Experimental improvement of flyash as a growth medium for plants through addition of selected solid wastes

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Preface:

The experimental work described in this thesis was carried out under the supervision of Dr. M. V. Fey of the Department of Geological Sciences, University of Cape Town from August to November 1996.

These studies represent original work by the author and have not been submitted for degree purposes to another University. Where use was made of the work of others, it has been acknowledged in the text.

Signed by candidate

Signature removed

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Abstract

Large quantities of coal are consumed in South Africa as a result of the generation of electricity and the manufacture of automotive fuel. A consequence of this was the production of more than 15 Mt of ash and associated coal combustion by-products in 1987 alone. This poses a large scale waste-disposal problem. Flyash, the major waste product is from South African coal sources, an alkaline, saline material the pozzolanic nature of which results in the formation of massive, compacted and cemented ash deposits which have significant environmental impacts. Efforts made to limit this impact by revegetation, in many locations throughout the world, have had limited success due to the mobility of phytotoxic concentrations of some elements, including As, B, Cr, Cu, Mo, Ni, S and Se. Flyash also has limited quantities of bioavailable Fe, Mn, P and Zn and these elemental limitations are associated with the alkaline nature of the flyash. Another element that is deficient, is N, it is unavailable in flyash as it is lost from coal during combustion. Aside from the chemical limitations to plant growth, the compacted nature results in low porosity which can limit plant available moisture. Plant root penetration is also impeded which limits nutrient uptake.

The basis of this study was to incorporate other selected waste materials into the flyash to produce, by co-disposal, a combined waste material that is geochemically inert and a satisfactory plant growth medium.

The ameliorants selected for inclusion in this study included interphase sulphur, a V-contaminated waste sulphur product from the sulphur recovery plant at the SASOL's Secunda petrochemical production facility and Catpoly, a spent catalyst consisting of phosphoric acid-impregnated diatomaceous earth, also obtained from SASOL's Secunda operation.

A beneficiated waste product, composted sewage sludge, produced by the Kynoch Fertiliser Company in Cape Town, was also utilised as an ameliorant and it was expected to contribute plant nutrients and improve soil physical properties. The final ameliorant was a nutrient *solution* introduced to provide required plant growth nutrients, including N, P, K and Mg, that might be absent or reduced in the other combined ameliorants.

Analyses of the ameliorants was carried out to ascertain the properties of the raw materials to be used in this study and to determine the proportions of the different ameliorants that should be used in the different combinations. The pH values of aqueous extracts of combinations of ameliorants produced by combining amended flyash and deionised water in a 2.5:1 ratio. The Ph values obtained ranged between 6.14, for a combination of Catpoly/sewage sludge/fertiliser treatment, to 9.08 for the unamended flyash. Variations in the EC values ranged from 0.961 $mScm^{-1}$ for unamended flyash to 3.44 $Mscm^{-1}$ for a sewage sludge/sulphuric acid/fertiliser treatment, where sulphuric acid was used as a proxy for elemental S. Alkalinity varied significantly, with the Catpoly treatment having the highest value of 3.962 mmol l^{-1} $CaCO_3$ (equivalent) while the lowest value occurred for the sulphuric acid treatment at 1.921 $mmol^{-1}$ $CaCO_3$ (equivalent). The flyash, sewage sludge and Catpoly were analysed by XRFS, which showed that while the highest values for most elements are contained in flyash, the Catpoly contains 53% P_2O_5 and composted sewage sludge contains the highest concentrations of Cu, Cl, Mn, Pb, S, Se and Zn, when compared with flyash, and Catpoly. The leachable fraction of elements from flyash was determined from a nitric acid leach. It was revealed that the levels of available As, Se, Mo and Hg were below detection limits and that Pb, Cr, Ni, Zn, Cu, V, Mn, B and Fe showed substantial level of availability, among these potentially toxic elements.

Lead was found to have the lowest value and increasing to the highest value for Fe, through the elements in the order listed. Analysis of major elements required for plant growth revealed that sulphuric acid treatments produced elevated Ca and SO_4^{2-} concentrations. Catpoly treatments resulted in reduced Na and K concentrations but significantly increased PO_4^{3-} and increased HCO_3^-. Measurable concentrations of NO_3^- only occurred in treatments containing fertiliser or sewage sludge plus fertiliser and NH_4^+ only as a result of Catpoly/fertiliser treatments.

Certain physical properties of the growth media were examined and it was found that the moisture holding capacity reduces with repeated wetting/drying cycles but is increased by the addition of composted sewage sludge to the flyash.

A plant growth trial was performed, using ryegrass planted on the different ameliorant combinations, and it was determined that the best growth response was achieved through the combination of fertiliser and composted sewage sludge. This result was consistent with elemental analyses conducted on plant tissue which revealed that the sewage sludge treatment, when used in combination with fertiliser, corrected a Zn deficiency from 1 to 26 mg kg^{-1} dry matter, in the flyash only treatment, and that the fertiliser supplied plant available N as indicated by analysis of the media. Most of the treatments, with the exception of the treatments containing composted sewage sludge plus fertiliser, composted sewage sludge plus sulphuric acid plus fertiliser and the composted sewage sludge only treatment, resulted in levels of plant assimilated B that could produce B toxicity with foliar B concentrations ranging from 422 to 1777 mg kg^{-1} dry matter. Examination of the leaf tips at the earliest stages of growth revealed necrotic zones consistent with B toxicity.

Interactions occurred between ameliorant effects. The combination of composted sewage sludge and fertiliser was found to suppress B and Mo concentrations in plant material and increased plant Zn and P. The interaction between fertiliser and acidic ameliorants resulted in a reduction in the elevated foliar B produced by fertiliser treatments alone. The case of Mo was different, since sewage sludge or Catpoly combined with fertiliser served to reduce plant Mo concentrations, while fertiliser and sulphuric acid treatments increased the Mo content. To increase plant concentrations of Zn, sewage sludge together with either an acidic ameliorant or fertiliser were required to maximise the uptake of Zn by ryegrass. In general, all of the treatments produced sufficiently foliar concentrations of K, P, Mg, Ca, Na and Fe for plant growth without reaching excessive levels.

The limits imposed on plant growth were therefore associated with three identifiable effects: the B and Mo concentration in plant material were consistent with those known to be toxic in most of the treatments; the concentration of plant Zn in over half of the treatments was sufficiently low to be deficient; and salinity induced by treatment of flyash with sulphuric acid was also sufficient to be a further probable cause of reduced growth.

During the growth trial, sulphuric acid was used as a proxy for the elemental S provided as a waste material due to the slow oxidation rate of elemental S. A separate study was instituted to investigate the rate of S oxidation at two rates: 6000 and 12 000 mg S kg^{-1} flyash. The study also considered the effect that sewage sludge had on the rate of S oxidation. It was found that sewage sludge improved the rate of S oxidation but at the maximum S application rate the oxidation was limited.

The oxidation of elemental S reduced the pH from 8.92, in the case of the unamended flyash, to 7.23 in the case of the 12 000 mg S kg^{-1} application rate combined with composted sewage sludge.

This investigation has shown that it is possible to create improved plant growth conditions by ameliorating flyash, but selection of ameliorants influences the effect on plant growth. Relative to dry matter yields produced in unamended flyash, the combination of composted sewage sludge and fertiliser produces a strong positive growth response. The use of acidic ameliorants, such as Catpoly or elemental S generally result in a negative response. The combination of composted sewage sludge plus fertiliser results in flyash with improved chemical and physical properties making it more suitable for use as a plant growth medium.

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Flyash - an introduction

The generation of electricity has resulted in the production of large volumes of coal combustion by-products world-wide (Vance, 1996; Dzeletovic and Filipovic, 1994; Carlson and Adriano, 1993; Mattigod *et al.*, 1990; Sharma *et al.*, 1989; Phung *et al.*, 1979). These products can be divided into a number of different categories with the most important being, in a South African setting, flyash and bottom ash. Flyash is of a uniform grain size and is collected from the flue gas stream by electrostatic precipitators while bottom ash is the coarser grained ash that remains in the boilers (Carlson and Adriano, 1993).

It is predicted that, by the turn of the century, more than 120 Mt of flyash will be produced by the US alone (USEPA, 1988 cited in Carlson and Adriano, 1993). In South Africa, Orren *et al.* (1987) reported that 14 Mt of flyash and 1.5 Mt of associated bottom ash was produced in 1987. Generally speaking, only about 20% of ash is used in agriculture and industry (Carlson and Adriano, 1993), which leaves a large scale waste disposal problem for the remaining ash. Most flyash is stored in ash dams, having arrived as a slurry from the electrostatic precipitators. The ash is then allowed to settle. The environmental impact of these ash dams may be divided into three distinct categories: aesthetic, physical and chemical.

The aesthetic impact in South Africa results from the fact that large, unvegetated ash dams are often poorly concealed within the surrounding countryside (Engelbrecht, 1987). The physical impacts of ash dams on the environment are twofold: firstly, large unvegetated structures disrupt the airstream resulting in the creation of dustclouds which intrude onto the surrounding countryside (Engelbrecht, 1987); and secondly, ash dams occupy large areas of land which is no longer available for agricultural production or as a wildlife habitat. The chemical impacts of South African ash dams can be divided into three categories: salinity effects, toxic elemental concentrations and alkalinity effects. Leachate from ash dams can contribute elevated concentrations of potentially toxic elements which are mobilised under the chemical conditions prevailing in the flyash and which migrate into ground and surface waters (Carlson and Adriano, 1993; Mattigod *et al.*, 1990; Sharma *et al.*, 1989; Phung *et al.* 1979; Orren *et al.*, 1987). The most straightforward approach to reducing the environmental impact of ash dams is to revegetate them. This strategy transforms the barren, unappealing dump and reduces its aesthetic impact on the landscape. Another advantage of revegetation is that of dust control (Engelbrecht, 1987), since plant cover will tend to prevent the entrainment of dust by airstreams.

The chemical and physical attributes of flyash are generally not conducive to the growth of plants, however, and the objectives of this dissertation are therefore:

i) To review the literature on flyash properties and their influence on plant growth; and

ii) To investigate, by means of short term laboratory and controlled environment plant growth experiments, the opportunities for co-disposal of certain solid waste products with flyash as a possible means of enhancing the revegetation of flyash dams.

Chapter 1: Flyash properties and their influence on the growth of plants - a literature review

1.1 Introduction

Any soil is a complex system that is capable, to varying degrees, of adsorption, exchange, adhesion, swelling, shrinkage, flocculatity and capillarity (Hillel, 1982). To be of value as a soil material, flyash must contain sufficient major and trace elements in a bioavailable form to provide plants with their growth requirements. However, the concentration of elements should not be so high as to cause phytotoxicity. The soil must contain enough water to enable the plants to meet their metabolic requirements after evaporative losses have occurred. It must also act as a thermal buffer to minimise the impact which temperature changes in the atmosphere may have on plants growing in the soil. The soil solution must be of a low enough concentration that plants do not experience osmotic stresses and pH conditions must be within the range that plants can tolerate. Soil structure must allow the penetration of roots for access to nutrients and water and must also provide structural stability for the plant. A soil must also represent a suitable habitat for decomposer organisms since their presence is vital to enable nutrient cycling to operate effectively (Wild, 1993). As long as flyash can meet these criteria, it will be practical to utilise it as a soil. If these conditions are not met, it may be possible to alter its properties by the addition of an appropriate ameliorant (Hodgson and Buckley, 1975).

1.2 Chemical and physical properties of flyash

1.2.1 Factors contributing to the alkalinity of flyash

The pH values obtained from aqueous solutions of flyash in equilibrium with water vary significantly. Sharma *et al.* (1989) noted that the pH of flyash suspensions depends on the concentration of soluble salts present in the flyash, the coal source from which the flyash was derived, the lagooning process that the flyash has been subjected to and the weathering stage that the flyash has attained.

The effect of salts can be explained by the conversion of carbonate salts, such as calcite and magnesite, to oxides during the combustion of coal (Townsend and Gillham, 1975; De Groot *et al.*, 1989 cited in van der Hoek *et al.*, 1994). During the transport and lagooning process these oxides hydrolyse, resulting in an increase in pH (Sharma *et al.*, 1989). As the flyash dries the hydroxides in the flyash react with atmospheric CO_2 resulting in a reduction in pH (Townsend and Gillham, 1975; Rippon and Wood, 1975; Howard *et al.*, 1977; Warren and Dudas, 1992).

Carlson and Adriano (1993) note that coals with a low S content result in the formation of flyashes with alkaline pH values. Generally, fresh, alkaline flyashes have a pH greater than 11 (Petruzzelli *et al.*,1986; Shukla and Mishra, 1986; Townsend and Gillham, 1975; Maree, 1987), stabilising to approximately 8 as a consequence of weathering (Townsend and Gillham, 1975).

South African flyash data of relevance to this project have been published by Maree (1987), Wyrley-Birch *et al.* (1987) and Orren *et al.* (1987), who report pH values of about 12 for aqueous suspensions of South African-derived flyash.

Because the degree of water saturation that the flyash has experienced (Carlson and Adriano, 1991) influences the proportion of ionic species remaining in the flyash, the lagooning process affects the pH. This effect is coupled with weathering processes because soluble salts may go into solution during the lagooning process and be removed from the flyash as the solution drains from the dam. As time passes, this effect continues to operate, with meteoric water continuing to leach mobile species from the ash (Scanlon and Duggan, 1979).

1.2.2 Elemental composition and mineralogy

Carlson and Adriano (1993) describe flyash as a complex heterogenous material. It is generally considered to be a ferro-aluminosilicate consisting predominantly of the elements Al, Si, Fe, Ca with lesser amounts of K and Na (Sharma *et al.*, 1989). All of the remaining naturally occurring elements are also present in flyash (Sharma *et al.*, 1989; Carlson and Adriano, 1993) but occur in minor quantities, with the trace elements being preferentially concentrated on smaller particles (Phung *et al.*, 1979, Sharma *et al.*, 1989, Carlson and Adriano, 1993). Mattigod *et al.* (1990) reported that K, Na, Mg and S are enriched in flyash compared to their concentrations in soil while Connor and Shacklette (1975, cited in Phung *et al.*, 1979) observed a similar situation for B, Pb, Co, Cr, Ni, Cd, Mo, Se and As concentrations.

A consequence of this is that plants grown on flyash may develop toxicity symptoms if the pH renders the elements chemically mobile and bioavailable (Phung *et al.*, 1979; Carlson and Adriano, 1993).

The silicate phase in unweathered flyash consists of glass, quartz and mullite ($Al_6Si_2O_{13}$), each present in similar proportions. Hematite (Fe_2O_3), magnetite (Fe_3O_4) and spinel ($MgAl_2O_4$) form the Fe phases, while the Ca phases are represented by anhydrite ($CaSO_4$) and lime (CaO) and the dominant Mg phase is periclase (MgO). Weathering results in the production of secondary minerals such as gypsum ($CaSO_4.2H_2O$), portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$) (Mattigod *et al.*, 1990; Willis, 1987; Lesch and Cornell, 1987; Bosch, 1990).

1.2.3 Mobility and bioavailability of elements in flyash

Flyash particles are predominantly spherical due to their having formed at high temperatures in the flue gas stream. Fine (<53 μm) spherical particles tend to sorb more of the heavy metals, due to their high surface area (with the exception of Pb, Cd and Co) than the >150μm fraction (Sharma *et al.*, 1989). The smallest particles (<2 μm) have the highest concentrations of potentially toxic trace elements such as: Cr, Cd, Pb, Ni, Se and As (Natusch *et al.*, 1974). Heavy metals attached to the surface of flyash particles may be more readily leached than the major elements structurally bound within particles (Sharma *et al.*, 1989).

The major controlling influence over elemental mobility in flyash solutions is pH. The high pH values attained in alkaline flyash result in enhanced mobility of B, Ba, As, Cr, Cu, Ni, Se and Zn, but Cd, Fe, Pb, Mn and Hg are rendered immobile (Sharma *et al.*, 1989).

A factor that also affects elemental mobility is the solubility of major elements (Mattigod *et al.*, 1990), which controls the mobility of many trace elements due to sorption and precipitation-dissolution mechanisms. For example, van der Hoek *et al.* (1994) report that the mobility of As and Se is related to the solubility of Ca minerals such as portlandite. In summary, virtually all of the elements will be retained by an ash dam but the exceptions are significant: S, As and possibly Cr, B, Se, and V. This necessitates additional leachate treatment to prevent these elements gaining access to surface and groundwaters (Sharma *et al.*, 1989; van der Hoek *et al.*, 1994).

While the composition of flyash suggests that it should provide most of the elements required for plant growth, with N being the only species obviously deficient (Sajwan, 1995; Sharma *et al.*, 1989), the prevailing pH results in many elements being rendered immobile. Gray and Schwab (1993) also noted that P can be made unavailable to plants by the precipitation of large amounts of P as calcium phosphate to the extent that more than 1000 kg P ha^{-1} added as fertiliser may be required to provide enough P to support plant growth.

Manganese mobility is also affected and Mn deficiency symptoms may occur (Carlson and Adriano, 1991). Because B, Ba, As, Cr, Cu, Ni, Mo and Se are rendered more mobile under alkaline conditions (Sharma *et al.*, 1989) they are also more bioavailable, which could be beneficial in cases where these elements are nutrients required for plant growth. Carlson and Adriano (1993) reported that high pH values present in flyash reduced the availability of Cu, Fe, Mn and Zn to plants while As, Se and V tended to be accumulated by plants. It is evident that in flyash, a problem arises with the narrow window that exists between deficiency and toxicity.

B toxicity commonly occurs in plants grown on flyash or flyash solutions (Bradshaw and Chadwick, 1980, cited in Carlson and Adriano, 1993; Maree, 1987; Shukla and Mishra, 1986). A similar effect was obtained by Shukla and Mishra (1986) who also noted elevated concentrations of B, Cu, Mn and Zn in plants grown hydroponically in flyash solutions. These concentrations inhibited germination in seeds and reduced plant growth rates. In some of the plants the concentrations were high enough to induce lethal effects, the incidence of which depended on the concentration of the solution and the period over which the plant was in contact with the solution.

Alkaline conditions can also result in deficiencies in essential trace elements such as Cu, Fe, Mn and Zn (Carlson and Adriano, 1993). A deficiency in Cu may result from elevated Mo concentrations which inhibit Cu uptake by plants, a condition known as molybdenosis (Davies *et al.*, 1971, cited in Sharma *et al.* 1989; Olsen, 1972, cited in Kabata-Pendias and Pendias, 1984).

Petruzzelli *et al.* (1986) observed a reduction in the concentration of plant-assimilated Cu, Cr and Zn during a study of wheat grown in flyash amended soils and found that the soil type and the organic matter content of the soil affected the extent to which metals were taken up by plants. Petruzzelli *et al.* (1986) also reported that heavy metals were segregated between the roots of plants and their foliage where soil concentrations forced plants to assimilate more of an element than required. The excess remained stored in the roots while foliage concentrations were not elevated. A consequence of this is that while plants are forced to take metals up from the soil, any animals browsing or grazing on their foliage need not necessarily be affected by the high concentrations of metals in the soils.

1.2.4 Texture and structure

Flyash occurs as approximately 70% silt or fine sand-sized particles (Townsend and Gillham, 1975) and its chemical nature imparts to it another quality: pozzolanic activity (Townsend and Gillham, 1975; Mattigod *et al.*, 1990; Carlson and Adriano, 1993). A pozzolanic material is one that reacts at ordinary temperatures to form stable cementitious compounds (Mattigod *et al.*, 1990). The combination of these two qualities results in a very fine grained material (Sharma *et al.*, 1989) with a tendency to become cemented and compacted (Carlson and Adriano, 1993; Townsend and Gillham, 1975). This often reduces the permeability of flyash, limiting the access of water to the subsurface (Sharma *et al.*, 1989) and making it difficult for root development to occur. This results in an adverse environment for plant root penetration (Hodgson and Buckley, 1975; Engelbrecht, 1987; Carlson and Adriano, 1993) which can result in the loss of plant cover due to erosion on steep surfaces where the vegetation layer slides off in heavy rains (Engelbrecht, 1987). Carlson and Adriano (1993) commented that the surface of a flyash dam will generally be compacted as a consequence of sedimentation from suspension, limiting subsequent access of meteoric water once the dam has drained.

1.2.5 Availability of water to plants

The properties of flyash control the availability of water, to plants using flyash as a growth medium, in a number of ways. Because flyash may have a high concentration of soluble salts, the osmotic potential can increase to a point where plants are unable to abstract water (Carlson and Adriano, 1991).

Many workers have utilised flyash as a soil ameliorant and the effect of flyash on the availability of water to plants has been most studied in this context. Carlson and Adriano (1993) noted that sandy soils amended with flyash showed an improvement in water holding capacity and Sharma *et al.* (1989) found that, at low flyash concentrations, the water holding capacity of soils was improved due to the silt-like qualities of flyash. At higher concentrations of flyash, however, its pozzolanic properties resulted in soil grains being cemented, impeding water passage. Chang *et al.* (1977, cited in Carlson and Adriano, 1993) also observed that the pozzolanic nature of flyash caused silt to become cemented, which resulted in reduced permeability. The increase in water holding capacity imparted by the flyash did not result in observed increases in plant growth, since this extra water is so tightly held as to be unavailable to plants (Chang *et al.*, 1977, cited in Carlson and Adriano, 1993).

Plank *et al.* (1975, cited in Carlson and Adriano 1993) showed an improvement in plant available moisture due to flyash but this was offset by phytotoxic effects. Maree (1987) commented that the reduction in hydraulic conductivity after addition of flyash may almost completely prevent drainage. This has an equally detrimental effect on plant growth as a result of waterlogging.

1.3 The effects of flyash on the growth of plants

1.3.1 Seed germination

The establishment of plants directly onto flyash-amended material is not always successful. Toxic effects may result in a delayed germination response in seeds.

In addition, a significantly higher mortality rate has been found in seedlings which have germinated in unamended soil treated with flyash extract Shukla and Mishra, (1986). Scanlon and Duggan (1979) found that plants survived better on flyash where it had been amended with either compost or soil. Mulhern *et al.* (1989, cited in Carlson and Adriano, 1993) explained the mortality of plants on an ash dam in terms of poor moisture retention, elevated temperature of the ash and the presence of a compacted layer 6-10 cm below the surface.

1.3.2 Factors limiting plant growth directly on ash dams

The limiting factors governing the establishment of vegetation on ash disposal sites are:
the lack of N and available P in the ash; toxicity due to high salinity, pH and concentrations of phytotoxic trace elements; and to the impervious, compacted or cemented layer that often occurs 6-10 cm below the surface (Carlson and Adriano, 1993).

Scanlon and Duggan (1979) utilised eight woody plant species to assess plant growth in flyash. After three growing seasons approximately half of the trees were still living. The conclusions from this study were that different plant species are capable of growing in different conditions and before vegetation can be utilised to revegetate an ash dam, an investigation should be undertaken to determine the suitability of the species involved. Carlson and Adriano (1991) undertook a similar study, but investigated trees that had been self sown on to an ash dam that had been abandoned 20 years prior to the study. Like Scanlon and Duggan (1979), they concluded that careful selection of species must be made, based on local conditions, prior to planting. In weathered flyash, elemental deficiencies are less likely to occur.

This is partly due to the fact that although fresh flyash is sterile, it acquires a bacterial population from lagooning waters and the atmosphere during weathering which promotes the onset of N fixation in the flyash (Rippon and Wood, 1975). Weathering involves reactions with atmospheric CO_2 so that neutralisation of the extreme alkalinity present in fresh flyash can occur (Carlson and Adriano, 1993). This reduction in alkalinity can increase the availability of some elements, especially P which, if present as a Ca phosphate solid phase, will become more soluble as pH decreases (Wild, 1988).

The poor draining characteristics of flyash can result in anaerobic conditions in the flyash (Maree, 1987). When combined with the reduction in alkalinity, this can result in an increase in the available Mn through reduction of unavailable Mn species (Davies and Jones, 1988).

Elemental uptake in plants grown on flyash directly or in soils amended with flyash shows some consistent trends, but also some variability, which appears to be due to variation in the composition of the flyash. Townsend and Gillham (1975) reported elevated foliar B levels which may persist for long periods, producing toxicity symptoms. Orren *et al.* (1987) encountered B toxicity in lettuce plants grown hydroponically in flyash extract. Adriano *et al.* (1980, cited in Sharma *et al.*, 1989) and Carlson and Adriano (1993) list a number of elements including B, Mo, As, Se, Cu, Zn, Co, Cr, Ni and Pb that are concentrated in plant material grown on flyash relative to unaffected plant material. Adriano *et al.* (1980) extend their list of elements that tend to be concentrated to include S, Cl, Al, Ba, Cs, Rb, Sr, V, W, Fe, Mn, P, K, Ca, Mg, F, Na and Sb. The degree to which some of these elements are concentrated, however, may be inconsistent between experiments, which may be related to variations in the flyash, as reported for Mn by Carlson and Adriano (1993).

1.4 Amelioration of flyash for plant growth

It has been mentioned previously that extreme values of pH, a lack of available nutrients and toxicity of certain elements are some of the prime factors limiting the revegetation of flyash dumps. Two ameliorants which are relevant to SASOL's Secunda operation are: elemental S, produced as a by-product of the sulphur recovery process requiring safe disposal in view of its potentially hazardous impurities, and sewage sludge, which again may require careful disposal in view of its metal content. The remainder of this review will briefly examine, the literature relevant to the possible amelioration of flyash with these materials.

1.4.1 Oxidation of elemental sulphur

Previous work has involved the use of elemental S to acidify alkaline, calcareous soils through bacterial oxidation of the S (Bole, 1986; Modaihsh *et al.*, 1989; Neilsen *et al.*, 1993; Cifuentes and Lindemann, 1993). The composition, mineralogy and pH of the weathered flyash makes it comparable with the calcareous soils and extrapolation of the findings to flyash-plant systems would seem to be justified.

Oxidation of S in soils by microorganisms occurs due to the presence of bacteria (Cowell and Schoenau, 1995), yeasts (Falih and Wainwright, 1995), fungi (Cifuentes and Lindemann, 1993) and actinomycetes (Wainwright *et al.*, 1984, cited in Cifuentes and Lindemann 1993). Chemolithotrophic sulphur bacteria are specially adapted to oxidise S, but different strains of these have different substrate requirements.

Autotrophic bacteria are able to utilise atmospheric CO_2 as a C source and oxidise the S during carbohydrate metabolism, while heterotrophic bacteria require organic C for their carbohydrate metabolism (Tisdale *et al.*, 1985).

Neilsen *et al.* (1992) noted a correlation between the extent of S-induced pH reduction and soil texture. As a consequence of their physiology, autotrophic bacteria will oxidise S less effectively in a compacted and cemented flyash dam where the air space is reduced by the fine particle size, high water potential (Janzen and Brettany, 1987b) and the impeded water passage (Chang *et al.*, 1977, cited in Carlson and Adriano, 1993).

Oxidation of S by heterotrophic bacteria is likely to be enhanced by the addition of organic matter (Cifuentes and Lindemann, 1993; Cowell and Schoenau, 1995; Tyagi *et al.*, 1994) but may still be limited by the fine grain size and pozzolanic nature of flyash if this allows the system to become anaerobic (Maree, 1987).

While there are many species of sulphur oxidising bacteria with different ranges of optimal efficiency for the oxidation of S, the most rapid oxidation of S occurs in acidic conditions (Tisdale *et al.*, 1985). Despite this, oxidation will still occur at pH values of 8.4, which is representative of the pH of a leached flyash dam (Carlson and Adriano, 1991). Two different bacteria would tend to be involved in the oxidation process. An important S oxidising species is *Thiobacillus thiooxidans,* an acidophilic bacterium with an optimum pH operating range of 3.5-4.5. The initial oxidation of S in flyash would therefore need to be initiated by a less acidophilic species such as *Thiobacillus thioparus,* which operates between pH 6-8 (Tyagi *et al.*, 1994). Janzen and Brettany (1986) note that the oxidation of elemental S depends on the degree of dispersion of S through the soil and on the degree to which the S is divided.

In the more finely divided particles, the surface to volume ratio is maximised and more bacteria can gain access to the S. Dispersion is important as S is hydrophobic and tends to agglutinate into larger grains within which bacteria cannot proliferate. To maximise the rate of reaction, large grains must be dispersed.

The oxidation of S is a self-limiting process because when the rate of oxidation is high, the acidity produced causes pH to become rate-limiting, irrespective of the amount of S still available (Cowell and Schoenau 1995, Chapman, 1989). As the acid produced reacts with alkalinity present in the growth medium the pH increases and oxidation may proceed again (Cifuentes and Lindemann, 1993). The rate of removal of acidity by reaction with alkaline mineral phases present in the flyash, therefore is likely to place a limit on the maximum rate at which S oxidation may occur.

1.4.2 Sewage sludge

The addition of composted material such as composted sewage sludge can improve soil in several ways. Sewage sludge adds nutrients to the soil and increases soil organic matter content

(Joost *et al.*, 1987). The increase in organic matter provides an energy source for bacteria so that nutrient cycling can accelerate (Carlson and Adriano, 1993). Another effect of the addition of sewage sludge is an increase in water holding capacity (Joost *et al.*, 1987; Seaker and Sopper, 1988; Kriesel *et al.*, 1994). Sewage sludge is a slightly acidic waste material (Joost *et al.*, 1987; Sajwan *et al.*, 1995) and its addition may therefore reduce the pH of some soils. Sewage sludge amended soils have an improved capacity to act as a thermal buffer and these soils are also less susceptible to erosion (Seaker and Sopper, 1988).

As the sewage sludge decomposes, some decomposition products leach into the underlying material which promotes soil formation and further enhances soil structure and soil fertility (Joost *et al.*, 1987).

While sewage sludge may enhance a growth medium, it also has two significant drawbacks: the first is that it contributes to soil salinity (Sajwan *et al.*, 1995). The second, and probably more important, is that it may contain elevated concentrations of a number of heavy metals and other undesirable elements such as Cd, Cr, Cu, Ni, Pb, Pd, Pt, Sb, Se, Sn, W and Zn (Berti and Jacobs, 1996; Petruzzelli *et al.*, 1989; Joost *et al.*, 1987; Sajwan *et al.*, 1995). Despite the acidic nature of sewage sludge the sorption capacity for the heavy metals is considerable, so that the bioavailable fraction is usually smaller (Berti and Jacobs, 1996; Petruzzelli *et al.*, 1989).

Seaker and Sopper (1988) found that inorganic fertiliser applied to soil produces an immediate growth response in plants but the advantage of sewage sludge is that over lengthy periods, sewage sludge amended soils retain their C and N significantly better than inorganic fertiliser amended soils and display a more gradual and more prolonged release of nutrients (Kriesel *et al.*, 1994).

Because flyash and sewage sludge each have a number of detrimental qualities that might be neutralised by combining them, a number of studies have been carried out to determine the effects of co-disposing these waste materials.

Kriesel *et al.* (1994) suggest that mixed wastes containing sewage sludge and flyash serve as nutritionally balanced soil amendments with respect to N, P and K, and that flyash can sorb soluble N and prevent it from leaching to groundwater. Cifuentes and Lindmann (1993) noted that biomass, organic amendments and soil organic C content have been related to rates of S oxidation rate and that a synergistic effect occurs between heterotrophic S oxidisers that produce thiosulphate and autotrophic thiosulphate oxidisers, resulting in a more efficient conversion of S to SO_4. Cowell and Schoenau (1995) recommended the use of elemental S with sewage sludge in flyash remediation. This is because the sludge increases the rate of oxidation of the S and this would further assist in reducing the pH of the flyash/sewage sludge sulphur mixture to near-neutrality. The benefits of combining the waste products may include a more balanced nutrient content, lower contaminant solubility, delayed availability of nutrients to plants and a less easily quantifiable characteristic: improved soil quality, through increases in moisture holding capacity and porosity (Kriesel *et al.*, 1994).

Sajwan *et al.* (1995) investigated the use of sewage sludge-flyash mixtures as a soil ameliorant. The supply of N and P from the sludge to the ash and the immobilisation of sludge-derived heavy metals by the flyash are examples of the potential benefits of such co-disposal.

1.5 Conclusions

Examination of the literature has revealed a number of physical and chemical properties that are characteristic of flyash, but which could potentially restrict plant growth. Other materials, which are often considered to be waste products, have physical and chemical properties that when combined with those of flyash, would interact and result in a combined material with properties far less detrimental to plant growth.

The flyash produced in the South African setting tends to be of an alkaline nature as a consequence of the concentrations of soluble salts present in the ash. The ionic species responsible for this alkalinity include Ca, Mg, K and Na salts and these ions produce very strongly alkaline conditions in the ash as a consequence of the hydrolysis of oxides.These oxides are produced both during coal combustion and during the weathering process that occurs once flyash has been deposited in ash dams. The pH in fresh alkaline flyash is generally greater than 11 and as a result of weathering, declines to approximately 8 with the precipitation of calcite. In some situations where sodium salts are present in the ash, the resulting pH tends to remain higher.

Because flyash often consists of approximately 70% silt or fine sand-sized particles, the structure tends to be quite massive. When this massive structure is combined with the pozzolanic nature of flyash, the resulting cemented body creates an impenetrable mass that plant roots often find difficult to gain access to. Furthermore, common engineering practice is to compact the flanks of ash dams to create a wall which can better retain the ash slurry that is pumped into the dam.

This further compounds the difficulty associated with revegetation as heavy rain can result in plant cover being flushed off steep, compacted flanks because vegetation is unable to penetrate the ash material to sufficient depth to maintain anchorage under these conditions.

Flyash consists of a complex heterogeneous ferro-aluminosilicate material containing both minerals and glass. Associated with the finest particles present in the ash are high concentrations of heavy metals and metalloid elements. These elements can be mobilised because flyash is susceptable to weathering and originally sorbed to the surface of minerals, are released when the minerals dissolve. The alkaline conditions present in the ash tend to promote the retention of some heavy metals, such as Cd, Fe, Pb, Mn and Hg, but others, such as Cr, V, Cu, Zn and Ni have an increased mobility. Also of concern is the fact that metalloids, such as As, S, Se and Mo form oxy-anions which readily mobilise so that leachate from ash dams may contribute to potential hazards further down a catchment area. Another element with both elevated concentrations in flyash, and exhibiting increased mobility when associated with sodic salt concentrations is B. Boron toxicity is a common occurrence in plants encountering flyash, either as a growth ameliorant or as a growth medium.

