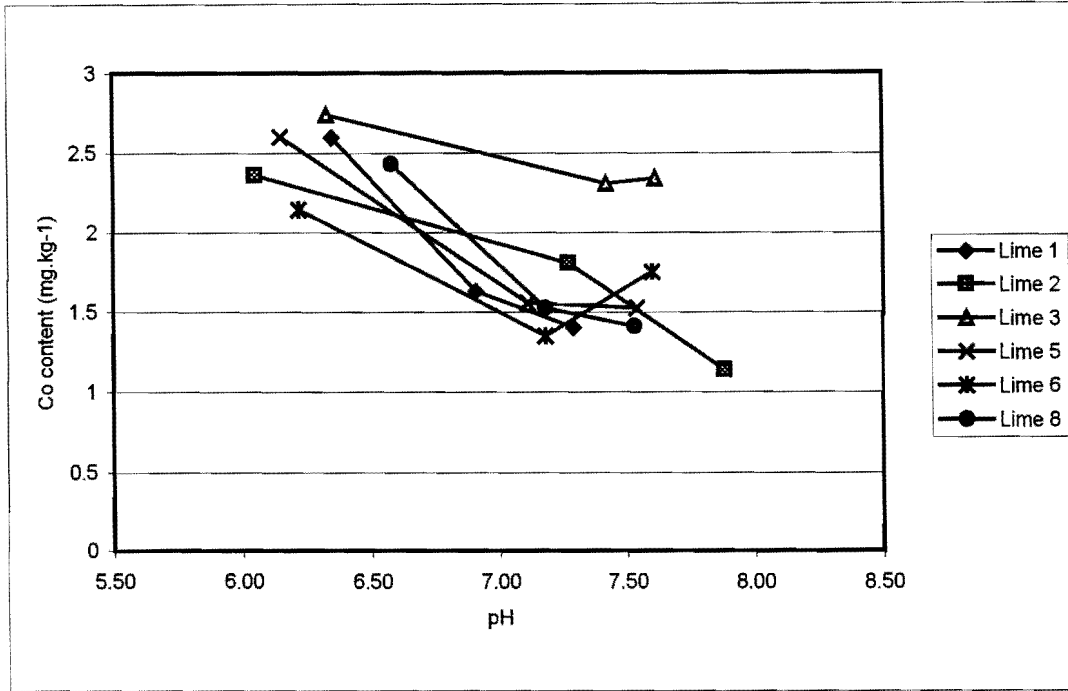


Figure 2.5. Co content of spinach leaves for each lime at the average pH value.

