CHAPTER 1

INTRODUCTION

A review on soil acidification, soil nutrient depletion and the need for soil amelioration using coal combustion byproducts and organic wastes.

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1.1 Introduction

Numerous environmental, nutritional and cultural factors effect plant production. None of these factors act independently and sometimes management factors are more important than the actual amount of fertiliser applied. The role of the soil in this regard is certainly not unimportant. Soil acidity and soil–fertility, on smallholder farms as well as in commercial farming, are the fundamental root causes for the declining per capita food production. The continued threat to the world's land resources is exacerbated by the need to reduce poverty and unsustainable farming practices (Sanchez *et al*, 1997).

During the past decade, food security has not been a global priority, but studies have shown that food security is one of the main global concerns as we move into the next century. Settlements were first supported by inherent soil fertility. As populations grew, this fertility was gradually depleted by crop-harvest removals, leaching and soil erosion, especially where farmers were unable to sufficiently compensate for these losses by returning nutrients to the soil via crop residues, manures and mineral fertilisers (Shepherd and Soule, 1998).

Agricultural and industrial activities have greatly accelerated the pace of soil acidification. In agriculture, the increasing use of nitrogenous fertiliser and the oxidation of organic residues under cultivation combined with incorrect management practices are important contributors to acidification of soils. The burning of fossil fuels and industrial pollution ("acid rain") have also contributed substantially to the acidification of many natural and agricultural ecosystems (Wang *et al.*, 2000).

Soil acidity affects plant development by influencing the availability of certain elements required for growth (Tisdale and Nelson, 1975). Soil acidity is a property of the greatest importance to the plant producer and one that is easily corrected if dealt with immediately after detection.

Liming soil is an ancient agricultural practice to ameliorate soil. Limestone (calcite, dolomite or a combination) is basically the main liming material used to date, with the infrequent use of quicklime, hydrated lime and byproducts such as slag and gypsum (for sub-soil amelioration). Current levels of pollution mean that more lime is now required to offset acidification, but extensification is likely to result in a cessation or reduction of liming for economic reasons, while afforestation may result in increased acid deposition and acidification (Goulding and Blake, 1998).

Although liming is usually an effective counter to soil acidification, liming acid soils does not always make economic sense. Many low –input agricultural systems (e.g. subsistence farming practices and extensive grazing lands) cannot use large amounts of lime and remain economically viable.

The mobility of lime in the soil is characterized, as being very slow, and by incorporating lime into the surface to ameliorate acid sub-soils, can be very slow and difficult to justify. A liming material is characterized as a material containing Ca and Mg compounds which are capable of neutralizing soil acidity (Barber, 1967). Amelioration of the entire rooting zone is not always economically viable or practical for most crops. Attempts to modify the profile below the conventional plow depth, either with deep plows or specialized equipment, have not proved encouraging in terms of yield response (Farina and Channon, 1988a).

In terms of reducing environmental impacts, the losses of nitrogen to waters from arable land can be greatly reduced by converting arable land to unfertilized, low intensity grassland, by introducing riparian buffer strips and, less effectively, by reducing fertiliser inputs and/or planting a cover crop. However, the abandonment of arable land and the natural regeneration of woodland result in increased acid deposition and soil acidification (Johnston *et al*., 1986; Goulding and Blake, 1998. and, in the case of extreme acidification, the mobilization of aluminium (Al) and other potentially toxic metals and their consequent uptake by the trees (Goulding and Blake, 1993; Goulding and Blake, 1998).

South Africa is characterized by a poor agricultural resource base, while the current population of 40 million continues to grow (Rethman *et al*., 1999b). Sustainable increases in food production are difficult on this limited resource base. The effective use of acidic soils is also critical in many areas. Therefore, increased food production is urgently required to improve both national and household food security (Truter and Rethman, 2000).

Practices, which focus on reducing inputs, provide an important link between the needs of commercial farmers and those involved in subsistence agriculture. With commercial systems, the aim is to reduce inputs for economic/environmental reasons. Subsistence farmers have similar aims, but, in this case, it is because they have restricted access to inputs.

Soil acidification is, therefore, a serious socio-economic concern. Very few countries can afford the decline in food production, which often accompanies the changes, which are taking place in our soils. Nutrient management practices affect the viability of agricultural ecosystems. Many of the factors influencing nutrient flows in agriculture lie beyond the farm and are the result of the way we live. Nutrient management strategies based on the return of nutrients from plant and animal wastes back to the soil will require radical changes to both agriculture and society. External sources of plant nutrients will, therefore, continue to be an essential part of agriculture as we strive to replace the nutrients lost in successive crop harvests. Farmers must, nevertheless, be made aware of the need to increase the cycling of nutrients within agricultural ecosystems. Ways must be found to return plant residues to the soil. To help manage nutrient flows, it may be necessary to develop nutrient balances based on soil and plant analyses.

In many rural development areas, farmers are not always able to obtain or use lime to treat their acidic or nutrient depleted soils, because they lack appropriate transport infrastructure and it can become very expensive. The possible use of alternative liming materials, which are economically more viable and more easily accessible, should, therefore, be investigated.

1.2 Nature and extent of acidification and soil nutrient depletion

Acid soils occupy about 30 % of the worlds ice-free land area. Acidity is a major degradation factor of soils and covers extensive areas in the tropical and temperate zones (Baligar and Fageria, 1997). In South Africa 15 % of the soils, or 16 million hectares (Beukes, 2000) available for dry land cropping, are classified as dystrophic and much of the yield instability in the higher potential, eastern parts of the South Africa is attributable to shallow root development and consequent susceptibility to short duration midsummer droughts (Farina and Channon, 1988b).

Soil acidity affects plant development by its influence on the availability of certain elements required for growth (Tisdale and Nelson, 1975). Maize (*Zea mays* L.) is the third most important cereal grown in the world. In South and Central America, maize is grown mostly on acidic soils. On these soils, yields are limited by deficient levels of available P, Ca and Mg, and toxic levels of Al and Mn (Baligar *et al.*, 1997a). Growth –limiting factors in acid soils include deficiencies (N, P, Ca, Mg, Mo, Zn) and toxicities (Al, Mn, Fe, H) of different elements. Management practices, such as acidifying effects of N fertilizers, removal of cations by harvested crops, increased leaching and run-off of cations and leguminous crops (N_2 fixation) have resulted in the lowering of natural soil pH (Baligar and Fageria, 1997). Soil acidification and indirectly nutrient depletion is an ongoing natural process. In natural ecosystems the rate of acidification is largely determined by the loss of base minerals (Ca, Mg, K) from the soil by leaching. The central problem of acid soil management lies in the constraints, which arise from the soil condition. The most serious of these is that at low pHs; acids (H^+) can release soluble aluminum (Al) and manganese (Mn) from soil minerals. Both Al and Mn have direct toxic effects on many plants (Beukes, 2000).

In a wide range of acidic Natal soils, exchangeable Al^{3+} rather than adsorbed H^{+} has been shown to be the main source of acidity (Moberly and Meyer, 1975). Orchard (1972) discovered that with a few exceptions, the EAI (exchangeable aluminum index) value increased with depth and this raises the troublesome problem of the need for subsoil liming. Sufficient exchangeable Al^{3+} in the subsoil will preclude healthy root development.

Al concentrations can be sufficiently high in acid soils, with pH values of 5.5 or below, to be toxic to plants (Ahlrichs *et al*, 1990). Aluminum acts by restricting root extension growth. All except the most tolerant crops suffer root damage at concentrations of 2-3 ppm Al^{3+} in the equilibrium soil solution. Plant sensitivities to Al can nevertheless be expressed secondarily through changes in water and nutrient supply, which occur in response to Al, and induced changes in root development. Acid soils are generally unable to supply critical plant nutrients (Ca, Mg, P, K, and Mo). The fundamental reaction underlying soil acidification involves the replacement of exchangeable base cations (Ca, Mg, and K) present in the soil solution by protons (H^{+}) as already mentioned.

The implication for yield reduction during periods of moisture stress, when subsoil reserves remain largely inaccessible to crops because of poor root penetration is obvious. Acid soils usually lack appropriate levels of N (nitrogen) to support healthy plant growth and the application of N fertiliser is a common practice for sustainable crop production in acid soil regions (He *et al*, 1999a).

In various plant species, Al can interfere with uptake and efficient use of essential nutrients (Baligar *et al.*, 1987, 1989, 1993a, b. 1996;Baligar and Bennet, 1986; Foy, 1992; Baligar and Fageria 1997). The Al inhibition of nutrient uptake in sorghum included Mg, Ca, K, N, Fe, P and Zn, while in maize it included K, Mg, Ca, P, Fe and Zn. Both of these crops were grown at 41 % soil Al saturation. It appears that Al influences uptake of various nutrients differently in different species. In general, the uptake of cationic elements in the leaves and stems of soybean plants cultivated on acid soil became higher than those of plants cultivated on normal soil during the late period of growth. However, the effect of soil acidification on the uptake of the anionic element, Se, is quite different from that on the cationic elements. The uptake of Se by plants cultivated on normal soil was higher than that of plants cultivated on acid soil at all four harvest points. The uptake behavior of these elements in soybean was discussed in relation to their adsorption behaviour on the same soil as was used for soybean cultivation. The growth of tomato plants was seriously affected by the soil acidity and lowering of uptake of elements was observed for the plants cultivated on acidified soil (Wang *et al.*, 2000). Plant demand, in addition to nutrient status of shoots (internal ionic concentrations), had profound effects on nutrient accumulation in plants. Differences in growth and nutrient uptake among cultivars/ genotypes in the presence, or absence, of phytotoxic levels of Al have been related to shoot demand, nutrient absorption and translocation, and dry matter production potential per unit of nutrient absorbed (Atkinson, 1990; Foy, 1992; Gerloff and Gabelman, 1983: Vose, 1984; Baligar and Fageria, 1997).

In a study on peanuts, peanut roots were little affected by soluble Al concentrations, which severely limited cotton (*Gossypium sp.*) root growth. Manganese may also become toxic to plant growth in acid soil (Labanauskas, 1966; Blamely and Chapman, 1982), particularly under flooded or waterlogged conditions (Graven *et al*, 1965; Blamely and Chapman, 1982).

Forage production in southeastern Australia is often well below potential. Poor productivity in the higher rainfall zones has often been attributed to effects of soil acidity and phosphorus deficiency on N_2 fixation by legumes in pasture swards. Difficult terrain and lack of suitable equipment commonly prevents the incorporation of lime or phosphatic fertilizers in permanently grazed pastures, and amelioration of soils in these situations must rely upon surface applications. A study was initiated in New South Wales, Australia, to investigate the effect of surface applied lime and superphosphate on N_2 fixation and growth of subterranean clover (*Trifolium subterraneum*). Eighteen months after treatment application, liming had increased surface soil pH and significantly decreased the concentrations of $CaCl_2$ extractable aluminium and manganese at all sites. While, pasture growth and subterranean clover content were increased by lime or superphosphate applications (Peoples *et al.*, 1995).

In addition to the direct effects of soil acidity on plants, the growth of legumes may be reduced indirectly through the depression of nodulation and nitrogen fixation. (Adams and Pearson, 1967; Munns *et al*, 1977a; Blamely and Chapman, 1982). Poor nodulation of soybeans (*Glycine max* (L.) Merr) in acid soil has been attributed to an Al induced Ca deficiency (Sartain and Kamprath, 1975; Blamey and Chapman, 1982).

The effects of low soil pH and lime applications on nodulation and nitrogen fixation in subterranean clover (*Trifolium subterraneum* L.) were examined in field and glasshouse experiments in south-west Australia. Field data from a number of broad acre pastures indicated that soil acidity, combined with high soil aluminium, reduced clover dependence on nitrogen fixation (% Ndfa) and that the addition of lime increased soil pH, reduced extractable aluminium concentrations below phytotoxic concentrations and increased plant nodulation. Glasshouse experiments also demonstrated positive effects of liming in reducing extractable aluminium and increasing total N_2 fixation and % Nfda, but beneficial effects on N_2 fixation were partly offset by counteractive effects on symbiosis through increased nitrogen mineralization at high lime application rates. Where companion ryegrass (*Lolium rigidum* Gaudin) was pot cultured with subterranean clover soil mineral N, released following liming, was absorbed preferentially by the grass, resulting in increases in % Nfda of the associated clover (Unkovich *et al.*, 1996).

Acidification of soil induces a change in the chemical state of the cations from bound to labile, the labile cationic species being readily absorbed by plants. The importance of its effect on the root absorption of trace elements by various plant species was studied with respect to plant nutrition. It was demonstrated that when the soil pH changed, the cations were absorbed by colloids. Furthermore, the effect of soil pH on element concentration and uptake by maize was studied. The contents of Fe, Mn and Zn in both shoots and roots of dwarf French beans, were inversely proportional to rhizosphere acidity (Wang *et al*, 2000). Heavy metals artificially added to acid environments often exhibit high bioavailability, accumulating in the edible part of plants. The bioavailability of these elements to plants deserves investigation in order to reduce the toxic and radiation hazards to humans through the food chain (Wang *et al.*, 2000).

1.3 Causes and effects of acidification and soil nutrient depletion

Before the discovery of plant nutrients, soil amelioration and fertilisation were, by force of circumstance, biological, i.e. done with substances taken from nature. After the discovery of plant nutrients, the chemical concept of fertility displaced the biological one. The implications of chemical fertilisation – inefficiency, deterioration in product quality, diminishing productivity of soils and negative effects on the environment- have created an urgent need for the study of fertility as a result of the activity of the bio-cycles of the ecosystems. With the aid of the advances of modern science, we can understand the defects and deficiencies of the chemical concept of fertility and return the biological concept of fertility to its proper place. This in turn is a good starting point for reproductive research and developmental work towards an ecologically sustainable agriculture and forestry (Oikarinen, 1996).

Soil acidification is the consequence of the formation or input of acids. Carbonate and silicate rocks are weak bases. Soils cannot, therefore, acidify as the consequence of rock weathering (exception: sulfide rocks, the content of sulfides in silicate rocks is usually neglible). Rainwater of pH > 5 possess alkalinity and cannot, therefore, acidify soils. The main acid sources remaining are the life processes of organisms. Since man has changed the acid/base status of aerosols, cloud water and all types of precipitation from alkalinity to acidity, the rate of acid deposition has to be considered as well.

With respect to the life processes of the organisms existing in an ecosystem, the soil represents the reaction vessel. The second aspect of soil acidification is represented by the chemical reactions taking place in this reaction vessel.

A few common management practices, such as application of acid forming N fertilisers, increased leaching and run off of cations, N fixations by legumes and cation removal by harvesting crops all contribute to soil acidification. Application of N fertilisers are essential for good crop yields, particularly on acid soils where the organic matter is low. Nitrogen fertilisers in the NH_4^+ form have long been recognized as increasing soil acidity (Tisdale and Nelson, 1975) due to the release of H^+ with plant absorption of NH_4^+ and with nitrification of NH_4^+. (He *et al*, 1999a). Acid (H^+) inputs into agricultural ecosystems revolve largely around the use of nitrogen (N) fertilisers. The guidelines classifying the acidification potential of different N fertilizers are well established. The scope for managing acid conditions in agricultural ecosystems, therefore, largely revolves around the input of ammonium (NH_4^+) and the output of nitrate (NO_3^-) ions in biological cycles. The central principle in reducing acid input (N cycle) involves matching the N supply to plant demand and reducing leaching losses of NO_3^- from the system to near zero. (Beukes, 2000)

It is well known that when ammonium is changed to nitrate as result of the nitrification process, hydrogen ions are released and this contributes to acidification. It has also been noted that ammonium sulphate and ammonium phosphate are theoretically twice as acidifying as limestone ammonium nitrate (du Plessis, 1986).

Chemical instability of clay minerals is as result of the saturation of H^+, which with time can lead to high lime requirements due to the wide range of Al forms that accumulate between clay layers (Jackson, 1960; Fouchè, 1979). It is for this reason that, the higher the concentration of clay in the soil, the more acid cations (Al^{+3}, H^+ .... etc.) can be absorbed.

In Germany mine soils formed of carboniferous and sulfurous overburden are classified as " sulfurous mine soils". They remain vegetation free for decades and may only be used for plant production after soil amelioration (Katzur and Haubold-Rosar, 1996).

Increased coal mining during the past two decades and a better recognition of the problem have resulted in more frequent identification of acidic spoil problems. Acidification of spoil material is primarily due to oxidation of iron sulfide minerals. Oxidation and hydrolysis occur when pyritic (FeS_2) overburden is disturbed and brought to the surface during mining. The formation of sulfuric acid by oxidation and hydrolysis of FeS_2 results in drastically reduced pH.

Acidic conditions limit mined land revegetation through: **(i)** plant toxicity by elements that become more available to plants at a low pH, **(ii)** restriction of root growth into acidic spoil material, **(iii)** reduction in the number of free living and symbiotic N fixing organisms, and **(iv)** increased populations of microorganisms that oxidize Fe and S (Barnhisel, 1977; Alexander, 1964; Arminger *et al.*, 1976; Taylor and Schuman, 1988).

1.4 Purpose of Amelioration

In acid soils, poor plant growth may result from deficiencies and toxicities of a number of elements. Low soil pH is generally accepted as an indicator of conditions under which some other soil property may limit crop growth rather than as a primary cause of poor root growth (Adams and Pearson, 1967; Coleman and Thomas, 1967; Blamely and Chapman, 1982).

In intensive agricultural systems, agronomic practices have evolved around minimizing the impact of soil constraints on the plant. Within this paradigm, lime was the starting point for transforming many millions of hectares of acid soils into productive farmlands and its use remains a cornerstone of acid soil management. In view of this wide-spread use of lime to treat acid soils, it is appropriate to note that while lime is effective in reducing toxicities (Al^{3+}) by neutralizing acidity (H^{+}) and contributing to the soil's base status (Ca, Mg) it will not halt the acidification process. Lime applications will, therefore, need to be repeated periodically if the desired soil condition is to be maintained. The use of lime is thus a recurring cost of production (Beukes, 2000).

