

**THE POTENTIAL OF LIME-STABILIZED AND CHEMICALLY-FIXED MUNICIPAL
SEWAGE SLUDGES FOR LAND APPLICATION AS LIME OR NITROGEN SOURCES**

by

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(ABSTRACT)

Lime-stabilized and chemically-fixed sludges have been inadequately characterized for utilization as amendments to acid soils. Laboratory incubation studies were employed to evaluate calcium carbonate equivalence (CCE) and nitrogen (N) mineralization rates of these sludges when applied to three acid Typic Hapludults from Virginia. Greenhouse studies were conducted to evaluate the effect of increasing sludge application rates on growth of corn. The CCE of the lime-stabilized and chemically-fixed sludges were 30.9 and 58.1%, respectively. Application of sludges to soils resulted in rapid neutralization of soil acidity. Added organic-N was mineralized at an average rate of 32% in surface soils. Based on N mineralization, application rates of lime-stabilized and chemically-fixed sludges will be limited by CCE for most soils. Corn yields on the Glencg and Tatum soils were improved by addition of the sludges and remained within 95% of maximum at 118 and 160%, respectively, of the rate predicted to raise soil pH to 6.5. Zinc deficiencies were induced at the highest sludge application rates. Corn yields were higher when soils were amended with lime-stabilized or chemically-fixed sludges than when amended with CaCO_3 because the sludges contained Zn and other nutrients. Lime-stabilized and chemically-fixed sludges are good sources of lime which will supply N at the rate of approximately 32% of applied organic-N but overapplication of these sludges to meet the N needs of corn will probably result in Zn deficiency on all but the most acid soils.

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Chapter I

INTRODUCTION

Lime-stabilization of sewage sludges is a modification of a process which has been in use for hundreds of years. Lime has traditionally been added to manures to reduce odors and fly populations. Today, lime is frequently used to raise the pH of sewage sludges above 11.5 to stop biological activity and kill many of the human pathogens associated with sewage sludge. This is known as lime-stabilization. Another process which has recently been employed to stabilize sludges involves the addition of Portland cement which causes the sludge to thicken to a clay-like consistency and reduces the pathogen content. This process is one type of chemical-fixation of sludges.

Little is known about the effect of lime-stabilized or chemically-fixed sludges on soil chemical properties or what value they may have as nutrient sources. The author found only one publication dealing with the application of lime-stabilized sludges to soil. This publication (USEPA, 1975) dealt with the effects of application of lime-stabilized sludge to land and subsequent growth of barley on soils with pH values from 6.7 to 7.9. The data indicated that micronutrient deficiencies were present prior to sludge application. Effect of lime-stabilized sludge on soil acidity was not dealt with and N-mineralization rates were not examined. These data are necessary in order to provide the fullest benefit from the use of these sludges on agricultural soils.

Disposal of sewage sludges by land application is a practice which is growing in popularity. Application of manures to agricultural land is a time honored practice for improving soil fertility, soil physical properties and soil-plant water relations. Applications of sewage sludge to soils provide all of the benefits that manures provide, but sometimes problems result from the overapplication of sludge or the use of contaminated sludges. Use of contaminated sludges may be prevented by proper analysis of the sludge prior to application but overapplication of good-quality sludge can also be detrimental. If sludge contaminants are not rate limiting, nitrogen (N) content usually is. The problem is that different sludges supply different percentages of N depending on previous treatment. Over application of N can result in contamination of surface and groundwater with nitrates (NO_3^-) which may result in eutrophication of surface water and methemoglobinemia if drinking water is contaminated.

Lime-stabilized and chemically-fixed sewage sludges have been inadequately characterized. These sludges may contain enough lime to serve as lime sources even though they may not qualify as agricultural liming materials. If they neutralize soil acidity, will they increase soil pH to a level at which yields will be reduced? Will lime or N be the factor which limits application rates? At what rate is N mineralized from these sludges? Finally, what is the effect of these sludges on crop growth when they are applied to agricultural land?

The objectives of this research were as follows:

1. To investigate N-mineralization characteristics of lime-stabilized and chemically-fixed sludges from the Blue Plains sewage treatment plant near Washington, DC,
2. To determine the suitability of the lime-stabilized and chemically-fixed sludges as lime sources, and
3. To investigate the effect of lime-stabilized and chemically-fixed sludge addition to acid soils on soil acidity and crop growth.

Chapter II

REVIEW of LITERATURE

Wastewater Treatment

The main objectives of wastewater treatment are to remove suspended and dissolved solids, human pathogens and other components which make the water unsafe or objectionable to discharge into the environment. Although there are many treatment alternatives, a typical mechanical wastewater treatment system is depicted in Figure 1 on page 4.

Preliminary treatment (not shown) consists of a bar screen to remove objects larger than 2.54 - 4.45 cm and a grit chamber which reduces the flow to about 30 cm s^{-1} allowing sand and gravel to settle out while maintaining organic particles in suspension. Preliminary treatment helps protect machinery from damage. Preaeration may also precede primary treatment in order to reduce odors (Virginia Sewerage Regulations, 1977).

