

THE UNIVERSITY OF CALGARY

RECLAMATION OF AGRICULTURAL SOILS
CONTAMINATED WITH ELEMENTAL SULPHUR

BY

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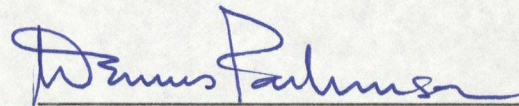
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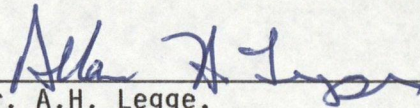
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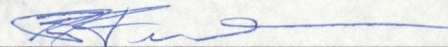
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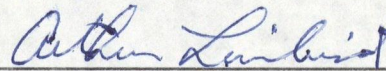
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ABSTRACT

Reclamation potential of contaminated soil from beneath a sulphur block basepad was evaluated in three 62-day greenhouse trials. The effect of lime and/or manure additions to pots of soil containing four different levels of total sulphur were tested through characterization of soil and leachate chemistry and growth of reed canarygrass.

Unamended soils were acidic and contained high levels of soluble aluminum and available ammonium. Lime addition to sulphur-contaminated soils resulted in the maintenance of a neutral soil pH throughout the experiment and decreased available phosphorous levels. Manure amendment did not significantly increase soil pH or lower soluble aluminum concentrations. Leachates produced from pots containing acid soils were acidic, while those produced from neutralized soils were neutral.

No plant growth occurred in pots containing unamended, sulphur-contaminated soil. Lime applications were not effective in promoting plant growth at soil sulphur levels above 4%. This may be due to pore space reduction due to the physical presence of the lime. Soils amended with manure alone, did not produce any plant growth.

Soils contaminated with elemental sulphur should be treated with smaller initial lime applications over an extended time period than is currently practised. Prompt liming of soils contaminated with elemental sulphur is, however, recommended to minimize acidic leachate production.

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CHAPTER 1

INTRODUCTION

1.1 SULPHUR CYCLING IN SOILS

Sulphur is an essential nutrient for both plants and animals (Coleman 1966). The element has six valence electrons and can exist in the free state (valence of zero) or in a number of inorganic and organic compounds. The majority of sulphur in soils is normally in the organic form. Estimates of organic sulphur in agricultural soils vary from 75% (Brown 1982) to over 95% (Nyborg 1978; Tabatabai 1984) of the total sulphur content. Organic fractions of sulphur in soil have been separated into three main categories: (1) HI-reducible S, (2) carbon-bonded S, and (3) unidentified S (residual or inert) (Tabatabai 1984). Sulphate is the most common inorganic form of sulphur found in soil, accounting for approximately 40% of the inorganic fraction (Alexander 1977). It exists in soil as easily soluble SO_4^{2-} , adsorbed SO_4^{2-} , insoluble SO_4^{2-} , or as insoluble SO_4^{2-} , co-precipitated with calcium carbonate (Wainwright 1984). Other forms of inorganic sulphur ions found in soil solution include sulphur trioxide (SO_3^{2-}) and sulphides (S^{2-}) (Brady 1984). Sulphide usually accounts for less than 1% of the total sulphur present in soils (Scott 1985).

Much of the information about sulphur in soils has resulted from studies carried out on sulphur deficient soils (Stewart et al. 1985; Li and Caldwell 1966). Sulphur deficiencies in soil have been noted with increasing frequency, especially over the last ten years

(Tisdale et al. 1985). Positive responses to sulphur fertilization have been documented worldwide (Tabatabai 1984).

Sulphur usually enters agricultural soil from four sources: (1) weathering products from parent material, (2) fertilizer additions, (3) atmospheric SO_2 that is absorbed by plants and/or soil, and (4) organic matter decomposition (Hausenbuiller 1978). Loss of sulphur from soil results from: (1) leaching into the groundwater, (2) uptake by plants, and (3) volatilization (Brown 1982).

Sulphur transformations in soils are thought to result primarily from microbial activity, although chemical processes are possible (Wainwright 1984). The major microbial processes are mineralization, immobilization, oxidation, and reduction. Mineralization involves the breakdown of large organic sulphur molecules into smaller units and finally into inorganic sulphate. The mechanisms of sulphur mineralization are not well understood (Scott 1985). It is believed that sulphur behaves similarly to nitrogen in that 1 to 3% of soil organic sulphur is mineralized and a similar amount of sulphate is immobilized (Nyborg 1978). Immobilization involves uptake of inorganic sulphur by microorganisms and the conversion of the sulphur into organic compounds (Scott 1985). Oxidation involves the conversion of reduced forms of inorganic sulphur compounds to sulphate. This process will be discussed in detail in Section 1.3. The final sulphur transformation process mediated by microorganisms involves the reduction of sulphate and intermediate compounds to sulphide. This specialized process generally takes place only in anaerobic soils.

Sulphur is considered an essential plant nutrient along with nitrogen, phosphorous, and potassium. As plants can only assimilate sulphur in the sulphate form (Pepper and Miller 1978), the mineralization process described above is an important part of the sulphur cycle. Sulphur is required by plants for a number of processes including the synthesis of sulphur-containing amino acids and formation of chlorophyll (Wainwright 1978). Crops vary in their sulphur requirements as they do in their requirements of other nutrients. Agronomic crops generally require about the same amount of sulphur as they do of phosphorous (Tabatabai 1984). As both sulphur and nitrogen are required for protein synthesis, the amount of available nitrogen can affect plant sulphur requirements.

1.2 SOURCES OF ELEMENTAL SULPHUR CONTAMINATION

Localized areas exist where contaminant levels of sulphur are found in soil. Although this situation does not occur on a large scale, the effects of high levels of sulphur in soil merits investigation. Elemental sulphur occurs naturally in aerated soils only in specialized situations such as in the hot springs regions in Yellowstone, USA (Fliermans and Brock 1972). Elemental sulphur may be deposited on soil in contaminant levels as a result of industrial processes. For the purposes of this work, contaminant amounts of sulphur in soil will be considered as those levels that exceed 1% total sulphur.

Two primary sources of contaminant levels of sulphur exist; (1) high SO₂ emissions from industrialized facilities such as sour gas or coal processing plants (Wainwright 1978), and (2) elemental sulphur deposition from industrial facilities. The effects of SO₂ emissions on terrestrial ecosystems have been and continues to be investigated (Wainwright 1980; Hutchinson and Havas 1980; Legge et al. 1978).

It has been estimated that 2000 to 3000 hectares of Alberta soils have pH values below 2.0, due to elemental sulphur deposition (Nyborg 1982). Elemental sulphur additions to soil will cause a reduction in soil pH and can, therefore, be used to correct nutrient deficiency symptoms caused by high soil pH. Addition of contaminant levels of elemental sulphur which result in soil pH values of 2.0 to 3.0 will, however, detrimentally alter biological and other chemical properties (Bertrand 1973).

The central role of the oil and gas extraction industry in the economy of Alberta is well known. Hydrocarbons extracted from a reservoir that has a significant amount of H₂S are referred to as sour oil or sour gas. Alberta produces 95% of Canada's elemental sulphur by converting the H₂S present in sour oil and gas to elemental sulphur through a controlled oxidative method called the Claus Process (Hyne 1977).

The majority of sour gas plants built in the 1950's to early 1970's stored elemental sulphur by pouring molten sulphur into a large block. The block was poured on top of a basepad, which was also usually formed from molten sulphur. Many of the sulphur basepads were

poured directly onto soil, with minimal ground preparation. This method of stockpiling was used to store sulphur inventory until a market for the commodity developed (Klemm 1972). There are approximately 105 block basepads at 34 locations in western Canada (Hyne and Schwalm 1983). The total area of basepads is estimated to be 100 hectares. These basepads range from a few hundred to 50,000 m² in area (Hyne 1986). Since 1980, few, if any, new basepads have been established in western Canada. Therefore, most blocks have been in place for at least ten years.

The market for elemental sulphur has been strong for the last five years. Since 1968, Canada has been the world's largest exporter of elemental sulphur (Klemm 1972). Over fifty percent of sulphur consumed in the western world is used to produce nitrogen and phosphate fertilizers (Tisdale et al. 1985).

As a result of the increased sales demand and declining reserves in older sour oil and gas fields, sulphur blocks are being depleted. Projections by Alberta Sulphur Research Limited indicate that little sulphur block inventory will remain in western Canada by the late 1980's or early 1990's (W. Schwalm, pers. comm.). Sour gas processing facilities built from the late 1970's onwards have selected other means, such as prilling or keeping the sulphur molten, to handle sulphur due to production difficulties and environmental problems associated with the blocks.

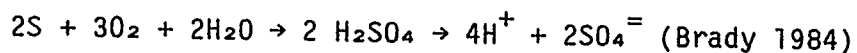
There are two sources of elemental sulphur contamination associated with blocks: (1) the deposition of sulphur dust on soil up to 4 km downwind of the facility, and (2) sulphur remaining in the

soil after the block and basepad have been dismantled (Nyborg 1978). In both cases, soils become acidified and may eventually become devoid of vegetation.

The cleanup and reclamation of former sulphur block basepad sites can be a difficult process if the basepad was poorly prepared. As much as 20% total sulphur may remain in the soil once the initial cleanup phase is completed. Little information is available about the biological, chemical, and physical condition of soils underlying sulphur basepads. Data collected to date indicate that the soils are highly acidified and that large amounts of sulphate-sulphur can accumulate and be leached into underlying soils (Leitch and Nyborg 1985). Reclamation of these soils is necessary to arrest the generation of excess soil acidity and related biological and chemical changes as well as the potential leaching of nutrients and metals through the soil profile into groundwater resources.

1.3 MICROBIAL OXIDATION OF SULPHUR IN SOILS

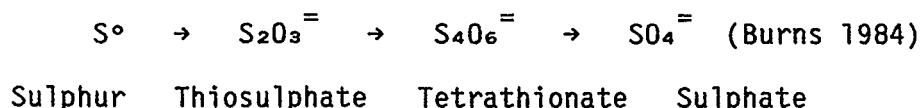
Elemental sulphur is inert and will have no effect on soil processes. It does not, however, lie dormant in the soil. Through both chemical and biological oxidation, sulphuric acid is formed. The general reaction describing the oxidation of elemental sulphur to sulphuric acid is as follows:



Once formed, the sulphuric acid does not remain stable in the soil. The breakdown of sulphuric acid to sulphate and hydrogen ions is the

final step in the oxidation process that results in acidification of the soil. As shown in the above equation, for every sulphate ion produced, two hydrogen ions are also produced. The production of hydrogen ions will increase soil acidity and can result in a lowering of soil pH. The degree to which the soil is acidified will depend on the amount of elemental sulphur present and the degree to which oxidation takes place.

Although it has been shown that elemental sulphur can be oxidized in soil slowly by chemical means, microbiological oxidation is considered to be more rapid and of greater importance (Pepper and Miller 1978). Numerous microorganisms are capable of oxidizing sulphur, including members of the autotrophic genus Thiobacillus, heterotrophs such as the fungi and the actinomycetes, as well as other autotrophs such as the colourless, filamentous sulphur bacteria, and the photosynthetic sulphur bacteria (Wainwright 1984; Burns 1984). It has been documented that only Thiobacillus and some heterotrophs play an important role in sulphur oxidation in most agricultural soils (Germida et al. 1985; Wainwright 1984). There are two intermediary sulphur compounds formed during the biological oxidation of elemental sulphur to sulphate. The sequence is listed below:



While microorganisms such as Thiobacillus thiooxidans are capable of carrying out the complete oxidation process, other microorganisms such

as I. thioparus and I. novellus can only oxidize certain inorganic and organic sulphur salts (Burns 1984).

A major difference between autotrophic and heterotrophic sulphur oxidation is that the autotrophs gain energy from the process. Autotrophic sulphur oxidizing organisms are capable of using the energy produced that results from the oxidation of reduced sulphur compounds (Wainwright 1984). In contrast, the inability of heterotrophic bacteria to gain energy from the process has been demonstrated since the 1950's (Wainwright 1984). Oxidation of sulphur by heterotrophs is thought to occur incidental to their growth and metabolism. The biochemical means of sulphur oxidation by heterotrophs is not well understood.

There are five sulphur oxidizing species of Thiobacillus that have been well characterized (Brady 1984). Environmental requirements and tolerances of these species vary considerably. For example, I. thiooxidans are extremely tolerant of acidity and function best in the pH range of 2.0 to 3.0 (Rao and Berger 1971), while I. thioparus is only capable of functioning in a neutral pH range (Starkey 1966). Although both I. thiooxidans and I. thioparus are both obligate autotrophs, I. novellus is a facultative autotroph and can grow on organic substances (Burns 1984). I. kabobis, described by Reynolds et al. (1981) was isolated from acidic soil adjacent to a sulphur stockpile located in Alberta.

It is generally accepted that extreme reductions in soil pH will cause decreases in microbial diversity (Alexander 1977). It is believed that few organisms are capable of maintaining normal

functions at soil pH levels of 2.0 to 4.0 (Wainwright and Killham 1980). Below soil pH levels of 2.0, extremely limited microbial activity occurs (Alexander 1977). Bryant et al. (1979) demonstrated a reduction in total bacterial numbers in a soil adjacent to a sulphur block that had a pH of 3.0. Although there have been bacteria isolated from soils that have pH values of 3.0 (Bryant et al. 1979), sulphur-oxidizing fungi have not been recovered from soils heavily contaminated with sulphur due to isolation difficulties. Recent development of general isolation media for sulphur-oxidizing heterotrophic bacteria and fungi (Wainwright 1978) should allow characterization of all microorganisms involved in sulphur oxidation at acidic pH levels.

Studies investigating the primary factors governing the oxidation rate of sulphur in soils have been conducted for both sulphur deficient soils and sulphur-contaminated soils. In all cases, it has been concluded that particle size, soil temperature and soil moisture are the three main factors governing oxidation rates (Bettany and Janzen 1985; Wainwright 1980).

The rate of elemental sulphur oxidation decreases as particle size increases (Laishley and Bryant 1985). This is a major factor to be considered when investigating reclamation options for soil located below former sulphur block basepads. Particle sizes of sulphur will range from microscopic to centimetres in diameter. Oxidation rates will, therefore, depend on the relative distribution of sulphur particle sizes at each site. Small particles of sulphur, from 5 to 50 μm in diameter, will be quickly converted to sulphate, while

pellets measuring 1 to 3 mm in diameter will be oxidized very slowly (Nyborg 1983).

Sulphur oxidation rates increase with increasing temperature up to about 40°C. Optimal temperatures for oxidation lie between 30° and 40°C (Li and Caldwell 1966). Wainwright (1980) extends the optimal range down to 23°C. Bettany and Janzen (1985) found that oxidation rates dropped sharply at both high and low soil moisture extremes and that the optimal soil moisture tension for sulphur oxidation was 10 to 200 kPa, depending on soil texture. Wainwright (1980) reports that optimal oxidation occurs when soil moisture levels are close to field capacity.

Sulphur oxidation has been documented in areas surrounding natural gas plants (Maynard et al. 1983; Nyborg 1978). The degree of oxidation that has taken place below a sulphur block prior to dismantling has not been documented. Optimal oxidation rates are not likely under these blocks, due to varying particle size, sub-optimal average annual temperature, possible lack of oxygen, and potentially reduced moisture levels.

1.4 EFFECTS OF CONTAMINANT LEVELS OF ELEMENTAL SULPHUR ON SOIL PROCESSES

It is thought that soils acidified by elemental sulphur do not differ significantly from naturally acid soils, except that the rapid acidification that can take place with elemental sulphur deposition may induce sudden and unknown changes in plant nutrient availability (Nyborg 1982). It appears that the decrease in soil pH

resulting from sulphuric acid production is responsible for many of the documented changes in soil processes (Rechcigl and Sparks 1985; Hilal et al. 1985). A decrease in soil pH can lead to: (1) an increase in the mobilization/dissolution of metals such as aluminum, iron, and manganese into the soil (Winterhalder et al. 1984), (2) a decrease in the cation exchange capacity (CEC) (Bache 1980), (3) impaired cycling of nitrogen (Rorison 1980), and (4) reduced availability of phosphorous (Brady 1984; Halstead et al. 1963).

It has been reported that plant growth on agricultural soils is impaired when soil pH is less than 5.5 (Webber et al. 1977; Hoyt and Turner 1975). Numerous studies have concluded that the major factor contributing to growth reduction is aluminum toxicity (Foy 1984). Toxicity of iron and manganese also affect plant growth and soil processes (Francis 1982; Klemm 1972). If metals such as aluminum, iron, and manganese go into soil solution at reduced pH, it would also be expected that these metals would be leached more readily from the soil. It might be anticipated that not only would there be an effect on plant growth, but also a health risk from metal contamination of local groundwater supplies. Knowledge of the chemical composition of leachates produced from soils heavily contaminated with elemental sulphur would indicate whether or not metals are mobile within the soil solution.