In a pot experiment conducted by Moberly and Meyer (1975), using soil of the Balgowan series, it was founded that the greatest responses in sugar cane growth were achieved from the addition of wattle ash or lime. A heavy application of aluminum salts caused a marked depression in yield and induced severe phosphorus deficiency symptoms. The main reason for yield improvement, following application of either wattle ash or lime, appears to have been due to a reduction in the amount of exchangeable aluminium, and to the improved utilization of phosphorus at the higher soil pH values induced by such treatments (Moberly and Meyer, 1975).

One of the many pot experiments carried out was designed to compare the relative efficiencies of limestone and calcium metasilicate on acid soils from the Natal Midlands (Du Preez, 1970). All treatments caused a substantial reduction in exchangeable Al in the soil. In an experiment with levels of superphosphate, the growth response to phosphorus in the presence of limestone was greater than the conventional method of analysis indicated it would be (Meyer, 1974; Moberly and Meyer, 1975).

The ameliorant lime can also have a positive effect on sugar cane quality according to Moberly and Meyer (1975). The nitrogen status increased considerably, as measured by the third leaf N content, which was 2.21% and 2.53 % for the control and the limed treatments respectively (Moberly and Meyer, 1975).

Liming does not markedly reduce P- fixing capacity but over liming reduces P availability to plants (Baligar *et al.*, 1997b). The influence that liming has on P availability is that high P-fixing capacity of many soils is commonly ascribed to the presence of active Fe and Al which form very insoluble precipitates with phosphates. If this view is valid, it follows that once active Fe and Al have been suppressed by liming there should be a marked reduction in P-fixing capacity and hence an improvement in the availability of applied P (Orchard, 1972).

Previous work indicated that the application of limestone and CCB's (Coal combustion by-products) increased P availability efficiency (the amount of plant yield produced (mg) per unit of extractable P (mg) and P utilization (amount of plant yield produced per unit of P in the plant (mg). (Baligar *et al.*, 1997b; He *et el.*, 1997a, b; He *et al* 1999b). Either limestone or CCB application increased the availability of soil P to plants, probably due to a more developed root system resulting from the alleviation of Al toxicity and increased availability of Ca (Baligar *et al.*, 1997b; He *et al*, 1999b). It can, therefore, be said that the application of CCB's and limestone to acidic soils results in healthier plants with a better developed root systems due to higher soil pH and increased Ca and Mg supply. The better developed root systems result in an enhanced P availability and P utilization efficiency of ryegrass and thus improved plant-soil relationship of P in acid soils (He *et al.* 1999b).

Ultimately the most common, and in most cases the most effective, way of remediation of mineral deficiencies and toxicities in acid soils is by applying lime. Lime significantly increased grain yields of annual crops and consequently improved nutrient uptake. The degree of liming must be based on reducing toxicity of Al and Mn and increasing soil pH to provide Ca and Mg, which are lacking in acid soils. The effectiveness of liming has been related to the nature and fineness of the material, the extent of incorporation, and the depth of placement. Lime has very low mobility in soil and is only effective in that part of the soil profile, with which it comes in contact (Baligar *et al*, 1997b).

The supply of adequate levels of nutrients is a prerequisite for higher yields in acid soils. Shoot and root growth of the common bean (*Phaseolus vulgaris* L.), maize (*Zea mays* L.) and soybean (*Glycine max* L. Merrill) were markedly reduced in the absence of N, P and K. Phosphorus was the most limiting factor for crop production on such soils. The addition of adequate nutrients and liming was essential for achieving reliable crop yields, but these inputs are costly. Optimizing nutrient efficiency is an increasingly important aspect of crop production based on economic and environmental concerns. The efficiency of nutrient acquisition, transport, and utilization by plants grown in soil are controlled by

(i) the capacity of the soil to supply the nutrients and
(ii) the ability of plants to adsorb, utilize, and remobilize the nutrients.

Efficiency of supply, acquisition, transport, and utilization varies with soil, genotype/cultivars of various crop species, and environmental factors. These various processes involve closely synchronized events at the soil-plant-root interface and within roots, stem and leaves. Optimizing nutrient use efficiency is an increasingly important aspect of crop production based on economic and environmental concerns (Baligar and Fageria, 1997). It is thus necessary to develop nutrient balances based on soil and plant analyses.

In discussing optimum soil conditions for root development one should be aware that growth and functioning of roots are closely linked to that of the shoots through various reciprocal relationships and numerous feedback systems (Baxter and West, 1977; Wiersum, 1980; Kotzè and du Preez, 1988). Although the importance of a large volume of soil for root development has frequently been demonstrated (Cockcroft and Wallbrink, 1966; Kotzè and du Preez, 1988), less soil is needed if soil conditions favoring uptake are provided. (West, 1978; Kotzè and du Preez, 1988). At higher soil pH values the incidence of trace element deficiencies increase rapidly (Hilkenbäumer and Kohl, 1968; Kotzè and Joubert., 1980; Kotzè and du Preez, 1988).

In acid soils, the most important nutrient deficiencies are likely to be those of Ca and Mg (Coleman and Thomas, 1967; Howard and Adams, 1965; Blamey and Chapman, 1982), as well as P, due to fixation (Hsu, 1965; Smith, 1965; Blamey and Chapman, 1982). Molybdenum availability is also decreased under acid soil conditions and may be alleviated by liming (Davies, 1945; Blamey and Chapman, 1982). With regard to toxicities, soluble aluminium, through its detrimental effect on root growth, is widely held to be a major cause of poor plant growth in many acid soils.

Many studies have shown soil amelioration to be of benefit in peanut (*Arachis hypogae* L.) production (Reid and Cox, 1973; Snyman, 1972; Walker, 1975; Blamey and Chapman, 1982). In general, results have shown that the benefit of soil amelioration, particularly with respect to kernel quality, has been due to improved calcium nutrition (Bledsoe and Harris, 1950; Colwell and Brady, 1945; Reid and York, 1950; Snyman, 1972; Blamey and Chapman, 1982). This emphasis on Ca as a nutrient results from the poor translocation of Ca from tops to the developing pod, which has a high Ca requirement (Bledsoe *et al*, 1949; Muzino, 1965; Blamey and Chapman, 1982)

A conclusion drawn from the studies conducted by Blamey and Chapman (1982) on peanuts, is, that rhizobia may have different tolerances to soil acidity factors than the host plant. Low pH has reduced the growth of rhizobia (Virtanen and Miettinen, 1963; Blamey and Chapman, 1982), but at the time previous research (Keyser and Munns, 1979a,b; Blamey and Chapman, 1982) indicated that Al was more toxic to rhizobia of the cowpea group than was low pH, high Mn levels or low levels of Ca and P.

It was concluded that depressed nodulation at high Al concentrations resulted in N deficiency, which reduced growth to a greater extent than the limitation imposed by Al concentrations on the host species (Blamey and Chapman, 1982). The application of gypsum has also been found to decrease yields through the induction or accentuation of Mg deficiency (Plant, 1953; Blamey and Chapman, 1982) and Al, Mn and Fe toxicity (Fried and Peech, 1946; Blamey and Chapman, 1982). Liming would tend to increase Mo availability through increased soil pH while gypsum applications might have the opposite effect through the antagonistic effect the sulphate ion on Mo availability (Reisenauer, 1963; Blamey and Chapman, 1982).

The application of lime and gypsum resulted in significantly increased exchangeable Ca levels in the soil during the investigation of soil amelioration on peanuts. Lime was more efficient than gypsum in increasing exchangeable Ca in the 0 – 150 mm soil layer, possibly because of the higher Ca concentration in the lime (34 %) than in the gypsum (20%) and because of the leaching of Ca when applied as gypsum to this soil. (Farina and Channon, 1988a; Blamey and Chapman 1982). Concomitant with the observed increase in soil pH (KCl), liming significantly decreased Al saturation. Gypsum applications, on average, only slightly reduced exchangeable Al, but substantially decreased Al saturation through an increase in exchangeable Ca rather than a reduction in exchangeable Al. In all seasons, liming significantly increased the effective cation exchange capacity (CEC) in the 0 – 150 mm soil layer (Blamey and Chapman, 1982).

Unlike the sunflower seedlings, in which the beneficial effect of liming on seedling growth was evident within one week of emergence (Blamey, 1975a; b; Blamey and Chapman, 1982), the early growth of the peanut plants appeared unaffected by soil amelioration treatments. It was only after three months of growth that the plants in the unlimed plots appeared to be retarded in comparison with plants in plots, which had received lime. The plants in the unlimed plots showed a general chlorosis, which became more severe as the season progressed.

Gypsum applications did not appear to alleviate this chlorosis. By the end of the season the chlorotic plants on gypsum treatments were visibly less vigorous than those in the limed plots. This suggested that the poor growth in the unlimed plots might have been associated with a N deficiency, a hypothesis supported by examination of the roots. In the unlimed pots, nodulation was extremely poor although root growth *per se* appeared unaffected by soil acidity factors (Blamey and Chapman, 1982). The tendency for gypsum to depress nodulation as recorded by Mann (1935) was almost entirely due to the annual application of this ameliorant and, while significant, was not as marked as the beneficial effect of liming on nodulation (Blamey and Chapman, 1982).

The marked increase in protein concentration in peanut kernels due to liming, mentioned earlier, reflects the beneficial effect of liming on nodulation. Furthermore, concomitant with the slightly depressing effect of gypsum on nodulation, gypsum also slightly decreased the kernel protein content (Blamey and Chapman, 1982). Lime applications significantly increased exchangeable Ca^{2+} and Mg^{2+} and the effective CEC, and decreased exchangeable Al^{3+}, but did not alter K^+ content in the soil (Wilms and Basso, 1988).

Annual gypsum applications increased Ca uptake significantly, while Mg and K uptake were only slightly decreased and Mn uptake increased. The effective CEC of the soil increased with pH, by liming, as expected (Keng and Uehara, 1973; Reeve and Sumner, 1972). Liming significantly increased groundnut and peanut hay yields whereas gypsum applications were either of no significant benefit or tended to decrease hay yields. Liming significantly increased pod and kernel yields by 60 to 117% (Blamey and Chapman, 1982). A conclusion drawn from these results was that Ca, as a plant nutrient, was a limiting factor to kernel yield of groundnuts (Blamey and Chapman, 1982). Liming was also beneficial in increasing kernel size, as shown by the highly significant increase in 100-kernel mass in all seasons.

The objective of amelioration is a sustained improvement in soil reaction. Lime requirement for the achievement of a certain pH-value is calculated from acid-base-balance (SBB) (Katzur and Haubold-Rosar, 1996).

Taylor and Schuman (1988) reported that during their study on amending acidic mine spoil to aid revegetation, their first crop increased when acidic spoil was either amended with lime or covered with topsoil. When no topsoil was placed over the spoil all levels of added lime resulted in higher biomass than that produced with no lime.

Reduction of subsoil acidity usually leads to deeper rooting, thereby increasing water uptake by plants during drought periods (Fouche, 1979). Root development is severely restricted in the presence of even very small amounts of active Al. Moisture reserves remain untapped in times of stress unless Al^{3+} in the subsoil is eliminated (Baligar and Fageria, 1997).

The root elongation of lucerne (*Medicago sativa*. L) in acid soils amended by gypsiferous coal combustion by-products was investigated in a glasshouse study. (Wang *et al.*, 1999). Lime, fluidised bed boiler ash (FBA), and flue gas desulfurisation gypsum (FGDG) were mixed into the surface 50 mm. Lucerne was grown on each column after it was leached with 400 mm of water. While the lime treatment had no effect on root elongation in the acidic subsurface, the FBA and FGDG treatments significantly improved lucerne root penetration into the subsurface, which was dominated by permanently charged clay minerals. Lime should be applied to neutralize the topsoil acidity, while gypsum is used as subsurface soil acidity ameliorant. FBA, which contains both lime and gypsum, can meet these requirements (Wang *et al.*, 1999).

1.5 Methods and Mechanisms of Amelioration

Lime requirement is most appropriately defined in terms of the minimum soil-pH value above which no significant crop response can be expected from additional liming. Besides affecting pH, liming is inevitably bound up with such factors as CEC, the degree of base saturation, buffer capacity, Al and Mn toxicities and P availability. Maximum response to lime is obtained at the point where active Al is effectively suppressed. Crop response to liming is ascribed to the elimination of Al toxicity as a growth-limiting factor rather than to improved P availability (Orchard, 1972).

Reeve and Sumner (1970a) suggested that the first consideration in attempting to improve yields must be the removal, or suppression, of exchangeable Al^{3+} in order to eliminate its known toxic affect. They further postulated that if exchangeable Al^{3+} is the main source of soil acidity, the amount present would be directly related to the lime requirement. It appears that sensitive crops are already adversely affected in poorly buffered soils. In a factorial experiment, conducted by Reeve and Sumner (1970b), four different levels of lime were used, the two highest levels being in excess of the amount required to eliminate all active Fe and Al. On average, yields at the two higher liming rates were depressed, which was interpreted as evidence that liming in excess of the quantity required for suppressing Al^{3+} could interfere with P availability. By using ameliorants other than lime (gypsum and Silene, a calcium silicate), it was possible to separate Al toxicity from other nutritional effects, particularly the availability of P to the crop. They showed that although lime eliminated exchangeable Al^{3+}, it failed to reduce P fixation significantly (Orchard, 1972).

The mechanism of neutralization entails the reaction of $CaCO_3$, which can be quite complex, especially when different combinations of reactive components are present in the soil.

$CaCO_3$ reacts in water as follows:

$$\mathbf{CaCO_3 + H_2O \text{ -------------}> Ca^{++} + HCO_3 + OH \text{ ....(1)}}$$

The rate of the reaction, as well as $CaCO_3$ in solution is directly related to the rate at which OH and HCO_3 are removed from the solution. Therefore the H^+ ions in solution will determine if the Ca^{++} in solution increases as well as the solubility. In acid soil the concentration of H^+ ions is a function of the replaceable H^+ ions and the hydraulic rate of Al and Fe hydroxyl polymers. The reaction of $CaCO_3$ in acid soil can theoretically take place as follows:

$$\mathbf{2CaCO_3 + 2H_2O \longrightarrow 2Ca^{++} + 2OH + 2HCO_3 \text{ ....(1)}}$$

$$\mathbf{\text{Clay}\left]\begin{array}{l}\text{---Al (OH)}\\ \text{--- H}\\ \text{--- H}\end{array}\right. + 2Ca^{++} \longrightarrow \text{Clay}\left]\begin{array}{l}\text{--Ca}\\ \\ \text{-- Ca}\end{array}\right. + Al(OH)^{++} + 2H^{+} \text{ .... (2)}}$$

From (1) and (2)

$$\mathbf{Al(OH)^{++} + OH \longrightarrow Al\,(OH)_2^{+} \longrightarrow Al\ hydroxyl\ polymers}$$

$$\mathbf{H^{+} \quad + \quad OH \longrightarrow H_2O}$$

$$\mathbf{H^{+} \quad + \quad H_2CO_3 \longrightarrow H_2CO_3 \longrightarrow H_2O \ + \ CO_2\uparrow}$$

All exchangeable forms of Al and H^{+} are immediately neutralized after it is replaced from the clay mineral complex (Fouchè, 1975).

Liming acid soil to neutralize Al helps to increase CEC, and such increases in CEC reduce potential leaching losses of K. However, if liming materials (Ca or Mg) are applied in forms other than carbonates or oxides, more leaching of K may occur because Ca and Mg compete on the exchange sites with K. If the anion associated with cations is chloride or sulphate, K might be removed from soil (Baligar and Bennet 1986; Baligar and Fageria, 1997). It has been determined by Hackland *et al*., (1976) that there was improved nodulation in *Trifolium africanum* Ser., when liming a low pH soil high in exchangeable Al, with no improvement being recorded in a low pH soil low in exchangeable Al. Over- liming of low buffer-capacity soils results in lime-induced deficiency of K, Mg, P, and micronutrients (von Uexhall, 1986; Baligar and Fageria, 1997).

Gypsum on the other hand, is a widely occurring material that has been used for many years as a soil conditioner and ameliorant for sodic and heavy clay soils and as a nutrient source of Ca and S for plant growth (He *et al*, 1999b).

Gypsum may reduce the detrimental effects of surface and subsoil acidity on the root growth of plants by

(i) providing needed Ca (Ca leaching to lower layers),
(ii) increasing the ratio of Ca and Al activity in soil solution,
(iii) forming nontoxic $AlSO_4^-$ and physical removal of Al due to leaching of aluminium sulfate.
(iv) sorption of sulfate to hydrous oxides of Fe or Al to release hydroxyl ions which raises soil pH, and
(v) enhancing ionic strength of soil solution that leads to reduced Al activity.

Reduction of subsoil acidity usually leads to deeper rooting, thereby increasing water uptake by plants during drought periods. The direct effects of lime include

(i) increased Ca and Mg content and

(ii) increased pH.

Increased pH improves P and Mo availability and, to some extent, reduces the availability of Mn, Cu, Fe, and Zn

The chemical barrier to root development existing in the sub-soils of acid soils is a subject of increasing interest. In order to better understand the factors involved in the amelioration of subsoil acidity, the effects of calcium sulphate, phosphogypsum and calcium carbonate on the properties of solid and liquid phases of subsoil samples and on the growth and nutrient uptake by maize (*Zea mays* L.) were evaluated (Carvalho and Raij, 1997). Calcium carbonate reduced activity of Al^{3+} because of the increase in pH. The subsoil samples presented severe restrictions for maize root growth and all three treatments were equally effective in increasing root development, which could be attributed to the supply of calcium and a combined effect of the amendment in reducing the activity of Al and increasing the activity of Ca in the soil solution in the other soils. As a consequence the three treatments increased in the same manner water, N and K uptake from the subsoil and the dry matter production of maize (Carvalho and Raij, 1997).