Primary treatment of wastewater usually consists of sedimentation in a tank called a primary clarifier where wastewater solids are allowed to settle or float to the surface. Chemical coagulants may be added at this point to aid in the removal of suspended solids and P. Solids removed at this

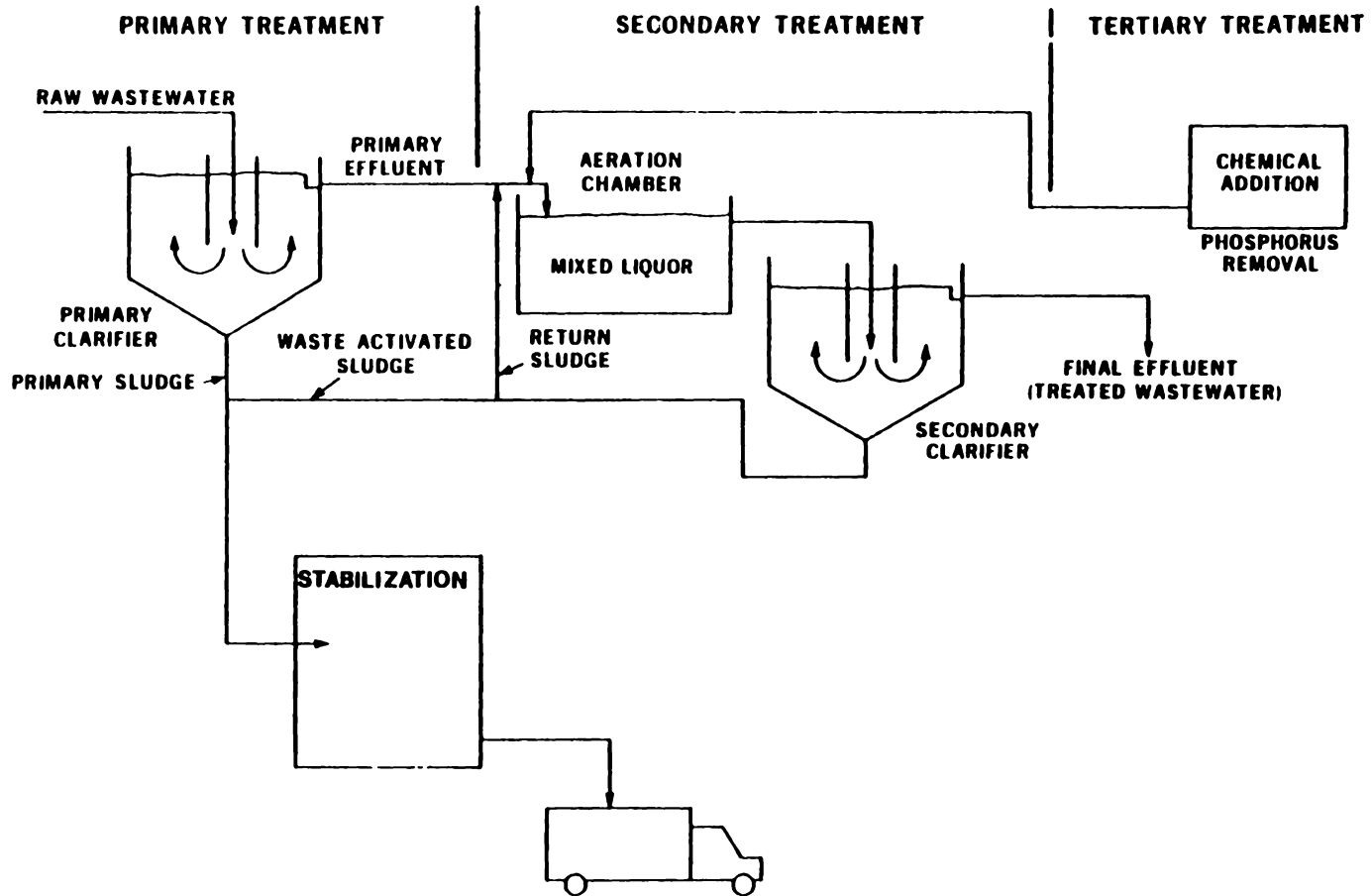


Figure 1. Mechanical wastewater treatment (adapted from Black, et al., 1984).

stage are termed primary sludge. The water from which the solids were removed is called primary effluent and still contains significant amounts of suspended solids and dissolved substances not removable by sedimentation (Vernick and Walker, 1981).

