

**ALKALINE HUMIC SUBSTANCES AND THE AMELIORATION OF
AN ACID SULPHATE SOIL AND COPPER-CONTAMINATED MINE TAILINGS**

BY

KELLY ANN SENKIW

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Soil Science
The University of Manitoba
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ABSTRACT

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Soil obtained from the Keld Series is acidic and its B horizon demonstrates acid sulphate soil characteristics and high levels of exchangeable aluminum. In addition, mine tailings from an abandoned gold mining site were found to be hazardous to the surrounding environment due to high acidity and often toxic levels of heavy metals.

Liming is the conventional method of improving acid soils by addition of acid-consuming material such as calcium carbonate. A new product, an alkaline humic substances extract (HS) from the waste material of coal mining, was produced and made available. Its use as an organic amendment for acid degraded lands was assessed in comparison to calcium carbonate.

Three laboratory studies were completed. The first was an evaluation of the acidity of the Keld Series soil by determination of its lime requirement. The Ah and Bmg horizons have $\text{pH}_{\text{H}_2\text{O}}$ of 5.0 and 3.9, respectively. Two methods were used and three lime requirements were calculated for each horizon. The buffer method accompanied by the conventional calculation of lime requirement, and the titration with strong base yielded similar results. The average of these two lime requirements for the soil from the Ah and Bmg horizons were 8.6 and 19.76 g $\text{CaCO}_3 \cdot \text{kg}^{-1}$, respectively, and these rates were used in the subsequent study.

The second study was a 9-week incubation of soil from the Ah and Bmg horizons of the Keld Series Pedon. The soils were amended with two treatments, alkaline humic substances and

lime. Titrations of soil versus the alkaline HS (liquid suspension) were completed to determine the rate of addition of the organic amendment. The Ah horizon received one application of HS, whereas the Bmg horizon received split applications of HS to avoid inundation.

The lime was most effective at increasing the pH and exchangeable calcium in soil from both horizons. Lime and HS both reduced the total acidity in both horizons compared to the control. The alkaline HS had little effect on the exchangeable calcium and magnesium cations in both horizons. The HS amendment resulted in a slightly depressed soil organic carbon content (SOC) in the Ah horizon, but the CEC was unaffected. In HS-treated soil from the Bmg horizon, the SOC was doubled to 2.1% and CEC was increased by $8.0 \text{ cmols (+)} \cdot \text{kg}^{-1}$. The lime and HS amendments both reduced NH_4OAc -exchangeable Al in the Bmg horizon from $106.8 \text{ mg} \cdot \text{kg}^{-1}$ to zero, by Day 21 of the incubation. The Al extractable by $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ CaCl}_2$, which is an estimate of plant-available Al, was $22.7 \text{ mg} \cdot \text{kg}^{-1}$ in the lime-amended soil and $13.5 \text{ mg} \cdot \text{kg}^{-1}$ in the HS-amended soil after 63 days, relative to $150 \text{ mg} \cdot \text{kg}^{-1}$ in the control.

Finally, the alkaline HS extract was applied to acid, copper-contaminated mine tailings. The total copper content of the tailings was above $2000 \text{ mg} \cdot \text{kg}^{-1}$, approximately a third of which was in the water-soluble and exchangeable forms. Lime produced the highest increase in pH. The alkaline HS raised the pH of the tailings and altered the distribution of copper among six fractions; the free, toxic copper pool was greatly reduced and was redistributed to more tightly-bound and plant-unavailable pools such as organically-bound and precipitated fractions. These observations were more pronounced when the humic substances were added in combination with wheat straw.

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I dedicate this thesis to my parents.

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1. INTRODUCTION

The earthen materials found above coal seams in a mine are generally termed overburden. The layer found directly above a coal seam, lignite, is derived from very old plant and animal matter. This material contains large amounts of organic carbon, and therefore may be useful as an amendment to soils that have been degraded or have low fertility. Examinations of the oxidized lignite collected from coal mines in Northern Alberta by Luscar Ltd. have shown the presence of large organic molecular compounds that resemble soil humic substances (mainly the fulvic and humic acids) in their complexity. Some preliminary investigations into the use of the lignite as a soil amendment found that the materials were ineffective in altering soil physical properties because they were insoluble and inert (Shaykewich 2000). Subsequent laboratory testing was undertaken to extract an active portion of the organic materials and their (chemically active) charged functional groups. A process to obtain such an extract, herein termed alkaline humic substances (HS), was developed by Luscar, Ltd. The resulting product was a liquid suspension of colloidal organic material, with a pH of 10.5. The research described herein was prompted by the question: what is the potential of this active HS extract to improve degraded soils?

Soil organic matter (SOM) has been investigated for many years. SOM is of great interest to researchers because of its demonstrated abilities to improve many aspects of a soil's chemical, physical, and biological properties. Organic matter acts as a binding material in soil aggregation and improves soil structure. Humic substances contain many surface functional

groups that contribute to the cation exchange capacity of soils. The charged functional groups also contribute to soil fertility by attracting and holding essential nutrients and micronutrients. Also, the SOM itself is an energy source for soil organisms and plants. The internationally accepted procedure for extraction of soil humic substances from SOM involves fractionation by solubility in alkali and acid. The HS obtained from leonardite for this study was extracted in a similar manner. It must be noted that the extract is not, and does not contain, soil humic substances. However, the alkaline extract of HS may be a desirable organic amendment if the humic substances benefit the soil environment as SOM is known to do.

A small area of western Manitoba is dominated by an acid sulphate (AS) soil. The Keld Series soil has developed on pyritic shales. The A horizon has a pH of approximately 5.0, while the B horizon has a pH of 3.5. Despite having a thick, dark A horizon, these lands are not very productive because of their low pH, and accompanying Al and Mn toxicity. The amount and kinds of acidity vary in soils. This is usually divided into active, i.e. free protonic acidity, and reserve acidity comprising exchangeable hexa-aquoaluminum, $\text{Al}^{3+} \cdot 6\text{H}_2\text{O}$, and even more stable and fixed hydroxy-Al forms.

Soil acidity is commonly alleviated by applying liming materials, which act to increase the pH to within the ideal range of 6 – 7.5. However, an inherent property of AS soils is the generation of sulphuric acid upon oxidation of pyritic minerals. Thus, liming is a long-term solution to raise the pH, but repeat applications of lime are necessary each time the previous addition is neutralized. An alkaline HS extract has the potential to act as a liming agent when applied to the soil, with the additional benefits of supplementing organic carbon and nutrient levels. The HS may also sustain the increased pH for a longer time than conventional liming, thereby reducing the need for repeated applications of the amendment.

In order for a new technology or amendment to be accepted as beneficial for acidic soil reclamation, several points have to be observed. The products have to be affordable, available, and must alleviate the pH. Furthermore, the product should immobilize Al^{3+} , or otherwise render this potentially toxic element non plant-available. When other harmful heavy metals can also be immobilized, the product would indeed be promising as an amendment. The product itself should not be phytotoxic. Lastly, if it could contribute to the soil condition via adding organic matter, and improving the vigour of beneficial microbial activity, for example, this would be an additional advantage.

Several closed mines are located within Nopiming Provincial Park in Manitoba. The land surfaces at the site of the Central Manitoba Mine are covered by coarse mine waste materials that contain high amounts of heavy metals (Renault et al. 2000). The pH of the tailings varies from 4 to 8. The sample of acid mine tailings used in this study had a pH of 3.45 and average copper content of $2300 \text{ mg Cu kg}^{-1}$. In low-pH portions of the tailings, much of the copper is in a highly labile form and is potentially toxic to plants. This is evidenced by the very sparse natural revegetation of the mine tailings that have lain undisturbed for over 70 years. Any reduction of the toxic forms of copper within the acidic tailings may improve the environment to the point where revegetation is possible. The alkaline HS amendment may help to achieve this in several ways. Any increase of pH would reduce the amount of soluble or free copper in the tailings by precipitation, complexation, or redistribution into chemical forms that are less bioavailable (Sims 1986; Alva et al. 2000). Additionally, free copper could be removed from solution by complexation reactions with the functional groups of the organic amendment. Finally, the organic amendment itself is an energy source for soil microorganisms. The potential boost in

biological activity will further improve the tailings' suitability to support growth by improving both physical and chemical aspects of the environment.

The layer of overburden above coal seams is a highly organic material. Chemically-active HS can be extracted from this inert material through a process of chemical modification. When used as an amendment to low-quality soils, the HS may offer some of the same, extremely valuable, benefits that natural SOM confers upon soils. The laboratory studies herein were initiated to investigate the ability of the alkaline HS extract to ameliorate the adverse chemical conditions of two acid soils. Chapter Three describes the assessment of acidity in the top two horizons of the Keld Series Soil. Two methods were used to determine the lime requirements of the soil horizons. The subsequent study reports the results of a laboratory incubation, where alkaline HS and lime amendments were applied to the Keld Soil, and selected chemical properties of the soil horizons were monitored. Specifically, the objectives were to raise the pH, and eliminate or reduce the amount of free aluminum in the Keld Series acid sulphate soil. The investigations were extended to include other earthen materials. In Chapter 5, copper-contaminated mine tailings were amended with alkaline HS, fresh wheat straw, a combination of HS and wheat straw, and lime. After 24 weeks of incubation, the tailings were analysed to determine the effects of the amendments on the distribution of copper, and to assess the potential lability of the copper.

2. LITERATURE REVIEW

This review will concentrate on the amelioration of acidic lands, as defined by an increase of soil pH and reduction of the associated toxicities of metals. Liming is the conventional method of alleviating the low pH and associated metal toxicities encountered in acidic soils and is usually conducted using agricultural lime or calcium carbonate. However, there exists a large volume of organically-rich lignite from coal mines, which may be useful an amendment for degraded soils. The oxidized lignite, termed leonardite, is available and contains humic substances that can be chemically extracted and formulated into an alkaline suspension.

2.1 Leonardite from Coal Mining

Lignite, a decomposed organic material, is a low-grade coal. One type of oxidized lignite that is found above coal seams is termed leonardite. Leonardite cannot be used as fuel and is usually stored on-site as waste piles. Leonardite contains a higher amount of carboxylic acid groups than lignite (O'Donnell 1973). Lignites are rich in organic carbon, and usually have high C/N ratios (El-Abedine and Hosny 1982).

Lignite and leonardite, in unaltered and modified forms, have been used as a soil amendment in attempts to improve soil physical or chemical properties (El-Abedine and Hosny 1982; Gati 1982; Lobartini et al. 1992; Whiteley and Williams 1993; Shaykewich 2000), such as to increase organic matter, ameliorate soil acidity, remediate mine spoils, and improve plant

growth and yield. These investigations were often inconclusive. For example, the addition of lignite was shown to increase cation exchange capacity (CEC), and soil organic matter content (SOM) (El-Abedine and Hosny 1982), but lignite has been shown to be resistant to microbial degradation (El-Abedine and Hosny 1982). It therefore persists in the soil. Whiteley and Pettit (1994) reported that the addition of colloidal humic substances from lignite suppressed the microbial decomposition of wheat straw.

Recent attempts at using leonardite for agricultural purposes did not show any increase in crop yield (Shaykewich 2000; Dilk 2002). Further to those investigations, it was discovered that leonardite contains moieties of humic substances that could be extracted (personal communication, Tee Boon Goh, Professor, Dept. of Soil Science, The University of Manitoba). Thus, an alkaline extract of leonardite powder, containing humic substances (HS), was made available for evaluation as an amendment for degraded acidic soils. There is no published literature on the chemical extraction process used, but some proprietary data is available that documents that the commercial alkaline HS contains fulvic- and humic-acid-like substances.

Evaluations of some commercial humic substances have been documented by Malcolm and MacCarthy (1986) and Lobartini et al. (1992). Bailey and Lawson (1965) found similar functional groups in humic acids (HAs) extracted from lignite and soil organic matter (as cited by Whiteley 1993). Ayuso et al. (1997) performed chemical and spectroscopic analyses on humic acids from organic wastes, leonardite (at pH = 3.20) and peat. The more humified materials, specifically leonardite and peat, are more oxidized and contain higher aromaticity, and lower amounts of nitrogen compounds than the organic wastes. The total acidity was higher in the more decomposed leonardite, peat and commercial HA samples, and with more carboxylic groups than phenolic groups. The peat, leonardite and commercial HAs displayed more

homogeneity in molecular weight fractions, with greater amounts in the intermediate range (Ayuso et al. 1997). Malcolm and MacCarthy (1986) concluded that the commercial HAs they examined were similar to leonardite humic acid. They also noted that commercial humic substances should not be used in experiments as substitutes for natural soil humic substances.

The alkaline HS used here, provided by Luscar Ltd., is not natural soil humus or organic matter but its performance and function when added to degraded soils should be evaluated in light of known beneficial effects of humus, as reported in the following sections.

2.2 Soil Organic Matter and Humic Substances

There are many definitions pertaining to soil organic matter and its components. Humus is defined by Stevenson (1982) as, “the total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their ‘partial decomposition’ products, and the soil (living) biomass”. He employs humus and soil organic matter synonymously. Alternately, some authors include living biomass (microorganisms and living plant and animal tissues) in their definitions of soil organic matter (Brady and Weil 1996). They further defined humus as “the amorphous and colloidal mixture of complex organic substances no longer recognizable as plant tissues”.

Humus contains a wide variety of complex compounds, and can be divided into two categories: humic substances and nonhumic substances. The humic substances are dark-coloured substances with relatively high molecular weights. In the soil, plant residues and complex compounds are decomposed by soil organisms. The resultant smaller compounds are used by microorganisms, and polymerized into larger and more complex chemical structures (Brady and Weil 1996). These structures interact with other compounds in the soil (*i.e.* nonhumic

substances) to produce stable, resistant humic substances. Nonhumic substances are compounds produced by microorganisms that can be biochemically classified, such as carbohydrates, amino acids, fats, organic acids, etc. (Stevenson 1982; Brady and Weil 1996).

Humic substances can be further subdivided based on their solubility in acids and bases. The groupings are termed humin, humic acids, and fulvic acids. Humic acids contain more carbon and less oxygen than fulvic acids. The molecular weights of humic and fulvic acids range from a few hundred to 300 000 (Schnitzer and Khan 1972). Humic and fulvic acids are heterogenous in size and structure. They are colloidal, i.e. very small in size, with relatively large surface areas. The conformation of humic molecules is generally considered to be long-chain, coiled molecules, although the shape may change slightly due to pH and ionic strength changes (Stevenson 1982). A variety of extractants have been used to isolate humic substances from soils. They include strong bases, neutral salts, and organic chelates, among others. The percentage of organic matter extracted ranges from 20 to 80%, with the strong bases extracting up to 80%. It is difficult to isolate humic substances because they may be intimately complexed with nonhumic substances or clay particles, or may be altered by the reagent.

Humus is often treated with NaOH or $\text{Na}_4\text{P}_2\text{O}_7$ to extract humic polymers from the soil (Schnitzer 1982). The extract obtained can then be fractionated based on its solubility. Three major fractions are obtained: humin, insoluble in alkali; humic acid, soluble in alkali, insoluble in acid; and fulvic acid, soluble in alkali, soluble in acid. These fractions can further be purified.

2.2.1 General Characteristics of Humus

Organic matter is dynamic, meaning that compounds are constantly being degraded and synthesized by microorganisms within the soil environment. The amount of organic matter at a

steady-state equilibrium in a soil depends upon the five soil forming factors: climate, time, vegetation, parent material, and topography (Stevenson 1982). Some portions of organic residues are easily decomposed. There are also resistant fractions of organic matter that remain in the soil for hundreds to thousands of years. The stability of separated humus components varies as well. The humin and humic substances fractions are approximately equal in stability, while the fulvic acid portion is less stable (Stevenson 1982). Therefore, humic substances are almost ubiquitous on the surface of the Earth. They occur in soils, natural waters, composts, sediments, peatlands, lignites, brown coals, and elsewhere (Stevenson 1982).

2.2.2 Roles of Humus and Humic Substances in Soils

Organic matter performs many roles in the soil. It promotes physical properties such as soil tilth and water retention by facilitating aggregation and thus improving structure. The large surface areas of humic substances contribute to the cation exchange capacity, allowing more nutrients to be held in positions where they are available to organisms. Micronutrient-organic matter complexes may also benefit plant growth. The ability of a soil to buffer pH changes is improved by organic matter. As organic matter is degraded, more nutrients such as nitrogen, phosphorus and sulphur are released and accessible to plants. Soil organisms also use organic matter as a carbon source.

The presence of reactive functional groups, mainly aliphatic and aromatic alcohol and carboxyls, on the surfaces of humic molecules permits chemical bonding reactions to occur (Schnitzer and Skinner 1965). Humic molecules may be linked to each other, to nonhumic compounds, or to the surfaces of clay particles.

In addition, humic and fulvic acids are capable of chelating metals. Mortensen (1963) presented much evidence to support the metal complexing ability of soil organic matter in his classic review paper. The oxygen-containing functional groups of humic substances, especially the -OH and -COOH groups on aromatic rings, provide sites for bonding and chelation (Schnitzer and Skinner 1965). A hydrated aluminum ion can bind to humic substances via a water bridge, electrostatic attraction, formation of a coordinate bond with one functional group, or formation of a bond with more than one functional group (chelation). The latter two bonds are the strongest (Sposito 1989).

A hydrated aluminum ion can act as a link between humic polymers, if the oxygen atoms are shared between the aluminum and humate. Aluminum can also connect a humic molecule and a clay particle or an oxide, again by sharing oxygens. These reactions are pH-dependent. The organic matter-aluminum complexes can be soluble or insoluble (Schnitzer and Skinner 1964). Humate-aluminum complexes are more likely to precipitate due to their high molecular weight (Sposito 1989).

2.3 Acidity in Soils

Soil acidity or alkalinity is indicated by pH, the negative logarithm of proton activity in an aqueous solution. Generally, soils with pHs between 6 and 7.5 are considered optimal for plant growth, since within this range, all essential nutrients are plant-available (Brady and Weil 1996).

McBride (1994) delineated four types of acidity: reserve, non-exchangeable, exchangeable, and active. The reserve acidity is a large pool, and is defined as all titratable

acidity from the solid phase. It is the sum of exchangeable and non-exchangeable acidity. Non-exchangeable acidity is the bound H and Al that can not be replaced by a neutral salt extractant like 1.0 M KCl. Non-exchangeable acidity is provided by hydrolysis of weak acids on organic matter, organically complexed Al, Al polymers in partially chloritized clays, and hydroxy-Al or -Fe oxides. The acidity that can be displaced by a neutral salt is termed the exchangeable acidity (Thomas and Hargrove 1984). Cation exchange, organically complexed Al, adsorbed Al^{3+} , and easily dissociated acid functional groups on organic matter contribute to exchangeable acidity. Finally, active acidity is associated with the solution phase, and is comprised of free Al^{3+} and H^+ ions. Total (titratable) soil acidity is the sum of active and reserve acidity. The quantity of reserve acidity greatly exceeds active acidity within soils (Brady and Weil 1996).

All soil components that constitute the reserve acidity also contribute to natural soil buffering ability by resisting changes in pH. Oxides of Al & Fe, Al-organic complexes, soluble Al, and clays buffer a change in pH by consuming or releasing protons (Sposito 1989). At soil pH below 5.5, dissolution of aluminosilicate clays and Al-oxides occurs. These events release monomeric Al^{3+} and hydroxy aluminum into solution. Then, the two products can either adsorb to the exchange complex and liberate base cations, or undergo hydrolysis below pH 5. Soluble, monomeric Al^{3+} is the most toxic form, and occurs at pHs below 4 (Figure 2.1). Acidity is also produced if Al^{3+} undergoes polymerization by forming hydroxyl bridges (Hsu 1989).

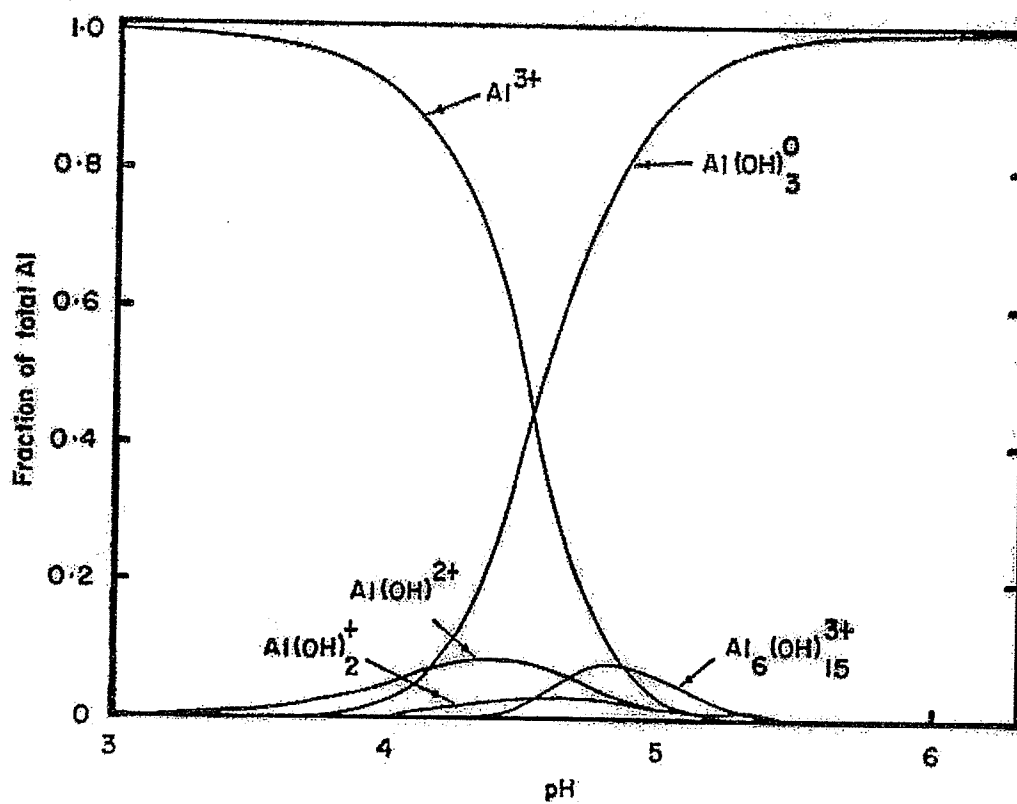
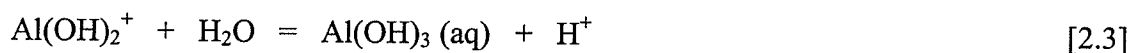


Figure 2.1 The fraction of Al present in each hydrolysis species as a function of solution pH. (Dalal, 1975).

2.3.1 Acidity and Aluminum Chemistry

There is no doubt that aluminum chemistry is of overriding importance in acid soils of pH less than 5.0 (Jackson 1963; Schwertmann and Jackson 1964; Thomas and Hargrove 1984). Large amounts of exchangeable H^+ do not occur in acid soils. As protons are adsorbed onto the exchange complex, they begin to attack the mineral. The proton is consumed in the production of a H_2O molecule, and is accompanied by the release of soluble Al^{3+} (Jackson 1963). The aluminum ion may then be strongly adsorbed, or, the hydrolysis of the free aluminum cation (Al^{3+}) further acidifies the soil solution (Thomas and Hargrove 1984; Bohn et al. 1985) (Equations 2.1, 2.2, and 2.3).



The many possible fates of aluminum within soil contribute to the complexities of studying aluminum and its reactions in a soil matrix. Aluminum is present in soil solution in different chemical forms, from $Al^{3+} \cdot 6H_2O$ (conveniently, Al^{3+}), which is the most toxic, to polynuclear, precipitated and chelated compounds, depending upon the pH (Jackson 1963; Sawhney 1968; Barnhisel and Bertsch 1982; Goh and Huang 1984). Consequently, the solubility and thus toxicity of aluminum varies.

Aluminum hydroxy complexes present in the interlayers of 2:1 expansible clays can be solubilized in acidic soil but are not as toxic to plants and organisms as monomeric Al^{3+} (James et al. 1983; Di Pascale and Violante 1986). Aluminum may also form complexes with various ligands. Ligands such as fluoride, oxalate, citrate, and fulvic acid increase the solubility of Al. Those that decrease the solubility of Al are phosphate, sulphate, hydroxyl and polymeric silicate (McBride 1994).

2.3.2 Acid Sulphate Soils

Acid sulphate soils are found throughout the world, mostly concentrated along coastal areas of the tropics. Some acid sulphate soils have been discovered in upland areas such as Texas (Carson and Dixon 1983), Maryland (Wagner et al. 1982) and Canada. The occurrence of acid sulphate soils across Canada, including the Keld Series soil of Manitoba, has been documented repeatedly (Ehrlich et al. 1959; Clark et al. 1961; Pawluk 1971; Ross and Ivarson 1981). The acid sulphate soils of Saskatchewan and Manitoba have formed on Cretaceous marine shales that contain iron sulfides (Mermut et al. 1985; Ross et al. 1988). The shale is overlain and mixed with glacial till, which in some areas has been completely consumed by the soil acidity.