Charges on weak-acid exchange sites such as in poorly-ordered aluminosilicates and hydrous oxides are strongly pH dependent (Bache 1980). These acids become dissociated at high pH and undissociated at

low pH. Therefore, CEC and the associated ability of soil to store reserves of nutrient cations, drops as soil pH decreases (Bache 1980).

There have been a number of published reports on the effects of reduced pH on nitrogen cycling in soils (Jackson 1967; Wainwright 1980). The majority of researchers report a decrease in nitrification with decreasing soil pH (Jackson 1967; Nyborg and Hoyt 1978).

Nitrosomonas and Nitrobacter, which are both autotrophs and are largely responsible for the transformation of ammonium to nitrite and of nitrite to nitrate, respectively, are particularly sensitive to acidity (Rechcigl and Sparks 1985). Not all authors, though, have reported reduced nitrification with decreasing pH (Wainwright 1980; Tabatabai 1985), possibly due to a limited drop in soil pH. It is also possible that low nitrification rates measured in acid soils may be the result of heterotrophic action (Rechcigl and Sparks 1985).

Contradictory results concerning nitrogen mineralization in acid soils have been published. Rechcigl and Sparks (1985) and Alexander (1980) report that conversion of soil organic nitrogen to ammonium does not appear to be affected by a drop in soil pH, while Francis (1982) suggests that acidification of forest soils may lead to significant reductions in nitrogen mineralization. Ammonification is not as sensitive to soil acidity as is nitrification since numerous heterotrophs are involved in the ammonifying process (Alexander 1980). A high concentration of ammonium in acid soils has often been measured (Alexander 1980; Rorison 1973; Tabatabai 1985), possibly the result of a breakdown of the nitrification process (Rorison 1973) rather than the result of increased mineralization. It has been suggested that

ammonium toxicity may be a growth limiting factor in acid soils (Foy et al. 1978).

The availability of phosphorous to plants varies with pH (Rorison 1973). At low pH values, reaction of the soluble phosphorous ion, H_2PO_4^- , with soluble iron, aluminum and manganese results in the formation of insoluble phosphorous compounds (Brady 1984). Plant availability of phosphorous is, therefore, drastically reduced. Some evidence also exists for a decrease in mineralization of phosphorous in acid environments (Halstead et al. 1963).

If contaminant levels of sulphur are present in the soil and oxidation conditions are favourable, contaminant levels of sulphate may also accumulate as a result of the dissociation of sulphuric acid. While some of the sulphate ions may be leached from the soil solution into groundwater, adsorped onto the soil matrix, or removed from the soil solution through uptake by vegetation, the remainder of the sulphate ions will be in the soil solution. This increase in soluble sulphate ions will result in an increase in soil conductivity, due to the increase in dissociated anions capable of conducting a current. Increased soil conductivity may, in turn, limit plant growth (Hausenbuiller 1978; Brady 1984).

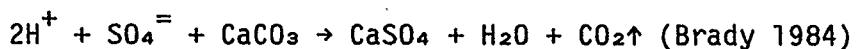
1.5 RECLAMATION OF SOILS CONTAMINATED WITH ELEMENTAL SULPHUR

Realizing that the major factor affecting soils contaminated with elemental sulphur is the acidity produced from sulphur oxidation, neutralization of this acidity is required to achieve successful reclamation. Realizing also that an acidic soil pH has, in most

cases, been maintained for an extended period of time, the soil may also require re-inoculation with microorganisms that operate within a neutral soil pH regime.

1.5.1 The Use of Lime as a Reclamation Aid

Liming is an ancient agricultural practice (Barber 1984). Many soils that are slightly acid are neutralized with lime to promote plant growth (Brady 1984). The neutralization reaction that takes place when calcium carbonate is added to an acid soil is as follows:



While it is well documented that soils made acid as a result of crop management practices such as fertilization can be reclaimed by amending the soil with calcium carbonate (Martini and Mutters 1985; Sims and Ellis 1983), no trials have been undertaken to reclaim soils that have been heavily contaminated with elemental sulphur. It is, therefore, not known whether procedures used to reclaim slightly acidified soils can be used to reclaim heavily contaminated soils.

Oxides, hydroxides, or carbonates of calcium and magnesium are added as liming materials to acid soils to replace the hydrogen and aluminum ions with metallic cations. These compounds are known as agricultural limes (Brady 1984). Limestone is the main liming material used (Barber 1984). It can be calcite, dolomite, or a mixture of both minerals. The advantage of using a carbonate lime over a hydroxide lime is that the soil pH will not increase to a

strongly alkaline value if too much lime is applied. Calcium hydroxide must be applied cautiously to a soil due to its strongly alkaline nature. Bertrand (1973) found that the best liming material for neutralizing soils made acid as a result of elemental sulphur-contamination was calcium carbonate.

As a result of the neutralization reaction that occurs in a limed acid soil, calcium sulphate, or gypsum, will be formed. This is a highly insoluble compound in soil. Bertrand (1973) reported that calcium carbonate with any more than 5% magnesium carbonate contamination was not suitable for reclamation purposes. Magnesium sulphate, also formed as part of the neutralization process, is soluble in soil and can lead to an elevation in the concentration of soluble salts in the soil solution.

There are a number of different ways to determine the amount of lime required to neutralize an acid soil. Differences in recommended rates of lime originate, in part, from differing levels of soil acidity. Most of the lime requirement work has been based on soils that have become acidified as a result of climatic influences and agricultural practices. Little work has been done with agricultural soils that have been heavily contaminated with elemental sulphur. It has been reported that the addition of calcium carbonate at a rate of four times the measured level of elemental sulphur was necessary to control acidification of soil (Adamczyk-Winiarska et al. 1975). The highest level of elemental sulphur in their soil was 1%. Lime requirement tests can be carried out on soil that is to be neutralized by incubating the soil with known amounts of lime and measuring the

soil pH response (Page et al. 1982). There are also procedures available where the soil is added to a specified buffer mixture and the pH of the resultant mixture is taken. By consulting a table that compares the soil-buffer pH with that of the desired soil pH, lime recommendations can be read directly (Page et al. 1982).

Another method of determining a lime requirement is based on chemical stoichiometry. On the basis of molecular weight, a little more than three times the amount of calcium carbonate will be required to neutralize the potential acidity generated by the amount of total sulphur detected (Hyne 1986). When dealing with a soil that has only small amounts of sulphur (less than 1%) present, the 3:1 rule would seem quite practical. However, soils located below former basepads may contain as much as 20% by weight of total sulphur. This would require a lime application of 60% by weight to the soil. It is not known if such an application would allow successful reclamation, while neutralizing produced acidity.

There have been a number of reports on the effect of liming acid soils. The literature is divided about the beneficial and detrimental effects of liming. For example, the amount of available phosphorous has been reported as being both reduced (Sherchand and Whitney 1985; Sims and Ellis 1983) and increased (Pombo and Smith 1986; Curtin and Smillie 1986) with lime applications.

Concern has also been expressed that at very high liming rates, such as those required to reclaim soil contaminated with more than 1% elemental sulphur, applications of calcium carbonate may create a soil salinity problem (C. Palmer, pers. comm.). It is not

known if there would be any other disruptions of soil processes with the addition of the required amount of lime to neutralize and reclaim soil upon which a former sulphur basepad and block had existed.

It has also been reported that the application of lime stimulates microbial oxidation of sulphur resulting in additional acid generation (Backes et al. 1985; Bertrand 1973). It is thought that the application of lime creates a more favourable soil environment, by raising the pH, for the sulphur oxidizers to survive and operate. Sulphur oxidation will continue until the soil pH has been lowered enough that the responsible microorganisms can no longer operate. Upon re-liming, the rate of sulphur oxidation will again increase due to the increase in soil pH.

1.5.2 The Use of Manure as an Amendment

A primary concern with soils that have been contaminated for a long period of time is that toxic levels of metals such as aluminum, manganese, and iron may be present. In addition, valuable nutrients such as nitrates may be easily leached from the acid soil. It is known that organic compounds are capable of forming complexes with metals such as aluminum by processes such as surface absorption and chelation (Hoyt and Turner 1975). Required plant nutrients may also be bound and slowly released from organic matter during decomposition (Hausenbuiller 1978). While Hoyt and Turner (1975) concluded that organic matter additions to acidic soils are not a satisfactory long term alternative to the addition of lime as a neutralizing agent, the combination of lime and organic matter may present the best long and

short term solution to reclaiming sulphur-contaminated soils. The organic matter should not only serve to bind toxic metals until the lime has reacted with enough of the oxidized sulphur to alter the soil pH, but it should also serve to improve soil structure and re-inoculate the soil with a variety of microorganisms that may not have been able to tolerate the previous soil pH values of approximately 2.0. Wright et al. (1985) found surface applications of organic matter in the form of cattle manure effective in reducing subsoil acidity. Ahmad and Tan (1986) found that while wheatstraw applications were somewhat effective in alleviating aluminum toxicity in an acid soil, the combination of lime and organic matter was a more effective treatment.

1.6 EVALUATION OF "CAPPING" THE CONTAMINATED SOIL

Another technique that is being considered within the oil and gas industry as a potential reclamation option is the application of a "cap" of uncontaminated soil over limed, sulphur-contaminated soil. Determinations of the amount of lime required to neutralize the contaminated soil are made and the prescribed amount of lime is incorporated into the soil. A "cap" of fill or topsoil material is then placed over the site and the area is seeded. The advantage of this system is that plant establishment should be rapid. A possible disadvantage of the procedure is that if the subsoil does re-acidify, it will be difficult to ensure that additional lime incorporation reaches the target area. Acidic leachate may also be produced from

the limed, contaminated soil, causing a potential hazard to local groundwater supplies.

1.7 OBJECTIVES OF THIS PROJECT

The problem of reclaiming soils that are heavily contaminated with elemental sulphur is specific to a small part of one industry, the oil and gas industry. Although the problem is not widespread, it is dissimilar enough from related issues such as soil acidification from acid precipitation or crop fertilization to require individual research effort. No other soil acidification problem requires a similar magnitude of amendment to neutralize the potential acidity that may be generated in soils that have underlain a former sulphur block and basepad.

It is important to determine the effect of elemental sulphur contamination on soil and on the quality of leachate being produced from these soils. Data produced from investigating these two aspects of sulphur-contaminated soils will aid in the determination of potential environmental and health risks resulting from these soils. It is also important to characterize the soil microorganisms that are capable of oxidizing the elemental sulphur and are contributing to the soil acidification process. This will provide initial information required to assess the degree to which sulphur oxidation takes place in these highly contaminated soils.

The preliminary step in determining a reclamation solution for these sites is to investigate the feasibility of applying lime to neutralize all potential generation of acidity. The feasibility of

such applications must be evaluated from two aspects; the physical application of the required quantities as well as an assessment of the growth potential of the amended soils. In addition, the potential effects of applying manure as an amendment to these soils should be evaluated. Information in the literature suggests that manure may be a beneficial amendment to these soils as a possible source of slow-release plant nutrients as well as a source of potential microbial inoculum.

Finally, the effectiveness of "capping" a limed sulphur-contaminated soil requires evaluation. Aspects of the investigation included assessment of both the growth potential of the soil and the characterization of the leachate produced from such a mixture.

The specific objectives of this project are outlined below:

1. to determine the effect of sulphur contamination on plant growth and on a number of soil chemical properties such as pH, conductivity, available nutrients, total sulphur, extractable aluminum, lime requirement, cation exchange capacity, and sodium absorption ratio;
2. to determine the effectiveness of applications of lime alone and with manure to sulphur-contaminated soil in ameliorating soil conditions and encouraging plant growth;
3. to determine leachate characteristics from sulphur-contaminated soils, both unamended and amended;

4. to characterize the sulphur-oxidizing organisms capable of operating in a soil heavily contaminated with elemental sulphur; and
5. to assess the effectiveness of "capping" a limed, sulphur-contaminated soil with clean soil on the acidity and salinity of generated leachates as well as on the reclamation potential of these soils.

CHAPTER 2

MATERIALS AND METHODS

2.1 LOCATION OF STUDY SITE

Soil samples were taken near a sour gas plant located near Innisfail in south-central Alberta. Agriculture is the primary land use in the area. The soil is a Benalto Silt Loam belonging to the Black Chernozem order (Peters and Bowser 1960) and has developed on glacial till.

A sulphur block basepad was constructed at the gas plant site in 1960. Block preparations consisted of stripping the topsoil and removing surface biomass. A basepad composed of approximately 1 m of sulphur was poured directly on the topsoil stripped surface. Sulphur was poured in the form of a block on top of the basepad. Between 1960 and 1985, sulphur inventory was both added and removed from the block, depending on market conditions. By 1985, the sulphur block had been removed and only the basepad remained. Sulphur-contaminated soil was removed from below a freshly exposed portion of basepad material.

Uncontaminated soil was taken from a farmer's field located $\frac{1}{2}$ km north of the gas plant. In order to obtain uncontaminated soil from approximately the same depth as contaminated soil, topsoil was stripped prior to sampling. Based on neutral soil pH values and total sulphur measurements of less than 0.5%, it was concluded that no significant soil acidification had occurred at the uncontaminated soil location. According to the area soil survey map (Peters and Bowser 1960), both locations are within the same soil unit. Soil pits, 15 cm

in depth, were dug at both sampling locations. Excavated soil was transported back to the University where it was spread out on plastic sheets to air-dry. Once dried, the soil was put through a 4 mm sieve.

2.2 GREENHOUSE TRIALS

2.2.1 Experimental Set-Up

The greenhouse pot experiment consisted of three consecutive growth trials to determine the effects of four levels of soil sulphur on aboveground biomass and selected soil chemical parameters. Two leaching trials were also run. The four levels of sulphur-contaminated soil were prepared by mixing the following proportions of uncontaminated soil with contaminated soil: (1) 100% uncontaminated soil; (2) 66.7% uncontaminated soil, 33.3% contaminated soil; (3) 33.3% uncontaminated soil, 66.7% contaminated soil, and (4) 100% contaminated soil. Soil mixture homogeneity was achieved by the use of a portable concrete mixer. Grab samples of the homogeneous soil were taken and analyzed for total sulphur and extractable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$. Based on nutrient requirements from preliminary sampling, all pots were fertilized with 55 $\mu\text{g N/g}$ soil as an aqueous solution of ammonium nitrate. Results indicated that no phosphate additions were necessary.

Within each level of sulphur, four treatments were imposed: no treatment; addition of lime; addition of lime and manure; and addition of manure alone. Lime, in the form of agricultural grind CaCO_3 , was added at a rate of three times the detected total sulphur. Organic matter was added as cattle manure at a rate of 40 tonnes/ha.

Sixteen pots comprised one replicate (4 sulphur levels x 4 treatments). There were 5 replicates in each trial for a total of 80 pots. Open draining pots, 20 cm wide x 15 cm deep, were used with attached collection containers. Each trial was 62 days long. Pots were randomized on a weekly basis to eliminate position growth effects. Pot soil samples were taken at experiment initiation, between each trial, and at the end of the experiment. Table 2.1 summarizes the chemical parameters determined with each set of soil and leachate samples.

Pots were seeded with 50 seeds of reed canarygrass (Phalaris arundinacea) which corresponds to a seeding rate of 12.7 kg/ha. Reed canarygrass was selected for use in this pot experiment due to its moderate salt tolerance and its ability to tolerate a variety of moisture conditions (Watson et al. 1980). The ability of the grass to spread via rhizome production was also considered an asset for this experiment. Once germination was completed, pots were individually watered to approximately 2/3 of their previously determined field capacity (~23%). At the end of each trial, aboveground biomass of each pot was clipped, dried for 48 h in an 80°C oven, and yield was recorded. Following each trial, soil from each pot was air dried, cultivated by thorough mixing, and soil samples (c. 100 g) were taken for chemical analysis. The remaining soil was replaced in the pot.

2.2.2 Leachate Collection

At initiation and completion of the third growth trial, all pots were watered, by weight, to approximately field capacity plus

TABLE 2.1 Summary of soil and leachate chemical parameters that were determined for greenhouse trials. Asterisk (*) indicates work that was carried out. ND indicates that the parameter was not determined.