Chemical coagulants may be added to the primary clarifier or the aeration chamber to facilitate the removal of suspended solids and P, but are normally added just prior to dewatering and are termed sludge conditioners. Some common chemical coagulants used to treat wastewater are alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), ferric chloride (FeCl_3), lime ($\text{Ca}(\text{OH})_2$) and polyelectrolytes (Clark et al., 1977; Vernick and Walker, 1981). Alum has been used for decades and reacts with available alkalinity (CO_3^{2-} , HCO_3^- , OH^-), P and suspended solids but is currently used only to enhance P removal. Alum sludges are harder to dewater than biological sludges (Vernick and Walker, 1981). Ferric chloride also reacts with alkalinity, P and suspended solids, and is highly corrosive. Mixtures of ferric chloride and lime are often used because of improved dewatering properties. Lime addition is a highly reliable coagulation process that has been used for over a century. The primary reasons for its use in wastewater treatment are for removal of P and suspended solids but it is also effective in the removal of toxic metals from the wastewater (Boynton, 1980; Baes and Mesmer, 1976). If biological wastewater treatment such as waste activation is to follow, low lime levels may be used which elevate the wastewater pH to 9 or 10 (Vernick and Walker, 1981). Addition of lime to the primary clarifier generally doubles the amount of solids generated through increased efficiency and the weight of the lime. High lime coagulation elevates the wastewater pH to about 11. The amount of sludge produced may be five or six times that produced in primary clarifiers utilizing gravitational thickeners only. The sludge increase represents a large increase in solids removal efficiency. High lime coagulation lends itself very nicely to lime stabilization of sludge solids but if the sludge is to be treated biologically, the pH must be reduced with CO_2 or acid. Elevation of the wastewater pH to between 10.8 and 11.5 converts virtually all of the ammonium (NH_4^+) to ammonia (NH_3) and aids in the removal of NH_4^+ through volatilization in NH_3 stripping towers (Vernick and Walker, 1981; Clark et al., 1977).

Secondary treatment is designed to remove suspended solids and dissolved organics (USEPA, 1979). The most popular method is the activated sludge process which mixes aerobic

microorganisms with the primary effluent in an aerobic environment which is maintained by constant aeration. The microorganisms utilize organic compounds as food in the 3-8 h of aeration after which the "mixed liquor" is transferred to the secondary clarifier. In the secondary clarifier, the microorganisms settle and are drawn off the bottom as waste-activated sludge. In the waste activation process, volatile compounds are partially driven off and metals precipitated in the sludge (Vernick and Walker, 1981). Part of the sludge is added back to the aeration chamber as inoculum for a new batch of mixed liquor, while the excess is mixed with the primary sludge to receive sludge treatment. The treated wastewater is drawn off the top and may be discharged if it meets requirements based on BOD, and suspended solids (Virginia Sewerage Regulations, 1977) or the effluent may be required to receive tertiary treatment. The wastewater effluent is disinfected, usually with chlorine, prior to discharge (Virginia Sewerage Regulations, 1977).

Municipal sewage sludge often contains wastes from storm drains, food processing and industry. Some industrial wastes contain heavy metals and toxic organic chemicals. A large percentage of sewage sludge solids may be derived from domestic waste and much of this may originate from the use of domestic garbage disposals (Anderson et al., 1971). Human wastes also comprise a significant percentage of the solids and are a source of human pathogens in sludge. Most pathogens settle out of wastewater with the solids in primary clarification (USEPA, 1979; Vernick and Walker, 1981).

Liquid sludge makes an excellent medium for the growth of microorganisms (because of the organic constituents mentioned above) and is very putrescible. Wastewater treatment plants are required to stabilize many of the organic components present in sludge prior to disposal (USEPA, 1979). Acceptable methods of sludge stabilization reduce the biological activity of the sludge and reduce the content of human pathogens. The most common methods of stabilization include aerobic and anaerobic digestion, composting, heat treatment (pasteurization), high lime treatment and pressure chlorination. Heat treatment and composting, through the heat evolved, are the only processes which completely destroy pathogens, the most resistant being the ova of the intestinal nematode (roundworm), Ascaris lumbricoides (Teletzke, 1978). Anaerobic digestion is a good method of reducing pathogens, but lime stabilization is better (Vernick and Walker, 1981). Pressure

chlorination kills pathogens but at the risk of forming toxic chlorinated hydrocarbons (Symons et al., 1975). Anaerobic digestion, composting and other biological sludge stabilization methods are the only methods which reduce sludge volume.

Lime stabilization of municipal sewage sludge is a procedure which involves the addition of hydrated lime ($\text{Ca}(\text{OH})_2$) to liquid sludge until the sludge reaches a pH of approximately 12 and maintains a pH above 11.5 for 2 h (USEPA, 1979; Virginia Sewerage Regulations, 1977). It is a widespread, highly reliable method which has been in use for over 100 y (Vernick and Walker, 1981). Although it increases the amount of sludge for disposal, it reduces sludge odors (Clark et al., 1977), increases sludge dewaterability and is highly compatible with lime clarification (Vernick and Walker, 1981; USEPA, 1979). Lime stabilization causes only a temporary reduction in microbial populations since equilibration with atmospheric CO_2 will lower the pH and allow microbial populations to regrow (Eikum and Paulsrud, 1975). Regrowth may require months, however.