Acid sulphate soils can be recognized by a low pH (between 3 and 4) and the presence of basic ferric sulphates such as jarosite (van Breemen 1982). The presence of *Thiobacillus ferrooxidans*, an iron oxidizing microorganism, may also signal an acid sulphate soil.

A newly drained pyritic soil is termed a raw acid sulphate soil according to Dent and Pons (1995). The acid generated inhibits rooting and the soil remains strongly acid. These soils are common along coastal areas, which are subject to tidal flooding. Dent and Pons (1995) also

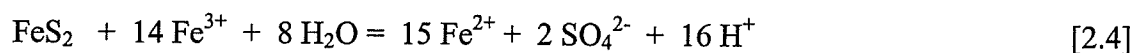
defined ripe acid sulphate soils, as those that have aged and undergone soil profile development. The soil is not regularly flooded, and the water table has dropped to below the zone of pyrite accumulation. The characteristics of these types of profiles are described as follows.

The bottom of the profile consists of parent material including pyrite, under reducing conditions. This layer is coloured grey and often waterlogged. Moving upwards, pale yellow mottles of jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, are often visible in soil above the zone of active acid production. Jarosite is a basic ferric sulphate that forms in oxidized environments of pH 2 – 4 (van Breemen 1982). In acid sulphate soils of western Canada, it has been found that natrojarosite, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, is present in relatively higher proportions than jarosite (Ross and Ivarson 1981). Rust coloured mottles of goethite may also be present amongst the jarosite minerals in this ripe soil horizon. On top of this is a horizon containing red or dark mottles (ferric oxides: goethite or hematite), with a pH of approximately 4 and large amounts of exchangeable aluminum (Dent and Pons 1995). The profile is capped with a dark-coloured topsoil. As such a profile ages, the pyrite and jarosite zones will move downwards.

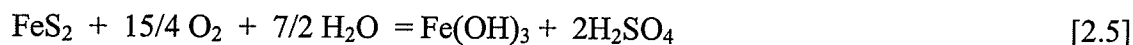
It is very important to note that pyrite-containing soils in reduced conditions have the ability to produce acid if the environment changes. These soils are termed Potential Acid Sulphate Soils, and they must be considered with as much gravity as actual Acid Sulphate Soils in any land use decisions since a simple lowering of the water table can lead to pyrite oxidation and acid sulphate soil conditions.

Three components are needed for the development of acid sulphate soils: sulphur, reducing environmental conditions to form pyrite, followed by oxidative conditions. The chemical or biological oxidation of pyrite (FeS_2) produces sulphuric acid (Bloomfield and Coulter 1973; van Breemen 1982).

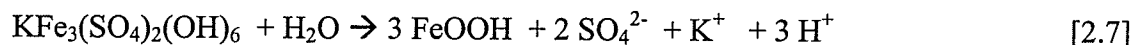
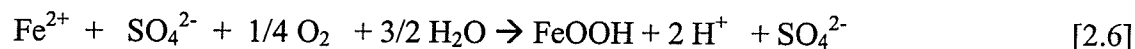
Pyrite can be chemically oxidized by oxygen, or by dissolved iron (III), the latter being the faster reaction (van Breemen 1982), as seen in Equations 2.4 and 2.5.



For each mole of pyrite oxidized, two moles of acidity are generated (Equation 2.5).



The iron from pyrite forms goethite in the soil, either directly or through jarosite (fool's gold), (van Breemen 1982), as seen in Equations 2.6 and 2.7.



If carbonates are not present to neutralize the acid, basic iron sulphates such as jarosite are formed in the soil (Bloomfield and Coulter 1973). During acid sulphate weathering, jarosite hydrolyses to gypsum, and ferric oxides (i.e. goethite) (De Kimpe and Miles 1992). These hydrolysis products are present in the zone above the jarosite in a soil profile. Sodium, magnesium, calcium, and aluminum may also form sulphates within the soil.

Depending on the soil's inherent buffering capacity, the resulting sulphuric acid may rapidly increase the acidity of the soil matrix.

2.3.3 Challenges in Management of Acid Sulphate Soils

The major problem encountered in acid sulphate soils is the extremely low pH that is caused by the sulphuric acid. Dent and Pons (1995) state that the pH of acid sulphate soils may decrease to as low as 2. This, in turn, leads to aluminum toxicity. If the parent material contains manganese, the toxicity of the solubilized Mn^{2+} is also a major problem for plant growth. Foy (1984) reviewed the physiological effects of Al^{3+} , Mn^{2+} and H^+ toxicities in acid soil. He concluded that toxicities are often due to more than one factor. In general, Al^{3+} has been reported to injure root membranes and structures, while Mn^{2+} toxicity is evident in above-ground vegetation (Foy 1984).

Strong acidity in acid sulphate soils also affects soil minerals themselves. Many authors have investigated the mineralogy of acid soils. Lynn and Whittig (1966) documented the deterioration of clay minerals in acidified sediments that had drained for 60 years. According to Barnhisel and Rotromel (1974), the sulphuric acid attacks the edges of clay minerals. Ross et al. (1988) studied the Keld Series soil, which is subject to acid sulphate conditions. They concluded that the layer silicates have undergone extensive mineral weathering, especially near the top of the profile. Similar results regarding clay mineral weathering have been published by Pawluk and Dudas (1978), Carson and Dixon (1983), and Ross et al. (1985). Weathering of silicates will release iron and aluminum to soil solution, enhancing any problems due to these metals (Pawluk and Dudas 1978).

The use of clay soils with acid generating properties as landfill covers is problematic (Fanning and Burch 1997). In addition to an increased risk of leaching of the wastes, erosion of the clay cover is also possible. Perched water in the soil above the clay layer acidifies as it moves down the side slopes of the landfill. The acid water discharges at the sides or footslope of

the landfill, and is potentially toxic to vegetation. The addition of liming materials to the topsoil covering the clay layer does not necessarily prevent acidification from occurring (Kargbo et al. 1993; Fanning and Burch 1997).

Furthermore, acid sulphate soils often have elevated salinity levels as a result of the sulphate salts produced during the oxidation of sulphidic minerals. Soil salinity can cause unfavourable environmental or agricultural conditions, depending upon the land use of the acid soils in question. Mermut and Arshad (1987) concluded that the oxidation of sulfides and the hydrolysis of natrojarosite are sources contributing to the salinity at the surface of southeastern Saskatchewan soils. Fanning and Burch (1997) described a reclamation attempt where the exclusion of tidal waters from a saline acid sulphate soil in West Africa simply exacerbated the problems of severe acidification and salinity.

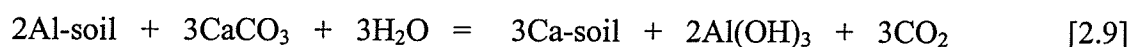
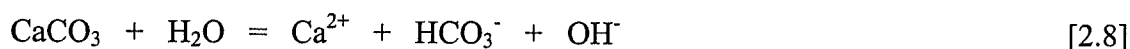
Other studies have shown that arsenic is often substituted for sulphur in pyrite, and is released upon pyrite weathering (Dudas 1984; Dudas 1987). The arsenic seems to be associated with iron released from arseno-pyrite weathering. Ross et al. (1988) reported arsenic levels of 18-25 mg kg⁻¹ in the Keld Series soil, which is approximately three times the background level of soils.

Mining is an activity that brings rock from underground to the earth's surface. If the mined material is contained in or surrounded by sulphur ores or rocks, the generation of acid often occurs upon exposure to air. Acid mine drainage has been recognized for several decades. The problem is not just the acid water, but that many heavy metals that can become soluble and mobile at low pH (Dixon et al. 1982). Barnhisel and Massey (1969) characterized some Eastern Kentucky coal mine spoils; four of the seven samples contained very high levels of iron, manganese, copper and zinc. Massey and Barnhisel (1972) continued their investigations into

these mine spoils. They concluded that, in addition to Fe, Al, and Mn toxicity, heavy metals such as Ni, Cu, and Zn must also be considered as possible barriers to revegetation in mined areas. High levels of copper, gold, and other metals were found in the geochemical analyses of some mine tailings from noble metal exploration in Manitoba (Renault et al. 2000).

2.4 Liming Acid Soils

The conventional method of raising soil pH is by adding lime to soil (McLean 1982). Common liming materials are calcite, dolomite, calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂) (Brady and Weil 1996). According to Bohn et al. (1985), the dissolution of calcium carbonate yields one hydroxyl ion in acid soils, as seen in equation 2.8. The generalized reaction of lime with an acid soil is shown in equation 2.9 (Thomas and Hargrove 1984).



Lime has a rapid effect on the soil pH, which is often stabilized within two weeks of addition (Osei 1993; Riggs et al. 1995). In leaching studies by van der Watt et al. (1991) and Noble et al. (1995), the application of calcium carbonate to acid soil increased the pH of the topsoil. However, the calcium carbonate was ineffective in improving subsoil acidity due to its low solubility. Thus, the incorporation of lime is important to ensure neutralization of acidity and reduction of Al toxicity at depth (Osei 1993).

As pH increases, the solubility of metals is reduced as the chemical forms change and precipitation occurs. For example, at pH above 5.5, exchangeable Al combines with OH^- to precipitate as gibbsite or fixed hydroxy-Al phases (Schwertmann and Jackson 1964). Evans and Kamprath (1970) reported reductions of solution Al and increases in corn yields after the addition of lime. Similarly, lime (CaCO_3) reduced KCl-extractable Al and improved soybean growth in an Al-toxic soil (Ahmad and Tan 1986). A decrease in solubility of toxic Al, Fe, and Mn will occur as the pH increases after lime addition (McLean 1982).

McLean (1982) defines the Lime requirement (LR) as the amount of lime (or other base) required to neutralize the acidity of an acid soil to a selected, more alkaline condition. A conventional laboratory determination of LR is a three-month incubation of a soil with varying amounts of lime (Alabi et al. 1986; Offiah and Fanning 1994).

Despite the fact that liming is an obvious solution to low soil pH, there are several disadvantages related to liming acid soils. Field variability in texture and pH may result in over- or under-liming the soil. Overliming may lead to deficiencies of trace elements in nutrient-poor and weakly-buffered soils (McLean 1982; Brady and Weil 1996). Repeat applications of lime to acid soils are necessary once the added amount has been neutralized. This is an even greater issue in acid sulphate soils, where acidity is being actively produced, rather than the acidity occurring solely as a result of loss of exchangeable bases from the soil. If large amounts of lime are needed, the cost can be excessive. This is especially true when there are no sources of lime nearby, and transportation must be factored into the liming costs.

2.4.1 Use of Organic Materials as Amendments for Acid Soil

Pocknee and Sumner (1997) found conflicting effects of organic matter additions on soil pH in the literature. They concluded that the ability of some organic materials to raise the pH is due to the base cations contained in the amendment. Hoyt and Turner (1975) attributed the higher pH and crop yield obtained upon addition of alfalfameal to an acid soil to the formation of Al-OM complexes. However, the effects lasted only a few months before returning to previous levels.

Schnitzer and Skinner (1963*a,b*) reported the formation of complexes between Al and OM in their investigations of the Bh horizon of a podzol soil. It has been shown that soils with high OM contents have lower Al-toxicity (Evans and Kamprath 1970; Hargrove and Thomas 1981). Additions of organic material to acid soils caused a reduction of exchangeable Al (Hoyt and Turner, 1975; Ahmad and Tan 1986).

There have been several studies investigating the use of calcium-saturated, coal-derived products to ameliorate soil acidity. van der Watt et al. (1991) applied a suspension of calcium-fulvate to the soil surface in an attempt to alleviate acidity in the subsoil. After leaching, it was reported that the product improved pH throughout the soil profile. Noble et al. (1995) examined the use of two coal-derived organic products as liming agents in a leaching study on an acid podzol soil with high levels of exchangeable aluminum. They found that the organic amendments increased pH and exchangeable Ca at depth. In addition, the amendments decreased the levels of toxic Al and Mn. Some of the exchangeable Al was leached from the column, however, precipitation of Al also occurred as the pH increased (Noble et al. 1995; Noble and Randall 1998). Further to the study in 1995, Noble and Randall (1998) investigated the effect of use of two coal-derived organic amendments compared to lime on the yield and

composition of wheat plants in an acid soil. They concluded that plant growth was improved with all amendments. The pH was raised and exchangeable Al and Mn were reduced. However, this was attributed mostly to precipitation of solid Al-phases as the pH increased, rather than the increased complexation by the coal-derived products (Noble and Randall 1998).

3. COMPARISON OF THREE LIME REQUIREMENTS DETERMINED FOR AN ACID SULPHATE SOIL

Abstract

The Ah and Bmg horizons of the Keld Series soil, an acid sulphate soil, have pH (1:1 in water) 5.0 and 3.9, respectively. Lime requirement (LR), the amount of lime required to neutralize the soil to pH 7.0, was determined by the SMP Single-Buffer Method, and by titration of soil with sodium hydroxide. Two calculations of LR, first by estimation of average slope and second by formula, were determined from the SMP data; while a third was computed from the titration curves. The closest agreement of lime requirements obtained was between the SMP Method accompanied by LR calculation using the formula, and the titration method. The results from the slope, formula, and titration calculations are, respectively, 42, 24, and 21 tonnes CaCO_3 ha^{-1} of Ah soil. For the Bmg horizon, the corresponding results are 66, 49, and 54 tonnes CaCO_3 ha^{-1} of Bmg soil. The LRs from the SMP formula and titration methods are similar, but the unconventional determination of LR that was attempted by using the average slope from the SMP method is not recommended.

3.1 Introduction

Acid sulphate soils form when parent materials containing sulphidic minerals are present in a reduced environment. Upon exposure to oxidizing conditions, sulphuric acid is produced. The pH of the soil decreases drastically, to as low as 2, rendering crop production difficult or impossible. A common problem associated with acidic soils is the increased mobility of toxic ions such as aluminum and manganese (Barnhisel et al. 1982; Foy 1984). Additional environmental problems result when acid sulphate soils with clayey textures are used as landfill covers (Kargbo et al. 1993; Fanning and Burch 1997).

Soil belonging to the Keld Series is found in western Manitoba, and has formed on sulphidic clay shales (Ross et al. 1988). In the field, this soil is often misclassified as a Chernozem, but according to the Canadian System of Soil Classification, it is a Brunisol (Agriculture Canada Expert Committee on Soil Survey 1987). The Ah and Bmg horizons of this soil have approximate pH values (1:1 in water) of 5.0 and 3.9, respectively. Further evidence of the acid sulphate character of the soil is the presence of pale-yellow jarositic minerals at depths of 50 cm.

Liming is the conventional method of raising the pH of acidic soils, to create a more favourable environment for plant growth. Studies by Osei (1993) and Riggs et al. (1995) show that lime addition has a rapid effect on soil pH, resulting in a more alkaline pH that often stabilizes within two weeks. However, liming acid sulphate soils is a short-term solution. As long as the sulphidic minerals and oxidizing conditions are present, the continued production of acidity will neutralize the added liming material.

Lime requirement (LR) is defined as the amount of lime or other base required to neutralize the acidity (both dissociated and undissociated) of an acid soil to a selected, more alkaline condition (McLean 1982). Thus, pH is not an adequate indicator of the LR of a soil, because the active acidity is only a fraction of the soil's total acidity, the remainder of which is reserve acidity. The lime requirement allows us to quantify the amount of total acidity in the soil, including active acidity in solution and reserve acidity which is slowly released over time.

A traditional and reliable laboratory determination of LR is performed by incubating a soil with varying amounts of lime for a period of three months (Alabi et al. 1986; Offiah and Fanning 1994). This approach is time consuming, and its results may be influenced by moisture content, carbon dioxide levels and air pollutants. Numerous efforts were made to create a fast, yet accurate, method of estimating lime requirement. The Shoemaker, McLean and Pratt (SMP) method was developed in 1961. It is a buffer test for soils expected to have high LR and high levels of exchangeable aluminum (McLean 1982). The SMP method is often used due to its speed and simplicity (Webber et al. 1977; Owusu-Bennoah et al. 1995). A buffer solution of known pH is added to 5 g of acid soil. The pH of the soil-buffer mixture is taken after 30 minutes and the depression of the buffer pH is used to obtain the lime requirement. The change in pH can be used with the SMP LR Reference Table, or can be inserted directly into an empirical equation to generate the LR (Shoemaker et al. 1961; McLean 1982). A third approach to determining LR is by use of titration curves. The data of soil pH versus moles of liming material (usually a basic solution) is particularly useful in soils of clay texture, whereupon a slow titration can reveal the quantity of acidity in various buffer ranges due to the presence of different kinds of hydroxy polymers (Schwertmann and Jackson 1964). Hence, three buffer ranges are

recognized, and they are:

- I pH 3.5-4.5, exchangeable H^+ ;
- II pH 4.5-5.5, exchangeable aluminum; and
- III pH 5.5-7.5, fixed aluminum-hydroxy polymers. (Schwertmann and Jackson 1964)

It is noteworthy that soil pH is an intensity factor, whereas LR and exchange acidity are capacity factors of soil acidity. Thus pH may not be, and usually is not, a satisfactory measure of the total soil acidity that includes fixed and exchangeable forms.

In this study, three techniques for estimating the lime requirement of an acid soil were investigated, and compared.

3.2 Materials And Methods

3.2.1 Soil Characteristics

Soil samples were collected from a site near Keld, Manitoba (SW 03 25 20 W), on May 25th, 2000. The soil profile description and a photograph of the profile are given in Appendix A. Selected soil properties are displayed in Table 3.1.

The Ah and Bmg horizons were chosen for study. The Ah horizon is only slightly acidic, and does not display acid sulphate characteristics. However, it was selected because it is of interest to see how any field-applied amendments will affect the surface soil. The Bmgj and Bmg horizons have low pH (3.9). The layer designated Bmgj is only 5 cm deep, therefore more soil from the Bmg horizon was collected and mixed with the Bmgj during sampling.

Table 3.1 Selected properties of the Keld Series soil profile

Horizon	Depth (cm)	pH (1:1 soil:water)	Texture	% O.M.
Ah	0-20	5.00	CL	9.2
Bmgj	20-25	3.95	CL	n/d ^z
Bmg	25-45	3.95	C	1.8
BC	45-55	3.50	C	1.1
Cg1	55-75	3.40	C	n/d
Cg2	>75	n/d	C	n/d
Shale - P.M.		2.45		

^zn/d - not determined.

3.2.2 Shoemaker-McLean-Pratt Single Buffer Method (SMP)

The lime requirements of the Ah and Bmg horizons were determined by the SMP Single-Buffer Method (Shoemaker et al. 1961; McLean 1982). This procedure was selected because it was designed for soils of high lime requirement and considerable exchangeable aluminum. During the experiment, the SMP Buffer of known pH is combined with a sample of acidic soil. The change in pH of the buffer is used to indicate total acidity of the sample, by referring to the SMP Table (Table 3.2).

Table 3.2 Calibrations to determine lime requirement of the surface 20 cm of mineral soil using the SMP single-buffer method

Soil-buffer pH	Desired pH			
	7.0	7.0	6.5	6.0
Amendment required to reach desired pH (metric tons ha ⁻¹)				
	Pure CaCO ₃	Ag-Ground limestone ^z		
6.8	2.4	3.2	2.7	2.3
6.7	4.1	5.3	4.7	3.8
6.6	5.3	7.6	6.5	5.3
6.5	7.0	10.1	8.5	7.0
6.4	9.0	12.3	10.5	8.5
6.3	10.5	14.6	12.3	10.1
6.2	12.1	16.8	14.3	11.6
6.1	13.4	19.2	16.1	13.2
6.0	15.2	21.5	18.1	14.8
5.9	17.2	23.8	20.1	16.3
5.8	18.6	26.2	21.9	17.9
5.7	20.1	28.5	23.9	19.5
5.6	21.8	30.6	26.0	21.0
5.5	23.3	33.2	28.0	22.8
5.4	25.3	35.4	30.0	24.4
5.3	26.7	37.8	31.8	26.0
5.2	28.5	40.1	33.8	27.6
5.1	30.2	42.5	35.8	29.1
5.0	31.8	44.8	37.8	30.6
4.9	33.6	47.2	39.9	32.3
4.8	34.9	49.5	41.6	33.8

^z Ag-Ground lime of 90%, plus total neutralizing power or CaCO₃ equivalent, and fineness of 40% < 100-mesh, 50% < 60-mesh, 70% < 20-mesh, and 95% < 8-mesh. (from McLean 1982).

3.2.2.1 Preliminary SMP Test. The SMP Buffer, p-nitrophenol-triethanolamine-chromate-acetate, was prepared as outlined by McLean (1982), and its initial pH was 7.7. The pH of a 5 g soil sample was measured in water (1:1). Ten milliliters of buffer solution was added to the same vial. The samples were agitated at 150 oscillations/min. for 10 min, then stood for 30 min., and were lightly swirled by hand before measuring the soil-buffer pH. While the soil-buffer pH readings for the Ah horizon were within the range on the SMP Reference Table (Table 3.2), the soil-buffer pH values for the Bmg horizon were so low that they did not reach the minimum value listed in the table. Therefore, an additional 10 mL of buffer solution was added to all samples, followed by another 10 minutes of agitation. After standing for 30 min., the soil-buffer pH was again measured. The time between measurement of the first soil-buffer pH and return of samples to shaker was approximately 40 min.

3.2.2.2 Actual SMP Test. Based on the above outcome for the Bmg horizon, it was decided to repeat the experiment on the Ah and Bmg horizons with a slight change in procedure. This time, the initial amount of buffer added was 20 mL, instead of 10 mL. For this experiment, the buffer solution had an initial pH of 7.5. The experiment was carried out in duplicate for each horizon. The estimated time between measuring pH_w , adding buffer, stabilizing flasks, and starting shaker was ~20 min. When measuring soil-buffer pH after shaking and standing, the electrode was placed in the clear supernatant above the settled soil.

3.2.3 Titration with Sodium Hydroxide Method

The titration method was employed as a means of verifying the results obtained from the SMP Method. Titration of 5 g soil with 0.05 mol L^{-1} NaOH was completed during a time period of approximately seven hours, in duplicate for each soil horizon. The initial soil pH was determined in water (1:1) (McLean 1982). A stirrer was inserted into each beaker, and a measured volume of NaOH was added from a burette. After ten minutes, the pH was recorded, and the process was repeated at approximately 10-minute intervals until the pH reached 8.0. The pH electrode was rinsed with distilled water between samples, and rested in pH buffer solution when not in use.

3.2.4 Calculation of Lime Requirements

3.2.4.1 Calculation of LR from SMP Slope Method. The lime requirement is usually read directly from the SMP Reference Table (Table 3.2). This was not possible for the Bmg horizon, as the soil-buffer pH measured was below the minimum value in the Reference Table. Therefore, all lime rates were calculated using the results of the SMP Buffer test employing an initial 20 mL of buffer and 5 g soil. Because of the use of twice the amount of buffer required by the SMP single-buffer procedure, an adjustment of values in the Reference Table was necessary. This was accomplished by first plotting the Reference Table values of soil-buffer pH vs. lime rate (columns 1 & 2 in Table 3.2) and calculating the average slope. For each 0.1 reduction in pH, an average of 1.6 tonnes of lime ha^{-1} is needed to attain a pH of 7.0. The difference between the initial and final soil-buffer pHs could then be multiplied by the average slope of $1.6/0.1$ to obtain a lime requirement in tonnes of $\text{CaCO}_3 \text{ ha}^{-1}$. As 20 mL of buffer was used for each 5 g of soil in

this experiment, it cannot be assumed that the slope will remain 1.6/0.1. With 20 mL of buffer, the reduction in soil-buffer pH will be less than that of a sample with 10 mL of buffer. Thus, for samples with 20 mL buffer, the average slope was assumed to double to 3.2/0.1. As a result, to calculate a lime requirement (in tonnes of $\text{CaCO}_3 \text{ ha}^{-1}$), the difference of the initial and final soil-buffer pHs was multiplied by 3.2/0.1. This is an unusual method of calculating LR with SMP data, but was performed with the intent of verifying the result versus that obtained with the standard method of LR calculation described next.

3.2.4.2 Calculation of LR from SMP Formula Method. The second determination of lime requirement was calculated with the empirical formula published by Quigley and Reid (1995) (Equation 3.1). The formula is a mathematical expression of the recommended LRs (in pure CaCO_3) that are provided in the SMP Reference Table (Table 3.2). Three values obtained during the SMP Single Buffer Method, namely pH_d and m_{SMP} , and the final soil-buffer pH measured during the SMP experiment, are inserted into the equation. The result is a lime requirement in tonnes of pure $\text{CaCO}_3 \text{ ha}^{-1}$.

$$\text{LR} = [-50.820 + (13.378 \times \text{pH}_d) - (1.928 \times \text{pH}_d \times \text{pH}_{\text{SMP}}) + (7.315 \times \text{pH}_{\text{SMP}})] \times (10/m_{\text{SMP}} \times 8/6) \quad [3.1]$$

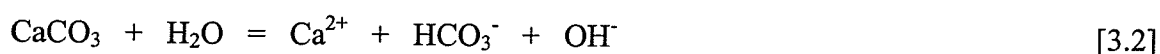
where pH_d = desired pH of soil (usually 7.0)

pH_{SMP} = soil-SMP buffer pH measured

m_{SMP} = mass of soil used

The second-to-last term in the equation ($10/m_{\text{SMP}}$) has been labeled “the dilution factor”. Generally, the mass of soil used is 5 g, which gives a dilution factor of two ($10/5$). In this experiment, where 20 mL of buffer was used, the dilution factor was altered to four ($20/5$). Although Quigley and Reid (1995) do not provide restrictions or guidelines for using this formula, it was noted that they altered the dilution factor in one of their experiments. Thus, it is believed that adjusting the dilution factor in the formula will not drastically affect the resulting lime requirement.