Parameter	Soil Series				Number of Replicates Analyzed
	A	B	C	D	
pH	*	*	*	*	5
Conductivity	*	*	*	*	5
Texture	*	ND	ND	ND	2
Al	*	ND	ND	*	3
CEC	*	ND	ND	*	3
SO ₄ -S	*	*	*	*	3
Lime requirement	*	ND	ND	ND	3
PO ₄ -P	*	*	*	*	3
NO ₃ -N	*	*	*	*	5
NH ₃ -N	*	*	*	*	5

Parameter	Leachates		Number of Replicates Analyzed
	Initiation 3rd Growth Trial	Completion of 3rd Growth Trial	
pH	*	*	5
Cond.	*	*	5
NO ₃ -N	*	*	5
NH ₃ -N	*	*	5
SO ₄ -S	*	*	5
PO ₄ -P	*	*	5
ICP - Al, Fe, Mn	ND	(selected samples)*	2

150 g. Following drainage into collection containers, leachate was collected. Selected subsamples from the second trial were acidified for metal analyses. Leachate samples were filtered through Whatman GF/A filters. Filtrates were analyzed for chemical parameters noted on Table 2.1. The pH and conductivity measurements were taken immediately following collection and filtration using a Fisher Accumet digital readout pH meter and an Industrial Instruments Inc. conductivity bridge meter, respectively. The nitrogen, phosphorous, and sulphur concentrations of the filtrates were determined using a Technicon II Auto Analyzer. Description of the modules is presented in Section 2.2.3. Samples were either analyzed within 48 hours of collection or frozen for analysis at a future date.

2.2.3 Soil Chemical Analyses

Soil samples for chemical analyses were air dried and passed through a 2 mm sieve. The following analytical procedures were used to characterize the soils. Unless noted in the descriptions below, all procedures were conducted as outlined by McKeague (1978).

A. pH

Forty mLs of water were added to 20 g of soil. The slurry was stirred initially and at 15 and 30 minutes. Samples then sat undisturbed for 30 minutes after which the pH of the soil:water mixture was determined using a Fisher Accumet digital readout pH meter.

B. Electrical conductivity

The soil:water suspension prepared for pH measurement was filtered through a Whatman GF/A filter. Electrical conductivity measurements of the filtrate were taken using an Industrial Instruments Inc. conductivity bridge meter.

C. Nitrogen analysis

Ten g of soil were extracted with 50 mL of 2 N KCl and shaken for 30 minutes. After filtration through a Whatman GF/A filter, the extract was analyzed colorimetrically on the Technicon II Auto Analyzer. Any extracts with a pH of less than 5 were raised to pH 5.0 by addition of sodium hydroxide. This neutralization was necessary to conform to operating requirements of the nitrate and ammonia modules.

Ammonium present in the soil extract was measured on the Technicon using the Berthelot Reaction (Technicon 1977). A green coloured compound, which is measured, occurs when a solution containing an ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite.

In the automated determination of nitrate, extracted nitrate is reduced to nitrite by a copper-cadmium reductor column (Technicon 1978). The reduced ion then reacts with sulphanilamide. The resultant diazo compound then combines with N-1-naphthyethylenediamine dihydrochloride to form a red colour, which is measured.

D. Phosphorous analysis

Ten g of soil were extracted with 50 mLs of modified, medium-strength Bray solution and shaken for 5 minutes. After filtration through a Whatman GF/A filter, the extract was analyzed colorimetrically on the Technicon using the reaction of ammonium molybdate in an acid medium to form molybdophosphoric acid (Technicon 1976). Reaction of this acid with ascorbic acid then forms a molybdenum blue complex which is measured.

E. Sulphate analysis

Ten g of soil were extracted with 0.1 M CaCl_2 and shaken for 30 minutes. After filtration through a Whatman GF/A filter, the extract was analyzed colorimetrically on the Technicon autoanalyzer.

The sulphate-containing extract is reacted with barium chloride to form barium sulphate (Technicon 1978a). Uncomplexed barium reacts with methylthymol blue to form a blue coloured chelate. Uncomplexed methylthymol blue is gray. The amount of uncomplexed methylthymol blue is equal to the sulphate present.

F. Total sulphur analysis

Total sulphur concentrations were determined using a Leco SC132 system. Within this system, samples are combusted at approximately 1400°C in an oxygen atmosphere. Sulphur present in the sample is oxidized to SO_2 which is then measured by an infrared detector. A microprocessor formulates the analysis results which are then displayed on the control console.

The instrument was calibrated using sulphur-containing coal standards. To ensure that these standards were applicable for soil samples being analyzed, sulphur-containing soil standards were also prepared. Known quantities of soil containing non-detectable levels of total sulphur were combined with 99.996% pure sulphur prills so that total sulphur concentrations in the soil standards ranged from 0.05% to 16%. All soil samples and materials used for the soil standards were ground to pass through a 30 mesh sieve.

G. Lime requirement

Lime requirements of the initial soil samples were determined using the Shoemaker, McLean and Pratt (SMP) single-buffer method (Page et al. 1982). Ten g of soil was mixed with 10 mL of distilled water. Twenty mL of buffer solution was added to the soil suspensions. The mixture was shaken for 10 minutes and allowed to stand for 30 minutes, after which the pH of the soil-buffer solution was read. The required level of agricultural ground limestone was determined from Page et al. (1982).

H. Particle size distributon

Estimates of sand, silt, and clay fractions in initial soil samples were determined using a soil hydrometer (Black 1965). The determination of the fractions is based on Stoke's law which states that the velocity of a particle settling in a liquid is directly proportional to its size and density (Brower and Zar 1977). Once the

soil sample percentage of each fraction is known, soil texture can be determined using a textural class triangle (Hausenbuiller 1978).

One hundred mL of Calgon solution and 300 mL of distilled water were added to 40 g of soil and allowed to soak overnight. The suspension was then homogenized in an electric mixer, transferred to a cylinder, and brought to 1 L volume. The suspension in the cylinder was thoroughly mixed with a plunger. Hydrometer readings were taken at a series of time intervals ranging from 30 sec to 18 h. The percentage of each fraction was calculated according to the equations in McKeague (1978).

I. Extractable aluminum

Ten g of soil were extracted with 20 mL 0.01 M CaCl_2 , shaken for 10 minutes, and filtered through a Whatman GF/A filter (Hoyt and Webber 1974). Each 20 mL extract was fixed with 0.1 mL HNO_3 . Acidified extracts were analyzed for aluminum using an atomic absorption spectrophotometer.

J. Soluble cations

The concentrations of Ca^{2+} , Mg^{2+} , and Na^+ in the initial and final sets of soil samples were determined in saturated extracts. A saturated paste containing soil and water was prepared and allowed to stand overnight. The paste was then filtered under vacuum and the resulting filtrate was analyzed for Ca^{2+} , Mg^{2+} , and Na^+ by atomic absorption. The sodium absorption ratio (SAR) was calculated according to the following equation

$$\text{SAR} = [\text{Na}^+]/([\text{Ca}^{2+} + \text{Mg}^{2+}]/2)^{1/2}$$

where all concentrations are in meq L^{-1} .

K. Cation exchange capacity

Ten g of soil was extracted with 50 mL of 1N NH_4OAc shaken and allowed to stand overnight. The soil was then leached with portions of NH_4OAc until the extract volume was 225 mL. The extract was filtered through a Whatman No. 42 filter. The filtrate was then analyzed for exchangeable Ca^{2+} , Mg^{2+} , and K^+ using atomic absorption spectrophotometry. The cation exchange capacity is the sum of exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$ expressed in $\text{meq } 100 \text{ g}^{-1}$.

2.2.4 Leachate Chemical Analyses

Leachate chemical analyses were determined using the same instruments used for soil analyses as described in Section 2.2.3. In addition, 15 subsamples of the second leachate collection (20 mL) were acidified with 0.1 mL HNO_3 . These samples were then analyzed for Al, Fe, and Mn using an inductively coupled plasma spectrophotometer.

2.3 MESH POT EXPERIMENT

The experiment was designed to evaluate the effectiveness of "capping" a limed soil containing sulphur with a layer of uncontaminated soil. Soil for this experiment was collected from the same sites as the soil used in the greenhouse trials but was not air-dried or sieved. This experiment was conducted outdoors. Two depths of pots

were used; 15 cm and 30 cm. All pots were 20 cm wide, had mesh bottoms, and rested on collection vessel. This allowed leachate produced as a result of precipitation to be collected.

The 15 cm deep pots contained 10 cm of limed, contaminated soil and a cap of 5 cm of uncontaminated soil. The 30 cm deep pots contained 20 cm of limed, contaminated soil and a cap of 10 cm of uncontaminated soil. Three replicate pots of each depth were used. Lime, in the form of agricultural grind CaCO_3 , was added to the contaminated soil at a rate of three times the measured soil total sulphur.

The experiment was initiated in September 1985. In the spring of 1986, all 6 pots were seeded with the following 5 salt tolerant grass species; reed canarygrass (Phalaris arundinacea), tufted hair grass (Deschampsia caespitosa), foxtail barley (Hordeum jubatum), slender salt-meadow grass (Puccinellia distans), and Nuttall alkali grass (Puccinellia nuttalliana). Aboveground biomass was harvested in September 1986 and the 80°C dry weights were recorded.

Leachates collected throughout the one year experiment were analyzed for pH and electrical conductivity using procedures outlined in Section 2.2.3.

2.4 SOIL DILUTION PLATING

An attempt to isolate sulphur-oxidizing organisms present in soil below the sulphur block basepad was made using a variety of media. Following the procedure outlined by Wainwright (1978), a series of basal agar media with sulphur overlays were prepared. The

basal media included Czapek-Dox media used to isolate fungi, starch-casein media used to isolate actinomycetes, and plate-count agar used to isolate heterotrophic bacteria (Wollum 1982). Media developed by Wieringa (1966) were used to isolate autotrophic microbes. An overlay media, outlined in Wieringa (1966), was then poured over all basal mediums. This overlay consisted of a bentonite clay/elemental sulphur mixture which was suspended in the appropriate basal media mixture.

Soil dilution plates were prepared by pipetting 0.1 mL of 10^{-2} to 10^{-4} dilutions of soil homogenized in quarter strength Ringer's solution onto all four types of plates. Production of clearing zones in the overlay generated from utilization of elemental sulphur by the microbes would indicate that isolated organisms were capable of oxidizing elemental sulphur. The dilution plates were left at room temperature for 1 month. At the same time, media designed to isolate autotrophic sulphur oxidizers were inoculated with a pure culture of Thiobacillus albertis.

2.5 STATISTICAL ANALYSIS OF DATA

All data were tested for significance with a two-way analysis of variance (ANOVA) and Scheffe multiple range test. Homogeneity of variances for all data sets was tested using the $F_{\max}$ -test. Log transformations of data sets were performed when necessary. Notation of transformed data is made where appropriate.

There was a significant interaction between the two factors (reclamation trials and sulphur levels) in all analyses of variance.

Values for each measured parameter were, therefore, tested individually against all other values for the same parameter in the Scheffe multiple range test. The accepted level of significance for all tests was $p < 0.05$.

CHAPTER 3

RESULTS

3.1 GREENHOUSE TRIALS

Data collected from the greenhouse trials will be presented in Section 3.1. Separate subsections will deal with: (1) verification of the soil sulphur present, (2) aboveground biomass yields from growth trials, (3) soil chemical characterization, and (4) leachate chemical characterization. Because lime was added to the soil in proportion to sulphur concentration, no lime was added to control soils. Therefore, the only amendment added to control soils was manure.

3.1.1 Total Sulphur in Soil Mixtures

Expected total sulphur concentrations of soils were verified using samples taken from all pot mixtures. The total sulphur concentration of unlimed soil correlated closely with expected values based on the ratios of clean:contaminated soil (Table 3.1). Reduced sulphur levels were detected in limed soils, especially at high levels of lime. The hypothesis that this was an instrument detection problem and not a true difference between soils within each level was tested by preparing 2 sets of standards. The first set contained known amounts of sulphur and soil while the second set contained known amounts of sulphur, soil, and lime. Results from this investigation

TABLE 3.1. Expected* and observed total sulphur concentrations in the soil mixtures used for the growth trials. Data are means (n=25) $\pm$ standard deviations.

Clean: Contaminated Soil Ratio	Expected Total Sulphur Values (%)	Reclamation Treatments (observed total sulphur values (%))			
		No Treatment	Lime	Lime and Manure	Manure
3:0	0.0	<0.1	<0.1	<0.1	<0.1
2:1	4.0	4.7 $\pm$ 0.5	4.2 $\pm$ 0.7	3.7 $\pm$ 0.5	4.8 $\pm$ 0.4
1:2	8.0	9.8 $\pm$ 1.0	7.7 $\pm$ 0.5	7.4 $\pm$ 0.9	9.6 $\pm$ 0.9
0:3	12.0	14.9 $\pm$ 0.8	10.8 $\pm$ 0.9	10.7 $\pm$ 0.8	14.2 $\pm$ 1.1

*based on clean:contaminated soil ratios

confirmed that the presence of lime inhibited sulphur detection by the Leco SC 132 (Table 3.2). Given this observation and the fact that soil within each sulphur level for the four reclamation treatments was taken from the same homogenized, bulked sample, it is unlikely that significant differences existed between total sulphur values within each level. Small differences that may have been present, due to varying particle sizes of elemental sulphur and any variation within bulked samples, would be insignificant compared to differences in total sulphur among the four sulphur levels.

3.1.2 Aboveground biomass

Although absolute amounts of biomass varied with trial number, general growth response trends were similar for all three trials (Table 3.3). No growth occurred in either untreated or manure-treated soils that contained detectable amounts of sulphur. Good growth was recorded in all control pots.

Reed canarygrass only grew in sulphur-contaminated soil when lime was applied. However, the presence of lime in contaminated soil did not ensure successful plant establishment. In all three trials, biomass for the soil containing 14% sulphur was not significantly different from zero for the calculated Scheffé 95% confidence interval. In the last 2 trials, aboveground biomass in the 9% sulphur treatments was significantly lower than that in control soils. Compared to grass growth in control soils in trial 3, biomass in the limed 4% sulphur soil was reduced by 50%, while there was a 75% yield

TABLE 3.2. Differences in detection of known amounts of sulphur between limed and unlimed soils. Data are means (n=10) $\pm$ standard deviations.

Expected S Values (%)	Observed Sulphur Values (%)	
	Soil and Sulphur	Soil, Sulphur, and Lime
4.0	3.6 $\pm$ 0.3	3.5 $\pm$ 0.5
6.9	7.1 $\pm$ 0.7	6.5 $\pm$ 1.3 ¹
8.0	7.6 $\pm$ 1.4 ²	7.6 $\pm$ 0.6
12.0	12.8 $\pm$ 0.7	10.3 $\pm$ 0.9
16.0	15.3 $\pm$ 0.7	13.6 $\pm$ 1.3

¹ n = 5

² n = 9

TABLE 3.3. Aboveground biomass (g dwt pot⁻¹) of reed canarygrass grown in soils containing four sulphur levels upon which reclamation treatments were superimposed. Data are means (n=5) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime + Manure	Manure
a) Trial 1				
<0.1	2.32 $\pm$ 1.08	1.62 $\pm$ 0.62 ^a	3.06 $\pm$ 0.65 ^b	3.17 $\pm$ 0.83
4	0.00	2.80 $\pm$ 0.80 ^b	1.97 $\pm$ 0.87 ^{ab}	0.00
9	0.00	0.55 $\pm$ 0.51 ^a	1.06 $\pm$ 1.11 ^{ab}	0.00
14	0.00	0.00	0.05 $\pm$ 0.11	0.00
b) Trial 2				
<0.1	5.61 $\pm$ 1.39	5.59 $\pm$ 0.64 ^{bc}	6.90 $\pm$ 1.07 ^c	7.18 $\pm$ 0.65
4	0.00	2.41 $\pm$ 0.98 ^{ab}	3.64 $\pm$ 1.37 ^b	0.00
9	0.00	0.43 $\pm$ 0.21 ^a	0.75 $\pm$ 0.56 ^a	0.00
14	0.00	0.03 $\pm$ 0.02	0.03 $\pm$ 0.03	0.00
c) Trial 3				
<0.1	7.15 $\pm$ 1.09	6.78 $\pm$ 0.91 ^b	6.71 $\pm$ 1.44 ^b	5.76 $\pm$ 0.96
4	0.00	2.00 $\pm$ 0.73 ^a	2.60 $\pm$ 0.54 ^a	0.00
9	0.00	0.79 $\pm$ 0.35 ^a	0.80 $\pm$ 0.65 ^a	0.00
14	0.00	0.03 $\pm$ 0.07	0.30 $\pm$ 0.26	0.00

¹ Two-way ANOVA was applied only to data from the 2 lime treatments and the first 3 soil sulphur levels. MSE for each trial was (1) 0.6178, (2) 0.7929, and (3) 0.7171 respectively. Significant differences amongst means were detected by the Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

reduction in the limed, 9% sulphur soil. Addition of manure to limed, sulphur-contaminated soils did not significantly improve yields.