Burge and Parr (1978) showed that NH_3 liberated from lime-stabilized sludge at high pH is responsible for stabilization and pathogen reduction is not a direct result of low H^+ ion content. Ova of intestinal nematodes appear to be the most resistant to lime stabilization (Teletzke, 1978). Lime is also the cheapest and safest chemical which can produce a stabilized sludge (Farrel et al., 1974). Lime stabilization adds 50-250 mg lime L^{-1} liquid sludge, depending on solids content and "should provide a premium-quality agricultural liming material" (Boynnton, 1980).

Chemical sludge "fixation" processes are normally reserved for industrial waste treatment but have been utilized in the treatment of municipal sewage sludge. Most processes depend on a cementitious reaction to encapsulate and immobilize hazardous constituents in a cement-like matrix. In fact, Portland cement often constitutes a large fraction of added ingredients. Chemfix Technologies, Inc. also reports the addition of Na-silicates to facilitate the hardening process (Meehan et al., 1986). These sludges are generally structurally adequate for landfilling (Taub and Roberts, 1978). The addition of Portland cement to sewage sludge may lend some liming properties to the sludge because the largest portion of Portland cement is CaO (lime) (Peray, 1979; Portland Cement Association, 1975). This type of sludge contains very few parasites (Meehan et al., 1986)

The largest component of sludge by weight is almost always water. Since sludges vary tremendously with respect to water content from plant to plant, as well as from day to day within a single plant, the concentration of the various sludge components should be reported on a dry weight basis so that sludges may be compared (Sommers and Nelson, 1978). In order to reduce the volume of wastewater solids to be disposed, wastewater treatment plants often remove a large portion of the water in liquid sludge, producing a product called dewatered sludge. Anderson et al. (1971) noted that the volume of a sludge which is 5% solids is reduced to less than one half its original volume at 80% water and one sixth at 70%. The most common method of mechanical sludge dewatering is vacuum belt filtration (Vernick and Walker, 1981). Other methods include centrifugation and drying beds. Use of coagulants can affect dewatering efficiency. Use of alum decreases sludge dewaterability, while lime and ferric chloride increase dewaterability. Activated sludge is difficult to dewater (Vernick and Walker, 1981).

Sludge Disposal

The ultimate fate of sewage sludge depends on many variables, including location, climate, soils, land availability and popular sentiment concerning sewage sludge. Conventional disposal options include landfilling, trenching, incineration, pumping to lake bottoms, ocean dumping and land spreading of liquid or dewatered sludge. The first five options represent a net waste of crop nutrients, while land spreading utilizes a waste material as a resource. Incineration of sludge requires use of auxiliary fuel but can yield process steam and be nearly pollution-free if a second burn is utilized, but often air pollution is a problem. Incineration is also one of the most expensive alternatives (Vernick and Walker, 1981). Virginia Sewerage Regulations (1977) cite land application as the most logical, useful, cost-effective and environmentally responsible alternative to municipal sewage sludge disposal.

Sewage sludges have been used to supplement commercial fertilizers (Sommers and Nelson, 1978). They contain substantial amounts of N and P but are low in K (Sommers and Nelson, 1978). They also contain substantial but highly variable quantities of Ca, Mg, S and micronutrients necessary for plant growth (Sommers, 1977). Sewage sludges also contain variable quantities of potentially toxic metals such as Cd but usually at very low levels (Sommers, 1977). Applications of sewage sludge improves soil physical properties and increases the organic matter content (Kladivko and Nelson, 1979; Epstein, 1975). Many farming techniques such as plowing encourage the oxidation of soil organic matter and, as a result, many agricultural soils are very low in organic matter. Soil humus, a resistant form of soil organic matter, plays an important role in soil water relations and helps reduce runoff while increasing infiltration and water retention (Follette et al., 1981). It also serves as the principal source of anions essential for plant growth such as SO_4^{2-} and MoO_4^{2-} and increases the soil CEC by a factor of 5 to 10 times that of clay (Follette et al., 1981).

Application of sludge to agricultural land is a practice which is growing in popularity. About 31% of the sludge produced in the US in 1979 was land applied (USEPA, 1979). Problems can arise from overapplication and application of contaminated sludges. Application of sludges in excess of the crop N requirements may result in the leaching of NO_3^- into the groundwater (O'Brien and Mitsch, 1980). Sludges may also be contaminated with toxic organic chemicals or heavy metals and potential exists for problems from these compounds when applied as sludge.

Potentially toxic metals do not pose a hazard to the food chain unless they become concentrated in the edible portion of the plant (Chaney, 1973). Most potentially toxic metals cause a reduction in crop growth before they become concentrated enough to pose a threat to the food chain. The most hazardous exception is Cd which can accumulate in grain and other edible portions of crops without a noticeable reduction in growth (Chaney, 1973). For this reason, Cd applied as sludge is limited on an annual basis and sludge with 25 mg Cd kg^{-1} or more is not approved for land application in Virginia. Cumulative Cd application in Virginia is limited on the basis of soil CEC (Table 1 on page 10) (Virginia Sewerage Regulations, 1977).