In peanuts, the use of gypsum has been widespread because of its ability to supply readily available Ca to the developing pod (Snyman, 1972; Walker, 1975; Blamey and Chapman, 1982). Since gypsum has no neutralizing ability, the reduction in exchangeable Al possibly resulted from the replacement of Al by Ca (Blamey and Chapman, 1982)

If little pH increase is noticed with high lime applications, according to Wilms and Basso (1988), it is beyond the high buffering capacity of the soil, but by the decreasing solubility of the employed limestone with increasing soil pH. Only 61%, 51% and 32% of the total Ca^{+} and Mg^{2+} applied with the three lime rates in one of their experiments (Wilms and Basso, 1988), were recovered in the soil as exchangeable nutrients. Additional soil analyses indicated the rest apparently remained as carbonate. The ameliorative application of lime, fertiliser or brown coal ash should be incorporated intensively into the soil to a depth of 60 cm, but would be better to a depth of 100 cm. Amelioration included a mineral fertilisation with N, P, and K (Katzur and Haubold-Rosar, 1996).

An important consideration when liming is that the extent that lime is incorporated in acid topsoil, would also affect the subsoil. In previous studies conducted by Orchard (1972), the depth of cultivation had not exceeded 20 cm and it was found that even 14 years after the initial application, the effect of lime had barely penetrated 25 cm below the plough depth. The effectiveness of liming has been related to the nature and fineness of the material, the extent of incorporation, and the depth of placement. Lime has very low mobility in soil and is only effective in that part of the soil profile with which it comes into contact (Fouchè, 1979).

Vertical movement of surface incorporated lime is extremely slow in most highly weathered soils and specialized management strategies are required in order to reduce the detrimental effects of sub-soil Al (Farina and Channon, 1988b). Anions (sulfate, chloride, nitrate) are known to promote downward movement of lime in an acid soil profile (Fouchè, 1975).

In the investigation of ameliorating acid soils in the South African sugar industry, Moberly and Meyer (1975) reported a superior growth of cane in areas that were associated with the windrows of wattle brush, which were burnt prior to land preparation. The analyses of these soils, containing wattle ash, showed highly significant reductions in acidity and labile Al, and increases in the amounts of exchangeable Ca, Mg, P, Si and K. Examination of the associated sugarcane third leaf analytical data showed similar increases in nutrient levels, particularly in regard to P and K.

Acidification effects the root environment and stunts root growth, leading to decreased efficiency of water use and reduced crop yields. The various options for treating soil acidity are not mutually exclusive nor is one approach necessarily superior to the other. The different options (lime, gypsum, coal combustion by-products, nutrient cycling and etc.) can however, be combined in different ways to provide a variety of possible solutions to the problem. A more flexible approach to soil acidity, is necessary to accommodate the broad range of practical perceptions and economic constraints which must also be taken into account when seeking optimum solutions to the soil acidity conundrum.

Coal combustion by products (CCB's) have been widely used as cost effective amendments for acid soils. It holds true that ashes have several advantages, and their application is recommended (Katzur and Haubold-Rosar, 1996). Although information is needed on the proper combination of CCB's with chemical fertilisers or other organic and inorganic amendments to improve the productivity of acid soils, the application of CCB's alone slightly raised soil pH and markedly increased soil exchangeable Ca, whereas dolomitic limestone alone raises the soil pH from 4.0 to 5.6 and provides the soil with considerable amount of exchangeable Mg in addition to Ca in a experiment conducted by He *et al*, (1999a).

Regarding amendment of nutrient depleted soils, many studies have demonstrated the ability of sewage sludge to restore degraded lands (Sopper, 1992), while most studies have focused on nutrient supply to plants from sewage sludge, or liming value in the case of alkaline stabilised sludge (Lindsay and Logan, 1998).

Land application of sewage sludge is projected to increase in European countries because of the ban on sea disposal starting in 1999 and increases in wastewater treatment lasting into the new millennium, from the EU Wastewater Treatment Directive (Commission of the European Communities, 1991). Sewage sludge can be a valuable source of plant nutrients such as N, P, and S, and the organic matter contained in the sludge also can help improve soil physical conditions such as; reduced runoff, increased infiltration, which in turn results in increase biomass growth and quality. Of the major environmental problems associated with the land use of sewage sludge is the addition of potentially toxic heavy metals in soils and possible pathogenicity. Repeated applications of heavy metal-contaminated sewage sludge can result in an accumulation of such toxic metals in the soil. Once accumulated, heavy metals are highly persistent in the topsoil, and can cause potential problems such as phytotoxicity, injury to soil microorganisms and elevated transfer to food chain (McGrath *et al*., 2000). Heavy loadings of biosolids may also result in the contamination of groundwater by nitrates, if the application rate exceeds the nitrogen demand of the vegetation.

Some authors advocate the sludge protection hypothesis, which states that the sludge-borne heavy metals are maintained in chemical forms of low bioavailibility by the inorganic components of the sludge, and that the specific metal absorption capacity added in sludge will persist as long as the heavy metals of concern persist in the soil (Corey *et al.*, 1987; Chaney and Ryan, 1993). According to this hypothesis, sludge-borne heavy metals should become less bioavailable with time as surface-absorbed metals become occluded. In contrast, others believe that the sludge-derived OM contributes significantly to the metal absorption capacity, and the slow mineralization of the OM could release metals into more soluble forms (McBride, 1995). Because the decomposition of sludge OM is often associated with an acidification of the soil, if this is uncorrected, further increases in the bioavailibility of the sludge-borne heavy metals would be expected (McGrath *et al.*, 2000).

The development of technologies that can be used to produce soil ameliorants with unique properties that can also be beneficially used to address problems associated with conventional sludge disposal practice, while simultaneously creating a new conduit for ash utilization, are extremely important.

1.6 The use of flyash as a soil amendment

Landfilling is the traditional method of fly ash disposal, but the dual factors of increased cost and stricter legislation have prompted research into alternative methods of disposal or utilization of this waste material (Kriesel *et al.*, 1994; Jackson *et al.*, 1999). Over the years, numerous studies on the use of fly ash as a soil amendment have been conducted, and several review papers on this subject have been written (Adriano *et al.*, 1980).

Land application of coal combustion residue wastes, particularly fly ash, to agricultural land may offer a waste-recycling alternative to current landfill disposal. Although fly ash, like the parent coal from which it was derived, contains almost every naturally occurring element, plant nutrition with this complex material is not straight forward, as demonstrated by contrasting reports in the literature. Although containing neutralization value, these materials may be beneficial in reclamation efforts, providing essential macro- and micronutrients (K, B, Mo and Zn) and improving acid mine spoil physical characteristics (Carlson and Adriano, 1993; Abbott *et al*, 2001).

The physical and chemical properties of coal ashes are dependent on the coal's geological origin, combustion conditions, efficiency of particulate removal, and degree of weathering before final disposal. Coal residues, applied on cropland, are not practical sources of essential plant nutrients N, P, and K. They can, however, effectively serve as a supplementary supply of Ca, S, B, Mo and Se to soils. Fly ash could also be an effective amendment in neutralizing soil acidity as previously mentioned. Many of the observed chemical and biological effects of fly ash applications to soils resulted from the increased activities of Ca^{2+} and OH^- ions. The accumulation of B, Mo, Se and soluble salts in fly ash-amended soils appear to be the most serious constraints associated with land application of fly ash to soil. Lignitic coals are characteristically high in S contents and consequently can produce ashes that are low in pH. On the other hand, lignite's can have lower S contents, but higher Ca and Mg and produce ashes characteristically high in pH. Ashes with pH as low as 4.5 and as high as 12.0 have been reported (Adriano *et al.*, 1980)

Fly ash is basically an amorphous ferro-alumino silicate, which is also characteristically high in Ca, Mg, Na and K. Virtually all natural elements are present in coal ash in trace amounts. There is a general consensus that most trace elements increase in concentration with decreasing size of fly ash particles (Adriano *et al.*, 1980). In the dry state, all ashes lack any form of aggregation, and tended to be noncoherent, suggesting that both wind and water erosion may be a significant problem on unstabilized surfaces (Aitken *et al.*, 1984).

While coal residues show promise as liming agents and sources of many plant nutrients, several factors need to be explored before its extensive utilization can be recommended: (i) loss of applied and indigenous soil N as a result of increased soil pH, (ii) fixation of P and other micronutrients, e.g., Zn, due to the adsorption on the amorphous ferro-alumino silicate matrix of fly ash, (iii) accumulation of As, Mo, and Se microbial activity, and (v) use of coal residues in conjunction with high carbonaceous materials such as sewage sludge, peat, and animal manures (Adriano *et al*., 1980)

The most widely accepted disposal practices for fly ash are by holding it in settling ponds, stockpiling, and landfilling. High-rate land application of fly ash is also a potential disposal method (Adriano *et al*., 1980)

Research in a number of countries has indicated that some ashes may have agronomic potential as liming agents (Doyle 1976; Hodgson *et al*. 1982; Aitken *et al*., 1984), boron (B) fertilisers (Mulford and Martens 1971; Plank and Martens 1974; Aitken *et al*., 1984) and as a physical amendment for soils (Doyle 1976; Chang *et al*. 1977; Aitken *et* al., 1984).

However, large-scale application of coal ash to agricultural land is uncommon in most countries (Hodgson and Holliday, 1966; Adriano *et al*., 1980; Wong and Wong, 1989). The reason being that the economics of waste disposal, are usually associated with adverse effects to soils and growing plants. Detrimental effects on plants are usually caused by excessive B, increasing salinity and alkalinity from high application rates, especially the unweathered ashes (Adriano *et al*., 1980).

A small percentage of the ash residues produced in many countries of the world will be used as basic constituents for cement and concrete manufacturing. The remaining residues will be disposed of in ash lagoons or landfill sites. However, insufficient availability of land has caused difficulties in finding new disposal sites. Hence utilization of coal residues for crop cultivation would be a very useful additional benefit in the handling of these wastes (Wong and Wong, 1989).

Current disposal practices (landfilling, surface impoundment, placement in mines and quarries) can potentially affect air and water quality through fugitive dust, or runoff and leaching of fly ash constituents to surface and ground waters. Agronomic acceptance of fly ash to soils is generally low due to the high costs of transporting and land spreading, low N and P content, high salinity, and environmental concerns over potentially toxic elements (mainly B, but also Mo, As and Se) (Carlson and Adriano, 1993; Abbot *et al*, 2001).

The alkaline nature of fly ash has led to an examination of its use as a liming agent to replace reagent grade $CaCO_3$ on acidic agricultural soils and coal mine spoils (Martens, 1971; Moliner and Street, 1982; Wong and Wong, 1989). Furthermore, the enriched macro- and micronutrients which fly ash contains enhance plant growth in nutrient-deficient soils (Plank and Martens, 1974; Martens and Beahm, 1978; Wong and Wong, 1989).

Because fly ash is relatively enriched in trace elements, it has been successfully applied to alleviate micronutrient deficiencies as well (El-Mogazi *et al.*, 1988; Jackson *et al.*, 1999). Fly ash amendments have been used to correct plant nutritional deficiencies of B (Martens, 1971; Ransome and Dowdy, 1987; Schumann and Sumner, 2000), Mg (Hill and Lamp, 1980; Schumann and Sumner, 2000), Mo (Doran and Martens, 1972; Elseewi *et al.*, 1980; Schumann and Sumner, 2000), S (Elseewi *et al.*, 1978b, 1980; Hill and Lamp, 1980; Schumann and Sumner, 2000), and Zn (Martens, 1971; Schnappinger *et al.*, 1975; Schumann and Sumner, 2000).

Fly ash alone, as previously mentioned, is a poor source of the macronutrients such as N and P (Carlson and Adriano, 1993; Jackson *et al.*, 1999). Nitrogen is volatilized during the process of coal combustion, while most fly ash P is relatively unavailable (Bradshaw and Chadwick, 1980; Jackson *et al.*, 1999). Notwithstanding these facts, land application of fly ash is still viewed as an attractive alternative means of disposal (Jackson *et al.*, 1999). In addition, unweathered fly ashes (no previous contact with water) contain high concentrations of soluble salts and increased concentrations of soluble B (Carlson and Adriano, 1993; Jackson and Miller, 2000).

Fly ash and lime have been used to treat acid soils and mine spoils in the past (Barber, 1967; Capp 1978; Adriano *et al.*, 1980; Taylor and Schumann, 1988). Fly ash amendment of soils and mine spoils have shown inconsistent effects on plant production and on the uptake of many of the plant nutrients and trace elements (Adriano *et al.*, 1980; Taylor and Schumann, 1988). This inconsistency in observed plant response and element content is related to the source of fly ash, quality of fly ash, and the nutrient status of the soil or spoils being treated. Fly ash amendment of soils has, in some instances, resulted in

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increased plant production when nutrient deficiencies were corrected by the addition of the fly ash (Adriano *et al.*, 1980; Taylor and Schumann, 1988).

The toxic effect of applying fly ash on soil has also been demonstrated by the decrease in microbial activity. Application of ash at 12% of the soil volume, seriously inhibited soil microbial respiration in the soil under investigation (Wong and Wong, 1986; Wong and Wong, 1989). These effects would diminish after long-term weathering in ash lagoons or disposal sites (Jones and Lewis, 1960; Ciravolo and Adriano, 1979; Wong and Wong, 1989).

1.6.1 Effect of fly ash on soil properties

In general it appears that fly ash can have significant beneficial effects in addressing certain problems in soil quality. For example, the high pH of low S coal fly ashes has found application in the use of fly ashes as liming agents, while the predominantly silt-sized nature of fly ash has been used to improve soil physical properties (Carlson and Adriano, 1993; Jackson *et al.*, 1999).

Past studies have also revealed several drawbacks to the use of fly ash as a soil amendment. The most commonly cited detrimental effects are salt toxicity and high available B (Carlson and Adriano, 1993; Jackson *et al.*, 1999). In addition, many researchers have noted an increased availability of trace elements in fly ash-amended soil (Tolle *et al*, 1983; Jackson *et al.*, 1999).

A study to evaluate various rates of fly ash application (0-80 Mg ha^{-1} equivalent) on soil pH, soil and plant nutrient levels, and plant growth using representative acidic clay and sandy soils from Southern Ontario was conducted by Cline *et al.*, (2000). After 90 days of soil incubation, the highest rates of fly ash increased soil pH, but had no significant effect on hot-water extractable B. Dry weights of plants grown in the same soil types were unaffected by fly ash rates

In a field study (1993-96) the benefits of applying unusually high rates of coal fly ash as a soil amendment to enhance water retention of soils without adversely affecting growth and marketability of the turf species. (Centipedegrass) was assessed by Adriano and Weber (2001). The high levels of soluble salts, indicated by the electrical conductivity (EC) of soil extracts, in tandem with an apparent phytotoxic effect from boron (B), apparently inhibited initial plant establishment as noted by substantially lower germination counts in treated soil. However, plant height and rooting depth were not adversely affected, as were the dry matter (DM) yields throughout the study period. Ash treatment did not significantly influence water infiltration rate, bulk density, or temperature of the soil, but substantially improved water-holding capacity (WHC) and plant-available water (PAW) (Adriano and Weber, 2001).

Coal fly ash has physical and chemical characteristics that make it useful as a soil amendment. One of the more important of these being the potential to permanently improve the soil water relations of sandy, drought-prone soils. Changes in the infiltration rate and water holding capacity of a sandy soil after application of high rates (up to 950 tons ha^{-1}) of a Class F fly ash were examined. Fly ash amendment not only increased water-holding capacity but also increased plant available water by 7-13% in the 100-300 kPa range. These results suggest fly ash amendment may have the potential to improve crop production in excessively drained soils by decreasing drainage and increasing the amount of plant available water in the root zone (Gangloff *et al.*, 1997).

The application of fly ash altered the soil texture and increased water holding capacity, pH and electrical conductivity and extractable amount of P, Ca, Mg, S, Fe, Mn, Zn, Cu, B and Al but decreased soil particle density and available soil N in a study conducted by Khandkar *et al.* (1999).

Of the essential plant nutrients, the concentrations of S, Mo and B in plant tissues have been shown to increase consistently with ash applications to soil. Concentrations of the non-essential trace elements Al, Se and Sr were also consistently increased. Arsenic, Ba, Cs, Rb, W, and V also showed an accumulative pattern with ash applications (Adriano *et al.*, 1980).

An increase in soil pH increases the availability of soil Mo owing to decreased retention of the molybdate anion by hydrous hydroxide and oxides of Al and Fe (Jones, 1972; Reyes and Jurinak, 1967; Wong and Wong, 1990). This accumulated Mo content did not, however, cause any observable symptoms of phytotoxicity. However, elevated concentrations of Mo in the animal diet have been known to induce a physiological disorder commonly referred to as molybdenosis (Erdaman *et al*., 1978; Wong and Wong, 1990). It has been suggested that a Mo concentration of 5-10 $ug\ g^{-1}$ could be toxic to cattle (Gather *et al*., 1975; Wong and Wong, 1990).

Sandy soil with fly ash incorporation might accumulate Mo to levels well above this critical range. In sandy loam the level was, however, much lower than the critical value. This might be due to the adsorption of Mo on clay and humus materials in soil (Davis, 1980; Wong and Wong, 1990).

It has been suggested that fly ash, when applied as a soil amendment, would increase soil temperature. However, no quantitative data has been provided to support this hypothesis. This hypothesis was tested on four fly ash treatments (0, 100, 200, and 400 t ha^{-1}) applied to clay loam soil in a randomized block design. Bi-hourly soil temperatures were measured on three summer days over two years, and afternoon temperatures were measured on randomly selected spring days at five-, 10-, and 20-cm depths in the four fly ash treatments. Fly ash decreased the percent clay, soil water content, and soil heat capacity. Contrary to previously expected trends, fly ash amendment did not significantly increase mean daily soil temperature under dry conditions. Generalizations in the literature regarding the influence of fly ash on soil temperature, bulk density, and water-holding capacity must be considered carefully since they generally relate only to coarse to medium textured soils (Hammermeister *et al*., 1998a).