Flyash has sufficient concentrations of most elements required for plant growth, with the exception of N and bioavailable P. The concentration of P present in flyash is often theoretically sufficient to sustain plant growth but P can be rendered bio-unavailable by precipitation of Ca phosphate salts. One advantage of the alkaline conditions in flyash is that many of the elements present are trace elements required for plant growth and the rate at which they are mobilised in the flyash limits their availability thereby matching the plants requirement for growth.

Flyash controls the availability of water to plants in two main ways. Where plants are grown directly on flyash the concentrations of soluble salts can increase the osmotic potential of the root environment resulting in plants experiencing salt stress. The pozzolanic character of flyash can also limit water availability to plants by reducing the permeability of the growth medium.

Seeds planted in flyash may show delayed germination and often higher rates of mortality. The survival of plants grown on flyash is often species dependant at the initial stage of revegetation, but as weathering proceeds, bacterial population increases and the nutrient cycling improves so too do plant survival rates. As dissolved salts are leached, the osmotic stresses decline resulting in a less unfavourable plant environment. Despite this removal of dissolved salts through leaching, plants grown on flyash may contain elevated concentrations of B, Mo, As, Se, Cu, Zn, Co, Cr, Ni, Pb, S, Cl, Al, Ba, Cs, Rb, Sr, V, W, Fe, Mn, K, Ca, Mg, F, Na and Sb.

The combination of flyash with other solid waste products can correct some of these less desirable effects on plant growth. By combining elemental S with flyash, bacterial oxidation of the S to produce acid can be exploited to neutralise the extreme alkalinity of flyash. The rate of S oxidation is dependant on the removal of salts produced by the acid-base reactions and is limited by excessively low pH. The dispersion of S and the grain size also affect oxidation rate since oxidation rate is proportional to surface area available to bacteria to gain access to S. Because S oxidation is also dependant on soil moisture and air content, the addition of sewage sludge increases the oxidation rate by increasing both the porosity and moisture holding capacity of the flyash.

The addition of organic matter also improves flyash fertility by leaching decomposition products into underlying layers of flyash. Sewage sludge has elevated heavy metal concentrations but by combining sewage sludge with flyash, the immobilising effect of the alkalinity combined with the sorbtive nature of the organic matter limits the bioavailable proportion of these metals. This produces a growth medium that is much more suitable for plant growth because of the delayed release of nutrients to plants. Because sewage sludge provides both N and P to the flyash after amendment, the combined material will then possess a more satisfactory nutrient profile for the establishment of vegetation.

It would appear that by treating flyash with other potentially hazardous waste material, a medium suitable for the growth of plants and for the stabilisation of flyash dams can be produced. By revegetating ash dams, aesthetic improvements to the landscape, combined with geochemical and physical stabilisation of the flyash mass can be achieved and soil formation on the surface of the dam can be encouraged.

1.6 Outline of research approach

Based on this review of the literature, experimental work has been carried out to determine whether flyash could be altered to make it a more suitable growth medium for plants. In this regard the experimental work needed to answer several key questions:

1) Can the usual growth limitations imposed by flyash be overcome by combining it with selected available waste products?
2) Which treatment is the most effective?
3) Are there any interactions between combinations of ameliorants?
4) Do the ameliorants have any effect on the uptake of undesirable elements by plants?

To answer these questions, an assessment was made of a selection of ameliorants. This analysis included a chemical and physical characterisation of the ameliorants that enabled the proportions of the various ameliorants required to produce conditions that resulted in a more suitable growth medium for plants. To assess the effect of the various ameliorants, a number of treatments of the flyash including combinations of the ameliorants were placed in pots which were planted with ryegrass in an effort to determine growth responses. At the end of the plant growth trial, after determining dry matter yields for the various treatments, geochemical analyses were performed on the foliage to determine variations in elemental uptake from the various growth media.

A separate trial took place to determine the rate of oxidation of the elemental waste S, both amended with composted sewage sludge and unamended. From this S oxidation trial, the changes in pH, EC and extent of SO_4 production were also determined to examine whether S dosage and the presence of sewage sludge affected the rate of S oxidation.

As a result of this investigation it was possible to answer the key questions posed above and to determine whether co-disposal of selected solid ameliorants was able to result in production of a more satisfactory environment for the production of ryegrass.

Chapter 2 Preparation and characterisation of plant growth media based on flyash and selected conditioners

2.1 Introduction

One of the objectives of this study was to test the disposal of certain organic or acidic waste products by using them as physical and/or chemical conditioners of flyash, with the potential added advantage of ameliorating some of their adverse properties as well as those of flyash. By examining each of these waste products, an understanding may be gained as to the effect that each is likely to have on plants growing in contact with them. Furthermore, a knowledge of the chemical properties of each waste product should allow predictions to be made as to how combining them may reduce detrimental effects on plant growth in particular (Duggan and Scanlon, 1974) and the environment in general.

The flyash utilised as a growth medium in this study was provided by Sastech R & D and originated from the steam and electricity generating plants at the SASOL Sasolburg petrochemical production facility. The interphase-sulphur and the Catpoly (waste catalyst) were derived from SASOL's Secunda plant while the composted sewage sludge was provided by Kynoch Fertiliser Company and was obtained from their treatment of municipal sewage from the Milnerton Municipality.

Flyash is generally understood to limit plant growth due to a number of physical and chemical properties. These include compaction, crusting and cementation due to salinity induced dispersion effects and the pozzolanic nature of the flyash and these properties limit root penetration (Rowell, 1988b; McBride, 1994; Sharma *et al.*, 1989; Engelbrecht, 1987).

Reductions in moisture holding capacity and soil permeability occurring in flyash (Sharma *et al.*, 1989; Maree, 1987) restrict plant growth by limiting the ability of plant roots to obtain necessary moisture. The lack of organic matter in flyash limits the bacterial population development that is so essential for nutrient cycling (Klubek *et al.*, 1992).

Elevated pH can cause imbalances in nutrient availability, such as reduced N, P , Cu, Fe, Mn and Zn levels in growth media, while elevated levels of As, B, Ba, Cr, Mo, Se and V may occur. These effects may result in the development of toxicity or deficiency symptoms in plants grown in flyash or flyash amended soils (Marshner 1990; Townsend and Gillham, 1975; Adriano *et al.*, 1980 cited in Carlson and Adriano, 1993; Sajwan, 1995; Carlson and Adriano, 1993; Orren *et al.*, 1987; Shukla and Mishra, 1985; Maree, 1987). Shukla and Mishra (1985) noted that one of the major influences of flyash on plant growth was the development of osmotic stresses set up by high concentrations of salts present in the flyash. This can result in reduced germination yields for seeds either planted or self sown onto flyash dumps (Shukla and Mishra, 1985) or reduced biomass production due to production of smaller leaves to minimise transpiration losses (Shalhevet, 1993).

Because the flyash used in this study is approximately 20 years old (pers.comm. M. Ginster, 1996) and has been subjected to the leaching effects of rainwater over this time, the concentrations of many elemental species will be altered (Ghodrati *et al.*, 1995). By quantifying the chemical properties of the flyash used as a growth medium in this study, an indication could be obtained as to which other studies of a similar kind reported in the literature were comparable. This also allowed an estimation to be made of the proportion of total elemental concentrations which are bioavailable in the various media . This information is important in understanding which properties need to be considered as an indication of the effects of codisposal.

The approach adopted in this study differs from most others reported in the literature involving growth of plants on flyash. Previous work either involved plant growth on unamended flyash, or flyash was utilised as a soil ameliorant. This study differs in that flyash was amended by combining selected waste products. The growth performance of plants grown on the ameliorated flyash mixtures was then investigated.

To enable the key questions to be answered satisfactorily, geochemical analyses of plant material and growth media were performed. The waste products used as soil ameliorants were analysed to identify potential sources of undesirable elements that became incorporated into the plants. The flyash to be used as a growth medium during this study was obtained from SASOL's Secunda gasification plant and had been exposed to the elements in an ash dam for approximately 20 years since its deposition (pers.comm. M. Ginster, 1996). Over this time it has been subject to the influences of leaching by rainfall and reaction with atmospheric gases. As a result, its mineralogy, pH and physical properties have had time to equilibrate with their surroundings. It was expected that 20 years of weathering would moderate the most extreme of the undesirable plant growth conditions to a certain extent. In an effort to increase the availability of elements required by plants for growth, alkalinity present in the flyash had to be neutralised. For this purpose, two acidic waste products generated by SASOL's process were combined with flyash.

Interphase sulphur is a waste sulphur product generated as part of the gasification process (pers. comm. M.Ginster, 1996) and it may contain concentrations of vanadium up to 2% (pers.comm. M.V.Fey, 1996). However, a preliminary, non-quantitative XRF scan performed prior to the commencement of this study showed the available sample to contain only negligible quantities of V. The intention behind amendment with interphase sulphur was that it was expected to oxidise to sulphuric acid in the flyash and the acidity generated would alter the pH of the flyash to be more suitable value for plant growth. During some preliminary work carried out before the commencement of this project (pers.comm. Dodds, 1996), it was found that sulphur oxidation in flyash was a slow process, probably due to low bacterial populations or bacterial respiration rates in the flyash (Rippon and Wood, 1975, Klubek *et al.*, 1992). As a consequence, sulphuric acid (AR) was used to simulate the acidifying effect of sulphur oxidation.

The second acidic waste product utilised in the growth trials was a waste catalyst (Catpoly) also sourced from SASOL's Secunda operation. This catalyst consisted of phosphoric acid impregnated diatomaceous earth and has a pH of approximately 1 when placed in a 10:1 water: Catpoly suspension. Due to the low availability of P in flyash the possibility that this product might improve plant growth by increasing available P both through amending the pH of the growth medium and by providing additional P was anticipated.

Had these products been disposed of by dumping in a landfill site the potential production of acidic leachate under the influence of rainfall is a likely consequence. However, by codisposing acidic waste products with alkaline flyash, the extreme effects can be neutralised and result in both a safer disposal mechanism and a more suitable environment for plant growth.

Flyash is generally considered to be deficient in both P and N (Carlson and Adriano, 1993) however, another ubiquitous waste product exists that has high concentrations of these and other elements required for plant growth: sewage sludge (Petruzelli *et al.*, 1989; Sajwan *et al.*, 1995). The sewage sludge utilised as an ameliorant in this study was in fact a beneficiated waste product. Kynoch Fertilisers operate a manufacturing plant that composts the sewage sludge produced by the Milnerton Municipality with bark and fine wood chips from a local sawmill. The elevated concentrations of heavy metals that often render sewage sludge unsuitable for application to agricultural land (Sajwan *et al.*, 1995; Petruzelli *et al.*, 1989; Berti and Jacobs, 1996; Joost *et al.*, 1987), are reduced by dilution and are immobilised by sorption onto the organic matter in the final product.

The addition of composted sewage sludge to flyash is likely to improve flyash as a growth medium because as well as making required growth elements available to plants, sewage sludge tends to improve the water-holding capacity of the growth medium (Joost *et al.*, 1987). Another advantage that amelioration with composted sewage sludge provides is that it increases the rate of acidification in a several ways.

Addition of sewage sludge provides an acidifying effect in its own right due to its inherently mild acidity (Sajwan *et al.*, 1995) and sewage sludge increases the rate of bacteriological S oxidation which further assists in the neutralisation of alkalinity in the flyash. Sewage sludge is metabolised by bacteria which results in an increased partial pressure of CO_2 in the growth media. As this CO_2 dissolves in the soil solution, the pH of the growth medium reduces (Drever, 1988).

The final ameliorant utilised in the plant growth trial was an inorganic fertiliser mix of N, P, K and Mg salts. While this ameliorant is not a waste product, it was applied because inorganic fertiliser is routinely used to improve growth production on agricultural land and if the only growth limitation is presented by mineral deficiencies, then it should be corrected with this ameliorant. Mineral deficiencies could have developed as a result of the PFA (pulverised fuel ash) itself being poor in required elements, or rainwater leaching having reduced the concentration of K and Mg, originally present in the flyash. This required investigation.

The experimental work carried out during this study consisted of three parts. Firstly, the prepared PFA growth media were analysed for characterisation purposes and to determine whether any elemental species were likely to be unavailable to plants.

The second part of the study (reported in chapter 3) consisted of a plant growth trial where ryegrass was planted in flyash treated with the ameliorants mentioned above. This was undertaken to allow the key questions to be answered. The combinations of ameliorants used are shown in Table 2.1 and a more detailed description of the rates of application are presented in Table 3.2.

Table 2.1 Factorial combinations of treatments used in the plant growth trial to determine growth responses to ameliorated flyash.

Treatments	Control	Composted sewage sludge	Inorganic fertiliser	SS + fertiliser
Control	none	SS	F	SS + F
Sulphuric acid	A	SS + A	F + A	SS + F + A
Catpoly	CP	SS + CP	F + CP	SS + F + CP

A:	H_2SO_4
CP:	Catpoly
SS:	10% composted sewage sludge
F:	N, P, K and Mg salts as inorganic fertiliser

As a result of the combinations of these ameliorants there were 12 different treatments and each was examined as a growth medium. By harvesting the plant material and determining the dry mass of the yield, an indication of the success of the codisposal exercise could be obtained. The digestion and analysis of the plant material provided an indication of the extent to which trace elements were taken up from the growth media and a comparison could be made of the elemental composition of plants exposed to any particularly effective treatments.

The third part of the study (chapter 4) was an investigation into the rate of sulphur oxidation in the flyash mixtures to assess acidifying effects due to oxidation. This arose from the anticipated delay in S oxidation and it was decided to quantify the rate of S oxidation in flyash, both alone and in the presence of composted sewage sludge.

2.2 Materials and methods

2.2.1 pH and electrical conductivity

For the purposes of this study, a 1:2.5 soil:liquid ratio was adopted for the determination of pH and EC, as used by Hissink (1930, cited in van Lierop, 1990). The pH was determined in both deionised water and 1M KCl, the latter to minimise any junction potential or suspension effects in the extracts. After combining the soil and liquid the mixture was stirred then left to stand for 30 minutes before determining pH and EC. The pH was determined using a Crison micro pH 2001 instrument after calibration with standard buffer solutions. The EC was determined from the 1:2.5, soil:water mixtures, on a Crison micro CM 2201 instrument which was calibrated against an EC standard solution before use. The pH and EC meters both contain temperature correction mechanisms to compensate for variations in temperature during measurement.

2.2.2 Alkalinity

The determination of alkalinity was performed on soil extracts that were obtained from composite subsamples of the replicates prepared for each treatment used in the growth trial. The extracts were obtained from 1:1 soil:water ratio using 20g of soil because the saturated pastes yielded insufficient extract. The suspensions were shaken for 1 hour then stood overnight. The samples were then centrifuged for 30 minutes at 6 000 rpm and the supernatant decanted and filtered.

The alkalinity was then determined by automatically titrating 5ml of filtered supernatant with 0.025M HCl to an endpoint of pH 4.5. Rhoades (1982) suggests that such an automatic titration should be performed using full titration curve display mode to allow the location of the CO_3^{2-} and HCO_3^- inflexion points to be determined.

However, for all of the extracts on which these titrations were performed, the initial pH lay between 6.00 and 7.86. Because this fell within a pH range where HCO_3^- is the dominant species, the titration utilised an endpoint of pH 4.5 and assumed that all carbonate species were present as HCO_3^-. The titrations were performed with a shut-off delay of 30s to account for the effects of any residual buffering capacity during the titration, and the solutions were agitated by a teflon coated magnetic stirrer during the titration as recommended by Rhoades (1982).

2.2.3 Total elements

The total element concentrations present in the constituent waste products were analysed by x-ray fluorescence spectroscopy (XRFS). The analyses were performed using a Philips X'Unique II and processed using in house software at the University of Cape Town. Analyses were performed on pressed powder discs produced from 7 subsamples taken from flyash, one composted sewage sludge sample and one Catpoly sample. The pressed powder discs were prepared using 16g of sample, with 20% (4g) wax incorporated as a binder. The trace element analyses were performed quantitatively but the major element analyses were only semi-quantitative due to matrix effects within the pressed powder discs. Due to these problems, four fused discs were subsequently prepared and used for major element analysis. The samples were analysed for the following elements: Al, As, Ba, Bi, (C), Ca, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Nb, Na, Ni, P, Pb, Rb, S, Se, Si, Sr, Ti, Th, U, V, W, Zn, Y, Zr.

2.2.4 Extractable elements

An indication of the bioavailable proportion of elements present in the growth media was obtained in two ways. The first approach involved High Performance Ion Chromatography (HPIC) on the 1:1 soil extracts prepared for the alkalinity titrations mentioned previously in section 2.2.2. The soil extracts provide the water soluble portion of species present in the growth media, representing the most rainwater leachable and bioavailable portion of any species present in the media. The second approach involved a more aggressive leaching method using a nitric acid solution, giving an indication of species that are likely to be leached under the influence of mildly acidic rainwater (van der Hoek *et al.*, 1994; Bo Shi and Sengupta, 1995-96) over a far longer time period.

2.2.4.1 HPIC analysis of soil extracts

The instrument used for the analyses was a Dionex DX300 suppressed IC system which was coupled to an AL-450 chromatography software package. An HPIC-AG4A column was used as a guard column with an HPIC-AS4A-SC separator column. Ions are separated using a stationary phase ion exchange resin contained in a column with a different column for anions and cations. The eluent used to move the ionic species through the exchange column was a 1.7 mM $NaHCO_3$ / 1.8 mM Na_2CO_3 buffer, which prevents the accurate determination of carbonate species. These were determined separately by the alkalinity titration (section 2.2.2). The ionic species analysed for during the HPIC analyses included cations: Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+} and anions: Cl^-, Br^-, NO_3^-, SO_4^{2-} and PO_4^{3-}. The sample loop volumes are 25μl for cations and 50μl for anions. The running times for the column operating at a flow rate of 1ml min^{-1} were approximately 15 minutes for cations and 8 minutes for anions. Prior to analysis, all samples were filtered through a 0.2μm millipore filter and diluted to an EC value of <100 μS cm^{-1}. The regenerant used for the column was 25mmol H_2SO_4.

2.2.4.2 ICP analysis of nitric acid leached flyash

A flyash sample was sent to AECI Research Laboratory in Modderfontein, Johannesburg, for semi-quantitative ICP-AES analysis of 29 elements. A sample of flyash (10g) was suspended in 100ml 0.1 M nitric acid and shaken for 15 minutes. The suspension was then filtered and analysed by ICP-AES.

2.2.5 Moisture holding capacity (MHC)

The moisture holding capacities of the growing media were determined in two different ways. The first technique used is described by Fey (1993) and consists of adding sufficient water to allow the sample to reach its "sticky point" (ie. the water content at which the surface of the soil in a beaker glistens when equilibrium saturation has been reached), weighing a subsample and oven drying to determine the quantity of water present. MHC is then determined to be 50% of the water added to reach the sticky point. A second, more reliable method was also used. About 250g of flyash was placed in a transparent column and 50ml of water was added to the surface and allowed to soak in overnight.

The water volume was selected on the basis that the column would not saturate all the way to the base so that when a sample was taken from approximately half way down the wetted portion of the equilibrated column, it would be at moisture holding capacity. A weighed sample of the wetted material was taken, oven-dried at 110°C and weighed again to determine MHC. The precision of the method was calculated by repeating the determination in triplicate.

The effect of wetting and drying cycles on the MHC of flyash was determined using a column of ash and determining the MHC in the same way as described above. The same sample was then reincorporated into the ash column and the determination repeated. This cycle was repeated 3 times.

In an effort to determine the effect of composted sewage sludge on MHC, the MHC of a number of flyash/sewage sludge mixtures was investigated in the same way as the unamended flyash. The composted sewage sludge/flyash mixtures from the evaporation loss trial (section 2.2.7

below) were used so that the composted sewage sludge content varied from 0-50%. Because the mixtures used were investigated at the conclusion of the wetting/drying cycles involved in the evaporation loss trial, the results must be compared with those from the triple sequence of flyash wetting/drying due to the cementation and compaction that occurs during such cycles (Townsend and Gillham, 1975; cited in Carlson and Adriano, 1993).

2.2.6 Particle size distribution

A particle size analysis was performed on flyash and a sample of flyash amended with 10% composted sewage sludge using a Malvern Mastersizer "S" particle size analyser located in the Chemical Engineering Department at UCT. The analysis involves dispersing 1g of sample in water and maintaining the water in an agitated state so that the particles remain in suspension. A laser beam is passed through this suspension and the output signal is received and processed using an internal software package to relate the particle size distribution to the degree of obscuration of the laser beam. During the analyses a 2.40 mm diameter laser beam was used and the obscuration value was maintained at approximately 30%.

2.2.7 Evaporation rates

A major influence on the ability of plant species to colonise flyash is the availability of water. It was considered that the addition of composted sewage sludge to flyash could increase the plant-available water in the growth medium (Kriesel *et al.*, 1994). In an effort to quantify the impact of composted sewage sludge on the ability of the ameliorant combination to retain moisture against the effects of evaporation a separate investigation was carried out. The evaporation rate study was also proposed to determine what proportion of any effect on the growth trials involving composted sewage sludge could be attributed to geochemical or nutrient effects rather than moisture availability. If addition of sewage sludge allowed the growing medium to retain more water but made it unavailable to plants,no improvement in the growth medium would have been attained.

The study was designed to include a range of sewage sludge contents. A control of unamended flyash was included and then treatments of 10, 20, 30, 40 and 50% composted sewage sludge thoroughly mixed with the flyash were included. An additional treatment of 10% sewage sludge applied to the surface of the pots was included to determine the effect of mixing the sludge into the flyash. All pots were watered to the same mass, which corresponded to 75% MHC for unamended flyash. This was done in an effort to simulate the nonselective effect that rainfall would have but for a more complete assessment trials would need to be done involving pots watered to a uniform proportion of MHC for each of the treatments. To aid the statistical analysis three replicates of each treatment were included.

Each pot consisted of 300g of the prepared growth medium and was placed in pots of approximately 70mm height and 100mm diameter resulting in a surface area for evaporation of approximately 7 800 mm^2. The pots were watered to 75% of moisture holding capacity as determined above (section 2.2.5) resulting in the addition of 103g of water to each pot. During the trial, each pot was watered back up to a gross mass of 411g twice daily and the amount of water lost due to evaporation recorded. This regime was maintained for the first three days and then no further water was added and the rate of water loss due to evaporation continued to be recorded until the moisture content reached approximately 30% of MHC. This exercise was then repeated.

The conditions in the phytotron were the same as those described in the growth trial in section 3.2. The effect of the draught caused by the phytotron ventilation system on the evaporation rate cannot be underestimated.

The quantity of water applied during the seven day duration of the trial corresponded to approximately 28mm. When this precipitation rate is extrapolated for six months it corresponds to 730mm of rainfall. The annual rainfall in the Secunda area occurs predominantly over the summer months and was reported by Bester (1993) as 685mm so the evaporative losses during this trial are as reasonable a simulation as can be expected from pot trials in a phytotron.

2.3 Results and discussion

2.3.1 pH and EC

A consequence of reducing the pH of the growth media by codisposal of other waste products may be to increase elemental availability in the soil solution, both of required (Cifuentes and Lindemann, 1993) and potentially hazardous elements (Bo Shi and Sengupta, 1995-96). The increase in availability of these elements is also likely to result in an increase in the EC of the soil solution, so care must be taken to ensure that osmotic stresses are not a consequence of lowering of the pH, as this could be detrimental to plant growth (McBride, 1994).

The pH and EC values of the various raw materials investigated are shown in Table 2.2. These values are quite varied and any combination of them must be carefully planned with due consideration being given to any geochemical consequences of their combination.

Table 2.2 pH and EC values for different waste materials

Sample	$pH(H_2O)$	pH(KCl)	$EC/mScm^{-1}$
flyash	8.64	8.54	0.71
sulphur	4.45	4.22	1.33
Catpoly	1.12	0.90	34.30
sewage sludge	4.56	4.36	2.54

The pH and EC values of mixtures of flyash and other ameliorants are presented in Table 2.3. The amount of acidifying material required to alter the pH of a flyash suspension to pH 6 was used in the experimental work, while the quantity of composted sewage sludge added to flyash was 10%. Examining Table 2.3 reveals the strongly acidic nature of the Catpoly which results in the largest pH reductions for any of the ameliorants used alone. While the composted sewage sludge is mildly acidic, the addition of it to flyash reduces the pH by a lesser amount. The sulphuric acid used in lieu of elemental S also has a lesser pH reducing effect.

McBride (1994) describes saline soils as those whose $EC > 4\ mScm^{-1}$, $ESP < 15$ and typical pH < 8.5. These artificial soils would therefore not be classified as saline and are unlikely to be detrimental to plant growth on the basis of salinity alone.

Table 2.3 pH in H_2O and in 1M KCl and EC values for mixtures of flyash and ameliorants.

Treatment	pH(H_2O)	pH(KCl)	EC/mScm^{-1}
control	9.08	8.66	0.96
A	8.10	7.84	3.13
SS	8.11	8.00	1.06
CP	6.38	6.33	0.79
F	8.42	8.44	1.13
F+A	7.78	7.80	3.36
CP+F	6.31	6.29	1.47
SS+F	7.83	8.87	1.50
SS+CP	6.31	6.01	1.45
SS+A	7.58	7.52	3.23
SS+A+F	7.58	7.46	3.44
CP+SS+F	6.14	6.11	1.74

control = flyash only, A = sulphuric acid, SS = composted sewage sludge, CP = catpoly, F = fertiliser

2.3.2 Alkalinity

The results of the alkalinity titrations are shown below in Table 2.4 and are expressed as mmol $CaCO_3$ kg^{-1} to a pH of 4.5. The data falls into two distinct groups, the untreated flyash and the fertiliser treated, sulphuric acid treated and sewage sludge treated flyash all have an alkalinity of between 384 and 792 mmol $CaCO_3$ kg^{-1} but any treatments containing Catpoly show values between 685 and 792 mmol $CaCO_3$ kg^{-1}. The extreme acidity of the Catpoly appears to have resulted in the production of increased alkalinity in the various treatments. The reason for this is probably due to the precipitation of calcium phosphate minerals as a result of dissolution of pre-existing calcite by the phosphoric acid from the Catpoly which will result in an increase in dissolved CO_2 species. Because of the pH of the different flyash mixtures used the predominant species will be HCO_3^- (Drever, 1988). This explanation based on dissolution of pre-existing Ca minerals is supported by thermodynamic data as the $\Delta_f G$ values demonstrate that hydroxyapatite is more stable at 25°C than calcite, gypsum, anhydrite or portlandite and so the dissolution of any of these species to precipitate hydroxyapatite is favoured (Drever, 1988).

Table 2.4 Alkalinity titrations data for flyash combined with different ameliorants

Treatment	Alkalinity/ mmol $CaCO_3$ kg^{-1} @ pH 4.5
none	477
A	384
F	444
CP	792
SS	648
SS+A	484
SS+F	544
SS+CP	743
F+A	442
CP+F	772
CP+SS+F	685
SS+A+F	462

2.3.3 Total elements

The results of the XRF analysis of the flyash, catpoly and composted sewage sludge are shown in Table 2.5. Examination of the data confirms the literature suggestion that flyash is a calcium

Table 2.5 Results of XRF analyses of flyash, Catpoly, and composted sewage sludge

major elements/ %	Fe2O3	TiO2	BaO	CaO	K2O	Cl	S	P2O5	SiO2	Al2O3	MgO	Na2O	Total
PFA	2.66	1.56	0.14	4.75	0.54	0.07	0.22	0.29	52.20	27.87	1.28	0.90	92.48
SS	0.66	0.20	0.03	1.63	0.32	0.60	2.03	0.77	10.18	1.85	0.28	0.01	84.56
CP	0.65	0.06	0.01	0.11	0.31	0.43	0.97	53.43	17.31	1.54	0.55	0.26	75.63

trace elements/ppm	W	Cr	Mn	Ni	V	Zn	Cu	Co	Sr	Rb
PFA	7	240	291	81	149	68	70	19	76	33
SS	0	146	505	31	23	738	191	6	4	12
CP	0	70	43	51	50	24	9	0	2	9

trace elements/ppm	Mo	Pb	U	Th	Nb	Zr	Y	Se	Bi	As
PFA	2	95	13	48	40	436	76	3	5	23
SS	3	102	0	0	3	104	4	13	3	12
CP	5	0	0	0	1	11	2	0	0	24

ferro-alumino silicate. As expected, flyash has significant Ca, Na, Mg and S concentrations. These are the elements which are expected to be the most mobile and to occur as salts. Flyash contains some of most of the elements with P being the predicted exception. However, it is the metalloids such as Mo, Se, Bi and As that are of concern since they become mobile at higher pH values, although amelioration should render them immobilise as the pH declines. The concentrations of metals such as Cr, Mn, Ni, V, Zn Cu and Pb will have to be carefully monitored as they too are expected to become more mobile as the pH is lowered. Another concern expressed in relation to Yugoslavian flyash is the presence of radionuclides (Dzeletovic and Filipovic, 1993). It can be seen here that U and Th do occur and their concentrations and mobilities will have to be considered along with those of the other metals.

The analysis of the Catpoly reveals little in the way of surprises. It is likely to be a good potential source of P and contains some other elements that are likely to occur as soluble salts, such as Mg, K and some S. It has less Na than the flyash but contains more than the sewage sludge. Catpoly contains significant quantities of Cr, Mn, Ni, Zn and Cu so the neutralisation of its acidity is likely to be beneficial to the immobilisation of these metallic species.

The sewage sludge analysis also confirms the expectations that the literature provokes: sewage sludge is a sorbent medium for metals so the concentrations of Zn, Cu and Mn in particular are not unexpected. The alteration of pH during growth trials should serve to immobilise these species still further but it should be borne in mind that only a small portion of the total metal concentration present in sewage sludge is bioavailable at any given time so this is not expected to cause any problems (Petruzelli *et al.*, 1989).

2.3.4 Extractable Elements

2.3.4.1 HPIC analyses of aqueous soil extracts

In Table 2.6 (cations) and Table 2.7 (anions), the SAR values are calculated according to formula obtained from McBride(1994):

sodium adsorption ratio: $SAR = [Na^{+}] / ([Ca^{+2}]+[Mg^{+2}] / 2)^{1/2}$

where ionic concentrations are expressed in $mmol_c\ l^{-1}$

Table 2.6 Cation concentrations from aqueous extracts of flyash treated with different ameliorants

Treatment	Na^+ mg/kg	K^+ mg/kg	NH_4^+ mg/kg	Mg^{+2} mg/kg	Ca^{+2} mg/kg	SAR	Σ cations/ $mmol_c\ l^{-1}$
control	226	27	0	77	146	3.74	24
A	223	29	0	274	525	7.88	59
F	266	46	0	116	203	14.88	32
CP	187	19	0	256	133	9.47	36
SS	207	41	0	113	199	8.51	29
SS+CP	187	25	0	331	151	9.33	44
F+A	287	51	0	336	609	10.46	72
CP+F	231	30	23	346	141	12.07	48
SS+F	247	60	0	154	264	8.30	38
SS+A	206	36	0	275	580	8.84	61
SS+A+F	256	54	0	317	633	2.059	70
CP+SS+F	204	36	19	321	211	2.052	48

Control = flyash, A = sulphuric acid, F = fertiliser, CP = catpoly, SS = sewage sludge

Table 2.7 Anion concentrations from aqueous extracts of flyash treated with different ameliorants

Treatment /mg l^{-1}	Cl^-	NO_2^-	NO_3^-	HCO_3^-	SO_{4-2}	PO_4^{-3}	Σ anions/ mmol$_c$ l^{-1}
control	216	bdl	105	89	659	bdl	23.2
A	209	bdl	94	72	2291	bdl	56.6
F	234	bdl	877	83	689	bdl	36.5
CP	193	bdl	97	148	665	712	45.8
SS	209	bdl	209	120	653	bdl	53.9
SS+CP	199	bdl	199	138	643	754	30.0
F+A	270	51	270	82	2357	bdl	69.4
CP+F	242	bdl	242	144	692	960	64.7
SS+F	232	bdl	232	101	631	bdl	60.4
SS+A	199	bdl	199	90	2160	bdl	40.8
SS+A+F	235	bdl	235	86	2159	bdl	58.7
CP+SS+F	220	bdl	879	128	630	920	72.7

Control = flyash, A = acid, F = fertiliser, SS = sewage sludge, CP = catpoly, bdl=below detection limits. Note: catpoly = phosphoric acid impregnated diatomaceous earth

Examination of the HPIC analyses reveals that these growth media pose no sodicity hazard (McBride, 1994) nor would they pose any hazard in terms of alkalinity to any soil receiving leachate, but the pH is likely to influence the growth of plants in this medium by altering elemental mobilities and as a consequence, may induce chlorosis due to deficiencies in Fe and Mn and deficiencies in Cu and P (Rowell, 1988b). Because all of the EC values are < 4 mS cm^{-1}, even for non salt-tolerant crops, salinity is unlikely to be a cause for concern (McBride, 1994).

Table 2.6 shows the influence of ameliorants on concentrations of individual ionic species. The addition of fertiliser solution results in the highest Na^+ and K^+ concentrations

and contributes some Ca^{2+}. The addition of fertiliser alone does not result in detectable concentrations of PO_4^{3-} but when combined with Catpoly the extra P present results in detectable PO_4^{3-} concentrations. The absence of PO_4^{3-} is probably due to the precipitation of Ca phosphate minerals (Wild, 1988) but as Catpoly provides a much higher concentration of PO_4^{3-} there is sufficient still present in the soil solution after the precipitation reaction has reached equilibrium to register a detectable concentration during HPIC analysis.

Catpoly treatments of flyash results in the highest PO_4^{3-} levels, as mentioned above, but also shows the highest HCO_3^- concentration which is likely to have resulted from the dissolution of calcite by the acidity present in the Catpoly. The lowest levels of Ca^{2+}, Na^+ and K^+ occur with Catpoly, the Ca^{2+} can be explained by phosphate precipitation but Na an K produce quite soluble salts so that is unlikely to be an explanation in this instance.