Treatments with zero values and biomass values for the 14% sulphur soils were not included in the ANOVA, as inclusion of these data invalidated the assumptions of an ANOVA (Zar 1984).

3.1.3 Soil Chemical Characterization

A. pH measurements

Prior to the growth trials, the pH of all soils was neutral (i.e., pH 6.0–7.5), except the values for unlimed sulphur-contaminated soils (Table 3.4). The pH of these acid soils significantly decreased with increasing soil sulphur concentration. At the conclusion of the first trial, the pH of the 9% and 14% sulphur-containing soils were no longer significantly different. Throughout the experiment, there were no pH differences amongst any of the limed, sulphur-contaminated soils. Manure additions to limed and unlimed soils did not alter soil pH values.

Throughout the three growth trials, the pH of limed soils remained neutral, while the pH of unlimed sulphur-contaminated soils decreased. The greatest pH decrease in these soils occurred during the first growth trial. The pH of untreated control soils decreased slightly over time, while the pH of manure-treated control soil remained stable.

TABLE 3.4. The pH of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means (n=5) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	6.35 $\pm$ 0.02 ^d	6.37 $\pm$ 0.06 ^d	6.42 $\pm$ 0.04 ^d	6.42 $\pm$ 0.04 ^d
4	4.36 $\pm$ 0.02 ^c	7.22 $\pm$ 0.10 ^e	7.25 $\pm$ 0.12 ^e	4.48 $\pm$ 0.05 ^c
9	3.22 $\pm$ 0.06 ^b	7.17 $\pm$ 0.06 ^e	7.16 $\pm$ 0.08 ^e	3.39 $\pm$ 0.02 ^b
14	2.27 $\pm$ 0.04 ^a	7.19 $\pm$ 0.02 ^e	7.20 $\pm$ 0.03 ^e	2.37 $\pm$ 0.04 ^a
b) Following 1st growth trial				
<0.1	6.01 $\pm$ 0.09 ^c	5.94 $\pm$ 0.05 ^c	6.19 $\pm$ 0.09 ^c	6.24 $\pm$ 0.06 ^c
4	2.29 $\pm$ 0.25 ^b	7.04 $\pm$ 0.06 ^d	7.09 $\pm$ 0.04 ^d	2.41 $\pm$ 0.22 ^b
9	1.86 $\pm$ 0.17 ^a	7.09 $\pm$ 0.02 ^d	7.11 $\pm$ 0.03 ^d	1.79 $\pm$ 0.06 ^a
14	1.59 $\pm$ 0.08 ^a	7.11 $\pm$ 0.03 ^d	7.15 $\pm$ 0.02 ^d	1.56 $\pm$ 0.12 ^a
c) Following 2nd growth trial				
<0.1	5.80 $\pm$ 0.29 ^c	5.94 $\pm$ 0.07 ^{cd}	6.34 $\pm$ 0.28 ^d	6.31 $\pm$ 0.11 ^d
4	2.09 $\pm$ 0.12 ^b	7.14 $\pm$ 0.05 ^e	7.12 $\pm$ 0.06 ^e	2.06 $\pm$ 0.08 ^b
9	1.61 $\pm$ 0.12 ^a	7.23 $\pm$ 0.04 ^e	7.22 $\pm$ 0.02 ^e	1.61 $\pm$ 0.09 ^a
14	1.48 $\pm$ 0.04 ^a	7.22 $\pm$ 0.03 ^e	7.28 $\pm$ 0.02 ^e	1.48 $\pm$ 0.07 ^a
d) Following 3rd growth trial				
<0.1	5.90 $\pm$ 0.23 ^c	5.99 $\pm$ 0.09 ^{cd}	6.34 $\pm$ 0.22 ^d	6.33 $\pm$ 0.10 ^d
4	1.92 $\pm$ 0.12 ^b	7.12 $\pm$ 0.03 ^e	7.07 $\pm$ 0.02 ^e	1.97 $\pm$ 0.08 ^b
9	1.71 $\pm$ 0.08 ^a	7.10 $\pm$ 0.02 ^e	7.10 $\pm$ 0.03 ^e	1.63 $\pm$ 0.07 ^{ab}
14	1.42 $\pm$ 0.10 ^a	7.06 $\pm$ 0.04 ^e	7.06 $\pm$ 0.04 ^e	1.39 $\pm$ 0.17 ^a

¹ Data in each trial were analyzed by two-way ANOVA. MSE for each trial was (1) 0.00322, (2) 0.01217, (3) 0.01495, and (4) 0.01219. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different (p < 0.05).

B. Conductivity values

Control soils had the lowest conductivity (E.C.) values of all soils throughout the experiment (Table 3.5). The conductivity of limed soils for the three growth trials was within an acceptable range ($E.C. \leq 4.0 \text{ mS cm}^{-1}$) for supporting plant growth (Hausenbuiller 1978). Unlimed soils from the 14% sulphur level were the only soils with E.C. values greater than 4.0 mS cm^{-1} in the first sampling.

While there was little change in the E.C. of limed soils over time, the E.C. of untreated and manure-treated, sulphur-contaminated soils increased between experiment initiation and completion of the first growth trial. No similar increases in E.C. occurred again. From the end of the first growth trial to experiment termination, the E.C. of all unlimed, sulphur-contaminated soils was greater than 4 mS cm^{-1} .

In all trials, the conductivity of limed soils was significantly lower than that of unlimed, contaminated soils. Following the first growth trial, no significance differences existed between limed, sulphur-contaminated soils. The application of manure to soils did not significantly affect conductivity values.

C. Nitrogen availability in soils

Available nitrogen, determined as KCl-extractable nitrate-nitrogen and ammonium-nitrogen, was measured in soils used in the greenhouse experiment. Nitrate values of samples taken prior to experiment initiation had less variation among the 5 replicates

TABLE 3.5. Conductivity values (mS cm^{-1}) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	0.36 ± 0.02^a	0.38 ± 0.02^a	0.55 ± 0.02^b	0.56 ± 0.03^b
4	1.89 ± 0.06^c	1.84 ± 0.11^c	2.04 ± 0.11^c	2.03 ± 0.06^c
9	2.73 ± 0.09^e	2.29 ± 0.04^d	2.45 ± 0.03^{de}	2.93 ± 0.06^e
14	4.82 ± 0.27^f	2.32 ± 0.03^d	2.51 ± 0.04^{de}	4.47 ± 0.19^f
b) Following 1st growth trial				
<0.1	0.58 ± 0.12^a	0.66 ± 0.17^a	0.70 ± 0.15^a	0.60 ± 0.15^a
4	10.0 ± 2.2^{cd}	2.40 ± 0.07^b	2.54 ± 0.07^b	9.1 ± 1.8^c
9	15.3 ± 2.5^d	2.37 ± 0.10^b	2.50 ± 0.08^b	18.3 ± 3.7^d
14	21.2 ± 3.2^d	2.32 ± 0.11^b	2.44 ± 0.07^b	21.2 ± 5.3^d
c) Following 2nd growth trial				
<0.1	0.87 ± 0.28^a	0.65 ± 0.10^a	0.71 ± 0.38^a	0.64 ± 0.14^a
4	14.1 ± 1.8^c	2.44 ± 0.07^b	2.59 ± 0.11^b	13.5 ± 1.4^c
9	21.8 ± 3.5^d	2.36 ± 0.07^b	2.47 ± 0.08^b	23.4 ± 2.6^d
14	24.3 ± 3.8^d	2.29 ± 0.07^b	2.47 ± 0.08^b	23.1 ± 5.1^d
d) Following 3rd growth trial				
<0.1	0.64 ± 0.29^a	0.49 ± 0.09^a	0.45 ± 0.28^a	0.48 ± 0.11^a
4	15.7 ± 2.7^c	2.72 ± 0.35^b	2.54 ± 0.11^b	15.6 ± 1.6^c
9	18.0 ± 2.0^c	2.50 ± 0.08^b	2.55 ± 0.08^b	19.8 ± 1.6^c
14	21.5 ± 5.0^c	2.39 ± 0.08^b	2.61 ± 0.09^b	23.3 ± 7.3^c

¹ Data in each trial were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00010 (2) 0.00302, (3) 0.00250, and (4) 0.00320. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

than did samples from the last three sampling periods (Table 3.6). In the first sampling period, limed soils had significantly higher nitrate values than unlimed soils. This general trend continued in the second sampling period, although, due to high variance within replicate determinations, the differences were not significant.

Nitrate values for the 4% unlimed, sulphur-contaminated soils in the final two sampling periods significantly increased compared with limed soils. Nitrate levels in all other soils were not significantly different from those in control soils.

Nitrate values of the unlimed, 9% and 14% sulphur soils dropped between the first and second sampling periods. Nitrate values for limed soils did not drop until the third sampling period. Manure addition to soils did not affect nitrate values. Nitrate values in the control soils decreased between the third and fourth sampling period. Between these two sampling periods, two pot leaching trials were carried out.

Values for ammonium-nitrogen varied much less amongst trials than did nitrate-nitrogen values (Table 3.7). Ammonium levels in control soils dropped gradually over time, unlike nitrate levels. Trends in ammonium levels were similar for all four sampling periods. Ammonium concentrations in limed soil did not differ significantly from control samples. In contrast, all unlimed sulphur-contaminated soils had significantly higher ammonium levels than the control soils. The addition of manure did not affect soil ammonium levels.

TABLE 3.6. $\text{NO}_3\text{-N}$ ($\mu\text{g g}^{-1}$) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	44.1 $\pm$ 1.1 ^{cd}	44.1 $\pm$ 1.9 ^{cd}	64.6 $\pm$ 1.0 ^{de}	64.6 $\pm$ 7.6 ^{de}
4	29.7 $\pm$ 1.8 ^b	70.8 $\pm$ 2.1 ^e	113.4 $\pm$ 2.1 ^f	47.6 $\pm$ 1.3 ^{cd}
9	25.4 $\pm$ 3.0 ^{ab}	56.4 $\pm$ 3.0 ^{de}	90.3 $\pm$ 7.4 ^{ef}	39.8 $\pm$ 0.9 ^c
14	20.4 $\pm$ 3.6 ^a	52.3 $\pm$ 2.7 ^d	90.4 $\pm$ 2.7 ^{ef}	35.3 $\pm$ 3.6 ^{bc}
b) Following 1st growth trial				
<0.1	64.7 $\pm$ 28.8 ^b	76.0 $\pm$ 16.8 ^b	65.9 $\pm$ 19.2 ^b	62.9 $\pm$ 21.4 ^b
4	15.9 $\pm$ 4.3 ^{ab}	35.9 $\pm$ 37.4 ^b	93.3 $\pm$ 59.1 ^b	31.5 $\pm$ 9.8 ^b
9	2.9 $\pm$ 2.7 ^{ab}	37.9 $\pm$ 34.7 ^b	36.3 $\pm$ 25.2 ^b	4.1 $\pm$ 2.2 ^{ab}
14	1.4 $\pm$ 0.2 ^a	4.9 $\pm$ 5.1 ^{ab}	14.4 $\pm$ 20.4 ^{ab}	4.4 $\pm$ 7.2 ^{ab}
c) Following 2nd growth trial				
<0.1	24.6 $\pm$ 24.4 ^a	51.1 $\pm$ 20.2 ^b	13.5 $\pm$ 14.4 ^{ab}	10.1 $\pm$ 12.0 ^{ab}
4	42.0 $\pm$ 7.5 ^b	3.9 $\pm$ 1.1 ^a	5.8 $\pm$ 4.2 ^{ab}	48.1 $\pm$ 5.9 ^b
9	2.9 $\pm$ 1.0 ^a	3.3 $\pm$ 0.7 ^a	3.2 $\pm$ 0.8 ^a	10.1 $\pm$ 8.6 ^{ab}
14	2.8 $\pm$ 0.9 ^a	1.8 $\pm$ 1.2 ^a	1.8 $\pm$ 1.4 ^a	4.4 $\pm$ 1.9 ^a
d) Following 3rd growth trial				
<0.1	2.1 $\pm$ 0.4 ^a	3.8 $\pm$ 4.5 ^a	2.3 $\pm$ 0.4 ^a	2.2 $\pm$ 0.5 ^a
4	23.6 $\pm$ 18.0 ^b	3.8 $\pm$ 0.8 ^a	2.7 $\pm$ 0.4 ^a	48.8 $\pm$ 22.5 ^b
9	3.6 $\pm$ 0.5 ^a	2.6 $\pm$ 0.7 ^a	2.1 $\pm$ 0.7 ^a	10.7 $\pm$ 15.8 ^{ab}
14	2.2 $\pm$ 0.3 ^a	1.6 $\pm$ 0.3 ^a	1.3 $\pm$ 0.2 ^a	2.9 $\pm$ 0.5 ^a

¹ Data in each trial were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00096 (2) 0.12235, (3) 0.07120, and (4) 0.04098. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

TABLE 3.7 $\text{NH}_4\text{-N}$ ($\mu\text{g g}^{-1}$) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	22.1 $\pm$ 4.5 ^{ab}	20.7 $\pm$ 1.5 ^{ab}	18.8 $\pm$ 3.3 ^a	18.4 $\pm$ 4.0 ^a
4	44.0 $\pm$ 2.0 ^c	29.3 $\pm$ 1.2 ^b	25.3 $\pm$ 2.3 ^a	37.9 $\pm$ 1.1 ^{bc}
9	59.3 $\pm$ 12.0 ^{cd}	39.6 $\pm$ 4.5 ^{bc}	35.2 $\pm$ 3.6 ^{bc}	58.3 $\pm$ 2.3 ^{cd}
14	78.5 $\pm$ 3.8 ^d	52.6 $\pm$ 3.0 ^c	50.7 $\pm$ 2.2 ^c	79.8 $\pm$ 2.6 ^d
b) Following 1st growth trial				
<0.1	12.7 $\pm$ 2.8 ^a	16.8 $\pm$ 4.0 ^a	8.6 $\pm$ 1.7 ^a	10.3 $\pm$ 3.5 ^a
4	97.0 $\pm$ 23.1 ^b	9.4 $\pm$ 2.4 ^a	11.0 $\pm$ 2.0 ^a	125 $\pm$ 17 ^b
9	109. $\pm$ 13 ^b	13.1 $\pm$ 2.9 ^a	11.3 $\pm$ 3.3 ^a	134 $\pm$ 17 ^b
14	146 $\pm$ 12 ^b	11.0 $\pm$ 7.0 ^a	8.8 $\pm$ 4.0 ^a	178 $\pm$ 37 ^b
c) Following 2nd growth trial				
<0.1	6.9 $\pm$ 0.9 ^a	7.0 $\pm$ 1.2 ^a	6.1 $\pm$ 0.8 ^a	6.5 $\pm$ 1.3 ^a
4	139 $\pm$ 14 ^b	5.7 $\pm$ 0.9 ^a	5.5 $\pm$ 0.7 ^a	165 $\pm$ 16 ^b
9	158 $\pm$ 23 ^b	5.7 $\pm$ 0.5 ^a	6.2 $\pm$ 1.9 ^a	216 $\pm$ 38 ^b
14	193 $\pm$ 61 ^b	4.5 $\pm$ 0.5 ^a	4.5 $\pm$ 0.6 ^a	197 $\pm$ 83 ^b
d) Following 3rd growth trial				
<0.1	4.4 $\pm$ 0.4 ^a	4.5 $\pm$ 0.6 ^a	4.6 $\pm$ 0.9 ^a	4.3 $\pm$ 0.1 ^a
4	191 $\pm$ 53 ^b	4.6 $\pm$ 0.4 ^a	4.8 $\pm$ 0.5 ^a	243 $\pm$ 14 ^b
9	264 $\pm$ 27 ^b	3.6 $\pm$ 0.4 ^a	3.5 $\pm$ 0.2 ^a	290 $\pm$ 8 ^b
14	223 $\pm$ 16 ^b	4.7 $\pm$ 0.6 ^a	3.3 $\pm$ 0.5 ^a	193 $\pm$ 51 ^b

¹ Data in each trial were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00242, (2) 0.01706, (3) 0.00967, (4) 0.00305. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

D. Phosphate values

Observed trends in phosphate-phosphorous levels were similar for all sampling periods (Table 3.8). Phosphorous concentrations in untreated and manure-treated soils remained constant as soil sulphur concentration increased, with one exception. Samples of the 4% sulphur soil taken following the first and second growth trials had lower phosphorous concentrations than those at higher sulphur levels.