3.2.4.3 Calculation of LR from Titration. The lime requirement was determined from the titration curve as follows. The number of moles of hydroxyl ions required to neutralize the soil’s pH from its initial value to 7.0 was calculated. To determine liming rate, the following principle was used: one mole of calcium carbonate yields one mole of hydroxyl ions when applied to acid soils, thereby neutralizing only one mole of acidity, according to the acid neutralization (Bohn et al. 1985), shown as:



3.3 Results and Discussion

3.3.1 SMP Single Buffer Method

The soil-buffer pH measurements from the SMP procedures are displayed in Table 3.3. In the preliminary test, when 10 mL of buffer was added to 5 g of soil from the Ah horizon, the

pH of the buffer was reduced from 7.7 to 5.3 (Table 3.3). This final soil-buffer pH is within the values provided in the SMP Reference Table, making it possible to read the LR for this soil (26.7 tonnes $\text{CaCO}_3 \text{ ha}^{-1}$ in Table 3.2). However, when the same procedure was applied to the Bmg horizon, the final soil-buffer pH was 4.0. This was lower than the minimum pH of 4.8 listed on the SMP Reference Table. Therefore, no lime requirement was obtained from the experiment using 5 g of Bmg soil and 10 mL of buffer.

Table 3.3 pH values of soil obtained by SMP Buffer tests for Ah and Bmg horizons

Horizon	Sample No.	pH (1:1 soil:water)	Soil-buffer pH #1 (10 mL buffer ^z)	Soil-buffer pH #2 (20 mL buffer ^y)
Ah	1	5.1	5.3	6.0
	2	5.1	5.3	6.4
	3	5.2	5.3	
Bmg	1	4.0	4.0	5.3
	2	4.0	4.1	5.6
	3	4.0	4.0	

^z initial SMP buffer pH = 7.7.

^y initial SMP buffer pH = 7.5.

When the initial amount of buffer solution added to 5 g of soil was increased to 20 mL, the soil of the Ah horizon depressed the pH of the buffer from 7.5 to an average of 6.2 (Table 3.3). The corresponding buffer pH values for the Bmg horizon were from 7.5 to 5.5. The less-acidic surface horizon depressed the pH of the buffer by an average 1.3 pH units, while the Bmg horizon depressed it by 2.0 pH units. The average soil-buffer pH values were used with the SMP Slope method, and Equation 3.1, (both modified for 20 mL buffer as described in the previous

section) to obtain lime requirements for the two horizons (Table 3.4).

3.3.2 Titration with Sodium Hydroxide

The titration curves for the slightly acidic Ah horizon and the more acidic Bmg horizon are depicted in Figures 3.1 and 3.2, respectively. The Ah horizon is seen to contain total acidity (up to pH 7.5) equivalent to that neutralizable by 11.5 mL of 0.05 mol L⁻¹ NaOH, or 0.575 mmoles, per 5 g soil (or 115 mmoles(+) kg⁻¹). The bulk of this total acidity between pH 5.5 to 7.5 is attributable to non-exchangeable hydroxy-Al. As suspected, the more acidic Bmg horizon contained the equivalent of 1.15 mmoles of acidity per 5 g soil (or 230 mmoles(+) kg⁻¹), neutralizable by 22.7 mL of 0.05 mol L⁻¹ NaOH. Of this, the proportions ascribable to non-exchangeable hydroxy-Al (pH 5.5 - 7.5), exchangeable Al³⁺ (pH 4.5 - 5.5), and exchangeable hydronium (pH 3.5 - 4.5) are 6:3:1.

During the titration, the time between additions of base was held constant between 10 and 20 minutes, during which it was assumed that all added base had reacted with the soil acidity. Although a long titration period was used in this study (7 hours), there is no doubt that a longer titration period would result in higher lime requirements as found by Bohn et al. (1985). It is thus unknown if the titration was of sufficient duration to permit completion of chemical reactions. The most accurate determination would require a complete mineralogical investigation that would include the stability and structure of the Al in the interlayers (Goh and Huang 1985).

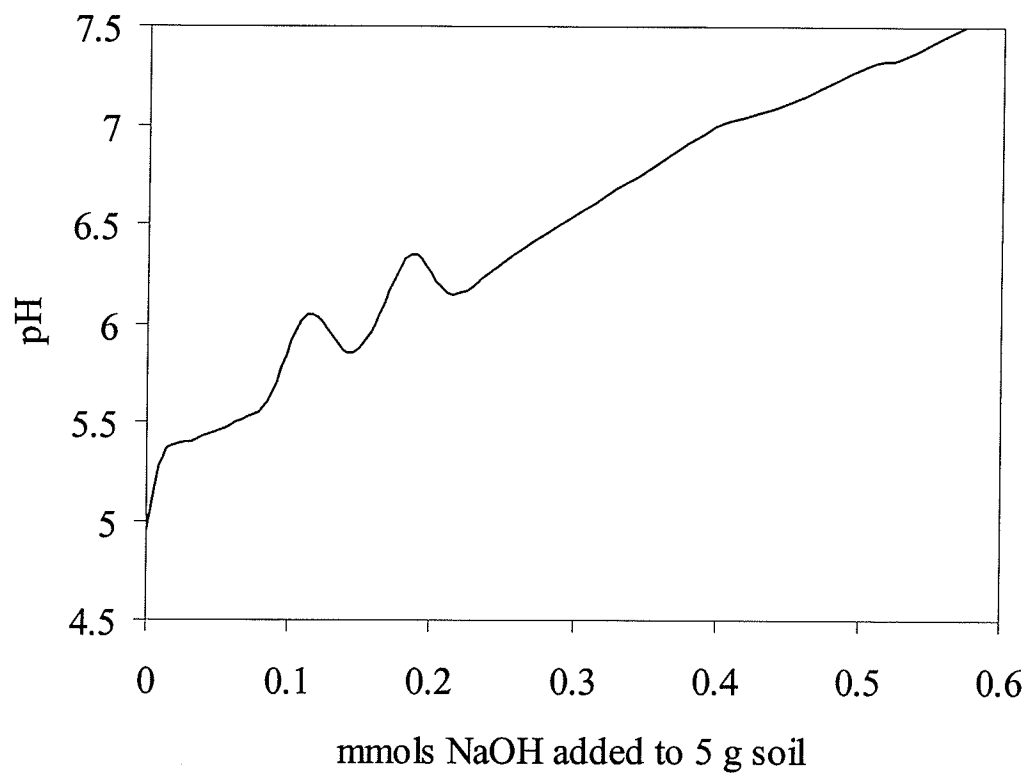


Figure 3.1 Acid neutralization curve of the Ah horizon, Keld soil.

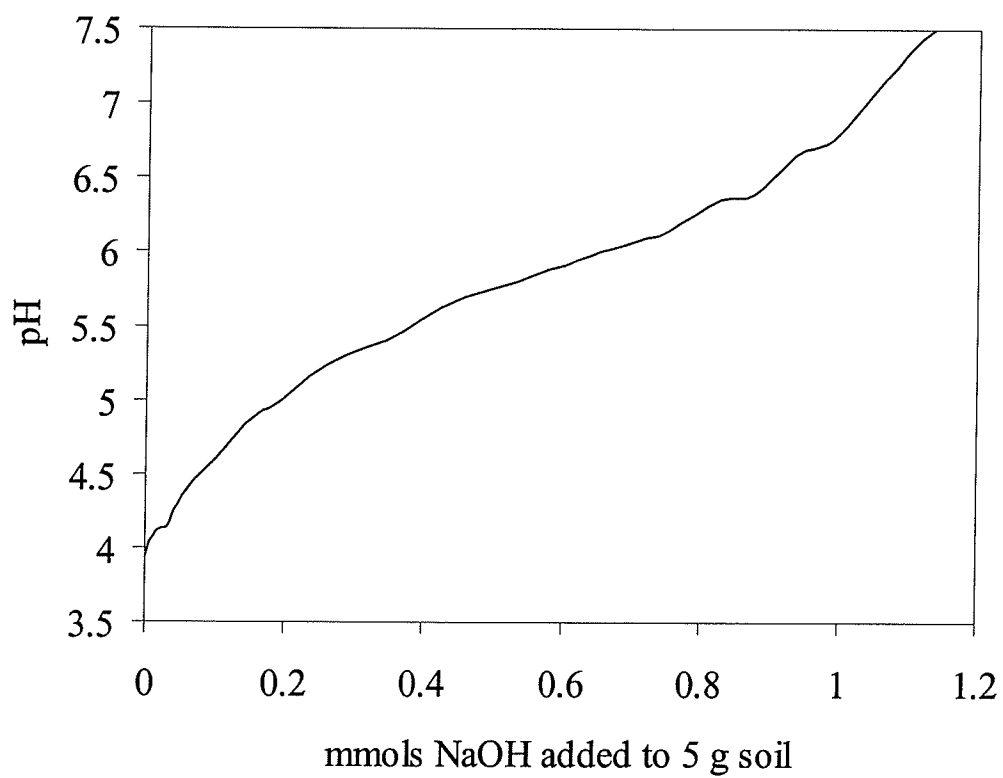


Figure 3.2 Acid neutralization curve of the Bmg horizon, Keld soil.

3.3.3 Comparison of Lime Requirements

The LR obtained by using the SMP Slope Method was calculated with the intent of checking it against the LR from the SMP Formula (Equation 3.1) and by titration. A statistical comparison among the three LRs was not conducted. The unusual calculation by SMP Slope does not appear to provide an accurate estimate of lime requirement, as seen by comparison to the LRs estimated by the SMP Formula and titration (Table 3.4). The LR was overestimated in both the slightly acidic Ah horizon and the strongly acidic Bmg horizon. One reason for the overestimation of LR obtained by the SMP Slope calculation is the alteration of the average slope from the LR values in the SMP Reference Table. It was assumed that doubling the amount of buffer would have the effect of doubling the average lime requirement, which is represented by the average slope obtained from a plot of the SMP Reference Table values. This unconventional extrapolation of the data proved to be erroneous and is hardly surprising since log functions such as pH are not linear.

Table 3.4 Lime Requirement rates (pure CaCO_3) required to achieve neutralization of the Ah and Bmg horizons to pH 7.0, as determined by three methods

Method for LR	LR for Ah		LR for Bmg	
	g kg^{-1}	tonnes $\text{ha}^{-1} \text{ z,y}$	g kg^{-1}	tonnes $\text{ha}^{-1} \text{ z,y}$
1. SMP Slope	16.0 ± 3.5	41.6 ± 9.1	25.2 ± 2.6	65.6 ± 6.8
2. SMP Formula	9.2 ± 3.6	24.0 ± 9.3	18.8 ± 2.7	48.8 ± 7.0
3. Titration with NaOH	8.0 ± 0.1	20.8 ± 0.2	20.7 ± 0.1	53.8 ± 0.4

^z estimated B.D. for Ah and Bmg are 1.3 g cm^{-3} and 1.35 g cm^{-3} , respectively.

^y depth of 20 cm.

The SMP procedure requires two pH measurements, the initial and final pH of the buffer. During the experiments, the pHs of samples from the Ah horizon were always measured first. Thus, the samples from the Bmg horizon may have been in contact with the buffer solution for a longer time than the Ah samples. Quigley and Reid (1995) found a disadvantage of the SMP method is the reduced precision of the pH electrode when immersed in SMP buffer solution. This may confound some results, although no large differences in pH measurements were noted in this experiment.

Laboratory methods of predicting the lime requirements of acid soils are not error-free. The SMP method may overestimate the amount of lime needed (Curtin et al. 1984). Despite this finding, Offiah and Fanning (1994) noted that laboratory lime requirements often underestimate the field requirement due to poorer mixing and eolian losses of the amendment in the field, and strongly acid soils below the ploughing depth. This is especially true for acid sulphate soils that are actively generating sulphuric acid. Lime requirements must also consider the effect of potential acid sulphate soils containing sulphidic minerals, that may become active (acid-generating) due to changing environmental conditions (Barnhisel et al. 1982).

It is known that the SMP Single-Buffer and titrations are reliable methods of estimating the LR of acid soils with high amounts of exchangeable Al and organic matter content below 10% (McLean 1982). In this study, two LRs were calculated with information from the SMP Single-Buffer soil-pH measurements. Although there was no statistical comparison of the three LRs obtained for each horizon, the findings confirm that the use of the SMP method accompanied by the formula yields a LR that is close in magnitude to the LR from the titration. Due to the unconventional calculation used to attempt a determination of the LR when 20 mLs of

SMP buffer was employed; and in light of the fact that the SMP formula to obtain LR yielded a result much more comparable to the LR from the reliable titration method; the unconventional calculation of LR by SMP Slope as used here does not appear to be valid and is not recommended for the Keld Series soil from the Ah and Bmg horizons.

Of the two lime requirements obtained by the SMP Formula (Equation 3.1) and by neutralization due to 0.05 mol L^{-1} NaOH titration, the SMP Formula method has the advantage of saving time. The titration method requires a careful analysis of the titration curves to estimate the amount of acidity in Buffer Ranges I, II, and III. In Buffer range I (between pH 3.5 - 4.5), exchangeable or active H^+ is estimated. Buffer range II (pH 4.5 - 5.5) estimates exchangeable Al^{3+} , and in Buffer range III (pH 5.5 - 7.5), fixed polymeric hydroxy-Al, i.e. the reserve acidity, is measured. The method is tedious, but accurate and reliable. The SMP Formula and the Titration predict that the Bmg horizon requires two to approximately two-and-a-half times the amount of lime as the Ah horizon (Table 3.4).

Overall, the predicted lime requirements are very high, which is typical of acid sulphate soils. In this experiment, the target pH was 7.0. This desired pH can be slightly lowered without risking harm to plants. This would reduce the lime needed, as aluminum mobility decreases above pH 5.5, and soils near pH 6.0 or 6.5 are generally productive. It is important to note that the recommended rate of lime will neutralize the soil's total acidity, which includes active and reserve acidity. The high field rates of lime may not be practical, but the total amount does not have to be added all at once.

3.4 Conclusions

It is known that acid sulphate soils are non-productive due to low pH and high levels of plant-available aluminum and manganese. Liming is often used to increase the pH of acid soils. The SMP Single Buffer Method with 20 mL of SMP buffer accompanied by the Formula of Quigley and Reid (1995) with adjustment of the dilution factor, and the soil-base titration are both acceptable methods of determining the lime requirement of acid sulphate soils, as the two results were very similar. However, the unconventional LR calculation using the average slope of the SMP Reference Table values produced the highest value in all replications and is not recommended.

4. ALKALINE HUMIC SUBSTANCES AND THE AMELIORATION OF AN ACID SULPHATE SOIL

Abstract

An acid sulphate soil located in Manitoba has low pH and high amounts of soluble aluminum. An alkaline extract of humic substances from leonardite was investigated as a potential liming agent for the Ah and Bmg horizons of the Keld Series soil. Two treatments, alkaline HS and lime (CaCO_3) were applied to soil from the Ah and Bmg horizons in a laboratory experiment. Soil pH, titration curves, organic carbon content, cation exchange capacity and exchangeable basic and acidic cations, and CaCl_2 -extractable aluminum were determined on four sampling days during the 63-day incubation.

The two treatments were effective in raising the pH and reducing total acidity in both soil horizons, compared to the control. In the soil from the Bmg horizon, the alkaline HS treatment also enhanced the soil organic carbon content and the CEC. The exchangeable Mn was reduced by lime in both soil horizons. The HS amendment lowered exchangeable Mn in the Ah horizon but raised it in the Bmg horizon, compared to the controls. Both amendments significantly reduced the amount of exchangeable Al in the acid Bmg horizon.

4.1 Introduction

Acid soils (here meaning soils of $\text{pH} \leq 6.0$) pose many challenges to plant growth and crop production. Problems in low pH soils include toxicity from aluminum and manganese, and nutrient deficiencies (Ca, Mg, P). Soils contain two kinds of acidity, reserve and active. The acidity from fixed, Al-hydroxy polymers is termed reserve acidity. Active acidity refers to the free protons in soil solution, and is measured by pH, the negative log of H^+ ions.

One type of acid soil in particular, known as acid sulphate soil, restricts the range of agricultural crops that can be grown and is difficult to manage due to its inherent chemical properties (i.e. immense active and reserve acidity). The parent material contains pyritic minerals that, upon oxidation, produce sulphuric acid. As a result, the pH can decrease to as low as 2 (Dent and Pons 1995). The resulting soil acidity and associated problems of aluminum and manganese toxicities hinder agricultural production.

Acid sulphate soils have also been documented in inland regions of North America. In western Manitoba, sulphidic clay shales are the parent material upon which the Keld Series soil has formed (Ross et al. 1988). This soil series has a thick Ah horizon of pH 5.0, and soil acidity increases with depth. The B horizons are sulphidic (i.e. pyritic) in nature and upon oxidation, they become sulphuric, hence, the acid sulphate nature of the Keld Series.

In the previous chapter, the lime requirements of the Ah and Bmg horizons of the Keld Series soil were determined. Chapter 3 formed the basis for the use of liming amendments in the amelioration of adverse acid sulphate soil chemistry, which is mainly low pH and the associated aluminum and manganese toxicities to plant growth. Common liming materials are limestone (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), $\text{Ca}(\text{OH})_2$, and CaO .

Many studies have focused on the effects of organic matter on exchangeable Al^{3+} in soils (Schnitzer and Skinner 1963*b*; Thomas and Hargrove 1984). Organic materials have been shown to alleviate Al toxicity in acid soils. Evans and Kamprath (1970) reported that higher organic matter content in soils reduced the amount of Al in solution at a given pH. Hoyt and Turner (1975) investigated the use of organic materials in a very acid soil as an alternative to lime.

The hypothesis in this chapter is that an alkaline organic amendment may neutralize the soil acidity and prevent accelerated weathering of the soil minerals, thereby decreasing the potential bioavailability of toxic metals, such as aluminum, Al^{3+} . There may be additional benefits from the humic materials contained in the amendment, including improved physical (soil aggregation) and chemical (nutrient reserve) properties.

The first objective of the study was to determine if alkaline humic substances (HS) extracted from leonardite can raise the pH of the Keld acid sulphate soil for a sustained period of time. The second objective was to ascertain if the amounts of soluble aluminum and manganese metals can be reduced to levels that pose low risks of toxicity. The effectiveness of the alkaline HS was compared to that of a common liming material, calcium carbonate.

4.2 Materials and Methods

A laboratory incubation study was conducted using experimental units of 50 g of soil (oven-dry basis) in 150 mL beakers. There were two soil horizons, three treatments, four sampling days, and three replications, for a total of 72 beakers. After the application of all amendments on Day 0, the beakers were covered loosely with aluminum foil caps, and placed on the laboratory countertop. The beaker weights were monitored every two days, and distilled

water was added to adjust the moisture contents, if necessary. On the sampling days, beakers were removed and the soil was used for the analyses described in Section 4.2.3.

4.2.1 Description of the Acid Sulphate Soil

Soil from the Ah and Bmg horizons of the Keld Series pedon was used for this laboratory incubation study. The two horizons are considered as separate soils in the interpretation of results. The Ah horizon had a pH of 4.80, and the pH of the Bmg horizon was 3.45. The texture of both horizons is clay loam. Selected properties of the Keld Series soil used in this study is shown in Table 3.1 (Chapter 3, this thesis), and the profile description and photograph are in Appendix A. During the study, the moisture content was held constant at ~20% (g/g).

4.2.2 The Amendments

Two treatments were compared against the control. They are described below. The control treatment was supplied with 10 mL of water to each beaker of 50 g O.D. soil, to attain a moisture content of 20%.

The organic amendment provided by Luscar Ltd., was an alkaline suspension of humic substances extracted from leonardite (referred to hereafter as HS). Properties of the leonardite material are presented in Appendix B. The amendment was a liquid formulation with a pH of 10.5. Earlier observations that the direct application of the modified leonardite may be harmful to soil microorganisms prompted the decision to dilute the amendment before application to soil. The original solution of HS was diluted 1:1 with distilled water, and the resulting pH was 10.1, before applying to soil.

The rate of HS amendment for this study was based on the preliminary titrations of 5 g soil (Ah or Bmg) in 5 mL water versus the HS (diluted 1:1). These titrations were completed over six hours. Initially, the titration curves obtained were used to determine the amount of HS needed to attain a target pH of 7.0. However, the volume required would cause flooding if added to soil. Thus, the target pH was revised to 5.5, a level at which Al mobility would be reduced to very low amounts. Subsequently, titration curves indicated the amounts of amendment required to attain a pH of 5.5 were 7.5 mL and 39 mL per 50 g of soil from the Ah and Bmg horizons, respectively. A rate of 10 mL of HS amendment was applied to soil from the Ah horizon. This amount was expected to raise the pH of the soil to at least 5.5. In the case of the Bmg horizon, a one-time application of 39 mL of liquid HS to 50 g of soil would still cause flooding. Therefore, split applications of HS were used. The first application of 10 mL HS was on Day 0, and further additions of 10 mL HS each were applied on Days 14 and 46. On the final sampling day, Day 63, the beakers containing soil from the Bmg horizon that was treated with HS had received a total of 30 mL HS. All applications of HS were added to the soils with an autopipette, and samples were thoroughly mixed. The moisture content during incubation was maintained at approximately 20% (v/w).

The calcium carbonate amendment (referred to hereafter as Lime) was a reagent-grade fine powder. The rates of CaCO_3 were obtained from the lime requirement (LR) experiments (Chapter 3, this thesis). In the lime requirement study, the LR calculated from the SMP method was slightly higher than the LR obtained from the titration curve for the Ah soil horizon. The reverse was observed for the Bmg soil horizon. Thus, the average of two rates obtained by the SMP Single-Buffer and Titration Methods was taken as the rate of CaCO_3 for each soil horizon. The rates of calcium carbonate amendment are 0.430 g and 0.988 g CaCO_3 per 50 g of Ah and

Bmg soils, respectively. The lime was thoroughly mixed into soil that had been wetted to approximately 20% gravimetric moisture content.

4.2.3 Chemical measurements

Subsamples of soil were collected after selected periods of incubation (Table 4.1) and the following chemical analyses conducted:

4.2.3.1 $\text{pH}_{\text{CaCl}_2}$. The pH of soil in $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ was measured following the procedure outlined by McLean (1982). After addition of 5 mL $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ to 5 g soil, the mixture was shaken by hand for 30 seconds. After 10 minutes, the pH of the supernatant was recorded with a Fisher Scientific Accumet® model 15 pH meter and an Orion Ross® Sure-flow pH electrode.

Table 4.1 Schedule of Events During Incubation Study

	Ah Soil	Bmg Soil
Application of amendments	Day 0	Day 0
First Sampling	Day 7	Day 12
Addition of 10 mL HS to Bmg	n/a	Day 14
Second Sampling	Day 21	Day 21
Titration curves	Day 27	Day 26
Third Sampling	Day 42	Day 42
Addition of 10 mL HS to Bmg	n/a	Day 46
Final Sampling	Day 63	Day 63
Titration curves	Day 69	Day 68
SOC Determination	Day 71	Day 82

4.2.3.2 Measurement of Total Acidity and Buffer Ranges. Titrations of 5 g soil vs $0.05 \text{ mol L}^{-1} \text{ NaOH}$ were completed in triplicate on Days 27 and 69 for the Ah horizon, and on Days 26

and 68 for the Bmg horizon. The initial soil pH in water (1:1) was determined after 10 minutes (McLean 1982). A magnetic stirrer was added to the sample, and the pH electrode was positioned beside it. A known volume of NaOH was added from a burette, and after approximately one minute of stirring, the pH was recorded. The titrations were stopped when the pH reached 8. Average titration curves were calculated from the results.

4.2.3.3 Soil Organic Carbon. The soil organic carbon was determined on the initial, untreated Ah and Bmg soil horizons, and after the incubation (Ah on Day 71, and Bmg on Day 82). The method employed was a modification of the Nelson and Sommers (1975) procedure. The Rapid Dichromate Oxidation Technique, was developed by Ibrahim and Goh (In Press, Commun. Soil Sci. Plant Anal.) after finding that the high digestion temperature of the Nelson and Sommers method caused the thermal decomposition of dichromate and high blank values. This new method achieves complete oxidation of organic carbon, and yields comparatively better results than the method of Nelson and Sommers (1975). The differences between methods are: using 10 mL of conc. H_2SO_4 instead of 7.5 mL; and heating at 140°C for 30 min. using a hotplate and cold finger condenser, compared to Nelson and Sommers' heating at 150°C for 30 min. with a block digester.