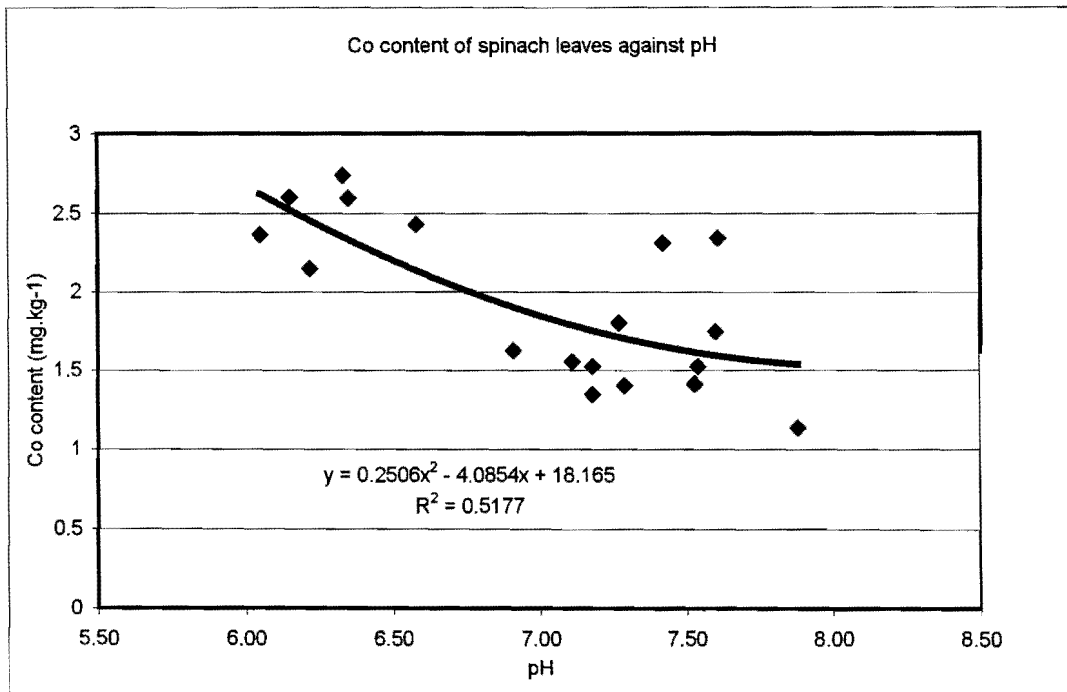


Figure 2.6. Trend in Co uptake across nine limes at the average pH value.

From Fig. 2.6 a very clear pH dependant Co uptake is discernable. The NH₄-EDTA extraction of Co (Table 2.12) of some of the soils yielded values generally two to three-fold higher than the levels in the plant. In this case it would seem that NH₄-EDTA was a relatively good indication of the amount of Co potentially available to the plant. Furthermore, these values seem to indicate a high background level in the soil, which would explain the levels in the plants when compared to the levels in the limes.

TABLE 2.12. NH₄-EDTA extraction (Co) on soil ameliorated with Limes 3 and 6, seven months after lime application.

Rate	NH ₄ -EDTA extractable Co (mg.kg ⁻¹)	
Control	3.885	
	Lime 3	Lime 6
1	3.899	4.068
2	4.203	4.333
3	4.206	4.390

The small variation in the values for the Co-content of spinach indicates that all the values are rather close and that there is no discernable trend with respect to a specific lime leading to a higher uptake.

Manganese

Table 2.13 indicates the amounts of lime added to the pots to attain the desired pH, the Mn content of some of the limes as well as the increase in Mn concentration per pot. The values from the ICP-MS semi-quantitative scan differed very substantially from the values of the subsequent determination due to the scan's inability to accurately depict levels as high as those in the limes. The scan results are not indicated. From the subsequent determinations (only four) it is clear that the limes contained very high levels of Mn.

In Table 2.14 the concentration of Mn in the leaves of the spinach is indicated. Figures 2.7 and 2.8 indicate the Mn concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively.

TABLE 2.13. Manganese content of limes and amounts of lime and Mn added per pot.

Lime no	Rate	Mn Content of Lime (mg.kg ⁻¹)	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg ⁻¹)
1	1		5.94	3.60	
	2		15.16	9.10	
	3		24.38	14.60	
2	1	8050.00	6.89	4.10	7.40
	2		17.59	10.60	18.88
	3		28.30	17.00	30.38
3	1	10450.00	5.41	3.20	7.54
	2		13.81	8.30	19.24
	3		22.22	13.30	30.96
4	1		3.60	2.20	
	2		9.20	5.50	
	3		14.80	8.90	
5	1		6.95	4.20	
	2		17.74	10.70	
	3		28.54	17.10	
6	1	6550.00	5.91	3.50	5.16
	2		15.09	9.10	13.18
	3		24.26	14.60	21.19
7	1		3.79	2.30	
	2		9.68	5.80	
	3		15.56	9.30	
8	1		7.43	4.50	
	2		18.98	11.40	
	3		30.52	18.30	
9	1		5.47	3.30	
	2		13.97	8.40	
	3		22.47	13.50	
10	1		7.30	4.40	
	2		18.65	11.20	
	3		30.00	18.00	
11	1	12800.00	3.70	2.20	6.31
	2		9.45	5.70	16.13
	3		15.21	9.10	25.96
12	1		8.70	5.20	
	2		22.21	13.30	
	3		35.73	21.50	

The values are high when compared to natural levels of 10-500 mg.kg⁻¹ and the “reference plant” levels from Table 2.2 of 200 mg.kg⁻¹. The levels fall into the top end of the range of Mn levels found in spinach grown on soils in India (Bhattacharjee, *et al.*, 1998), which ranged from 31 to 979 mg.kg⁻¹.