Short-term laboratory studies have indicated that the addition of unweathered fly ash to soil, can stress microbial populations and their activities, but effects of fly ash addition at the field scale are not known. In a study where field plots received 0 or 505 tons fly ash ha^{-1} were subsequently cropped to a fallow-corn-wheat rotation or continuous fescue (*Festuca arundinacea* Schreb.). Twenty months later, during the wheat phase of the rotation, the plots were sampled (0-15 cm) and assayed for activity of soil enzymes (dehydrogenase, alkaline phosphatase, arylsulfatase, and denitrifying enzymes); numbers of aerobic heterotrophs, ammonium oxidizers, denitrifiers, and bradyrhizobia; and N mineralization, nitrification, and denitrification potentials. Nitrification potentials doubled in fly ash-amended soils, and numbers of denitrifiers were 200-fold higher in fescue-cropped, fly ash- amended soils relative to fescue-cropped, non-amended soils. No other large differences in microbial populations or activities were, however, found. The lack of detrimental effects on microorganisms in the field was possibly due to reductions in fly ash's soluble salt and trace element concentrations with time, the mild alkalinity of the fly ash used in this study, and the positive responses of crops to fly ash amendment (Schutter and Fuhrmann, 1999).

In a greenhouse study conducted by Taylor and Schumann (1988), the aim was to determine the effectiveness of lime and fly ash as soil amendments, for increasing the pH of acidic mine spoil material, and to determine the effects of these amendments on aboveground biomass, root biomass and distribution, and plant element content of two crops of barley. They concluded that the fly ash and lime amendments were both effective in raising the pH of the acid spoil from 2.7 to an average of 6.9. These amendments, in conjunction with topsoil, resulted in significantly greater aboveground plant production (Taylor and Schumann, 1988).

Capp (1978) found that a single application of fly ash was effective in raising the pH of acid soils and improved the plant nutrient status and water holding capacity of the soil. In comparison, lime applications to acid soils have been reported to decrease the solubility of P and increase exchangeable Ca and Mg (Brady, 1974; Taylor and Schumann, 1988)

Wong and Wong (1989) reported that the application of fly ash to both sandy and sandy loam soils caused an upward shift in soil pH. The rate of increase was more gradual at lower application rates, i.e. at 3, 6 and 12% of the soil volume. However, at 30% of the soil volume, the pH increased markedly from 7.26 to 12.50 for sandy soil and 6.66 to 12.20 for sandy loam. Moreover, the increase in pH for sandy soil was greater ($P<0.05$) than that of sandy loam at 3, 6 and 12% application rates, indicating that sandy loam had a better buffering capacity at lower levels of ash amendment. At 3 and 6% application rates, seed germination of both species grown in sandy soil was enhanced by the addition of fly ash while significant reductions ($P<0.05$) were observed at 12 and 30% application rates. However, both crops cultivated in sandy loam were similar for all treatment groups; except for 30% fly ash-treated soils, which showed significant reductions in germination ($P<0.05$) when compared with the control. Germination of both *Brassica parachinensis* and *B. chinensis* at 30% ash-amended soil was drastically reduced throughout the observation period. However, at 3 and 6% application rates, seed germination rate was enhanced (Wong and Wong, 1989).

Potential limitations of fly ash's agronomic use include its low levels of N, excessive levels of B, high salt levels and their strongly alkaline pH values. Their alkaline nature is not considered a problem, since most of the ashes are poorly buffered and, if they were added in small amounts to acid sands or loams, the equilibrium pH would be nearer to the initial soil pH (Aitken *et al.*, 1984).

Perhaps the most limiting factors in fly ash utilization on land, are unfavorable changes in the soil's chemical equilibrium including increases in pH, salinity, and levels of certain toxic elements. As a result of the hydrolysis of CaO and MgO, coal ashes, which are characteristically high in oxides of Ca and Mg, will increase the soil pH. The final pH of the fly ash-water suspension could be as high as 12 or greater. Even a moderate application rate can increase the soil pH markedly. Following the application of fly ash to soil at a rate of 8% by weight, Page *et al.* (1979) observed that the pH of a calcareous soil was also elevated form 8.0 to about 10.8, and that of an acidic soil shifted from 5.4 to about 9.9. The calcareous soil's higher buffering capacity was responsible for the smaller pH change. The high pH lingered until the end of a 12-month cropping of alfalfa (lucerne). This "reserve" alkalinity in fly ash makes its neutralizing capacity persist for some, as yet undetermined, time (Adriano *et al.*, 1980).

Laboratory studies showed that an alkaline fly ash was chemically equivalent to approximately 20% of reagent-grade $CaCO_3$ in reducing soil acidity and supplying plant Ca needs (Phung *et al.*, 1978; Adriano *et al.*, 1980). However, depending on the source of fly ash and the extent to which it is weathered, its neutralizing capacity could range from none to very high (Doran and Martens, 1972; Adriano *et al.*, 1980). Elseewi *et al.* (1978a) also found marked increases in Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-} and B in the saturation extracts of fly ash-treated acidic and calcareous soils cropped with lettuce. Plant availability of many other nutrient elements may also be affected by the shifting of soil pH. Reduced plant uptake or deficiency symptoms of P and Zn have also been observed on fly ash-treated soils (Mulford and Martens, 1971; Schnappinger *et al.*, 1975; Elseewi *et al.*, 1978a; Adriano *et al.*, 1978; Adriano *et al.*, 1980).

Soil salinity could increase substantially when soils were amended with unweathered fly ash (Page *et al.*, 1979; Mulford and Martens, 1971; Elseewi *et al.*, 1978a; Phung *et al.*, 1978; Adriano *et al.*, 1978; Adriano *et al.*, 1980). Weathering of fly ash before application significantly reduces the salinity impact on soils. Lagooning, stockpiling, and leaching considerably reduced the soluble salt and B contents of fly ash (Hodgson and Townsend, 1973; Townsend and Gillham, 1975; Adriano *et al.*, 1980). Under normal storage conditions, the stabilization may take several years (Plank and Martens, 1974; Adriano *et al.*, 1980). Therefore, the concentration of B in fly ashes is highly variable (Adriano *et al.*, 1980).

Wong and Wong (1990) observed that an addition of ash at a high rate, raises the pH of sandy soil and sandy loam from 7.3 and 6.7 to 9.7 and 8.6, respectively. As compared with 0% ash treatment, yields were found to be significantly higher for 3% ash-amended sandy soil, while yields at 12% level were significantly lower.

An increase in fly ash application rates caused a considerable increase in both pH and EC of soils. The pH shifted from 7.3 on the control to 9.7 for sandy soil and from 6.7 to 8.6 for sandy loam at the highest application rate of 12%. The initial increase in soil pH after ash amendment was attributed to the release of Ca, Na, Mg and OH ions from fly ash (Hodgson *et al.*, 1982; Wong and Wong, 1990). It has been suggested that Ca was the major element soluble in water. Calcium oxide in ash in relatively constant and in contact with water, CO_2 is absorbed leading to the precipitation of $CaCO_3$. Residual pH effect after cropping was found to be more obvious for sandy soil than for sandy loam. Nevertheless, the pH was still much higher than that of the control without ash amendment (Wong and Wong, 1990).

It has been estimated that 1 million ha of land remain virtual wastelands due to damage incurred from strip mining of coal (Fail and Wochok, 1977; Adriano *et al.*, 1980). The resultant acidic spoils are infertile and often support only sparse vegetation, subjecting them to severe erosion. Fly ash has been demonstrated to be effective in reclaiming these areas (Capp and Spencer, 1970; Capp and Gilmore, 1973; Fail and Wochok, 1977; Adriano *et al.*, 1980).

When spoil areas are reclaimed, the quantities of fly ash, which may be applied usually, exceed those for cropland disposal. The quantities of fly ash required to reclaim spoil areas depend upon the pH of the fly ash, the degree to which it is weathered, and the pH of the spoil to be reclaimed. For example, spoil areas having a pH of 4.4. to 5.0 were reclaimed by fly ash at rates of 70 metric tons ha^{-1} (Fail and Wochok, 1977; Adriano *et al.*, 1980) while on spoils with pH values of 2.0 to 3.5 rates from 335 to 1790 metric tons ha^{-1} were used (Adams *et al.*, 1972; Adriano *et al.*, 1980). Where unweathered fly ashes are applied at high rates, a stabilization period of about 1 year is required to establish uniform plant growth (Martens and Beahm, 1978; Adriano *et al.*, 1980). However, where weathered fly ash is applied, uniform growth of crops frequently occurs the season following the initial fly ash application. Studies reported by Martens and Beahm (1978), showed no yield reduction of corn grain each year following five repeated applications of weathered fly ash at rates of 144 metric tons ha^{-1}, whereas at much lower rates of unweathered fly ash (48 to 96 metric tons ha^{-1}) the yield of corn grain was substantially reduced. At the same application rate unweathered fly ash produces a much higher pH and/or salt content in the soil-fly ash mixture than does weathered fly ash. High salinity and pH, which tends to be buffered out with time, therefore accounts for growth depressions which occur immediately following applications of unweathered fly ash to soils (Adriano *et al.*, 1980).

1.6.2 The effects fly ash have on plant growth

As previously mentioned, fly ash disposal is a major problem in and around thermal power plants. A study was conducted to test fly ash suitability for application to agricultural soils in a definite proportion for better plant growth. While lower application rates of fly ash enhanced seed germination as well as seedling growth, higher application rates either delayed or inhibited these processes drastically. Fly ash application to the agricultural soils increased Ni plant uptake but reduced that of Cr and Cu (Singh *et al.*, 1997).

While fly-ash amendments may also cause phytotoxicity, due to excesses of micro-nutrients such as B, only As, Mo, and Se have been reported to accumulate in plants to levels that could be potentially toxic to grazing animals (Doran and Martens, 1972; Elseewi *et al.*, 1980; Tolle *et al.*, 1983; Elseewi and Page, 1984; Schumann and Sumner, 2000). Fly ash application may also decrease plant uptake of elements such as Cd, Cu, Cr, Fe, Mn, and Zn (Schnappinger *et al.*, 1975; Adriano *et al.*, 1982; Petruzzelli *et al.*, 1986; Schumann and Sumner, 2000). Phosphorus concentrations in plant foliage were often reduced by fly ash applications (Elseewi *et al.*, 1980; Moliner and Street, 1982; Schumann and Sumner, 2000). These effects were attributed to an increase in soil pH by the ash. (Martens *et al.*, 1970; Schumann and Sumner, 2000). These conflicting results are understandable, given the high variability in the fly ash samples (Schumann and Sumner, 2000).

Corn (*Zea mays* L.) plant emergence, grain yield, percent moisture, and harvest index were not significantly influenced by fly ash applications. However, soybean [*Glycine max* (L.) Merr.] yields treated with 50 tons ha^{-1} fly ash increased by as much as 35 and 31% in comparison with untreated and lime control treatments, respectively. Selenium and boron, which can be the rate-limiting elements for maximum permissible loading rates of fly ash for soil amendments, did not accumulate in plants in quantities that would be of concern for plant health or animal and human consumption (Cline *et al.*, 2000).

Fly ash has shown potential as a soil amendment and a source of trace elements beneficial to plants. However, agricultural utilization of fly ash has been restricted due to variability in chemical composition, elemental toxicity, induced nutrient imbalances in plants, and inconsistent response of vegetation to fly ash amendment. Fly ash was applied to reclaimed mine soil near Edmonton, Alberta, at rates of 0, 25, 50, 100, 200, and 400 t ha^{-1}. Boron concentration in plant tissue increased significantly to toxic levels with symptoms evident at early stages of barley development and increasingly severe at later stages. Toxicity symptoms were, however, less severe for bromegrass and alfalfa (Hammermeister, *et al.*, 1998b).

Root growth of wheat seedlings (*Triticum aestivum*) and trace element levels in ryegrass (*Lolium multiflorum*) were determined in acid soils treated with 1.25 to 80 kg ha^{-1} of various coal combustion by-products. Low application rates of by-products did not inhibit wheat seedling root growth. Ryegrass concentrations of Cu, Zn, Ni, Pb, Cd and Cr were similar in treated and untreated soil. Boron, Se, As and Mo were increased in the treated soil, but Se from fly ash treatments was the only potential food chain risk from a single application of these materials (Wright *et al.*, 1998).

At a high pH, the extractability of trace elements might be reduced, which might result in reducing the availability of certain essential elements. This would in turn affect the plant growth through a deficiency toxicity complex (Hodgson and Holliday, 1966; Wong and Wong, 1989). On the other hand, it has been well documented that low levels of trace elements in aqueous solution would cause inhibition and delay in seed germination (Adriano *et al.*, 1973; Wong and Bradshaw, 1981; Wong and Wong, 1989), and trace elements in fly ash-treated soil may potentially inhibit seed germination and early growth (Vollmer *et al.*, 1982; Wong and Wong, 1989)

A fly ash extract, in the lower concentration rage of 0.5 to 1.0% (wet volume), as reported by Shukla and Mishra (1986) had no significant effect on germination and seedling growth of corn and soybeans. Higher concentrations of fly ash extracts, however, had deleterious effects on the percentage germination, viability, number of roots, shoot and root length, fresh weight and dry weight of seedlings of both the crops (Shukla and Mishra, 1986).

Khandkar *et al.*, (1999) reported that soil application of fly ash increased the concentration of all the nutrients. A conclusion drawn from the investigation was that fly ash can be used to correct S and B deficiency in acid soils.

Wong and Wong (1989) conducted a study where fly ash was applied at rates of 0, 3, 6, 12 and 30% (on a dry weight basis) to a sandy soil and a sandy loam. After application of fly ash, germination of *Brassica parachinensis* and *B. chinensis* seeds in 3 and 6% treated sandy soil was enhanced, while those in 12 and 30% treated sandy soil and 30% treated sandy loam showed a significant (P = 0.059) reduction. In general, the dry weight production of crops was enhanced and the lengths of first leaves, shoots and cotyledons were longer in the 3% amendment but reduced in 12 and 30% amendment for both soil types. The results indicated that low ash amendment at 3% improved young seedling growth of both crops, but high ash amendment (12 and 30%) produced adverse effects on growth. The increased pH would alter the availability of micro nutrients to plants. The yields at 12 and 30% amendment levels were significantly ($P<0.05$) lower than the control for all groups except *B. chinensis* at 12% amendment ($P<0.05$). Moreover, sandy loam produced higher yields than sandy soil due to its better nutrient status (Wong and Wong, 1989).

With *B. chinensis,* the 3% ash treatment in sandy soil enhanced all these growth criteria while no significant difference was observed for sandy loam except for shoot length. However, shoot length, cotyledon length and length of first leaf were decreased with increasing concentration of ash amendment. With *B. parachinensis* growth of first leaf was enhanced at 3% application rate for both soils as compared with the control. However, no significant difference was observed between 3% treatment group and the control for both shoot and cotyledon lengths, although better seedling growth was observed for crops growing on sandy loam than those on sandy soil (Wong and Wong, 1989).

In general, the toxic effect of coal fly ash caused delay and reduction in seed germination for both crops on both soils. However, the toxic effect on seed germination was more obvious for sandy loam than for sandy soil. However, the vegetable crops grown on soil with fly ash in further studies did not exhibit any symptoms of metal toxicity or metal deficiency (Wong and Wong, 1989).

Field and greenhouse studies both indicate that many chemical constituents of fly ash may benefit plant growth and can improve agronomic properties of the soil (Chang *et al.*, 1977; Adriano *et al.*, 1980). There were instances when increases in dry matter yields were obtained in the fly ash-amended soils, which were associated primarily with correction of either macro- and micronutrient deficiencies (Adriano *et al.*, 1980). Greenhouse studies in which an unweathered western U.S. fly ash was added to either calcareous or acidic soils at rates ranging up to 8% (by weight) produced higher yields of several agronomic crops (Page *et al.*, 1979; Adriano *et al.*, 1980). These yield increases were attributed to increased availability to plants of S from fly ash. Similarly, increases in alfalfa (*Medicago sativa*) yields were attributed to an alleviation of B deficiency by field application of fly ash (Plank and Martens, 1974).

Fly ash applied to acidic strip mine soils in several states increased the yields of many crops. These increases, apparently caused by increased plant nutrient availability (e.g. Ca^{2+}, Mg^{2+}), also prevented the toxic effects of Al^{3+} and Mn^{2+} and other metallic ions by neutralizing the soil acidity (Fail and Wochok, 1977; Kovacic and Hardy, 1972; Capp and Engle, 1967; Adriano *et al.*, 1980).

Because the N content of fly ash is usually zero and its P content is quite insoluble, these nutrients should be added to sustain good growth when fly ash is applied (Adriano *et al.*, 1980)

Increased N concentrations in plant tissues have been observed in some cases, especially when poorly burned coal was used (Page *et al.*, 1977; Adriano *et al.*, 1978; Adriano *et al.*, 1980). The major plant nutrients (P, K, Ca and Mg) were affected inconsistently by ash application. Most studies indicate that fly ash application caused no substantial changes and in some cases even lowered plant tissue P concentrations. Deficient P levels in plant tissues were also observed (Adriano *et al.*, 1978). It was shown that P in the fly ash was considerably less available to plants than the P from monocalcium phosphate (Martens, 1971; (Adriano *et al.*, 1980). Of the basic cations, Ca^{2+} and Mg^{2+} appeared to be taken up preferentially by legumes (Adriano *et al.*, 1978; Page *et al.*, 1979; Adriano *et al.*, 1980). Martens *et al.* (1970) demonstrated that K from KCl was slightly more available to plants than from fly ash. Inconsistencies in the uptake of K, Ca and Mg are probably caused by the interaction among these elements in the root-soil solution interface or within the plant system. For example, Ca and/or Mg can reduce K uptake by plants grown in fly ash-treated soils (Martens *et al.*, 1970; Adriano *et al.*, 1978; Adriano *et al.*, 1980). The micronutrients Mn, Zn, Cu and Fe for fly ash are not consistently available to plants. The increases in soil pH caused by ash application are likely to induce deficiencies of some of these nutrients (Adriano *et al.*, 1980).