All flasks except the non-heated blanks were arranged on a hotplate, attached to cold finger condensers, and heated to 140°C on a hotplate for 30 minutes. After the flasks cooled, they were diluted to approximately 100 mL with deionized water and titrated with 0.5N $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ solution to a bright green endpoint. Two non-heated blanks and two heated blanks were included at each determination.

4.2.3.4 Cation Exchange Capacity. Exchangeable cations were displaced by 1 mol L^{-1} NH_4OAc ($\text{pH} = 7$). Soil samples ($\sim 5 \text{ g O.D.}$) were agitated with 25 mL of NH_4OAc for 30 min. at 150 rpm , and left to stand overnight. The samples were then filtered through Whatman #42 filter paper on a Buchner funnel with a side-arm flask attached to a vacuum at low suction. Following five washings with 50 mL ethanol (95%), the exchange sites of the soil in the filter were assumed to be saturated with NH_4^+ cations. Potassium chloride solution was used to replace the NH_4^+ cations with K^+ . The leachate was collected and the NH_4^+ was measured. The amount of NH_4^+ displaced represents the number of negative sites in the soil, i.e. its cation exchange capacity.

A total of 60 mL of 1 mol L^{-1} KCl was used, in three exchanges. The leachate was collected, acidified with 1 mL of $3\% \text{ H}_2\text{SO}_4$, and made up to 100 mL with 1 mol L^{-1} KCl . The purpose of acidification before storage was to eliminate the chance of ammonia production and release upon opening the bottle. The ammonium was measured on a Technicon AutoAnalyser. Corrections for dilutions and soil moisture contents were applied and the CECs in $\text{cmols (+) kg soil}^{-1}$ were calculated.

Exchangeable cations were also determined. The leachates from the NH_4OAc exchange step of this procedure were stored in plastic, capped bottles at 4°C . The solutions were later analysed by Inductively Coupled Plasma Mass Spectrometry (ICP) for exchangeable base cations (calcium and magnesium), and acidic cations (aluminum and manganese).

4.2.3.5 Aluminum Extracted by CaCl_2 . A five-minute extraction of soil using 0.01 mol L^{-1} CaCl_2 , at a ratio of $1:5$ (soil:solution), was completed with the intention of measuring plant-available Al as per Hoyt and Webber (1974).

A subsample of soil was transferred to a 125 mL plastic bottle, to which 30 mL of 0.01 mol L⁻¹ CaCl₂ was added. All bottles were agitated in a reciprocal shaker, at a speed of 150 rpm for 5 min. The soil suspension was filtered through a Whatman #42 filter and made up to 50 mL using distilled water. The filtrate was acidified with 3 drops of conc. HNO₃ prior to storage (Bertsch and Bloom 1996).

Extractable aluminum was determined by the Aluminon method (Hsu 1963), with the modifications listed by Barnhisel and Bertsch (1982). An acid pre-treatment was applied to the soil extracts prior to the commencement of the aluminon procedure, to eliminate any organic chelates that could interfere with the colorimetric determination of aluminum (Weaver et al. 1968; Goh and Huang 1984). A 10 mL aliquot of the CaCl₂ soil extract was subjected to the acid pre-treatment described by Weaver et al. (1968). Ten millilitres of conc. HNO₃ and three millilitres of conc. H₂SO₄ were added to the CaCl₂ extract. The beakers were evaporated to dryness on a hotplate and the residues were heated to 450°C for 3 hours.

The aluminon-acetate buffer pH was adjusted to account for the acid pre-treatment by addition of 37 g of NaOH instead of 24 g (Wang and Wood 1973). The ashed residue was dissolved by 9 mL of 0.5 N HCl. Then, 14.4 mL of 0.3 N NaOH was added and the solution was made up to 50 mL with distilled water. The purpose of adding the base was to achieve a solution pH of between 2-3, as is required by the aluminon procedure (Hsu 1963). A 15 mL sample of the dissolved residue was transferred by pipette into a 50 mL volumetric flask. To reduce the interference of Fe(III), 1 mL of 0.5% ascorbic acid was added and the flasks were placed in a sand bath at 80 to 90°C for 30 minutes (Jayman and Sivasubramaniam 1974). After the solutions cooled, 25 mL of water was added to each. Then 10 mL of the aluminon-acetate buffer was added, and the solutions were made up to 50 mL with distilled water. Each flask was inverted

twenty times to ensure thorough mixing. The sample from the distilled water was placed into the reference cell of the spectrophotometer. The colour intensity was measured at 530 nm on a Biochrom Ultraspec® 3100 *pro* spectrophotometer and the concentration of aluminum was calculated from a standard curve.

4.2.4 Data Analysis

The soil horizons, Ah and Bmg, were considered two separate soils during the statistical analyses. The data were analysed as a split plot design, with treatments as the main plots (arranged as CRD), and time (sampling day) as the subplot factor. Analyses were done with the General Linear Model in the Statistical Analysis Software (SAS Institute 2000). The parameters were pH, CEC, exchangeable cations (Ca, Mg, Mn in the Ah horizon; the same cations plus Al in the Bmg horizon), and CaCl₂-extractable Al (Bmg horizon only). The analysis of variance tests (ANOVA) of the main plot (treatment) effects were carried out using “Rep (Trt)” as the error term. The treatments were found to act differently over time, thus the treatment means (control vs. HS vs. Lime) were compared on each sampling day (Days 7, 21, 42, 63). The multiple comparisons of treatment means on each sampling day were conducted using LSmeans with an adjustment for Tukey’s test, at a significance level of $\alpha = 0.05$.

4.3 Results and Discussion

4.3.1 $\text{pH}_{\text{CaCl}_2}$

The initial $\text{pH}_{\text{CaCl}_2}$ of the soil from the Ah horizon was found to be 4.80 (data not shown). The $\text{pH}_{\text{CaCl}_2}$ values of soil from the Ah horizon during the incubation study are shown in Figure 4.1. During the incubation, the variability of the control soil pHs (i.e. no amendment) was low, as the pH varied between 4.78 and 4.84.

The alkaline humic substances (HS) treatment raised the pH of the Ah horizon in the first seven days of the incubation, to 5.18 (Figure 4.1). There were no further additions of HS to the Ah horizon after the initial 10 mL was added on Day 0. The pH of the HS-treated Ah soil varied between 5.10 and 5.20 during the incubation period of 63 days. There was no gradual decline or increase in the pH as the experiment proceeded. Preliminary investigations into the liming ability of the alkaline humic substances had indicated that 7.5 mL of HS would augment the pH of soil from the Ah horizon to at least 5.5. The rate of HS applied to the Ah was 10 mL, so it was hypothesized that the pH could exceed 5.5 by the end of the incubation. This was not observed, as the highest pH attained during the experiment was 5.20 on Day 21. This may indicate that the amendment was able to neutralize some of the active acidity. Furthermore, it added to the soil's buffering capacity, by supplying surface functional groups which act to resist changes in the pH.

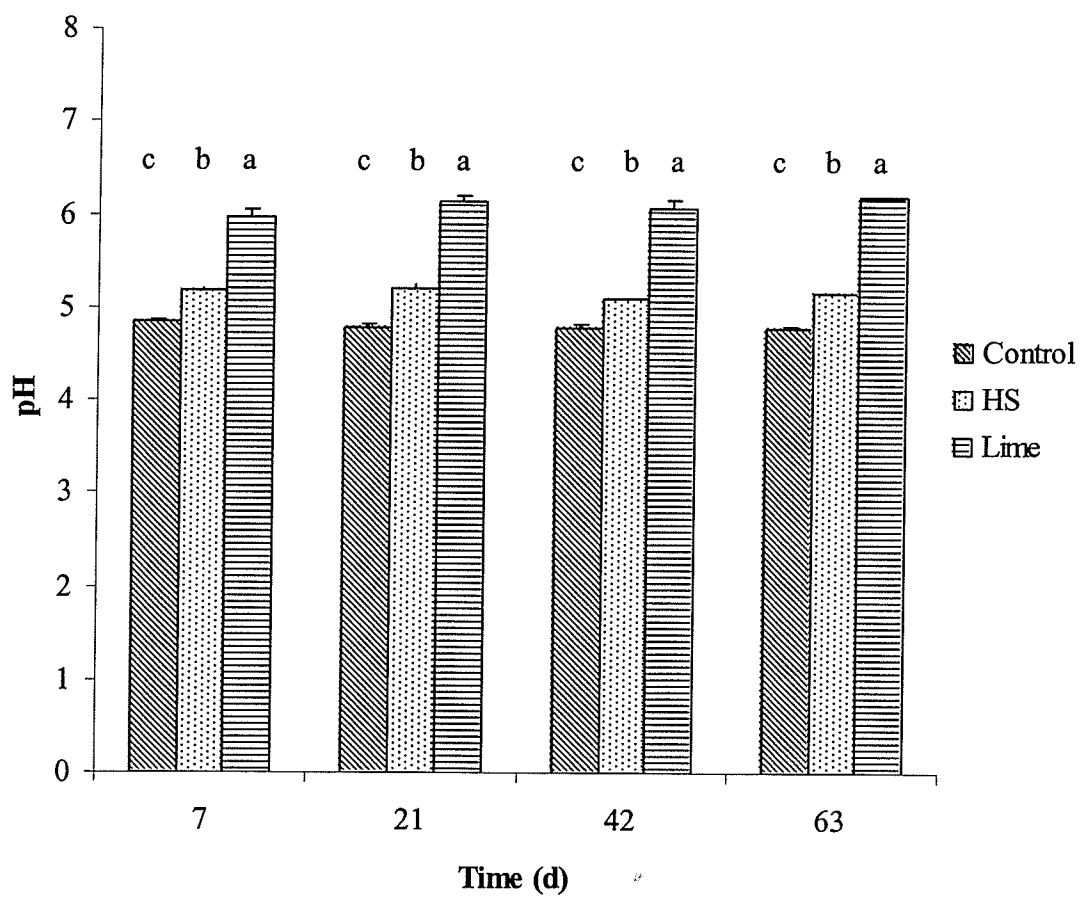


Figure 4.1 $\text{pH}_{\text{CaCl}_2}$ of soil from Ah horizon on sampling days during the incubation. (a-c values followed by the same letter within sampling date are not significantly different). Initial $\text{pH}_{\text{CaCl}_2} = 4.80$.

The lime treatment also dramatically increased the pH of the Ah horizon during the first seven days, from 4.80 to 5.98. The lime was rapidly consumed by the active acidity in the Ah horizon. The pH was highest on Day 63 at 6.20, indicating that the effect of lime was still strong 9 weeks after its application.

The three treatment means at each sampling day were compared by ANOVA. On all sampling days, the three treatment means were significantly different at $\alpha = 0.05$. The mean pHs within treatments were not compared across sampling days.

The $\text{pH}_{\text{CaCl}_2}$ values of soil from the Bmg horizon throughout the incubation period are presented in Figure 4.2. The initial soil pH of the untreated Bmg horizon was 3.45 (data not shown). When the first sampling occurred on Day 12, the pH of the control was 3.56, and it decreased slightly throughout the incubation, to a low of 3.40 on Day 63. This is possibly due to the production of sulphuric acid in the Bmg horizon soil during the incubation.

The pH of the HS-treated soil fluctuated between sampling days. The first 10 mL addition of HS on Day 0 increased the pH to 3.78 by Day 12 (Figure 4.2). The effect of a second addition of HS on Day 14 was a further increase in pH to 4.03 on sampling Day 21. A slight decrease to 3.96 occurred between days 21 and 42. The third addition of 10 mL of HS to the Bmg on day 46 increased the pH to 4.29 by Day 63. Preliminary investigations of the HS amendment had indicated that 39 mL of HS should increase the pH of soil from the Bmg horizon to approximately 5.5. After a total of 30 mL of HS was added to soil from the Bmg horizon in split applications from Day 0 to Day 42, the highest pH attained was 4.29 at the end of the incubation (Day 63).

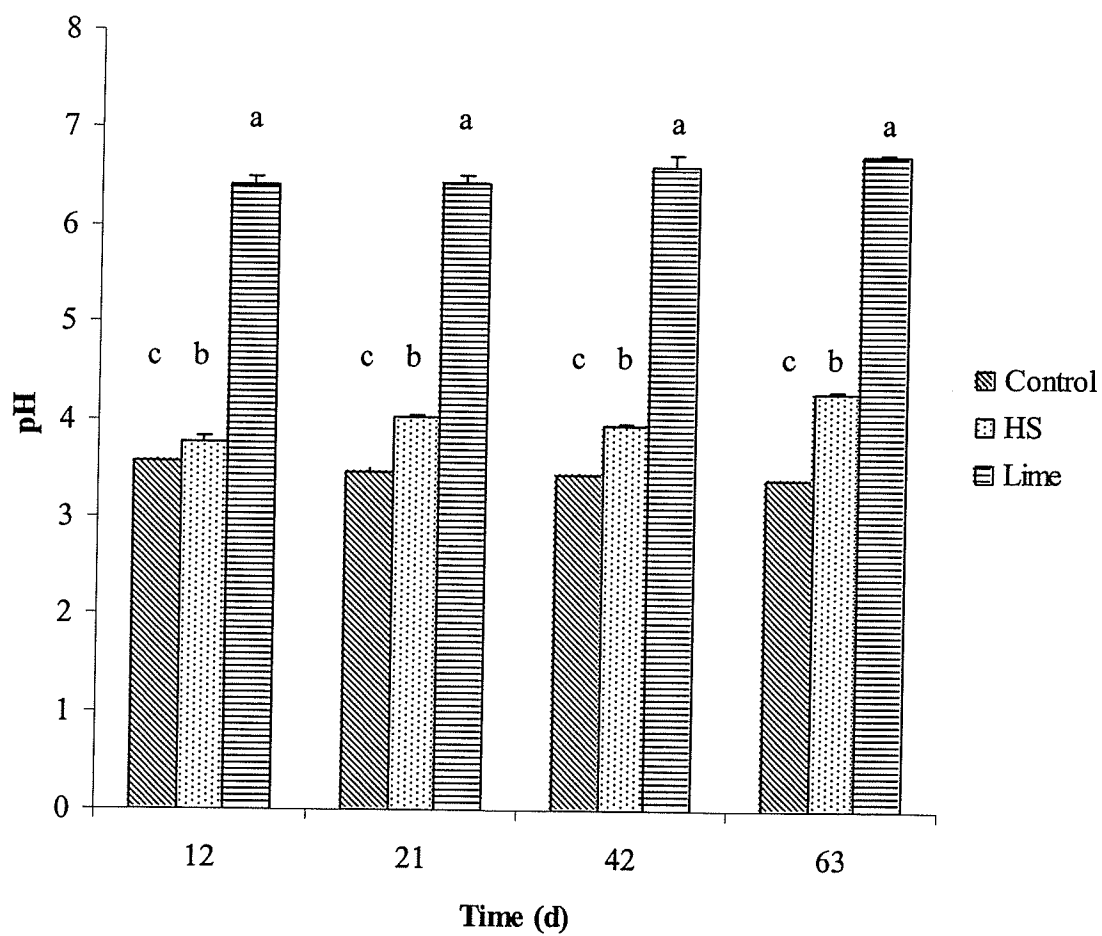


Figure 4.2 $\text{pH}_{\text{CaCl}_2}$ of soil from Bmg horizon on sampling days during the incubation. (a-c values followed by the same letter within sampling date are not significantly different). Initial $\text{pH}_{\text{CaCl}_2} = 3.45$.

The rate of HS amendment was determined with a goal of reaching a soil pH of 5.5, a level at which exchangeable Al^{3+} would be minimized or eliminated (Schwertmann and Jackson 1964). This pH was selected by examining the titration curves obtained from 5 g soil, 1:1 in water, versus NaOH (as described in the materials and methods section, this chapter). It is known that due to the salt effect, a measurement of pH in dilute salt solution (i.e. 0.01 M CaCl_2) is approximately 0.6-1 units lower than pH in water (McLean 1982). This could partially explain why the $\text{pH}_{\text{CaCl}_2}$ of HS-treated soil from Ah and Bmg horizons, (at 5.20 and 4.29 on Day 63, respectively) did not attain the desired pH of 5.5.

Soil from the Bmg horizon that received the lime treatment experienced a large increase in pH by Day 12, to 6.43. This pH was maintained until Day 21, and then increased to 6.74 by Day 63.

In both soils, the quantity of lime added was more than enough to neutralize the active acidity in soil solution. The effect of lime on pH was rapid and persisted for 63 days, but it is unknown how much longer the pH would have been sustained. This would depend upon the amount of reserve acidity in the soil, and how quickly it was being released to the soil solution. By contrast, a single application of approximately 40 mL of HS to the Bmg soil was found to be impractical, thus a total of three-10 mL applications were used. The results show that the rate of HS applied (10 mL HS to soil from the Ah, and 30 mL HS to soil from the Bmg) did not neutralize the acidity as much as a single dose of lime. However, other benefits due to the organic matter may have been accrued, as discussed in the following sections.

4.3.2 Titration Curves and Buffer Ranges

The titration curves for soil from the Ah horizon obtained on Days 27 and 69 are depicted in Figures 4.3 and 4.4. The curves are used for a more detailed examination of the types of acidity in soils, as represented by acidity in three buffer ranges defined by Schwertmann and Jackson (1964). Buffer range I, pH 3.5 - 4.5, is considered to be exchangeable H^+ . The acidity in Buffer Range II (4.5 - 5.5) is attributable to exchangeable Al^{3+} , while that in Buffer Range III is due to fixed Al-hydroxy polymers, and is an estimate of reserve acidity.

The acidity in each buffer range in the amended Ah soil on Days 27 and 69 is presented in Table 4.2. The control soil has the most acidity in Buffer Range III on both days, at 46 and 42 mmols (+) kg^{-1} , respectively, compared to the Ah horizon treated with HS and lime. The total acidity of the control was 69 mmols (+) kg^{-1} on Day 27, but only 46 mmols (+) kg^{-1} at the end of the incubation period. The total acidity of the HS-amended soil decreased from 32.3 to 19.3 mmols (+) kg^{-1} between the two titrations. The HS treatment reduced the acidity attributable to exchangeable Al^{3+} (Buffer Range II) to 0.40 mmols (+) kg^{-1} , when compared to the control. The lime treatment eliminated the acidity in Buffer Range II by Day 27, which was expected because the pH on Day 21 was 6.1. The total acidity of the lime treatment was approximately a third of the control on Day 27, and less than a quarter of the control by the end of the incubation (Table 4.2).

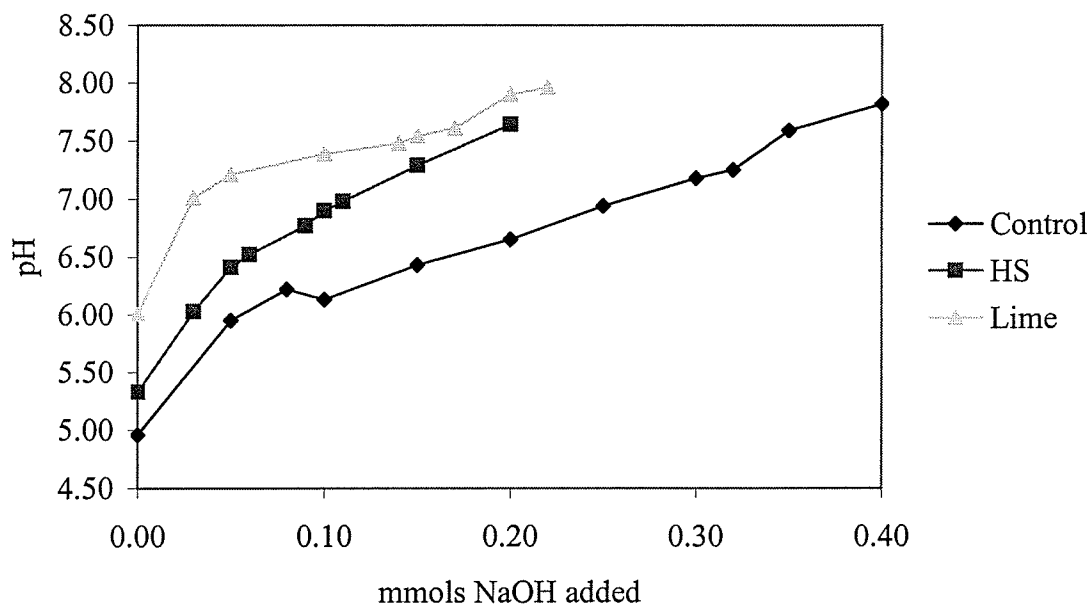


Figure 4.3 Mean titration curves of amended Ah horizon soil vs. NaOH after 27 days.

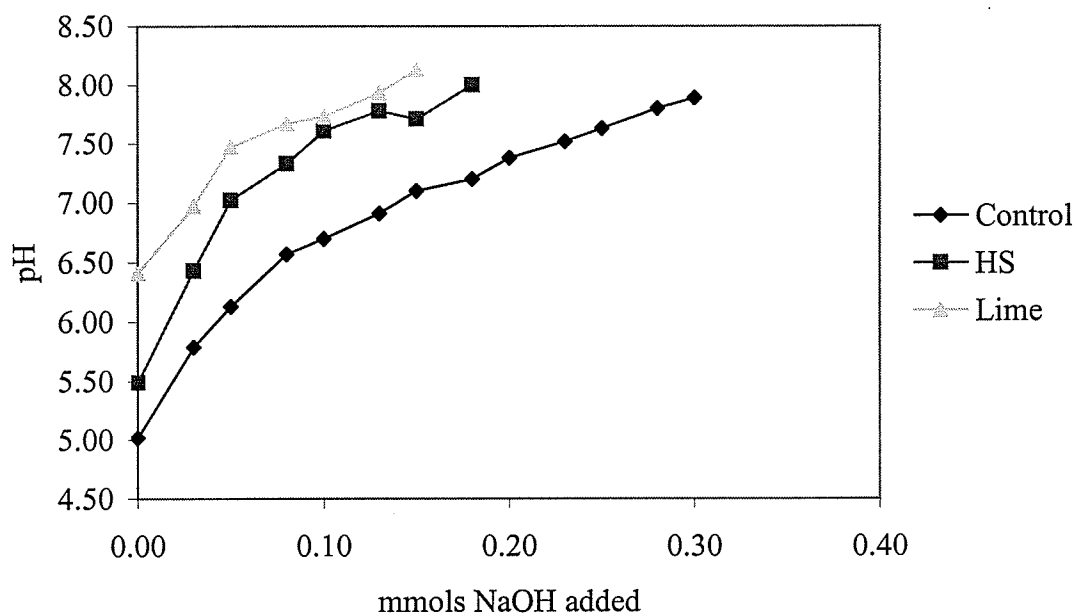


Figure 4.4 Mean titration curves of amended Ah horizon soil vs. NaOH after 69 days.

Table 4.2 Acidity in the three buffer ranges of amended Ah soil as determined by titration with 0.05 mol L⁻¹ NaOH

		Buffer Range I	Buffer Range II	Buffer Range III	
Days	Treatment	pH = 3.5 - 4.5	pH = 4.5 - 5.5	pH = 5.5 - 7.5	Total Acidity
(mmols (+) kg ⁻¹)					
Day 27	Control	0	22.67	46.33	69.00
	HS	0	1.47	30.73	32.20
	Lime	0	0	24.27	24.27
Day 69	Control	0	3.67	42.47	46.14
	HS	0	0.40	18.87	19.27
	Lime	0	0	10.87	10.87

The titration curves for the Bmg soil horizon obtained on Days 26 and 68 are shown in Figures 4.5 and 4.6. The Bmg soil horizon is more acidic than the Ah horizon, as seen by comparing with Figures 4.3 and 4.4. On Day 26, 6.2 mmols (+) kg⁻¹ was detected in Buffer Range I (Table 4.3). The total acidity in the Bmg control on Day 26 was 214 mmols (+) kg⁻¹, due mostly to the 174 mmols (+) kg⁻¹ contributed by the fixed Al-hydroxy polymers in Buffer Range III. This represents a substantial amount of reserve acidity in the soil. In contrast, the total acidity in the control at the end of the incubation was only 74 mmols (+) kg⁻¹, due to a large decrease in acidity detected in Buffer Range III. A plausible reason for this anomaly is that the hydroxy-Al that was responsible for Buffer Range III was unstable. The theory of the presence of unstable hydroxy-Al was confirmed later where it was found that the CaCl₂-extractable Al in the control soil of the Bmg horizon actually increased with the incubation time (Figure 4.16, discussed in Section 4.3.6). In addition, if incubation time affected the formation or stability of a hydroxy-Al phase in the soil, the length over which the titration was performed may not have been adequate to determine the acidity in the buffer ranges.