Lime addition to sulphur soils significantly decreased phosphorous levels. Manure addition to limed soils raised phosphorous values, but they still remained low compared with control soils. Lowest phosphorous values occurred in the highest sulphur-contaminated, limed soil. Manure addition increased phosphorous concentration in all soils.

E. Sulphate values

Sulphate values in control soils remained constant throughout the growth trials (Table 3.9). Sulphate levels measured in sulphur-contaminated soils were significantly higher in all trials compared with control soils. Sulphate concentrations in sulphur-contaminated soils increased with increasing soil sulphur level. All soils within each sulphur treatment contained approximately the same amount of sulphate prior to the first growth trial. From the end of the first growth trial to experiment termination, however, sulphate levels were significantly higher in the unlimed, sulphur-containing soils compared to the limed, sulphur-containing soils. Throughout the experiment, sulphate production was highest in the unlimed, sulphur-contaminated

TABLE 3.8 $\text{PO}_4\text{-P}$ ($\mu\text{g g}^{-1}$) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=3$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	21.3 $\pm$ 0.7 ^d	24.4 $\pm$ 3.8 ^d	46.7 $\pm$ 5.9 ^{def}	47.8 $\pm$ 5.3 ^{ef}
4	23.9 $\pm$ 1.5 ^d	9.3 $\pm$ 0.4 ^c	13.8 $\pm$ 2.3 ^{cd}	48.5 $\pm$ 1.7 ^{cf}
9	26.1 $\pm$ 1.8 ^{de}	4.4 $\pm$ 0.7 ^b	9.1 $\pm$ 0.9 ^{bc}	61.6 $\pm$ 1.0 ^{ef}
14	21.3 $\pm$ 1.0 ^d	1.3 $\pm$ 0.4 ^a	4.4 $\pm$ 0.7 ^b	55.2 $\pm$ 1.8 ^{ef}
b) Following 1st growth trial				
<0.1	21.2 $\pm$ 1.4 ^{bcd}	21.2 $\pm$ 0.9 ^{bcd}	40.0 $\pm$ 1.0 ^{cd}	37.1 $\pm$ 1.3 ^{cd}
4	6.2 $\pm$ 2.6 ^{ab}	7.6 $\pm$ 0.8 ^{ab}	14.2 $\pm$ 3.2 ^b	9.8 $\pm$ 3.2 ^b
9	17.8 $\pm$ 5.0 ^{bc}	5.1 $\pm$ 0.3 ^{ab}	10.4 $\pm$ 1.1 ^b	41.3 $\pm$ 7.6 ^{cd}
14	18.9 $\pm$ 3.5 ^{bc}	2.9 $\pm$ 1.1 ^a	6.0 $\pm$ 0.8 ^{ab}	49.2 $\pm$ 13.1 ^{cd}
c) Following 2nd growth trial				
<0.1	22.7 $\pm$ 1.4 ^{bc}	22.2 $\pm$ 1.5 ^{bc}	41.2 $\pm$ 2.8 ^{bc}	39.7 $\pm$ 1.8 ^{bc}
4	8.0 $\pm$ 4.9 ^{ab}	7.2 $\pm$ 1.8 ^{ab}	15.0 $\pm$ 4.0 ^{bc}	10.8 $\pm$ 7.1 ^{ab}
9	34.4 $\pm$ 4.9 ^{bc}	5.9 $\pm$ 1.1 ^{ab}	11.4 $\pm$ 0.4 ^{ab}	59.7 $\pm$ 8.4 ^{bc}
14	26.2 $\pm$ 4.7 ^{bc}	2.2 $\pm$ 1.0 ^a	4.1 $\pm$ 0.8 ^{ab}	56.0 $\pm$ 8.7 ^{bc}
d) Following 3rd growth trial				
<0.1	18.4 $\pm$ 1.6 ^{bc}	17.5 $\pm$ 0.4 ^{bc}	38.7 $\pm$ 2.3 ^{cd}	36.1 $\pm$ 1.6 ^{cd}
4	17.4 $\pm$ 11.6 ^{bc}	11.5 $\pm$ 0.2 ^{bc}	24.3 $\pm$ 2.1 ^{bcd}	26.2 $\pm$ 4.8 ^{cd}
9	28.3 $\pm$ 6.0 ^{cd}	9.2 $\pm$ 2.8 ^b	16.5 $\pm$ 5.6 ^{bc}	51.1 $\pm$ 3.4 ^{cd}
14	24.4 $\pm$ 4.7 ^{bcd}	0.23 $\pm$ 0.06 ^a	0.53 $\pm$ 0.11 ^a	48.8 $\pm$ 6.9 ^{cd}

¹ Data in each trial were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00371, (2) 0.00666, (3) 0.01945, and (4) 0.00808. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < .05$).

TABLE 3.9 $\text{SO}_4\text{-S}$ ($\mu\text{g g}^{-1}$) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=3$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	26 $\pm$ 25 ^a	22 $\pm$ 25 ^{2,a}	33 $\pm$ 10 ^a	61 $\pm$ 10 ^{2,a}
4	2840 $\pm$ 11 ^b	2400 $\pm$ 70 ^b	2450 $\pm$ 80 ^b	2770 $\pm$ 90 ^b
9	5220 $\pm$ 100 ^d	4310 $\pm$ 50 ^c	4330 $\pm$ 10 ^c	5210 $\pm$ 200 ^d
14	7860 $\pm$ 200 ^e	5610 $\pm$ 110 ^d	5530 $\pm$ 140 ^d	7440 $\pm$ 170 ^e
b) Following 1st growth trial				
<0.1	150 $\pm$ 50 ^a	200 $\pm$ 30 ^{2,ab}	490 $\pm$ 200 ^b	140 $\pm$ 30 ^{2,a}
4	27,450 $\pm$ 7840 ^d	7910 $\pm$ 60 ^c	7930 $\pm$ 70 ^c	23,160 $\pm$ 5620 ^d
9	39,080 $\pm$ 6010 ^d	7910 $\pm$ 110 ^c	8150 $\pm$ 40 ^c	41,750 $\pm$ 7560 ^d
14	33,320 $\pm$ 2450 ^d	7600 $\pm$ 70 ^c	7700 $\pm$ 110 ^c	32,550 $\pm$ 10,540 ^d
c) Following 2nd growth trial				
<0.1	990 $\pm$ 440 ^a	540 $\pm$ 240 ^{2,a}	620 $\pm$ 590 ^a	450 $\pm$ 190 ^{2,a}
4	38,480 $\pm$ 7340 ^c	7930 $\pm$ 230 ^b	8240 $\pm$ 110 ^b	34,670 $\pm$ 2380 ^c
9	50,450 $\pm$ 5440 ^c	8130 $\pm$ 140 ^b	8220 $\pm$ 220 ^b	55,150 $\pm$ 3240 ^c
14	35,280 $\pm$ 5220 ^c	7680 $\pm$ 50 ^b	7550 $\pm$ 450 ^b	38,940 $\pm$ 1810 ^{2,c}
d) Following 3rd growth trial				
<0.1	880 $\pm$ 370 ^a	470 $\pm$ 260 ^{2,a}	520 $\pm$ 620 ^a	310 $\pm$ 250 ^{2,a}
4	39,480 $\pm$ 7010 ^{bc}	8000 $\pm$ 150 ^a	8280 $\pm$ 70 ^a	42,440 $\pm$ 1250 ^c
9	42,740 $\pm$ 3060 ^b	8040 $\pm$ 90 ^a	8020 $\pm$ 70 ^a	45,560 $\pm$ 1390 ^c
14	28,470 $\pm$ 6770 ^b	7720 $\pm$ 50 ^a	7950 $\pm$ 160 ^a	32,550 $\pm$ 880 ^{bc}

¹ Data in each trial were analyzed by two-way ANOVA. Data from the initial and final trials were not transformed prior to analysis, although other data were log transformed. MSE for each trial was (1) 11356.9, (2) 0.00874, (3) 0.01849, and (4) 7297339. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < .05$).

² $n = 2$

soils. The presence of manure did not influence soil sulphate concentrations. Although the sulphate data did not pass the $F_{\max}$ test, it was assumed that the ANOVA was robust enough to withstand the heterogeneity of variances inherent in this data set.

F. Sodium adsorption ratio

All sodium adsorption ratios (SAR) were within acceptable limits for plant growth requirements (Bohn et al. 1979). There was little difference in SAR values amongst the sulphur levels and between reclamation treatments (Table 3.10). While SAR values did increase when manure was added to the soil, the presence of lime did not significantly affect SAR values at any sulphur level.

G. Cation exchange capacity

Observed trends in cation exchange capacity (CEC) were similar for both sampling periods (Table 3.11). Cation exchange capacities decreased with increasing levels of sulphur concentration. All soils containing sulphur had significantly lower CEC values than control soils.

Lime applications decreased on soil CEC values. Addition of manure had no effect on CEC values.

H. Soluble aluminum values

Aluminum concentrations in limed, sulphur-contaminated soils did not differ significantly from control soil values at either

TABLE 3.10. Sodium adsorption ratio (SAR) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are reported as means (n=3) $\pm$ standard deviations.¹

Soil. Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	0.70 $\pm$ 0.05 ^b	0.66 $\pm$ 0.05 ^b	1.08 $\pm$ 0.03 ^{cd}	1.17 $\pm$ 0.14 ^{cd}
4	0.40 $\pm$ 0.01 ^a	0.36 $\pm$ 0.01 ^a	0.74 $\pm$ 0.04 ^b	0.77 $\pm$ 0.02 ^b
9	0.38 $\pm$ 0.06 ^a	0.35 $\pm$ 0.04 ^a	0.82 $\pm$ 0.08 ^{bc}	0.84 $\pm$ 0.04 ^{bc}
14	0.33 $\pm$ 0.03 ^a	0.36 $\pm$ 0.03 ^a	1.02 $\pm$ 0.08 ^{cd}	0.86 $\pm$ 0.04 ^{bc}
b) Following 3rd growth trial				
<0.1	0.42 $\pm$ 0.04 ^{ab}	0.48 $\pm$ 0.04 ^{ab}	0.78 $\pm$ 0.10 ^{bc}	0.86 $\pm$ 0.08 ^{bc}
4	0.25 $\pm$ 0.01 ^a	0.28 $\pm$ 0.05 ^a	0.52 $\pm$ 0.09 ^{ab}	0.46 $\pm$ 0.06 ^{ab}
9	0.31 $\pm$ 0.04 ^a	0.27 $\pm$ 0.01 ^a	0.52 $\pm$ 0.02 ^{ab}	0.52 $\pm$ 0.06 ^{ab}
14	0.64 $\pm$ 0.06 ^{bc}	0.28 $\pm$ 0.01 ^a	0.48 $\pm$ 0.12 ^a	0.76 $\pm$ 0.13 ^{bc}

¹ Data in each trial were analyzed by two-way ANOVA. MSE for each trial was (1) 0.00269 and (2) 0.00473. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different (p < 0.05).

Table 3.11. Cation exchange capacity (meq 100g⁻¹) of pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means (n=3) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	39.7 $\pm$ 0.6 ^g	39.9 $\pm$ 0.3 ^g	39.6 $\pm$ 0.5 ^g	40.1 $\pm$ 0.5 ^g
4	32.3 $\pm$ 0.1 ^f	28.6 $\pm$ 0.2 ^e	29.1 $\pm$ 0.5 ^e	33.0 $\pm$ 0.5 ^f
9	25.4 $\pm$ 0.5 ^d	19.9 $\pm$ 0.1 ^c	20.8 $\pm$ 0.3 ^c	25.8 $\pm$ 0.2 ^d
14	17.4 $\pm$ 0.2 ^b	13.0 $\pm$ 0.3 ^a	13.9 $\pm$ 0.4 ^a	18.4 $\pm$ 0.4 ^{bc}
b) Following 3rd growth trial				
<0.1	40.7 $\pm$ 0.6 ^e	40.8 $\pm$ 0.6 ^e	41.0 $\pm$ 0.4 ^e	41.2 $\pm$ 0.4 ^e
4	28.6 $\pm$ 1.7 ^d	27.0 $\pm$ 1.4 ^d	28.6 $\pm$ 0.9 ^d	27.7 $\pm$ 1.1 ^d
9	20.9 $\pm$ 0.8 ^c	18.8 $\pm$ 0.3 ^{bc}	19.9 $\pm$ 0.3 ^c	21.7 $\pm$ 0.9 ^c
14	15.3 $\pm$ 0.3 ^{ab}	12.3 $\pm$ 0.5 ^a	13.2 $\pm$ 0.5 ^a	16.7 $\pm$ 1.0 ^{bc}

¹ Data in each trial were analyzed by two-way ANOVA. MSE for each trial was (1) 0.01606 and (2) 0.71416. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different (p < 0.05).

experiment initiation or completion (Table 3.12). Manure addition to limed, sulphur-contaminated soils did not influence measured soluble aluminum concentrations. Aluminum values in unlimed, sulphur-containing soils were significantly higher than those in limed soils.

Aluminum concentrations in unlimed, sulphur-contaminated samples taken at experiment initiation increased with increasing sulphur concentration. Sulphur-containing soils treated with manure had significantly lower aluminum values than did untreated soils.

At experiment completion, aluminum values were not significantly different in untreated and manure-treated, sulphur-contaminated soil. In addition, aluminum concentrations of unlimed soil did not increase with increasing sulphur. Aluminum concentrations increased in unlimed soils from experiment initiation to completion.

I. Soil texture

Texture measurements were determined for soil from each combination of sulphur level and reclamation treatment. The majority of soils were classified in the silt loam textural class (Table 3.13). This is in agreement with field observations that the top 30 cm of soil is silt loam (Peters and Bowser 1960).

According to Brady (1984), all determined textures fall into the medium texture class with the exception of clay loam and sandy loam soils. The control soil determined as a clay loam had a moderately fine texture, while the soil containing 14% sulphur amended with lime and manure had a moderately coarse texture.

TABLE 3.12. Soluble aluminum ($\mu\text{g g}^{-1}$) of pot soils used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are reported as means ($n=3$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 1st growth trial				
<0.1	0.33 ± 0.12^a	ND	0.27 ± 0.12^a	ND
4	1.0 ± 0.2^b	0.27 ± 0.12^a	0.33 ± 0.23^a	0.87 ± 0.12^{ab}
9	49.7 ± 7.5^d	0.27 ± 0.12^a	0.33 ± 0.12^a	13.4 ± 0.4^c
14	845.0 ± 27^e	0.27 ± 0.12^a	0.27 ± 0.12^a	62.2 ± 1.9^d
b) Following 3rd growth trial				
<0.1	0.47 ± 0.12^a	ND	0.67 ± 0.30^a	ND
4	3950 ± 536^b	0.47 ± 0.12^a	0.27 ± 0.12^a	4340 ± 197^b
9	4170 ± 506^b	0.27 ± 0.12^a	0.27 ± 0.12^a	4353 ± 254^b
14	2907 ± 549^b	0.33 ± 0.23^a	0.27 ± 0.12^a	3040 ± 410^b

¹ Data in each trial were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00166 and (2) 0.00258. Significant differences amongst log transformed means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

ND = not determined.

TABLE 3.13. Texture classification of soils used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed.

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
<0.1	Clay loam	Silt loam	Silt loam	ND
4	Silt loam	Silt loam	Loam	Silt loam
9	Silt loam	Loam	Loam	Silt loam
14	Loam	Loam	Sandy Loam	Silt loam

ND = not determined.

In general, no major texture differences were measured despite the varying levels of sulphur, lime, and manure present in the soils.

J. Lime requirement

The lime requirement of the soil mixtures was determined to compare actual amounts of lime added with that required to neutralize existing soil acidity. Soil-buffer pH measurements of the mixtures are presented in Table 3.14. Limed soils had the highest soil-buffer pH while unlimed, sulphur-contaminated soils had the lowest pH values. Lime requirement recommendations to neutralize the top 15 cm of soil to pH 7.0, as determined by Page et al. (1982), are presented in Table 3.15. Minimal amounts of lime were required to raise control soil pH to 7.0. No additional lime was required in the previously limed, sulphur-contaminated soil. The amount of lime required to neutralize unlimed, sulphur-contaminated soils increased with increasing soil sulphur level. The soil-buffer pH values for the unlimed 14% sulphur soil were below the lowest soil-buffer pH of 4.8 recorded in Page et al. (1982). Lime requirement values for soil-buffer pH's measured at the 14% soil sulphur level were estimated based on the assumption that for every 0.1 drop in pH unit, 1.05 times the amount of lime was required. This assumption was validated for lime requirement values within pH range of 5.0-4.8 in Page et al. (1982).