The treatments containing sewage sludge as an ameliorant have a slightly reduced Na^+ concentration while the K^+ concentration is increased. This excludes the Catpoly/sewage sludge treatment where the Catpoly causes a reduction in the K^+ concentration relative to the contol. The Mg^{2+} content is increased over that present in unamended flyash but is significantly lower than in other treatments. This may be due to organic complexation of the Mg^{2+} by the organic matter present in the sewage sludge (Kabata-Pendias and Pendias, 1984; Jenkinson, 1988). The addition of sewage sludge results in an increase in the NO_3^-, but the highest value occurs when sewage sludge is combined with sulphuric acid and fertiliser. The fertiliser makes a large contribution to the NO_3^- concentration without the effect of sewage sludge. The other impact that sewage sludge has is on the HCO_3^- concentration, which increases significantly due to bacterial oxidation of organic matter present in the sludge resulting in elevated concentrations of dissolved CO_2 (Rowell, 1988b).

The most obvious effect of sulphuric acid as an ameliorant is to significantly increase the SO_4^{2-} concentration. The concentrations of Na^+ and K^+ remain approximately constant while the Mg^{2+} and Ca^{2+} concentration increases when the acidified treatment is compared with unamended flyash. This effect is due to the concentration-charge rule (McBride, 1994).

A detectable concentration of NH_4^+ only occurs on the addition of fertiliser and the Catpoly ameliorant, both with and without sewage sludge being present, and this corresponds to a reduction in NO_3^- concentration from the value provided by fertiliser only. This suggests a bacterially mediated reduction in N species occurs, although this reaction requires reducing conditions to produce the NH_4^+ (McBride , 1994).

Charge balance as an indication of analytical accuracy was discussed by Murray and Wade (1996) who concluded that a charge imbalance of ± 2.5% was an acceptable level of experimental error. The charge imbalances in the HPIC analyses fall into two distinct groups, the first of which includes flyash treated with the following ameliorants: none, sulphuric acid, sewage sludge, fertiliser + acid, sewage sludge + acid + fertiliser. These treatments fall within an acceptable range of experimental errors while treatments with fertiliser, Catpoly, sewage sludge + Catpoly, Catpoly + sewage sludge + fertiliser and Catpoly + fertiliser fall outside the 2.5% limit.

In the case of the sewage sludge treatments, the imbalance may be caused by complexation of cations by organic matter and the presence of cations that were not considered in the preparation of standards.

2.3.4.2 ICP analysis of nitric acid leachate from flyash

Shown in Table 2.8 are the results of the ICP-AES analysis of the leachate produced during the leaching of flyash by nitric acid.

The data reveals that, as might be expected, Ca dominates the mobile elements with Al and Mg occurring in slightly lower concentrations. The next group of elements occurs in concentrations an order of magnitude lower and includes Fe, Na, P, K and Sr. The next group of elements occurs in concentrations that are a further order of magnitude lower and includes B, Cr, Mn, Ti, and V and the remainder of elements occur in still lower concentrations: Zn, Li, Cu, Ni, Pb, Co, Be, Cd and Ag.

Previous work has shown that plants grown on flyash or flyash amended soils can contain elevated concentrations of a number of elements including As, B, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Se, Ti and Zn (Townsend and Gillham, 1975; Sharma *et al.*,1989; Petruzelli *et al.*, 1986; Carlson and Adriano, 1993) while sewage sludge application is reported to result in elevated concentrations of elements such as B, Cd, Cu, Mn, Mo, Ni and Zn (Rodgers and Anderson, 1995). Comparison of these literature reports of elevated elemental concentrations present in plants grown on flyash and sewage sludge with the concentrations of potentially hazardous elements from the acid leached flyash reveals some correlations. After the growth trial, plant analysis was conducted to determine whether toxic concentrations of B, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti and Zn were present in the biomass.

Table 2.8 Semi-quantitative ICP-AES analysis of nitric acid leachate after leaching of flyash

Element	As	Se	Mo	Ag	Ti	Sr	Mg	Al
detection limit/ppm	0.5	1.0	0.1	0.01	0.01	0.01	0.01	0.04
concentration/ mg kg^{-1} PFA				0.1	790	1170	22400	34280

Element	Mn	Fe	Cr	V	Na	Be	B	Ca
detection limit/ppm	0.01	0.02	0.1	0.04	0.02	0.1	0.03	0.01
concentration/ mg kg^{-1} PFA	470	4610	160	210	4110	5.0	650	123500

Element	Cd	Cu	Sb	Pb	Bi	Li	Co	Sn
detection limit/ppm	0.01	0.04	0.2	0.2	0.5	0.01	0.1	0.4
concentration/ mg kg^{-1} PFA	1.0	40		30		40	6.0	

Element	Hg	Zn	Ni	P	K
detection limit/ppm	0.02	0.01	0.01	0.4	0.2
concentration/ mg kg^{-1} PFA		90	40	3180	1410

2.3.5 Moisture holding capacity (MHC) of flyash mixes

The moisture holding capacities for different flyash mix samples are shown in Table 2.9. The first value is from unamended 20 year old flyash (having been passed through a 5mm mesh). The following three determinations demonstrate the reduction in moisture holding capacity brought about by repeated wetting and drying cycles. This reduction can most likely be related to the pozzolanic nature of flyash (Carlson and Adriano, 1993).

The final set of data demonstrates the effect that varying additions of composted sewage sludge has on the moisture holding capacity of the flyash. This reduction in MHC for unamended flyash is consistent with the compacting and cementing that Carlson and Adriano (1993) relate to the pozzolanic nature of flyash. When sewage sludge is introduced into the flyash, the MHC increases by increasing the organic matter content of the flyash (Berti and Jacobs, 1996). Composted sewage sludge also reduces cementation that occurs as a result of the pozzolanic nature of flyash. This is because cations are being assimilated into organo-metallic complexes with sewage sludge derived humic substances, rather than precipitating as salts which cement ash grains together. By introducing fine sand sized particles and adding organic matter to flyash, the packing is disrupted and porosity is increased. As a consequence, the growth medium is more suitable for plant growth due to the availability of water and plant nutrients.

Table 2.9 Variation in moisture holding capacities (MHC) of flyash due to wetting and drying cycles and through the addition of composted sewage sludge.

Sample	MHC/g kg^{-1}
Variation of MHC with wetting/drying cycles:	
flyash, not having experienced any rewetting cycles	470
flyash after first rewetting/drying cycle	344
after second cycle	320
after third cycle	210
Variation of MHC with the incorporation of composted sewage sludge:	
0% sewage sludge, (flyash after 2 rewetting cycles)	320
10% sewage sludge	369
20% sewage sludge	426
30% sewage sludge	462
40% sewage sludge	511
50% sewage sludge	603

Increasing the MHC of a growing medium raises the soil moisture content available for plant growth and the addition of composted sewage sludge to flyash has been reported to improve the MHC of flyash (Joost *et al.*, 1987). This serves to alleviate salt and water stress by increasing water content and diluting any salts that are present in the soil, as well as by reducing the difficulty that plants have in abstracting water from the soil (Richardson and McCree 1985, cited in Shalhevet, 1993). An additional effect is to increase the availability of a number of nutrient elements including: Ca^{2+}, Mg^{2+} and K^+ (Schaff and Skogley, 1982; cited by Marschner, 1990) and P (Fleige *et al.*, 1981, cited by Marschner, 1990).

2.3.6 Particle size distribution

The particle size distribution curves of unamended flyash and flyash amended with 10% sewage sludge are shown in Figure 2.1. In the flyash sample the particle size distribution assumes a slight negative skew with approximately 8% of the grains occurring as clay, 33.5% as fine sand and the remaining 58.5% as silt sized grains (silt 3.9-62.5μm, using the Udden-Wentworth grain size scale after Pettijohn *et al.*, 1972). In the case of the 10% sewage sludge amended sample, the particle size distribution is similar but only 7% clay occurs, while 36% of the grains fall into the fine sand size range and approximately 57% occur as silt.

The particle size distribution shows an almost normal distribution for the flyash with only a slight negative skew, but when the 10% sewage sludge is added, a "shoulder" appears on the larger grain size region of the curve. The likely effect of sludge amendment, indicated by this broadening of the peak, is to create more pore spaces within the flyash. These are then available to retain more moisture or soil-air, consistent with the observed increase in moisture holding capacity with the addition of sewage sludge to flyash. Improvements in soil moisture and air space are necessary in flyash if it is to behave as a soil. The development of small aggregates in a soil is desirable and this is more likely to occur in a mixture of flyash and sewage sludge than flyash alone due to the massive, cemented structure likely to develop in response to the pozzolanic nature of flyash. Once sufficient pore space has developed, soil moisture and air are able to penetrate the material and this makes it more habitable for soil bacteria which play an essential role in nutrient cycling and fertility in soils (Wild, 1993).

The broadening of the grain size range discussed here is consistent with the improvement in the MHC that is obtained with the inclusion of sewage sludge (discussed in section 2.3.5). The particle size distribution observed here is consistent with distributions reported in the literature since between approximately 60% of the grains fall within the silt size range.

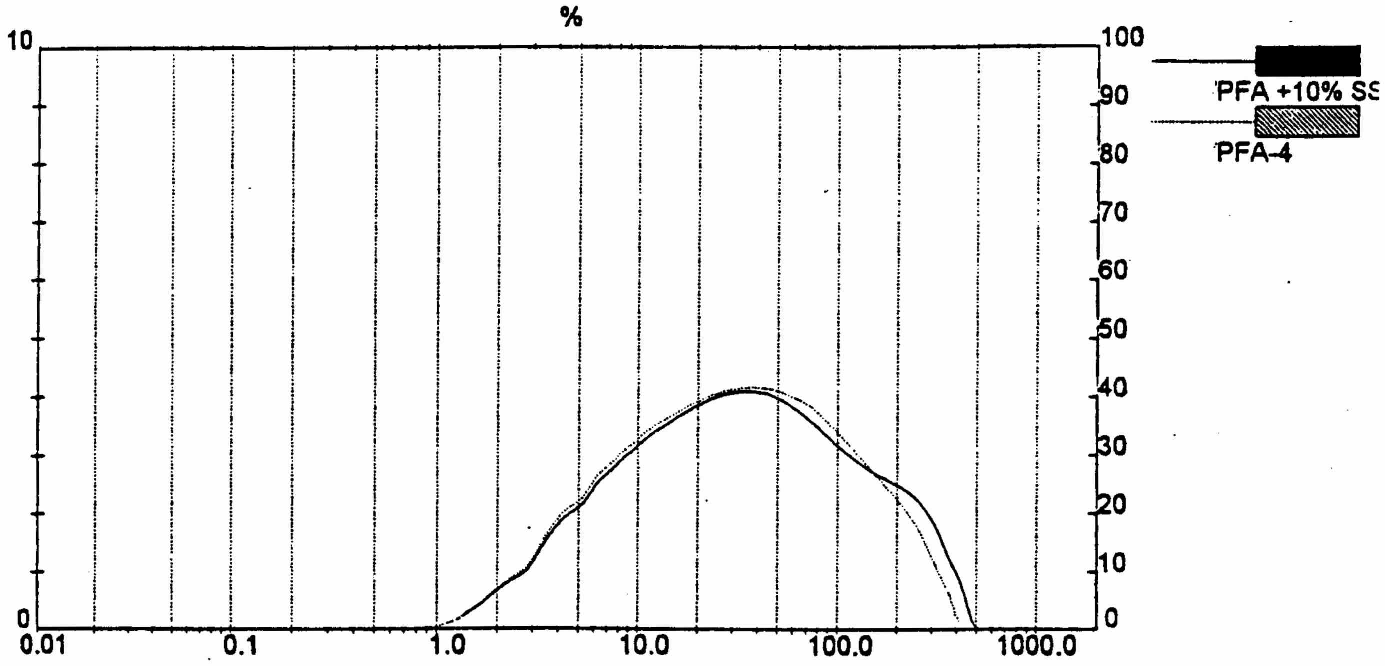


Figure 2.1 Particle size distribution curves of flyash alone. Superimposed on this is the curve from flyash amended with 10% sewage sludge.

The distribution of grain sizes in flyash varies significantly between different combustion plants and coal compositions from different countries. Dzeletovic and Radoslav (1995) report a Yugoslavian flyash as being predominantly sand sized grains (80-95%) while Sale *et al.* (1996) report only 37% sand sized grains and 54% silt, from a Canadian flyash.

Flyash from India as reported by Sharma *et al.* (1989) was predominantly silt (63%) but all of these flyash samples have a low clay percentage. South African flyashes analysed by Bosch (1990) showed some variation in grain size but silt forms the predominant particle size group.

2.3.7 Evaporation Rates

The quantity of water applied during the evaporation trial provides an equivalent amount of water applied as would have been supplied by 28mm of rain. This quantity of water was applied during the 1 week trial. Bester (1993) reported an average rainfall for the Secunda area of 685mm per annum falling over the summer months. This trial was aimed at simulating the wetting and drying cycles occurring during the summer growing season.

Rather than watering each flyash/sewage sludge mix to 75% of its individual moisture holding capacity, an approach was taken where the same mass of water was applied to each pot in the same non-selective manner in which rainfall occurs. As a result, all treatments were operating at a lower MHC than the unamended flyash. This is similar to a field situation in that the field capacity of all soils would only be reached after a particularly protracted period of rainfall. If an effort was to be made to characterise all of the sewage sludge/flyash mixtures more comprehensively, a trial would have to be carried out where each of the mixtures was wetted to its individual field capacity. However, since the other experiments in this study only utilise 10%

sewage sludge mixtures with flyash such an approach was considered to be beyond the scope of this project. Table 2.10 shows means and standard deviations of triplicate determinations of average evaporation rates for the different treatments.

Table 2.10 Rate of evaporation of water from flyash as a function of treatment with sewage sludge (raw data collected in triplicate).

Sewage sludge treatment/ % by mass	Mean evaporation rate/ mm day^{-1}	Evaporation standard deviation/ mm day^{-1}
none	3.87	0.107
10 (surface)	3.75	0.111
10 (mixed)	4.03	0.031
20	3.94	0.080
30	4.06	0.129
40	3.85	0.209
50	4.00	0.018

The complete data set was analysed using a Kruskall-Wallace test to determine if there was any significant difference between the treatments at the 95% confidence level. An outlying value in the 40% sewage sludge treatment showed significance but if this is taken as an outlier there is no significant difference between the treatments. The implication from this is that while more soil moisture would be available in the amended flyash watered to field capacity, the water would be as readily available to plants growing on the flyash mixes as it would in unamended flyash, because the tendency to lose water by evaporation is the same in all cases. Thus, the ability of plants to extract moisture from the fine grained flyash is unlikely to provide growth limitations.

2.4 Conclusions

Because flyash is a moderately alkaline material, decreasing its pH to limit the mobility of potentially toxic elements by combining it with selected waste materials was viewed as a measure that would render flyash dams geochemically more inert. At the same time it would provide a surface capable of supporting revegetation which would stabilise the surface against erosion, reduce dust emissions and allow the waste repositories to develop into a less obvious disturbance of the surrounding landscape. While decreasing the pH of flyash by combining it with sewage sludge, acidic waste catalyst or sulphur, may reduce the bioavailability of some metallic and metalloid species, it may also provide risk of elevated concentrations of other heavy metals mobilised under the new pH conditions. To offset this effect, the bioavailable concentrations of these metals may be reduced through the formation of organo-metallic complexes with composted sewage sludge (Hodgson *et al.*, 1966; Sanders, 1983; Geering *et al.*, 1969; Sims and Patrick, 1978; Jarvis, 1981, cited in Marschner 1990).

The chemical variability of the flyash is demonstrated by the observation that approximately 2/3 of the Cr present in the flyash was extracted by the nitric acid leaching for ICP analysis while the Mn concentration leached was significantly higher than the amount initially present in the sample, as determined by XRF.

It was found that the alkalinity determinations, moisture holding capacities and pH values are all quite variable so this chemical difference is not unexpected. Of the other metals, Cu and Pb appeared to be relatively immobile under the nitric acid leaching while Fe, Mn, V and Al appeared to be quite mobile.

The sorptive nature of the sewage sludge is expected to render any elevated concentrations of these metals immobile and sewage sludge amended flyash may also provide a more suitable environment for bacterial growth. Sewage sludge, therefore, may be a very valuable ameliorant. Bacteria are necessary for the cycling of nutrients. This is essential for plant growth so that the effect of the sewage sludge may prove to be doubly beneficial. The improved soil texture that results from the incorporation of composted sewage sludge should also enhance plant root development which would improve the ability of plants to assimilate nutrients from soil (Marschner, 1990). When this is combined with improvements in MHC and nutrient availability brought about by a lowering of pH, the synthetic soil should be a significantly better growth medium than unamended flyash.

Chapter 3 Investigation into the growth responses of ryegrass planted on flyash amended with various selected ameliorants

3.1 Introduction

Previous work dealing with flyash effects on plant growth has either concentrated on plants growing in flyash amended soils (Shukla and Mishra, 1985; Petruzelli *et al.*, 1987; Ghuman *et al.*,1994; Salé *et al.*,1996), using flyash, both with and without sewage sludge as a fertiliser or soil conditioner (Kriesel *et al.*,1994; Ghodrati *et al.*,1995), as a fertiliser, or on soil layers overlying flyash. Much less commonly has the study of plants growing directly on flyash been undertaken (Townsend and Gillham, 1975; Hodgson and Buckley, 1975; Scanlon and Duggan, 1979; Engelbrecht, 1987; Carlson and Adriano, 1991; Dzeletovic and Filipovic, 1995). The geochemical/chemical investigations are often hydroponic trials (Maree, 1987; Shukla and Mishra, 1985) or simply involved harvesting plant material without any effort to relate plant composition to growth medium composition (Howard *et al.*, 1977; Maree, 1987; Sajwan *et al.*,1995).

The pot trial in the present study was undertaken in an effort to satisfy two objectives: firstly, to produce a satisfactory growth medium for plants through the codisposal of two potentially hazardous waste materials, and secondly, to render these potentially harmful waste products geochemically inert so as to reduce their impacts on the environment.

Another consequence of the plant growth trial was expected to be the development of an explanation as to why some combinations of ameliorants were effective in promoting plant growth while others were not.

Rowell (1988b) advocated the addition of S to sodic, saline and alkaline soils because it decreased pH and resulted in increased Ca concentration through the dissolution of Ca minerals. This resulted in improvements in porosity as a result of reversal of dispersion which improved soil drainage. The addition of sewage sludge results in increases in soil organic matter which increases bacterially mediated nutrient cycling (Carlson and Adriano, 1993) while increasing soil moisture holding capacity at the same time (Seaker and Sopper, 1988). An added benefit of the addition of sewage sludge is the reduction in soil pH as a result of increases in dissolved CO_2 produced by bacterially oxidised organic matter. This also assists in restoring the flocculated state of the growth medium (Rowell, 1988b). The drawbacks of the addition of sewage sludge to growth media are increases in salinity due to the dissolved salts present in the sludge (Sajwan *et al.*, 1995) and the incorporation of elevated concentrations of potentially toxic metal ions (Kabata-Pendias, 1985). Despite this, the sorption capacity of sewage sludge is generally high enough to retain most of the heavy metals as long as the application rate and frequency is controlled (Petruzzelli *et al.*, 1989; Ekama, 1993; Schwegler, 1995; Berti and Jacobs, 1996). The addition of inorganic fertilisers to improve nutrient availability also results in rapid growth responses (Seaker and Sopper, 1988; Kriesel *et al.*, 1994) but has minimal effects on other soil properties of the growth medium.

Combinations of the ameliorants mentioned above, have been used in previous studies, but were used as either fertilisers or soil conditioners. Kriesel *et al.* (1994) used combined sewage sludge and flyash and proposed utilising it as a fertiliser with the advantage of slow elemental release and the ability to improve soil MHC. This resulted in some of the potentially toxic elements being made bioavailable as trace elements for plant growth. Sajwan *et al.* (1995) also used sewage sludge/flyash combinations as a soil ameliorant and found the combinations resulted in increases in N and P supply to plants when compared with soil, but excessive application resulted in reduced yields due to toxic effects. Wyrley-Birch *et al.* (1987) utilised a balanced combination of inorganic fertilisers and flyash as a nutrient supply for a hydroponic growth trial but despite this, the combination resulted in the growth of plants that was deficient in Zn and Mn while P, Mg, Zn, Mn and Cu also had low plant availability from the flyash. The combination of sewage sludge and S has been found to result in an increased rate of S oxidation (Cifuentes and Lindemann, 1993; Cowell and Schoenau, 1995) which resulted in a reduction in soil pH as discussed above. Based on these literature reports, the combination of these ameliorants with flyash was expected to produce a positive growth response from plants grown in these media.

The growth media produced from the combinations of ameliorants with flyash are variable in their compositions. Kabata-Pendias (1995) suggests that the trace metal status in soils depends on a number of factors including free calcite, soil texture, content of hydrous oxides and clay minerals, redox conditions, pH, CEC and soil organic matter. The pH ranges for the different growth media lie between 6 and 8 and the organic matter content of these treatments are also variable. This means that the trace metal contents of plants grown on these media should also be variable, based on Kabata-Pendias' parameters.

The determination of the most suitable treatment will need to consider both the dry matter yield and elemental uptake by plants before any conclusion is reached. While salinity effects are recognised as being potentially significant, a leaching trial was beyond the scope of this study.

3.2 Materials and methods

3.2.1 Components of growth media

The growth media utilised for this plant growth trial were based on flyash. The flyash was mixed with other ameliorants (as described in Chapter 2) to reduce the detrimental plant growth qualities of the flyash. The ameliorants used included sulphuric acid, Catpoly, composted sewage sludge and a solution of inorganic salts of selected nutrients to be applied as a fertiliser. The quantity of each acidifying ameliorant added was that required to reduce the flyash pH to approximately 6 (as reported in Chapter 2). Sulphuric acid was used to simulate the acidifying effect that oxidation of elemental S would provide, assuming 100% oxidation of the S. This was achieved by applying 73ml of 2.13M sulphuric acid per 900g flyash in each pot treated. Catpoly treatments required the application of 41g to provide the same level of pH adjustment. Composted sewage sludge was applied as 10% of the growth medium in the treatments it was applied to. The fertiliser treatment contained N, P, K and Mg and the details of quantities applied are shown in Table 3.1.

3.2.2 Experimental design

A factorial design (Rayner, 1969) was employed to compare the effect of the two different acidifying treatments and a control and to determine the extent of interaction between these and composted sewage sludge and inorganic fertiliser, both separately and when combined. To ensure sufficient degrees of freedom for a statistical analysis to be carried out, each treatment was performed in triplicate so that in total 36 pots were planted for the trial. The treatments applied to amend the flyash are set out in Table 3.1.

Table 3.1 Ameliorant combinations used as treatments of flyash in the plant growth trial

Treatment	None	Composted sewage sludge	Inorganic fertiliser	Composted sewage sludge + fertiliser
None	Control	SS	F	SS + F
Sulphuric acid	A	SS + A	A + F	A + F + SS
Catpoly	CP	SS + CP	CP + F	CP + F + SS

The abbreviations for the ameliorants listed in Table 3.1 are explained below.

Control:	900 g flyash per pot
A:	73ml of 2.13 M sulphuric acid
CP:	41g of Catpoly (phosphoric acid impregnated diatomaceous earth) per pot.
SS:	100g composted sewage sludge, combined with 800g of flyash per pot
F :	Inorganic fertiliser mix, containing 124mg N + 79mg P + 49mg K + 15mg Mg, added as 15ml of a solution containing $MgSO_4.7H_2O$, NH_4NO_3, $NaH_2PO_4.2H_2O$ and KCl.

On mixing, each pot had a total of 140ml of liquid added to bring it up to the desired MHC, either as distilled water alone or with sulphuric acid and/or fertiliser solutions.

3.2.3 Phytotron conditions

The light regime for the duration of the trial involved a 14-hour photoperiod. Incandescent lights came on at 06h00 and remained on for one hour. At 06h55 sodium and mercury vapour lamps came on in three stages to complete the simulation of sunrise. At the end of the day the metal lamps were shut down in three stages and at 19h00 the incandescents once again came on for one hour and at 20h00 the entire photoperiod was complete.

During the trial the temperature was maintained at 22 °C and fans provided a constant draft. The humidity was loosely maintained at about 50% with safeguards to ensure that it did not exceed 70% or drop below 30%.

3.2.4 Watering regime

The pots of treated flyash were lined with plastic bags to prevent drainage and watered twice daily using distilled water. The pots were planted at 35% of the MHC as determined in section 2.2.5 of Chapter 2 and the moisture content was increased to 60% of MHC 4 days after planting and then to 75% of MHC on the 19th day after planting and maintained at this level thereafter. The MHC was determined to be 457 g water kg^{-1} of air-dried flyash, as detailed in section 2.2.5.

3.2.5 Mixing of flyash treatments and potting and planting the seeds

Weighed quantities of the solid dry components of each treatment were placed in plastic with the air-dry flyash and thoroughly mixed. Any liquid additions, including sulphuric acid, inorganic fertiliser solutions and distilled water to raise the moisture content of the flyash mixes to the proportion of MHC required at planting, were then added and the contents of the bag were then once again thoroughly mixed. The bags were then placed into plastic pots of approximately 150mm diameter by 130mm in height.

For the growth trial it was decided to utilise Italian ryegrass (*Lolium multiflorum*) as the plant species and approximately 100 presoaked seeds were scattered onto the surface of each pot.

During the planting an additional 20ml of water was applied to obtain more contact between the seeds and the growth media. For the first seven days of the trial the pots were covered with a strip of paper towelling to improve humidity.

Ten days after planting, thinning to 50 seeds per pot was performed by pinching out surplus seedlings so as not to disturb the surface of the growth medium.

3.2.6 Harvesting, drying and determining dry matter yield

Harvesting was done 35 days after planting and consisted of cutting the foliage at a level of 1 cm above the soil surface to minimise contamination from the growth medium. This above-ground biomass was then oven-dried at 60°C for 48 hours to a constant mass and the dry mass was recorded. The triplicate determination of dry matter yield was then subjected to a Kruskall-Wallace analysis of variance and Mann-Whitney U-tests between individual treatments to determine if there were significant differences between yields grown on different flyash treatments.

3.2.7 Sample preparation and analysis

The dry samples were milled to pass a 20 mesh screen and ashed using the dry ashing technique described by Joners and Case (1990). A 0.5 g sample of dried plant material, or less in the cases where insufficient sample was available, was placed in a porcelain crucible which was then placed in a cool muffle furnace and brought to a temperature of 500°C. Joners and Case (1990) suggested that it should take 2 hours for the furnace to come up to temperature. However, the furnace utilised in this operation only required one hour to attain the required temperature. The method also suggested muffling in the furnace for 4-8 hours with an extra 2 hours if the crucibles were covered. It was found that the seals on the furnace excluded so much air that it was necessary to muffle for 11 hours with the furnace door being opened once at 5 hours to admit additional air, for complete ashing to occur, as indicated by an absence of dark, charred material in the ash.

The ash was retained in the crucible and dissolved in 10ml of dilute aqua regia (300ml conc. HCl + 100ml 55% HNO_3 made up to 1 l with deionised water).

To assist the dissolution process, the ash/ acid mix was heated at 70°C on a digestion block for 3 hours then made up to the original mass with acid after cooling. The acid solutions were then diluted to 50ml with deionised water and filtered prior to analysis which was carried out using ICP-AES instrumentation, for the following elements: Al, P, As, Se, Mo, V, Be, Li, Cd, Pb, Co, B, Cr, Cu, Sr, Zn, Ni, Si, Mg, Mn, Fe, Ca, Na, K.

3.3 Results and discussion

3.3.1 Dry matter yields

The dry matter yields from harvesting the ryegrass grown on the different flyash treatments showed obvious improvements in growth response (Figure 3.1).

The growth responses of all the treatments, except the pots treated with acid only, showed an improvement in dry matter produced over that of the control. The greatest improvement occurred in the treatment containing fertiliser plus composted sewage sludge. The results shown in Figure 3.1 show relative yields and are related to the mean dry matter produced by the fertiliser plus sewage sludge treatment. The dry matter yields for each pot are recorded in Appendix I and are displayed visually in Figure 3.2 as a bar graph showing dry matter yields and a photograph of the pots prior to harvesting. Examination of the yields reveals that the different

Treatment:

1 = acid (A)

2 = control

3 = Catpoly (CP)

4 = F+A

5 = Fertiliser (F)

6 = SS + CP

7 = CP + F

8 = SS + A

9 = Composted sewage sludge (SS)

10 = SS + CP +F

11 = SS + A + F

12 = SS + F

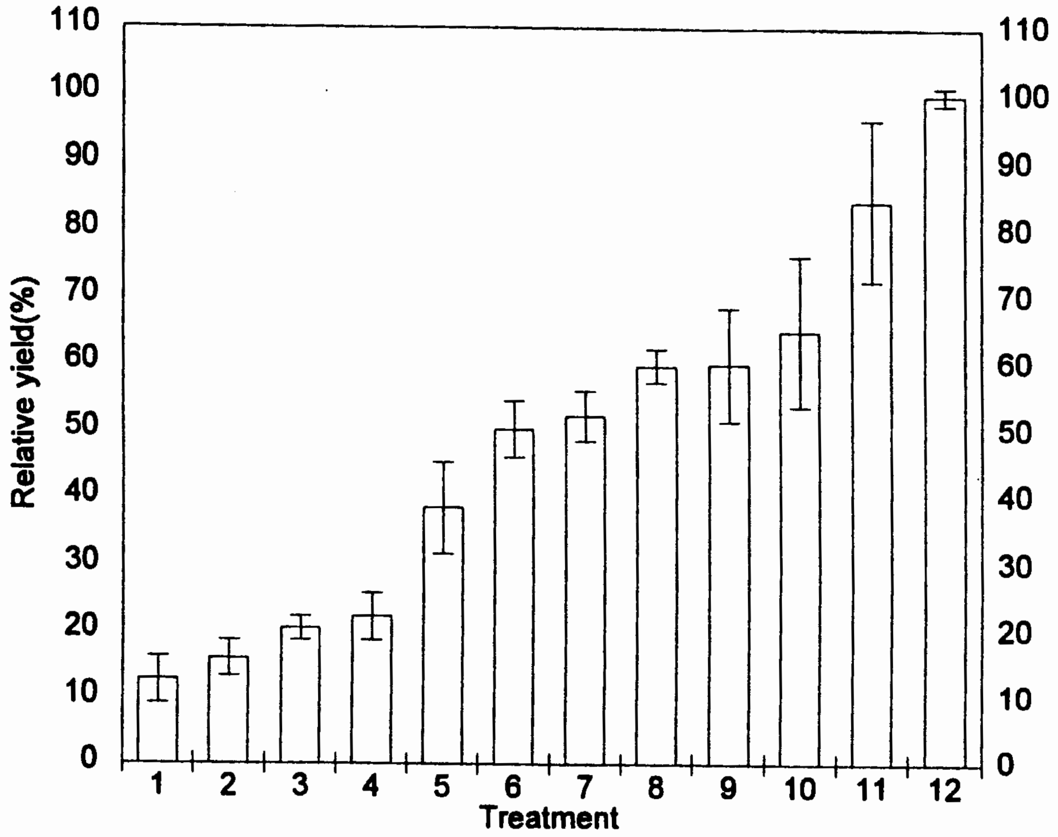


Figure 3.1: Relative dry matter production of ryegrass in flyash with different ameliorants.

Error bars in graph show +/- one SD.

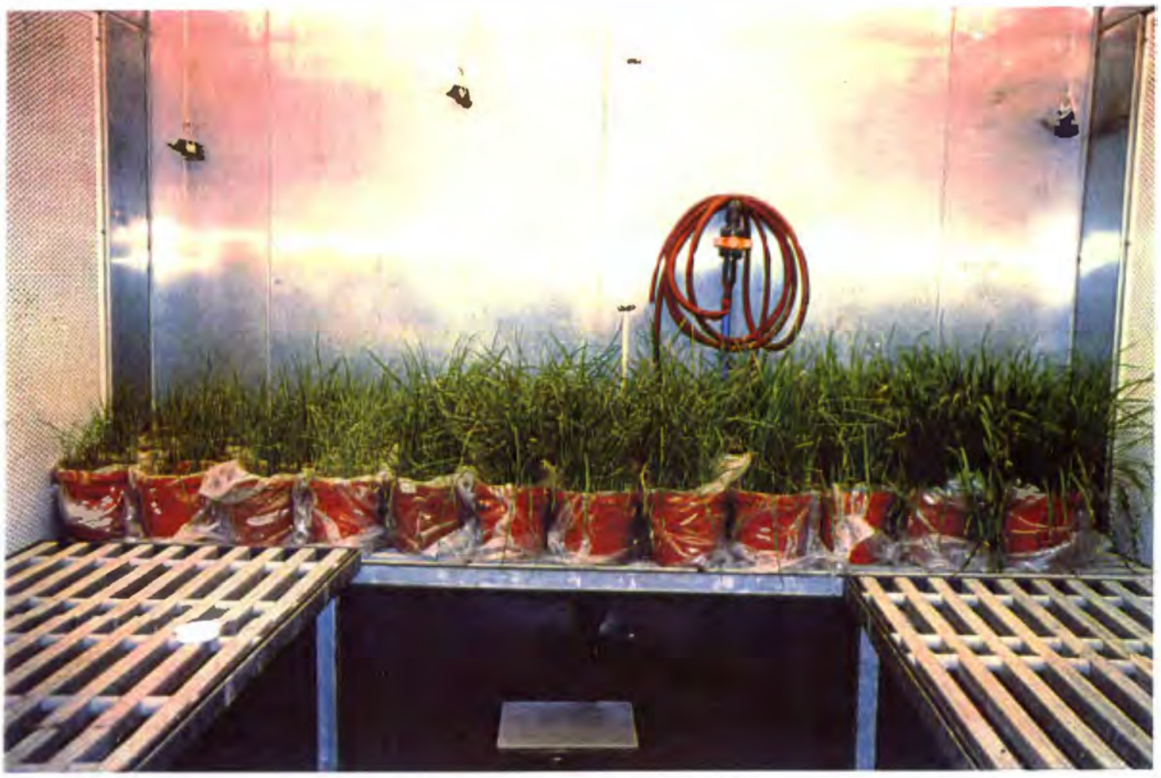
All yields expressed relative to the composted sewage sludge.

ameliorants have different effects on growth responses. Compared to the control, the sulphuric acid treatments result in a negative growth response while Catpoly, fertiliser and composted sewage sludge all produce a positive one with the response from sewage sludge being the best for all of the individual amendments.