Table 1. Maximum application of metals to soils used for food chain crop production.

Metal	Soil Cation Exchange Capacity ¶		
	< 5	5-15	> 15
	----- (kg ha ⁻¹) -----		
Zn	250	450	1000
Cu	125	250	500
Ni	50	100	200
Cd	2.5	5	10
Pb	450	1000	2000

Virginia Sewerage Regulations, 1977.

¶ cmoles kg⁻¹

Several factors control plant availability of applied metals. As with the micronutrients Zn, Cu, Fe and Mn the bioavailability of other heavy metals from soils is controlled by soil pH, redox potential, organic matter and hydrous oxides of Fe, Al and Mn (Sommers and Nelson, 1978). Soil pH is probably the most important factor regulating the availability of most heavy metals because it directly affects metal solubility. Raising pH reduces the solubility of Mn, Zn, Cu, Fe, Cd and Al (Baes and Mesmer, 1976).

Reducing the solubility of indigenous metals promotes the precipitation of hydrous oxides of Fe, Al and Mn. Due to the amphoteric nature of these hydrous oxides, raising the pH of the system shifts the net charge to a less positive state (Jackson, 1963). This increases the CEC and attracts positively charged metal ions from solution which may cause occlusion of the heavy metals in the hydrous oxide structure (McKenzie and Osmond, 1977). Co-precipitation may account for much of the disappearance from soil solution of heavy metals applied to soils. Raising soil pH also increases soil CEC, especially in the soil organic matter component, which helps to remove heavy metals from soil solution. A decrease in pH of sludge treated soils may result in the release of toxic heavy metals (Chaney, 1973). Similarly, a reducing environment, which occurs when soils remain wet for extended periods or when manures are applied to soils (Miller et al, 1985), can cause a reduction in the oxidation state of Fe^{3+} and Mn^{4+} and increase their solubility. The dissolution of Fe and Mn from hydrous oxides may result in a release of co-precipitated heavy metals.

Landspreading of sewage sludge is a practice which is growing in popularity and could be hazardous if not controlled. In order to protect the environment and minimize problems with land spreading of municipal sewage sludge, the USEPA has set forth guidelines, and each state has its own set of rules which are frequently more stringent than EPA guidelines. Virginia adopted sewage regulations in 1977 which govern land spreading of sewage sludge (Virginia Sewerage Regulations, 1977). Only class A sludge may be spread on agricultural land. Class A sludge must be stabilized and "shall not contain heavy metals or other undesirable components that:

1. may be harmful to crop production
2. result in crops containing components harmful to consumers

3. render soil unsuitable for further land use
4. degrade existing groundwater.”

The regulations provide for the evaluation of long and short term chemical effects of sludge application on land and groundwater. They require adequate provisions for the prevention of air and water pollution and soil contamination from spreading sludge. Choice of crops intended for human consumption is restricted to non-root crops and crops not eaten raw so that health hazards are prevented. Location of the spreading area should be remote from dwellings, water supplies and shellfish areas; and runoff into surface waters must be controlled. In general, “Disposal of sludge shall be in such a manner as not to cause health hazards, destroy vegetation, create odor and/or vector problems, render the soil unsuitable for future land use or create other nuisances.”

Soils to which sludges are applied should have at least 0.4 m to a seasonal water table or rock, should be 61 m from wells and 15.25 m from surface waters and should not be steep. Loading rates of sludge-borne metals, Table 1 on page 10, are based on soil CEC (neutral, normal NH_4OAc) (Virginia Sewerage Regulations, 1977; USEPA, 1983) because this is an easily obtainable measurement related to other soil parameters which control metal availability (Sommers and Nelson, 1978). Soils must be limed to pH 6.5 or above before sludge application and maintained above pH 6.2 after application to reduce the solubility of heavy metals. Loading rates are usually based on N, but this depends on the crop and sludge composition.

Lime-stabilized and chemically fixed sludges may have enough lime to be utilized as effective soil-liming agents. Loading rates for these sludges may be limited on agricultural soils by the sludge’s effectiveness in neutralizing soil acidity. It is possible that these sludge materials may produce the required soil pH (6.5) upon application to acid soils and at high rates may even raise the pH enough to cause yield reductions due to micronutrient deficiencies.

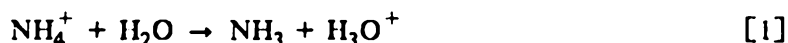
Nitrogen

A number of transformations involving N may occur when sludge is applied to soil. Even before the sludge is applied NH_3 may volatilize from the sludge in transport to the application site. Ammonia may also volatilize after application (Terry et al., 1978). The bulk of the total-N applied as sludge is usually organic and is mineralized to NH_4^+ by soil microorganisms. In most aerobic soils, NH_4^+ is microbially transformed to nitrite-N (NO_2^-) and then to NO_3^- . Under anaerobic conditions, NO_3^- may be denitrified to gaseous, plant unavailable forms such as N_2 and N_2O (Alexander, 1977).