TABLE 3.14. Soil-buffer pH measurements, as determined by Shoemaker, McLean and Pratt (SMP) method, of pot soil mixtures at experiment initiation. Data are means (n=3) $\pm$ standard deviations.

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
<0.1	6.67 $\pm$ 0.04	6.76 $\pm$ 0.03	6.80	6.82 $\pm$ 0.07 ¹
4	5.95 $\pm$ 0.04	7.24 $\pm$ 0.03	7.22 $\pm$ 0.02	6.08 $\pm$ 0.02
9	5.32 $\pm$ 0.05	7.27 $\pm$ 0.02	7.27 $\pm$ 0.02	5.60 $\pm$ 0.22
14	4.18 $\pm$ 0.08	7.30 $\pm$ 0.03	7.30 $\pm$ 0.01	4.37 $\pm$ 0.05

¹ n = 2

TABLE 3.15. Lime requirement recommendations (tonnes ha⁻¹) for pot soil mixtures as determined by SMP method. Recommendations are based on amount of agricultural grind limestone required to obtain a pH of 7.0 in top 15 cm of soil.

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
<0.1	4.0	2.4	2.4	2.4
4	16.1	not required	not required	16.1
9	28.4	not required	not required	23.0
14	66 (est.) ¹	not required	not required	60 (est.) ¹

¹Estimated values extrapolated from Table 12.1 (Page et al. 1982).

The amount of lime actually applied to the pots is presented in Table 3.16. Lime values from Tables 3.15 and 3.16 can be directly compared for the various soil sulphur levels. The amount of lime applied to pots exceeded that required to neutralize existing soil acidity by at least ten-fold for all soil sulphur levels.

For both the 9% and 14% sulphur levels, the soil-buffer pH values were higher for manure-treated soil than for untreated soil. This resulted in a corresponding decrease in lime requirement for the manure-treated soils at these two sulphur levels.

3.1.4 Leachate Chemical Characterization

Data for leachates produced both prior to and following the third growth trial are presented in the following six subsections. Addition of manure to soils did not produce statistical differences in parameters measured in the produced leachates. In the second leaching episode, data from limed, 14% sulphur soil were excluded from statistical analyses as only one replicate remained in the experiment.

A. pH of leachates

Similar trends in pH values were produced from both leaching episodes (Table 3.17). Three distinct groups of pH measurements were separated statistically. Leachates produced from unlimed, sulphur-contaminated soils were strongly acidic. The pH of leachates generated from control soils were mildly acidic, while the pH of leachates produced from limed, sulphur-contaminated soils were neutral. There

TABLE 3.16. Actual amounts of lime applied to pot soils (tonnes ha^{-1}) to neutralize acidity produced by oxidation of elemental sulphur.

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
<0.1	NA	NA	NA	NA
4	NA	288	276	NA
9	NA	555	534	NA
14	NA	893	857	NA

NA = not applicable

TABLE 3.17. The pH of leachate produced from pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means (n=5) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 3rd growth trial				
<0.1	5.3 $\pm$ 1.0 ^{bc}	4.6 $\pm$ 1.2 ^b	5.1 $\pm$ 0.9 ^{bc}	5.8 $\pm$ 1.0 ^{bc}
4	1.7 $\pm$ 0.2 ^a	7.2 $\pm$ 0.3 ^c	6.8 $\pm$ 0.7 ^c	1.8 $\pm$ 0.1 ^a
9	0.9 $\pm$ 0.2 ^a	7.0 $\pm$ 0.2 ^c	6.9 $\pm$ 0.3 ^c	0.9 $\pm$ 0.1 ^a
14	0.5 $\pm$ 0.1 ^a	6.9 $\pm$ 0.2 ^c	7.1 $\pm$ 0.1 ^c	0.5 $\pm$ 0.1 ^a
b) Following 3rd growth trial				
<0.1	4.9 $\pm$ 0.7 ^b	5.0 $\pm$ 0.2 ^b	5.5 $\pm$ 0.5 ^b	5.3 $\pm$ 0.3 ^b
4	1.3 $\pm$ 0.4 ^a	7.1 $\pm$ 0.4 ^c	7.3 $\pm$ 0.1 ^c	1.4 $\pm$ 0.2 ^a
9	1.0 $\pm$ 0.1 ^a	7.3 $\pm$ 0.2 ^c	7.4 $\pm$ 0.1 ^c	1.0 $\pm$ 0.1 ^a
14	0.7 $\pm$ 0.1 ^a	7.5 ²	7.5 $\pm$ 0.1 ^c	0.7 $\pm$ 0.2 ^a

¹Data in both trials were analyzed by two-way ANOVA. MSE for each trial was (1) 0.31922, and (2) 0.07568. Significant differences amongst means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different (p < 0.05).

² n = 1

were no significant differences in leachate pH within any of these three groups.

B. Leachate conductivity

Similar trends in conductivity values existed for both leaching episodes (Table 3.18). Conductivity values were highest in leachates produced from unlimed, sulphur-contaminated soil. Within this group, conductivity values increased with increasing total sulphur concentration. Leachates from limed, sulphur-contaminated soil were at least ten-fold lower than those from their unlimed counterparts. There were no significant differences in conductivity values amongst leachates produced from limed, sulphur-containing soils. Leachate from control soils had the lowest conductivity values of the experiment. No major changes in the magnitude of conductivity values occurred over time.

C. Soluble nitrogen concentrations in leachates

Similar trends in nitrate and ammonium values occurred in both leaching episodes (Tables 3.19 and 3.20). Leachates produced from control soils and from limed, sulphur-contaminated soils were not significantly different. In the first leaching trial, more nitrate-nitrogen was produced from these soils than ammonium. Leachates produced in the second trial from the control and limed, sulphur-contaminated soils contained similar concentrations of nitrate and ammonium-nitrogen.

TABLE 3.18. Electrical conductivity (mS cm^{-1}) of leachate produced from pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 3rd growth trial				
<0.1	1.42 ± 0.72^a	1.16 ± 0.34^a	0.91 ± 0.38^a	1.20 ± 0.35^a
4	33.0 ± 5.12^c	3.21 ± 0.13^b	3.41 ± 0.14^b	31.9 ± 4.87^c
9	74.0 ± 18.0^d	3.54 ± 0.17^b	3.79 ± 0.20^b	70.8 ± 13.3^d
14	141 ± 21^e	3.13 ± 0.43^b	4.41 ± 0.19^b	143 ± 14^e
b) Following 3rd growth trial				
<0.1	0.62 ± 0.32^a	0.66 ± 0.30^a	0.49 ± 0.35^a	0.69 ± 0.35^a
4	47.4 ± 7.64^c	3.16 ± 0.36^b	3.34 ± 0.16^b	42.1 ± 3.8^c
9	61.0 ± 10.1^c	3.47 ± 0.22^b	3.66 ± 0.24^b	57.6 ± 4.8^c
14	108 ± 22^d	2.58^2	3.86 ± 0.36^b	124 ± 22^d

¹Data were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00438, and (2) 0.00398. Significant differences amongst log transformed means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

² $n = 1$

Table 3.19. $\text{NO}_3\text{-N}$ ($\mu\text{g mL}^{-1}$) in leachate produced from pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 3rd growth trial				
<0.1	30.3 $\pm$ 14.3 ^{bc}	42.1 $\pm$ 22.0 ^c	21.1 $\pm$ 10.4 ^{bc}	15.1 $\pm$ 7.0 ^{bc}
4	291 $\pm$ 39 ^d	16.8 $\pm$ 6.6 ^{bc}	19.3 $\pm$ 5.8 ^{bc}	418 $\pm$ 85 ^d
9	408 $\pm$ 73 ^d	9.8 $\pm$ 4.0 ^b	11.1 $\pm$ 3.6 ^{bc}	398 $\pm$ 95 ^d
14	660 $\pm$ 74 ^d	1.5 $\pm$ 2.0 ^a	7.7 $\pm$ 1.9 ^b	618 $\pm$ 87 ^d
b) Following 3rd growth trial				
<0.1	0.43 $\pm$ 0.29 ^{2,a}	11.4 $\pm$ 3.7 ^{3,b}	ND	0.25 $\pm$ 0.21 ^{3,a}
4	473 $\pm$ 84 ^c	0.53 $\pm$ 0.06 ^{2,a}	0.67 $\pm$ 0.50 ^a	578 $\pm$ 119 ^c
9	522 $\pm$ 119 ^c	0.83 $\pm$ 0.42 ^a	0.40 $\pm$ 0.17 ^a	515 $\pm$ 107 ^c
14	674 $\pm$ 104 ^c	ND	1.3 $\pm$ 1.7 ^a	706 $\pm$ 151 ^c

¹Data were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.02545, and (2) 0.01304. Significant differences amongst log transformed means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

² $n=3$

³ $n=2$

ND = not determined

Table 3.20. $\text{NH}_4\text{-N}$ ($\mu\text{g mL}^{-1}$) in leachate produced from pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 3rd growth trial				
<0.1	0.46 ± 0.22^{ab}	0.50 ± 0.13^{ab}	0.44 ± 0.20^a	0.36 ± 0.25^a
4	547 ± 68^c	0.81 ± 0.33^{ab}	1.3 ± 0.4^{ab}	861 ± 162^{cd}
9	1177 ± 384^d	1.36 ± 0.27^{ab}	1.9 ± 0.3^b	1264 ± 317^d
14	1841 ± 238^d	1.1 ± 0.6^{ab}	1.9 ± 1.0^b	1668 ± 241^d
b) Following 3rd growth trial				
<0.1	0.53 ± 0.27^a	0.52 ± 0.18^a	$0.58 \pm 0.22^{2,a}$	0.41 ± 0.21^a
4	925 ± 110^b	0.35 ± 0.09^a	0.39 ± 0.34^a	1034 ± 164^{bc}
9	1275 ± 213^{bc}	0.48 ± 0.09^a	0.44 ± 0.16^a	1548 ± 173^{bc}
14	1729 ± 284^c	0.16^a	0.74 ± 0.54^a	2065 ± 373^c

¹Data were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.00696, and (2) 0.00489. Significant differences amongst log transformed means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

² $n=3$

³ $n=1$

Leachates produced from unlimed, sulphur-contaminated soils contained elevated levels of both nitrate- and ammonium-nitrogen. Nitrate values remained constant as soil sulphur levels increased, whereas ammonium levels increased with increasing soil sulphur concentration. Nitrate and ammonium concentrations within this group of leachates remained constant over time.

D. Phosphate concentrations in leachates

Phosphate-phosphorous concentrations in leachates from limed soils were not significantly different than those from control soils (Table 3.21). Similar to the ammonium and nitrate data, elevated phosphate levels were found in leachate from unlimed, sulphur-contaminated soils. There was no clear trend in phosphate concentration with increasing soil sulphur concentration.

Similar trends in phosphate values existed for both leaching episodes. No major changes in the magnitude of phosphate values occurred over time.

E. Sulphate in leachates

Trends in sulphate concentrations of leachates were similar for both two leaching trials (Table 3.22). Sulphate levels were highest in leachates produced from unlimed, sulphur-contaminated soils. Limed soils contained the next highest levels, while leachates from control soils had the lowest sulphate concentrations. These three groups were all statistically separate from each other.

Table 3.21. $\text{PO}_4\text{-P}$ ($\mu\text{g ml}^{-1}$) in leachate produced from pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.¹

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 3rd growth trial				
<0.1	0.17 ± 0.12^a	0.15 ± 0.08^a	0.59 ± 0.20^a	0.44 ± 0.09^a
4	53.0 ± 16.2^b	0.36 ± 0.04^a	0.57 ± 0.10^a	71.9 ± 55.8^b
9	169 ± 40^c	0.46 ± 0.14^a	0.66 ± 0.09^a	225 ± 36^c
14	116 ± 25^{bc}	0.48 ± 0.12^a	0.72 ± 0.11^a	183 ± 47^c
b) Following 3rd growth trial				
<0.1	0.17 ± 0.16^a	0.15 ± 0.14^a	$0.37 \pm 0.18^{2,a}$	0.35 ± 0.22^a
4	96.6^a	0.12 ± 0.02^a	0.28 ± 0.04^a	123 ± 22^{2c}
9	161 ± 24^{cd}	0.16 ± 0.02^a	0.31 ± 0.05^a	232 ± 37^d
14	78.1 ± 17.1^b	0.33^3	0.35 ± 0.06^a	147 ± 34^c

¹ Data were analyzed by two-way ANOVA following log transformation. MSE for each trial was (1) 0.01150 and (2) 0.00342. Significant differences amongst log transformed means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

² $n=3$

³ $n=1$

Table 3.22. $\text{SO}_4\text{-S}$ ($\mu\text{g mL}^{-1}$) in leachate produced from pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Data are means ($n=5$) $\pm$ standard deviations.

Soil Sulphur (%)	Reclamation Treatments			
	No Treatment	Lime	Lime and Manure	Manure
a) Prior to 3rd growth trial				
<0.1	660 $\pm$ 380 ^{ab}	470 $\pm$ 180 ^b	430 $\pm$ 310 ^a	590 $\pm$ 260 ^{2,ab}
4	38,120 $\pm$ 10,790 ^c	1560 $\pm$ 50 ^b	1640 $\pm$ 80 ^b	37,400 $\pm$ 8090 ^c
9	82,010 $\pm$ 26,460 ^c	1540 $\pm$ 40 ^b	1600 $\pm$ 60 ^b	81,700 $\pm$ 12,640 ^c
14	90,700 $\pm$ 11,670 ^c	1390 $\pm$ 280 ^b	1610 $\pm$ 100 ^b	55,760 $\pm$ 23,780 ^c
b) Following 3rd growth trial				
<0.1	330 $\pm$ 200 ^{2,a}	260 $\pm$ 120 ^a	460 $\pm$ 350 ^{3,a}	340 $\pm$ 230 ^a
4	50,870 $\pm$ 26,190 ^{4,c}	2320 $\pm$ 250 ^b	2380 $\pm$ 90 ^b	77,560 $\pm$ 11,630 ^{3,c}
9	85,460 $\pm$ 5840 ^c	2450 $\pm$ 260 ^b	2620 $\pm$ 230 ^b	82,540 $\pm$ 22,890 ^c
14	67,200 $\pm$ 7850 ^c	ND	3080 $\pm$ 640 ^b	63,860 $\pm$ 16,210 ^c

¹ Data in each trial were analyzed by two-way ANOVA, following log transformation. MSE for each trial was (1)0.02656, and (2)0.03909. Significant differences amongst log transformed means were detected by Scheffé multiple contrast test. Values in each trial followed by the same letter(s) are not significantly different ($p < 0.05$).

² $n = 4$

³ $n = 3$

⁴ $n = 2$

ND = not determined

Sulphate data collected from leachate trials did not pass the $F_{\max}$ test. It was assumed that the ANOVA was robust enough to withstand the heterogeneity of variances inherent in these data sets.

F. Soluble aluminum, iron, and manganese in leachates

Unlike other leachate data, metal determinations were made only on selected samples taken following the third growth trial. The effect of manure was not investigated in terms of soluble metals in the produced leachates. As only two replicate determinations were made, an ANOVA was not conducted.

From the mean values presented in Table 3.23, it can be noted that leachates from limed soils contained lower levels of measured soluble metals than leachates from control soils. No trend in these leachate metal concentrations was noted with changing soil sulphur levels. Leachates from unlimed soils contained higher levels of soluble aluminum, iron, and manganese than did leachates from control soils. Highest leachate levels of metals were recorded from pots containing unlimed 9% sulphur-contaminated soil. Further investigation would be required to determine if this trend is merely a function of low sample replication.

3.2 MESH POT EXPERIMENT

The average total sulphur concentration of basepad soil used for this experiment was $5.6 \pm 0.5\%$. Lime was added in a 3:1 ratio to this soil based on a presence of 6% sulphur. The topsoil cap

Table 3.23. Soluble aluminum, iron, and manganese ($\mu\text{g mL}^{-1}$) in leachates produced from selected pot soil used for growth trials involving four sulphur levels upon which four reclamation treatments were superimposed. Leachates were produced following the third growth trial. Data are means ($n=2$) $\pm$ standard deviations.