3.3.2 Examination of interactions between ameliorants

When the amendments are mixed, the interactions between the amendments alter conditions with the different combinations. While the effects of some combinations of amendments were super-additive, only the three treatments that combined sewage sludge and fertiliser resulted in a greater yield than that produced by sewage sludge alone. As a generalisation, the addition of sulphuric acid or Catpoly resulted in a decrease in yield, with the exception being the combination of Catpoly and fertiliser. The superadditivity of the sewage sludge and fertiliser treatment is likely to result from a combination of complementary provision of required elements and some physical soil effects by the sewage sludge. Sewage sludge will increase soil moisture and combining this with bacterial enhanced nutrient availability results in significantly improved growth responses.

Both of the acidifying ameliorants appear to detract from the additive effects of sewage sludge and fertiliser when combined, possibly as a result of additional salinity created by acid reacting with previously precipitated minerals and re-dissolving them to the detriment of the plants. These ameliorants interact in different ways with sewage sludge and fertiliser. The combination of Catpoly and fertiliser has an additive effect, implying that the two ameliorants are complementary, with one providing a growth requirement that is lacking in the other.



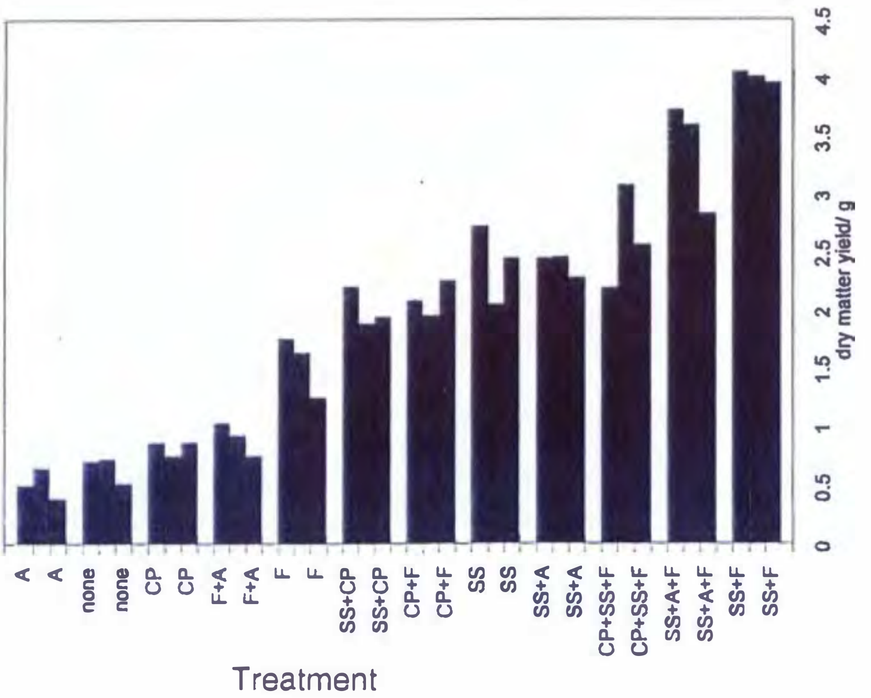


Figure 3.2:The photograph of the pots in the phytotron arranged in terms of increasing yield as can be seen from the graph showing dry matter yields for the individual treatments. The yellow necrotic leaf tips are evident in all of the treatments.

The acid when combined with fertiliser has a detrimental effect on the growth response provided by the fertiliser alone. This suggests that the effect of the Catpoly is more than just an acidity effect and may be related to the P that the Catpoly introduces to the growth medium. When these ameliorants interact with sewage sludge the situation is reversed. In this case, the Catpoly reduces the yield of the sewage sludge. This is probably brought about by an excess of P, since both Catpoly and sewage sludge are able to provide P to soils.

The Catpoly provides in excess of 25 000 mg kg^{-1} P (Figure 3.3) and Wild (1988) reports that soils generally contain between 130 to 700 mg kg^{-1}, so that the level of application of P provided by treatment with Catpoly is likely to be well above that required for optimal plant growth and in fact may inhibit growth. Kabata-Pendias and Pendias (1984) note that P combines with trace metals to produce a fungicidal effect which will result in a reduction in biological activity in the growth medium and, as a consequence, trace elements may be less available to plants.

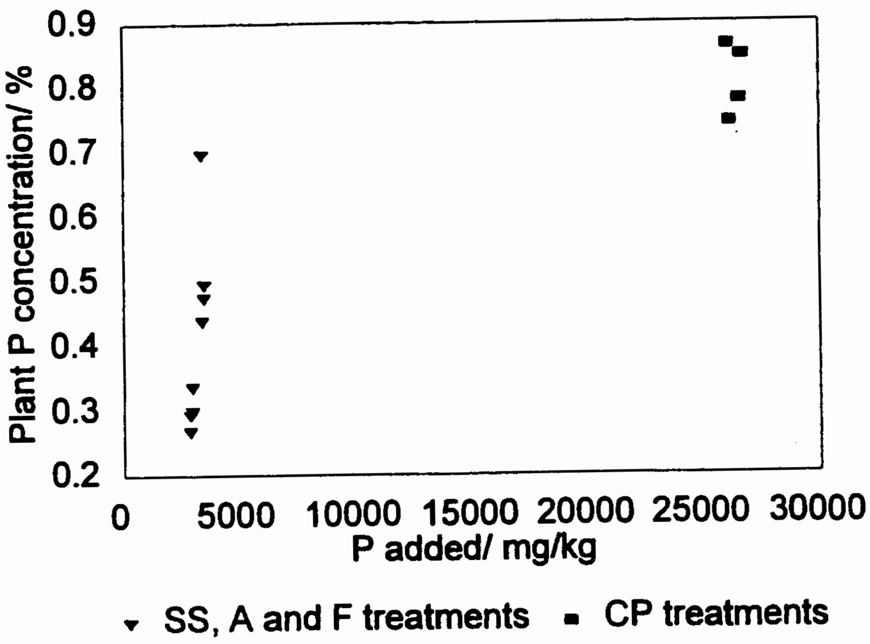


Figure 3.3: Plant P uptake vs quantity applied

The uptake of trace elements can be reduced by the antagonistic effect of P on a large number of elements (Kabata-Pendias and Pendias, 1984). In some instances, however, this antagonistic effect may be reversed and P acts synergistically to assist in elemental uptake. The interaction of sewage sludge and acid is virtually insignificant with a reduction in relative dry matter production of 0.25%.

3.3.2.1 Statistical significance of dry matter yields produced during the plant growth trial

A statistical analysis was performed on the ameliorant treatments to determine if there were any significant different differences in the growth yields. The analysis was performed using the STATISTICA software package and the Kruskall-Wallace test, which is the non-parametric equivalent of a one-way analysis of variance. The Kruskall-Wallace test produced a P-value of 0.0012. Because the P-value is less than both 0.05 and 0.01, the H_0 is rejected at both the 95 and 99% confidence levels. This means that the population distribution functions are not identical and that significant differences exist between the dry matter production of different treatments. In an effort to determine between which treatments the differences are significant, the Mann-Whitney u-test was employed and the results are shown in Table 3.2.

All of the treatments, with the exception of the acidified flyash, had P-values of close to or less than 0.05, which implies significant differences between the treated and untreated flyash at the 95% confidence level. Because the P-values are so close to 0.05, the differences are significant, but not greatly so while the acid treatment showed no significant difference between the growth it produced and the untreated flyash yield.

Table 3.2: P-statistics for growth responses to different treatments performed on flyash

If P<CL(0.05), reject Ho and accept that a significant different exists between treatments at the 95% confidence level

Treatment	A	CP	F	SS	F+A	F+CP	SS+CP	SS+A	SS+F	CP+SS+F	SS+A+F
none	**0.126**	0.046	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
A		0.046	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
CP			0.046	0.046	**0.369**	0.046	0.046	0.046	0.046	0.046	0.046
F				0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
SS					0.050	**0.275**	**0.127**	**1.000**	0.050	**0.513**	0.050
F+A						0.050	0.050	0.050	0.050	0.050	0.050
F+CP							**0.275**	0.050	0.050	**0.127**	0.050
SS+CP								0.050	0.050	**0.127**	0.050
SS+A									0.050	**0.513**	0.050
SS+F										0.050	0.050
CP+SS+F											**0.127**
SS+A+F											

A: sulphuric acid
CP: acidic waste catalyst
F: inorganic fertiliser
SS: composted sewage sludge

Bold type signifies no significant differences exist between treatments.

Significant differences occurred when comparing treatments but the most significant differences occurred between Catpoly treatments and the others. The only treatment that the Catpoly yield was not significantly different to, was the fertiliser plus acid treatment.

Examining the effects which showed significant differences reveals that, with the exception of the Catpoly treatments, all the other statistically significant differences are determined on the basis of P-values of 0.050, which implies that any differences are only marginally significant. The treatments that do not display significantly different yields may be divided into a number of groups: the lowest yielding treatment combinations include the control and the sulphuric acid treatment. The next pair are also lower yielding treatments: Catpoly only and fertiliser plus acid. The third group are the intermediate yielding treatment combinations and include sewage sludge, sewage sludge plus acid, sewage sludge plus Catpoly, sewage sludge plus acid plus fertiliser, sewage sludge plus Catpoly plus fertiliser and the final treatment in this group, Catpoly plus fertiliser. The highest yielding treatment, containing sewage sludge plus fertiliser, performs significantly better than all of the other treatments.

3.3.3 Elemental concentrations in ryegrass grown on amended flyash

The elemental concentrations present in the ryegrass grown on amended flyash show some characteristic effects with different ameliorants and are shown in Table 3.3.

While it is important to note that the sufficiency ranges cited here (Table 3.3) apply to plants in general, they will give a general indication of the range of concentrations required for optimal plant growth.The concentrations of P present in all the plants are in the sufficiency range. The treatments containing Catpoly all result in much higher P concentrations, in the order of four times the sufficiency level. Potassium concentrations in plant material all fall above the sufficiency threshold, with most treatments containing approximately double that required for satisfactory plant growth.

The Mg concentrations produced by all of the treatments are well above the sufficiency threshold so that Mg deficiency is unlikely to have provided any restrictions to growth.

Most of the treatments result in Ca concentrations in the plant material that are within the sufficiency range for most plants. The exceptions are the Catpoly treatments which have lower Ca concentrations. This is probably due to Ca being less available due to precipitation as Ca phosphate minerals as a consequence of the surplus phosphate supplied by the Catpoly. It should be noted though, that elevated concentrations of heavy metals (Wallace *et al.*, 1966, cited in Marschner, 1990) or NaCl (La Haye and Epstein, 1971, cited in Marschner, 1990) requires that plants maintain a higher concentration of Ca in response to Ca being readily replaced by other cations at its binding sites.

Of the micronutrient elements, the plant tissue Fe concentrations fall within the sufficiency range, with exception of the sewage sludge and Catpoly treatments which occur below the sufficiency threshold. The Mn concentrations, with the exception of treatments containing Catpoly, which provide sufficient Mn for plant growth, result in plant tissue containing less than sufficient Mn for plant growth. The fertiliser, acid and fertiliser plus acid treatments produce plant material with Mn deficiencies. The Zn concentrations in plant material are also predominantly deficient, with the combination of sewage sludge and fertiliser being the only treatment to result in the plant tissue containing sufficient Zn for plant growth. The

Table 3.3: Composition of ryegrass (mean of three replications) in relation to treatment of flyash. Literature values for toxicity, sufficiency and deficiency shown for comparison.

Major nutrient elements	Elemental concentrations/ %				
Treatment	P	K	Mg	Ca	Na
control	0.2945	1.9123	0.3787	0.5156	1.3425
mean A	0.2686	1.9547	0.5395	0.5269	0.9449
mean F	0.3371	2.3319	0.4963	0.605	1.503
mean SS	0.4388	1.7246	0.3135	0.5189	1.0377
mean CP	0.8648	1.7948	0.5432	0.2323	0.5998
mean SS+CP	0.779	2.079	0.5484	0.2532	0.689
mean SS+A	0.6964	2.1608	0.418	0.5039	1.0097
mean F+A	0.3005	2.2189	0.609	0.5631	1.1681
mean CP+F	0.7442	2.4214	0.6332	0.2215	1.0457
mean SS+F	0.4945	1.9362	0.4198	0.5311	1.8943
mean CP+SS+F	0.8486	2.2731	0.8059	0.3006	1.2579
mean SS+A+F	0.4742	2.0086	0.5641	0.4888	1.5271
Toxicity threshold	2				2500-5000
Sufficiency threshold	0.2	1	2	5	
Deficiency threshold	0.3				
Analytical detection limit/ ppb	272	60	23	0.2	69

Micronutrient elements	Elemental concentrations/ mg/kg					
	Fe	Mn	Zn	Cu	B	Mo
Treatment						
control	139	27	1	39	1777	24
mean A	222	12	2	48	1647	14
mean F	242	18	4	11	1489	15
mean SS	96	22	5	26	422	5
mean CP	86	190	bdl	47	863	6
mean SS+CP	121	167	15	37	850	5
mean SS+A	156	30	16	41	780	4
mean F+A	290	14	1	40	1559	11
mean CP+F	127	143	7	7	940	4
mean SS+F	223	26	26	24	493	4
mean CP+SS+F	129	186	25	45	1103	4
mean SS+A+F	162	32	24	31	664	5
Toxicity threshold	>1000	300-500	100-400	20-100	50-200	10-50
Sufficiency threshold	100	50	20	6	20	0.1
Deficiency threshold		15-25	10-20	2-5	5-100	0.1-0.3
Analytical detection limit/ ppb	12	1.4	1.8	5.4	4.8	7.9

Non-essential trace elements	Elemental concentrations/mg/kg						
	As	Se	Pb	Sr	Ni	Si	Al
Treatment							
control	2	7	1	84	2	867	294
mean A	2	6	13	77	6	916	355
mean F	5	6	368	113	2	81	980
mean SS	1	4	2	68	bdl	58	104
mean CP	6	4	1	14	28	58	80
mean SS+CP	3	5	1	13	15	112	84
mean SS+A	1	8	2	70	5	75	101
mean F+A	2	7	2	80	2	2281	322
mean CP+F	1	7	2	9	32	72	84
mean SS+F	1	8	3	62	1	88	170
mean CP+SS+F	4	4	2	16	12	63	141
mean SS+A+F	1	6	2	62	bdl	73	180
Toxicity threshold	5-20	5-30	30-300	30	10-100		50-200
Sufficiency threshold							
Deficiency threshold							
Analytical detection limit/ ppb	53	75	42	0.8	15	31	15

Toxicity, sufficiency and deficiency values for plants in general, derived from:

McBride (1994)
Kabata-Pendias and Pendias (1984)
Wild (1993)
Logan and Chaney (1983)
Ayers and Westcot (1985)

A: sulphuric acid
F: fertiliser
SS: composted sewage sludge
CP: Catpoly

concentration of Cu in the leaves reaches potentially toxic concentrations in all treatments except the Catpoly plus fertiliser and the fertiliser treatments. Similarly, the B concentrations in the leaf material in all treatments falls within the toxic range.

The Mo concentrations are all above the sufficiency threshold with the control, acid, fertiliser and fertiliser plus acid treatments producing plant material with Mo concentrations within the toxic range. The As, Se, Sr and Al concentrations are often above the toxic threshold while for the heavy metals, Pb and Ni, apart from one treatment that elevates the concentrations into the toxic range, their concentrations are below toxic thresholds.

3.3.4 The effect of different ameliorants on elemental concentration in plant material

Some general trends occur as a result of the addition of individual ameliorants: the addition of Catpoly results in approximately three times the concentration of P present in control plant material and an increase in the Ni and Mn concentrations. This effect can be related to the decrease in pH which usually results in increased metal availability. The addition of Catpoly also results in a reduction in concentrations of Sr, Ca and Na in plant material and this is likely to result from precipitation of Ca and Na phosphate salts. Because Catpoly contains very high amounts of P, as can be seen from the XRFS analysis of Catpoly shown in Table 3.4, it is not surprising that the P concentrations in plants grown on Catpoly-amended flyash are approximately three times those from plants grown on unamended flyash.

The addition of composted sewage sludge results in one consistent effect: plants grown in sewage sludge amended flyash display reduced B concentrations. This could result from the presence of organic matter in the sewage sludge. Gluskoter *et al.*(1977, cited in Kabata-Pendias

Table 3.4: Results of XRF analyses of flyash, Catpoly, and composted sewage sludge and calculated compositions

major elements/ %	Fe2O3	TiO2	BaO	CaO	K2O	Cl	S	P2O5	SiO2	Al2O3	MgO	Na2O	Total
PFA	2.66	1.56	0.14	4.75	0.54	0.07	0.22	0.29	52.20	27.87	1.28	0.90	92.48
SS	0.66	0.20	0.03	1.63	0.32	0.60	2.03	0.77	10.18	1.85	0.28	0.01	84.56
CP	0.65	0.06	0.01	0.11	0.31	0.43	0.97	53.43	17.31	1.54	0.55	0.26	75.63
PFA + SS	2.46	1.42	0.13	4.44	0.52	0.12	0.40	0.34	48.00	25.27	1.18	0.81	91.69
PFA + CP	2.57	1.49	0.13	4.55	0.53	0.09	0.25	2.61	50.68	26.72	1.25	0.87	91.75
PFA + SS + CP	2.36	1.35	0.12	4.22	0.51	0.14	0.45	2.66	46.21	23.96	1.14	0.78	90.90
soil concentrations	0.5-5	0.1-0.9		0.0008-0.003	0.01-4.0			0.014-0.07			0.0005-0.2	0.63	

trace elements/ppm	W	Cr	Mn	Ni	V	Zn	Cu	Co	Sr	Rb
PFA	7	240	291	81	149	68	70	19	76	33
SS	0	146	505	31	23	738	191	6	4	12
CP	0	70	43	51	50	24	9	0	2	9
PFA + SS	7	231	312	76	136	135	82	18	69	31
PFA + CP	7	233	280	80	145	66	68	18	72	32
PFA + SS + CP	6	223	303	75	131	137	80	17	65	30
soil concentrations			10-4250	1-660		10-622	1-323		18-3500	
(mean)			500	30		50	20		200	

trace elements/ppm	Mo	Pb	U	Th	Nb	Zr	Y	Se	Bi	As
PFA	2	95	13	48	40	436	76	3	5	23
SS	3	102	0	0	3	104	4	13	3	12
CP	5	0	0	0	1	11	2	0	0	24
PFA + SS	2	96	12	43	36	403	69	4	5	22
PFA + CP	2	91	12	46	38	417	72	3	4	23
PFA + SS + CP	2	92	11	41	34	382	65	4	4	22
soil concentrations	0.013-17	1.5-189						0.005-2.32		0.4-95
(mean)	2	30						0.4		8

Soil concentrations sourced from:	Kabata-Pendias (1985) Wild (1988) Tisdale et al. (1985)

and Pendias, 1984) suggested that B is an element that has a particularly high affinity for organic matter. As a consequence of this, the elevated organic content of sewage sludge may provide a sorptive medium to reduce the bioavailability of B.

The use of sulphuric acid as an ameliorant has a varied effect. When flyash is acidified, there is no significant effect on the B content compared to unamended flyash. Fertiliser has a similar effect. A different effect arises when Catpoly or sewage sludge are added to flyash as ameliorants: the B concentration reduces. As a consequence, the B content of ryegrass grown on amended flyash is, approximately, a sum of these separate effects.

The effect of the addition of fertiliser to flyash impacts on the elemental concentrations of plant material grown on amended flyash in several ways. The addition of fertiliser increases Al uptake by the plant, but sewage sludge and Catpoly tend to decrease it so that a cancellation of effects may occur. An increase in Fe and a slight increase in P also result from the addition of fertiliser. This is not surprising, since fertiliser was expected to provide plant available P. The level of foliar P is, however, significantly less than that provided by Catpoly. The K content of plants grown on fertiliser-amended flyash is increased, but sewage sludge combined as an ameliorant with either acid or Catpoly increases foliar K to a far greater extent. The Mg content of the ryegrass is improved by the addition of each of the ameliorants, but the combination of Catpoly, sewage sludge and fertiliser has the greatest effect.

Foliar Cu was reduced in some cases due to the addition of fertiliser, but sulphuric acid counters this reduction when these two ameliorants were combined. The combination of fertiliser and sewage sludge does not alter plant K concentrations, whereas acidifying with either Catpoly or sulphuric acid increases plant K content, as mentioned above, but the quantity of K alters less than the concentrations of many other elements.

The addition of ameliorants appears to have little effect on the uptake of As and Se. The Mo content of plants grown on unamended flyash is reduced by all the ameliorants. It is interesting to note that the three treatments with the highest foliar Si content are flyash only, flyash and sulphuric acid and flyash with acid and fertiliser. It should, however, be borne in mind that Si present in ashed plant material is not all likely to dissolve during the acid digestion so that the plant Si concentrations should be viewed in a comparative, semi-quantitative sense, rather than an absolute indication of the Si originally present in the plant tissue. Tinker (1981, cited in Kabata-Pendias, 1984) suggests that Si uptake by grasses is a passive process which implies that the plant concentration of Si is proportional to the soil solution concentration. Kabata-Pendias (1984) suggests that Si solubility increases with increasing pH and this is consistent with the observed Si concentration in the unamended flyash treatment, since it has the highest pH value. The flyash and acid treatment has a pH of 8.10, so the high Si concentration is also not surprising. The treatment with the highest Si concentration is difficult to explain as it has an intermediate pH value (7.78) while three other sewage sludge treatments had higher pH values but had lower Si contents in the plant matter. Silica interacts with the uptake of other elements (Kabata-Pendias, 1984), with plant contents of B, Mn and Fe having been reported to be reduced by Si.

In the present case, the Mn concentrations are reduced by those treatments which resulted in the highest Si contents, but the uptake of B and Fe appear to be unaffected.

3.3.5 Factors influencing dry matter yield in ryegrass grown in amended flyash

The influence of different growth media on the production of dry matter is a complex, with the growth response representing an interaction of the different factors involved. Yield is influenced by both the chemical and physical conditions prevailing in the growth medium, with pH and salinity playing important roles in addition to direct nutritional effects. Also important are the elemental concentrations in the medium and the proportion of these elements which is available to plants.

3.3.5.1 The effect of pH on dry matter yield

The pH of the growth medium influences plant growth mainly through its mobilising or immobilising effect on elemental species. For example, higher pH values result in reduced bioavailable concentrations of P, Fe, Mn and Zn (Rowell, 1988a). Associated with alkaline soils there may be detrimental effects on the predominant cationic species. Calcareous soils often induce chlorosis in plants due to deficiencies in Fe. Plant-available P is also reduced due to precipitation of Ca phosphate minerals. If Na is the dominant cation, then osmotic stress and Na toxicity may also constitute a problem (Rowell, 1988a). Kabata-Pendias and Pendias (1984) note that reductions in the availability of metals occurs, with Zn, Ni and Pb mobility being reduced by high pH conditions. The solubility of Cu at high pH increases from its minimum at a pH of approximately 7.5 (Kabata-Pendias and Pendias, 1984). The treatments that resulted in the least reduction in pH in the growth medium are the control, acid only, fertiliser only and the sewage sludge only treatments.

The predictions made about likely effects of alkaline conditions are consistent with the observations for Cu concentrations. None of the four treatments that produced the highest pH growth conditions reduced the plant Cu concentration below the toxicity threshold. The effect of elevated pH on Mn and Zn concentrations was to produce lower plant concentrations than the treatments which resulted in lower pH growth media such as Catpoly, or combinations of ameliorants. The control, acid-treated and fertiliser-treated pots had higher plant Fe concentrations than the sewage sludge or Catpoly treatments, suggesting that factors other than pH influenced plant Fe content. The P level is also influenced by other factors, as can be seen from the low P content in the control and the acid treated pots, but the sewage sludge and fertiliser treatments had increased P concentrations. In the lowest pH treatment (CP+SS+F), the Fe concentration was reduced whereas the P, Mn, Zn and Cu concentrations were increased, as might have been predicted.

3.3.5.2 The effect of salinity on dry matter yield

The second factor to be considered for its influence on yield is salinity. It should be borne in mind however, that the plant species utilised for the growth trials could have a strong bearing on the growth response to salinity. In this case, the Italian ryegrass selected is a moderately salt tolerant species and is also moderately B- and Na-tolerant (Ayers and Westcot, 1985). Rowell (1988b) observes that moderately salt tolerant crops will tolerate EC values of up to 8 mS cm^{-1} without loss of yield. This is confirmed by Ayers and Westcot (1985), who suggest that moderately salt tolerant crops should produce a relative crop yield of approximately 95% under the most saline conditions produced during these growth trials (EC of 3.36 mS cm^{-1} in the fertiliser plus acid treatment, Table 2.3).

The relative yields for all treatments apart from sewage sludge plus fertiliser and sewage sludge plus acid plus fertiliser (shown in Figure 3.1) show the yields are well below 95% indicating that factors other than salinity influenced dry matter yield during the course of this study.

3.3.5.3 The effect of growth media composition on dry matter yield

Growth medium composition has an effect on both dry matter yield and composition. Examination of the extractable element concentrations of the unamended flyash (Table 2.8) and the HPIC analyses carried out on aqueous extracts from the various growth media, reveals that the presence of some ionic and elemental species is related to improved dry mass yields. Table 3.4 shows the results of XRFS analysis of the flyash, composted sewage sludge and Catpoly. Beneath these analyses are calculated values for the composition of the growth media when mixed in the proportions described in section 3.2.2. Also included in Table 3.4 are literature values for a range of soil elemental compositions to allow an understanding to be gained of which elements are likely to be excessive or deficient in the artificial growth media used in this study. Table 3.4 shows that the concentrations of Ca, P, Mg, Na, Ni, Cu, Pb and Se present in most of the growth media are higher than those normally present in soils. By examining the relative yields shown in Figure 3.1 (and the raw data from Appendix I) and relating them to the ionic concentrations in Tables 2.6 and 2.7, two correlations may be obtained. When regression analysis is performed on the NO_3^- concentrations against dry matter yield, a significant correlation results, with the r^2 value for the correlation being 0.67, where n=12.

This is consistent with Marschner's (1990) suggestion that N affects plant growth more than any other plant nutrient, where the soil N concentration is high, so that the resulting positive correlation is not unexpected.

The other correlation between soluble ionic species and dry matter was that of K^+ (r^2 of 0.39, where n=12), which, however, was not significant at the 95% confidence level.

When relationships are sought between the foliar composition and the yield some significant correlations do emerge. Figure 3.4 shows plots of the concentrations of P, Mo, B, Zn and K against yield of ryegrass. Regression analysis of the foliar P vs yield plot produced an r^2 value of 0.28 (n=36). The P data are subdivided into two groups because of the extreme concentration of P provided by the addition of Catpoly. The Catpoly treatments are therefore excluded from the regression analysis. Rowell (1988a) suggests that P availability is often low in calcareous soils and according to Marschner (1990), P should constitute 3000-5000 mg/kg of plant mass, with Wild (1993) suggesting that 2000 mg/kg is adequate for plant growth. The P content present in the plant material grown during this trial is in the range of 3000-8500 mg/kg. Elevated P levels may inhibit starch synthesis, according to Marschner (1990), and this may explain the reduced yields of the Catpoly-treated flyash mixtures. The plants grown on these treatments have the highest P concentrations but have reduced yields when compared with the same treatments excluding Catpoly, so that an excess of P could be implicated in reduced yield.

Soil P concentrations commonly range between 130-700 mg kg^{-1} (Wild, 1988). The unamended flyash contains 0.127% P while the composted sewage sludge contains 0.336% P while the fertiliser solutions applied 87.7 mg kg^{-1} P to the flyash. Catpoly contains 23.3% P, so because of the high concentration of P available from Catpoly treated flyash, the growth response of the ryegrass is not a simple linear one due to a saturation effect. This effect is explained by Michaelis-Menten kinetics (Tisdale et al., 1985) and occurs as a steep initial curve that levels out in an asymptotic manner. Examination of Figure 3.3 reveals a steep initial curve where dry matter is produced with additional P provided but when the Catpoly treatments provide more P than the plants are able to assimilate efficiently, the dry matter production levels off. The dry matter yields indicate that optimum combinations of P and other elements are provided by

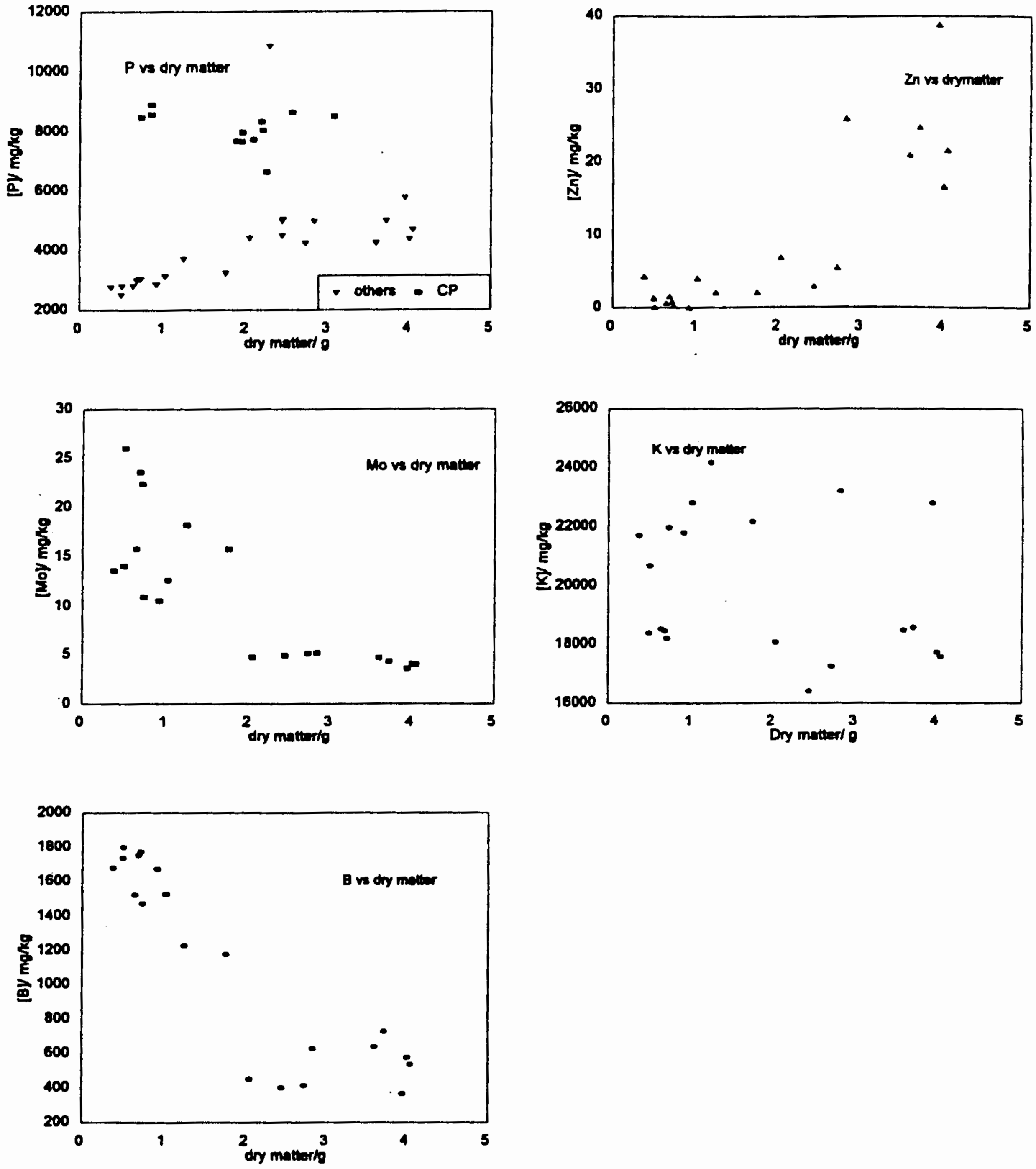


Figure 3.4: Variation in elemental concentration with dry matter produced

combinations of sewage sludge and fertiliser and when additional P is provided it does not result in increased yield.

The Catpoly ameliorant has such a large impact on plant available P for two reasons: firstly, as Table 3.4 showed, Catpoly contains in excess of 20% P and equally importantly, the mobility of P and hence the availability of P to plants is maximised in the pH range of 6 to 6.5, which coincides with the pH of the Catpoly treated growth media. Had a lesser amount of Catpoly been used, the pH would have remained higher and the Catpoly would have acted as more of a slow release source for P. An aspect of P metabolism that has particular relevance here is a report by Kabata-Pendias and Pendias (1984), that P inhibits the uptake of heavy metals by plants. Because the elevated concentrations of heavy metals in both flyash and sewage sludge are problematical, efforts to reduce plant uptake of heavy metals must be considered before plant material could be used in food production for humans or livestock.

Kabata-Pendias and Pendias (1984) note that P interacts antagonistically with a number of elements, including Al, As, B, Be, Cd, Cr, Cu, Fe, Hg, Mo, Mn, Ni, Pb, Rb, Se, Si, Sr and Zn as mentioned previously. This interaction would serve to limit the uptake of heavy metals by plants. The correlation between foliar concentrations of P and Ni has an r^2 value of 0.52 (n=12), and the correlation between foliar P and Fe gives an r^2 value of 0.45 (n=12), so there is some suggestion of influence by P limiting the uptake of some heavy metals. A complicating factor is the influence of organic matter on the mobility of heavy metals too. The interaction between metallic cations and organic matter has been reported for Mo (Marschner, 1990), Cu, Fe, Mn (Tisdale *et al.*, 1985) and Pb (Kabata-Pendias, 1984).

3.3.5.4 Interactions between foliar elemental composition and dry matter yield

Examination of the scatter plot for Zn vs dry matter production (Figure 3.4), shows a positive correlation between the two. The r^2 value of 0.61 (where n=36), confirms this correlation and shows the significance of this correlation. When the sufficiency concentrations for foliar Zn (shown in Table 3.3) are examined in conjunction with the positive correlation between Zn concentration and dry matter production, it becomes clear that the provision of Zn by sewage sludge treatments serves to correct a deficiency in the growth media that are not treated with sewage sludge. This results in a positive growth response from the plants.