Elseewi *et al.* (1978b) concluded that the increases in yields of alfalfa (*Medicago sativa*) and bermudagrass (*Cynodon dactylon*) were due to the correction of S deficiency in soils; they demonstrated further that fly ash-derived S was as effective as gypsum-derived S. The S content of swiss chard *(Beta vulgaris)*, maize (*Zea mays*), and beans (*Phaseolus vulgaris*) were also increased by fly ash treatments irrespective of soil and ash type (Elseewi *et al.*, 1978b; Adriano *et al.*, 1978; Adriano *et al.*, 1980). Although the Mo increases in plant tissues were not directly associated with improved yields, they do indicate the high plant availability of fly ash Mo. Doran and Martens (1972) reported equal plant availability of fly ash Mo and $Na_2MoO_4 \bullet 2H_2O$. They suggested that high fly ash inputs to soil could increase Mo in forage crops to levels potentially toxic to animals feeding on the forage. Higher soil pH can increase the availability of soil Mo due to less retention of these anions by oxides of Al and Fe (Adriano *et al.*, 1980).

Boron in fly ash is also readily available to plants. In fact numerous investigators (Holliday *et al.*, 1958; Cope, 1962; Hodgson and Townsend, 1973; Townsend and Gillham, 1975; Elseewi *et al.*, 1978a; Ciravolo and Adriano, 1979; Adriano *et al.*, 1980) considered B to be a major limiting factor for successful cropland utilization of ashes, especially when they are not fully weathered. Since B compounds in soils are quite water soluble, the weathering of fly ash by allowing adequate drainage should reduce the detrimental effects of B on plants. Once fly ash is added into the soil, B toxicity to plants may last for an extended period of time as a result of gradual hydrolysis of the B compounds. Townsend and Gillham (1975) estimated that, under field conditions, it might take at least 2 to 3 years to reduce the phytotoxic effects of B in fly ash-treated soil to an acceptable level. When the fly ash was completely weathered, it did not lead to any detectable B toxicity symptoms (Ciravolo and Adriano, 1979; Adriano *et al.*, 1980). Crops also exhibit varying degrees (0.5 to 10.0 ppm B in soil extracts) of tolerance to B in soils (Bingham, 1973; Adriano *et al.*, 1980). If the hot water-soluble B in fly ash exceeds 20 ppm, most agronomic crops grown on the fly ash-amended soil may show visual symptoms of B toxicity. For more sensitive crops, yields may also be affected (Davies *et al.*, 1971; Adriano *et al.*, 1980). Some B-sensitive crops, such as peas (*Pisum sativum*), beans (*Phaseolus vulgaris)* and barley (*Hordeum vulgare)* may even exhibit B toxicity symptoms when hot water-soluble B in soil exceeds 7 ppm (Townsend and Gillham, 1975; Adriano *et al.*, 1980).

Since fly ash supports microbial population, legumes usually require inoculation with Rhizobia before planting. Yellow sweet clover (*Melilotus officinalis*) and white sweet clover (*Melilotus alba*) were found growing voluntarily and abundantly in several fly ash landfills in New York (Gutenmann *et al.*, 1976; Adriano *et al.*, 1980). Many potential hazardous elements including Se were found to rapidly accumulate in vegetative tissues. Winter wheat (*Triticum aestivum*) grown on a deep bed of fly ash produced grains containing 5.7 ppm Se (dry wt) as compared to 0.02 ppm in the control (Stoewsand *et al.*, 1978; Adriano *et al.*, 1980).

Selenium concentrations in plant tissues consistently increased with fly ash treatment. This increase was shown to be roughly proportional to either the rates of fly ash application or Se content of fly ash (Furr *et al.*, 1976; Furrr *et al.*, 1977; Straughan *et al.*, 1978; Adriano *et al.*, 1980). Although many trace elements in fly ash are considered potentially detrimental to plants, only B has been associated with any significant reductions in crop production (Cope, 1962; Elseewi, 1978a,b; Adriano *et al.*, 1980). Conversely Cd, Co, Cr, Cu, F, Ni, and V in fly ash have not been shown to be deleterious to plants. Molybdenum and Se are essentially non-toxic to plants at input levels expected from fly ash but their uncontrolled accumulation in plant tissues would be a potential hazard to livestock animals. Although small amounts of Mo and Se are essential in animal nutrition, continuous consumption of forage with elevated Mo and Se contents may induce physiological disorders in livestock. Selenium is required in the diet of animals in the range of 0.04 to 0.2 ppm, while Mo is required at levels <1.0 ppm to prevent nutritional imbalance (Adriano *et al.*, 1980). Molybdenum concentrations ranging from 5 to 20 ppm and Se concentrations ranging from 4 to 5 ppm are potentially hazardous (Comm. On MBEEP, 1976; Adriano *et al.*, 1980).

High alkalinity, high salinity and enhanced concentrations of toxic elements in coal fly ash are the three major constraints in using fly ash for agricultural crops (Cope, 1962; Hodgson and Holliday, 1966; Townsend and Gillham, 1975; Elseewi *et al.*, 1978a; Page *et al.*, 1979; Phung *et al.*, 1979; Wong and Wong, 1990). Despite these constraints, no phytotoxic symptom has ever been reported for plants growing in ash-amended soil except for boron toxicity (Hodgson and Holliday, 1966; Ciravolo and Adriano, 1979; Aitken and Bell, 1985; Wong and Wong, 1990). The relatively large concentrations of K, Ca, Mg, Fe, Zn, B, Mo, S and Se in fly ash were found to be readily available for plant uptake and alleviated deficiencies for these elements for deficient soils (Martens, 1971; Doran and Martens, 1972; Schnappinger *et al.*, 1975; Elseewi *et al.*, 1978a; Ciravolo and Adriano, 1979; Wong and Wong, 1990).

However, inconsistent results on crop yield have been reported from different regions of the world (Furr *et al.*, 1976; Ciravolo and Adriano, 1979; Elfving *et al.*, 1981; Moliner and Street, 1982; Aitken and Bell, 1985; Wong and Wong, 1990). This may be due to the heterogeneity of the physical, mineralogical and chemical properties of fly ash, which in turn depend on the composition of the parent coal, combustion condition, efficiency of emission control device, storage and handling of fly ash and climate (Adriano *et al.*, 1980; Ramsden and Shibaoka, 1982; Wong and Wong, 1990).

Hence, favourable crop response will depend directly on a proper combination of soil types, plant species and regional practice. In Hong Kong, the increasing cost of fly ash disposal and the lack of land for landfill make the land application option more acceptable (Wong and Wong, 1990).

Establishment of vegetative cover through sound reclamation procedure is essential to maintain effective control of erosion and stream pollution. Revegetation of areas where adverse conditions such as steep slopes and highly acidic spoil materials occur is not always accomplished without major regrading operations and treatment of the spoil with soil amendments. Maintenance of a proper balance of physical, chemical and biological factors is essential to the satisfactory survival of planted species. Amendments such as lime, fertiliser and mulch have become common place and much attention has been given to the utilization of waste materials such as compost, sewage sludge, manures and bark as potential amendments. These remarks are directed to a procedure whereby coal waste areas can be stabilized and restored with the aid of fly ash, a by-product of electric power generation (Capp *et al.*, 1975).

The coal ash is often not suitable for agricultural uses due to the high cost of handling and transportation from the source, very low C and N contents, and usually high pH and toxic B contents (Adriano *et al.*, 1980).

Moreover, the addition of organic wastes such as sewage sludge, chicken manure or compost will increase the organic carbon content in soil receiving ash amendment. This will initiate soil microbial activities for the cycling of nutrients (Wong and Wong, 1986; Wong and Wong, 1990). The high N and P contents in these wastes may also reduce the need for inorganic fertiliser. Fly ash mixed with an organic waste will be an attractive and economical option that should be considered (Wong and Wong, 1990).

1.7 Agricultural Utilization of Biosolids

Biosolids are not necessarily untreated raw sewage materials. They are the treated residuals from domestic wastewater treatment processes. Biosolids have undergone screening (to remove large inorganic materials) and grit removal (to remove small inorganic material). The remaining highly organic material is then processed in a manner certified by the Environmental Protection Agency (EPA) to destroy pathogens. Pathogen destruction may involve anaerobic digestion, aerobic digestion, heating, drying, or pH adjustment (Barry *et al.*, 1995).

Local authorities, both overseas and in South Africa, are continually searching for environmentally acceptable, as well as beneficial and economical, means of disposal of sewage sludge. Biosolids that have not undergone pathogen destruction cannot be land applied (Barry *et al.*, 1995). Land application of sludge is not common in many countries since very little research has been carried out under local conditions. While extensive overseas studies can provide some guidance to the potential for sludge utilization, ultimately sludge management practices should be developed on local soils under local conditions.

Existing regulations set limits for the content of heavy metals in sewage sludge as well as the maximum annual and cumulative loadings to land. These loadings are primarily based on health risk assessments (pathogenic micro-organisms) and soil contamination aspects (heavy metals) with some consideration of soil properties, but not soil sorption parameters. The amount of sludge applied to soil influences the composition of the soil solution, and since the movement of heavy metals within soils is mainly in the solution phase, chemical factors that control the distribution of metals between the solid and solution phase influence the mobility of heavy metals. Some of the soil chemical reactions controlling mobility of heavy metals and phosphorus are in fact adsorption /desorption processes (Barry *et al.*, 1995).

Restoration of semi-arid grasslands is going to depend upon restoration of soil C and N resources. Restoration efforts in semiarid grasslands commonly use inorganic N and P fertilisers (Black and Wight, 1979; White *et al*, 1997). The goal is to increase plant growth and litter production, which ultimately could lead to an increase in soil C and N resources. However, N and P fertilisers are costly and as much as 94 % of the inorganic N added to soils in southwestern USA, as an example, can be lost during the first year after application (Westerman and Tucker, 1979; White *et al.*, 1997).

Use of bio-solids (e.g., municipal sewage sludge) has been shown to aid in the sustainable revegetation and reclamation of mined lands when applied with or without a suitable liming agent (Joost *et al.*, 1987; Pichtel *et al.*, 1994; Barnhisel and Hower, 1997; Cravotta, 1998; Abbott *et al.*, 2001). Sewage sludge is a source of organic matter, a pool of slow-release essential nutrients (N and P), and microorganisms (Cravotta, 1998; Abbott *et al.*, 2001).

In a study on the potential release of macro-nutrients from soil, phosphorus (P) was identified as one of the key elements in the eutrophication of inland waters (OECD, 1982), municipal sewage treatment plants have been required to reduce point sources of P pollution. The treatment process removes soluble P, which, consequently, ends up in sewage sludge. The annual production of sewage sludge in Sweden, for example, and this is presumably similar for other countries, should be sufficient to fertilize 9 % of the agricultural land in Sweden (2

800 000 ha) at the recommended rate of 1 ton (dry weight) ha^{-1} yr^{-1} (SEPA, 1995). The addition of this amount of sludge would result in the import of 30 kg P ha^{-1} yr^{-1}, whereas the average amount of crop-P removed at harvest is only 13 kg P ha^{-1} yr^{-1} (Granstedt and Westberg, 1992; Rydin and Otabbong, 1997). Sewage sludge in landfills must, therefore, be regarded as a potential source of nonpoint P pollution (Rydin, 1996)

Rangeland restoration through surface application of biosolids (municipal sewage sludge) is an increasingly common practice. In a study conducted by (White *et al*, 1997) nitrogen mineralization potentials were significantly higher ($P< 0.05$) in the 45 and 90 tons ha^{-1} applications after nine years, indicating that site fertility remained higher even though most soil chemical properties were returning to untreated levels (White *et al*, 1997).

Long-term benefits to rangelands are the desired result of biosolid application, in addition to the direct benefit realized from its disposal. The benefit is expected to occur through increased primary production resulting in more above- and below –ground litter, which in combination with soil microbial production contributes to soil OM through the process of decomposition. The increase in N minerilization with increasing rate of biosolids application (significant for the 45 and 90 tons ha^{-1} applications) nine years after application is a very good indicator that long term benefits in site productivity may be realized from surface-applied biosolids. Although biosolids are recognized for increasing N availability after addition to soils (Garza *et al*., 1986; Wiseman and Biblike, 1998; White *et al*., 1997), these results indicate that the frequently measured short term increase in N availibility and productivity, may indeed extend for much longer periods, which is the desired result. There may be no long-term benefit from applications in excess of about 45 tons ha^{-1}. This rate would be recommended because it minimizes the contribution of metals relative to higher application rates yet maximizes the long term nutrient benefit (White *et al*., 1997).

The near universal short term response to N application to rangelands is an increase in site productivity, regardless of whether the N is in the form of inorganic fertilisers or biosolids (Aguilar *et al*., 1994; Fresquez *et al*., 1990a,b, 1991; Loftin and Aguilar, 1994; Wester *et al*., 1996; White *et al*., 1997). However, a short-term response may not lead to long-term benefits. Soils often respond to N additions with further increases in mineralization of indigenous soil-N, a response known as the "priming effect" (Woods *et al*., 1987; White *et al*., 1997), which is seen as a short term increase in productivity. Addition of N stimulates decomposition of indigenous soil OM, as shown by an increase in CO_2 liberation from fertilised soils. This results in a short-term decrease in soil OM and a short-lived pulse of productivity. If repeated frequently, fertiliser-N applications deplete soil OM, resulting in long-term declines in potential site productivity (DeLuca and Keeney, 1993; White *et al*., 1997).

Plant growth may also be stimulated following biosolids application to semiarid calcareous soils due to increased availability of essential micronutrients (O'Connor *et al*, 1980; White *et al*, 1997). If biosolids were readily incorporated into the soil through movement of fine biosolid particulates and/or stimulation of plant growth, it could provide the nutrient resources necessary for long-term recovery of degraded grasslands (White et al., 1997).

The water soluble, DTPA (diethylenetriaminepentaacetic acid)- extractable metals and other properties associated with biosolids application increased through the first four years after application and then declined by the eighth year. Soil fertility, as measured by the N mineralisation potentials of the soils, remained significantly higher nine years after the biosolids applications of 45 and 90 tons ha^{-1} (White *et al*., 1997).

Soil microbial communities also increased following application of biosolids and the soils with 45 and 90 tons ha^{-1} treatments had significantly more fungal biomass relative to controls after four growing seasons (Dennis and Frequez, 1989; Frequez and Dennis, 1989; White *et al*., 1997). This increased growth by vegetation and soil microorganisms would in part account for a decline in essential water-soluble nutrients.

Soil fertility is also related to soil biota. Microbes and fungi are the major agents in the decomposition of organic matter and soil stabilization, and serve to increase the availability of plant nutrients, and fix nitrogen from the atmosphere. Martensson and Witter (1990) reported retarded N_2 fixation in soil treated with biosolids. In general, long term studies have found N_2 fixation by free living heterotrophic bacteria and free living cyanobacteria was inhibited by metals in applied biosolids (McGrath *et al.*, 1995; White *et al.*, 1997), but most studies were in soils with lower pH, which could significantly increase metal toxicity to microorganisms over the slightly basic soils used in this study. Nitrogen fixation by free-living soil microorganisms provides small, but perhaps essential, inputs to grassland ecosystems (Herman *et al.*, 1993; White *et al.*, 1997).

As part of the continuing effort to understand potential toxicity of heavy metals in sewage sludge on the growth of legumes, the effects of sludge on *Rhizobium leguminosarum* bv. *Trifoli* and N_2 fixation were examined. Reddy *et al.* (1983) investigated the survival of *Bradyrhizobium* in a newly sludge-amended soil and observed a decline in bacterial populations. They concluded that the decrease in viability of *Bradyrhizobia* was because of heavy metal toxicity. However, Madariaga and Angle (1992) reported that a rapid decline in the soil population of *Bradyrhizobium*, soon after application of sludge, might be due to the presence of toxic concentrations of soluble salts in the sludge (Ibekwe *et al.*, 1995).

Heckman *et al.* (1986, 1987) reported that an increase in dry matter yield and N_2 fixation of soybean [*Glycine max* (L.) Merr.] was related to the residual content of N in soil originating from sludge applied 10 years earlier. The number of *Bradyrhizobia* in the same sludge-amended soil was found to increase with increasing rates of sludge addition to soil (Kinkle *et al.*, 1987; Ibekwe *et al.*, 1995), although *Bradyrhizobium* is more resistant to heavy metals than *Rhizobium* (Ibekwe *et al.*, 1995).

The presence of large numbers of rhizobia in the soil may be one of the most important factors that determine efficient nodulation. As noted by Giller *et al.* (1989), by increasing rhizobial concentrations added to contaminated soil above 10^7 cells g^{-1}, effective nodulation is observed because sufficient numbers of cells survive to nodulate their host. Giller *et al* (1989) reported that inoculation with effective Rhizobium resulted in effective N_2 fixation, which enhanced the potential of nodulation in the metal-contaminated soil.

The present study also demonstrates that legumes still benefit from sewage sludge applied 18 years previously. This was illustrated by the increase in dry matter yield of plants grown on the sludge-amended soils. Application of sewage sludge to land planted to legumes is a beneficial practice and with appropriate caution should be encouraged (Ibekwe *et al.*, 1995).

Improper land use practices, including overgrazing, can lead to a severe reduction in plant cover and soil productivity. This process, known as desertification, is especially common in arid and semiarid regions with sparse vegetation cover. A loss of vegetative cover can increase the erosion potential of the soil and soil erosion can accelerate the process of desertification by removing the topsoil, which is relatively rich in plant nutrients and organic matter. If the cycle of degradation is not disrupted, a grassland can degrade to a desert-like system which might be virtually be impossible to restore (Naveh, 1988; Klein, 1989; Loftin and Aguilar, 1994).