TABLE 2.14. Manganese content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Mn (mg.kg^{-1})	pH
1	1	4.33	915.0	6.35
	2	4.71	603.0	6.91
	3	8.96	576.0	7.29
2	1	5.2	796.5	6.05
	2	8.86	652.5	7.27
	3	10.67	535.5	7.88
3	1	5.93	990.0	6.33
	2	6.42	702.0	7.42
	3	9.26	688.5	7.61
4	1	5.68	945.0	6.05
	2	9.16	652.5	6.55
	3	9.38	454.5	7.34
5	1	6.16	900.0	6.15
	2	6.89	490.5	7.11
	3	8.49	504.0	7.54
6	1	5.19	895.5	6.22
	2	7.35	418.5	7.18
	3	7.2	535.5	7.60
7	1	8.33	1050.0	6.19
	2	12.84	733.5	7.02
	3	14.66	612.0	7.86
8	1	3.26	1110.0	6.58
	2	6.85	558.0	7.18
	3	7.94	540.0	7.53
9	1	5.98	931.5	6.37
	2	9.32	571.5	6.95
	3	9.94	702.0	7.43
10	1	5.5	886.5	6.25
	2	7.44	616.5	6.79
	3	11.04	549.0	7.21
11	1	5.51	930.0	5.91
	2	8.03	706.5	6.78
	3	9.79	630.0	7.27
12	1	3.19	886.5	6.12
	2	8.75	625.5	6.78
	3	9.66	679.5	7.60

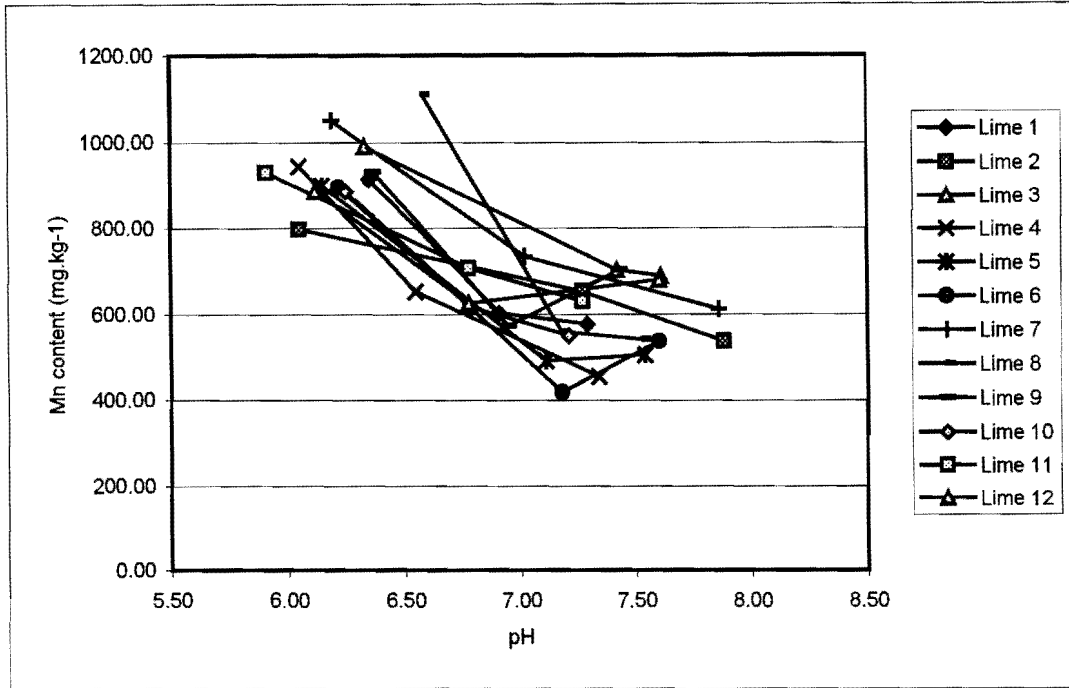


Figure 2.7. Mn content of spinach leaves for each lime at the average pH value.