The Zn deficiencies present in some of the treatments can be explained by two effects reported by Kabata-Pendias and Pendias (1984). The first is that at higher pH values, Zn tends to be immobilised by adsorption, which is consistent with the low Zn concentrations present in the control, sulphuric acid, fertiliser and the fertiliser plus acid treatments, all of which have pH values of approximately 8.

The second effect is the tendency of Zn to be immobilised by clays and soil organic matter (Kabata-Pendias and Pendias, 1984). In this instance, rather than immobilising Zn, the organic matter provided by the sewage sludge provided Zn by releasing Zn that was already sorbed during the production of the composted sewage sludge.

Wild (1988) notes that P can induce Zn deficiency, however, examining the data produced as part of this trial to determine the extent of any correlation leads to the conclusion that in the interactions of P with Pb and Zn there is no correlation as the r^2 values are 0.15 and 0.14 (n=12), respectively. This shows that P does not appear to have any effect on the Zn concentrations obtained here. This is surprising though as Marschner (1990) reported that Zn deficiencies occur where the Zn/P ratio reaches approximately 200. In this study the range in Zn/P ratios is from 190 to more than 8500. According to this criterion all but two of the treatments should be Zn deficient. This correlates well with the dry matter yield, as the sewage sludge/fertiliser treatment and the sewage sludge/acid/fertiliser treatment are not deemed to be Zn deficient, according to the Zn/P ratio, and they have the highest drymass yields. An explanation for the deficiency being not well correlated with P comes from the influence that other factors have on Zn immobilisation. Marschner (1990) notes that Zn sorbs to calcite present in soils, and in this calcareous medium, this may be a significant factor. Tisdale *et al.*(1985) suggests that Zn forms insoluble hydroxides and carbonates at high pH values and this too will limit plant availability.

The B concentrations present in all of the plants exceed the toxicity threshold reported in Table 3.3 (McBride, 1994). This is not unexpected as plants grown on flyash have previously been reported as having developed B toxicity symptoms (Carlson and Adriano, 1993).

The correlation between B concentration and dry matter yield is a negative one, as may be seen in Figure 3.4. As might be expected with an excessive concentration, the plants with the lowest B concentrations produce the best growth response, because B is after all a trace element. The r^2 value for the correlation is 0.47, where n=36. This value shows the significance of the interaction between B concentration and yield. The most effective treatments for the growth media, with regard to B, are those that reduce the bioavailable B concentration.

Kabata-Pendias and Pendias (1984) note that the addition of $Ca(H_2PO_4)_2$ and sulphuric acid to B toxic soils reduces plant available B. In this study the sulphuric acid does reduce the B concentration in plants, but not as much as other treatments. The Catpoly treatments, which are likely to indirectly to produce $Ca(H_2PO_4)_2$ by reacting with and dissolving Ca minerals present in the flyash, does have a greater effect on the B content of plants. Plants grown on Catpoly treated pots experience an approximately 50% reduction in plant B concentration when compared with the control.

Part of the problem with B in the flyash which is to be used as a growth medium is that B is a very mobile element (Kabata-Pendias and Pendias, 1984). Boron forms soluble oxyanions which allows the B to be readily taken up by plants. The sodicity of the flyash compounds the B problem since B may become co-precipitated with Mg and Ca hydroxides and also precipitates as sodium and calcium metaborate (Kabata-Pendias and Pendias, 1984). The Ca salt is relatively insoluble, but the Na one is soluble, in flyash much of the Ca is precipitated as Ca phosphate minerals and the Na is mobile so that the Na-metaborate is likely to form and retain B mobility.

The most effective immobilising amendment for B is composted sewage sludge. The sewage sludge treatments produce plant material with approximately 25% of the B present in the control, even when other ameliorants offset some of this B immobilisation, the resulting treatment still has a reduced B concentration in the plant matter.

It is interesting to note that different plant species are able to grow under conditions where they accumulate elevated B concentrations. John *et al.* (1977, cited in Kabata-Pendias and Pendias, 1984) reported spinach, admittedly with a reduced yield, but growing with B concentrations of 348 to 990 ppm B. This is consistent with field observations of wild spinach growing on the flanks of a flyash dam in Secunda (Figure 3.5).

Figure 3.5 Flyash dam associated with SASOL's Secunda gasification operation showing wild spinach growing on the flanks of the ash dam

Like B, Mo is extremely mobile under high pH conditions and its uptake by plants is directly proportional to increasing pH (Wild, 1988). The regression of the foliar Mo vs yield was significant (r^2 of 0.44, n=36) and this can be can be seen from the scatter plot in Figure 3.3. Mo becomes immobilised by organic matter in the same way as B does, although it is less readily complexed by organic matter than B (Kabata-Pendias and Pendias, 1984). Molybdenum also becomes precipitated by $CaCO_3$ or other divalent cations (Kabata-Pendias and Pendias, 1984) and this is consistent with the observed concentrations in the different treatments.

Foliar Mo concentrations are reduced in treatments containing sewage sludge and this is consistent with sorption by the organic matter as reported by Kabata-Pendias and Pendias (1984). Treatments containing Catpoly also have a reduced foliar Mo concentration and this is likely to be due to precipitation of MoO_4^{2-} as Ca salts (Davies and Jones, 1988) where Ca^{2+} ions are released by dissolution of Ca minerals by phosphoric acid present in the Catpoly.

3.3.5.5 Boron toxicity occurring as a consequence of plants growing in flyash or sewage sludge amended growth media

Boron toxicity is often a consequence of plants associated with flyash or sewage sludge (Townsend and Gillham, 1975; Hodgson and Buckley, 1975; Shukla and Mishra, 1986; Sale *et al.*, 1996; Carlson and Adriano, 1993; Ghodrati *et al.*, 1995).The concentration of B associated with phytotoxicity varies between plant species and McBride (1994) suggests toxic concentrations occur in the range of 50 - 200 mg kg^{-1}. Kabata-Pendias and Pendias (1992, cited in Sale *et al.*, 1996) however, describe ryegrass with B concentrations of 430 mg kg^{-1} and not showing B toxicity symptoms. This is consistent with the findings of Bester (1993), who found that ryegrass grown on two different soil types developed B toxicity symptoms once the plant dry matter concentration reached 514 - 708 mg kg^{-1}, depending on the soil type. The plant materials grown during this trial contained B concentrations in the range of 400 to 1600 mg kg^{-1}. This indicates that, with the exclusion of the sewage sludge plus fertiliser, sewage sludge only and sewage sludge plus acid plus fertiliser treatments, all the other treatments would be expected to produce toxicity symptoms. The correspondence of the best dry matter yields with sub-toxic B concentrations is apparent. The two highest yielding treatments, sewage sludge plus fertiliser and sewage sludge plus acid plus fertiliser have leaf B concentrations below the highest of the two B toxicity thresholds reported by Bester (1993). The sewage sludge only treatment has the fourth highest dry matter yield and has the lowest B content. The only treatment to result in high growth yields accompanying a phytotoxic B concentration is Catpoly plus sewage sludge plus fertiliser. This treatment produced the third highest yield but has B concentrations in foliage of 1103 mg kg^{-1}, which is well above the toxic threshold. The reason for this yield under potentially adverse conditions may be related to the ameliorants present.

Catpoly reduced the pH and increased the P content while the fertiliser provided N, K and Mg. As a consequence, elemental deficiencies were unlikely to occur for these elements. A similar situation arises for Zn since sewage sludge coupled with the acidifying effect of the Catpoly provides plant available Zn. The toxic effects due to the elevated B concentration are likely to be reduced due to sufficiency in other growth requirements.

Kabata-Pendias and Pendias, (1984) suggest that toxicity symptoms include plants accumulating B at leaf tips or margins and these portions become chlorotic and progressively necrotic with browning of leaf tips and decaying of growing points. Sale *et al.*(1996) note that B toxicity symptoms included white leaf tips, necrosis enlarged and advancing down leaf margins with random areas on leaves becoming chlorotic and then enlarging to form necrotic spots. These observations are consistent with all of the pots grown during the plant growth trial as all displayed necrotic leaf tips and at earlier stages, mottled, chlorotic patches towards the ends of the leaves, which progressively became necrotic as may be seen in Figure 3.6. Figure 3.2 also shows the necrotic leaf tips, which are due to B toxicity, and are present in all of the pots. Davies and Jones (1988) note that B in soils is sometimes associated with organic matter and this is consistent with observations made during the growth trial where the lowest plant B content occurs where the flyash is treated with composted sewage sludge only. Because at higher pH values B forms soluble borate salts, the flyash treated with acidifiers, such as sulphuric acid and Catpoly, should have tended to reduce the B mobility, but this was not reflected in the B concentrations in plant matter shown in Table 3.3.

Figure 3.6: Ryegrass grown on amended flyash, displaying necrotic leaf tips and patches within the necrotic region.

3.5.5.6 Explanations for the effectiveness of different ameliorants

The treatment that provides the best growth is sewage sludge plus fertiliser and this can be explained in terms of the chemical and physical properties of the amendments. The addition of composted sewage sludge results in an increase in plant available N, Zn and P. Sewage sludge also reduces the availability of B and Mo which were present in potentially phytotoxic concentrations in the control. The treatments containing fertiliser also received additional N and P but often resulted in additional salinity being introduced to the soil solutions, but based on the yields produced, not in sufficient quantities to limit plant growth response.

The other two ameliorants resulted in a detrimental effect on plant growth and like the beneficial treatments, the explanation has both a chemical and physical basis. Treatments containing Catpoly experienced reduction in B and Mo in plant material, but increases in the Cu, Mn and Ni concentrations of the plant material. The most detrimental effect of Catpoly treatments was the excessive supply of P which resulted in reduced yields. The treatment of flyash with sulphuric acid does not appear to mobilise nutrients to the extent anticipated and the overall effect appears to be an increase in salinity which may be sufficient to inhibit plant growth.

3.3.6 Variation in concentrations of other elements that show no clear effect on plant growth

Literature sufficiency values for K in plants varies, with Marschner (1990) suggesting that for optimal growth, plants require K to occur as 2-5% of the dry weight of plant material, while Wild (1993) suggests 1% and Bennett (1993) offers a range of values for sufficiency in turfgrasses of 1-2.5 %. In the plant material produced during this study, K occurs as between 1 and 3% of the plant matter. This is probably sufficient to ensure that plants are not developing K deficiency symptoms, but with the growth media used in this study other growth limitations are likely to restrict growth before K has any effect.

For optimal plant growth, Mg should constitute approximately 0.5% of the plants dry mass (Marschner, 1990). Because in this trial, Mg constitutes approximately 0.3-0.8% of the dry mass, any excess Mg will be stored and improve the nutritional quality of plants (Marschner, 1990) and this could prove to be useful if grasses grown on ash dams were ever to be utilised for stock feed, assuming all other elemental concentrations were satisfactory.

Elevated Ca is useful for detoxifying other mineral elements in plants (Marschner, 1990) and foliar Ca content varies from between 0.1 to more than 5% depending on growing conditions. The plant matter produced here falls within the range of 0.2-0.6% Ca, so the Ca concentration should be sufficient. It should be noted though, that elevated concentrations of heavy metals (Wallace *et al.*, 1966, cited in Marschner, 1990) or NaCl (LaHaye and Epstein, 1971, cited in Marschner, 1990) requires that plants maintain a higher concentration of Ca in response to Ca being readily replaced by other cations from its binding sites.

Wild and Jones (1988) report that Na is not an essential element for plant growth except in the case of some salt tolerant species. This contradicts Brownell (1979, cited in Marschner, 1990), who suggested that Na is a micronutrient for C_4 plants and in this case where ryegrass is the species grown, which is a C_4 plant, Na is an essential micronutrient. Sodium also may replace K in osmotic roles and the maintenance of turgor so in this situation (Wild and Jones, 1988), where K is not limiting, Na is unlikely to have any beneficial effect on plant growth so that the

Na concentration range of 2-7% Na is not likely to have any significant positive effect on the growth of ryegrass.

The critical level for Fe deficiency in plant leaves is 50-150 mg/kg and Fe deficiency occurring as so called lime-induced chlorosis is a common problem in calcareous soils (Marschner, 1990) and these flyash growth media could be considered as calcareous soils so this is worth considering. Examination of the Fe levels in the leaves demonstrates that Fe deficiency may be a problem in up to half of the treatments because the Fe levels fall within the range of 85-300 mg/kg.

Manganese deficiency is unlikely to be a cause for concern in most of these amended flyash growing media, with the only exceptions being the acid only and the fertiliser plus acid treatments. Usually Mn deficiency is restricted to highly leached tropical soils or high pH soils with high organic matter content, neither of which applies to flyash, even if ameliorated with sewage sludge at the rates used here. Critical deficiency of Mn occurs in the range of soil concentrations of 10-20 mg/kg. All of the other growing media used here fall within the range of 15-200 mg/kg Mn so it is possible that the treatments using acid, fertiliser and fertiliser plus acid were deficient in Mn, which correlates well with the reduced dry matter yields. It is important to note that Mn availability in plants is negatively correlated with increasing pH and positively correlated with increasing organic matter (Kabata-Pendias and Pendias, 1984). This is in good agreement with the highest Mn concentrations occurring in flyash amended with Catpoly and sewage sludge. Wild (1988) also suggested that there should be a correlation between P and Mn and the r^2 value for this is 0.79 (n=12), displaying support for the influence of P on the immobilisation of heavy metals.

The Cu concentrations in plant matter are relatively constant compared to the control with the only exceptions being the fertiliser and fertiliser plus Catpoly treatments that result in a reduction in Cu concentration.

In the case of Sr and Al, the concentrations are relatively constant for all treatments except Catpoly which causes a drop in the Sr and Al concentrations. In the case of Ni the values are relatively constant until Catpoly is added, but it has the opposite effect to the Sr and Al situation in that the Ni concentration increases noticeably.

The concentration of Pb remains relatively constant, but the mean value reported for the fertiliser treatment includes one outlier value that is two orders of magnitude larger than the other two pots which had received the same treatment. The acid treatment is the only other treatment to provide an increased Pb concentration and this consistent with predictions made by Kabata-Pendias and Pendias, (1984) suggesting that lowering pH would increase the mobility of divalent cations. Other divalent cations, such as Zn and Ni, must have been influenced more by other effects opposing the mobilising effect as their concentrations do not appear to obviously increase. The concentration of Si in the plant matter remained comparatively constant for all treatments except the control, acid only and fertiliser plus acid where the values increased. The concentrations of Se and As remain approximately constant for all treatments but the As concentration is lowered by the effect of composted sewage sludge. Analyses were performed for Be, Cr, Co, Cd and V but the values obtained were consistently below detection limits.

3.4 Conclusions

The amendments to flyash as a growth medium by combining different ameliorants resulted in improvements in dry mass yield in all cases except the sulphuric acid only treatment. The most significant improvement was produced by the combination of composted sewage sludge and fertiliser. The reason for this is probably due to improvements in plant available N, Zn and reduction of B concentration to below the toxic threshold. While P and K may also be improved the correlation is not so clear. The sewage sludge plus fertiliser treatment also had the effect of reducing phytotoxic concentrations of B and Mo. Other physical soil improvements may also have occurred too with improved MHC, permeability and increases in bacterial populations but they are much more difficult to quantify.

The acidifying treatments resulted in no increases in yield over that produced by the sewage sludge plus fertiliser. The likely reasons for this are twofold: in the case of the Catpoly a gross excess of P was provided to the growth medium and this resulted in excessive P being present and resulted in an inhibition to further productivity. In the case of the sulphuric acid treatment a dramatic increase in salinity resulted in the EC value tripling and then approaching a critical level for moderately salinity tolerant plants and this resulted in a reduction in yield.

No evidence was found of a beneficial effect of the inclusion of the acidifying ameliorants without further work being undertaken to correct the excess salinity or elevated P concentrations generated by these ameliorants. Clear evidence exists for the benefit of using composted sewage sludge especially in combination with inorganic fertiliser.

Chapter 4 Assessment of the potential for oxidation of elemental sulphur in flyash by laboratory incubation

4.1 Introduction

The use of sulphur to acidify soils has been widely practised (Cifuentes and Lindemann, 1993; Cowell and Schoenau, 1995; Tyagi *et al.*, 1994; Chapman, 1989; Modaihsh *et al.*,1989; Bole, 1986; Neilsen *et al.*, 1993; Janzen and Brettany, 1987a). Some work had been done prior to the commencement of this study (pers. comm. H.A. Dodds, 1996) which indicated that the rate of oxidation of S added to flyash was likely to be too slow to make it feasible as a treatment in the growth trial, as reported in Chapter 3. A separate trial was therefore instituted to investigate the rate of S oxidation in flyash as well as the influence of amending flyash with composted sewage sludge, since the presence of sewage sludge has been reported to significantly accelerate oxidation of sulphur (Cowell and Schoenau, 1995). The purpose of this trial was to ascertain the extent to which S oxidation would lower the pH of the flyash as this was expected to result in a number of improvements to flyash as a medium for plant growth. A lowered pH would be expected to increase the availability of P, Fe, Mn and Zn to plants (Rowell, 1988a) while reducing the availability of Cu, B (Kabata-Pendias and Pendias, 1984) and Mo (Wild, 1988). While Chapter 3 reports that the addition of sulphuric acid resulted in increases in soil salinity, Rowell (1988b) suggested that the incorporation of S and organic matter would improve soil porosity. This, would in turn, enhance leaching and thus make it possible to remove excessive sodicity, so that the acidification may still prove to be beneficial for plant growth in a situation where free drainage and leaching occur.

In this situation, the usefulness of elemental S as a potential ameliorant of alkaline flyash could be confirmed.

4.2 Materials and methods

4.2.1 Preparation of pots for sulphur oxidation trial

The investigation into the oxidation of sulphur in flyash involved six different treatments, as can be seen in Table 4.1.

Table 4.1 Treatments utilised during the sulphur oxidation trial

Pot Contents	Quantities
flyash only	1000g PFA
flyash + sulphur	1000g PFA + 6g S
flyash + double sulphur	1000g PFA + 12g S
flyash + composted sewage sludge	900g PFA + 100g SS
flyash + composted sewage sludge + sulphur	900g PFA + 100g SS + 6g S
flyash + composted sewage sludge + double sulphur	900g PFA + 100g SS + 12g S

The ameliorants utilised during this experiment consisted of elemental S and composted sewage sludge. The quantity of S added was an equivalent amount to that contained in the sulphuric acid added during the plant growth trial, described in Table 3.2. Because this quantity of S assumes 100% S oxidation, a rate which was thought unlikely to occur in reality, a second S treatment was undertaken utilising double the quantity of S.

To improve bacterial oxidation of the S, a pinch of soil was added to each mixture to provide an inoculation of soil bacteria in case they were not naturally present in flyash (Rippon and Wood, 1975; Klubek *et al.*, 1992; Carlson and Adriano, 1993). However, as this flyash was 20 years old, the bacterial populations are likely to have increased in keeping with Odum's postulate (Odum, 1969) that "diversity increases with maturity".

As can be seen from Table 4.1, the experiment was designed to allow comparison of the effect of composted sewage sludge on S oxidation at the two different rates of S application. Where composted sewage sludge was utilised as an ameliorant, it was applied at the rate of 10% by mass, and replaced an equal mass of flyash, so as to retain an equal total mass for the treatment.

In each case, the flyash and ameliorants were combined in a plastic bag and were mixed by shaking extensively to ensure homogeneity of composition. Each treatment was then subdivided into eight 100 cm^3 plastic pots. Each pot was wrapped in paper to exclude light passing through the side walls of the pots, since this may have resulted in increased soil temperatures or even photo-oxidation of sulphur that would not have occurred below the surface in a soil column. After the individual pots were prepared, they were watered to 60% of the MHC determined for the flyash after the first wetting/drying cycle, as shown in Table 2.9. The reason that the lower MHC value was chosen is, that with such small pots, it was important to avoid creating anaerobic conditions, under which bacterial oxidation would decline or cease entirely. During the trial, the pots were watered daily to an accuracy of plus or minus 2g of the original mass after potting.

The oxidation took place in the phytotron under the same conditions described for the plant growth trial in section 3.2.3 and the trial lasted for eight weeks. Each week, a single container from each treatment was removed from the phytotron for analysis.

4.2.2 pH and EC analyses

Weekly pH determinations in both 1M KCl and in deionised H_2O were carried out and EC determinations were made (section 2.2.1). Samples were obtained after tipping the entire pot contents out onto a sheet of paper and thoroughly mixing with a spatula. The precision of the pH measurements was determined in a separate investigation detailed in Appendix II.

4.2.3 HPIC analyses for SO_4 concentration in amended flyash

Sulphate was determined by ion chromatography, as described in chapter 2, in a 1:1 aqueous suspension of each of the treatments, sampled in the first and eighth weeks. These suspensions were shaken for 30 minutes, then centrifuged for 30 minutes at 6000 rpm and the supernatant decanted off. The supernatant was then diluted to give an EC of <100 µS cm^{-1} before filtration through a 0.2µm filter, prior to analysis by ion chromatography.

4.3 Results and discussion

4.3.1 Results of sulphur oxidation trial showing variation in pH, EC and SO_4 concentrations

The results of the sulphur oxidation trial are shown in Figure 4.1 and in Table 4.2. The graphs of the pH and EC (Figure 4.1) allow a visual interpretation to be made of changes in pH and EC that occurred over time and these can be related to the changes in SO_4^{2-} concentrations from Table 4.2.

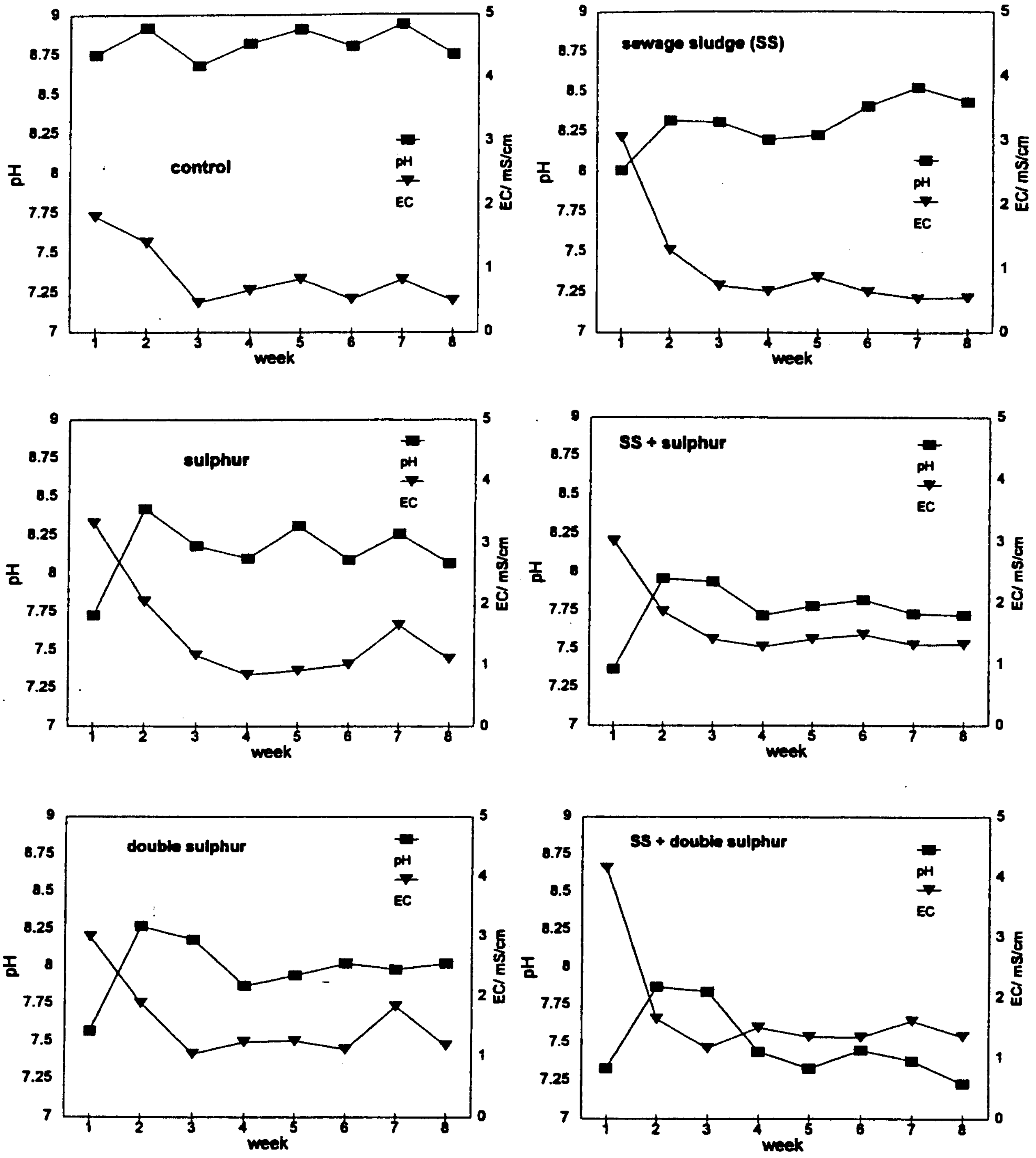


Figure 4.1: The variation of pH and EC with time of suspensions of flyash subjected to different treatments

Table 4.2 Variation in SO_4^{2-} concentration (mg l^{-1}) over the period covered by the S oxidation trial

Treatment	Week 1	Week 8
flyash only	52	313
sulphur	845	870
double sulphur	1167	1280
sewage sludge	60	6
SS + sulphur	845	1286
SS + double sulphur	2113	2150

4.3.2 Variation in pH with differing amendments to flyash

The pH determinations were made in both deionised H_2O and 1M KCl but the values are similar enough that discussion of the results is based around the pH (H_2O) and the pH (KCl) results have been consigned to Appendix I. The pH results, in all cases except unamended flyash, begin with an initial dip in pH from the value occurring in the unamended flyash, due to acidification when the acidic ameliorants were added to the flyash. The pH then increases over the following week. While no pH and EC measurements were taken from freshly mixed ameliorant combinations, one sewage sludge/double S sample was prepared to give an indication and this value is combined with those of the individual ameliorants and they are shown in Table 4.3.

Table 4.3 Variation in pH and EC values of the unmixed materials and a mixed combination of composted sewage sludge and double S.

	$pH(H_2O)$	pH(KCl)	EC/ $mScm^{-1}$
PFA	8.64	8.54	0.71
Sulphur (S)	4.45	4.22	1.33
Composted sewage sludge (SS)	4.56	4.36	2.54
Freshly mixed SS+double S	6.79	not determined	1.03

The immediate acidic effect, assumed to have been operating in the first week as suggested by the low pH of the freshly mixed sewage sludge/double S treated sample shown in Table 4.3, is countered by the alkalinity present in the flyash which results in an increase in pH over subsequent weeks until an equilibrium value is obtained.

In the case of the sewage sludge/double S treatment, the pH rose from 6.79 at mixing to a maximum of 7.87 in the second week, then down to a mean value of 7.37 in the following weeks (Figure 4.1). The values observed in the second week are the maxima obtained by most of the acidification treatments before pH declined to an equilibrium value. While some pH oscillations were observed in some weeks, these were either due to variations in the flyash composition or to differences in the amount of water present in the flyash mixture. Huberty and Haas (1940) and Chapman (1941, both cited in Van Lierop, 1990) note that differences in water content can make a difference of up to 0.5-1.5 pH units. The pH in the unamended flyash, as might be expected, remained the highest of all the treatments with a consistently high mean value, averaging $pH(H_2O)$ 8.82 for the whole trial.

The treatment with sewage sludge showed the next highest pH. Here, the mean pH value was 8.35, excluding the first week (where pH is low due to the acidic nature of the sludge). The mean equilibrium pH values of all S treated samples were calculated without including the initial pH value. The values obtained for sewage sludge treated samples are lower at both S application rates, when compared to the samples treated with S only. For the samples containing a S concentration equivalent to that of the plant growth trial, the mean pH values were 8.16 for the S only treatment and 7.75 for the sewage sludge treated sample. In the double S treatment, however, the values were 7.97 for the S only and 7.37 for the sewage sludge treated sample. This is clear evidence that the addition of sewage sludge results in a greater reduction in pH than the addition of S alone. Part of this effect may be due to the mildly acidic nature of the sewage sludge, but a far more likely cause is the bacterial oxidation of S once the acidity introduced by the sewage sludge has been neutralised by the flyash.

Normally, the pH of a weathered flyash suspension is around 8 (Townsend and Gillman, 1975). This is consistent with soils containing free $CaCO_3$, which have a pH in the range of 7.0-8.4 (Rowell, 1988a). Drever (1988) commented that most natural waters in equilibrium with calcite have a pH in the range of 7.3-8.4, where P_{CO2} is in the range of 10^{-2}-$10^{-3.5}$ atm. Preliminary analyses in this study demonstrated that calcite was indeed present in the flyash. This evidence was obtained from both the ubiquitous "fizzing" of dilute HCl on the flyash, as well as a preliminary XRD scan (Appendix I). If equilibration with calcite was the only factor influencing the pH, then the pH should lie in the range of 7.0-8.4 as mentioned above.

However, the mean pH of unamended flyash is 8.82, which suggests that some other form of alkalinity is present. The sodic nature of the amended flyash mixtures suggests that it is likely to be sodium bicarbonate. Rowell (1988a), notes that soils containing Na_2CO_3 have a pH between 7 and 10.5, although most dissolved CO_2 will be present as HCO_3^- at the pH range discussed here (Drever, 1988). This is consistent with the pH values observed here. As a consequence it is likely that the pH of the system is being influenced by both $CaCO_3$ and $NaHCO_3$.

Oxidation of S results in a drop in pH initially, as might be expected because S oxidation occurs more rapidly under higher pH conditions and the rate of acidification increases until bacterial metabolism ceases (Janzen and Brettany, 1987b; Chapman, 1989). Cifuentes and Lindemann (1993) report that in a calcareous soil, which flyash might reasonably be compared with, the buffering capacity of the calcite causes the pH to climb again. This allows the oxidation process to recommence, but at a lower rate than the initial stage when there was abundant S available. These dynamics eventually result in an equilibrium pH value between that associated with the lower S oxidation rate and that associated with the buffering capacity of the calcite present.

Sulphur oxidation in calcareous soils is a slow process which may take years to go to completion (Cifuentes and Lindemann, 1993). Lindemann *et al.* (1991) note that even with high S concentrations, the pH of a calcareous soil only reduced to a value in the range of 7.4-7.6.

Janzen and Brettany (1987a) suggest that there is a limit to the quantity of S that can be oxidised by bacteria growing in any particular medium and this threshold is controlled by a combination of soil properties such as pH, porosity, grain size, initial extractable SO_4, organic carbon, P and soil moisture.

A factor that is likely to influence the extent of HCO_3^- production in these systems is the bacterial production of CO_2 during respiration. Heterotrophic bacteria produce CO_2 during their metabolic respiration of organic carbon. This will result in an elevated P_{CO2} in the soil air and a higher concentration of HCO_3^- in soil solution. The HCO_3^- concentrations in the flyash systems (Table 2.7) reveal that sewage sludge amended flyash has an elevated HCO_3^- concentration, as predicted. Furthermore, the presence of P increases the rate of bacterial oxidation of S (Modaihsh *et al.*, 1989; Janzen and Brettany, 1987a) so that in a field trial where P is supplied, either as inorganic fertiliser or as Catpoly, the HCO_3^- concentration is likely to be even higher than where P is absent. The acidifying effect of S oxidation would therefore need to be rapid to overcome this, or as Lindemann *et al.* (1991) suggested, the availability of micronutrients or P to plants would not increase sufficiently for efficient plant growth.

4.3.3 Variation of electrical conductivity (EC) with time as result of different amendments

All of the EC values displayed a consistent downward movement during the first two weeks but then levelled out at an equilibrium value, so a mean is calculated. The high initial EC value is probably due to high ionic concentrations in the flyash mixture as a result of the initial introduction of water during the preparation of the trail pots.

Dissolution of preexisting crystalline mineral species may also have occurred as a result of the production of sulphuric acid by S oxidation. As time progressed, precipitation resulted in reduction in the quantity of ions remaining in solution. As expected, the unamended flyash produces the lowest mean EC value at 0.63 mS cm^{-1}, while the sewage sludge amended sample was not a great deal higher with a value of 0.66 mS cm^{-1}.

The production of sulphuric acid results in an increase in the EC value (Modaihsh *et al.*, 1989) due to the dissolution of previously crystalline minerals (Cifuentes and Lindemann, 1993). Calcareous soils, which should include these flyash mixtures, tend to precipitate sulphate (Cifuentes and Lindemann, 1993) and phosphate salts (Gray and Schwab, 1993), which will decrease the EC to a value controlled by the solubility of the salts present. Lindemann *et al.* (1991) suggested that addition of high S concentrations would only result in a low to moderate increase in EC (in the order of 2 mS cm^{-1}) due to the slow rate of S oxidation. In this study, the addition of sewage sludge accelerated the oxidation rate so that an increase in ionic species is likely to have occurred which in turn may increase available micronutrients, contrary to the suggestion of Lindemann *et al.* (1991).

These results are not surprising as Cifuentes and Lindemann (1993) reported that the addition of sewage sludge would tend to increase the EC of a soil. Since flyash is a considerably more saline medium than most soils, the proportion of salts present in the sewage sludge that become dissolved in the soil solution appears to be minimal. Thus the sewage sludge amelioration of flyash appears to have a minimal impact on the EC value of the combined mix. Once S is added to the flyash, though, the EC values increased.

Ignoring the high EC values during the first week, the single S treated flyash has a mean EC value of 1.12 mS cm^{-1} and the double S treatment has an EC value of 1.27 mS cm^{-1}. When the flyash was treated with sewage sludge in combination with S, the single S sample has a mean EC value of 1.37 mS cm^{-1} while the double S treatment is 1.39 mS cm^{-1}. The freshly mixed double S/sewage sludge mixture had an EC value of 1.03 mS cm^{-1}. The additional salinity present at the end of the first week, as indicated by an EC value of 4.15 mS cm^{-1}, could be due to bacterial oxidation of S and the dissolution of pre-existing minerals in the sulphuric acid produced by the oxidation.