Soil organic matter plays a key role in inhibiting the process of desertification (El-Tayeb and Skujins, 1989; Parr *et al.*, 1989; Loftin and Aguilar, 1994). Organic matter improves infiltration of precipitation, soil water holding capacity, and nutrient availability, all of which are important to plant recovery. Any successful attempt at grassland restoration will need to increase retention of precipitation and control runoff and erosion, increase plant growth, and re-establish a stable pool of soil organic matter. Biosolids are an excellent choice for a soil amendment, it is readily available, contains many plant nutrients, and has excellent soil conditioning capabilities when it is incorporated into the soil (Alloway and Jackson, 1991; Glaub and Golueke, 1989; Parr *et al.*, 1989; Loftin and Aguilar, 1994). Epstein (1973) reported that sewage sludge, or sludge compost, (at application rates of 5-10 % by weight) increased moisture retention at all matric potentials and increased aggregate stability (Lindsay and Logan, 1998).

Clapp *et al.* (1986) evaluated the results of 23 published studies and concluded that sludge application reduced bulk density (p_b), and increased total porosity and moisture retention. Clapp *et al* (1986) also attributed the observed effects to organic matter additions. In a green house study with four Ohio soils, Logan *et al* (1996) found that a one-time application of 25 % by weight of digested sewage sludge improved soil physical properties as measured by p_b, porosity, moisture retention, aggregate stability, shrinkage, and saturated hydraulic conductivity (K_s) (Lindsay and Logan, 1998). Sludge additions generally improved the soil properties measured. Had the sludge been added to a soil with poorer physical properties, beneficial effects on physical properties would probably have been greater. Stable organic matter content, which was increased, likely contributed to improving many of the soil physical properties (Lindsay and Logan, 1998).

Sludge amended spoil generally has higher rates of plant biomass production than non-amended spoil (Seaker and Sopper, 1982; Anderson and Birkenholz, 1983; Heckman *et al.*, 1987; Rodgers and Anderson, 1995). Yield responses often are not linearly related to levels of sludge amendment. For example, Pietz *et al.* (1982) reported that corn yields (*Zea mays* L.) were not linearly related to the amount of liquid anaerobically digested sewage sludge added to the spoils, but it followed a quadratic response to increasing amount of sludge amendment. Similarly, Rodgers (1987) reported that biomass production of prairie switchgrass (*Panicum virgatum* L.) and Indian grass [*Sorghastrum nutans* (L.) Nash] grown in a glasshouse exhibited a quadratic response to increasing levels of sludge applied to strip mine spoil. Soluble salt concentration may have limited plant growth at the high sludge amendments in both of these studies (Pietz *et al.*, 1982; Rodgers, 1987; Rodgers and Anderson, 1995). The toxic effect created by high concentrations of soluble salts is due to a decrease in available moisture to the seeds or growing plants (Ashby *et al.*, 1979; Jastrow *et al.*, 1984; Smith *et al.*, 1986; Rodgers and Anderson, 1995)

The potential for high concentrations of soluble salt to limit plant growth at high levels of sludge application is high, especially where soils are subjected to periodic drying. These conditions are more likely to occur in the field. When various application rates of municipal sludge (11-202 tons ha^{-1}) were tested in the field, Seaker and Sopper (1982) found hay yield to be higher on all sludge-amended strip mine sites than undisturbed farmland, but the rate of 134 tons ha^{-1} had the highest yield. Keefer *et al.* (1983) also tested various types of ameliorants on abandoned strip mine sites, including 45 and 90 tons ha^{-1} of sewage sludge. They found that only the addition 90 tons ha^{-1} increased the yield of grasses. Based on their research and other studies, they recommended that sludge amendments not exceed a one-time application of 100 tons ha^{-1} to prevent growth inhibition during the first years following field application (Rodgers and Anderson, 1995)

A surface application of biosolids to semi-arid grasslands has been shown to increase aboveground plant cover (assuming these systems are water and/or nutrient limited) (Frequez *et al*, 1990a; Loftin and Aguilar, 1994) and a subsequent decrease in surface runoff and soil erosion (Aguilar and Loftin, 1992; Loftin and Aguilar, 1994). Although, surface applications of biosolids made no direct input to soil organic matter (carbon), increases in soil organic matter could have occurred as an indirect result of increased plant nutrient availability and subsequent belowground productivity (Loftin and Aguilar, 1994).

Mine spoil is often characterized as having low fertility, organic matter, water holding capacity, and soil biological activity, yet it is used as a coversoil in surface mine revegetation when topsoil is lacking (Reddell and Milnes, 1992; Thorne *et al.*, 1998). Spoil created from open pit surface mining is a mix of soil and rock produced from excavations of ore veins and is generally devoid of physical and biological attributes associated with a developed topsoil (Thorne *et al.*, 1998). Since revegetation objectives may not be met if a suitable soil environment is not provided, amendments such as sewage sludge and arbuscular mychorrhizal fungi are often added to mine spoil to help create a functional soil (Lambert and Cole, 1980; Topper and Sabey, 1986; Joost *et al.*, 1987; Sabey *et al.*, 1990; Thorne *et al.*, 1998). These amendments may add plant nutrients and help re-establish biologically driven nutrient cycles that benefit the establishment of revegetation species on mine spoil (Johnson and McGraw, 1988; Hetrick *et al.*, 1994; Thorne *et al.*, 1998).

Few studies with sewage sludge have examined the effects of application rates that might range from < 10 tons ha^{-1} for agronomic uses to one-time large rates of several hundred tons per hectare for reclamation, or soil conditioning. In the study reported by Lindsay and Logan (1998), an existing field experiment with multiple rates from 7.5 to 300 tons ha^{-1} (Logan *et al.*, 1997a; Lindsay and Logan, 1998), was sampled and selected soil physical properties were measured. A previous study on the site had shown significant improvements in soil physical

properties with a one-time application of 500 tons ha^{-1} of N-Viro Soil, an alkaline stabilized sewage sludge (Lindsay and Logan, 1998).
Sewage sludge collected from waste –water treatment plants supplies N and P, provided long-term fertility (Topper and Sabey, 1986; Thorne *et al.*, 1998), and shortened the time period for development of biological cycles critical for sustained plant growth (Seaker and Sopper, 1998).

1.7.1 Heavy metal bioavailability in biosolid amended soils

Land application of biosolids is still not completely accepted in the scientific community as a beneficial disposal option (McBride, 1995; Brown *et al.*, 1997), with concern persisting over the fate and phytoavailability of biosolids-applied trace metals over time. Studies of metal movement in biosolid-amended soils have generally shown little or no movement through the soil profile with significant exceptions (Darmody *et al.*, 1983; Dowdy and Volk, 1983; Emmerich *et al.*, 1982; Kuo and Baker, 1980; Legret *et al.*, 1988; Robertson *et al.*, 1982; Welch and Lund, 1987; Brown *et al.*, 1997).

The need for regulation arose, in part, from the heavy metals in biosolids that could potentially enter the food chain through plant uptake. As a result, many studies have investigated the effects of biosolids applied to grasslands used for agricultural production (Barkay *et al.*, 1985; Brendecke *et al.*, 1993; Obbard *et al.*, 1994; O'Connor *et al.*, 1980; Soon *et al.*, 1978; 1980; Wild *et al.*, 1991; White *et al.*, 1997). These practices involve one or more applications of biosolids that are usually mechanically incorporated into the soil prior to crop production. However, even with the frequency of biosolids addition to agricultural soils, the effects on long-term bioavailability and movement of metals in soil profiles are incompletely understood (Alloway and Jackson, 1991; White *et al.*, 1997).

Biosolids application for agricultural practices differs significantly from current practices in rangeland restoration where biosolids are generally an one-time surface application to minimize soil and vegetation disturbance. Semi-arid rangelands frequently have neutral or slightly basic soils, which reduces metal toxicity considerably compared to soils with lower pH (McGrath *et al.*, 1995; White *et al.*, 1997).

Municipal biosolids are often rich in aliphatic and aromatic acids, polysaccharides, proteinaceous material, humic substances, and organic sulfonates (Holtzclaw and Sposito, 1978; Holtzclaw *et al.*, 1980; Boyd *et al*, 1980; Baham and Sposito, 1983; Han and Thompson, 1999). Application of biosolids to soil is expected to affect the content and composition of soluble organic carbon, which in turn, could influence the speciation, mobility, and fate of metals in the amended soil (Han and Thompson, 1999). Biosolid amendments could increase the mobilization of hydrophillic, low-molecular-weight compounds in a soil while at the same time limiting the mobility of organic colloids. Therefore, the mobility of trace metals (which are often associated preferentially with hydrophillic organic compounds) could be enhanced, while the mobility of hydrophobic organic pollutants (more likely to be associated with colloidal organic matter) could be reduced (Han and Thompson, 1999).

The observed movement of metal(s) and alkalinity may be linked to the formation of fulvic acid-metal complexes that become increasingly more soluble at elevated pH levels. Although statistically significant, the movement of metals was limited and occurred only after very high rates of biosolids had been applied. There is no indication that metal movement would occur in fields receiving agronomic rates of biosolids (Brown *et al.*, 1997).

Chang *et al.*, (1984) found more than 90 % of the biosolid-borne metals accumulated in the plough layer (top 15 cm of soil) and there was no significant increase below the 30 cm depth in plots treated for six years with biosolids (up to 320 tons of biosolids ha^{-1} total application). It is generally assumed that biosolids-borne trace elements will not leach below the plough layer in amended soils. The AB-DTPA extractions did detect movement but only zink (Zn) showed consistent increases below the plough layer. An increase in extractable trace elements does not necessarily foretell environmental –contamination or pose a public health threat (Barbarick *et al*, 1998).

It has been suggested that sludge-applied metals, and cadmium (Cd), in particular, are mainly associated with sludge organic matter in the soil (McBride, 1995). Minerilization of sludge organic matter may release metals into bioavailable forms that may harm sensitive crops and microbes. To address this possibility, more information is needed on the long-term chemical forms of trace metals in continuously cultivated agricultural soils that received multiple sewage sludge applications. Significant amounts of sludge borne trace metals were added to agricultural soils during a 20-year watershed study at the Rosemount Experimental Station near Rosemount, Minnesota (Dowdy *et al.*, 1994; Sloan *et al.*, 1997). Studies have reported large differences between calculated soil profile metal concentrations based on biosolids loadings and those determined by chemical analysis (Berti and Jacobs, 1996; Dowdy *et al.*, 1994; Sloan *et al.*, 1997). However, Dowdy *et al*, (1994) were unable to account for large movements of heavy metals to soil depths of 1.0m 14 years after massive biosolids applications (Sloan *et al.*, 1997). Concentrations of Cd, Ni and Zn in lettuce were most highly correlated ($P<0.001$) to metal concentrations in one or more chemical fractions.

Bidwell and Dowdy (1987) observed significant linear and quadratic effects of biosolids loading during the six years after biosolids applications. This suggests that a fraction of biosolid-derived Cd becomes less available with time when applied at high rates. Land application of biosolids at agronomic rates increased dissolved organic carbon (DOC) concentrations in soils (Sloan and Basta, 1995; Sloan *et al.*, 1997). It is possible that high DOC concentrations in soils which received large biosolids amendments initially inhibited precipitation of Cd, but as biosolid organic matter stabilized and DOC concentrations decreased, subsequent Cd precipitation decreased Cd bioavalability. Plant uptake of biosolid-derived Ni and Zn showed similar trends. Nickel and Zn were not taken up by lettuce to the same extent as Cd, but tissue concentrations of both metals were increased three to four times with the highest biosolid loading. During the three years biosolids were applied , the Ni and Zn content of corn (*Zea mays* L.) silage increased linearly with biosolid application rate (Dowdy *et al.*, 1983; Sloan *et al.*, 1997). In a study on metal movement in soils over a period of nine years, there was a decline in extractable metals after 8years and it was suggested that this could possibly be as a result of increased binding with soil particles and lower extraction efficiency. Thus metals could still be present, but less-readily extracted (White *et al.*, 1997). In a study conducted in Australia, on estimating sludge application rates to land, it was concluded that elements Cd, Ni and Cu were all retained to a greater extent in the surface horizon, most likely due to their affinity for organic matter (Barry *et al.*, 1995).

Heavy metal phyto-availability is inversely related to pH (Logan and Chaney, 1983; Narwal *et al.*, 1983; NRC, 1996; Basta and Sloan, 1999), and land application of biosolids can increase crop uptake of heavy metals in acidic soils (Corey *et al.*, 1987; Logan and Chaney, 1983; Mahler *et al.*, 1980; Basta and Sloan, 1999). Federal regulations before 1993 (USEPA, 1979; Basta and Sloan, 1999) and many current state regulations do not permit land application of biosolids to agricultural land with soil pH < 6.5. These regulations require soil to be limed to pH > 6.5 before land applications of biosolids to agricultural land to reduce heavy metal solubility and bioavailability (USEPA, 1979; Basta and Sloan, 1999). Liming acidic soils that have received biosolids application reduces plant uptake of Cd, Zn, and to lesser extent Cu and Pb (Braillier *et al.*, 1996; Logan and Chaney, 1983; Mahler *et al.*, 1987; Basta and Sloan, 1999).

Alkaline biosolids, produced when biosolids are treated with alkaline materials to kill pathogens, have a relatively high $CaCO_3$ and may serve as a liming material (Little *et al.*, 1991; Basta and Sloan, 1999). Because alkaline biosolids are effective as liming material, the application of alkaline biosolids resulted in less plant uptake of Cd (Brown and Brush, 1992; Basta and Sloan, 1999) and Cd, Cu, Ni, and Zn (Mulchi *et al.*, 1987; Basta and Sloan, 1999). The application of non-alkaline biosolids to non acidic soils, only increased barley (*Hordeum vulgare* L.) shoot Cu and Zn (Luo and Christie, 1998; Basta and Sloan, 1999). Current federal regulations (USEPA, 1993; Basta and Sloan, 1999) do not require liming acidic soils to pH > 6.5 before application of biosolids. Also, new federal regulations define an exceptional quality (EQ) biosolid that contains low levels of heavy metals and pathogens (USEPA, 1993; Basta and Sloan, 1999) and which can be land applied with minimal regulatory oversight.

Whether plant metal concentration follows a linear or a plateau-type response to metal loading may depend on plant species (McGrath *et al.*, 2000). Cadmium and Zn are usually the most bio-available heavy metals of sludge origin (Alloway 1995; Berti and Jacobs, 1996; Sloan *et al.*, 1997; McGrath *et al.*, 2000). Cadmium is of major concern in terms of the transfer into the food chain, whereas Zn can cause harmful effects to plants and soil micro-organisms well below the concentration in soil that is permitted to build up under the USEPA-503 regulations (Chandri *et al.*, 1993: Lubben *et al.*, 1991; McGrath *et al.*, 1995; Sanders *et al.*, 1987; McGrath *et al.*, 2000).

The concentrations of total Zn and Cd in the sludge-amended plots decreased markedly after sludge applications were terminated, mainly because of lateral soil movement. Although OM from sludge decomposed rapidly during the initial years after sludge was applied, about 15 % of sludge OM still remained in the soil 23 years after the termination of sludge applications (McGrath *et al.*, 2000). The concentrations of Zn and Cd in both vegetative and storage tissues of eight crops correlated linearly with soil total metal concentrations. Plant species differed markedly in the transfer efficiency of Zn and Cd from soil to plants (McGrath *et al.*, 2000).

Wastewater pre-treatment programmes over the last 15 years have significantly reduced biosolids heavy metal content, and amounts of EQ biosolids produced have increased (NRC, 1996; Basta and Sloan, 1999). These changes may result in application of EQ to acidic soils. Information on soil solution and bio-available heavy metals in acidic soils treated with EQ biosolids is limited. Perhaps land application of EQ biosolids to acidic soils will have minimal effect on heavy metal bioavailability. Land applications of alkaline EQ biosolids on acidic soil may be comparable to application of limestone and have little effect on heavy metal bioavailability (Basta and Sloan, 1999). Soil solution Cd and Zn and plant uptake of heavy metals were greater for non-alkaline anaerobic – digested biosolids than alkaline lime stabilized biosolids. In general, EQ biosolids increased soil solution Cd and Zn and plant uptake of heavy metals compared with limestone treatment. Increasing application rate of alkaline biosolids to achieve soil pH > 5 decreased soil solution heavy metal and bioavailability despite larger heavy metal loadings to the soil. High application of lime-stabilized biosolids had similar dissolved Cd and Zn as soil treated with limestone that did not receive any biosolids. Soil solution Cd and Zn increased with time after application of EQ biosolids; this increase was small for lime stabilized biosolids but large for alkaline biosolids. Many state regulations prohibit application of biosolids to acidic soil to reduce risk of heavy metal mobility and phytotoxicity. Although this is a prudent practice for nonalkaline biosolids, application of EQ alkaline biosolids to acidic soil to achieve final soil pH > 5 will minimize risk from soil solution Cd and Zn and plant uptake of heavy metal (Basta and Sloan, 1999).

If the pathogen reduction process in sewage sludge treatment involves the addition of hydrated lime and/or an alkaline substance, resulting in a pH 12 material, a built in source of alkalinity is realized (Abbott *et al.*, 2001), and can be regarded as a possible amendment for acidic and nutrient depleted soils.