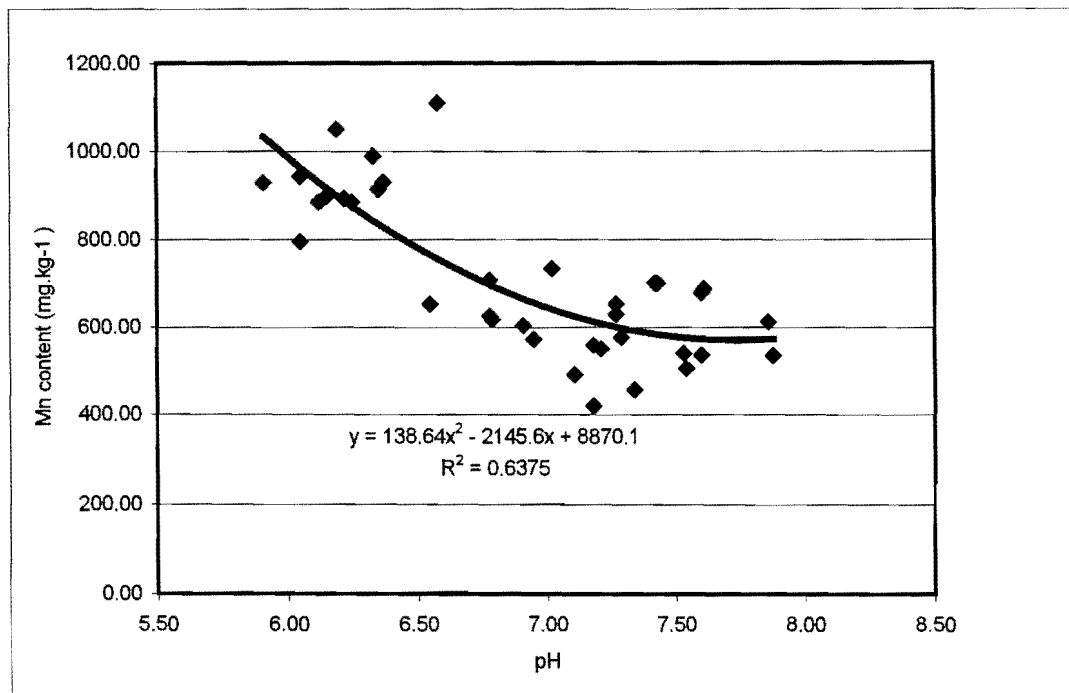


Figure 2.8. Trend in Mn uptake across nine limes at the average pH value.

The uptake of Mn was a function of pH as is seen in the clear pH trend in Fig. 2.8. As in the case of the previously discussed metals, the high concentration in the plants could be ascribed to the fact that conditions in pots exaggerate metal uptake. Again there is very little difference between the Mn concentrations of any of the plants grown on the different limes, which indicate that the Mn taken up must be from a background source and not the limes.

Other Heavy Metals

The spinach was also tested for other metals but these were not included in the study. These metals are Zn, Cu, Mo, and Ba, and their results are listed in Appendix 2.

CONCLUSION

Although the heavy metal levels in the spinach were relatively high in absolute terms, these high levels are ascribed to other factors than the metal content of the limes. The main factor being the effect of plants grown in pots and the possible exaggerated uptake of the metals.

In relative terms the values indicate small variation between high and low metal content limes, which would seem to indicate that there is no greater risk in using slags than using ordinary limes. The immediate risk concerning metal uptake from applied slags is therefore deemed to be low.

Differences between limes in terms of heavy metal uptake were also amplified in the same manner as the absolute heavy metal values were amplified by pot conditions, It is very probable that what seems to be large differences in some cases could in effect be very small differences in field conditions. This aspect would best be studied in more detail.

In most of the cases the metal concentration in the spinach decreased with increasing pH, as was expected from the literature.

Although the speciation of Cr has not been addressed in this study, it is of critical importance that the slags be tested with respect to the dominant species in soils after slag application. The toxicities of the two Cr species differ quite substantially, therefore speciation is important when referring to absolute concentrations.

Levels of the metals in the limes, although not posing an immediate threat, could become hazardous when large amounts of a specific slag is applied over a long period of time. As long as the soil's pH remains within relatively neutral boundaries, the metals will pose no threat. This situation could change when the soil is left to acidify or when it is acidified artificially through cultivation without further adequate lime inputs. Safe levels of metals in slags or liming materials should be determined by taking into account the natural acidity of the soils they are applied to, to prevent excessive application to soils that could acidify naturally to pH levels that could pose a hazard in metal bioavailability. This aspect definitely deserves further study.

The effect of growing plants in pots and the exaggerated uptake of metals could have contributed to the high levels found in the plants. The making of conclusions concerning heavy metal levels in plants grown in pots should therefore be done with the utmost care. A proper control treatment is an absolute necessity to assist in the making of sound deductions. The results gained from this study, however, could be compared meaningfully due to the difference between the limes in terms of their heavy metal composition as well as similarity in terms of their effect on pH of the soil.

Although EDTA has been suggested as an extractant that gives a good indication of the metals that are potentially plant available in soils, it would not seem to be the case in soils in pots for the elements tested.