Crop N requirement usually limits sludge application rates. If NO_3^- were "sorbed" by soil in a manner similar to P and K, then application rates could be much higher. However, microbial transformations in the soil convert organic-N, through a series of biological reactions, to NO_3^- which is a mobile anion in soils (Follett et al., 1981). If sludge applications result in soil NO_3^- levels which exceed crop utilization and gaseous losses, pollution of groundwater with NO_3^- may occur. This pollution can contribute to eutrication of surface waters and to human methemoglobinemia (oxygen starvation) if nearby drinking water is contaminated (Follett et al., 1981).

Ammonia Volatilization

Ammonia volatilization from solution proceeds according to the reaction:



and is controlled by diffusion (Skoog and West, 1979). As with other reactions, increasing the concentration of reactants or removal of products causes the reaction to proceed to the right by steepening the diffusion gradient. This explains why increasing concentrations of NH_4^+ causes more volatilization and, similarly, why soil drying increases NH_3 losses through volatilization (Terry et

al., 1978). Factors which can reduce the concentration of NH_4^+ in soil solution and thus reduce volatilization losses are depth to which NH_4^+ fertilizers are placed and the texture and CEC of the soil. As depth of application and CEC are increased, retention of NH_4^+ on the CEC is increased (Terry et al., 1978). Increasing clay content usually increases CEC. Raising the pH of a solution which contains NH_4^+ dramatically increases NH_3 volatilization (Fenn and Kissel, 1973; Terry et al., 1978) by removal of H_3O^+ . Ammonia has a dissociation constant of 1.76×10^{-5} (Skoog and West, 1979) which indicates that 50% of the initial NH_4^+ in solution will exist as NH_3 at pH 9.2. If the NH_3 produced is removed by changing the air above the solution (i.e. wind) then volatilization will be further promoted by removal of NH_3 (Terry et al., 1978). Raising the temperature also promotes NH_3 volatilization (Terry et al., 1978). Factors which promote NH_3 volatilization from sludge treated soil are: high sludge pH (Hoff et al, 1981), minimal incorporation (Hoff et al., 1981), wind, dry soil, coarse textured soil of low CEC, high soil pH, high application rates and hot summer temperatures.

Nitrogen Mineralization

Mineralization of organic-N from sewage sludge is a microbial process which can be accomplished by a large number of soil heterotrophs (Russel, 1973). Because of the large variety of microorganisms capable of mineralizing organic-N, the process is less dependant on soil conditions than other N transformations (Alexander, 1977). Terry et al. (1979) and Sommers et al. (1979) reported that soil type had little effect on N-mineralization rate of sludge treated soil. Nevertheless, N-mineralization rates have been shown to be affected by soil acidity, moisture levels, aeration status, fertility status, temperature and of course, total-N levels (Alexander, 1977). Under strongly acid conditions, soil fungi become the major mineralizers of organic-N and mineralization is lower than in slightly acid and alkaline soils, where actinomycetes and bacteria become the major mineralizers (Alexander, 1977). Organic matter levels influence N-mineralization since the mineralizers are heterotrophic. They are usually found in surface soils where organic matter is

present and are stimulated by additions of easily decomposable organic matter (Alexander, 1977) such as sludge. Total-N levels in soil influences "apparent" N-mineralization rates. Soils which contain enough N to supply the mineralizers with N do not generally exhibit substantial immobilization of N (Alexander, 1977).

Soil microorganisms respond to the addition of easily oxidizable C compounds such as those in sewage sludge by producing various enzymes which are excreted and are able to break down a wide variety of compounds (Alexander, 1977). Once outside the organisms body, the enzymes attack a variety of organic compounds including resistant, indigenous compounds such as humic acids and lignin. This phenomenon which may result in accelerated oxidation of indigenous resistant compounds has been studied and is called cometabolism or "the priming effect" (Ryan et al., 1973; Alexander, 1977). This process could explain the mineralization of organic-N in excess of the amount predicted when low rates of sludge are applied to land.

Mineralization of N from municipal sewage sludge-soil mixtures proceeds at rates which depend to a large extent on sludge, soil and climatic conditions (Sommers and Nelson, 1978). If sludge is treated by a process which biologically decomposes the sludge such as composting or anaerobic digestion, much of the readily decomposable compounds have been oxidized with the liberation of NH_4^+ . In the case of anaerobically digested sludge, the NH_4^+ percentage is increased and the organic component is decreased but enriched with resistant N compounds. Peterson et al. (1973) reported that 20-50% of the total-N in unlimed anaerobically digested sludge occurs in the NH_4^+ form. Nitrogen mineralization rates in soils treated with anaerobically digested or composted sludges are relatively low due to the preoxidation of nitrogenous compounds. In contrast, sludges which are not subjected to biological decomposition such as waste activated sludges contain a higher percentage of easily decomposable N compounds. The result is higher N-mineralization rates, initially, when these types of sludges are applied to land (Hsieh, 1981).