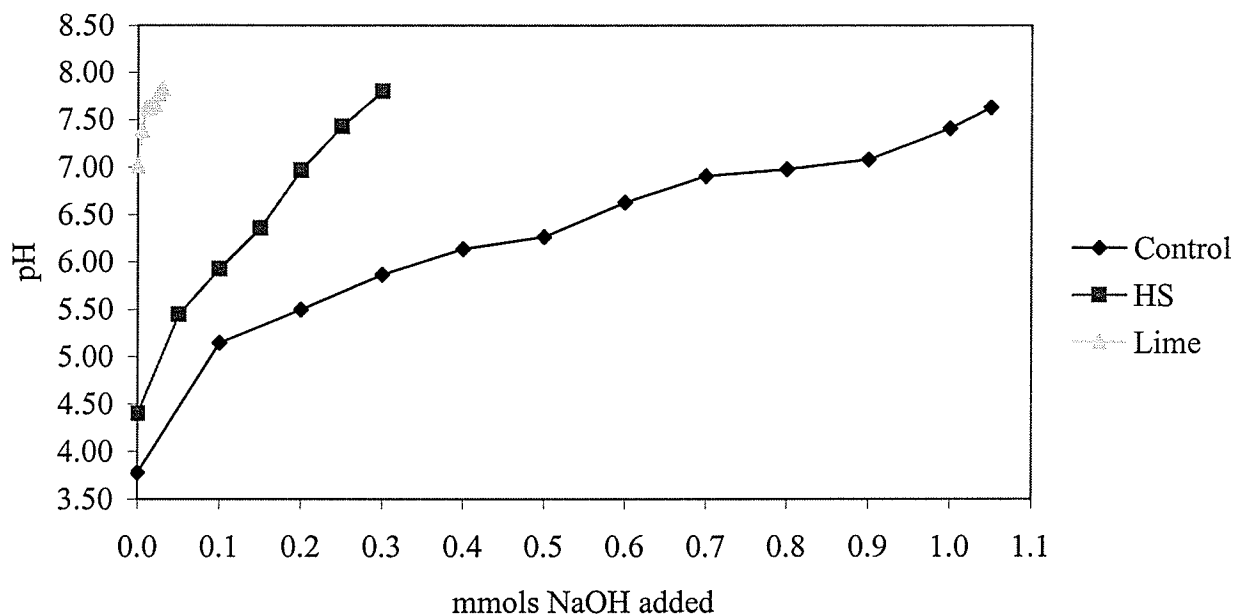


Figure 4.5 Mean titration curves of amended Bmg horizon soil vs. NaOH after 26 days.

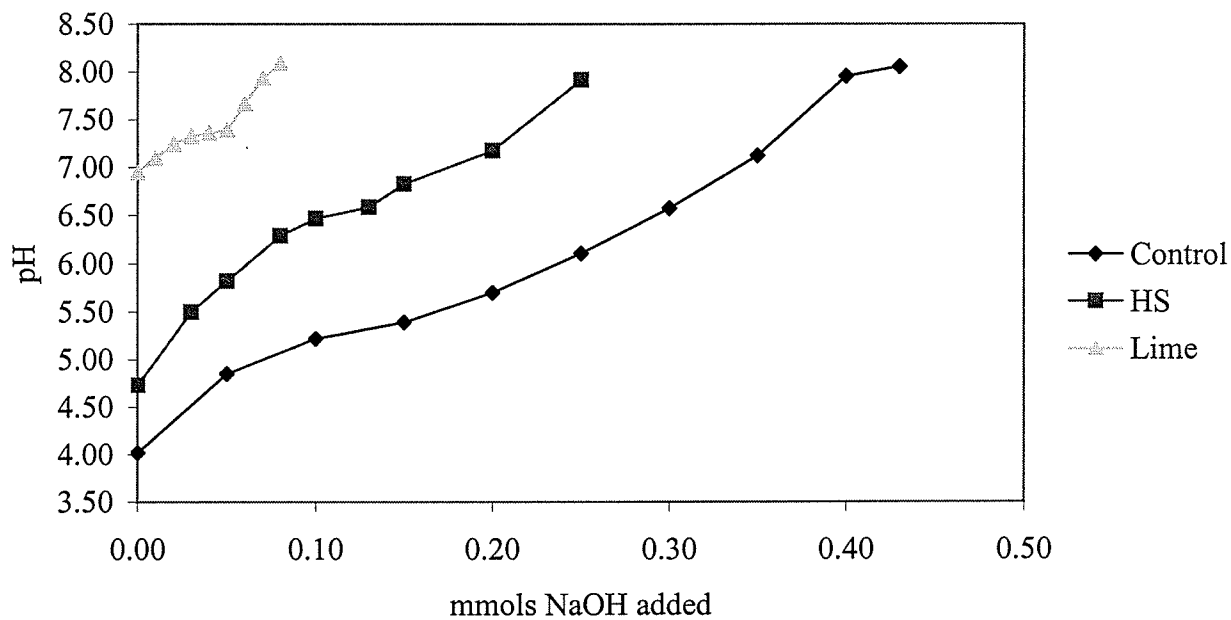


Figure 4.6 Mean titration curves of amended Bmg horizon soil vs. NaOH after 68 days.

The HS-amended soil contained only 1.0 mmols (+) kg⁻¹ of acidity from exchangeable H⁺ (i.e. in Buffer Range I) on Day 26, and none on Day 68. The HS was also able to reduce the acidity in the other buffer ranges between Days 26 and 68 (Table 4.3). The lime treatment was the most effective in reducing total acidity in the soil from the Bmg. The only acidity observed was in Buffer Range III and this was greatly reduced compared to the control and the HS treatment. It is noteworthy that the acidity in the third Buffer Range increased between Days 26 and 68 in the lime-amended soil, from 2.66 to 10.3 mmol (+) kg⁻¹ (Table 4.3).

The HS and lime treatments reduced the acidity in the Bmg soil compared to the control. The HS reduced the total acidity to 72 mmols from 214 mmol (+) kg⁻¹ on day 26; and to 45 mmols from 74 mmol (+) kg⁻¹ on Day 68. The lime treated soil contained 2.66 mmols (+) kg⁻¹ of total acidity on Day 26 and 10.3 mmols (+) kg⁻¹ on Day 68 (Table 4.3).

Table 4.3 Acidity in the three buffer ranges of amended Bmg soil as determined by titration with 0.05 mol L⁻¹ NaOH

		Buffer Range I	Buffer Range II	Buffer Range III	
Days	Treatment	pH = 3.5 - 4.5	pH = 4.5 - 5.5	pH = 5.5 - 7.5	Total Acidity
(mmols (+) kg ⁻¹)					
Day 26	Control	6.2	33.8	173.7	213.7
	HS	1.0	11.0	59.9	71.9
	Lime	0	0	2.66	2.66
Day 68	Control	3.58	29.84	40.9	74.32
	HS	0	5.47	39.67	45.14
	Lime	0	0	10.3	10.3

4.3.3 Soil Organic Carbon

Soil organic carbon was measured at the beginning and end of the incubation period only. Soil from the Ah horizon had an initial soil organic carbon (SOC) content of 6.37%. The determination of final soil organic carbon was carried out eight days after the incubation ended (on Day 71), but it is assumed that this time did not affect the results obtained. The final SOC values of the control, HS-amended and lime-amended soil from the Ah were 6.23%, 5.7%, and 6.04%, respectively (Table 4.4). The variability of the soil's initial SOC, and the final SOC of the control and lime treatments, were one order of magnitude higher than that of the HS-treated soil. No statistical comparison of SOC was done to assess if the differences among treatments were a result of random chance. However, the slight decrease in the average SOC upon the use of HS may be worrisome. It shows that despite using an amendment that contained humic substances, the SOC declined following the incubation. One probable cause could be increased mineralization and use of organic carbon by microbes. However, this has to be checked by further experimentation.

Table 4.4 Organic carbon content of the Ah and Bmg horizons before and after incubation

	Ah % SOC	Bmg % SOC
Day 0	6.37 ± 0.57	1.12 ± 0.05
Control	6.23 ± 0.55	1.25 ± 0.09
HS	5.70 ± 0.04	2.10 ± 0.10
Lime	6.04 ± 0.30	1.22 ± 0.06

The organic carbon content of the untreated Bmg soil was 1.12% (Table 4.4). The final SOC content was determined three weeks after the end of the incubation (Day 82). The final

SOC contents of soil from the control, HS and lime treatments were 1.25%, 2.10%, and 1.22%, respectively. The HS amendment increased the initial value of organic carbon within the Bmg soil horizon by a factor of two. In this soil, the variability of the SOC was much lower than that of the Ah soil. This observation is attributable to the facts that subsoils have lower organic matter content than topsoils, and thus there should be less variability within subsoil SOC content.

Shaykewich (2000) applied several rates of soluble leonardite powder to a clay loam topsoil with initial %OC of 1.5%. The results showed that the amendment significantly increased the %OC in the clay loam topsoil. This is contrary to what was observed in soil from the Ah horizon of the Keld Series, but is similar to what was observed in the Bmg horizon of the Keld Series.

4.3.4 Cation Exchange Capacity

The cation exchange capacity, CEC, determined by exchange with $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$, measured the exchangeable negative charge at pH 7. In addition, the measurement of exchangeable cations enabled an evaluation of the distribution and balance among basic and acidic cations in the Ah and Bmg horizons of the acid sulphate Keld Series.

The initial CEC of the untreated Ah horizon was $44.0 \text{ cmols (+) kg}^{-1}$ (Figure 4.7). During the incubation, the CEC of the control (no amendment) was found to vary from 42.4 to $45.4 \text{ cmols (+) kg Ah}^{-1}$, which is essentially within error of measurement. The HS treatment increased the CEC of soil from the Ah horizon, and the CEC varied from 45 to $47.6 \text{ cmols (+) kg}^{-1}$. The CEC of lime-amended soil was low on Days 7 and 21, at 41.1 and $42.8 \text{ cmols (+) kg}^{-1}$, respectively. But it increased to approximately the same as the control and HS on Days 42 and 63 (Figure 4.7). It is possible that the lower CEC values of the lime-amended soil on the first

two sampling days are due to a dilution effect. Lime (CaCO_3) is not known to be surface active in terms of CEC.

During this study, there was only a small variation in CEC of soil from the Ah among all treatments. The only statistical difference between the treatment CECs was on Day 7, where the HS treatment was significantly higher than the Lime. However, this difference diminished with time.

For the Bmg horizon, the CEC of the control ranged from 34 to 36.7 cmols (+) kg^{-1} during 63 days of incubation (Figure 4.8). The CEC of the HS-amended soil increased throughout the experiment, with the largest increase from 39.1 to 43.5 cmols (+) kg^{-1} occurring between the last two sampling days (days 42 and 63). The addition of 10 mL HS on Day 46 likely contributed to this increase in CEC. Statistically significant differences between the HS and lime treatments were observed on sampling days 42 and 63. On Day 63, the CEC of the HS-amended soil was statistically higher than both the control and the lime treatment.

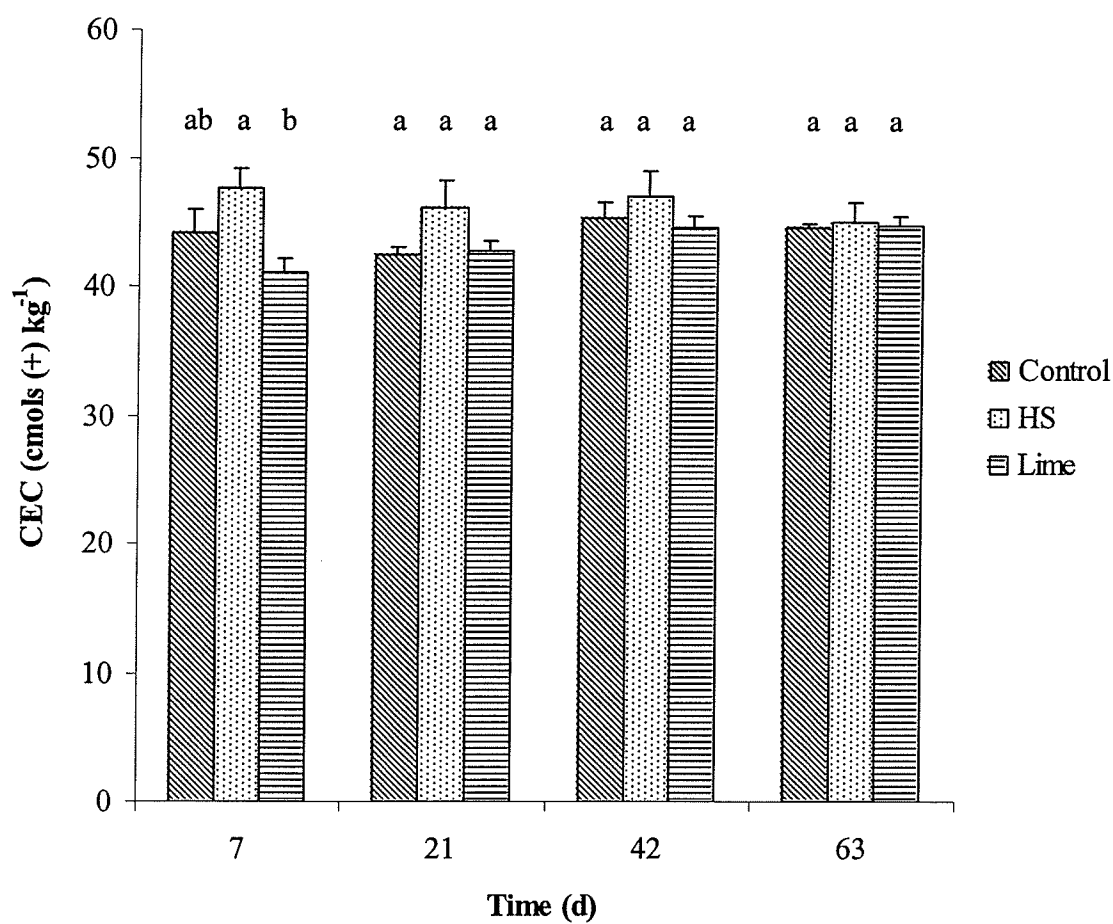


Figure 4.7 Cation exchange capacity of soil from Ah horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial CEC = 44.0 cmols(+) kg⁻¹.

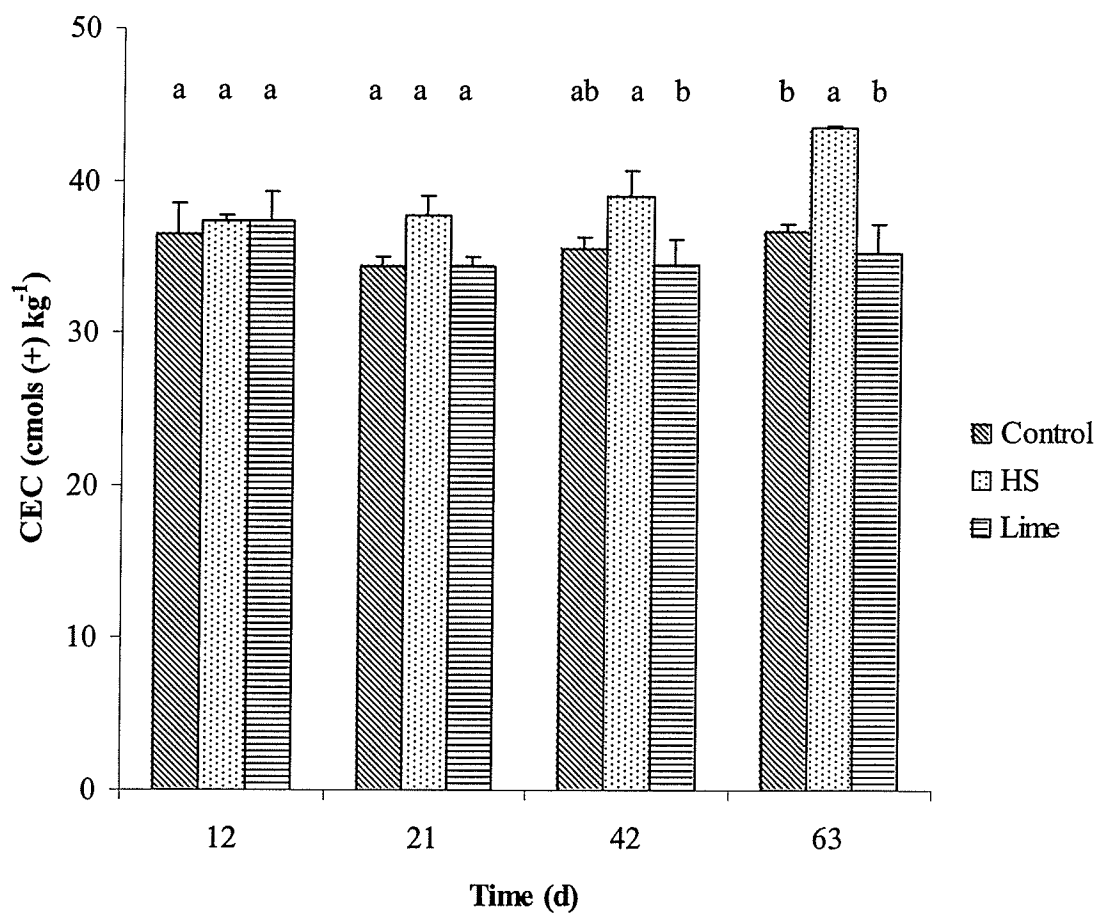


Figure 4.8 Cation exchange capacity of soil from Bmg horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial CEC = 35.5 cmols(+) kg⁻¹.

The CECs of the control & lime-amended soils were not expected to change during the incubation. The alkaline organic amendment is a colloidal suspension of HS, and as such, is expected to provide some active, charged sites where cation exchange may occur. However, in the Ah horizon soil, the HS was statistically higher than the control and Lime only once, on the first sampling day (Day 7). In the previous section, it was noted that the Ah amended with HS experienced a decrease in SOC. By contrast, these two findings are opposed since CEC is expected to decrease as SOC decreases. Therefore, the use of HS must have added some exchangeable negative charge to the Ah horizon soil, in the form of surface carboxyl or phenol groups, so that even though SOC was found to decrease, the CEC was maintained or slightly increased.

In the HS-amended soil from the Bmg horizon, there was an overall trend of increasing CEC with time (Figure 4.8). On Day 63, the SOC of the HS amended soil was statistically higher than both the control and the lime-amended soil. The Bmg horizon has a lower initial organic carbon content than the surface Ah horizon (Table 4.4). Therefore, the addition of 30 mL HS amendment made a significant contribution to the SOC and the CEC of the Bmg soil horizon, as compared to the effects of the 10 mL addition of HS to the Ah horizon.

4.3.5 Distribution of Basic and Acidic Cations

The exchangeable calcium in the untreated Ah was approximately 3200 ppm (16 cmol (+) kg^{-1} OD soil) during the incubation (Figure 4.9). The exchangeable calcium of the HS-treated soil was just above 3000 ppm on the first three sampling days, but had decreased slightly to 2860 ppm on Day 63. As expected, the addition of CaCO_3 to soil boosted the exchangeable calcium measured, to 5500-6000 ppm on all sampling days. The Ca of the lime-amended soil

was significantly higher than the control and HS-amended soil on each sampling day. The finding of higher exchangeable calcium in the lime treatment was expected, since Ca from CaCO_3 can be increased by dissolution in $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$ in the absence of a common ion effect.

Untreated soil from the Ah horizon was found to contain approximately 850 ppm of exchangeable magnesium ($7.08 \text{ cmol (+) kg}^{-1} \text{ OD soil}$) (Figure 4.10). Across all treatments and all sampling days, the exchangeable Mg varied only slightly, from 825 to 935 ppm. There was a significant difference between treatments on Day 21. However, the measured values were within a small range on that day, at 926, 894, and 825 ppm, for control, HS and Lime, respectively.

In contrast to the Ah horizon, the exchangeable calcium in the untreated soil of the Bmg was found to vary from 702 to 773 ppm ($3.51 \text{ to } 3.87 \text{ cmol (+) kg}^{-1} \text{ OD soil}$) (Figure 4.11). This attests to the fact that acidic soil is low in basic cations, of which Ca^{2+} is by far the dominant kind. The exchangeable Ca in the HS-treated soil fluctuated between 828-910 ppm throughout the sampling days. Again, in a soil with a higher pH than the control (Section 4.3.1), there is less leaching of Ca^{2+} from the soil. As expected, the lime immediately increased the exchangeable Ca in the soil, by approximately 10 times compared to the control. The lime treatment was significantly higher than the control and HS at all sampling days.

The control Bmg contained approximately 250 ppm exchangeable Mg ($2.08 \text{ cmol (+) kg}^{-1} \text{ OD soil}$) (Figure 4.12). The HS amendment increased this value by an average of 27 ppm. The Lime treatment caused a gradual decrease in exchangeable Mg, from 210 ppm at Day 12, to 162 ppm on Day 63. At all sampling days, the HS treatment was significantly higher than the control, which was significantly higher than the lime.

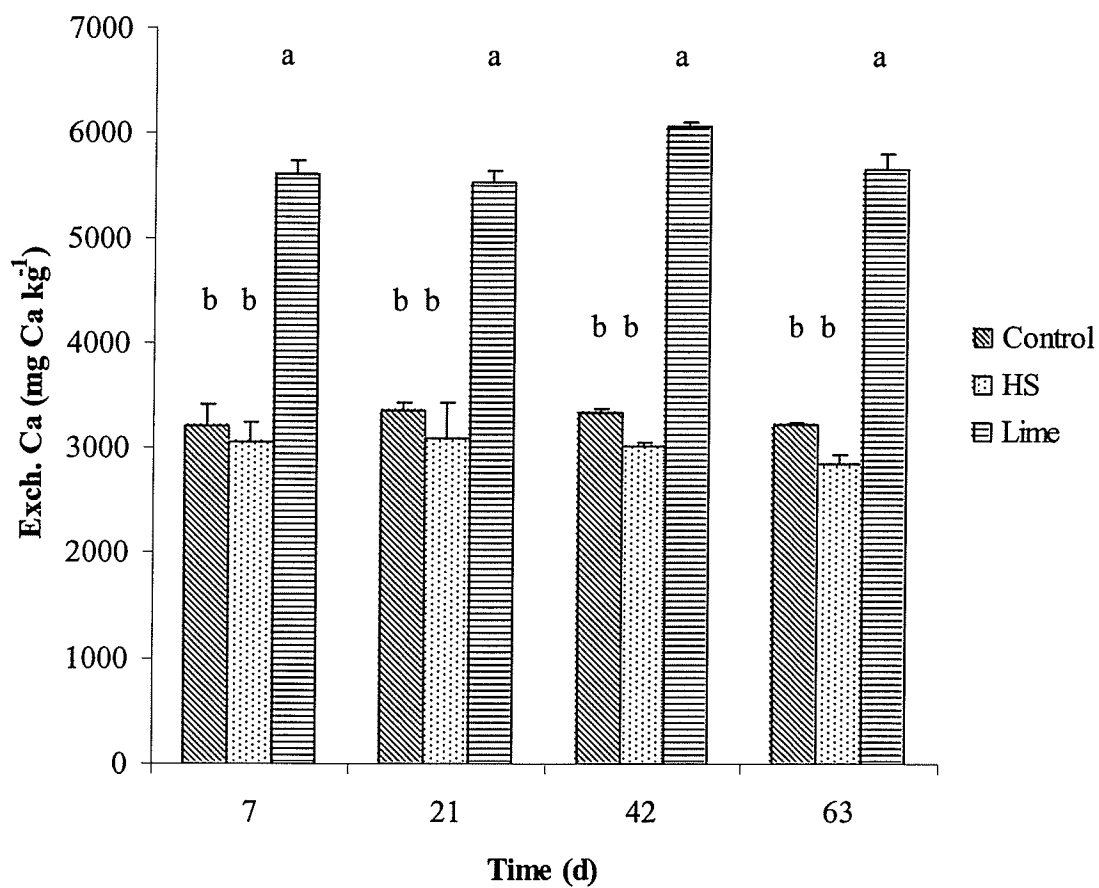


Figure 4.9 Exchangeable calcium in soil from Ah horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial Exch. Ca = 3058 mg kg⁻¹.