1.8 The Co-utilization of waste products to ameliorate acidic and nutrient depleted soils

Since the advent of nationwide advanced wastewater treatment in the late 1960's in the USA, much attention has been placed on the treatment and disposal, or use, of the residual solids of wastewater processing. Those solids, referred to as sewage sludge, and more recently biosolids, have traditionally been placed in municipal landfills, incinerated, ocean dumped, or applied to agricultural land. Lesser amounts have been used for reclamation of disturbed lands, and given away or sold for gardening or commercial horticulture. Before the 1980's, most sludge was biologically digested as a means of stabilizing the sludge organics and to reduce pathogens. In the 1980's, more advanced technologies for sludge treatment emerged that produced a pathogen free product and stabilized sludge organic matter. The two most widely used approaches are biological composting and alkaline stabilization. While composting relies on biological degradation, heat, and drying to kill pathogens and stabilize sludge organic matter, alkaline stabilization utilizes a combination of high pH, heat, and drying to achieve the same purpose. One of the alkaline stabilization technologies known worldwide is the patented N-Viro process. This process involves the mixing of partially dewatered sewage sludge (either digested, waste activated, or raw primary waste activated) with an alkaline material or blend of materials. Solids content of the sludge can vary from 15 to 40 % (Logan and Burnham, 1992; Logan and Harrison, 1995), and a number of industrial by-products can be used as alkaline reagents. These include cement kiln dust, limekiln dust, lime (CaO), limestone, alkaline fly ash, FGD, other coal burning ashes, and wood ash. The reagents are used alone or in combination (referred to as alkaline admixtures, AA), according to local availability and cost, so as to provide pH in the sludge-AA mixture >12, temperatures between 52 and 62°C, and solids content > 50 % for 12 h. The pH must remain > 12 for at least 3 days (Burnham *et al.*, 1992; Logan and Harrison, 1995). At this point, the final product has achieved the USEPA's classification for complete pathogen destruction (USEPA, 1993; Logan and Harrison, 1995). The material must be further dried, however, by windrowing to at least 60 % solids to produce a uniform, granular product if it is to be used beneficially. The material is usually windrowed a minimum of three times during a period of 3 to 7days. At this point, the material, if it also meets the federal sludge concentration limits for trace elements, and the vector attraction requirements (USEPA, 1993; Logan and Harrison, 1995), can carry the trademark N-Viro Soil.

There are > 30 operating N-Viro facilities in the USA, Australia, and England; and N-Viro Soil is used as a substitute for agricultural limestone, as a fertiliser, for land reclamation, as a soil amendment for landscaping, as an ingredient with other materials for the manufacture of synthetic topsoil, and as a substitute for soil for landfill cover (Logan, 1992; Logan and Burnham, 1992; Pierzynski and Schwab, 1993; Logan and Harrison, 1995).

N-Viro Soil has been previously characterized for lime, nutrient and trace element characteristics (Logan, 1992; Logan and Burnham, 1992; Logan and Harrison, 1993; Logan and Harrison, 1995), but no study has been made of the physical properties of these materials. Physical data is essential if these materials are to be used effectively as substitutes for soil in various applications (Logan and Harrison, 1995).

Previous work by Reynolds *et al* (1999) to determine the feasibility of converting waste disposal problems in South Africa into a soil beneficiation strategy, has proven viable. The co-utilization of fly ash and sewage sludge with added lime delivered a product termed SLASH (that contains 60 % fly ash, 30 % sewage sludge and 10% unslaked lime on a dry matter basis), which has beneficial soil ameliorant effects. Two problems experienced in the past were that, sewage sludge contained heavy metals and pathogens. As a result its use was restricted for agricultural land application. Secondly, fly ash production in countries which rely on coal for energy such as South Africa, presents a major problem to those responsible for the consequences and implications of disposing of such "waste" products (Truter *et al.*, 2001).

In South Africa approximately 28 million tons of ash is produced annually as a result of energy generation to meet the energy requirements of a population of 45 million people and growing. This largely untapped resource, together with the power utilities, is generally situated in areas with high agricultural potential, which are acidifying because of the effect of "acid rain" and agronomic practices. Only a small percentage of this fly ash resource is used in the cement, plastics, rubber and paint industry (Reynolds *et al*, 2002).

Sewage sludge on the other hand is classified as a toxic waste and it is produced at a rate of 800 tons/day dry mass in South Africa (Reynolds, 1996). These problems emphasize the need for co-utilization of wastes and thereby identify possible strategies for the safe disposal (use) of such waste products. Nutrient poor and acidic soils in South Africa are becoming more prevalent and many farmers require alternatives to the high priced conventional methods of soil amelioration currently in use (Truter *et al.*, 2001).

Lime added to sewage biosolids to reduce malodor and to kill pathogens often provides an effective means to also neutralize subsoil acidity when biosolids are applied to land at high loading rates. It is not clear if there is a significant effect when biosolids are applied at standard agronomic rates. This benefit appears to be greatest when lime-stabilized, undigested, biosolids are used. The metal movement observed in this study occurred only when highly contaminated biosolids or very high rates of biosolids were applied. The level of metal movement, although statistically significant, was limited enough to suggest that no adverse environmental effect would result from this movement. Based on the results of this study, it is highly unlikely that the agronomic use of biosolids would result in the movement of biosolids metals below the surface layer of soils.

However, as with fly ash, only a fraction of total nutrients (especially N and P) supplied by organic wastes are available to crops in a season, since they must be mineralized from organic to inorganic forms. Despite these limitations, sewage sludge and animal manures may be the most cost effective supplement for co-utilization with fly ash in crop fertilisation. Mixtures of fly ash with organic wastes already have a proven track record (Pitchel and Hayes, 1990; Belau, 1991; Schwab *et al.*, 1991; Sims *et al.*, 1993; Vincini *et al.*, 1994; Sajwan *et al.*, 1995; Wong, 1995; Schumann and Sumner, 2000), but the preparation of mixtures has usually proceeded by trial and error. The formulation and use of complex waste products could be greatly enhanced by improved prediction of nutrient supplies from components before they are combined (Schumann and Sumner, 2000).

Alkaline biosolids originate from treatment of sewage sludge with alkaline materials to kill pathogens. Two commonly produced biosolids are lime stabilzed sewage sludge and N-Viro Soil. Lime stabilized sewage sludge is produced when hydrated lime is used to raise the sewage sludge pH of 12 (USEPA, 1973,1992; Sloan and Basta, 1995). Alkaline cement kiln dust has been used to raise the sewage sludge pH and produce N-Viro soil. Alkaline biosolids can have relatively high $CaCO_3$ equivalencies (CCE) (Little *et al.*, 1991; Sloan and Basta, 1995) and may serve as potential liming amendments to alleviate Al toxicity in acid soils

The use of fly ash (FA) as a soil amendment is hindered by a lack of macronutrients in the ash and concerns about trace element availability. Mixing FA with an organic waste can increase macronutrients while reducing odor and improving material handling, but the trace element solubility requires investigation. A study conducted by Jackson *et al.*, (1999) examined the trace element solubility and availability resulting from land application of such mixed wastes. Two FA's were applied as mixtures with either poultry litter (PL) or sewage sludge (SS) to field plots at rates 100 and 120 tons ha^{-1} for FA/PL and FA/SS, respectively. Trace element uptake was monitored in maize (*Zea mays* L.)

leaf tissue and grain. Soluble B was initially >25 mg L^{-1} for one high B FA/PL mixture and led to initial toxicity in seedlings. Soil solution concentrations of dissolved carbon, P, As, Se, Mo, Cu, and Cr were increased in FA/PL field plots. Increased solubility was due to increased load in the FA/PL mixtures, while for Mo, Se, and Cr, mixing fly ash with poultry litter appeared to increase solubilisation from the ash when compared with an equivalent mass of FA mixed with sewage. Leaf tissue data confirmed an increase in available As from the FA/PL mixtures, while leaf tissue Se was more dependent on the total Se concentrations of the ash (Jackson, *et al.*, 1999).

Wong and Su (1997) performed an experiment, to evaluate the importance of pre-incubation on the stabilization of a soil-mix composed of coal fly ash and sewage sludge. Sludge was amended with ash at rates of 0, 5, 10, 35 and 50% (on a wet basis). Each ash-sludge mixture was mixed with a loamy soil at either 1:1 or 1:5 ash-sludge mixture: soil (wet volume) and then incubated under greenhouse conditions for 42 days. Ash amendment resulted in a decrease in EC, NH_4^+, PO_4^{3-} and Zn, but an increase in pH and B for most of the incubation period especially for soil with 35 and 50% ash-sludge mixture added at 1:1 (wet volume). Ammonium increased and then decreased, while PO_4^{3-} and NO_3^- remained relatively unchanged, in the first 14-21 days and then increased until the end of the incubation period. Soluble Cu of all treatments decreased at the end of incubation except for soil with 0% ash-sludge mixture at 1:5 (wet volume). With an increase in ash amendment rate, both seed germination and root growth of *Agropyron elongatum* in the soil extracts increased at each incubation period indicating the beneficial effect of the fly-ash-sludge mixture. However an incubation period of 21 days would be needed to obtain an optimum physico-chemical condition for plant growth.

Previous studies had shown that a combination of coal fly ash (10% wet weight) and lime (1% wet weight) amendment was effective in stabilizing biosolids by killing the pathogens and reducing heavy metal availability, and the product contained a high B content. It was, therefore, the aim of the study by Jiang *et al.*, (1999) to evaluate the suitability of the stabilized biosolids as a B fertiliser for a degraded acid soil with B deficiency in South China. An acid and B deficient loamy soil was amended with the stabilized biosolids at application rates of 6.4, 12.7, 25.5, 63.7 and 127.4 tons ha^{-1}, which were then compared to the same soil receiving an equivalent B fertiliser application rates of 0.9, 1.4, 2.2, 4.5 and 8.4 kg ha^{-1}, respectively. Soil hot water soluble B content and pH increased significantly with an increase in the amendment rate of the stabilised biosolids mixture.

Soil amended with the stabilised biosolids mixture had a significantly higher dry weight yield for both cucumber and corn than the control and its counterparts of soil with B fertiliser. The highest yield was obtained in the treatment with 5% stabilised biosolid mixture amendment. Boron concentrations in plant tissues increased according to the application rates of the stabilised biosolids mixture and B fertiliser. Cucumber was more sensitive than corn to both B deficiency and toxicity as indicated by the insignificant effect of B fertiliser application on dry weight yields of corn. The experimental results demonstrated that the stabilised biosolid mixture at an application rate of 63.7 tons ha^{-1} could act as a B fertiliser supplement for the acid loamy soil (Jiang *et al.*, 1999).

Prediction of plant nutrient supply from fly ash and biosolids (sewage sludge and poultry manure) may enhance their agricultural use as crop fertilisers. The resin method was useful for major nutrient (N, P, K, Ca, Mg, S) extraction from fly ashes and organic materials, particularly where mineralizable fractions of N and P under aerobic conditions are required. Extraction of fly ash with dilute-buffered nutrient solution was more successful because micronutrient recovery was improved, major nutrients were correlated to the resin method, and both addition and removal of nutrients were recorded. The overall nutrient supply from these extremely variable fly ashes was: Cu = Fe, B, Mo > Ca > S > Zn >Mn > N > Mg > P > K (high micronutrient, low macro nutrient supply). For biosolids, the macronutrients ranked: P > N, Ca > S > Mg > K (sewage sludges), and N > Ca, K > P > Mg > S (poultry manures). In mixtures of fly ash with 26% sewage sludge the order was: Ca > S > N > Mg > P > K, while in mixtures of fly ash and 13% poultry manure, the nutrients ranked: Ca > K, N, S > Mg > P. Optimal plant nutrition (especially N-P-K balancing) should be possible by mixing these three waste materials (Schumann and Sumner, 2000).

Solid waste such as sewage sludge containing fecal matter, as already discussed, is processed to reduce pathogens by at least 90% and converted to a useful product such as an amendment to agricultural land. By combining the waste with an acid such as concentrated sulfuric acid and a base such as fly ash, which exothermically reacts and thermally pasteurizes the waste and adds mineral value to the product can serve as such an amendment. Pozzolanic materials, such as fly ash agglomerate the product and after grinding, the particles can aerate soil. The calcium oxide in fly ash reacts with sulfuric acid to form calcium sulfate dihydrate, a soil amendment. The amount of sulfuric acid can be controlled to provide a product with acid pH, which is useful to neutralise alkaline soils such as those found in the Western United States of America (Edwin *et al.*, 1996).

In a study with biosolids (two from the same treatment plant) that had been processed three different ways; limed-undigested, limed-digested, and limed-compost. This allowed a comparison of the role treatment process on lime and metal movement. Slaked lime ($Ca(OH)_2$) was used during wastewater treatment for these materials. The $CaCO_3$ (CCE) equivalent of the limed raw and limed digested material was 40 %. The composted material had a CCE of 10 and 12%. At the 224 tons ha^{-1} loading rate, the limed –undigested and limed digested biosolids added the equivalent of 90 tons ha^{-1} $CaCO_3$. The composted biosolids added the equivalent of 25 tons ha^{-1} $CaCO_3$. Biosolid treatment processes may indirectly affect the acid neutralization potential of the biosolids. After incorporation into soil, undigested biosolids will have the highest organic matter decomposition, as it is the least stabile of the products used. This decomposition can occur in anaerobic microsites, leading to the formation of organic acids. These acids would be capable of forming soluble complexes with the Ca added in the liming material. This type of decomposition will be more likely to occur at the high loading rates used in this study than at agronomic loading rates. The potential for this type of decomposition and complex formation would be greatest for the undigested biosolids. This suggests that the undigested, digested, and composted materials would be increasingly less effective at neutralizing subsoil acidity. Although no direct measurements of this type of complex (Ca-fluvic acid) were made, the limed-undigested and limed digested biosolids were significantly more effective in neutralizing subsoil acidity than the calcareous control and the biosolids compost. When looking at the heavy metal concentrations, Cd concentrations for the biosolid treatments were not significantly different from those for the control at any of the measured depths. Concentrations fell below detection limits for all the treatments by the 20 to 30 cm depth. Lead concentrations for the biosolids treatments were significantly higher than for the control in the A horizon and remained elevated to the 30 to 40 cm depth. Below this depth, Pb concentrations were below those of the control soil (Brown *et al.*, 1997).

There was no detectable movement of metals below the 20 to 30 cm depth for the limed-digested biosolids treatments. It is highly unlikely that the agronomic use of biosolids would result in any migration of biosolid metals from the surface horizons at sites such as these. There are several factors that may account for the observed metals movement. Generally, movement of metals is thought to increase with reduced soil pH. At lower pH levels, concentrations of free metal ions increase and coarse soil texture facilitates movement of metal ions with soil water (Dowdy and Volk, 1983; Welch and Lund, 1987; Brown *et al.*, 1997).

Leachate concentrations of Al, Fe, Mn, K, Cu, Ni, and Zn were significantly reduced by lime-stabilized bio-solids application, whereas concentrations of Ca, SO_4, Mg, Cl, F, B, and P were increased. Leachate B increased with increasing neutral coal fly ash rate. Sequential selective dissolution indicated a transformation of Co, Cr, Cu, Ni, Pb, and Zn into less labile mineral pools with weathering (Abbott *et al.*, 2001).

Organic compounds are known to form inner sphere and multidenate complexes with heavy metals. The demonstrated preference for a particular metal will depend on the nature of the organic ligand and the relative concentration of heavy metals in the biosolid-soil-system (Hendrickson and Corey, 1981; McBride, 1989; Brown *et al.*, 1997). In general, organic ligands show a relative preference for Cu>Pb> Zn>Cd.

Metal movement is expected to increase with decreased soil pH and coarser soil texture, because these factors increase the solubility of metal ions and facilitate water movement. The importance of organic matter has been discussed both in relation to the formation of complexes that prevent movement of metals (Tyler and McBride, 1982; Brown *et al*., 1997) as well as the formation of complexes that solubilize metals (as organo-metal complexes) at higher pH levels (Kuo and Baker, 1980; Brown *et al*., 1997). It is possible that the same mechanism that facilitates Ca movement may permit the movement of trace metals through the soil profile (Brown *et al*., 1997).

Methods of processing sludge substantially modify metal leachability, as with the N-Viro process increasing the potential mobility of some metals (eg. Cu, Mo, and Ni) while decreasing the mobility of others (e.g. Zn and P) (Richards *et al*., 1997; McBride, 1998) Since the N-Viro process raises the pH of the sludge product to about 12, the high leachability Cu and Ni in particular may be due to the increased dissolved concentrations of organic matter that have been shown to bring strongly complexing metals into solution (Bruemmer *et al*., 1986; Evans *et al*., 1995; McBride and Blasiak, 1979; McBride, 1998). Metals that exist as oxyanions in soils, such as Mo, As and Se, are generally more soluble and bioavailable in soils at high than at low pH (O'Neil, 1990; Jones *et al*., 1990; Neal, 1990; McBride, 1998). Although the potential for leaching of heavy metals from sludge-treated soils has generally been considered to be low (McBride, 1995; McBride, 1998), studies at field scale and in soil columns indicate that rapid leaching of some metals occurs immediately following sludge application. (Lamy *et al*., 1993; Frankel *et al*., 1997; de Haan, 1980; McBride, 1998). The leachability of metal cations is due, at least in part, to complexation with dissolved organic matter (Camobreco *et al*., 1996; McBride *et al*., 1997; Temminghoff *et al*., 1997; Gerritse *et al*., 1982; McBride, 1998).

A leaching potential test of the ameliorant SLASH was conducted by Reynolds *et al.,* (2000) and shown to be within the TCLP (Toxicity Characteristics Leaching Procedure) guidelines. The TCLP leaching of the SLASH product showed that the heavy metals of the sewage sludge are immobilized within the fly ash component and do not leach out in either of the simulated conditions. Although the two methods gave similar results, it was noted that Mn, Mo, Ni, and Zn leached more in the TCLP leachate than in the acid rain leachate, while Cu leached less. This may be as a result of the differing pHs of the leachates (Reynolds *et al.*, 2002).

A field plot study, in which a single 500 tons ha^{-1} application of N-Viro sludge was made, showed significant decreases in total Cd, Ni, Cu, and particularly Pb, in the surface soil (0-15cm) over three years (Logan *et al.*, 1997b; McBride, 1998). Other examples of apparent losses in heavy metals, from surface soils following sludge application are described in McBride *et al* (1997). However, these studies in many cases involved heavy application rates, and losses of metals may be less significant at agronomic applications (McBride, 1998). The fact remains that direct application of non-alkaline sewage sludge is likely to increase heavy metal bioavailability in soil (Sloan and Basta, 1995).