Stanford and Smith (1972) showed that the relationship between cumulative N mineralized from organic matter increased linearly with the square root of incubation time. Cumulative N mineralized is expressed as a percent of organic-N applied. Stark and Clapp (1980) have demonstrated the linear relationship of N-mineralized with the square root of time for anaerobically di-

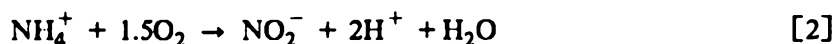
gested sludge-soil mixtures. O'Keefe et al. (1986) observed sludge treated soils to display two phases of N mineralization. The first was a rapid phase characterized by a decreasing quantity of N mineralized as time increased. The second phase was characterized by a nearly constant slope such as that described by Stanford and Smith (1972) indicating that equilibrium had been reached. These observations are in agreement with the observations of Hadas et al. (1986).

Two methods of studying N mineralization of sludge-soil mixtures are: incubation with periodic sampling (Parker and Sommers, 1983) and incubation of sludge-soil-sand mixtures with periodic leaching with a weak nutrient solution and analysis for N in the leachate (Stanford and Smith, 1972).

Nitrification

The fate of NH_4^+ applied in sludge or mineralized from organic-N depends on a number of conditions. As discussed, it may volatilize as NH_3 under favorable conditions or it may be immobilized by uptake by plants and soil organisms. Ammonium may also remain on the CEC, and is sometimes "fixed" permanently between platelets of mica, vermiculite and wedge-sites of hydroxy-interlayer vermiculite (King, 1976; Nommik and Vahtras, 1982). Ammonium "fixation" is favored by increasing soil pH (Nommik, 1957). Fixation is reduced by organic matter and is generally higher in subsoils (Nommik and Vahtras, 1982). Ammonium may also be oxidized by two genera of bacteria which work together to convert NH_4^+ to NO_2^- , another plant available form of N. Nitrosomonas spp are the soil bacteria responsible for the conversion of NH_4^+ to NO_2^- , a phytotoxic form of N (Alexander, 1977). Fortunately, there is a population of soil bacteria of the genus Nitrobacter spp which transforms NO_2^- to NO_3^- so soon after NO_2^- is produced that NO_2^- accumulation in soils is rare. Both genera are chemoautotrophic. Being autotrophic, their C source for the building of cell tissues is atmospheric CO_2 . Chemoautotrophs derive the energy needed for biosynthetic reactions and growth from the oxidation of inorganic materials. Nitrosomonas spp

and Nitrobacter spp are obligate chemoautotrophs and cannot utilize organic C for energy (Alexander, 1977). The reactions involved in the conversion of NH_4^+ to NO_3^- are:



and



mediated by Nitrosomonas spp and Nitrobacter spp, respectively (Alexander, 1977). The oxidation of NH_4^+ to NO_2^- involves the loss of 6 electrons from the -3 state of NH_4^+ to the +3 state of NO_2^- . The oxidation of NO_2^- to NO_3^- involves the loss of 2 electrons as the N is oxidized to the +5 state of NO_3^- . The electrons are the actual energy source for the bacteria (Follett et al., 1981). The fact that the Nitrosomonas spp change the oxidation state of N more than Nitrobacter spp means that the Nitrobacter spp derive less energy per unit of N and therefore must metabolize more substrate than Nitrosomonas spp in order to grow and reproduce (Follett et al., 1981). This helps to explain why NO_2^- rarely accumulates in the soil.

Nitrosomonas spp are tolerant of large concentrations of NH_4^+ -N (2000 mg kg^{-1} or more) and their optimum pH for growth and reproduction is around 8.7 (Follett et al., 1981). Under optimum laboratory conditions, Nitrosomonas spp have exhibited logarithmic growth (Alexander, 1977). This is rare in soil systems due to competition and other limiting factors. Nitrobacter spp on the other hand, are very sensitive to large concentrations of NH_4^+ especially at high pH (Follett et al., 1981), suggesting that they are subject to the bactericidal effects of NH_3 which is produced from NH_4^+ at high pH levels. Note that reaction 2, mediated by Nitrosomonas spp, is an acid producing reaction. Extended use of NH_4^+ producing fertilizers will result in lower soil pH (Follett et al., 1981). Nitrification rates typically decline rapidly below pH 6.0 and become negligible below pH 5.0. Liming may drastically increase nitrification rates in acid soils (Alexander, 1977).

Temperature is an environmental factor which regulates the growth and activity of nitrifying bacteria. Nitrification rates are slow below 5°C and above 40°C. This helps explain reduced

nitrification in winter and summer in temperate climates. Under certain conditions, this fact can be used to advantage by applying N fertilizers in the fall (Follett et al., 1981).