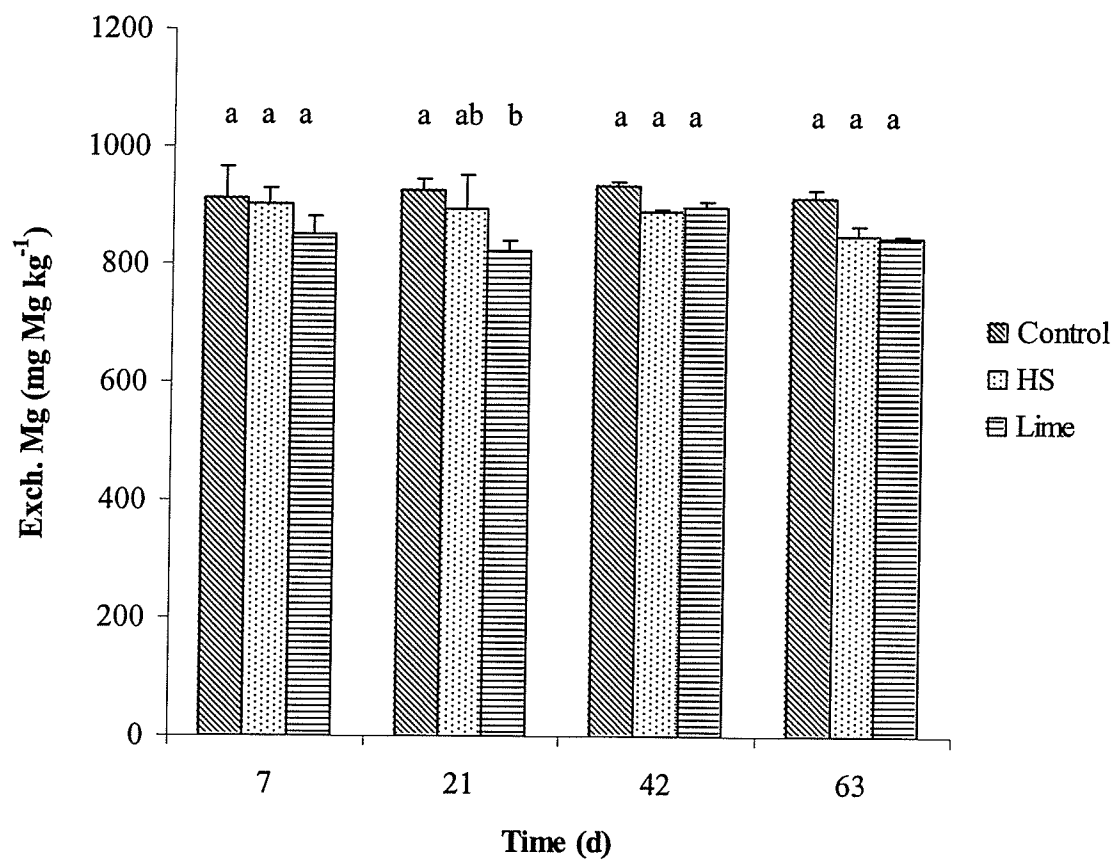


Figure 4.10 Exchangeable magnesium in soil from Ah horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial Exch. Mg = 853 mg kg⁻¹.

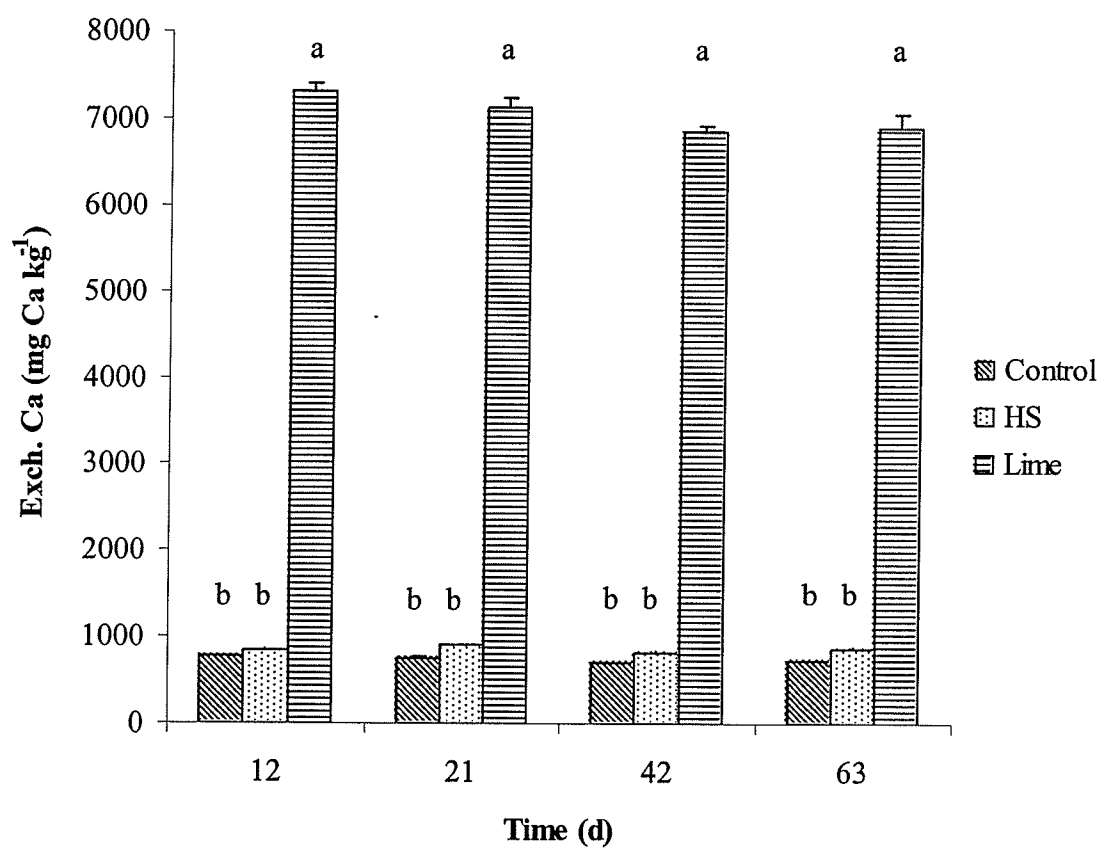


Figure 4.11 Exchangeable calcium in soil from Bmg horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial Exch. Ca = 716 mg kg⁻¹.

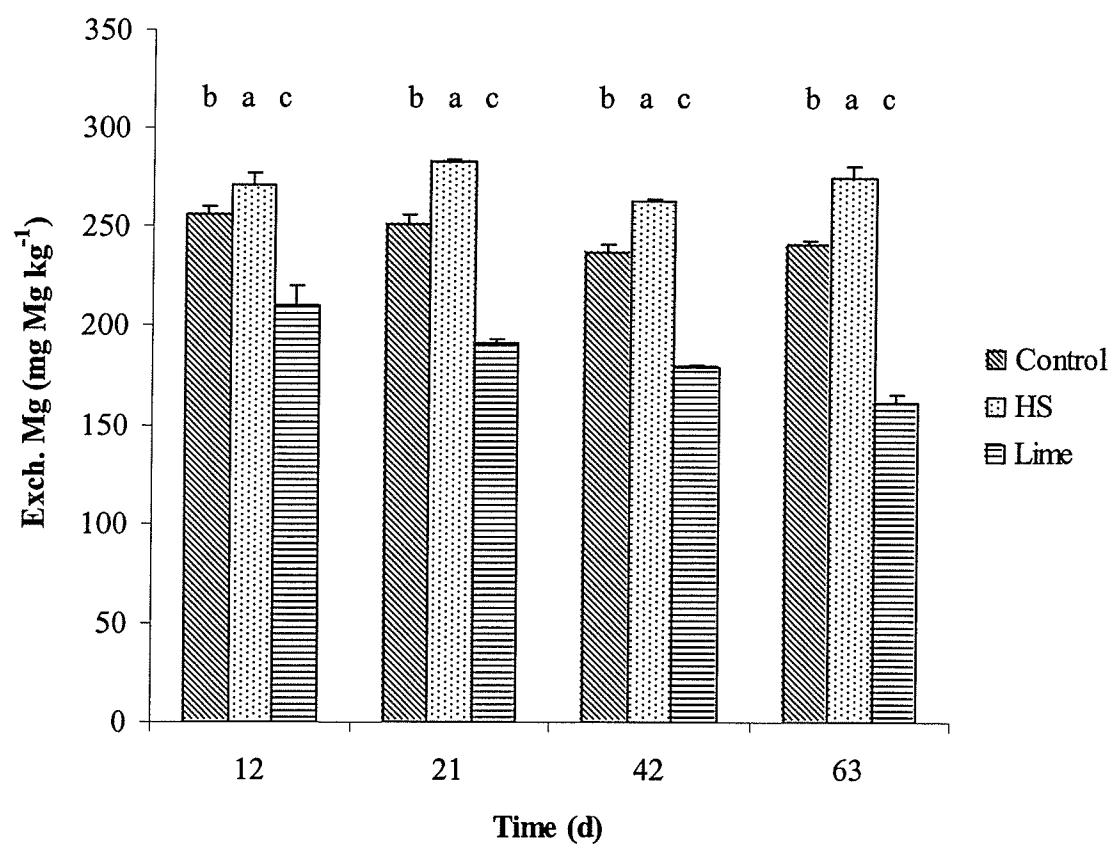


Figure 4.12 Exchangeable magnesium in soil from Bmg horizon on sampling days during the incubation.
(a-c values followed by the same letter within sampling date are not significantly different).
Initial Exch. Mg = 237 mg kg⁻¹.

Soil from the Ah horizon initially contained approximately 3.44 ppm of exchangeable Mn ($0.0125 \text{ cmol (+) kg}^{-1} \text{ OD soil}$). The amounts of exchangeable Mn detected in the Ah horizon soil are displayed in Figure 4.13. On the first sampling day, the control soil had increased to 4.70 ppm. At each sampling day, exchangeable Mn increased until it reached a high of 5.84 ppm on Day 63. The HS-amended soil contained 4.49 ppm exchangeable Mn on Day 7, which is elevated compared to the initial value in the Ah. Throughout the incubation, the exchangeable Mn in the HS soil was approximately 4.85 ppm. The lime treatment kept the Mn below 4 ppm at all sampling days, and was significantly lower than the control & HS. On Days 42 and 63, the Mn in the HS-amended soil was statistically lower than the control.

The Mn in the control Bmg soil was 1.21 ppm on Day 12 ($0.0044 \text{ cmol (+) kg}^{-1} \text{ OD soil}$), but gradually decreased to 0.97 ppm by the end of the incubation period (Figure 4.14). The HS-amendment raised the exchangeable Mn in the Bmg soil horizon by a factor of 2 to 2.8 compared to the control. The higher values, ranging from 2.29 to 2.87 ppm, were observed from the first sampling day and persisted throughout the incubation. The lime-amended soil contained only 0.33 ppm Mn on Day 12. The lime treatment reduced the exchangeable Mn to zero by Day 63, and was statistically lower than the control and HS at all sampling days. As the pH increased, the Mn combined with OH was precipitated out of the soil solution.

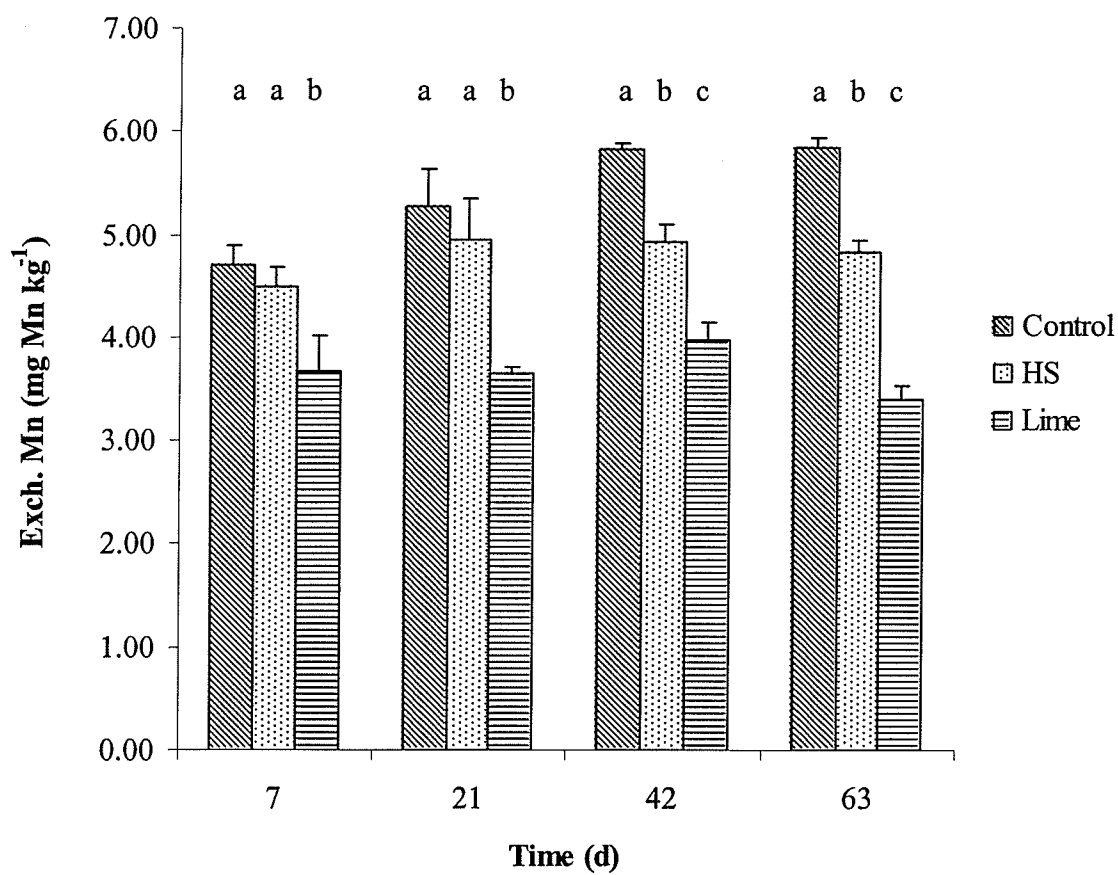


Figure 4.13 Exchangeable manganese in soil from Ah horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial Exch. Mn = 3.44 mg kg⁻¹.

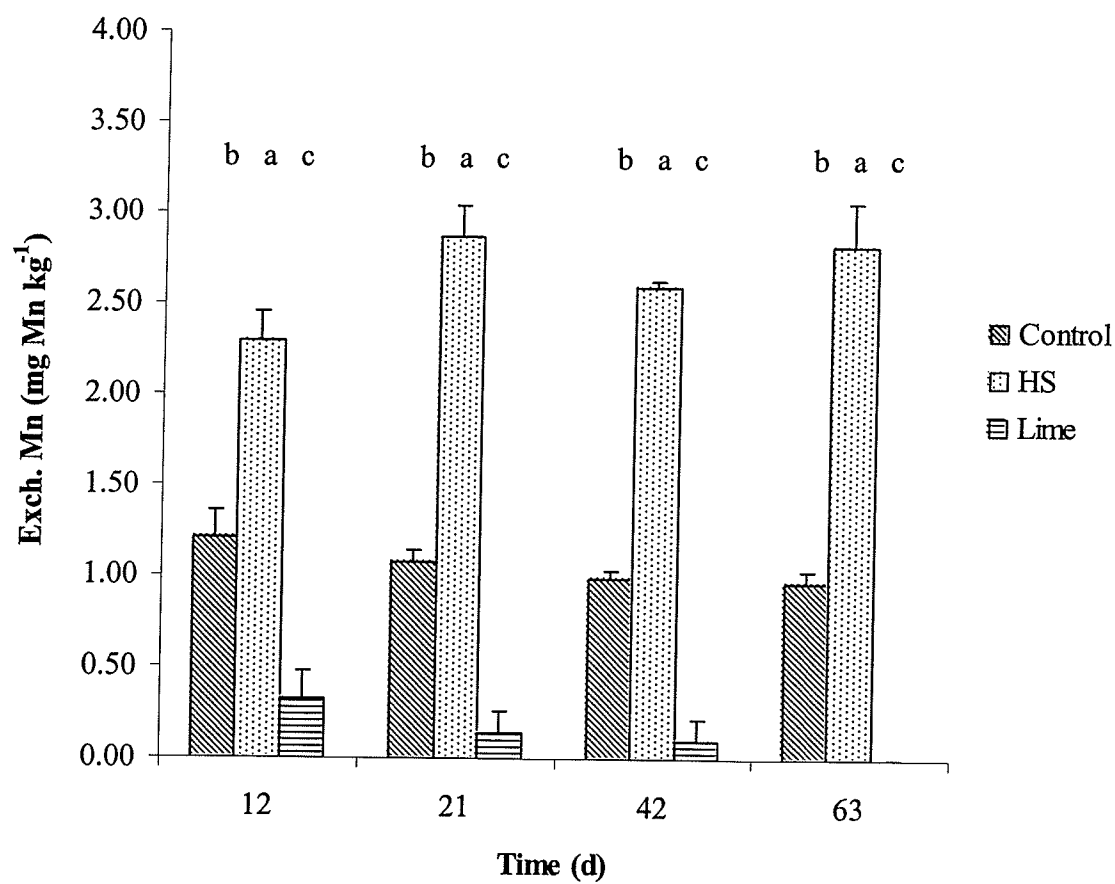


Figure 4.14 Exchangeable manganese in soil from Bmg horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial Exch. Mn = 0.94 mg kg⁻¹.

All NH_4OAc -extracts of soil from the Ah horizon yielded values of zero for exchangeable aluminum. The principal reason why there was no soluble aluminum detected in the Ah horizon is that exchangeable Al is not common in soils of $\text{pH}_{\text{H}_2\text{O}} > 5.5$ (Schwertmann and Jackson 1964). It is inferred from the $\text{pH}_{\text{CaCl}_2}$ measurements that the $\text{pH}_{\text{H}_2\text{O}}$ of the Ah was indeed greater than 5.5 throughout the incubation.

The NH_4OAc -exchangeable Al in the Bmg horizon is displayed in Figure 4.15. The initial value of exchangeable Al in the Bmg (Day 0, untreated soil) was 106.8 ppm ($1.187 \text{ cmol (+) kg}^{-1} \text{ OD soil}$). On Day 12, however, 232 ppm of exchangeable Al was detected in the control sample, and for the remainder of the experiment, all the control values were above 220 ppm ($2.444 \text{ cmol (+) kg}^{-1} \text{ OD soil}$). This is in agreement with previous investigations (Jackson 1963; Thomas and Hargrove 1984; Ross et al. 1988) that acid soils undergo proton attack, which leads to a release of structural Al from phyllosilicates so that Al-saturation of the clay fraction soon follows. After the addition of HS and lime, the Al decreased and by Day 12 was much lower than in the control, at 50 ppm and 10 ppm, respectively. Zero exchangeable aluminum was detected from the HS and Lime treatments on all successive sampling days. The lime was able to quickly reduce the exchangeable aluminum levels, similar to findings by Osei (1993). The HS amendment was also very effective at reducing soluble Al after Day 21 in this experiment.

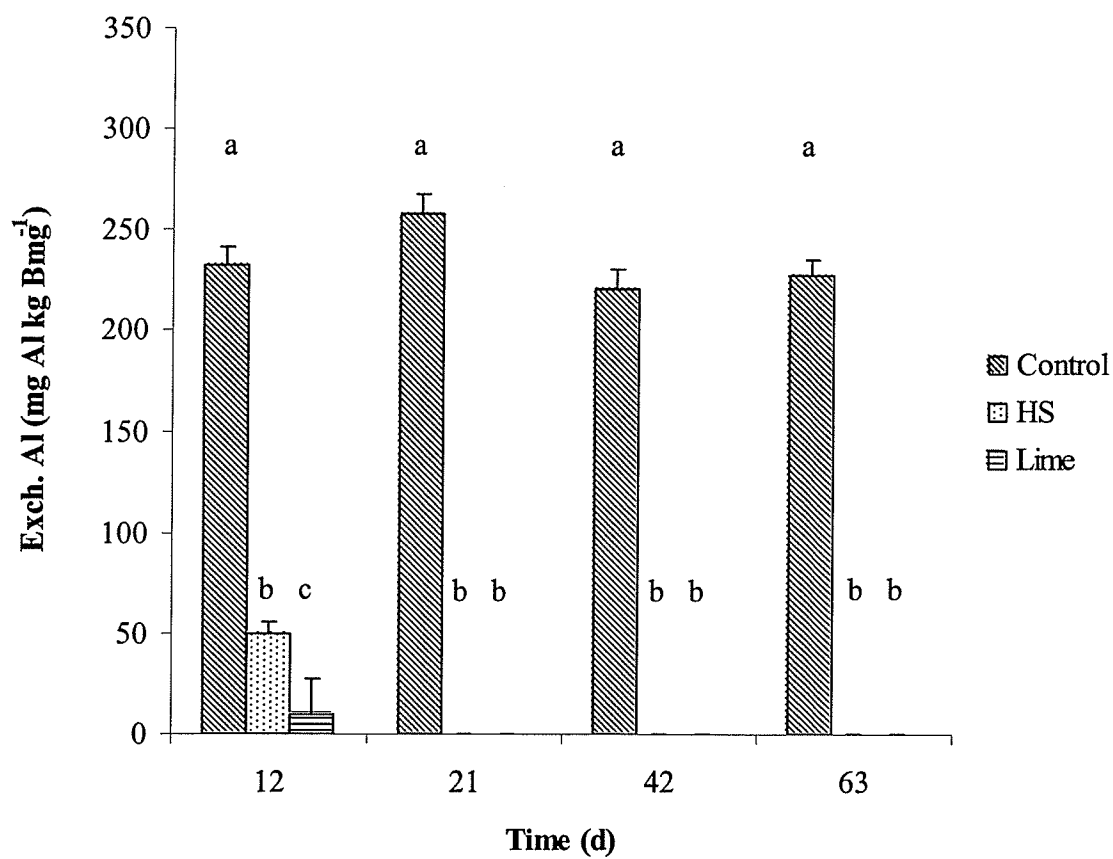


Figure 4.15 Exchangeable aluminum in soil from Bmg horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial Exch. Al = 106.8 mg kg^{-1} .

4.3.6 Aluminum Extracted by CaCl_2 from an Acid Sulphate Soil Horizon

Since Al chemistry and its toxicity to plants are paramount in acid soils (Thomas and Hargrove 1984) a further measurement of the Al in the Bmg horizon was conducted. Hoyt and Webber (1974), proposed the 5-minute, 0.01 mol L^{-1} CaCl_2 extraction as a rapid alternative to the previous methods of estimating plant-available Al and Mn, which outlined shaking times of 16 or 1 hours (Clark 1965; Hoyt and Nyborg 1972). In acid Canadian soils, the procedure resulted in high correlations between Al and crop yield. Its major advantage is saving time.

The results obtained by the CaCl_2 -extraction of soil from the Bmg horizon are depicted in Figure 4.16. The initial value in the untreated Bmg soil was 126.2 ppm, which is of similar magnitude to the value obtained from the NH_4OAc extract (106.8 ppm). In the control, the extractable aluminum ranged from a low of 122.4 ppm on Day 12, to a high of 175.9 ppm on Day 21.

The extractable aluminum in HS-treated soil was dramatically lower than the control soil levels. By Day 12 of the incubation, it had been lowered to 38.8 ppm. The addition of HS on Day 14 had little effect on extractable Al in the ensuing week, as it was 37.3 ppm on Day 21. The aluminum was further reduced between Days 21 and 42, and by Day 63 the value had decreased to 13.5 ppm.

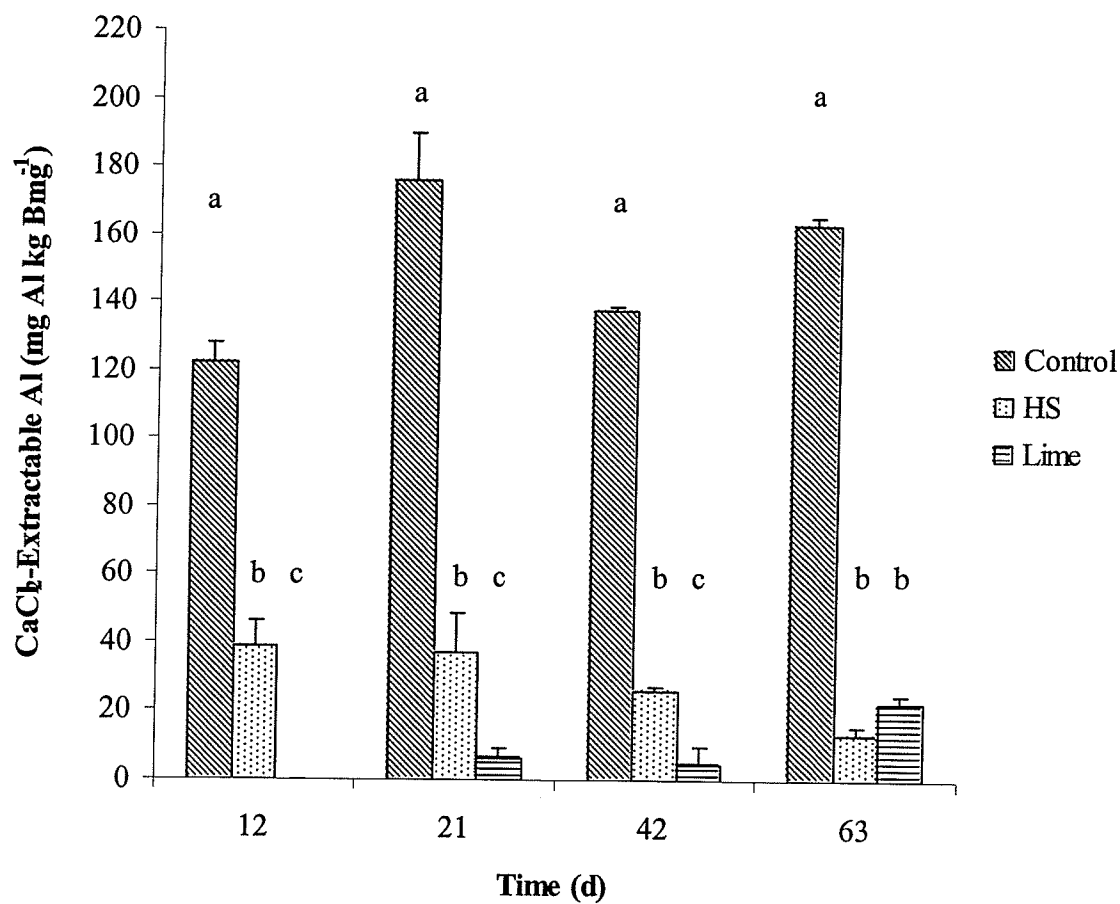


Figure 4.16 CaCl₂-extractable Al in soil from the Bmg horizon on sampling days during the incubation.