The general trend in the EC curves may be that any portlandite initially present in the flyash reacts with atmospheric CO_2 and becomes converted to calcite. Since calcite has a lower solubility this conversion results in a reduction in EC as the calcite precipitates (Snoeyink and Jenkins, 1980).

4.3.4 Variation in SO_4 concentration with different flyash treatments

The HPIC analyses of aqueous extracts taken from the different flyash and S treatments reveals obvious differences in the way the SO_4 concentrations altered over the 8 weeks of the study. The concentration of SO_4 is controlled by the rate of oxidation of S. The oxidation of S would continue and the pH would drop as the rate of S oxidation was affected by acidic conditions, which then limits the rate of bacterial metabolism (Gupta *et al.*, 1988, cited in Cowell and Schoenau,1995; Cifuentes and Lindemann, 1993). Cowell and Schoenau (1995) suggested that bacterial S oxidation occurred while the concentration of SO_4 remained less than 100 mg S kg^{-1} soil but once the SO_4 concentration exceeded this the rate of SO_4 production will level off.

Examination of the SO_4 values shows that oxidation of sulphur did occur, although it should be noted that the interphase sulphur contained 181 ppm SO_4, in an extract produced in the same manner as the flyash extracts. As a consequence, addition of sulphur to the flyash mixtures, even in the 0.6 or 1.2% proportions applied, resulted in a significant initial input of SO_4 to the flyash mixtures. In the flyash with no sulphur additions significant SO_4 production occurred during the trial and this is a reflection of the S content in the flyash. The XRF analyses, in section 2.2.3, showed that the flyash contains between 0.12 and 0.34% S and this is consistent with literature values of 0.1 to 1.5% (Sharma *et al.*, 1989) and 0.04 to 6.44% (Mattigod *et al.*, 1990), where the upper limits include acidic flyash sourced from high S coals. In both the single and double S treated flyash samples, in excess of 90% of the S was present as SO_4 at the end of the first week. This is due to SO_4 being added with the sulphur initially, followed by oxidation of both interphase S and flyash associated S.

If the flyash used was the most S rich, and the pot had only been subjected to the single S treatment, oxidation of the S present in the flyash may contribute as much as 57% additional S to that supplied by the treatment. It is evident though, that most of the S oxidation occurred during the first week since, over the following 7 weeks, only an additional 25 ppm of SO_4 was produced in the case of the single S treatment and 113 ppm in the double S treatment. In the case of the sewage sludge treatment, without further S, the SO_4 concentration drops to 10% of its initial concentration. A potential reason for this is found in the following 25°C thermodynamic data (Ebbing and Wrightson, 1993):

$$\begin{array}{ll}
SO_4 \rightarrow S + 2O_2 & -\Delta_f G_{(SO4)} = +741.99\ \mathrm{kJmol^{-1}} \\
2[\,C + O_2 \rightarrow CO_2\,] & \Delta_f G_{(CO2)} = 2[-394.4\ \mathrm{kJmol^{-1}}] \\
\hline
SO_4 + 2C \rightarrow CO_2 + S & \Delta_R G \;=\; -46.81\ \mathrm{kJmol^{-1}}
\end{array}$$

The Gibbs Free Energy for the overall reaction suggests that the C present in the sewage sludge should be able to reduce SO_4 to S which could account for the reduction in the amount of SO_4. The problem with this is that chemical kinetics are not taken into consideration here so this can only be suggested as a possible explanation. A more likely explanation is that the reduction of

SO_4^{2-} is a bacterially mediated process. Charlson *et al.* (1992) describe two widely recognised genera of bacteria, *Desulfovibrio* spp. and *Desulfotomaculum* spp., which are responsible for the production of H_2S from SO_4^{2-}. Other organisms then reduce this SO_4^{2-} to elemental S.

The addition of sewage sludge increased the rate of S oxidation over the 8 week period. In the case of the single S treatment, the final SO_4^{2-} concentration increased from 870 mg l^{-1}, where no sewage sludge was added, to 1286 mg l^{-1}, when sewage sludge was added. This data supports the suggestion that the addition of sewage sludge increases the rate of S oxidation. Composted sewage sludge provides chemoheterotrophs in the flyash with the required C to undertake the bacterial oxidation of S and is itself a source of S oxidising bacteria. Organic matter is not a metabolic requirement of chemoautotrophs, but, since chemoautotrophic oxidation of S in calcareous soils is slow, by stimulating chemoheterotrophs the overall oxidation rate can be increased (Cifuentes and Lindemann, 1993). When the quantity of S added was doubled, the quantity of SO_4^{2-} produced during the first week increased from 1167 mg l^{-1}, in the treatment lacking sewage sludge, to 2113 mg l^{-1}, where sewage sludge was added. At the eighth week, the SO_4 concentration in the double S treatment without sewage sludge, had risen to 1280 mg l^{-1}, comparable to the 1286 mg l^{-1} present in the sewage sludge treated sample with only the single dose of S.

The treatment with double S and sewage sludge had apparently approached its maximum SO_4^{2-} concentration as the value had only increased from 2113 mg l^{-1} in the first week to 2150 mg l^{-1} in the eighth week.

This is consistent with literature which notes that at higher S concentrations the oxidation rate reduces (Chapman, 1989). This is because the oxidation rate is pH sensitive. At higher S concentrations the local pH surrounding the oxidising bacteria can become too acidic for heterotrophic S oxidisers (Lawrence and Germida, 1988 cited in Chapman, 1989), resulting in either a reduction in activity or bacterial mortality (Gupta *et al.*, 1988, cited in Cowell and Schoenau, 1995). Janzen and Brettany (1987b) note that S oxidation is unaffected by the concentration of S within the application range of 50-4000 mg kg^{-1}, whereas Modaihsh *et al.*(1989) found that excessive S concentrations appear to be limiting, which appears to have occurred in this case when 12 000 mg S kg^{-1} was added in the double S treatment.

Rowell (1988b) suggests applying elemental S to aid in the reclamation of saline and sodic soils, however, Cifuentes and Lindemann (1993) suggest that S oxidation in calcareous soils is a slow process and may take years to go to completion. The addition of organic matter that Rowell (1988c) also suggested, would decrease soil pH as a result of dissolution of metabolically produced CO_2 in the soil solution. In the treated flyash, this mechanism appears to have had the additional effect of increasing the rate of S oxidation, as evidenced by the increased SO_4^{2-} present in sewage sludge treated flyash compared to that lacking sludge treatment.

Sewage sludge is an acidic substance (Sajwan *et al.*,1995) (Table 4.3) and its application to flyash lowers the pH of the system. This is evident by the comparison of pH in the treatments with and without sewage sludge and having the same quantity of S added. Sewage sludge application initially results in higher EC values in soils due to the addition of ionic species contained in the sewage sludge and because its acidity promotes the dissolution of previously crystalline salts (Rodgers and Anderson, 1995). In this experiment, EC values were initially higher in the sludge treated samples, but the apparent precipitation of salts ensured that the mean EC values for all the treatments were below 1.5 mS cm^{-1}. This ensured that the experimental growth media had EC values well below the level of 4 mS cm^{-1}, which is a threshold value for salinity hazard in soils (McBride, 1994; Ayers and Westcot, 1985). In fact, Rowell (1988b) points out that while 4 mS cm^{-1} poses a salinity hazard to salt sensitive crops, moderately tolerant crops, such as ryegrass, will tolerate salinity up to 8 mS cm^{-1}. The EC values from this study show that only one of the treatments had an EC value exceeding 4 mS cm^{-1} and that was only in the first week. After that, mineral precipitation resulted in a significant decrease in EC to acceptable levels for plant growth. It should be borne in mind that sulphuric acid treated flyash resulted in a reduced yield during the growth trial due to salinity effects.

Bole (1986) states that in the absence of leaching, S addition is not an effective treatment for the reduction of soil pH due to the increase in total salts which could adversely affect plant growth. In any field situation it is likely that some leaching would occur. This includes the surface of any ash dams treated with sewage sludge and S to improve soil conditions prior to revegetation. Rowell (1988b) pointed out an unexpected benefit of the addition of S and sewage sludge as ameliorants for saline or sodic soils.

Clays in such soils tend to disperse when they encounter waters of very low salinity, such as rainwater. The consequences of dispersion include clogged soil pores, crusting, reduced water percolation, surface crusting and soil erosion. By ameliorating flyash mixtures with organic matter and elemental S, Ca minerals present in the flyash dissolve and the clays are then able to flocculate, once again restoring soil porosity and allowing leaching to commence (Rowell, 1988b).

4.3.5 Comparison of results from the elemental sulphur oxidation trial with relevant data from growth media characterisation (Chapter 2)

The S oxidation trial was undertaken to provide data not expected to be available from the plant growth trial due to the anticipated slow oxidation rate for elemental S. Therefore, it is important to examine data from the characterisation section to determine how far the oxidation had proceeded at the end of the incubation trial. It is also necessary to make a comparison between the salinity produced by the acidification with sulphuric acid and that produced by bacterial oxidation of elemental S.

To make the comparisons valid, the material being analysed must be treated in the same manner in both cases. The pH and EC values recorded during the S oxidation trial were produced using a standard 2.5:1 water:flyash-mix ratio and were determined the day after the samples were extracted from the phytotron, in which the treated flyash had been maintained at 60% MHC. The growth media characterisation values were obtained from composite samples of each of the three pots with the same treatments. These samples were collected and stored after the flyash treatments were mixed and had therefore been sitting at 35% MHC for the three weeks between collection and production of the 1:1 extracts for SO_4 determination.

The pH and EC measurements were made after the composite flyash mixes had been stored for 4 days. Variation in pH values obtained from flyash is likely to occur as the pH of a 2.5:1 unamended flyash:deionised water suspension, which equilibrated for 30 minutes, varied for 8.64 to 9.08 from 4 different samples. This variability has already been reported in Chapter 2 but is important enough to comment on once more. To allow a comparison to be made between the SO_4 from the composite samples and those from the oxidation trial, the values obtained from the 1:1 extracts used for analysis of the composite samples were divided by 2.5 to produce the same flyash : water ratio. It must be borne in mind, that a better extraction is likely to have been obtained in the more dilute extract and these data were only produced to allow a comparison to be made and should only be considered to be semi-quantitative, at best.

In the unamended flyash treatments the composite sample pH was 9.08 while the samples taken during the S oxidation trial ranged from 8.68 to 8.94 which indicates little difference between the two samples. The EC value from the composite sample was 0.961 mS cm^{-1} and the S oxidation trial values began at 1.82 and reduced to 0.50 ms cm^{-1}. This suggests that the composite sample precipitation reactions, that reduce EC values, were incomplete when the sample was analysed. The SO_4 concentrations from the oxidation trial increased from 52 mg l^{-1} in the first week to 313 mg l^{-1} at the end of the trial, which compares with a value of 263 mg l^{-1} from the composite sample. The indication for the SO_4 values is similar to that proposed for the EC values, in that the S oxidation had not yet gone to completion, since 263 lies between 52 and 313 mg l^{-1}. The pH and EC values for the composite flyash mixtures are taken from Table 2.3. The SO_4 concentrations are from Table 2.7 and the raw data for the S oxidation trial is recorded in Appendix I.

In the sewage sludge treated flyash the pH value from the composite mix was 8.11, which compares with the range covered during the 8 week trial of pH 8.01 to 8.53. The EC values for the composite mix was 1.056 mS cm^{-1}, which lies within the range of 3.04 mS cm^{-1} reducing to 0.54 mS cm^{-1} at the end of the 8 week trial. In the case of the SO_4 concentration some variation occurs between the incubated sample which was exposed to airborne bacteria by the draft present in the phytotron. Sulphur reducing bacteria appeared to be able to colonise the pots resulting in a reduction in SO_4 concentration from 60 mg l^{-1} to 6 mg l^{-1}, while the composite sample, which was placed into a closed container after collection, had a SO_4 concentration of 261 mg l^{-1}.

The single S treated flyash is compared with the sulphuric acid treated composite. The pH value for the acid treated composite is 8.10 which compares with the range of values from the S oxidation which start at 7.73 in the first week and end at 8.07 having reached as high as 8.42 before subsiding again. The EC value for the acid treated flyash mix is 3.13 mS cm^{-1}, which relates well to the SO_4 concentration of 916 mg l^{-1}. The S oxidation trial produced less SO_4, 845 increasing to 870 mg l^{-1}, and has a similar EC range which started at 3.32 and dropped off to 1.11 mS cm^{-1}. This indicates that the S oxidation during the incubation study went almost to completion and the largest proportion of the oxidation occurred during the first week.

The combined sewage sludge and S treated flyash produced a pH range commencing at 7.37 and increasing to 7.72, which is comparable to the value of 7.58 obtained from the composite acid treated flyash mix. The composite mix produced a higher EC value, 3.23 mS cm^{-1}, than the incubation trial maximum of 3.01 mS cm^{-1}, which then reduced to 1.33 mS cm^{-1}.

This is consistent with the SO_4 concentration of 864 mg l^{-1}, which is higher than the 845 mg l^{-1} produced in the first week, but less than the increase to 1286 mg l^{-1} over the following weeks. From this data it appears that the rate of S oxidation is rapid during the first week and that over the following 7 weeks the remainder of the S is almost completely oxidised and that the sewage sludge itself contributed SO_4 to the flyash mixture. This is consistent with the increased EC resulting from the incorporation of sewage sludge into flyash shown in Table 2.3.

This data confirms that the treatment of flyash with sulphuric acid has a similar effect on the growing media as the inclusion of elemental S. Because of this, it is reasonable to use the sulphuric acid treated flyash as a proxy for the way in which flyash treated with elemental S is likely to have behaved.

4.4 Conclusions

The results of this study into oxidation rates for elemental S show that the bacterial oxidation of S is an effective technique to reduce the alkaline pH of flyashes. The most effective co-ameliorant for the S is composted sewage sludge. While the sludge may contribute to elevated salinity immediately after application, in a very short time the EC is low enough and does not present a salinity hazard to most plant species. The salinity produced as a consequence of the oxidation of elemental S to SO_4 appeared to inhibit plant growth response, as reported in Chapter 3. But, the combination of elemental S and composted sewage sludge has been demonstrated in this incubation trial to reduce salinity to levels that would not produce a decrease in growth yield of even moderately salt sensitive plant species (Ayers and Westcot, 1985).

Rowell (1988b) reported that the application of elemental S and organic matter may be used to reclaim sodic soils. Applying elemental S reduces the pH of the flyash and by combining it with sewage sludge to accelerate the rate of S oxidation the pH reduction is greater. The pH is further reduced as bacterial oxidation of the SOM increases the dissolved CO_2 content of the soil solution. This acidification will result in the dissolution of otherwise less soluble Ca minerals which encourages the flyash clay particles to flocculate and thus improves porosity. As a consequence of this, in a field setting, leaching by rainfall is likely to remove any residual elevated salt concentrations, thereby ensuring more suitable conditions for plant growth. The revegetation of ash dams has traditionally required careful selection of salt tolerant crops as the pioneer species (Carlson and Adriano, 1991; Dzeletovic and Filipovic, 1995; Bradshaw and Chadwick, 1980) but this may prove to be less important if the flyash is amended by application of elemental S and composted sewage sludge prior to planting, as such pre-treatment moderates the extremes of salinity and pH present in the unamended flyash.

Chapter 5 General Discussion

Flyash, in a South African context, is an alkaline, saline material, that in a weathered state has a pH of approximately 8. The alkaline nature results in mobility of a number of different elemental species including heavy metals such as Cr, Cu, Ni, V and Zn and metalloids such as As, B, Mo, S and Se. These elements have the ability to produce toxic responses in plants grown on them so that they may provide limitations to plants growing in flyash. Another potential growth limitation associated with plants grown in flyash is elemental deficiencies. Flyash has been associated with deficiencies in Cu, Fe, Mn, N, P and Zn.

The physical properties of flyash also have a significant limiting effect on plant growth. Flyash develops a massive structure that is often compacted and may be cemented due to the pozzolanic nature of the ash. This combination of qualities results in a material which plant roots often have difficulty penetrating and this limits elemental uptake and plant anchoring.

Another quality of flyash that influences plant growth is the availability of water. In flyash this can be associated with both the impermeable nature of the ash and osmotic stresses imposed by the salinity. The low porosity of flyash has been associated with dispersion of the clay sized particles under the influence of low EC rainwater and this results in clogging of pore spaces which limits permeability.

The examination of the chemical and physical properties of the flyash utilised during this study confirms the general observations discussed above, and efforts to correct these growth limitations by combining other selected ameliorants with flyash resulted, in some cases, in improvements in growth of the plants.

The addition of sulphuric acid, Catpoly and composted sewage sludge to the flyash resulted in reductions in the pH of the mixtures. This effect resulted in an increase in the bioavailability of Al, Fe and Mn. Catpoly increased the availability of Ni and Mn but reduced the plant assimilated concentrations of Al, B, Ca, Na and Sr. An additional effect of Catpoly is to greatly increase the availability of P to plants due to its high P content and pH. This resulted in smaller growth responses than were obtained from treatments providing less extreme supplies of additional P to the growth media. The addition of sulphuric acid resulted in an increase in EC and a reduction in plant dry matter yield due to salinity effects. The most significant effect of the addition of composted sewage sludge on plant elemental concentrations is a negative one. The sewage sludge has a capacity to adsorb elements and so limit toxic effects in the growth media. The concentrations of B and Mo were reduced by the treatment of flyash with sewage sludge and only increases in P and K resulted from this addition. The overall result of the growth trial demonstrated that most treatments produced plant concentrations of Ca, Fe, K, Mg, Na and P that indicated sufficiency in these elements but not high enough concentrations to have resulted in toxicity. Most of the treatments produced B concentrations high enough to have been phytotoxic and identification of "burnt", necrotic leaf tips on all of the plants demonstrated this effect, although some of the treatments were able to overcome this limitation better than others, with fertiliser plus sewage sludge producing the best yield.

The other growth limitation identified was Zn deficiency which required the combination of composted sewage sludge and an acidic ameliorant to make additional Zn available to overcome this deficiency.

The oxidation of elemental S to SO_4^{2-} results in a decrease in growth medium pH. It was determined during this study that an increase in the rate of oxidation of S could be achieved by the addition of composted sewage sludge to the flyash/ sulphur mixture. This increased rate of S oxidation was demonstrated by an increase in EC and SO_4^{2-} concentration. The reduction to pH was slightly superadditive as the pH of the sewage sludge plus S treatment was lower than the sum of the pH reductions demonstrated in the S or sewage sludge treatments individually.

There is a limiting feature associated with the S oxidation in that when the concentration of S becomes too high, the bacterial metabolic oxidation rate is inhibited. In the higher S application rate, also treated with sewage sludge, the maximum SO_4^{2-} concentration was reached during the first week. In the absence of composted sewage sludge, the oxidation of S was a slower process and the SO_4^{2-} concentration continued to increase throughout this study, but did not reach the level attained when both sewage sludge and elemental S were present. In this study it was found that the limiting S concentration for sewage sludge amended flyash occurred between 6000 and 12 000 mg kg^{-1} S added. This was shown by the SO_4^{2-} concentration in the higher S treatment not increasing between the first and eighth weeks while at the lower rate of S application, the SO_4^{2-} concentration continued to increase throughout the investigation.

The first key question raised at the commencement of this study enquired whether the usual growth limitations imposed by flyash could be overcome by combining flyash with selected available waste products. Based on the growth trial results it would appear that the growth limitations can in fact be overcome but the inclusion of inorganic fertiliser as an ameliorant assists with this in a short term growth trial like the one undertaken here. Over a longer term it may prove to be unnecessary to repeat applications of N once bacterial populations are increased under the influence of the addition of composted sewage sludge. However, this would require further work to be confirmed.

The second key question raised enquired which of the treatments was the most effective. In the timescale of this study the combination of composted sewage sludge with fertiliser and mixed into the flyash produced the best growth response.

The third and fourth key questions asked whether the ameliorants affect the uptake of undesirable elements by the plants and whether there are interactions between applied ameliorants. There are both synergistic and antagonistic interactions between ameliorants. Sewage sludge and fertiliser interact synergistically and results in a better dry mass yield than the sum of the improvements effected by each of the treatments separately, while of the other combinations of ameliorants, three interact subadditively and another three superadditively. To improve plant Zn concentrations requires the addition of composted sewage sludge, however, a combination of both sewage sludge and one of the acidic ameliorants or inorganic fertiliser results in a more substantial improvement. The combination of sewage sludge and fertiliser suppresses foliar B and Mo but increases plant uptake of Zn, N and P.

The treatment of flyash with fertiliser alone results in an increased plant uptake of B but when fertiliser is combined with either Catpoly or sulphuric acid, the B level is not elevated. In the case of Mo the interaction is a little different as fertiliser increases plant Mo levels but the treatment of flyash with fertiliser plus acid also results in elevated Mo concentrations. Suppression of these levels requires fertiliser to be combined with either sewage sludge or Catpoly. A beneficial antagonistic interaction is that between Catpoly and sewage sludge which produced a lower Mn level in plants than was obtained from Catpoly only as a treatment for the flyash.

Because this study was undertaken on both a small scale and a short time-frame there is more work that could be done in the future to follow up on this study. As mentioned previously, future work should examine the longer term improvements to soil fertility brought about by the inclusion of composted sewage sludge in the growth media and determine whether repeated applications of inorganic fertilisers are required. Decomposing sewage sludge may be able to provide sufficient plant available N for bacteriological cycling to maintain a sufficiently large N pool in the growth medium. The advantage of this approach is that N obtained from sewage sludge would be slowly released so that less anthropogenic input would be required to maintain the media. A final area that may warrant investigation to assist in revegetating flyash dams is the recontouring of the external profile of the dams. By altering the steep flanks of the dams to a more shallow angle the surface is less likely to slough off sheets or clumps of the grass under heavy rainfall due to any difficulties grass roots may have initially penetrating the compacted ash until a deeper soil layer has had an opportunity to develop. The added advantage is an aesthetic one as the dams then assume a less artificial appearance.

The utilisation of combinations of these, or similar ameliorants should enable safe co-disposal of potentially hazardous waste materials to result in improvements to the ability of flyash dams to be successfully revegetated. This in turn would reduce the effect of the ash dams on the environment by limiting dust and hydrosphere impacts and minimise the aesthetic impact at the same time. Despite the reduced yield produced by ryegrass grown in flyash treated with elemental S or Catpoly, if the primary objective of a revegetation project was to dispose of potentially hazardous acidic waste products, then the viability of such a codisposal exercise would place less importance on the reductions in yield. Under these circumstances, the geochemical immobilisation of potentially hazardous materials has been demonstrated to be quite viable and biomass production would be less of a priority.

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Appendix I: Complete data sheets and analytical equipment descriptions

I.i Preliminary XRD scan

A preliminary XRD scan was performed on the unamended flyash to confirm that the mineralogy of the weathered flyash was consistent with those reported in the literature (Carlson and Adriano, 1993; Bosch, 1990). The analysis was performed on a Philips PW3890 x-ray diffractometer with a graphite monochromator and scintillation detector using Cu Kα radiation (λ=1.542 Å). For the analysis, the machine settings were as follows:

Voltage: 40 KV
Current: 25 mA
Scanning range: 5° to 65°
Scanning speed: 0.1° 2θ step^{-1}
Count time: 1 s
Time constant: 1
Divergence slit: 0.1 mm
Scatter slit: 1.0°

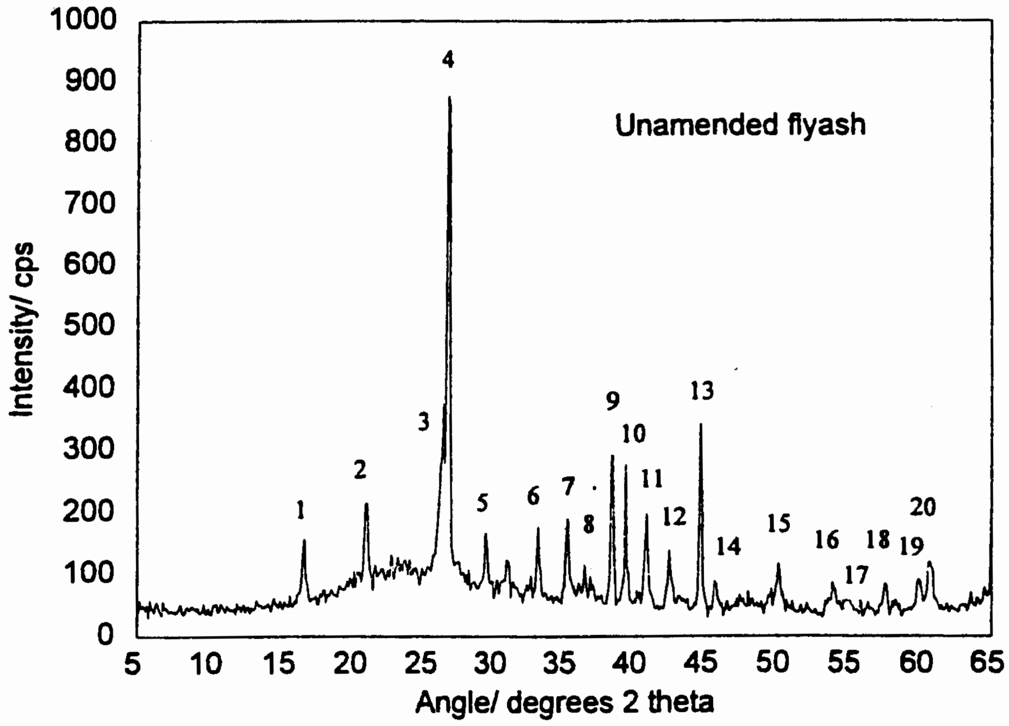


Figure I.i: Preliminary XRD scan of unamended flyash.
Legend shown in Table I.i.

Table I.i shows the legend to Figure I.i and reports the mineralogy responsible for the labelled peaks.

Table I.i : Legend to Figure I.i, indicating minerals corresponding to peaks on XRD scan.

Number	d-spacing/ Å	mineral(s)
1	5.39	mullite
2	4.210, 4.311	quartz, goethite
3	3.43	mullite
4	3.376	quartz
5	3.048	calcite
6	2.714	mullite, goethite
7	2.55	mullite
8	2.468, 2.462, 2.417	goethite, quartz, lime
9	2.338	aluminium sample holder
10	2.298, 2.292, 2.287	mullite, calcite, quartz
11	2.212	mullite
12	2.137	quartz, mullite
13	2.032	aluminium sample holder
14	1.981	quartz
15	1.824	quartz
16	1.704	lime, mullite
17	1.664, 1.675	quartz
18	1.603	mullite
19	1.549	quartz
20	1.530	mullite

I.ii Comparison of pH and EC measurements of amended flyash growth media at two different dilution rates used during this study

Table I.ii compares pH and EC values obtained from the 1:1 extracts used in the HPIC analyses with the standard 2.5:1 dilution ratio used in the remainder of the study.

Table I.i: The pH and EC values obtained from treated flyash mixtures at two different dilution rates.

Ameliorants	pH (1:1)	EC(1:1)/ mS/cm	pH H2O (2.5 : 1)	pH (KCl)(2.5 : 1)	EC(2.5 : 1)/ mS/cr
none	8.18	2.03	9.08	8.66	0.961
A	7.92	3.93	8.1	7.84	3.13
F	7.87	2.84	8.42	8.44	1.134
CP	6.21	2.36	6.38	6.33	0.788
F+A	7.6	4.74	7.78	7.8	3.36
CP+F	6.1	3.06	6.31	6.29	1.466
SS+F	7.54	3.22	7.83	7.87	1.498
CP+SS+F	5.97	3.37	6.14	6.11	1.742
SS	7.8	2.43	8.11	8	1.056
SS+A	7.53	4.25	7.58	7.52	3.23
SS+A+F	7.47	4.9	7.58	7.46	3.44
SS+CP	6.06	2.85	6.31	6.01	1.447

Ameliorants
A: sulphuric acid
F: major element nutrient solution
CP: Catpoly
SS: composted sewage sludge

I.iii Variations in alkalinity for flyash combined with various ameliorants

The results of the alkalinity titrations reported in Chapter 2 are shown in Table I.iii. The results are expressed in HCO_3^- concentrations (mmol kg^{-1}) and are then converted to mmol $CaCO_3$ equivalent at pH 4.5.

Table I.iii: Alkalinity titration data for amended and unamended flyash.

Composite Sample	[HCO3]/ mmol/kg	alkalinity/mmol CaCO3 @ pH4.
Flyash only	1.456	2.386
Flyash + sulphuric acid	1.172	1.921
Flyash + fertiliser	1.355	2.221
Flyash + Catpoly	2.417	3.962
Flyash + fertiliser + sulphuric acid	1.347	3.238
Flyash + Catpoly + fertiliser	2.356	2.418
Flyash + composted sewage sludge + fertiliser	1.658	2.718
Flyash + Catpoly + composted sewage sludge + fertiliser	2.089	3.713
Flyash + composted sewage sludge	1.975	2.208
Flyash + composted sewage sludge + sulphuric acid	1.475	3.862
Flyash + composted sewage sludge + sulphuric acid + fertiliser	1.41	3.425
Flyash + composted sewage sludge + Catpoly	2.265	2.311

Molecular mass, CaCO3 = 100g/mol
Molecular mass, HCO3 = 61 g/mol

$$\frac{\text{molecular mass, CaCO3}}{\text{Molecular mass, HCO3}} \; *[\text{HCO3}]/\text{ mmol/kg} = \text{alkalinity}$$

I.iv Results of XRFS analyses of flyash, composted sewage sludge and Catpoly

The results of the XRFS analyses performed on the individual components utilised in the growth media are displayed in Table I.iv and I.v. Table I.iv contains the major element analyses while Table I.v contains the trace elements.

Table I.iv: Major element analyses, performed by XRFS, of composted sewage sludge, Catpoly and flyash

Analyses performed on pressed powder discs with results expressed as %.

Sample	Fe_2O_3	TiO_2	BaO	CaO	K_2O	Cl	S	P_2O_5
SS	0.66	0.20	0.03	1.63	0.32	0.60	2.03	0.77
CP(20% wax)	0.52	0.05	0.01	0.09	0.25	0.34	0.77	42.74
PFA1	2.74	1.54	0.15	4.68	0.54	0.15	0.35	0.24
PFA2	2.42	1.56	0.14	4.83	0.56	0.03	0.30	0.22
PFA3	2.74	1.57	0.15	4.91	0.55	0.15	0.28	0.31
PFA4	2.66	1.56	0.15	4.75	0.55	0.05	0.15	0.29
PFA5	2.60	1.55	0.14	4.66	0.55	0.04	0.18	0.23
PFA6	2.53	1.53	0.14	5.02	0.57	0.03	0.12	0.22
PFA7	2.65	1.55	0.15	5.02	0.56	0.03	0.19	0.26

flyash replicates using glass discs:

Sample	Fe_2O_3	TiO_2	BaO	CaO	K_2O	Cl	S	P_2O_5
rep 1	2.62	1.56	bdl	4.67	0.55	bdl	bdl	0.28
rep 2	2.67	1.57	bdl	4.78	0.54	bdl	bdl	0.29
rep 3	2.72	1.56	bdl	4.86	0.54	bdl	bdl	0.29
rep 4	2.63	1.56	bdl	4.67	0.55	bdl	bdl	0.28

Analyses performed on pressed powder discs with results expressed as %.

Sample	SiO_2	Al_2O_3	MgO	Na_2O	H_2O	CO_2	C	totals
SS	10.18	1.85	0.28	0.01	bdl	bdl	66.00	84.56
CP(20% wax)	13.85	1.23	0.44	0.21	28.00	bdl	bdl	88.50
PFA1	48.92	26.17	1.22	0.67	6.66	bdl	bdl	94.02
PFA2	52.80	28.81	1.38	0.92	6.66	bdl	bdl	100.65
PFA3	51.77	27.65	1.24	0.78	6.66	bdl	bdl	98.77
PFA4	52.19	27.88	1.29	0.90	6.66	bdl	bdl	99.07
PFA5	51.59	27.63	1.32	0.84	6.66	bdl	bdl	97.98
PFA6	51.33	28.17	1.40	0.86	6.66	bdl	bdl	98.58
PFA7	50.96	27.33	1.37	0.85	6.66	bdl	bdl	97.56

flyash replicates using glass discs:

Sample	SiO_2	Al_2O_3	MgO	Na_2O	H_2O	CO_2	C	totals
rep 1	52.10	27.87	1.27	0.81	bdl	bdl	bdl	98.38
rep 2	52.27	27.96	1.31	0.81	bdl	bdl	bdl	98.84
rep 3	52.14	27.82	1.28	0.98	bdl	bdl	bdl	98.99
rep 4	52.27	27.83	1.27	0.98	bdl	bdl	bdl	98.84

bdl = below detection limit

Table I.v: Trace element XRFS analyses of flyash, composted sewage sludge and Catpoly discs

Trace element analyses performed on pressed powder discs and results expressed as ppm.

Sample	Cr	Mn	Ni	V	Zn	Cu	Co	Cd
SS	146	505	31	23	738	191	6	bdl
CP(20% wax)	70	43	51	50	24	9	bdl	bdl
PFA1	235	294	80	146	63	66	18	bdl
PFA2	243	286	84	153	74	73	21	bdl
PFA3	240	291	81	148	64	70	19	bdl
PFA4	236	286	79	146	66	70	19	bdl
PFA5	233	285	81	146	65	68	18	bdl
PFA6	249	295	85	156	78	73	20	bdl
PFA7	248	296	80	148	69	73	18	bdl

flyash replicates using glass discs for comparison with pressed powder results:

Results expressed as %.

flyash	Cr2O3/%	MnO/%	NiO/%
rep 1	0.0220	0.0310	0.0080
rep 2	0.0240	0.0340	0.0080
rep 3	0.0260	0.0340	0.0090
rep 4	0.0260	0.0360	0.0100

Trace element analyses expressed as ppm.

Sample	Sr	Rb	Ag	Be	B	Li	Mo	Pb
SS	4	12	bdl	bdl	bdl	bdl	3	102
CP(20% wax)	2	9	bdl	bdl	bdl	bdl	5	bdl
PFA1	75	33	bdl	bdl	bdl	bdl	2	89
PFA2	77	35	bdl	bdl	bdl	bdl	2	98
PFA3	77	32	bdl	bdl	bdl	bdl	2	98
PFA4	76	33	bdl	bdl	bdl	bdl	3	99
PFA5	75	33	bdl	bdl	bdl	bdl	3	90
PFA6	75	34	bdl	bdl	bdl	bdl	2	100
PFA7	75	33	bdl	bdl	bdl	bdl	2	94

Trace element analyses expressed as ppm.