Soil Sulphur (%)	Metal Measured	Reclamation Treatments			
		No Treatment	Lime	Lime and Manure	Manure
<0.1	Al	0.123 $\pm$ 0.106	ND	ND	ND
	Fe	0.731 $\pm$ 0.443			
	Mn	0.034 $\pm$ 0.004			
4	Al	778 $\pm$ 3	0.012 $\pm$ 0.001	ND	ND
	Fe	4817 $\pm$ 1439	0.124 $\pm$ 0.039		
	Mn	514 $\pm$ 34	0.008 $\pm$ 0.008		
9	Al	1082 $\pm$ 293	0.011 $\pm$ 0.000	ND	ND
	Fe	8220 $\pm$ 3224	0.119 $\pm$ 0.045		
	Mn	419 $\pm$ 169	0.005 $\pm$ 0.006		
14	Al	526 $\pm$ 163	0.008 ¹	ND	ND
	Fe	2554 $\pm$ 1055	0.016 ¹		
	Mn	13.8 $\pm$ 5.7	0.177 ¹		

ND = not determined

¹n = 1

placed on top of the limed soil contained non-detectable amounts of total sulphur. The only moisture received by the pots which were left outdoors throughout the one year trial was natural precipitation.

3.2.1 Aboveground Biomass

Aboveground biomass was harvested 105 days after seeding. All biomass yields were less than 1.0 g pot^{-1} , with the exception of reed canarygrass in the 30 cm deep pot⁻¹ (Table 3.24). Nuttall's alkali grass did not grow in the 15 cm deep pots. No significant differences were observed amongst the four grass species grown in the 15 cm deep pots. Yields in the 30 cm pots were somewhat higher than those in 15 cm deep pots. Reed canarygrass was the only species tested that had a significantly higher yield in the 30 cm deep pot compared with that in the 15 cm deep pot. Reed canarygrass in the 30 cm deep pot exhibited the greatest shoot production.

During harvest, it was noted that the majority of vegetation in all pots had senesced. Soil cores from top to bottom of each pot were taken. In all cases, grass roots had penetrated through the top-soil layer and extended through the entire pot depth.

Very little moisture (21.7 mm) was received in Calgary during August, 1986. The average precipitation recorded for August over the last 30 years is 55.4 mm. Given that good growth was observed during prior months when more moisture was received, and that grass roots were found throughout pot depths, plant dieback appeared to be related more to soil moisture levels than to the soil composition within pots.

TABLE 3.24. Aboveground biomass (g dwt pot⁻¹) of five grasses grown in two depths of mesh pots containing limed, sulphur-contaminated soil over which topsoil was placed. Data are means (n=3) $\pm$ standard deviations.¹

Depth of pots ² (cm)	Grass Species				
	Reed canarygrass	Tufted hairgrass	Foxtail barley	Slender salt- meadow grass	Nuttall alkali grass
15	0.24 $\pm$ 0.25 ^a	0.19 $\pm$ 0.25 ^a	0.10 $\pm$ 0.18 ^a	0.28 $\pm$ 0.28 ^a	0.00
30	2.33 $\pm$ 0.76 ^b	0.12 $\pm$ 0.08 ^a	0.83 $\pm$ 0.70 ^{ab}	0.82 $\pm$ 0.58 ^{ab}	0.21 $\pm$ 0.22 ^a

¹ Data were analyzed by two-way ANOVA. MSE was 0.18928. Significant differences among means were detected by Scheffé multiple contrast test. Values followed by the same letter(s) are not significantly different (p < 0.05).

² The 15 cm and 30 cm deep pots had 5 cm and 10 cm depth topsoil covers, respectively.

3.2.2 The pH and Conductivity Measurements of Leachates

The pH of leachates from both pot depths was neutral throughout the experiment (Table 3.25). The pH of 15 cm deep pots decreased below 6.5 on July 20 and July 26 but returned to pH 6.9 by the final sampling date. Although significant pH differences were highlighted by the Scheffé multiple contrast test, these differences are not biologically significant. Lime application to soil containing approximately 6% total sulphur neutralized all produced leachate for 15 cm and 30 cm deep pots.

No conductivity values over 3.0 mS cm^{-1} were recorded, indicating that the salinity of produced leachates was low (Table 3.26). Significant differences as detected by the Scheffé test are not biologically significant. No clear pattern was evident in terms of conductivity values with respect to either pot depth or time. The addition of lime to soil containing approximately 6% sulphur did not produce a saline leachate.

3.3 ISOLATION OF SULPHUR-OXIDIZING MICROBES

Microbial growth was evident on the four types of media. Clearing zones were not observed on plates inoculated with suspended soil nor on plates inoculated with pure culture of I. albertis. Therefore, enumeration of sulphur-oxidizing microorganisms was not possible.

TABLE 3.25. The pH of leachate produced over time from two depths of mesh pots containing limed, sulphur-contaminated soil over which topsoil was placed. Data are means (n=3) $\pm$ standard deviations.¹

Depth of pots ² (cm)	Sampling Dates (1986)					
	May 17	Jun 17	Jul 1	Jul 20	Jul 27	Sep 01
15	7.2 $\pm$ 0.1 ^b	6.9 $\pm$ 0.1 ^b	7.1 $\pm$ 0.1 ^b	6.2 $\pm$ 0.1 ^a	6.3 $\pm$ 0.1 ^a	6.9 $\pm$ 0.2 ^b
30	7.4 $\pm$ 0.1 ^b	7.3 $\pm$ 0.1 ^b	7.3 $\pm$ 0.1 ^b	6.7 $\pm$ 0.1 ^{ab}	6.9 $\pm$ 0.1 ^b	7.1 $\pm$ 0.2 ^b

¹ Data were analyzed by two-way ANOVA. MSE was 0.01666. Significant differences among means were detected by Scheffé multiple contrast test. Values followed by the same letter(s) are not significantly different ($p < 0.05$).

² The 15 cm and 30 cm deep pots had 5 cm and 10 cm depth topsoil covers, respectively.

TABLE 3.26. Conductivity of leachate (mS cm^{-1}) produced over time from two depths of mesh pots containing limed, sulphur-contaminated soil over which topsoil was placed. Data are means ($n=3$) $\pm$ standard deviations.¹

Depth of pots ² (cm)	Sampling Dates (1986)		
	May 17	Jun 30	Jul 01
15	2.67 $\pm$ 0.02 ^b	2.47 $\pm$ 0.75 ^b	2.77 $\pm$ 0.55 ^b
30	2.88 $\pm$ 0.23 ^b	0.61 $\pm$ 0.18 ^a	2.13 $\pm$ 0.34 ^{ab}
	Sampling Dates (1986) continued		
	Jul 20	Jul 27	Sep 01
15	2.06 $\pm$ 0.26 ^{ab}	2.14 $\pm$ 0.50 ^{ab}	1.90 $\pm$ 0.27 ^{ab}
30	1.57 $\pm$ 0.27 ^{ab}	0.90 $\pm$ 0.58 ^{ab}	0.93 $\pm$ 0.04 ^{ab}

¹ Data were analyzed by two-way ANOVA. MSE was 0.15584. Significant differences among means were detected by Scheffé multiple contrast test. Values followed by the same letter(s) are not significantly different ($p < 0.05$).

² The 15 cm and 30 cm deep pots had 5 cm and 10 cm depth topsoil covers, respectively.

CHAPTER 4

DISCUSSION

The discussion will follow the format of the experimental objectives outlined in the Introduction. Results obtained from work on each objective will be discussed sequentially.

4.1 EFFECT OF SULPHUR CONTAMINATION ON PLANT GROWTH AND SOIL CHEMICAL PROPERTIES.

No plant growth occurred in any untreated soils containing sulphur. Initial germination occurred, but plants were unable to survive to trial completion. All of these soils had a pH of less than 4.5. This is below the pH that Webber et al. (1977) reported as the minimum pH at which plant growth can successfully occur on agricultural soil. It is likely that the failure of plants to establish on these acidic soils was due to both direct and indirect effects of the low soil pH. Although it is not intended to document the specific reason for the failure of plants to become established on these acidic soils, observed changes in the soil chemistry of these soils compared to values recorded for control soils will be briefly discussed.

Within a soil that is heavily contaminated with elemental sulphur, microbial oxidation of sulphur to soluble sulphate will occur. A number of soil chemical properties are directly linked to the level of sulphur oxidation in soils. Throughout the growth trials, sulphate levels were higher in the unlimed, sulphur-contaminated soils (hereafter termed acid soils) than in the control soils.

Both pH and conductivity corresponded closely to sulphate levels in acidified soils. When the rate of sulphur oxidation slowed, so did the resultant production of sulphuric acid. Hence, the observed pH values also leveled off. It is postulated that the leveling off of sulphate values in the acid soils was the result of metal toxicities in the soil limiting or inhibiting the survival of sulphur-oxidizing microorganisms. Reduced rates of sulphur oxidation as a result of metal toxicity have been reported by Hart (1959). Levelling off of pH values occurred, however, at levels toxic to plant growth. The same trend was observed for soil conductivity. The major ion contributing to the soluble salt concentration in these soils would be sulphate. Although sulphate-sulphur is not phytotoxic, it can accumulate to the point where the soil becomes saline (Leitch and Nyborg 1985). Conductivity values leveled off when sulphate values plateaued. Conductivity values in the acid soils were, however, high enough to inhibit plant establishment. Reed canarygrass has been documented as growing in soils with conductivity values as high as 5 to 10 mmhos cm^{-1} (Watson et al. 1980). All of the acid soils in this study had conductivity values well above this range, with the exception of the data collected prior to the first growth trial and the 4% sulphur soils following the first growth trial.

Sulphur oxidation in acid soils was also indirectly related to other changes in soil chemical properties. Reductions in soil pH due to the production of sulphuric acid caused changes in other soil properties. High levels of soluble aluminum were measured in these

acid soils. Nyborg (1982) reported that soluble aluminum concentrations greater than 3-5 ppm would be harmful to vegetation. Although values of only 1.0 and 0.87 ppm were measured in the 4% sulphur soil prior to the first growth trial, aluminum concentration in the 4% sulphur soil was 3950 ppm following the third growth trial. Aluminum levels in the other acid soils were significantly higher than the toxic level of 20 ppm reported by Nyborg (1982). Soluble aluminum levels were, therefore, high enough to have prevented successful plant growth.

Nitrate levels in acid soils decreased relative to that in the control soils following the first growth trial. The decrease in nitrate levels corresponds well with the documented susceptibility of Nitrobacter to acid conditions (Rechcigl and Sparks 1985). However, there was an apparent stimulation in nitrate production in the 4% sulphur soils as measured by samples taken following the second and third growth trials. Other researchers have also reported evidence of nitrification in acid soils. Uhlen (1985) observed that nitrification had occurred in a highly organic soil at a pH of 4.5, while Curtin and Smillie (1986) reported evidence of nitrification in a soil that had a pH of 4.2. Rechcigl and Sparks (1985) speculate that any nitrification that does take place below a pH of 4.5 may be the action of heterotrophic organisms. From the data obtained in the present study it can only be speculated that nitrification was taking place in the unlimed 4% sulphur-contaminated soil even at a pH of 1.9.

In contrast, ammonium levels were higher in acid soils than in control soils. While this result has been reported in the literature (Rorison 1973; Rechcigl and Sparks 1985), the mechanisms of ammonium accumulation in acid soils are not well understood. While some report higher ammonium levels as a result of increased mineralization, it could be the result of impaired nitrification leading to an accumulation of ammonium. The data for both soluble forms of nitrogen indicate that normal cycling of nitrogen was impaired as a result of acidification.

Although a decrease in both phosphorous mineralization (Rechcigl and Sparks 1985) and the availability of soluble phosphorous (Leitch and Nyborg 1985) has been observed in acid soils, soluble phosphorous levels in acid soils in the present study did not differ significantly from those in control soils. This indicates that either the microorganisms responsible for transformation of organic phosphorous to inorganic phosphate are capable of operating under extreme acidity, or a chemical process such as acid hydrolysis of organic matter is responsible for the levels of soluble phosphorous in the acid soils. It also indicates that available phosphorous is not being bound as expected, due to the formation of aluminum and iron bound phosphates (Leitch and Nyborg 1985). Further investigations would be required to confirm this process and to identify whether it is biological or chemical in nature.

Differences in SAR between acid soils and control soils were significantly different, but not different enough to cause plant growth impediment. Sodium adsorption ratio values were statistically

lower in the acid soils indicating a different ratio of calcium, magnesium, and sodium cations in these soils compared with the control soils. The effects of sulphur and acidity on cation concentrations is beyond the scope of this thesis.

As reported in the literature (Gebhardt 1973), the cation exchange capacity (CEC) of acid soils was significantly lower than that of the control soils. This reduction in CEC is due to the reduction of exchange sites within the soil structure caused by both the breakdown of materials such as aluminosilicates at pH values below 5.5 (Gebhardt 1973) and the presence of soil sulphur that does not have any exchange capacity.

Sulphur contamination in soils that had underlain a sulphur block basepad caused a number of biological and chemical changes such as interrupted cycling of nitrogen, increased soil concentration of soluble sulphate and aluminum and increased soil acidity. These changes resulted in the soil being incapable of supporting plant growth.

4.2 EFFECTIVENESS OF LIME AND MANURE AMENDMENTS TO SULPHUR-CONTAMINATED SOIL

Lime alone and in combination with manure was applied to sulphur-contaminated soils to test their effectiveness in encouraging plant growth and ameliorating soil conditions.

Based on the results of this study, lime amendment may not ensure reclamation of soils heavily contaminated with elemental

sulphur. Productivity of reed canarygrass was significantly reduced in limed, sulphur-contaminated soil compared with that in the control soils. No growth was recorded in limed soils containing 14% sulphur. These results are not in agreement with Nyborg (1982) and Bertrand (1973) who reported that soils contaminated with elemental sulphur could be successfully reclaimed despite the requirements for heavy lime applications. Liming rates used by these two authors were determined in the same manner as in the present study. Bertrand applied 224 tonnes lime ha^{-1} to acidified soils of pH 1.4 and 2.1 and obtained successful crops of oats (Nyborg 1978). Nyborg (1982) reported that grasses grew well on soils that were limed with as much as 600 tonnes ha^{-1} . Liming rates for the sulphur-contaminated soils used in the present study were as high as 893 tonnes ha^{-1} .

Both Nyborg and Bertrand studied sulphur-contaminated soils obtained from areas adjacent to sulphur handling facilities rather than soils that had underlain a sulphur block basepad (as was the case in the present investigation). Total sulphur values in Bertrand and Nyborg's soils were $\leq 1\%$ and 10%, respectively. Comparable results from the present study do not agree that lime amendment of the contaminated soil will result in successful reclamation.

Differences between the soils used in the present project and those used in the two previous studies include the fact that soil taken from below the basepad may have been in contact with elemental sulphur for much longer than soils lying adjacent to sulphur handling facilities. In addition, the soil lying below the sulphur block

basepad for a minimum of twenty years would have been subjected to very different microclimatic factors than was soil that did not support a block of sulphur.

Other studies on the effects of liming acid soils have reported variable results, e.g. Timmer (1985) reported no plant growth effect of a hybrid poplar clone to liming (15 tonnes ha^{-1}) an acidified soil with a pH of 5.7 to neutrality. Grove and Sumner (1985) recorded yield depressions in corn associated with lime applications of up to 22.4 tonnes ha^{-1} . Negative growth responses to high lime rates are well documented (Haynes 1982). High rates of lime application are not unusual in agricultural soils which have been acidified through fertilizer use or climatic factors. However, rates denoted as high for these soils (i.e., 25 tonnes ha^{-1}) are at least ten-fold lower than lime additions incorporated into soils in this research.

Despite reports of organic matter reducing toxicities associated with acid soils (Hoyt and Turner 1975; Wright et al. 1985; Ahmad and Tan 1986), addition of manure to unlimed, sulphur-contaminated soils did not improve the growth of reed canarygrass. Organic matter may be beneficial in acid soils by complexing toxic levels of aluminum with organic compounds (Hoyt and Turner 1975). Although, in the first growth trial, manure additions did reduce the amount of soluble aluminum in the acid soils, aluminum levels were still greater than 20 ppm, the level reported by Nyborg (1982) as being toxic to plants. In samples taken following the third growth trial, there were no significant differences in the amount of soluble aluminum present in the acid soils whether they were treated with manure or not. Therefore, the

amount of manure that was added, 40 tonnes ha^{-1} , was not sufficient to complex a significant proportion of the available aluminum. It would appear impractical to reclaim heavily contaminated soils with organic matter alone. Ahmad and Tan (1986) concluded that the addition of lime in combination with organic matter was more successful in reducing aluminum toxicity than the addition of organic matter alone. Under the conditions set forth in the present study, addition of manure to limed soils did not significantly improve plant growth.