(a-c values followed by the same letter within sampling date are not significantly different).

Initial CaCl₂-extr. Al = 126.2 mg kg⁻¹.

Results from the first sampling day (Day 12) indicated that the lime treatment had eliminated the CaCl_2 -extractable aluminum. However, the aluminum values increased in the following weeks. By Day 63, the aluminum extractable by 0.01 M CaCl_2 was 22.7 ppm in the lime-amended soil. These results are surprising since the immobilization of aluminum as the pH of soil increases is quite well documented (Schwertmann and Jackson 1964; Dalal 1975). However, in those instances where the liming agents were very effective, the liming agent contained hydroxyl ions such as $\text{Ca}(\text{OH})_2$ or slaked lime, CaO . The Al is immobilized by precipitation of the very insoluble $\text{Al}(\text{OH})_3$, $K_{\text{sp gibbsite}} = 10^{-33.7}$. Where CaCO_3 had been used as the lime, it is postulated that the carbonate was consumed by the acid in the soil, and further production of acid, H^+ , (e.g. from pyrite oxidation) caused Al to be released without its combination with OH^- to form gibbsite.

Although the lime initially caused the largest and fastest decrease in extractable aluminum, this effect did not persist throughout the incubation period. The HS treatment was slightly more effective in reducing the potentially plant-available aluminum after 63 days when compared to lime, although the difference between the treatments was not statistically significant (Figure 4.16). In the HS-treated soil, the extractable aluminum decreased at each sampling. These results are in agreement with many other studies whereby reduced Al^{3+} toxicity is observed in acid soils amended with OM (Hoyt and Turner 1975; Ahmad and Tan 1986; Noble and Randall 1998). By the final sampling day, the HS treatment had lower extractable aluminum than the lime treatment, (13.5 vs. 22.7 ppm, respectively), although the difference was not statistically significant.

There is no threshold level of aluminum toxicity for plants, as the phytotoxicity of aluminum depends on soil factors (such as pH and OM content) and the plant species (Foy

1984). Hoyt and Webber (1974) reported yield reductions of 20-45% for barley, where the CaCl_2 -extractable Aluminum was 9-15 ppm. It is possible that the 13.5 ppm of aluminum extracted by CaCl_2 in soil from the Bmg horizon in this experiment may be phytotoxic. Other investigators (Goh et al. 1986) have reported that the degree of Al toxicity to wheat seedlings was dependent on the kind of organic acid present with Al in solution. When the Al^{3+} concentration is in the vicinity of 10 ppm, organic acids with chelating sites could reduce the toxicity of Al. In contrast, simple organic acids such as acetic acid that only formed monodentate complexes with Al actually increased the Al toxicity by virtue of the fact that Al-acetate complexes were soluble and available via plant roots. However, it is important to note that acid soils with higher organic matter have been shown to have lower Al toxicity, even if the pH remains low (ie. 4.2) (Evans and Kamprath 1970; Hargrove and Thomas 1981). This was most likely attributable to the formation of large organic-Al complexes that were not uptaken via plant roots.

4.4 Conclusions

Two amendments were applied to the Ah and Bmg horizons of the Keld Series acid sulphate soil in an incubation study of 63 days duration. The effects of an alkaline extract of humic substances (HS) from leonardite were examined and compared with lime. The lime treatment caused the highest increase in pH in both horizons. The HS raised the pH of the Ah horizon from 4.8 to 5.2 after 63 days, while the pH of the Bmg horizon was increased from 3.45 to 4.29. A slight decrease in the organic carbon content of the Ah horizon soil treated with HS was observed. However, the CEC was maintained. The organic carbon content of soil from the

Bmg was doubled with the addition of HS, and was accompanied by an increase in CEC. No exchangeable aluminum was detected in the untreated Ah horizon soil (pH = 4.80). In the Bmg horizon, the initial amount of 106 mg Al kg⁻¹ of exchangeable aluminum was reduced to zero by the lime and HS after 21 days. The lime and HS treatments were both able to significantly reduce the CaCl₂-extractable aluminum in the Bmg horizon. After 63 days, the HS-amended soil had slightly lower extractable aluminum than the lime, although this difference was not statistically significant.

Although the rate of HS amendment used in this experiment did not raise the soil pH to the target of 5.5, it was able to reduce the estimated plant-available aluminum (CaCl₂-extractable Al) in soil from the Bmg horizon. The use of an organic material as a liming agent may also provide the soil with additional benefits due to humic materials, such as improved soil aggregation and nutrient reserves. Thus, it appears as if the alkaline extract of HS has potential to be an effective amendment for acid soils with high amounts of soluble aluminum.

5. ALKALINE HUMIC SUBSTANCES INFLUENCE THE DISTRIBUTION AND LABILITY OF COPPER IN ACID MINE TAILINGS AFTER 24 WEEKS OF INCUBATION

Abstract

Acid, copper-contaminated mine tailings in Nopiming Provincial Park, Manitoba, pose a hazard to their surroundings. In environments with low pH, a large portion of the total copper can exist in the labile and potentially toxic water-soluble form, while the rest is distributed among chemical forms that are less bioavailable. Copper can be sequentially extracted from fractions in the tailings, in an effort to assess the potential lability and availability of the metal. Four amendments were applied to the tailings in an incubation study, and sequential extraction was used to examine the distribution of copper among six fractions. The control tailings were highly contaminated with copper, containing 564 mg kg^{-1} of water-soluble copper. The addition of wheat straw (WS) reduced this form to 305 mg kg^{-1} . The addition of an alkaline extract of humic substances from leonardite (HS) decreased the free copper to 72 mg kg^{-1} , while the combination of HS+WS reduced it to 30 mg kg^{-1} . The CaCO_3 amendment reduced free copper to near zero. The amendments increased the pH of the tailings in the order of Lime > HS+WS > HS > WS. Total copper in the tailings ranged from $1816\text{-}2275 \text{ mg kg}^{-1}$ by summation of copper in the six fractions. Total copper by acid digestion was $2257\text{-}2360 \text{ mg kg}^{-1}$. The efficiency of the sequential extraction method varied from 75 to 96%. Lime was the most effective at reducing the potential availability of copper, followed by HS+WS, then HS.

5.1 Introduction

Many regions in Canada have been mined for natural resources such as coal and industrial metals. The aboveground storage of mine tailings exposes previously buried minerals to the surface environment. Here, accelerated chemical and biological weathering can occur, with the associated risk of contamination by heavy metals (Barnhisel et al. 1982, Amacher et al. 1995). The presence of sulphur-containing minerals at mine sites is a precursor to the production of sulphuric acid by the process of oxidation, resulting in a pH as low as 3.5 (Dixon et al. 1982). Heavy metals such as Cu, Ni, Zn, Mn and Fe are often present in mine spoils, and their mobility and toxicity may be increased in acidic environments (Barnhisel et al. 1982). The potentially toxic combination of a low pH and dissolution of heavy metals are hazardous to vegetation and habitats bordering mine tailings. Hence the reclamation of mine spoils or tailings must involve a neutralization of pH, as well as a reduction of lability, availability and toxicity of free metal ionic contaminants.

Several mines operated within Manitoba in the early twentieth century, in the region that is now Nopiming Provincial Park. The visible remnants of the Central Manitoba Gold Mine, located along Provincial Highway #304, mark the mine site that was active from 1927 to 1937 (Appendix C). Today, the tailings cover an area of approximately 5400 m² and have remained virtually barren since the mine's closure, despite several recent attempts at revegetation on site (Renault et al. 2002). It is believed that revegetation has been limited by the acidity and extremely high concentrations of copper and other metals in the tailings (Renault et al. 2000). The acid portion of the tailings have a pH of 3 to 5, and contain, on average, 2300 mg kg⁻¹ total copper (by digestion) (Ibrahim and Goh, In Press, Commun. Soil Sci. Plant Anal.).

Merely knowing the total contents of heavy metals (such as copper) in a soil provides limited information about the potential behaviour and bioavailability of the metals. Soil texture, pH, organic matter content, and Fe/Mn oxides also influence the lability and bioavailability of copper. A heavy metal in soil can be associated with many of these soil components. Sequential extraction techniques have been employed to examine the distribution of metals, such as copper, among soil micronutrient pools (Shuman 1985; Sims 1986; Alva et al. 2000; Kabala and Singh 2001). Shuman (1991) describes six conceptual micronutrient pools in soils: water-soluble; exchangeable; precipitated as carbonate; associated with Fe, Mn, and Al-oxides; organically-bound; and residual (hereafter referred to as fractions F1 to F6). The water-soluble and exchangeable forms of metals are considered readily labile and available to plants, while the other forms can be considered relatively inactive or strongly bound (Alva et al. 2000).

Copper is a trace element that is essential to the nutrition of plants and animals. The average Cu content in soils is around 30 ppm with a range from 2-100 ppm (Aubert and Pinta 1977) and it is well-documented that excessive bioavailability of copper is toxic. In fact, the soil-plant continuum functions as a natural barrier against toxicity to animals. Plant growth (e.g. revegetation of copper-contaminated tailings) will either be greatly reduced or will cease before a dangerously toxic amount would be accumulated and transferred to animals via the food chain.

Studies using humic substances obtained from lignite as a soil conditioner or amendment are rare. Whiteley and Williams (1993) investigated a metal-contaminated mine spoil (pH = 5.1) after amendment with three forms of lignite: untreated lignite; and the insoluble and soluble extracts obtained after an oxidation treatment. The variable examined was the growth response of metal tolerant and non-tolerant cultivars of *Agrostis capillaris*. The authors concluded that the

lignite treatment may be a valuable reclamation tool, as it improved the survival of non-tolerant cultivars in a Cd-, Pb-, Zn-contaminated mine spoil.

Organic matter accounts for many useful functions in soils, sediments and natural waters (Aiken 1985). Humic substances constitute most of the organic matter in leonardite. It is of interest to investigate if the humic substances that can be obtained following alkaline chemical extraction will be of benefit in the reclamation of copper-contaminated mine spoils.

The objectives of this study are: (1) To assess the copper distribution among six defined fractions, and thereby approximate the lability and the bioavailability of copper, within the mine tailings; and (2) To investigate the potential of alkaline humic substances from leonardite, lime, and wheat straw amendments to reduce the lability and bioavailability of copper after incubation for 24 weeks.

5.2 Materials and Methods

Acid mine tailings were collected from the surface of the Central Manitoba Mine site in October, 2001. A photograph of the site is in Appendix C. The tailings were stored at room temperature in a covered, five-gallon plastic pail.

The mine tailings have a sandy loam texture, with 48.5% sand, 47.2% silt, and 4.3% clay. Their organic matter content is very low (2.1 g kg^{-1}), and total copper contents are extremely high ($2000 - 5000 \text{ mg kg}^{-1}$) (Renault et al. 2000; Ibrahim and Goh, In Press, Commun. Soil Sci. Plant Anal).

The experiment was designed to compare the effects of different organic amendments on the distribution of copper in the mine tailings. Humic substances (HS), fresh wheat straw (WS),

and lime (CaCO_3) were mixed with the mine tailings in four combinations. All experimental units were 200 g of mine tailings. For the HS treatment, 14 mL of liquid HS, (5.62% Organic Carbon), $\text{pH} = 10.5$, was added. The WS, containing 65.5% carbon, was ground by hand and 2.29 g was added to the tailings. The amounts of HS and WS applied corresponded to 4.0 and 7.5 g C kg^{-1} tailings, respectively. The third treatment was the combined addition of HS+WS, at the same rates. The lime was applied at a rate of 4 g CaCO_3 kg^{-1} tailings. Nitrogen (N) was added to all samples except the Control at the rate of 50 mg N kg^{-1} tailings. All samples were prepared in triplicate and placed in 500 mL plastic containers with lids. The samples were incubated at 20°C for 24 weeks and their moisture was maintained at 60% of the water holding capacity throughout the incubation period.

5.2.1 Fractionation of Copper

Total copper concentration of the tailings was determined following digestion of a sample with aqua regia. In addition, six fractions of copper (labeled F1 to F6) were extracted according to Salbu et al. (1998). After each step, the supernatant was separated by high-speed centrifugation for 30 min at 10,000 x g. The residue was washed with 10 mL of deionized water and the wash was combined with the supernatant. All supernatants were refrigerated until analysis for copper content by graphite furnace atomic absorption spectrophotometry. The sequential extraction was conducted in the following manner:

A two-gram subsample of tailings and 20 mL of deionized water were combined in a 50 mL polycarbonate centrifuge tube and shaken for 1 hour at 20°C. The supernatant containing the water-soluble copper, denoted Fraction 1 (F1), was collected and stored.

The F1 residue (i.e. the soil following F1 extraction) was extracted for 2 hours with 20 mL of 1 mol L⁻¹ ammonium acetate, pH 7 to obtain the exchangeable copper (F2) from the mine tailings. To obtain Fraction 3 (F3), the F2 residue was extracted for 2 hours on a shaker with 20 mL of 1 mol L⁻¹ ammonium acetate, pH 5. Fraction 4 (F4), the metal-associated (or specifically-sorbed) copper, was collected by combining the F3 residue with 20 mL of 0.04 mol L⁻¹ NH₂OH-HCl solution for 6 h in a 60°C water bath. To collect Fraction 5 (F5), the organically complexed copper, the F4 residue was extracted for 5.5 h in an 80°C water bath with 15 mL of 30% H₂O₂, pH 2. After cooling, 5 mL of 3.2 mol L⁻¹ ammonium acetate was added and the sample was shaken for 30 minutes. The solution was brought up to 20 mL with deionized water. Finally, all of the remaining copper in the sample was extracted into Fraction 6 (F6). The residue from F5 was allowed to dry for a few minutes. One gram of the residue was placed into a conical flask and digested with 10 mL of 7 mol L⁻¹ HNO₃ on a hotplate for 6 hours. After dissolution with 1 mL of 2 mol L⁻¹ HNO₃, the contents were made up to 10 mL.

5.2.2 Analysis for Copper Concentration

The copper concentration of all extracts was determined by graphite furnace atomic absorption spectrophotometry (AAS). Standard copper solutions were prepared in each of the matrices utilized in the sequential extraction procedure.

5.2.3 Data Analysis

The experiment was carried out as completely randomized design (CRD). The copper fractions (F1-F6), and total copper (by sum of fractions, and by digestion), were randomized among the treatments (Control, HS, HS+WS, WS, and Lime). Analysis of variance (ANOVA)

was performed using Statistical Analysis Software (SAS Institute 2000). Due to some missing data (unequal replications), the treatment LSmeans within each fraction were compared using the protected LSD test, at 95 % confidence interval for F1 – F4 ($\alpha = 0.05$), and at 90 % for F5 ($\alpha = 0.10$). (In SAS, comparison using LSmeans does not provide an LSD value.) The average total copper contents by sum and by digestion were compared by a paired t-test.

5.3 Results and Discussion

5.3.1 Effect of Amendments on pH of the Tailings

The pH measurements (1:1; soil:water) of the tailings after the incubation period of 24 weeks are listed in Table 5.1. The pH of the control tailings was 3.32. As expected, lime was the most effective treatment, raising the pH to 5.59. The HS alone augmented the tailings' pH to 4.5, whereas the WS alone increased the pH by a slight 0.6 units compared to the control. In comparison, the combined HS+WS treatment raised the pH to 5.02. The combination of HS+WS caused a 50-fold reduction in the acidity (i.e. 1.7 pH units), compared to the control.

Despite the fact that all four treatments were able to increase the pH of the mine tailings above the initial value of 3.32, the pH still remained in the acidic range. This means that following the application of the amendments containing HS at the rate used in this experiment, site rehabilitation by revegetation may still not be possible since the availability of heavy metals is expected to be high in acidic environments. Some plants may be able to tolerate the slightly acidic pH in the lime- and HS+WS- amended tailings, but further investigation is necessary to identify these plant species.

Table 5.1. pH of tailings and mean copper content in each fraction

Treatment ^z	pH	Copper in each fraction (mg kg ⁻¹)					
		F 1	F 2	F 3	F 4	F 5	F 6
Control	3.32	564 ± 151 <i>a</i>	16 ± 2.6 <i>c</i>	90 ± 1.1 <i>d</i>	207 ± 13 <i>d</i>	618 ± 199 <i>c</i>	321 ± 73
HS	4.5	72 ± 36 <i>c</i>	44 ± 6.8 <i>b</i>	171 ± 15 <i>c</i>	237 ± 21 <i>cd</i>	872 ± 240 <i>bc</i>	428 ± 38
HS+WS ^y	5.02	30 ± 0.8 <i>c</i>	63 ± 8.7 <i>a</i>	217 ± 31 <i>a</i>	334 ± 12 <i>b</i>	1185 ± 30 <i>a</i>	446 ± 11
WS	3.95	305 ± 6.3 <i>b</i>	45 ± 1.9 <i>b</i>	174 ± 3.9 <i>bc</i>	273 ± 6 <i>cd</i>	863 ± 102 <i>bc</i>	341 ± 62
Lime	5.59	7 ± 0.9 <i>c</i>	40 ± 3.8 <i>b</i>	197 ± 1.3 <i>ab</i>	430 ± 33 <i>a</i>	909 ± 179 <i>ab</i>	405 ± 68
ANOVA	df	Pr > F					
Trt	4	<.0001**	<.0001**	<.0001**	<.0001**	0.0701*	0.1300

a-d Mean values followed by the same letter (within columns) are not significantly different.

^z Treatments: Control, HS = Humic Substances, WS = Wheat Straw, Lime = CaCO₃.

^y For HS+WS, all Cu fractions are means of 2 replications.

* significant at p < 0.10

** significant at p < 0.05

5.3.2 Effects of Amendments on the Distribution of Copper

The total copper measured by fractionation in the control tailings was 1816 mg kg^{-1} (Table 5.2). Of this total, 31% or 564 mg kg^{-1} of Cu was found in F1, the water-soluble fraction. This is an extremely high amount, and is expected to be very toxic to organisms. The organically-complexed fraction (F5) contains the largest portion of copper in the untreated tailings (34%) (Table 5.1 and Figure 5.1).

The total copper extracted from the tailings treated with alkaline HS was 1824 mg kg^{-1} (Table 5.2). This was very similar to the amount of total copper obtained from the control. The water-soluble copper was drastically reduced from 564 to 72 mg kg^{-1} . The copper was redistributed into the other fractions, i.e. F2 to F6. The largest increase was observed in F5, which rose to 872 mg kg^{-1} compared to 618 mg kg^{-1} in the control, although this difference is not significant (Table 5.1). However, the observed increases in the copper content of the F2 and F3 fractions were significant compared to the control. Furthermore, if fractions F1 (water-soluble) and F2 (exchangeable) are indicative of the most available fractions of Cu, it is observed that the HS treatment may greatly reduce the availability of Cu to plants. The size of the residual copper pool (F6) in the HS treated tailings was the largest of all amendments, at 23%.

The fractionation procedure extracted almost 2300 mg kg^{-1} of total copper from the tailings treated with HS+WS. The soluble, toxic form of copper was reduced to 1% of the total copper extracted, or 30 mg kg^{-1} (Table 5.1 and Fig. 5.1). The organically bound copper comprised 52% of the distribution, and was significantly higher than the F5 of all other treatments. A total of 11.5 g C was added per kg tailings, which is the highest of all the treatments. Because organic matter provides surface sites for adsorption and complexation of copper, it is expected that increasing additions of carbon residues will correspondingly raise the

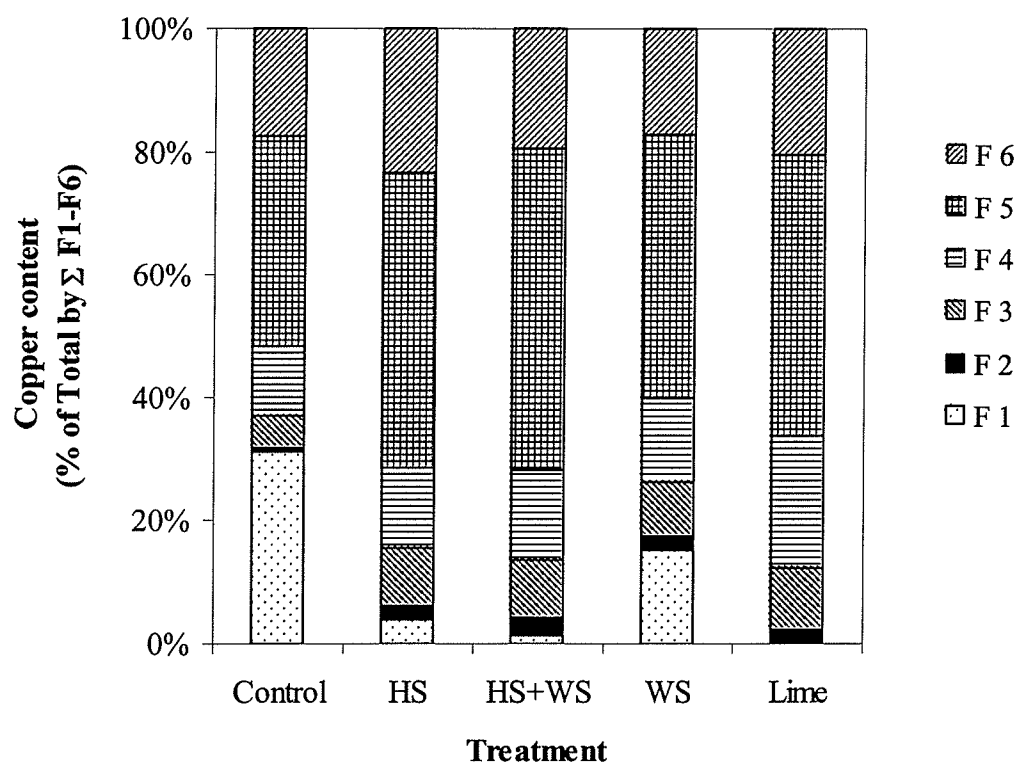


Figure 5.1 Relative distribution of copper among fractions after 24 weeks.

copper in F5. The HS+WS amendment was very effective at reducing the toxic forms of copper, while redistributing the copper to fractions where it is strongly held (F4, F5, F6) and thus considered to be less bioavailable.

When applied alone, the WS did not reduce the free copper as much as the amendments containing the alkaline HS. The water-soluble copper was reduced from 30% in the control, to 15% in the WS-treated tailings (Fig. 5.1). However, the 305 mg kg^{-1} of free copper (Table 5.1) was still extremely high, and poses a toxicity hazard to organisms. It is possible that the low pH of the WS-amended tailings may have limited microbial activity and the ability of WS carbon to play a role in immobilizing copper. In contrast, when WS was added in combination with HS, the water-soluble copper was reduced to 30 mg kg^{-1} . The slightly higher pH observed in the tailings that received the HS+WS treatment may have contributed to the reduction in F1. The pH may allow the carbon of the WS to be used by microbes, and thus through decomposition, the WS may provide some active surface sites to which Cu could be adsorbed or chelated.

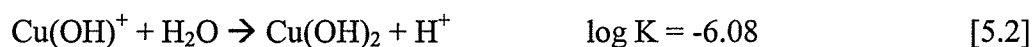
A total of 1989 mg kg^{-1} of copper was extracted from the tailings treated with Lime. The water-soluble copper was negligible, at only 7 mg kg^{-1} . This is a reduction of 80 times compared to the control. The copper was redistributed to all other fractions, with greatest gains in F4 and F6. The lime treated tailings had the largest increase in F4 of all the treatments, at 22% of the total distribution, compared to 11% in the control. This provides evidence that the F4 fraction obtained by this fractionation scheme extracts some carbonate bound copper, in addition to metal-oxide bound copper.

In this study, an amendment was considered effective based on several observations. First, if it elevated the pH of the tailings, then the lability of copper would be reduced (Sims 1986; Alva et al. 2000). The water-soluble copper is the most toxic form, followed by the

adsorbed and exchangeable forms. Thus, if an amendment reduced the copper in these fractions, it was considered beneficial in decreasing the potential for mobility and toxicity. A corresponding increase of copper in fractions where it is tightly bound or unavailable (i.e. F4, F5, and F6), was also considered a benefit. There is some uncertainty as to whether the carbonate-bound fraction (F3) is labile and available. This would depend on the pH, since the Cu sorbed by carbonates may have a transient existence in carbonate minerals. In an acidic environment the Cu may be released upon dissolution of the carbonate. Thus, fraction F3 represents a potentially mobile and available pool among the total copper.

The treatments HS, HS+WS, and Lime, all drastically reduced the F1 fraction of copper in the tailings (Table 5.1). The amount of water-soluble copper in the tailings amended with lime plunged to a nearly negligible amount of 7 mg kg^{-1} . The treatments containing modified leonardite (HS and HS+WS) were both highly effective compared to the control, with HS+WS outperforming HS alone (30 and 72 mg kg^{-1} , respectively).