Sample	U	Th	Nb	Zr	Y	Se	Bi	As	W
SS	bdl	bdl	3	104	4	13	3	12	bdl
CP(20% wax)	bdl	bdl	1	11	2	bdl	bdl	24	bdl
PFA1	14	47	40	442	75	2	3	21	8
PFA2	13	48	41	436	77	2	3	24	7
PFA3	12	49	40	445	77	3	5	24	8
PFA4	14	48	41	437	76	2	4	23	8
PFA5	13	47	40	437	75	3	7	23	5
PFA6	12	47	39	421	75	3	5	24	10
PFA7	13	48	39	434	75	4	5	23	6

bdl = below detection limit

I.v Results of HPIC analyses of aqueous extracts from flyash mixes used as growth media during plant growth trial

The results of the HPIC analyses, performed on the 1:1 aqueous extracts from the composite flyash mixtures described in Chapter 2, are shown here. These are the same combinations of ameliorants used in the plant growth trial for growing ryegrass. The results are expressed as mg l^{-1} of the ionic species and then converted to $mmol_c$ to allow the calculation of charge balance. Because the charge balance requires all anionic species to be included, the HCO_3^- concentrations taken from the alkalinity titrations are also included in the table. Table I.vi contains the data from the cations while Table I.vii contains the anion data.

Table I.vi: Cation data from HPIC analyses of aqueous extracts of flyash/ameliorant mixtures.

Ameliorants	Na / mgl/l	K	NH4	Mg	Ca	F	dry matter yield/g
none	226	27	bdl	77	146	5	0.64
acid	223	29	bdl	274	525	5	0.51
fertiliser	266	46	bdl	116	203	bdl	1.54
Catpoly	187	19	bdl	256	133	bdl	0.82
sewage sludge + Catpoly	187	25	bdl	331	151	bdl	2.01
sewage sludge	207	41	bdl	113	199	bdl	2.40
fertiliser + acid	287	51	bdl	336	609	bdl	0.89
Catpoly + sewage sludge + fertiliser	204	36	19	321	211	bdl	2.60
Catpoly + fertiliser	231	30	23	346	141	bdl	2.09
sewage sludge + fertiliser	247	60	bdl	154	264	bdl	4.00
sewage sludge + acid	206	36	bdl	275	580	bdl	2.39
sewage sludge + acid + fertiliser	256	54	bdl	317	633	bdl	3.38
deionised water	bdl	bdl	bdl	bdl	0.358	bdl	

Ameliorants	Na/ mmol c	K/mmol c	NH4	Mg	Ca	total cations
none	0.010	0.001	bdl	0.006	0.007	37.761
acid	0.010	0.001	bdl	0.023	0.026	107.921
fertiliser	0.012	0.001	bdl	0.010	0.010	52.093
Catpoly	0.008	0.000	bdl	0.021	0.007	64.016
sewage sludge + Catpoly	0.008	0.001	bdl	0.027	0.008	78.306
sewage sludge	0.009	0.001	bdl	0.009	0.010	48.506
fertiliser + acid	0.012	0.001	bdl	0.028	0.030	129.852
Catpoly + sewage sludge + fertiliser	0.009	0.001	0.001	0.026	0.011	84.722
Catpoly + fertiliser	0.010	0.001	bdl	0.028	0.007	81.818
sewage sludge + fertiliser	0.011	0.002	bdl	0.013	0.013	63.965
sewage sludge + acid	0.009	0.001	bdl	0.023	0.029	113.014
sewage sludge + acid + fertiliser	0.011	0.001	bdl	0.026	0.032	127.850

bdl = below detection limit

Table I.vii: Anion data from HPIC analyses of aqueous extracts of flyash/ameliorant mixtures.

Ameliorants	Cl	NO2	NO3	PO4	SO4/ mg/l	HCO3/M	charge balance	dry matter yield/g
none	216	bdl	105	bdl	659	0.0015	-1.07	0.64
acid	209	bdl	94	bdl	2291	0.0012	-1.71	0.51
fertiliser	234	bdl	877	bdl	689	0.0014	-1.25	1.54
Catpoly	193	bdl	97	712	665	0.0024	24.08	0.82
sewage sludge + Catpoly	199	bdl	544	754	643	0.0023	18.95	2.01
sewage sludge	209	bdl	530	bdl	653	0.0020	-5.30	2.40
fertiliser + acid	270	51	621	bdl	2357	0.0013	-4.55	0.89
Catpoly + sewage sludge + fertiliser	220	bdl	879	920	630	0.0021	23.21	2.60
Catpoly + fertiliser	242	bdl	394	963	692	0.0024	24.03	2.09
sewage sludge + fertiliser	232	bdl	1204	bdl	631	0.0017	-8.53	4.00
sewage sludge + acid	199	bdl	410	bdl	2160	0.0015	-4.31	2.39
sewage sludge + acid + fertiliser	235	bdl	1218	bdl	2159	0.0014	-4.16	3.38
deionised water	bdl	bdl	bdl	bdl	bdl			n/a

Ameliorants	F /mmol c	Cl	NO2	NO3	PO4	SO4	HCO3 /mmol c	total anions	charge balance
none	0.000	0.006	0.000	0.002	0.000	0.014	0.001	36.959	-1.074
acid	0.000	0.006	0.000	0.002	0.000	0.048	0.001	104.286	-1.713
fertiliser	0.000	0.007	0.000	0.014	0.000	0.014	0.001	50.808	-1.249
Catpoly	0.000	0.005	0.000	0.002	0.023	0.014	0.002	104.631	24.083
sewage sludge + Catpoly	0.000	0.006	0.000	0.009	0.024	0.013	0.002	114.926	18.951
sewage sludge	0.000	0.006	0.000	0.009	0.000	0.014	0.002	43.624	-5.298
fertiliser + acid	0.000	0.008	0.001	0.010	0.000	0.049	0.001	118.280	-4.664
Catpoly + sewage sludge + fertiliser	0.000	0.006	0.000	0.014	0.029	0.013	0.002	135.944	23.212
Catpoly + fertiliser	0.000	0.007	0.000	0.006	0.030	0.014	0.002	135.666	24.759
sewage sludge + fertiliser	0.000	0.007	0.000	0.019	0.000	0.013	0.002	53.914	-8.526
sewage sludge + acid	0.000	0.006	0.000	0.007	0.000	0.045	0.001	103.685	-4.305
sewage sludge + acid + fertiliser	0.000	0.007	0.000	0.020	0.000	0.045	0.001	117.630	-4.163

bdl = below detection limit

I.vi Results of semi-quantitative ICP-AES analysis of leachate from nitric acid leaching of flyash

The results of the ICP-AES analysis of the leachate, derived from the nitric acid leaching of flyash, are shown in Table I.viii.

Table I.viii Results from semi-quantitative ICP-AES analysis of nitric acid leachate produced after leaching flyash.

element	As	Se	Mo	Ag	Ti	Sr	Mg	Al
concentration /sample suspension/ mg l^{-1}	bdl	bdl	bdl	0.01	79	117	2240	3428
detection limit/ppm	0.5	1.0	0.1	0.01	0.01	0.01	0.01	0.04
concentration/ mg kg^{-1} PFA				0.1	790	1170	22400	34280

element	Mn	Fe	Cr	V	Na	Be	B	Ca
concentration /sample suspension/ mg l^{-1}	47	461	16	21	411	0.5	65	12350
detection limit/ppm	0.01	0.02	0.1	0.04	0.02	0.1	0.03	0.01
concentration/ mg kg^{-1} PFA	470	4610	160	210	4110	5.0	650	123500

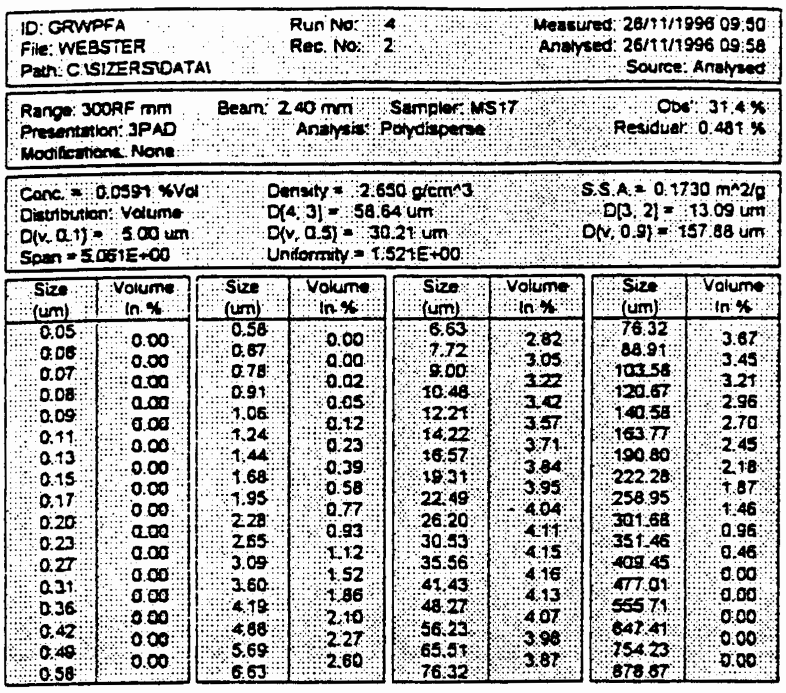
element	Cd	Cu	Sb	Pb	Bi	Li	Co	Sn
concentration/ sample suspension/ mg l^{-1}	0.1	4	bdl	3	bdl	4	0.6	bdl
detection limit/ppm	0.01	0.04	0.2	0.2	0.5	0.01	0.1	0.4
concentration/ mg kg^{-1} PFA	1.0	40		30		40	6.0	

element	Hg	Zn	Ni	P	K
concentration/ sample suspension/ mg l^{-1}	bdl	9	4	318	141
detection limit/ppm	0.02	0.01	0.01	0.4	0.2
concentration/ mg kg^{-1} PFA		90	40	3180	1410

I.vii Particle size distributions for unamended flyash and flyash containing 10% composted sewage sludge

The results of the particle size distribution analysis, described in Chapter 2, are shown in Tables I.ix and I.x and the data are plotted on the same axes for comparison in Figure x.x.

Table I.ix : Particle size distribution for unamended flyash.



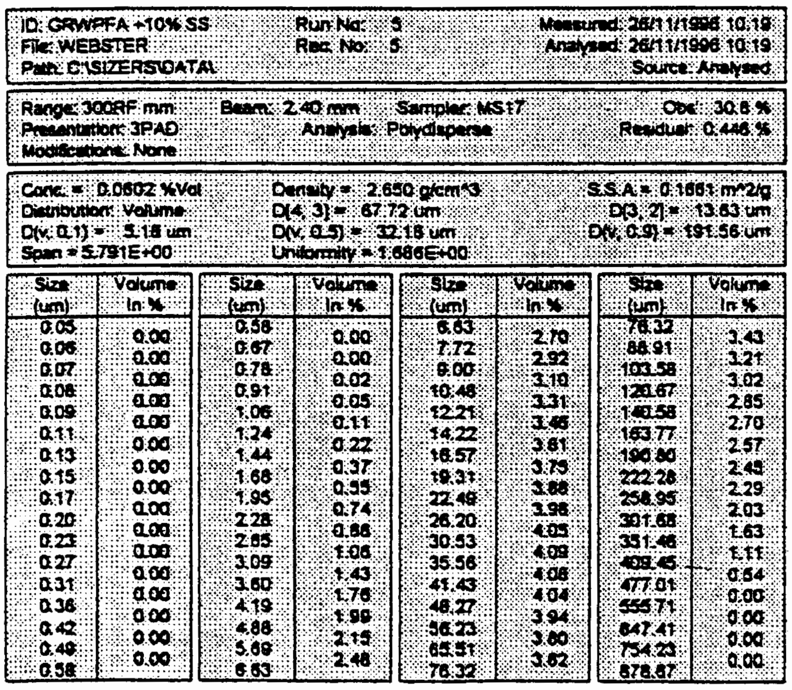
ID: GRWPFA Run No: 4 Measured: 26/11/1996 09:50
File: WEBSTER Rec. No: 2 Analysed: 26/11/1996 09:58
Path: C:\SIZERS\DATA\ Source: Analysed

Range: 300RF mm Beam: 2.40 mm Sampler: MS17 Obs': 31.4 %
Presentation: 3PAD Analysis: Polydisperse Residual: 0.481 %
Modifications: None

Conc. = 0.0591 %Vol Density = 2.650 g/cm^3 S.S.A.= 0.1730 m^2/g
Distribution: Volume D[4, 3] = 58.64 um D[3, 2] = 13.09 um
D(v, 0.1) = 5.00 um D(v, 0.5) = 30.21 um D(v, 0.9) = 157.88 um
Span = 5.061E+00 Uniformity = 1.521E+00

Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
0.05	0.00	0.58	0.00	6.63	2.82	76.32	3.67
0.06	0.00	0.67	0.00	7.72	3.05	88.91	3.45
0.07	0.00	0.78	0.02	9.00	3.22	103.58	3.21
0.08	0.00	0.91	0.05	10.48	3.42	120.67	2.96
0.09	0.00	1.06	0.12	12.21	3.57	140.58	2.70
0.11	0.00	1.24	0.23	14.22	3.71	163.77	2.45
0.13	0.00	1.44	0.39	16.57	3.84	190.80	2.18
0.15	0.00	1.68	0.58	19.31	3.95	222.28	1.87
0.17	0.00	1.95	0.77	22.49	4.04	258.95	1.46
0.20	0.00	2.28	0.93	26.20	4.11	301.68	0.96
0.23	0.00	2.65	1.12	30.53	4.15	351.46	0.46
0.27	0.00	3.09	1.52	35.56	4.16	409.45	0.00
0.31	0.00	3.60	1.86	41.43	4.13	477.01	0.00
0.36	0.00	4.19	2.10	48.27	4.07	555.71	0.00
0.42	0.00	4.88	2.27	56.23	3.98	647.41	0.00
0.49	0.00	5.69	2.60	65.51	3.87	754.23	0.00
0.58		6.63		76.32		878.67	

Table I.x : Particle size distribution for flyash amended with 10% composted sewage sludge.



ID: GRWPFA +10% SS Run No: 5 Measured: 26/11/1996 10:19
File: WEBSTER Rec. No: 5 Analysed: 26/11/1996 10:19
Path: C:\SIZERS\DATA\ Source: Analysed

Range: 300RF mm Beam: 2.40 mm Sampler: MS17 Obs': 30.8 %
Presentation: 3PAD Analysis: Polydisperse Residual: 0.446 %
Modifications: None

Conc. = 0.0602 %Vol Density = 2.650 g/cm^3 S.S.A.= 0.1661 m^2/g
Distribution: Volume D[4, 3] = 67.72 um D[3, 2] = 13.63 um
D(v, 0.1) = 5.18 um D(v, 0.5) = 32.18 um D(v, 0.9) = 191.56 um
Span = 5.791E+00 Uniformity = 1.686E+00

Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
0.05	0.00	0.58	0.00	6.63	2.70	76.32	3.43
0.06	0.00	0.67	0.00	7.72	2.92	88.91	3.21
0.07	0.00	0.78	0.02	9.00	3.10	103.58	3.02
0.08	0.00	0.91	0.05	10.48	3.31	120.67	2.85
0.09	0.00	1.06	0.11	12.21	3.46	140.58	2.70
0.11	0.00	1.24	0.22	14.22	3.61	163.77	2.57
0.13	0.00	1.44	0.37	16.57	3.75	190.80	2.43
0.15	0.00	1.68	0.55	19.31	3.88	222.28	2.29
0.17	0.00	1.95	0.74	22.49	3.96	258.95	2.03
0.20	0.00	2.28	0.88	26.20	4.05	301.68	1.63
0.23	0.00	2.65	1.06	30.53	4.09	351.46	1.11
0.27	0.00	3.09	1.43	35.56	4.08	409.45	0.54
0.31	0.00	3.60	1.76	41.43	4.04	477.01	0.00
0.36	0.00	4.19	1.99	48.27	3.94	555.71	0.00
0.42	0.00	4.88	2.15	56.23	3.80	647.41	0.00
0.49	0.00	5.69	2.48	65.51	3.62	754.23	0.00
0.58		6.63		76.32		878.67	

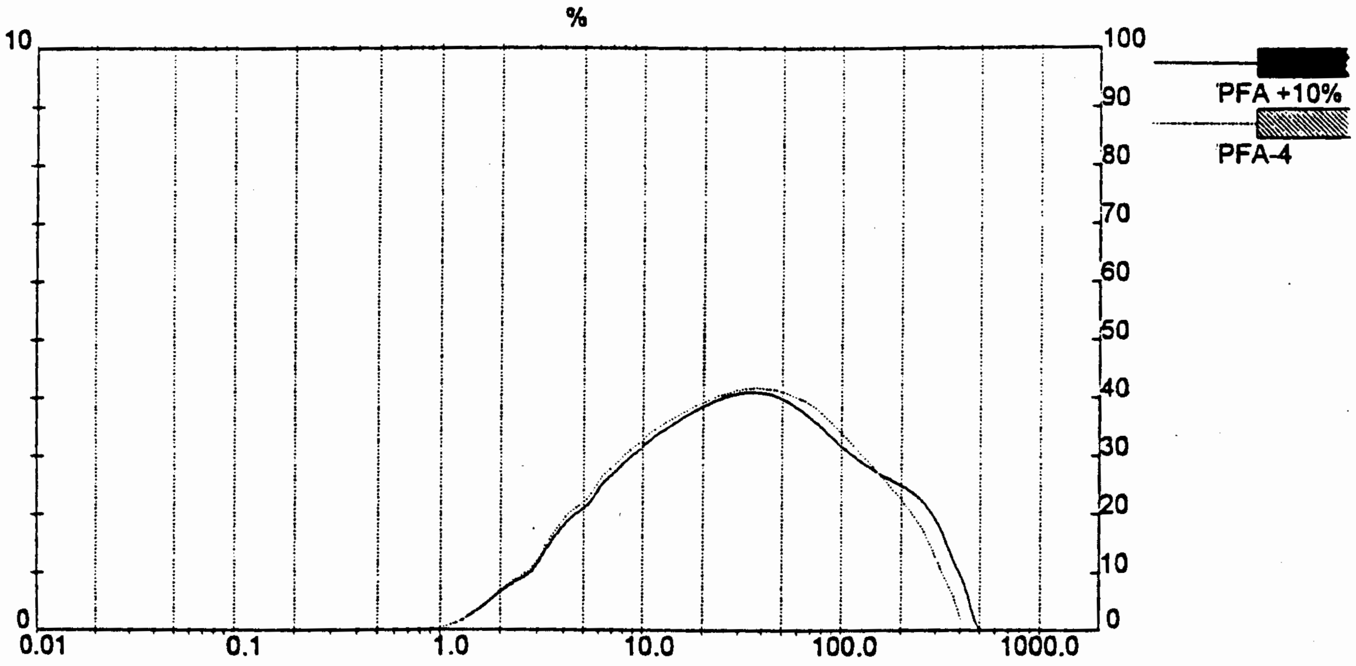


Figure I.ii: Plots of the particle size distributions of unamended flyash and flyash amended with 10% composted sewage sludge. The plot shows particle size, in µm, plotted against % of the grains that are present in the particular size range. The solid line shows the sewage sludge amended flyash, while the unamended flyash is represented by the dotted line.

I.viii Dry matter yields of ryegrass produced during plant growth trial

The complete data set, reporting the dry matter produced by individual pots during the growth trial, is shown in Table I.xi. The table shows individual pot yields, means for each treatment and standard deviations for treatments. Also shown is the additive effects present from combinations of ameliorants.

Table I.xi : Dry matter production for ryegrass produced o in response to different amendments

amendments	drymass/g	treatment mean/g	std.dev.
control	0.51	0.64	0.11
control	0.72		
control	0.69		
A	0.38	0.51	0.14
A	0.65		
A	0.50		
CP	0.86	0.82	0.07
CP	0.74		
CP	0.86		
F	1.24	1.54	0.27
F	1.63		
F	1.75		
SS	2.44	2.40	0.34
SS	2.04		
SS	2.72		
SS+A	2.27	2.39	0.10
SS+A	2.45		
SS+A	2.44		
SS+CP	1.94	2.01	0.17
SS+CP	1.88		
SS+CP	2.20		
SS+F	3.95	4.00	0.05
SS+F	4.01		
SS+F	4.05		
SS+A+F	2.83	3.38	0.48
SS+A+F	3.60		
SS+A+F	3.72		
CP+SS+F	2.55	2.60	0.45
CP+SS+F	3.07		
CP+SS+F	2.18		
CP+F	2.24	2.09	0.15
CP+F	1.95		
CP+F	2.08		
F+A	0.74	0.89	0.14
F+A	0.92		
F+A	1.02		

A:sulphuric acid
CP: Catpoly, acidic waste catalyst
F: inorganic salts fertiliser solution

I.ix Results of ICP-AES plant tissue analyses performed on ryegrass grown in variously treated flyash

Results of the analyses of the ryegrass grown on the 12 different amended flyash treatments are shown in Tables I.xii to I.xvii. These Tables contain the complete data set from the analyses of plant material. This plant material was produced during the growth trial described in Chapter 3. There are 36 analyses as each of the 12 different flyash treatments was performed in triplicate. Mean values of these analyses were determined and these were used in the discussions in Chapter 3.

Table I.xii: Foliar analyses of drymatter produced during growth trial, sheet 1.
Plant analyses by ICP-AES, elemental concentrations expressed as ppm.

Treatment	mass analysed/g	Al	P	As	Se	Mo	V	Be	Li
PFA	0.5	20.5	130.0	0.1	0.4	1.2	bdl	bdl	8.0
PFA	0.5	10.8	152.0	0.1	0.3	1.1	bdl	bdl	7.5
PFA	0.5	11.3	150.0	0.1	0.3	1.2	bdl	bdl	7.1
mean PFA		14.2	144.0	0.1	0.3	1.2	0.0	0.0	7.6
PFA+A	0.4	14.9	108.0	0.0	0.2	0.5	bdl	bdl	7.3
PFA+A	0.5	18.1	140.0	0.1	0.3	0.8	bdl	bdl	6.0
PFA+A	0.5	15.9	123.0	0.1	0.3	0.7	bdl	bdl	7.9
mean PFA+A		16.3	123.7	0.1	0.3	0.7	0.0	0.0	7.1
PFA+F	0.5	17.7	185.0	0.1	0.3	0.9	bdl	bdl	8.6
PFA+F	0.5	102.0	159.0	0.4	0.3	0.6	bdl	bdl	6.0
PFA+F	0.5	27.3	162.0	0.1	0.3	0.8	bdl	bdl	7.7
mean PFA+F		49.0	168.7	0.2	0.3	0.8	0.0	0.0	7.4
PFA+SS	0.5	5.5	225.0	0.1	0.2	0.2	bdl	bdl	4.9
PFA+SS	0.5	4.6	221.0	0.0	0.2	0.2	bdl	bdl	5.4
PFA+SS	0.5	5.5	212.0	0.1	0.2	0.3	bdl	bdl	5.1
mean PFA+SS		5.2	219.3	0.1	0.2	0.2	0.0	0.0	5.1
PFA+CP	0.5	3.9	429.0	0.2	0.2	0.3	bdl	bdl	6.4
PFA+CP	0.5	2.1	424.0	0.4	0.2	0.3	bdl	bdl	8.1
PFA+CP	0.5	6.0	446.0	0.3	0.2	0.3	bd;	bdl	6.8
mean PFA+CP		4.0	433.0	0.3	0.2	0.3	0.0	0.0	7.1
PFA+SS+CP	0.5	2.7	383.0	0.1	0.2	0.3	bdl	bdl	6.2
PFA+SS+CP	0.5	3.8	384.0	0.2	0.3	0.3	bdl	bdl	7.4
PFA+SS+CP	0.5	6.1	402.0	0.2	0.2	0.3	bdl	bdl	8.0
mean PFA+SS+CP		4.2	389.7	0.1	0.2	0.3	0.0	0.0	7.2

Table I.xiii: Foliar analyses of drymatter produced during growth trial, sheet 2.
Plant analyses by ICP-AES, elemental concentrations expressed as ppm.

Treatment	Cd	Pb	Co	B	Cr	Cu	Sr	Zn	Ni
PFA	bdl	0.0	bdl	83.7	bdl	1.5	4.1	0.0	bdl
PFA	bdl	0.1	bdl	88.8	bdl	2.9	4.0	0.0	0.2
PFA	bdl	0.0	bdl	87.7	bdl	1.3	4.2	0.1	bdl
mean PFA	0.0	0.0	0.0	86.7	0.0	1.9	4.1	0.0	0.1
PFA+A	bdl	0.9	bdl	65.8	bdl	2.8	3.4	0.2	0.5
PFA+A	bdl	0.1	bdl	76.1	bdl	1.5	3.9	0.0	0.3
PFA+A	bdl	0.8	bdl	85.5	bdl	2.1	3.2	0.1	0.1
mean PFA+A	0.0	0.6	0.0	75.8	0.0	2.1	3.5	0.1	0.3
PFA+F	bdl	0.2	bdl	61.4	bdl	0.7	5.2	0.1	0.1
PFA+F	bdl	54.9	bdl	103.0	bdl	0.6	7.3	0.4	0.2
PFA+F	bdl	0.1	bdl	59.0	bdl	0.4	4.5	0.1	bdl
mean PFA+F	0.0	18.4	0.0	74.5	0.0	0.6	5.6	0.2	0.1
PFA+SS	bdl	0.1	bdl	20.1	bdl	1.0	3.3	0.1	bdl
PFA+SS	bdl	0.1	bdl	22.5	bdl	1.3	3.2	0.3	bdl
PFA+SS	bdl	0.1	bdl	20.7	bdl	1.6	3.8	0.3	bdl
mean PFA+SS	0.0	0.1	0.0	21.1	0.0	1.3	3.4	0.3	0.0
PFA+CP	bdl	0.1	bdl	41.9	bdl	2.4	0.7	bdl	1.6
PFA+CP	bdl	0.1	bdl	51.7	bdl	2.0	0.6	bdl	1.6
PFA+CP	bdl	0.0	bdl	36.1	bdl	2.7	0.7	bdl	1.0
mean PFA+CP	0.0	0.0	0.0	43.2	0.0	2.3	0.7	0.0	1.4
PFA+SS+CP	bdl	0.1	bdl	26.1	bdl	1.3	0.6	0.6	0.8
PFA+SS+CP	bdl	0.1	bdl	59.4	bdl	2.5	0.7	0.9	0.8
PFA+SS+CP	bdl	0.1	bdl	42.0	bdl	1.8	0.7	0.7	0.7
mean PFA+SS+CP	0.0	0.1	0.0	42.5	0.0	1.8	0.7	0.7	0.8

Table I.xiv: Foliar analyses of drymatter produced during growth trial, sheet 3.
Plant analyses by ICP-AES, elemental concentrations expressed as ppm.

Treatment	Si	Mg	Mn	Fe	Ca	Na	K
PFA	51.9	187.0	1.0	8.4	244.0	621.0	961.0
PFA	32.7	172.0	1.4	5.8	246.0	602.0	911.0
PFA	41.6	195.0	1.6	6.0	265.0	744.0	924.0
mean PFA	42.1	184.7	1.3	6.8	251.7	655.7	932.0
PFA+A	35.6	225.0	0.5	10.9	230.0	368.0	850.0
PFA+A	20.9	277.0	0.8	11.1	266.0	410.0	926.0
PFA+A	70.0	241.0	0.5	8.1	227.0	529.0	906.0
mean PFA+A	42.2	247.7	0.6	10.0	241.0	435.7	894.0
PFA+F	4.3	271.0	0.7	9.5	288.0	840.0	1210.0
PFA+F	4.2	242.0	0.8	14.2	337.0	704.0	1180.0
PFA+F	3.7	232.0	1.3	12.6	283.0	712.0	1110.0
mean PFA+F	4.1	248.3	0.9	12.1	302.7	752.0	1166.7
PFA+SS	3.0	149.0	1.1	4.7	244.0	556.0	821.0
PFA+SS	3.1	167.0	1.3	4.8	256.0	533.0	903.0
PFA+SS	2.7	154.0	1.0	4.9	278.0	467.0	862.0
mean PFA+SS	2.9	156.7	1.1	4.8	259.3	518.7	862.0
PFA+CP	2.7	262.0	9.2	4.2	117.0	245.0	899.0
PFA+CP	2.7	284.0	9.1	3.7	113.0	391.0	917.0
PFA+CP	3.2	270.0	10.3	5.1	119.0	265.0	880.0
mean PFA+CP	2.9	272.0	9.5	4.3	116.3	300.3	898.7
PFA+SS+CP	7.3	261.0	8.8	5.9	127.0	283.0	950.0
PFA+SS+CP	6.5	273.0	8.1	6.4	122.0	353.0	1150.0
PFA+SS+CP	3.0	289.0	8.2	6.0	131.0	398.0	1020.0
mean PFA+SS+CP	5.6	274.3	8.3	6.1	126.7	344.7	1040.0

Table I.xv: Foliar analyses of drymatter produced during growth trial, sheet 4.
Plant analyses by ICP-AES, elemental concentrations expressed as ppm.

Treatment	mass analysed/g	Al	P	As	Se	Mo	V	Be	Li
PFA+SS+A	0.5	4.4	542.0	0.0	0.7	0.2	0.2	bdl	1.2
PFA+SS+A	0.5	4.2	254.0	0.0	0.2	0.2	bdl	bdl	5.2
PFA+SS+A	0.5	6.5	250.0	0.1	0.2	0.2	bdl	bdl	5.7
mean PFA+SS+A		5.0	348.7	0.1	0.4	0.2	0.1	bdl	4.0
PFA+F+A	0.5	15.6	152.0	0.1	0.4	0.5	bdl	bdl	8.0
PFA+F+A	0.5	14.2	143.0	0.1	0.4	0.5	bdl	bdl	7.3
PFA+F+A	0.5	18.6	156.0	0.1	0.4	0.6	bdl	bdl	7.7
mean PFA+F+A		16.1	150.3	0.1	0.4	0.6	bdl	bdl	7.7
PFA+CP+F	0.5	3.2	332.0	0.0	0.6	0.1	bdl	bdl	1.7
PFA+CP+F	0.5	4.5	399.0	0.1	0.3	0.2	bdl	bdl	10.2
PFA+CP+F	0.5	5.0	388.0	0.1	0.2	0.2	bdl	bdl	8.3
mean PFA+CP+F		4.2	373.0	0.1	0.4	0.2	bdl	bdl	6.8
PFA+SS+F	0.5	7.0	291.0	0.1	0.7	0.2	0.1	bdl	1.4
PFA+SS+F	0.5	8.7	219.0	0.1	0.3	0.2	bdl	bdl	8.7
PFA+SS+F	0.5	9.9	235.0	0.1	0.2	0.2	bdl	bdl	7.3
mean PFA+SS+F		8.5	248.3	0.1	0.4	0.2	bdl	bdl	5.8
PFA+CP+SS+F	0.5	8.1	432.0	0.2	0.2	0.2	bdl	bdl	13.0
PFA+CP+SS+F	0.5	6.9	425.0	0.1	0.2	0.2	bdl	bdl	10.7
PFA+CP+SS+F	0.5	6.2	416.0	0.2	0.2	0.2	bdl	bdl	12.3
mean PFA+CP+SS+F		7.1	424.3	0.2	0.2	0.2	bdl	bdl	12.0
PFA+SS+A+F	0.5	11.2	249.0	0.1	0.3	0.3	bdl	bdl	8.1
PFA+SS+A+F	0.5	6.0	213.0	0.0	0.2	0.2	bdl	bdl	7.5
PFA+SS+A+F	0.5	9.8	250.0	0.1	0.3	0.2	bdl	bdl	8.5
mean PFA+SS+A+F		9.0	237.3	0.1	0.3	0.2	bdl	bdl	8.1

Table I.xvi: Foliar analyses of drymatter produced during growth trial, sheet 5.
Plant analyses by ICP-AES, elemental concentrations expressed as ppm.

Treatment	Cd	Pb	Co	B	Cr	Cu	Sr	Zn	Ni
PFA+SS+A	0.3	bdl	bdl	51.9	bdl	4.0	4.5	1.3	bdl
PFA+SS+A	bdl	0.1	bdl	33.3	bdl	0.6	3.2	0.5	0.0
PFA+SS+A	bdl	0.1	bdl	31.9	bdl	1.6	2.9	0.6	0.7
mean PFA+SS+A	0.1	0.1	bdl	39.0	bdl	2.1	3.5	0.8	0.2
PFA+F+A	bdl	0.1	bdl	73.8	bdl	3.4	3.4	bdl	bdl
PFA+F+A	bdl	0.1	bdl	83.7	bdl	1.6	4.0	bdl	bdl
PFA+F+A	bdl	0.1	bdl	76.4	0.6	1.0	4.5	0.2	0.3
mean PFA+F+A	bdl	0.1	bdl	78.0	0.2	2.0	4.0	0.1	0.1
PFA+CP+F	0.2	bdl	bdl	0.3	bdl	bdl	0.3	0.9	1.8
PFA+CP+F	bdl	0.2	bdl	76.3	bdl	0.5	0.6	0.1	1.6
PFA+CP+F	bdl	0.1	bdl	64.8	bdl	0.5	0.5	bdl	1.5
mean PFA+CP+F	0.1	0.1	bdl	47.1	bdl	0.3	0.5	0.3	1.6
PFA+SS+F	0.2	bdl	bdl	18.5	bdl	1.4	2.4	2.0	bdl
PFA+SS+F	bdl	0.1	bdl	28.9	bdl	1.7	3.4	0.8	bdl
PFA+SS+F	bdl	0.3	bdl	26.8	bdl	0.5	3.6	1.1	0.2
mean PFA+SS+F	0.1	0.1	bdl	24.7	bdl	1.2	3.1	1.3	0.1
PFA+CP+SS+F	bdl	0.1	bdl	55.2	bdl	2.4	0.9	1.1	0.6
PFA+CP+SS+F	bdl	0.1	bdl	51.8	bdl	2.1	0.7	1.2	0.5
PFA+CP+SS+F	bdl	0.1	bdl	58.5	bdl	2.2	0.8	1.5	0.6
mean PFA+CP+SS+F	bdl	0.1	bdl	55.2	bdl	2.2	0.8	1.2	0.6
PFA+SS+A+F	bdl	0.1	bdl	31.3	bdl	1.6	3.2	1.3	bdl
PFA+SS+A+F	bdl	0.1	bdl	32.0	bdl	1.6	2.9	1.1	bdl
PFA+SS+A+F	bdl	0.1	bdl	36.4	bdl	1.6	3.3	1.2	bdl
mean PFA+SS+A+F	bdl	0.1	bdl	33.2	bdl	1.6	3.1	1.2	bdl

Table I.xvii: Foliar analyses of drymatter produced during growth trial, sheet 6.
Plant analyses by ICP-AES, elemental concentrations expressed as ppm.