The high pH of alkaline stabilized sludges creates chemical conditions conducive to the immediate mobilization of certain trace metals, notably Cu, Ni, and Mo. Conversely, the solubility of Pb, Cd, Ag, and Zn is initially very low at pH 12. Most of the soluble Cu exists as a Cu-amino complex formed with amines or amino acids. The high solubility of Cu and Ni did not decrease when the alkaline (pH=12) water extract was exposed to air, and CO_2 lowered the pH to 8.1. The stability of metal complex raises issues of leaching potential in the field, at least to surface waters or shallow ground-water, if alkaline-stabilized sludges are spread on sloping fields without incorporation, are stockpiled in the field, or are applied at heavy rates on coarse-textured soils. In deep and fine textured soils, the soluble Cu and Ni complexes may be adsorbed and prevented from leaching, but additional research is needed to determine the fate of these potentially mobile forms of metals in soils of varying pH and texture. Practices that do not immediately mix the product with soil, delaying the neutralization of the very high pH and minimizing the potential for adsorption reaction, are most likely to cause contamination of surface water (McBride, 1998). Boron phytotoxicity is probably the greatest potential problem to crops associated with high application rates of certain unweathered fly ashes to soil (Carlson and Adriano, 1993; Schumann and Sumner, 1999).

Hence, trace element availability from fly ash/organic waste mixtures may result from either of the mixture components and interaction between the two.

Studies conducted on fly ash/sewage sludge mixtures have focused on limiting the effect of fly ash in suppressing availability of trace elements from sludge. Cadmium uptake in sudangrass (*Sorghum vulgare* L) resulting from sewage sludge application was found to be reduced in the presence of fly ash (Adriano *et al*., 1982; Jackson *et al*., 1999), while Cd, Zn, and Mn uptake in tall wheatgrass (*Agropyron elongatum* (Host) Nevski) was reduced when sewage sludge potting medium was mixed with fly ash (Wong, 1995; Jackson *et al*., 1999). The liming effect of alkaline fly ash may reduce trace cation concentrations in the soil solution of fly ash / sewage sludge mixtures. The potential for leaching of trace elements from such waste applications is probably greatest immediately after application, but even then increased trace element concentrations were so transient that significant leaching would not be expected. Similarly, plant availability would be greatest if planting occurred immediately following waste application (Jackson *et al*., 1999).

Water retention characteristics are probably a combination of additives and interactive effects of the components in products like N Viro-Soils. Both sludge organic matter and alkaline admixture materials hold large amounts of water at high suction pressures as a result of microporosity and hygroscopic reactions. The field of study showed that almost all measured soil physical properties of a physically degraded mineral soil were improved by the one-time application of 500 tons ha^{-1} N-Viro soil. This application rate is in the range used for reclamation, urban soil amendments, and as a topsoil blend (Logan, 1992; Logan and Burnham, 1992; Logan and Harrison, 1995). Measurements were made one year after application, and it is not clear how long lasting the effects will be. Short-term improvements in soil physical properties from the application of organic amendments like manures, sewage sludge, and composts have been attributed to the organic amendments themselves and to the microbial production of humic substances. As the organics degrade, the effects diminish. The physical characteristics of N-Viro Soils, when compared with their chemical characteristics, suggest that chemical rather than physical attributes are likely to limit the use of these materials as soil substitutes. While high initial pH and acid neutralizing capacity, together with high soluble salt content place limitations on the use of N-

Viro Soils as soil substitutes, there appear to be no limitations due to their physical properties, and the soil amendment study suggests that the physical properties of degraded soils can be significantly improved with high rates of application of these materials (Logan and Harrison, 1995).

Alkaline biosolids may increase soil pH and precipitate toxic Al^{3+} as nontoxic $Al(OH)_3$ or other Al minerals. Lime stabilized sewage sludge may have organic C contents up to 25 % and the ability to complex soluble Al. Similar effects have been observed following the addition of sewage sludge to acid soil (Cavallaro *et al.*, 1993; Heil and Barbarick, 1989; Hue, 1992; Little *et al.*, 1991; Sloan and Basta, 1995). While sewage sludge may complex and detoxifies Al in acid soil, there is a possibility that it may also cause Mn toxicity. Addition of organic matter to soil may create a reduced environment and increase Mn solubility (Sloan and Basta, 1995). Lime stabilized sewage sludge generally undergoes minimal decomposition before disposal and consequently contains a large amount of easily oxidized organic C. Previous regulations governing land application of sewage sludge required liming soil to pH> 6.5 before application of sewage sludge (USEPA, 1992). Therefore, direct application of sewage sludge to acid soil has not always been possible. New regulations are not based on maintenance of soil pH (USEPA, 1993), and lime stabilized sewage sludge may serve as an alternate liming material (Sloan and Basta, 1995). Alkaline biosolids were as effective as agricultural lime for remediating acid soils. Soil pH increased linearly with alkaline biosolid rate and remained relatively constant from one to six months incubation. Mineralization resulted in a small decrease in soil pH with lime stabilized sewage sludge but this effect would be less prominent under field conditions. Alkaline biosolids decreased soluble and exchangeable Al to non-toxic levels. Chemical speciation of soil solution showed that alkaline biosolids decreased toxic Al^{3+} activity well below phytotoxic levels. Large decreases in soluble and exchangeable Al in alkaline biosolid-amended soils were due to increased soil pH. Alkaline biosolids decreased soluble Mn and the potential threat of Mn toxicity in acid soils amended with biosolids. Non-alkaline biosolids increased soil pH relative to unlimed controls, but remediation of the three acid soils was not achieved. The highest rate of non-alkaline biosolid addition did not increase soil pH above 4.7. Non-alkaline biosolids decreased soluble and exchangeable Al, but these decreases were much smaller than reductions realized by using alkaline biosolids. Soluble Mn was unaffected by lime stabilized sewage sludge soil additions. Although non-alkaline biosolids did not increase Mn toxicity risk, it did not decrease the potential threat of Mn toxicity in acid soils amended with biosolids.

Alkaline biosolids can remediate many of the problems associated with strongly acid soils. Alkaline biosolids showed similar effects on soil pH and Al chemistry as agricultural lime when applied at equivalent lime rates. Land application of alkaline biosolids to acid soils will result in more agronomic benefit than land application of non-alkaline sewage sludge. Increased soil pH from application of alkaline biosolids should minimize increased heavy metal bioavailability (Sloan and Basta, 1995).

There is evidence to suggest that the surface application of limed biosolids may neutralize subsoil acidity. A field study by Tester (1990) noted an increase in soil pH to 70 cm below the tilled depth following application of limed biosolids compost.

The acidity of the acid mine spoil, as indicated by the pH of the leachates, was effectively neutralized by lime stabilized biosolid amendment throughout the duration of the study conducted by Abbott *et al*., (2001).

A comparison of the pH changes with depth across all application rates of the limed-digested biosolids indicated that the 224 and 448 tons ha^{-1} rates significantly increased soil pH to levels greater than those for the calcareous control to the 50 to 60 cm depth. Results from this experiment suggest that the application of high rates of lime-stabilized biosolids is an effective means to correct subsoil activity. The effectiveness of limed stabilized biosolids may be related to a proposed mechanism involving the formation of fulvic acid-Ca complexes, which was previously discussed (Sposito *et al*., 1978; Tan *et al*., 1985; Brown *et al*., 1997).

The complexes formed with fulvic acids from the biosolids, which enhance movement of Ca as, previously discussed, are hydrophilic. The associated water molecules enhance movement of the complexes through the soil profile without being adsorbed onto colloid surfaces (DeConnick, 1980; Sposito *et al*., 1978; van der Watt *et al*., 1991; Brown *et al*., 1997). These processes occur at low soil pH.. It is not clear if the processes would be similar at elevated soil pH, and/or if the increase in soil pH might be associated with an increased rate of complexation. As these complexes are oxidized, Ca is able to increase the base status of the soil. Oxidation of the fulvic acids can also result in an increase in soil pH. Several factors have been proposed to explain the extent of metal movement through the profile of biosolids-amended soils. These include soil pH, soil texture, pores size, and organic matter content (Dowdy and Volk, 1983; Welch and Lund, 1987; Brown *et al*., 1997).

Phosphorus concentrations in plant foliage were often reduced by fly ash applications (Elseewi *et al*., 1980; Molliner and Street, 1982; Schumann and Sumner, 1999). These effects were attributed to an increase in soil pH by the ash and the formation of insoluble complexes (Gray and Schwab, 1993; Schumann and Sumner, 1999). Comparatively few studies have examined the prospects of crop fertilisation using mixtures. Preparation of mixtures has also usually proceeded by trial and error (factorial studies), whereas the formulation and use of complex waste products could be greatly enhanced by improved prediction of nutrient supplies from components before they are combined. (Schumann and Sumner, 1999). The contribution of fly ashes to maize nutrition in two pot experiments conducted by Schumann and Sumner (1999) was minimal, mainly because the major nutrients P and K, which are not readily available from fly ash and which were most urgently required in these soils. Soil P and Mg deficiencies were even exacerbated by fly ash applications, due to precipitation of P and cation imbalances caused from excess Ca compounds. About 50 % of these fly ashes also produced visible B phytotoxicity in maize, at application rates of 80 tons of fly ash ha^{-1}. Sewage sludge mixtures moderated some of the adverse effects of fly ashes on maize growth, but only poultry mixtures were able to match the maize growth achieved with fertilisation. It should be possible to further exploit these positive interactions by formulating fly ash-sewage sludge- poultry manure triple mixtures. Dewatered sewage biosolids are particularly K-deficient, while animal manures are a good source of this macronutrient. Responsible land application of fly ash and biosolid wastes requires a predictive procedure that permits the formulation of mixtures and rates to match nutrient requirements of soils and crops (Schumann and Sumner, 1999).

The extreme variability measured in these waste materials in terms of total nutrient concentrations, extractable nutrients, and relative nutrient balance agreed well with other studies, and reinforced the urgent need to characterize waste materials before mixing and use in crop fertilisation. The potential pitfalls of indiscriminate waste application to soil include (I) potential phytotoxicity from micronutrient excesses (especially B); (ii) shortages of essential major nutrients such as N, P, and K due to low supply; (iii) nutrient deficiencies caused by unfavourable fly ash pH, slow nutrient release, and fixation of other nutrients such as P already present in the soil solution; and (iv) induced nutrient deficiencies from the supply of elements in incorrect proportions. Most of these problems can be overcome by exploiting the complementary nature of fly ash, sewage sludge, and poultry manure, and additional nutritional benefits (especially N-P-K balancing) should be possible by mixing these three waste materials together (Schumann and Sumner, 2000).

Mixing of organic waste products such as sewage sludge or poultry litter with fly ash has been proposed to increase the macronutrient content of the resulting mixture while reducing odor and improving handling properties of the organic waste (Garau *et al.*, 1991; Vincini *et al.*, 1994; Schumann, 1997; Jackson and Miller, 2000). Field trials utilizing fly ash/ organic waste mixtures as fertilisers for maize (*Zea mays* L.) produced comparable yields to conventional fertilisation techniques (Schuman, 1997). However, while trace element availability from land application of fly ash is well documented (Adriano *et al.*, 1980; El Mogazi *et al.*, 1988; Carlson and Adriano, 1993), few studies have focussed on trace element availability from fly ash/ organic waste mixtures (Jackson and Miller, 2000).

At the present time, land application of poultry litter and sewage sludge are more common practices than land application of fly ash. Land application of animal wastes is a long-standing agronomic practice and animal wastes are often exclusively used as soil amendments (Sims, 1993; Jackson and Miller, 2000). However, in recent times poultry and livestock production has become concentrated in large-scale confinement enterprises with large concentrations of animals generating large quantities of waste, which is increasingly difficult to dispose of (Eck and Stewart, 1995; Jackson and Miller, 2000). For sewage sludge, it has been estimated that more than 25% of all sludge produced in the United States is land applied (Hue, 1995, Jackson and Miller, 2000). Trace element input to soil arising from sewage sludge land application is well documented (Lake *et al.*, 1984; Jackson and Miller, 2000) and is regulated under the USEPA's 503 regulations (USEPA, 1993; Jackson and Miller, 2000)

The use of alkaline products to stabilise and deodorise sewage sludge is not a new technology and dates back to early Roman times. Subsequent researchers have shown the advantages of alkaline disinfections in the substantial reduction of the inherent pathogen count in sewage sludge (Reynolds, 1996). The production process of SLASH was based on this principle. Fly ash was supplemented with a small amount of unslaked lime and was mixed with sewage sludge. The result is an odour free, pasteurised, soil-like product, which has growth enhancing properties, trace minerals from the fly ash and organics from the sewage sludge (Reynolds and Kruger, 2000)

The use of a soil ameliorant based on sewage sludge and fly ash has, therefore, definite agricultural potential. The ameliorant also has promising liming qualities, improving the pH and maintaining it for a minimum of 18 months. Although SLASH is seen as a good source of the nutrients required for plant growth, it does not contain a full range of nutrients. It is often virtually devoid of K for example, and the need will exist for supplementary fertilisation (Truter *et al.*, 2001).

Reynolds *et al.*, (1999), Rethman *et al.*, (1999a) and Rethman *et al.*, (1999b) have reported on the manufacture and use of a soil ameliorant for a variety of crops- including corn, beans, potatoes, spinach and a flower crop such as asters. These reports highlighted the use SLASH to eliminate the potential problems with disease organisms or heavy metal pollutants, while improving soil pH, Ca, Mg and P. The growth and productivity of such test crops was improved markedly under conditions of low fertility (Rethman *et al.*, 2001).

In a study on corn conducted on a soil where low fertility prevailed, the addition of SLASH enhanced early growth. In acidic soils the yield increased with the addition of SLASH. Where beans and potatoes were used as test crops, it was abundantly clear that soil type, liming and – in the case of potatoes – level of fertlisation were all more important than the level of SLASH application. Where fertility was limiting SLASH did have a beneficial effect, although it is unclear whether this should be ascribed to a fertility effect or to the effect that it had on pH. Under the experimental conditions employed it is evident that SLASH had no negative effect on the uptake of potentially toxic elements (Rethman *et al.*, 1999a).

The pot trials that Rethman *et al* (1999a) conducted with corn, potatoes and beans determined how SLASH could be used and how biomass and soil chemical properties could be influenced by SLASH. Other matters of concern were the possibility of translocation of heavy metals to the different plant components. Soil type, rate of SLASH application and plant species were identified as being important in this regard. It was concluded that wherever fertility was limiting, SLASH had a beneficial effect (Rethman *et al.*, 1999a; Truter *et al.*, 2001). At the low application rates used in these pot trials, it was found that no heavy metals had been translocated. Subsequent trials with higher application rates (up to 30 % of soil volume) were conducted and it was concluded that rates at 30 % were too high, compared to the 5-10 % treatments (Rethman *et al.*, 2000a; Truter *et al.*, 2001).

With the exception of sewage sludge, SLASH offered greater benefits than any individual ingredients. Sewage sludge, although offering better growth, cannot, however be recommended due to the potential pathogenicity of the sludge and heavy metal content and the fact that the heavy metals are not immobilized in the sludge, as they are in SLASH (Truter *et al.*, 2001).

SLASH has also had marked beneficial effects on productivity and root development of forages for as long as two years after initial treatment (Rethman *et al.*, 2001; Truter *et al.*, 2001). While this study emphasized the potential of such soil amelioration for improved forage productivity and root development. It also resulted in considerable interest in the potential use of such waste products to revegetate and restore productivity of disturbed soils (Rethman *et al.*, 2000b; Truter *et al.*, 2001).

The South African mining industry has been the backbone of the country's economy for much of the past century. Mining has, however, had major impacts on both agricultural resources and the urban environment. Rehabilitation of such impacted soils, which are often characterized by high acidity and low fertility, requires major inputs to ensure the successful establishment and sustainability of protective and restorative vegetation. The safe use of biosolids has been made feasible by combining them with coal combustion by-products (CCB's). The resultant product SLASH has been shown to have a positive effect on the pH, Ca, Mg, and P of a moderately acid agricultural soil (Rethman and Truter, 2001) and on the production of a range of vegetable and flower crops (Rethman *et al.*, 1999b).

A conclusion drawn from a study on the growth reponses of both grasses and legumes to SLASH, within the limited range of species that were evaluated, indicated that grasses (which are dependent on N and P) respond favourably to the N in SLASH, up to the highest levels of application. This N also has the advantage of having good persistence by virtue of its "slow release" properties and/or the favourable C: N ratio created when SLASH is used. In contrast the legume response (which is usually less dependent on applied N) is more closely correlated with pH and P status of the growing medium and optimum levels were much lower than with grasses. Finally it was emphasized that SLASH did not contain a full range of plant nutrients. Even at the high rates used in trials (50 – 600 tons ha^{-1}) regular monitoring of the soil and crops should be employed as the basis for determining the need for supplementary fertilisation. If low levels (100's kg ha^{-1}) are recommended, because of the high cost of transport, it is unlikely that the product will have any meaningful effect on pH, mineral status or organic matter content of the soil (Rethman and Truter, 2001).

The rationale behind such mixed wastes is that the mixture itself is a superior soil amendment to either component alone. The use of an organic waste addresses the deficiency of macronutrients in fly ash, while fly ash can act as a bulking agent for the organic wastes, substantially reduces odor and can offset soil acidity problems that may arise through continued land application of organic wastes. Although many studies have reported on the availability of trace elements arising through land application of fly ash, little work has been conducted on the potential changes in availability of trace elements that may occur through the application of mixed wastes. Sewage sludges applied to agricultural lands can be a source of trace elements upon land application (Lake *et al.*, 1984; Jackson *et al.*, 1999).

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.... In the light of the foregoing comprehensive literature review on the use of fly ash, biosolids and alkaline-biosolid mixtures as soil amendments, the agricultural SLASH programme was undertaken. This study entailed the monitoring and measurement of

- biomass production of ornamental sunflowers ,various grasses, legumes, forage- and grain crops in response to different treatments.
- multiple (intensive) cropping of treated soils
- root development.
- soil chemical properties.
- heavy metal and micro-nutrient levels.

to determine the

- optimal SLASH application rates
- long term residual effect of SLASH
- growth response of the various plant species to the waste products and the mixture (SLASH)
- tolerances and sensitivities to waste products and the mixture (SLASH).

The abovementioned research studies will be described and discussed in the following chapters.

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