Lime additions to sulphur-contaminated soils resulted in changes to various soil chemical parameters. The pH of all soils amended with lime increased to neutrality and remained neutral for the duration of the experiment. Neutralization of these soils raised the pH to a level where plant growth would not be impeded by direct or indirect effects of acidity.

Another important chemical parameter that could influence reclamation success is soil salinity as measured by conductivity. Bertrand (1973) found that the use of calcium carbonate containing greater than 5% magnesium carbonate resulted in levels of soluble salts which could hinder plant growth. The lime used for this experiment did not contain more than 5% magnesium carbonate (G. Crosby, pers. comm.). The conductivity values of all limed soils were below 4.0 mS cm^{-1} ; conductivities above this value are generally considered indicative of saline soils (Hausenbuiller 1978). The reduction in growth, therefore, was not due to elevated levels of soluble salts in the limed soils.

The general fertility status of the sulphur-contaminated soils was also altered as a result of liming. Liming resulted in an initial increase in nitrate-nitrogen values compared with control soils. Following this, nitrate values in all soils decreased during the course of the experiment, despite fertilization at the beginning of each trial. Although nitrate values were quite low, especially after the leaching trials, their levels in the limed soils did not fall below those in control soils. Given that reed canarygrass growth in the control soils was always lush, it does not appear that plant growth in limed soils was limited by a lack of nitrate-nitrogen. Ammonium concentrations in limed soils did not differ significantly from control soil values throughout most of the experiment. They were well below the values that occurred in the acid soils. Given the similarity of ammonium values in limed soils to those in control soils, levels of this plant nutrient did not cause the growth depression observed in the limed soils.

The major plant nutrient affected by liming was phosphate. In soil samples taken throughout the experiment, phosphate values in limed soils were significantly lower than those in control and acid soils. Various publications (Sims and Ellis 1983; Pombo and Smith 1986) report deficiencies or elevations in the status of available phosphorous as a result of lime applications. Overliming can result in phosphorous deficiencies (Brady 1984). The decreases in available phosphorous in limed soils is likely due to precipitation of insoluble

compounds containing phosphate and calcium. Results from this experiment clearly indicate a reduction in phosphorous in limed, sulphur-contaminated soils.

Reductions in aboveground biomass in the limed soils may have been due to a phosphate deficiency. Plants suffering from a lack of phosphate develop red stripes along their leaves (Agrios 1969) but no such symptoms were noted. Plants germinated in the limed pots, but would begin to dieback about two weeks later. The condition of these plants suggested that they were dessicating due to a possible lack of moisture but all pots were watered at two-thirds of their field capacity, so moisture should not have been a limiting factor.

There are two different types of acidity within a soil; active acidity and reserve acidity (Brady 1984). Active acidity requires immediate neutralization. In a soil that is heavily contaminated with elemental sulphur, a proportion of the soil acidity will be reserve acidity due to the presence of unoxidized elemental sulphur. The method initially used to determine lime application rates in this experiment assumes that all of the sulphur present in the soil will be oxidized. Lime was added on a chemical basis to ensure that all the generated acidity (i.e., active plus reserve acidity) would be neutralized. Therefore, the amount of lime added to the pots (present study) was a minimum of 10X greater than that required to neutralize the active acidity (i.e., overliming).

As has already been discussed, one of the main toxic effects of soil acidity is the elevated levels of soluble aluminum. Lime amendment of sulphur-contaminated soils reduced the level of soluble

aluminum to below 1 ppm. Therefore, the growth reduction in limed soils was not due to elevated levels of soluble aluminum.

Liming sulphur-contaminated soils did not result in significant changes in the ratio of sodium, calcium, and magnesium expressed as SAR. A decrease in SAR values in limed soils indicates an increase in calcium levels. The similarity of SAR values for all of the pot soils illustrates that this ratio is not an indicator of the chemical changes that are occurring as a result of amending sulphur-contaminated soils.

Cation exchange capacity of limed soils was initially reduced relative to both the control and untreated soils. Following the third growth trial, significant differences still existed between CEC values in limed soils and control soils. Liming did not restore cation exchange capacity to the previously acidified soils. This is due to the fact that neither the lime itself nor the sulphur in the soils have exchange capacity. Cation exchange capacity values measured in this experiment were within an acceptable range (D. McCoy, pers. comm.). Therefore, the reduction in CEC values in limed soils was not responsible for the decreased plant biomass measured in pots containing limed, sulphur-contaminated soil.

The addition of manure alone or in combination with lime did not affect many soil chemical parameters. The majority of changes in the sulphur-affected soils were due to the presence of lime rather than manure. Addition of manure alone did not significantly change chemical parameters compared with those of the acid soils. There were some exceptions to these generalizations, e.g., phosphorous values

were higher in all manure treated soils; prior to the growth trials available nitrate-nitrogen was higher in manure-treated soils; and SAR values were slightly higher in samples taken from manure-treated soils prior to the first growth trial. The addition of manure did initially improve some soil fertility levels, such as available phosphate and nitrate, but did not result in improved yields of reed canarygrass. It had been expected that the manure would be effective in reducing aluminum toxicities in the sulphur-contaminated soils and would also provide additional nutrients through the ongoing breakdown of organic material, but this did not appear to be the case.

In summary, lime amendment of a soil taken from below the basepad of a former sulphur block did reclaim the soil by improving soil chemical characteristics and plant growth. However, reclamation success was not complete in that aboveground biomass of reed canarygrass was reduced compared with control pots. From a plant growth perspective, no reclamation success was achieved in liming the 14% sulphur soil. It is postulated that the reduced yields measured on limed soils compared to those on control soils were due mainly to the physical presence of the lime itself. Although changes in soil texture were not quantitatively measured, soil structure changes were visually apparent. Overliming is known to reduce pore space (Brady 1984) and in the present study the soil became harder to break apart as the amount of added lime was measured. The consequences of less pore space are reduced water and air necessary for healthy root growth. Although root biomass was not measured quantitatively, roots

growing in limed soils were observed to be less developed than those in control soils. The observation that plants appeared to be dying of dessication also supports the hypothesis of overliming.

Poor growth in the limed soils may also have been due to micronutrient deficiencies. While some authors have reported that micronutrient deficiencies are not a problem in limed soils (Nyborg 1982; Folscher et al. 1986), others have measured lime-induced deficiencies (Timmer 1985). Micronutrients were not measured in the present study; consequently, no definitive conclusions can be made regarding this aspect. In the present study, the pH levels in all limed soils were very similar. Therefore, any micronutrient deficiencies that might be the result of soil pH status should have manifested themselves in the form of reduced yields for all levels of sulphur. This did not occur. The decrease in plant yields with respect to control soils was greater as sulphur and, correspondingly, lime levels increased. This suggests that the problem was directly associated with the lime applications.

The design of this experiment does not permit differentiation between the effects of lime itself compared with the effects of the combination of lime and sulphur in the soil on plant yield and soil chemistry. Much of the work done by Nyborg and Bertrand involved the addition of lime in excess of the required amount necessary to neutralize acid produced from elemental sulphur oxidation. In this experiment, however, lime was added at rates determined by the amount of total soil sulphur. Reduced plant yields and altered soil chemistry could conceivably be due to two possible factors: (1) the physical

presence of lime alone, or (2) a combination effect of the presence of both lime and sulphur in the soil.

There is a possibility that the sulphur-contaminated soils could be successfully reclaimed with a change in liming practices. As has already been discussed, neutralization of the active soil acidity required only a fraction of the actual amount of lime applied. Reduced initial applications of lime followed by additional applications as required, should minimize the possibility of overliming the soil. Further work is required to determine what levels of lime should be initially applied to soils containing high levels of elemental sulphur. Adequate liming is necessary to ensure neutralization of acidity produced as a result of any continued sulphur oxidation.

The addition of manure as an amendment is also recommended, despite the poor results achieved in this experiment. Consideration should be given to adding more manure throughout the reclamation process to progressively improve soil conditions. The addition of manure may be important in the re-inoculation of the soil with microorganisms that are capable of operating within a neutral soil pH range. Nutrient additions, as required, should be added in the form of fertilizers.

4.3 CHEMICAL CHARACTERISTICS OF LEACHATES

Pots used in the greenhouse growth experiments were also used for leaching trials. These trials took place before and after the third growth trial. The objective of the leaching trials was to characterize chemically the leachate produced from the various soil

mixtures. No attempt was made to relate plant nutrient concentrations in leachates with those measured in the soils.

Acidic leachates were produced from all unlimed, sulphur-contaminated pots, while leachates from limed pots were neutral. Leachate acidity increased with increasing sulphur level. pH values of less than 1.0 were recorded for the two highest sulphur levels. Sulphate concentrations occurred in acidic leachates in levels as high as 0.9% while concentrations in leachates from limed soils were measured in the $\mu\text{g mL}^{-1}$ level. Conductivity values were greater in leachates from unlimed soils than in those from control or limed soils. The increase in soluble salts present in acidic leachates was due to the presence of high levels of sulphate. High levels of other nutrients, such as nitrogen and phosphorous, were also present in acidic leachates. In contrast, nutrients leached from limed soils were not significantly higher than those from control soils.

Selected samples taken during the second trial were analyzed for soluble aluminum, iron, and manganese. Metal concentrations in leachates produced from limed soils were well below $1\mu\text{g mL}^{-1}$, while concentrations in the acidic leachates were recorded in the hundreds of $\mu\text{g mL}^{-1}$. These results indicate the potential for metal contamination from sulphur-contaminated soils that are not limed immediately following basepad removal. Leaving a soil that is heavily contaminated with elemental sulphur exposed and unlimed is not only a potential health hazard as a result of the metal concentrations that could potentially reach the groundwater, but also a drain of potentially available nutrients that are required for reclamation.

The results obtained in this study suggest that leachates from limed, sulphur-contaminated soils would not present a hazard to local groundwater supplies but acidic leachates from unlimed, sulphur-contaminated soils may contaminate groundwater. Chemical characterization of leachates from acidic soils illustrate the importance of quickly neutralizing contaminated soils.

4.4 SULPHUR OXIDATION IN SOILS

Attempts to characterize the microorganisms responsible for oxidizing sulphur in the soil taken from below the basepad were unsuccessful. No clearing zones of the sulphur-coated bentonite overlay, indicating the presence of sulphur-oxidizing microorganisms, were produced on agar plates designed to characterize the types of microbes active in elemental sulphur oxidation. Wainwright (1979) reported that this technique had been successfully used for forest soils located downwind of a coking facility. Upon re-examination of the plate preparations, it was noted that the pH of the final plates was neutral. From information in the literature, it was known that the only microorganisms involved in oxidizing sulphur in the soil used in the present study would be those that could tolerate conditions of extreme acidity (i.e., pH <4.0). These same microorganisms are not able to operate within the neutral pH range. Therefore, it is not unexpected that isolation attempts were unsuccessful. The lack of organisms isolated on the neutral plates suggests that no sulphur-oxidizing microorganisms that function in the neutral pH range were able to survive in the acidic soil.

Sulphur oxidation took place in the sulphur-contaminated soils used for the growth trials. Although rates of oxidation were not measured, trends in oxidation can be observed by examining both the soluble sulphate and soil pH data. Levels of soluble sulphate in all sulphur-contaminated soils increased between the first and second sampling periods, after which they leveled off. Greatest increases in sulphate production occurred in the lowest soil sulphur level. The magnitude of increases in sulphate were much greater in the unlimed soils than in the limed soils. While a decrease in pH occurred in the unlimed soils, the pH of the limed soils remained neutral. Sulphate levels in both limed and unlimed soils stabilized following the first growth trial, indicating that minimal sulphur oxidation occurred during the rest of the experiment. The pH of the unlimed soils also stabilized following the first growth period. It is postulated that the pH of the acidic soils fell below the tolerance limits of the acidophilic species of Thiobacillus (Hart 1959).

Particle size of the elemental sulphur governs, to a large degree, the rate of sulphur oxidation. The presence of sulphur in soils underneath a basepad is visually obvious, i.e., a proportion of the particles is macroscopic. Chunks of sulphur up to 10 cm in diameter are found in these soils and even under optimal conditions, complete oxidation of this material would take years (Bettany and Janzen 1985). Therefore, it appears unnecessary initially to lime the soil to counteract all of the potential acidity resulting from complete oxidation of the sulphur. Beverly (1986) found that actual oxidation

of elemental sulphur only lowered soil pH by one-fifth as much as was potentially possible.

Neutralization of sulphur-contaminated soil can increase rates of oxidation (Bertrand 1973). This, in turn, can result in re-acidification of the soils. Re-acidification of the limed, sulphur-contaminated soils did not occur in this experiment. As noted, the pH of the limed soils remained neutral throughout the trials. It is thought that the lack of re-acidification of soils was due to the absence of sulphur-oxidizing organisms capable of operating in neutral soil conditions and the presence of adequate lime levels to neutralize any produced acidity.

In summary, sulphur-oxidizing organisms were not isolated from soil taken beneath a sulphur block basepad due to application of an inappropriate technique. However, evidence does suggest that sulphur oxidation in these acid soils is possible. Liming of the soil to neutrality did not result in re-acidification of the soil.

4.5 EFFECTS OF "CAPPING" A SULPHUR-CONTAMINATED SOIL

One method for improving growth on a former sulphur block site might be to apply a cap of uncontaminated soil on top of limed, sulphur-contaminated soil. This would provide a hospitable environment for seed germination and initial root development. A potential disadvantage of this reclamation technique is the relative inaccessibility of the contaminated soil, if further treatment of that soil is deemed necessary.

The pots, designed to evaluate the effectiveness of the "capping" technique, were used for a reclamation trial to select the highest yielding salt tolerant grass. When the experiment was initially designed, it was thought that salt tolerant grasses would be the easiest plants to establish on the potentially saline, heavily limed soil. However, results from the greenhouse trials indicated that it was not the salinity from lime applications that was the concern. Results of the outdoor trial indicated that given the specific soil and climatic conditions, reed canarygrass produced the highest yield. Growth in the "capped" pots was not as good as expected. Dieback of the majority of plants occurred during the last month of the trial. Upon examination of the roots, which had permeated all the available soil, it was decided that plant senescence was due to an unusually hot, dry month rather than due to factors relating to the soil mixture composition.

The sulphur level used in the outdoor pot experiment was 6% which was significantly lower than the two highest sulphur levels used in the greenhouse experiment. The absence of control pots in the "capping" experiment does not allow a comparison of plant biomass grown in subsoil that is contaminated with elemental sulphur with biomass yields grown in uncontaminated subsoil. The use of a "cap" over limed soils heavily contaminated with sulphur is not recommended as a reclamation technique at the present time. More information is required about most effective liming techniques and the factors controlling sulphur oxidation. If a soil is low enough in sulphur that application of approximately three times the amount of lime will not

inhibit plant growth response, then there is no need for a "cap." If there is a substantial amount of sulphur in the soil, the application of appropriate amounts of lime to the subsoil may hinder proper root development once the roots enter the subsoil.

Leachate produced from pots set up to evaluate this technique were neutral in pH. Conductivities of the intermittently produced leachate were low, indicating that there were no measureable concentrations of sulphate in the leachate.

CHAPTER 5

CONCLUSIONS.

The following conclusions were drawn from results of the experiments conducted:

1. Plant growth did not occur in any untreated sulphur-contaminated soils;
2. Lime applications, at a rate of 3 parts lime:1 part total sulphur, were not effective in promoting plant growth at soil sulphur levels above 4%;
3. Reclamation of sulphur-contaminated soils by manure additions, alone, was not successful;
4. Nitrogen cycling, as determined by nitrate and ammonium measurements, was disrupted in unlimed, sulphur-contaminated soils;
5. Lime applications to sulphur-contaminated soils maintained soil pH values at neutrality.
6. Amounts of lime added to contaminated soil were a minimum of 10-fold higher than that required to neutralize the active acidity within the soil.
7. Reclamation failure of limed soils is postulated to be due to the physical presence of lime. A second possibility not tested in this experiment is that reclamation failure could also be due to a combined effect of both the lime and sulphur in the soil.

8. Further work on this reclamation problem should include a determination of actual lime requirement needs of sulphur-contaminated soils based on active acidity and a prediction of sulphur oxidation rates over time.
9. Acidic leachates were produced from all unlimed, sulphur-contaminated soils, while leachates from limed soils were neutral. Leachate acidity increased with increasing sulphur level.
10. Soils that have underlain a sulphur block basepad should not be left exposed and unlimed. Immediate liming to prevent potential migration of acidic leachate into the groundwater is recommended.

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