The amount of free copper in soil solution is very important because this form is readily absorbed by plant roots. In soil solutions with $\text{pH} < 6.0$, the dominant species of copper is the divalent cation, Cu^{2+} (Harter 1991). As the pH increases, two hydrolysis reactions occur fairly quickly.



If an amendment was able to increase the pH, the more unavailable chemical forms of copper such as $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, and even CuO would be formed.

The results show that all treatments caused some of the water-soluble copper to be redistributed from F1 to F2. However, the copper in F2 is still relatively labile, and still poses a toxicity threat because it may be released into solution via cation exchange, or may be subject to plant uptake. In a practical sense, it must also be noted that the quantities of copper held in the exchangeable fraction are very small when compared to the total copper in the tailings. For the Control and WS treatments, where F1 is very large, exchangeable copper contributes very little to the potentially toxic copper in the tailings. But, for treatments with small amounts of Cu in F1, namely HS, HS+WS, and Lime, F2 values are approximately equal to the amount of water-soluble copper, and thus they contribute more to potential toxicity or bioavailability. It was beyond the scope of this study to determine if the survival and growth of plants were curtailed following the addition of these amendments.

All treatments significantly increased the amount of copper in the carbonate-associated fraction, F3 (Table 5.1). Despite the statistical differences between treatments, the relative size of the F3 fraction only varied from 8.7 to 9.9% in all of the amended tailings (Fig. 5.1).

Examination of the organically-complexed fraction, F5, reveals several interesting observations. This was the largest pool of copper in all treatments, comprising 34 to 52% of the total copper (Fig. 5.1). The amount of organically-complexed copper ranged from 618 to 1185 mg kg^{-1} across all treatments, and the differences were found to be statistically significant at $p < 0.10$ (Table 5.1). As anticipated, the treatment that added the most organic material to the tailings, HS+WS, was the most successful at raising the copper in F5.

Copper ions in soil solution are often complexed with various inorganic or organic ligands. Complexation with organic acids or low molecular weight organic matter may solubilize copper and render it available for plant uptake or leaching (van der Watt 1991; Merritt and Erich 2003). On the other hand, complexation followed by precipitation with complex humic substances may immobilize the copper (Stevenson 1982).

5.3.3 Evaluation of the Efficiency of Sequential Extraction

Total copper was determined in two ways; by digestion with aqua regia, and by summation of copper in the six fractions. Total copper contents determined by digestion yielded mean values ranging from 2292 to 2442 mg kg⁻¹ across treatments, while that by summation of the six fractions ranged from 1816 to 2275 mg kg⁻¹ (Table 5.2). However, ANOVA showed that total copper contents by either method were not significantly different (Table 5.2). Overall, the digestion procedure extracted significantly more copper from the tailings than the sequential extraction, as illustrated by a paired t-test comparison ($p = 0.0004$, $df = 12$) (Table 5.2).

The efficiency of the sequential extraction compared to digestion is indicated as a percentage, with a range of 75 to 96 % across the treatments (Table 5.2). The higher amounts of total copper obtained by digestion can be attributed to the destructive properties of aqua regia. The dissolution of metal oxides by this strong extractant may have released occluded copper. In the sequential extraction, the first three extractants are not strong solvents. Thus, it is likely that they did not dissolve all of the copper into solution. The copper that was resistant to extraction during the fractionation procedure is evidently held very strongly within the tailings. As such, this “missing copper” can be considered unavailable, and thus unimportant with respect to copper lability in these mine tailings.

Table 5.2. Efficiency of sequential extraction procedure

Treatment	Total Cu by (Σ F1 to F6)	Total Cu by Digestion	% of Total Cu extracted by fractionation
	(mg kg ⁻¹)		
Control	1816 ± 411	2257 ± 47	80.24
HS	1824 ± 263	2442 ± 159	75.12
HS+WS ^z	2275 ± 14	2360 ± 64	96.45
WS ^y	2002 ± 154	2275 ± 83	84.23
Lime	1989 ± 200	2292 ± 61	86.70

ANOVA

Source	df	Pr > F	
Trt	4	0.3719	0.2263

Paired t-test

Source	df	P-value from paired t-test ^x
Method	12	0.0004

^z For HS+WS, all Cu fractions are means of 2 replications.

^y For WS, Total Cu by Digestion is a mean of 2 replications.

^x The P-value is the probability that the difference in Mean Total Cu by Sum of Fractions and by Digestion is significant.

5.3.4 Effect of Amendments on Potential Lability and Plant Availability of Copper

The water-soluble and exchangeable forms of metals in soils are considered to be plant-available (Shuman 1991; Alva et al. 2000). The free copper cation or its complexed species may be adsorbed to the negatively charged colloids within the soil. Attraction due to electrostatic forces is referred to as non-specific or outersphere adsorption. This copper is exchangeable using salt solutions because of its relatively weak adsorption onto non-specific exchange sites (Shuman, 1991). The F3 fraction, considered to be carbonate-bound, is sometimes included in this estimate, as metals in this fraction can become available under altered environmental

conditions (Kabala and Singh 2001). Alternately, copper may form covalent bonds with an OH⁻ ligand on a soil colloid, such as Fe, Mn, or Al oxides. If the copper forms two covalent bonds with the exchanger, the copper is strongly retained by the soil. This is termed specific adsorption. In this case, the copper is not salt-exchangeable.

The Lability Factor (LF) was employed as an aid in assessing the plant-availability of copper in the mine tailings. It is a relative index to compare metal lability among treatments. When F1+F2 are the only fractions considered to be labile at the time of fractionation, the control tailings have the highest lability, with an LF of 32% (Table 5.3). The lability factors for the HS and HS+WS treatments are 6.3 and 4%, respectively. The Lime treatment was more effective at reducing the F1 and F2 fractions of copper, resulting in a low LF of 2.4%.

Table 5.3. Copper Lability Factors for each treatment

Treatment	Lability Factor 1 ^z	Lability Factor 2 ^y
Control	31.92	36.88
HS	6.33	15.72
HS+WS	4.09	13.62
WS	17.50	26.21
Lime	2.39	12.31

^zLability Factor 1 = [(F1 + F2) / (Total Cu by Sum)] x 100

^yLability Factor 2 = [(F1 + F2 + F3) / (Total Cu by Sum)] x 100

If fraction F3 is also considered labile, then 37% of the relative distribution of copper in the control tailings is potentially toxic. Regardless, the resulting lability factors, Lability Factor 2, present the same pattern as described for Lability Factor 1 (Table 5.3). Hence, the treatments containing the alkaline organic amendment (HS and HS+WS) decreased the copper LF to less than half of its original value, and the Lime is slightly more effective than the HS+WS.

Caution must be taken when using a lability factor to interpret the potential movement or availability of metals in soil. It is useful as a discussion tool, but the mobility of copper in individual fractions is only assumed, and not measured. The copper extracted into each fraction, and its lability, will depend upon the individual soil and the metal fractionation procedure employed.

5.4 Conclusions

The study confirmed that the tailings from the Central Manitoba Mine site are highly contaminated with copper, containing approximately $2300 \text{ mg Cu kg}^{-1}$. The control tailings contained 564 mg kg^{-1} of water-soluble copper, which is readily labile and toxic. Approximately one-third of the total copper in the acid tailings is considered potentially toxic.

All amendments altered the distribution of copper. The Lime was the most effective at increasing pH, and decreasing soluble copper.

The two treatments containing alkaline, humic substances extracted from leonardite were also effective at reducing water-soluble copper. The addition of WS with the HS further reduced the water-soluble fraction. The treatment HS+WS also had the highest amount of copper in the organically-complexed fraction.

In conclusion, the alkaline humic substances extract used in this research may be a valuable addition to a reclamation strategy for acid, copper-contaminated mine tailings.

6. GENERAL SUMMARY AND DISCUSSION

At the outset, it must be pointed out that the project was designed to evaluate the potential of using alkaline humic substances from leonardite for the amelioration of acid soils. Leonardite is a waste material from coal mining. It is stored on-site and can easily be ground to a fine powder. Leonardite was previously found to be rather inert when applied to soils or plants for agricultural purposes (Shaykewich 2000; Dilk 2002). Therefore, in order to access potential benefits, the humic substances contained in leonardite powder have to be extracted. This is done by alkaline extraction¹ to obtain suspensions that are termed alkaline HS in this investigation. Due to the fact that the HS is alkaline, plus the fact that at high pH, humic substances are “activated” by deprotonation of acidic functional groups, it seemed reasonable that the HS be tested in order to evaluate its use in the amelioration of acid soils.

The investigations reported in Chapter 3 demonstrated the acidic conditions present in the Keld Series soil, specifically the Ah and Bmg horizons. Two of the three methods that were used to determine the lime requirements (LR) of the two horizons studied herein, namely titration and SMP Single-Buffer method with the LR Formula (Quigley and Reid 1995), gave results in close agreement with each other. Thus, the average of these two LRs calculated for each horizon was used as the rate of lime to be applied to the soil in the incubation study.

¹The process of extracting humic substances from leonardite is proprietary information, but it has been confirmed that following alkaline treatment, humic substances resembling humic and fulvic acids are present in the commercial formulation that is sold as a suspension.

completed in Chapter 4. The rates of lime applied to the soil from the Ah and Bmg horizons were equivalent to 8.6 and 19.76 g $\text{CaCO}_3 \cdot \text{kg}^{-1}$ soil, respectively.

An assessment of the accuracy of the LR determined in Chapter 3 (to reach $\text{pH} = 7.0$) can be done by observing the pH in lime-amended Ah and Bmg soil samples in Chapter 4. In the Ah horizon, the pH was raised from 4.80 to 6.2 after 63 days of incubation. The soil pH from the Bmg horizon was raised from 3.45 to 6.43 in 12 days, and had increased to 6.7 by Day 63. It is unknown if or how the pH would change in the lime-amended soils after this point in time. As expected, lime caused a rapid increase of soil pH (Osei 1993). It is interesting to note that the pH of soil from the Bmg was elevated faster than soil from the Ah horizon. This observation was attributed to the higher buffering capacity of the topsoil, since the Ah horizon contained more organic matter than the Bmg horizon. The pH of lime-amended soils at the end of the incubation did not reach 7.0, therefore it can be concluded that the LRs determined in Chapter 3 were underestimated. Barnhisel et al. (1982) noted the potential for underestimation of LRs obtained for acid sulphate mine spoils due to the presence of sulphidic minerals in the soil. Soil properties that contribute to buffering capacity, such as clay content and organic matter content, will buffer changes in soil pH and may have affected the LRs determinations in Chapter 3.

A similar assessment of the effectiveness of the rate of alkaline HS added, on the pH of soil from the Ah and Bmg horizons can be made. The rate was determined by titrations of soil vs. HS prior to the incubation study, for both horizons. Due to the volumes of HS liquid that were necessary to reach $\text{pH} = 7.0$ based on the titration curves, the desired final pH was lowered from 7.0 to 5.5. Soil samples (of 50 g) from the Ah horizon received 10 mL of HS (1:1). During the incubation, the pH was found to stay consistently between 5.1 and 5.2. The soil from the more acidic Bmg received a total of 30 mL HS in split applications. By Day 63, the pH had

increased to 4.3. It is unknown what pH changes would occur after Day 63 in either soil. The pH of the Ah and Bmg did not reach the target of 5.5. Hence, the soil vs. HS titrations did not sufficiently predict the HS needed, especially in the Bmg horizon. This finding reiterates evidence of a very acidic Bmg horizon in the Keld soil. Lime was more effective in raising the pH of the Bmg than alkaline HS.

The final $\text{pH}_{\text{CaCl}_2}$ in the Ah was 5.2, (thus $\text{pH}_{\text{H}_2\text{O}} \approx 5.5$) at which it is generally accepted that exchangeable Al is uncommon (Schwertmann and Jackson 1964). Initially, $126 \text{ mg} \cdot \text{kg}^{-1}$ of aluminum was extracted from the soil of the Bmg horizon by dilute calcium chloride, which is a method that estimates plant-available aluminum (Hoyt and Webber 1974). The lime eliminated the Al on Day 12, but Al was detected on the following three sampling days. The HS, applied in split applications, caused a reduction of aluminum, to $39 \text{ mg Al} \cdot \text{kg}^{-1}$ on Day 12. The extractable aluminum decreased on each successive sampling day. On the final day of the incubation, Day 63, the lime- and HS-amended soil contained 13.5 and $22.7 \text{ mg Al} \cdot \text{kg}^{-1}$ soil, respectively, and both were statistically lower than the control.

The relationship between the reduction of Al-toxicity with increasing organic matter has been documented by many researchers (Evans and Kamprath 1970; Hoyt and Turner 1975; Thomas and Hargrove 1981; Ahmad and Tan 1986). Ahmad and Tan (1986) reported that organic matter (wheat straw) was as effective as lime at reducing the toxicity of Al. The addition of a calcium-saturated organic product derived from coal reduced the acidity and extractable aluminum in an acid soil (Noble et al. 1995; Noble and Randall 1998). The decrease in exchangeable Al with increasing rates of OM was attributed to complexation; and formation of solid Al phases was also likely as the pH increased (Noble and Randall 1998).

Despite the fact that lime was more effective at raising the pH of the acid soil from the Bmg horizon, both the alkaline HS and lime were effective at reducing extractable Al at the end of 63 days. The increased efficiency of the alkaline HS must be due to complexation of free Al, and the probable associated reduction of Al toxicity in the newly formed Al-HS complexes.

Ahmad and Tan (1986) found that a combination of lime and wheat straw was more effective at reducing Al toxicity to soybeans compared to lime alone. However, the effects of combinations of HS and Lime were not investigated here. It is postulated that the addition of both together should raise the pH above 5.5, and may result in lower amounts of plant-available aluminum after 9 weeks compared to lime alone due to Al-OM complexation.

A benefit of lime application to soils is the provision of basic cations, calcium and magnesium, depending on the type of lime added (Riggs et al. 1995). As expected, the lime caused significant increases in exchangeable calcium in soil from both horizons. The quantity of exchangeable Ca in the alkaline HS-amended soil was approximately the same as the untreated soil in the Ah horizon, and was 100 ppm higher than the untreated soil from the Bmg horizon. The HS amendment slightly raised the exchangeable Mg in the Bmg, and had approximately the same effect as lime in the Ah horizon.

The content of basic cations in organic matter added to acid soil was found to be highly correlated ($r^2 = 0.92$) with the final soil pH (Pocknee and Sumner 1997). The amount of exchangeable bases was altered very slightly in HS-amended soil. A concomitant decrease in H^+ and Al^{3+} in soil amended with alkaline HS is further evidence of benefits of use of this extract as an amendment.

In Chapter 4, there were some contrasting results relating to cation exchange capacity and percent soil organic carbon content within the two soil horizons. In soil from the Ah horizon that

was amended with the alkaline HS, there was a decline in SOC. However the CEC was maintained. Thus, the HS must have added some negatively-charged exchange sites in the form of surface functional groups (e.g carboxyl) to the soil. In HS-amended soil from the Bmg, the SOC was doubled from 1 to 2%. Shaykewich (2000) reported that a modified leonardite amendment also significantly increased %SOC in a clay loam forest topsoil with initial %OC of 1.5% (Waitville Dark Grey Luvisol). The CEC of the mine tailings was not determined in Chapter 5 of this study. However, it is known that the mine tailings have low %SOC and are coarse-textured. Based on the observed increase in CEC of the Bmg, which is also strongly acidic and low in %SOC, it is postulated that the CEC of tailings amended with HS will increase, provided that the amendment was able to increase %SOC.

Following the success of alkaline HS extract in the reduction of free Al^{3+} in the Keld Series soil, the amendment was investigated for its reclamation potential in a degraded mine spoil. The final experiment (Chapter 5) was conducted to observe the effects of the alkaline HS extract on mine tailings contaminated with $\sim 2300 \text{ mg Cu} \cdot \text{kg}^{-1}$. Copper is known to strongly complex with OM (Stevenson 1982; Shuman 1991).

The untreated mine tailings had an initial pH of 3.32. Four treatments were applied and the tailings were incubated for 24 weeks. The application of wheat straw (WS) and lime raised the pH to 3.95 and 5.6, respectively. The HS amendment increased the pH to 4.5. However, when added in combination, the HS+WS increased the pH to 5.0.

Initially, the water-soluble and exchangeable copper comprised approximately one third of the total copper in untreated tailings. The water-soluble copper was reduced by amendments in the order of lime > HS+WS > HS > WS. Of the four treatments, the application of HS+WS resulted in the highest amount of copper found in the fraction considered to be organically-

bound. The availability of copper was not investigated here. However, the reduction of acidity and labile (most toxic) forms of copper demonstrated the potential benefits of using the alkaline HS extract in the reclamation of the mine tailings studied.

It is hypothesized that a combination of lime, HS and WS would probably be the most effective at ameliorating the mine tailings. The lime would quickly raise the surface pH of the tailings. The combination of older and newer organic matter would provide many surface exchange sites for complexation of copper and other metals. The variety of humic materials may also provide long and short-term available organic carbon and nutrients; while also improving the physical condition of the tailings.

Further research into the use of alkaline humic substances for the improvement of acid, degraded lands should take into account the following. The rates of HS used herein were based on attaining a soil pH of 5.5, and were limited by the liquid formulation of the product. Application of the original product without (1:1) dilution, or use of an alternate formulation such as a dehydrated, powdered form, may be more advantageous. If more HS could be applied due to a change in its formulation, the pH of the treated soil may reach the target pH of at least 5.5, the original target of 7.0, or somewhere in between. In addition, determination of the optimum rate of HS for desired benefits would facilitate the design of subsequent studies seeking to investigate the use of HS as an amendment. This may be accomplished by following the procedure for a conventional determination of lime requirement, where various amounts of HS are combined with soil or tailings and incubated for 3 months. The practicality of using the high rates of liquid HS (as required) in the field is questionable, due to flooding of the soil and possible salinization. Further, the cost of the HS may be prohibitive, as compared to lime or other organic materials. Also of interest would be the testing of combinations of treatments,

such as lime plus humic substances extract, to see if the soil chemistry could be further improved compared to either amendment alone.

Finally, the plant-availability of toxic metals was only estimated. The next step to assess bioavailability may be accomplished in several ways. A restricted number of plant species would allow a simple preliminary investigation into bioavailability of aluminum and copper. The selection of grasses or plants should consider those species that are native to the study area, and the tolerance of the species to soil acidity, as well as to metals of relevance (ie. those in the soil or tailings). Environmental conditions such as temperature and moisture can be controlled in greenhouse studies, therefore it may be preferable to conduct a greenhouse study before moving to field studies. Regardless of the experimental design, the effects of amendments on plant toxicity may be observed by monitoring above-ground and root biomasses, and yield. These values, accompanied by the measurement of soil chemical properties such as exchangeable or extractable metals, pH, and other pertinent properties, will provide information for assessing bioavailability of metals to plants grown on HS-amended soil.

7. CONCLUSIONS

The use of an alkaline extract of humic substances from leonardite as a liming agent for degraded, acid soils was investigated. The high lime requirements determined for the Ah and Bmg horizons of the Keld Series confirmed the acid conditions of this soil.

The application of lime (CaCO_3) caused the largest increase in pH and was the most effective at reducing acidity in the Keld soil and the mine tailings. The alkaline HS was able to raise the pH of the Keld soil Ah and Bmg horizons. It also raised the pH of the acid mine tailings. The treatment of HS + wheat straw (WS) raised the pH of the tailings more than HS alone.

Lime and HS were both able to eliminate the exchangeable Al in the Bmg horizon of the Keld Series soil after 21 days. The HS amendment was as effective as lime at reducing CaCl_2 -extractable Al (an estimate of plant-available Al) in the Bmg after 63 days.

The HS amendment altered the distribution of Cu among six fractions in the highly contaminated mine tailings, mainly by a large reduction of the water-soluble Cu and an increase in the organically-associated Cu. The combination of WS with HS further enhanced these observations, and resulted in slightly higher pH than HS alone.

The HS extract is not soil humus, but provided organic carbon to the acid Bmg horizon of the Keld Series soil and to the Cu-contaminated mine tailings. In light of the findings herein, it appears as if the alkaline extract of humic substances from leonardite, used as an amendment for

degraded lands, has demonstrated benefits for the amelioration of adverse chemical properties of an acid sulphate soil and Cu-contaminated mine tailings.

8. CONTRIBUTION TO KNOWLEDGE

The findings herein contribute to research and development into enhancing the usefulness of a mining waste product, leonardite. The new product that was tested, which is actually an alkaline extract containing humic- and fulvic-like acids, appears to be beneficial for the amelioration of the adverse chemistry of acidic soils; as supported by its observed abilities to raise the soil pH and reduce levels of exchangeable aluminum, and water-soluble copper.

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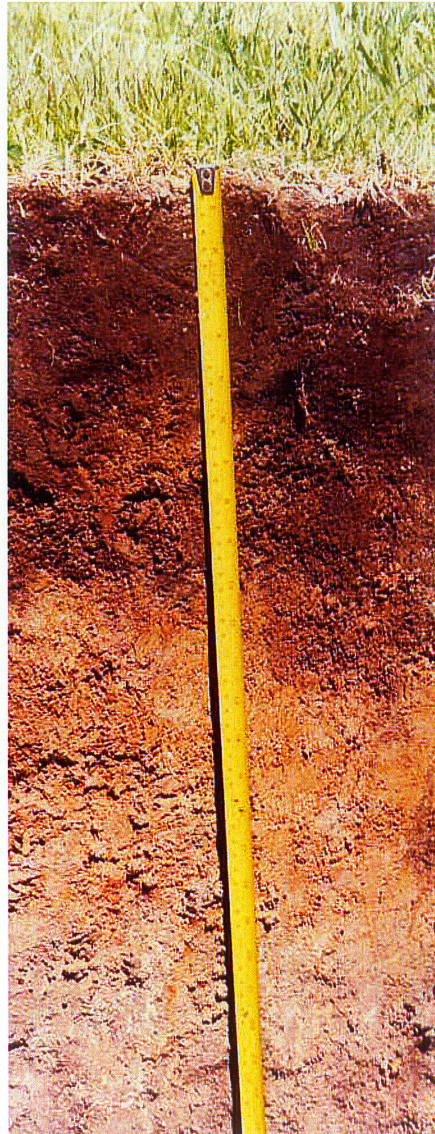
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10. APPENDICES

Appendix A. Profile Description and Photograph of the Keld Series Soil.

Soil Series	Keld Series	
Subgroup	Gleyed Sombric Brunisol	
Location	SW 03 25 20 W	
Date	May 25, 2000	
Topography	Level	
Drainage	Imperfect	
Vegetation	Natural vegetation, herbaceous species	
Parent Material	Extremely acidic lacustrine clay shales (sulphidic), overlain by glacial till	
Ah	0 - 20 cm	Black (10YR 3.0 2.0) clay loam; granular; sharp, wavy boundary to:
Bmgj	20 - 25 cm	Brownish black (10YR 4.0 2.5) clay loam; prismatic; wavy boundary to:
Bmg	25 - 45 cm	Dark brown-orange (7.5YR 4.0 2.0) clay; weak, medium subangular blocky; breaks easily; numerous orange iron mottles present (7.5YR 5.0 6.0); gradual boundary to:
BC	45 - 55 cm	Greyish (10YR 4.0 2.0) clay; prismatic; iron mottles as above; jarosite mottles also present (2.5Y 7.0 6.0); clear boundary to:
Cg1	55 - 75 cm	Greyish (10YR 4.0 2.0) clay; stratified; 10% of area covered by jarosite mottles (2.5Y 7.0 6.0); clear, smooth boundary to:
Cg2	> 75 cm	Greyish (10YR 4.0 2.0) clay; stratified; some shale-like fragments present; 60% of area covered by distinct jarosite mottles (5.0Y 7.0 6.0).



Keld Series Soil Profile 0-60 cm.

Appendix B. Selected Properties of the Leonardite Powder Used in the Extraction of Alkaline Humic Substances^z.

Select Chemical and Physical Properties:

pH _{H2O}	5.8
pH _{CaCl2}	4.2
Bulk Density	0.68 g·cm ⁻³
Grav. Moisture (w/w)	18.0%

Humic Acid and Fulvic Acid Contents^y:

Yield (HA + Ash)	27.2%
Ash in HA	9.7%
Yield (HA only) ^x	24.6%
Yield (FA + Ash)	3.0%

Characteristics of Humic Acid:

Total Acidity	8.3 meq · g HA ⁻¹
Carboxyl (-COOH)	4.0 meq · g HA ⁻¹
Phenolic (-OH)	4.3 meq · g HA ⁻¹

^z Laboratory examinations conducted by Dr. S.M. Lee. Department of Soil Science. The University of Manitoba.1999.

^y by SSSA Method on sample of 100 g.

^x Yield (HA only) = [Yield (HA + Ash)] - [Yield (HA +Ash)*(Ash in HA)].

Appendix C.



Aerial Photograph of Mine Tailings. Note the sparse vegetation.