Treatment	Si	Mg	Mn	Fe	Ca	Na	K
PFA+SS+A	3.7	207.0	1.5	4.6	262.0	551.0	1310.0
PFA+SS+A	4.7	203.0	1.4	11.8	247.0	496.0	982.0
PFA+SS+A	2.9	218.0	1.7	7.0	248.0	470.0	954.0
mean PFA+SS+A	3.8	209.3	1.5	7.8	252.3	505.7	1082.0
PFA+F+A	129.0	284.0	0.7	20.9	253.0	532.0	1100.0
PFA+F+A	173.0	296.0	0.6	9.2	280.0	601.0	1090.0
PFA+F+A	40.3	334.0	0.9	13.4	312.0	620.0	1140.0
mean PFA+F+A	114.1	304.7	0.7	14.5	281.7	584.3	1110.0
PFA+CP+F	4.2	300.0	6.7	8.2	107.0	591.0	1430.0
PFA+CP+F	3.5	340.0	7.9	5.3	115.0	510.0	1130.0
PFA+CP+F	3.1	312.0	6.9	5.6	111.0	471.0	1080.0
mean PFA+CP+F	3.6	317.3	7.2	6.4	111.0	524.0	1213.3
PFA+SS+F	4.0	194.0	2.0	5.5	295.0	1140.0	1150.0
PFA+SS+F	3.0	220.0	0.8	6.8	271.0	892.0	887.0
PFA+SS+F	6.3	218.0	1.1	21.2	279.0	822.0	880.0
mean PFA+SS+F	4.4	210.7	1.3	11.2	281.7	951.3	972.3
PFA+CP+SS+F	3.2	421.0	9.7	6.4	156.0	658.0	1140.0
PFA+CP+SS+F	3.3	374.0	8.7	7.0	138.0	625.0	1130.0
PFA+CP+SS+F	3.0	414.0	9.5	6.0	157.0	604.0	1140.0
mean PFA+CP+SS+F	3.2	403.0	9.3	6.4	150.3	629.0	1136.7
PFA+SS+A+F	3.3	310.0	1.6	7.2	244.0	732.0	1160.0
PFA+SS+A+F	3.9	268.0	1.4	8.5	241.0	766.0	926.0
PFA+SS+A+F	3.8	269.0	1.9	8.7	249.0	795.0	930.0
mean PFA+SS+A+F	3.6	282.3	1.6	8.1	244.7	764.3	1005.3

I.x Results of laboratory incubation trial to investigate the rate of oxidation of elemental sulphur in flyash

Included in Table I.xviii are the results of the laboratory incubation study investigating the rate of S oxidation in flyash. As reported in Chapter 4, the study examined the effect of doubling the quantity of S added and the influence of the addition of composted sewage sludge to the flyash.

Table I.xviii: Tabulated data from laboratory incubation trial into rates of oxidation of interphase S

	pH(H2O)	pH(KCl)	EC/ mS/cm	SO4/mg/l
Week	Treatment:	Unamended flyash		
1	8.75	8.57	1.82	52.00
2	8.92	8.87	1.42	
3	8.68	8.52	0.47	
4	8.82	8.76	0.67	
5	8.91	8.56	0.84	
6	8.80	8.50	0.52	
7	8.94	8.76	0.83	
8	8.75	8.60	0.50	313.00
Week	Treatment:	Sulphur		
1	7.73	7.61	3.32	845.00
2	8.42	8.61	2.05	
3	8.18	8.03	1.17	
4	8.10	8.31	0.85	
5	8.31	7.88	0.92	
6	8.09	8.33	1.02	
7	8.26	8.30	1.66	
8	8.07	7.92	1.11	870.00
Week	Treatment:	Double sulphur		
1	7.57	7.52	3.00	1167.00
2	8.27	8.28	1.89	
3	8.18	8.07	1.04	
4	7.87	7.93	1.24	
5	7.94	7.96	1.26	
6	8.02	8.11	1.11	
7	7.98	8.18	1.83	
8	8.02	7.91	1.19	1280.00
Week	Treatment:	Composted sewage sludge		
1	8.01	7.97	3.04	60.00
2	8.32	8.15	1.29	
3	8.31	8.24	0.73	
4	8.20	8.21	0.65	
5	8.23	8.07	0.87	
6	8.41	8.38	0.64	
7	8.53	8.29	0.53	
8	8.44	8.12	0.54	6.00
Week	Treatment:	Composted sewage sludge + sulphur		
1	7.37	7.35	3.01	845.00
2	7.96	7.82	1.86	
3	7.94	7.87	1.41	
4	7.72	7.73	1.29	
5	7.78	7.71	1.41	
6	7.82	7.85	1.48	
7	7.73	7.93	1.32	
8	7.72	7.58	1.33	1286.00
Week	Treatment:	Composted sewage sludge + double sulphur		
1	7.33	7.17	4.15	2113.00
2	7.87	8.74	1.64	
3	7.84	7.55	1.16	
4	7.44	7.39	1.50	
5	7.33	7.24	1.35	
6	7.45	7.37	1.35	
7	7.38	7.42	1.62	
8	7.23	7.11	1.36	2150.00
Analysis of sulphate present in interphase sulphur before mixing with flyash				181.00

Appendix II: Precision and accuracy determinations

II.i Precision and accuracy of pH and EC measurements

Because pH and EC measurements were carried out on the same suspensions during this study, any precision and accuracy discussion must relate to both procedures. The soil : water ratio proposed by Hissink (1930, cited in Van Lierop, 1990) of 1:2.5 was utilised throughout this study, although some preliminary pH and EC measurements were carried out on the 1:1 aqueous growth media extracts. These were not compared with any of the standardised pH or EC determinations. The suspensions were allowed the 30 minutes to equilibrate that Van Lierop (1990) recommended for calcareous soils, before any measurements were made. The Crison micro pH 2001 meter used was equipped with an automatic temperature compensating electrode. Before use the meter was calibrated with standard buffer solutions of pH 4.00 and 7.02, although when the higher pH values for unamended flyash were being determined a standard buffer of pH 10.01 was used. The measurements were repeated until the value had stabilised and then duplicated to ensure repeatability. It must be recognised that only one sample of each growth medium was taken on each occasion which is why a separate pH precision study was undertaken and is discussed in the next section.

To ensure the precision and accuracy of EC measurements, the Crison micro CM 2201 EC meter, equipped with an immersion glass-platinum cell and automatic temperature compensating electrode, was calibrated with a standard 0.01 M KCl solution before and after the readings were taken. Like the pH measurements, the EC readings were allowed to stabilise and then duplicated to ensure repeatability. As a consequence, the repeatability of measurements made are within 0.1 ms cm^{-1} when operating in this range and within 5µS cm^{-1} when operating in the finer range.

Each time pH measurements are to be made the pH meter is calibrated against a known pH standard and the internal temperature correction system of the meter is able to correct for differences in registered pH brought about by temperature changes. In spite of these measures being taken to ensure that the accuracy of pH measurements are as good as conditions and equipment allow, no effort had been made to investigate the precision of pH measurements made on any samples. To overcome this limitation an investigation was made into the repeatability of pH measurements made on some flyash samples collected during the S oxidation trial. Despite samples being air dried before pH analyses were carried out, there was a concern that microbial respiration might alter the pH of the samples.

To investigate the possibility of this effect altering the measured pH, one weeks subsample was taken as a representative of each treatment. The original pH(H_2O) was combined with pH analyses taken from three triplicate samples, from the same pot, on two subsequent occasions and a set of triplicate repeats where the same samples were left in water for an additional 30 minutes. This resulted in 10 determinations being made for the pH of each subsample.

The results of the precision study are shown below and give some indication about the precision to which pH values may be confidently expressed. Table II.i shows the minima, maxima, means and standard deviations of the precision study for pH measurements.

Table II.i Statistical analyses of replicability of pH(H_2O) measurements

flyash treatment	mean	STD deviation	minimum value	maximum value
flyash only	8.70	0.06	8.59	8.77
sewage sludge	8.28	0.09	8.14	8.38
SS + sulphur	7.70	0.07	7.58	7.78
SS + double sulphur	7.26	0.10	7.10	7.44

All of the pH values determined during the precision study fall within two standard deviations (99% CL) of the mean values of the 10 measurements taken. On this basis it can be assumed that all of the pH measurements taken during the sulphur oxidation trial are representative of the pH of the flyash mixtures being sampled. The evidence that the largest standard deviation rounds to 0.1 of a pH unit suggests that pH values should be confidently quoted to no more than one significant figure.

II.ii Precision and accuracy of automatically performed titrations

During the characterisation study a number of titrations were carried out to determine the quantity of different ameliorants required to be combined to amend the pH of a combination of ameliorants and flyash. A Radiometer Copenhagen TTT85 titrator was used and coupled to an ABU 80 Autoburette, a pHG201 Ph glass electrode and a REF401 calomel reference electrode. Like the pH meter, this instrument was calibrated with standard buffers with values of pH 4.01, 7.00 and 10.01. Two different temperatures of at least 10°C difference were also required to ensure the accuracy of the calibration.

After calibration, titrations were performed with different ameliorants to determine a consistent concentration for a 0.5g sample suspended in 10 ml of deionised water. For Catpoly the titration was performed in triplicate and a mean concentration of 0.2306 mM was obtained with a standard deviation of 0.0343. The titration for flyash was repeated 17 times due to significant variability in the endpoint but the resulting mean concentration was 0.8739 mM with a standard deviation of 0.102 which indicates the variability of flyash composition. To gain some indication of the precision obtained by the instrument rather than of variation in the samples, titration was performed with diluted Titrisol sulphuric acid. A mean value of 0.02265 mM concentration was obtained with a standard deviation of 0.000466 for the 4 samples. This indicates a reasonable level of precision for the instrument to the point where values produced by titration can be assumed to be correct to within 20% of the determined value. This level of accuracy is consistent with what would be obtainable from acid-base indicators according to Manahan (1986), but is ignoring errors in the accuracy of titrating using burettes where endpoints can only be determined to within 0.01 ml (Manahan, 1986) which, in this case, would be an order of magnitude less accurate than what this automatic system obtained with a 5ml sample volume. For wet chemical titrations to be comparable, a significantly larger volume of sample would be necessary. In this situation, limits to the quantity of growth media available would have made this impracticable.

II.iii XRFS analysis

Analyses of individual ameliorants prior to mixing was performed by XRFS at the University of Cape Town Department of Geological Sciences. A Philips PW1480 wavelength dispersive spectrometer was used. The samples were all prepared as pressed powder discs for analyses. The trace elements were analysed quantitatively and the majors semi-quantitatively due to infinite thickness difficulties. The major element totals produced were too low to be of value for the flyash samples. Fused discs were made and run for comparison with the pressed powder disc analyses as described in Tables I.iv and I.v for the major elements and trace elements respectively. A comprehensive description of the tubes used for analysis of different elements, lower limits of detection and calibration curves are all included in the attached document (Appendix III): Instrumental parameters and data quality for routine major and trace element determinations by WDXRFS, Willis (1995).

The low totals that resulted from the infinite thickness difficulties require that the analyses be only considered to be semi-quantitative as, despite efforts to improve the totals, all of the analyses remained low.

II.iv HPIC

Analyses of aqueous extracts from the growth media and from the S oxidation trial were analysed by HPIC in the Department of Geological Sciences at the University of Cape Town. The instrument used for the analyses was a Dionex DX300 suppressed IC system which was coupled to an AL-450 chromatography software package. An HPIC-AG4A column was used as a guard column with an HPIC-AS4A-SC separator column. Ions are separated using a stationary phase ion exchange resin contained in a column, with a different column being used for anions and cations. The eluent used to move the ionic species through the exchange column was a 1.7 mM $NaHCO_3$/ 1.8 mM Na_2CO_3 buffer, which prevents the accurate determination of carbonate species. These were determined separately during the alkalinity titrations (section 2.3.2). The ionic species analysed for during the HPIC analyses included the following cations: Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+} and anions: Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}. The sample loop volumes are 25µl for cations and 50µl for anions. The running times for the column at a flow rate of 1 ml min^{-1} was approximately 15 minutes for cations and 8 minutes for anions. Prior to analysis, all samples were filtered through a 0.2 µm millipore filter and diluted to an EC value of <100µS cm^{-1} . The regenerant used for the column was 25 mM H_2SO_4. The calibration curves produced before the analyses were performed and all of the r-values for the regression lines are at least 0.99 and in many cases 0.999, so that the accuracy of the determinations of concentrations present is within 1%. The precision of the anion analyses determined at 10 different times over 3 different days and the RSD values range from 1-10% indicate an acceptable level of precision.

II.v ICP-AES

The ICP-AES analyses of the plant matter were performed on a Jobin Yvon 138 Ultrace ICP spectrometer from the Department of Archaeology at UCT. The spectrometer operates at the following settings:

Power:	1 kW
Pressure- Ar gas:	3.5 bar
RF :	27.12 MHz
Sample uptake:	2.0 ml min^{-1}
Observation height:	15 mm above coil
Aerosol flow rate (Ar):	0.4 l min^{-1} and 0.8 l min^{-1} (Na and K)
Plasma gas flow rate (Ar):	0.1 l min^{-1}
Coolant gas flow rate (Ar):	12 l min^{-1}

Samples were analysed in triplicate and RSD values less than 10% were considered to have attained acceptable precision and didn't necessitate re-analysis. Over the 755 analyses performed the mean RSD value was 5.45. The RSD standard deviation, however, was 11.86 which indicates the spread of values that had occurred and in some cases required rerunning. Willard *et al.*(1988) commented that while ICP's have very low detection limits, there is the possibility that sample contamination may occur where samples of high concentration interfere with the analysis of subsequent, lower concentration samples due to the long wash-out time brought about by the low gas and liquid flow rates. This is why the triplicate analyses of each sample was required with an acceptable RSD value being defined at 10% and not requiring a repeat of the analysis.

II.vi MHC precision for flyash

During the characterisation section of the study (chapter 2), some difficulty was experienced in obtaining consistent MHC values. As a consequence a triplicate determination of MHC for unamended flyash was undertaken with the individual MHC values being 464, 465, 444 g kg^{-1}. The mean value determined from this investigation was 457 g kg^{-1} with a standard deviation of 12 g kg^{-1}.

Appendix III

DEPARTMENT OF GEOLOGICAL SCIENCES

UNIVERSITY OF CAPE TOWN

INSTRUMENTAL PARAMETERS AND DATA QUALITY FOR ROUTINE MAJOR AND TRACE ELEMENT DETERMINATIONS BY WDXRFS

J P WILLIS

INFORMATION CIRCULAR No. 14

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MAJOR ELEMENTS

Nine major elements, Fe, Mn, Ti, Ca, K, P, Si, Al and Mg (with Ni and Cr when Ni and Cr concentrations exceed ~2000 ppm) are determined using fusion disks prepared according to the method of Norrish and Hutton (1969). The disks are analyzed on a Philips PW1480 wavelength dispersive XRF spectrometer with a Mo/Sc x-ray tube. Fe, Mn and Ti are measured with the tube at 100 kV, 25 mA. The other elements are determined with the tube at 40 kV, 65 mA. Peak only measurements are made on the elements Fe through Mg. Sodium is determined using powder briquettes, the x-ray tube at 40 kV, 65 mA, and with backgrounds measured at −2.00 and +2.00°2θ from the peak position. Analytical conditions are given in Table III.i.

Fusion disks made up with 100% Johnson Matthey Specpure SiO_2 are used as blanks for all elements except Si. Fusion disks made up from mixtures of Johnson Matthey Specpure Fe_2O_3 and $CaCO_3$ are used as blanks for Si. Intensity data are collected using the Philips X40 software. Matrix corrections are made on the elements Fe through Mg using the de Jongh model in the X40 software. Theoretical alpha coefficients used in the de Jongh model for all other elements on the analyte element are calculated using the Philips on-line ALPHAS programme. Na_2O is not included in the matrix corrections in de Jongh model, and no matrix corrections are made to the sodium intensities.

Table III.i Analytical conditions for determination of major elements using a Philips PW1480 WDXRF spectrometer.

Element/line	Collimator	Crystal	Detector	PHS		Counting time (s)	Concentration range *	RMS	No. of standards
				LWL	UPL				
FeKα	F	LiF(220)	FL	16	70	150	0 - 17	0.118	14
MnKα	F	LiF(220)	FL	15	70	150	0 - 0.22	0.005	14
TiKα	F	LiF(200)	FL	28	70	150	0 - 2.75	0.020	14
CaKα	F	LiF(200)	FL	36	70	20	0 - 12.5	0.037	14
KKα	F	LiF(200)	FL	36	70	50	0 - 15.5	0.057	14
PKα	C	GE(111)	FL	25	75	100	0 - 0.36	0.008	14
SiKα	C	PE(002)	FL	32	74	100	0 - 100	0.408	14
AlKα	C	PE(002)	FL	25	75	80	0 - 17.5	0.136	14
MgKα	F	PX-1	FL	30	74	150	0 - 46	0.095	14
NaKα	F	PX-1	FL	30	78	200	0 - 9	0.189	15

* = all concentrations expressed as wt% oxide

$$RMS = \sqrt{\frac{1}{n-k} \sum \left(Conc_{given} - Conc_{calc} \right)}$$

where

n = no. of standards

k = no. of calibration coefficients, *i.e.* 2, the slope and intercept of the calibration line.

$Conc_{given}$ = recommended concentration for an element in a standard

$Conc_{calc}$ = concentration of an element calculated from the best-fit calibration line

First order calibration lines, with intercept, are calculated using all data points, including blanks. Calibration plots for Fe_2O_3, CaO, SiO_2 and MgO are given in Figures III.i - III.iv.

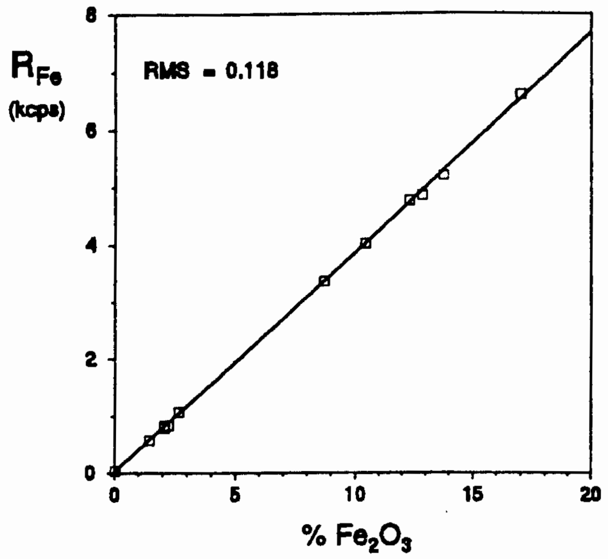

Figure III.i. **Calibration plot for Fe_2O_3 using "Norrish" fusion disks.**

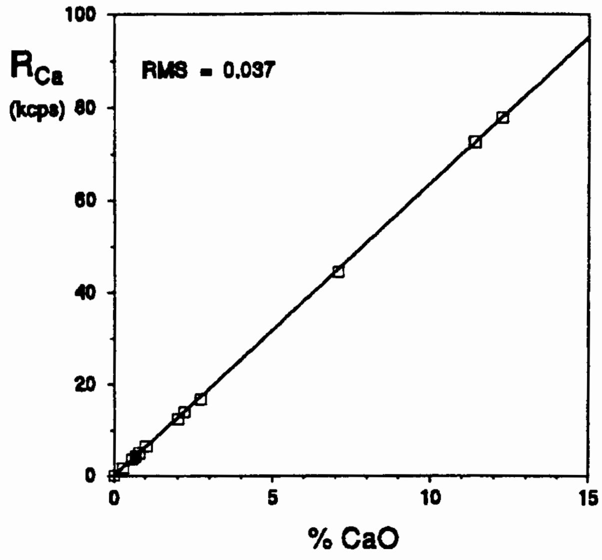

Fig III.ii **Calibration plot for CaO using "Norrish" fusion disks.**

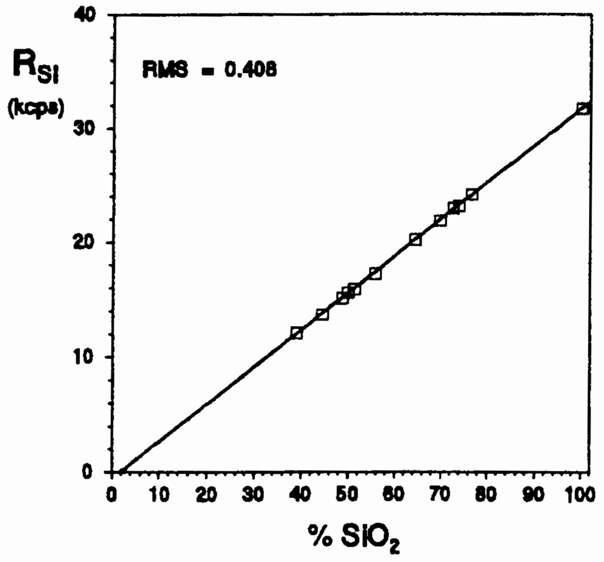

Fig III.iii **Calibration plot for SiO_2 using "Norrish" fusion disks.**

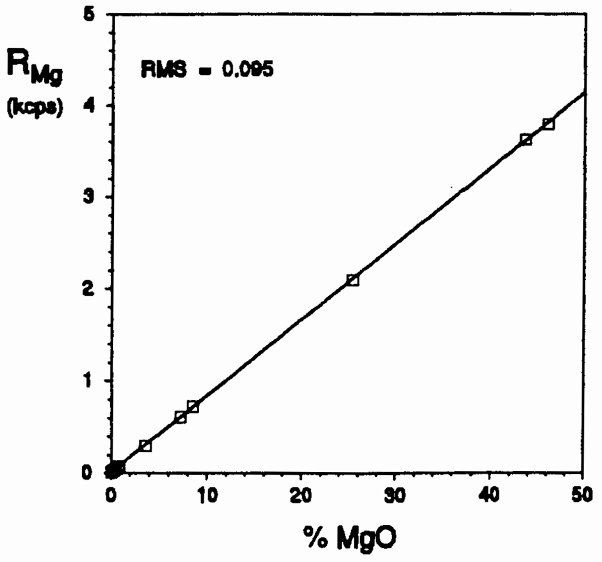

Fig III.iv **Calibration plot for MgO using "Norrish" fusion disks.**

TRACE ELEMENTS

Trace elements are determined on powder briquettes using a series of x-ray tubes. Analytical conditions are listed in Tables III.ii and III.iii.

Table III.ii. **X-ray tubes and tube and x-ray path settings for the determination of trace elements using a Siemens SRS303AS and Philips PW1480 WDXRF spectrometer.**

Spectrometer	Element/line	X-ray tube		X-ray path
		Target	kV - mA	
SRS303AS	RhKαC	Rh	60 45	Vacuum
SRS303AS	MoKα	Rh	60 45	Vacuum
SRS303AS	NbKα	Rh	60 45	Vacuum
SRS303AS	ZrKα	Rh	60 45	Vacuum
SRS303AS	Y Kα	Rh	60 45	Vacuum
SRS303AS	SrKα	Rh	60 45	Vacuum
SRS303AS	U Lα$_1$	Rh	60 45	Vacuum
SRS303AS	RbKα	Rh	60 45	Vacuum
SRS303AS	ThLα$_1$	Rh	60 45	Vacuum
SRS303AS	PbLβ$_1$	Rh	60 45	Vacuum
PW1480	ZnKα	Au	60 45	Vacuum
PW1480	CuKα	Au	60 45	Vacuum
PW1480	NiKα	Au	60 45	Vacuum
PW1480	CoKα	W	50 55	Vacuum
PW1480	MnKα	W	50 55	Vacuum
PW1480	CrKα	W	50 55	Vacuum
PW1480	V Kα	W	50 55	Vacuum
PW1480	BaLα$_1$	Cr	50 55	Vacuum
PW1480	ScKα	Cr	50 55	Vacuum

Table III.iii. **Instrumental conditions for determination of trace elements using a Siemens SRS303AS and Philips PW1480 WDXRF spectrometer.**

Element /line	Collimator	Crystal	Detector	PHS LWL UPL	Counting time (s)	Background position(s) relative to peak position	Concentration range *
RhKαC	F	LiF(220)	SC	0.6 1.5	200		
MoKα	F	LiF(200)	SC	0.7 1.7	160	-0.8 +0.65	0 - 5.2
NbKα	F	LiF(200)	SC	0.5 1.6	160		0 - 268
ZrKα	F	LiF(200)	SC	0.5 1.6	160		0 - 1210
YKα	F	LiF(200)	SC	0.5 1.6	160	-0.61 +0.54	0 - 143
SrKα	F	LiF(200)	SC	0.5 1.6	160	+0.60	0 - 440
ULα_1	F	LiF(200)	SC	0.5 1.6	160		0 - 15
RbKα	F	LiF(200)	SC	0.5 1.6	160	+0.53	0 - 530
ThLα_1	F	LiF(200)	SC	0.5 1.6	160		0 - 51
PbLβ_1	F	LiF(200)	SC	0.4 1.4	160	+1.27	0 - 40
ZnKα	F	LiF(220)	FS	20 80	200	-1.08 +4.24	0 - 235
CuKα	F	LiF(220)	FS	20 80	200	+4.44	0 - 227
NiKα	F	LiF(220)	FS	20 80	200	+2.52	0 - 630
CoKα	F	LiF(220)	FL	15 75	200	+1.00	0 - 116
MnKα	F	LiF(220)	FL	15 75	200	-2.30 +4.70	0 - 1700
CrKα	F	LiF(220)	FL	15 75	200	-4.10 +2.90	0 - 465
VKα	F	LiF(220)	FL	13 67	200	+3.40	0 - 640
BaLα_1	F	LiF(200)	FL	25 75	200	-5.20	0 - 2680
ScKα	F	LiF(200)	FL	25 75	200	-2.78	0 - 54

* = all concentrations expressed as part per million (ppm or mg.kg^{-1})

The RhKα Compton peak is used to determine the mass absorption coefficients of the specimens at the RhKαC wavelength (Figure III.v) and the calculated values are used to correct for absorption effects on the Mo, Nb, Zr, Y, Sr, U, Rb, Th, Pb, Zn, Cu and Ni analyte wavelengths. Primary and secondary mass absorption coefficients for the Co, Mn, Cr, V, Ba and Sc analyte wavelengths are calculated from major element compositions using the tables of Heinrich (1986). Mass absorption coefficient corrections are made to the net peak intensities, (gross peak intensities corrected for dead time losses, background and spectral overlap), to correct for absorption differences between standards and specimens. No corrections are made for enhancement, which could be small but significant (<~5% relative) for the elements Cr, V, Ba and Sc in certain specimens, depending on their concentrations of Fe, Mn and Ti.

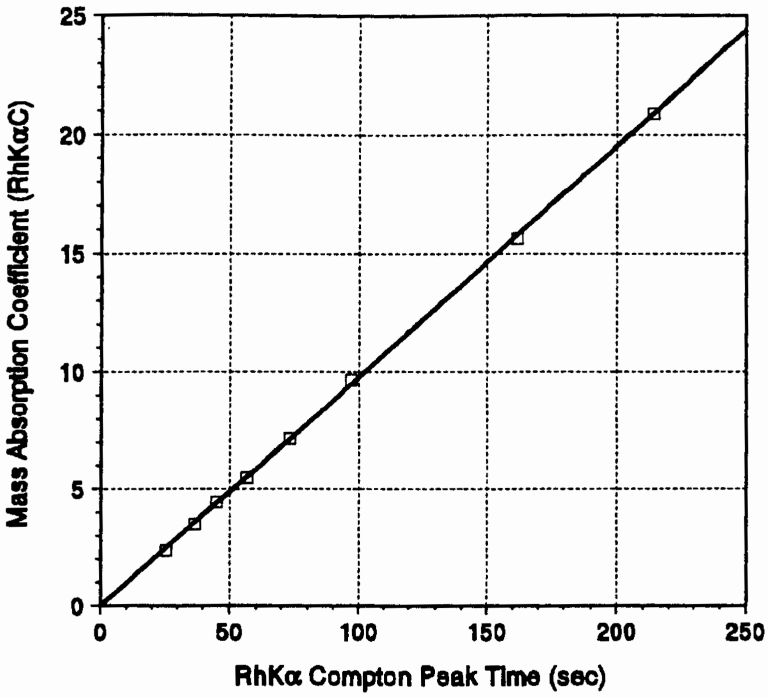

Fig III.v **Calibration line for determination of mass absorption coefficients at the RhKαC wavelength. RhKαC peak time is the time required to accumulate 400 000 counts on the RhKαC peak using the fixed count method.**

Measured intensity data are processed through the computer program TRACE to correct gross peak intensities for background and spectral overlap and to make mass absorption coefficient corrections according to the methods outlined in Duncan *et al.* (1984). First order calibration lines with zero intercept are calculated using six or more international rock standard reference materials (SRMs) for each element. The one standard deviation (1 σ) error due to counting statistics and the lower limit of detection is calculated for each element in each specimen.

Table III.iv lists the given and calculated concentrations for selected elements in a number of rock SRMs, which gives an indication of the accuracy of the trace element data. Table III.v lists the one standard deviation counting error and lower limit of detection for each of the elements in an acidic (low Fe, Ca and Mg, high Si) rock and in a mafic (high Fe, Ca and Mg, low Si) rock. Because of the difference in mass absorption coefficients between the two types of specimen the counting error and lower limit of detection will be slightly higher in mafic rock specimens. The two examples given cover the range of mass absorption coefficients found in the majority of geological rock, soil and sediment specimens.

The counting error and lower limit of detection are calculated using the following formulae:

$$1\sigma \; error \; (in \; ppm) = Conc \times \frac{\sqrt{\frac{I_p}{T_p} + \frac{I_b}{T_b}}}{I_n}$$

and

$$LLD \; (in \; ppm) = \frac{6}{m}\sqrt{\frac{I_b}{T_{total}}}$$

where Conc = calculated concentration in ppm
m = net peak / concentration
I_p = gross peak count rate in cps
I_b = background count rate under the peak in cps
I_n = $I_p - I_b$ = true net peak count rate in cps
T_p = counting time for peak in seconds
T_b = total counting time for background in seconds
T_{total} = $T_p + T_b$

N.B. I_b is the calculated background *plus* any corrections for spectral interference, and is equal to $I_p - I_n$.

Table III.iv Given and calculated trace element data (all values in ppm) for some rock SRMs.

Element	QLO-1		BHVO-1		W-2		STM-1		BIR-1	
	Given	Calc	Given	Calc	Given	Calc	Given	Calc	Given	Calc
Mo	2.6	3.5	1.0	0.8	(0.6	0.5	5.2	3.1	(0.5	<0.8
Nb	10	11	19	19	7.9	7.4	268	267	0.6	0.9
Zr	185	190	179	181	94	95	1210	1220	16	19
Y	24	25	28	28	24	23	46	47	16	17
Sr	336	329	403	395	194	195	700	689	108	109
U	1.9	2.3	0.4	<1.6	0.5	<1.2	9.1	8.8	0.01	<1.2
Rb	74	71	11	9.7	20	20	118	114	0.3	<0.6
Th	4.5	4.0	1.1	1.8	2.2	2.7	31	31	0.03	<1.5
Pb	20	20	2.6	3.1	9.3	8.5	18	17	3	3.1
Zn	61	61	105	106	77	79	235	242	71	69
Cu	29	25	136	139	103	108	(4.6	2.1	126	132
Ni	(5.8	1.8	121	127	70	72	(3	1.7	166	170
Co	7.2	7.6	45	44	44	43	0.9	<1.9	51	52
Mn	720	690	1300	1290	1260	1240	1700	1600	1320	1280
Cr	(3.2	3.6	289	312	93	100	(4.3	3.2	382	404
V	54	44	317	314	262	257	(8.7	<1.6	313	306
Ba	1370	1430	139	138	182	191	560	589	7.0	10
Sc	8.9	10.3	31.8	33.9	35	36	0.6	0.5	44	39

(n.n = value given for information only

Table III.v Calculated trace element data, 1 σ counting error and lower limit of detection (all values in ppm) for two rock specimens having different mass absorption coefficients.

Element	JR-2			JB-1a		
	Calc	1 σ	LLD	Calc	1 σ	LLD
Mo	4.1	0.2	0.6	1.8	0.3	0.7
Nb	19	0.1	0.4	28	0.2	0.5
Zr	87	0.1	0.3	152	0.2	0.4
Y	51	0.2	0.6	24	0.2	0.6
Sr	8.2	0.1	0.4	444	0.3	0.5
U	11	0.3	0.9	2.3	0.4	1.2
Rb	303	0.2	0.4	39	0.2	0.6
Th	34	0.4	1.1	9.8	0.5	1.4
Pb	24	0.5	1.3	7.5	0.6	1.8
Zn	28	0.2	0.6	84	0.4	0.9
Cu	1.1	0.3	0.8	55	0.5	1.1
Ni	1.3	0.3	0.8	139	0.7	1.3
Co	<1.2	0.4	1.2	37	0.9	2.3
Mn	878	1.7	1.2	1100	2.0	1.8
Cr	1.6	0.4	1.3	406	1.5	2.0
V	1.7	0.4	1.2	193	1.4	3.0
Ba	28	0.6	1.5	523	1.8	3.3
Sc	6.0	0.2	0.5	26	0.4	0.9

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