The process of nitrification is intimately linked to the supply of molecular oxygen (O_2) as shown in Reactions 2 and 3. The O_2 is utilized as their terminal electron acceptor and the rate of nitrification is maximized when the concentration of O_2 is equal to that of the atmosphere (about 20%) (Follett et al., 1981). The rate drops slowly as the concentration of O_2 is reduced to about 5% and rapidly below that. Conditions which reduce the concentration of O_2 in soil, such as increasing soil depth and displacement of soil air with water, will cause a marked reduction in the rate of nitrification. Nitrifying bacteria need moisture but are more tolerant of a dry environment than a wet one (Follett et al., 1981).

Immobilization

The addition of organic matter to soils has been observed to result in the disappearance of NO_3^- under certain conditions. In well-drained soils, the addition of organic matter which is low in N may result in N immobilization. This occurs when the ratio of C to N in added organic matter exceeds 25 because the inorganic N is assimilated by the heterotrophs for carbohydrate metabolism (Alexander, 1977).

Denitrification

The O_2 shortage produced by wet conditions is aggravated by addition of easily decomposable organic matter. This stimulates intense activity of heterotrophic microorganisms resulting in the rapid utilization of soil O_2 and the production of large quantities of metabolic CO_2 . In wet soils, the addition of organic matter may result in the disappearance of NO_3^- because of another N transformation, denitrification. Denitrification is mediated by a relatively few species of bacteria,

mostly Pseudomonas spp, Bacillus spp and Paracoccus spp. These common soil bacteria are aerobic but use NO_3^- as their terminal electron acceptor for growth in the absence of O_2 (Alexander, 1977). Denitrification may proceed in microsites of well-drained soils, especially when O_2 supply is less than microbial demand such as when easily decomposable organic matter is added. Other environmental factors which influence denitrification include NO_3^- concentration, temperature and pH. The higher the concentration of NO_3^- , the higher the rate of denitrification (Alexander, 1977). Temperatures above 25°C are considered optimum for denitrification and the process proceeds up to 65°C but does not operate above 70°C (Follett et al., 1981). The rate of denitrification is markedly reduced below 10°C and is practically inhibited at 2°C (Alexander, 1977). Soil acidity strongly inhibits denitrification in many soils but the relationship varies from soil to soil so that a pH range in which denitrification is inhibited for all soils is difficult to define (Alexander, 1977; Follett et al., 1981).

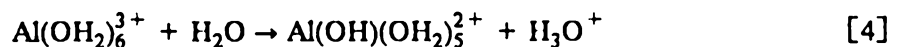
Soil Acidity

Soil acidity is probably the single most limiting factor to agricultural production in the southeastern United States. It effects mineral nutrition, CEC, clay mineralogy and release of potentially toxic elements such as Cu, Zn, Mn and especially Al. The severity of the soil acidity problem in the southeast is due primarily to the combination of high temperature and precipitation. Warm, moist conditions favor plant growth which tends to stimulate growth and activity of heterotrophic soil microorganisms which decompose plant residues. Respiration of these organisms elevates soil CO_2 levels.

Development and Chemistry of Soil Acidity

Carbon dioxide liberated by respiration reacts with water to form carbonic acid (Lindsay, 1979) and has been shown to decompose clay minerals (Jackson, 1960; Jackson, 1963). Acid decomposition of this type may eliminate smaller particles of montmorillonite (Jackson, 1960). In the course of decomposition, SiO_4 groups accept protons to form water soluble silicic acid (H_4SiO_4) which may be lost to leaching in permeable soils. The remaining bicarbonate ion may decompose to yield OH^- and CO_2 or may combine with an exchangeable cation and leach through the profile (Black, 1968). It is true that most of the carbonic acid that is formed in a soil decomposes and the CO_2 is lost to the atmosphere, but over geologic time, especially in soils with reasonable internal drainage, carbonic acid can liberate large quantities of Al and aid in the removal of exchangeable bases by leaching. Since Al is a trivalent cation, it is held more strongly on the exchange complex than mono and divalent cations and tends to accumulate in older soils as these cations and H_4SiO_4 are lost to leaching (McLean, 1971; Jackson, 1963). This effect becomes more noticeable as average annual precipitation increases (Black, 1968).

Aluminum in soils, especially acid soils, tends to become 6-coordinated with water and/or hydroxyls. In solution, Al tends to hydrolyze according to reactions of the type:



which has a $\text{p}K_1$ of approximately 5.0 (Coleman and Thomas, 1967). Therefore, in more acidic solutions the reaction is driven to the left and Al tends to be higher charged. The reaction is driven to the right in solutions with pH higher than 5.0 (especially dilute systems) favoring hydrolysis and the production of acid. Thus Al is considered an acidic cation and, indeed, has a weak acid strength approximately equal to acetic acid (Jackson, 1960). Hydrated Al ions are thought to be stable as single ions in solutions that are sufficiently acid since the individual, positively charged ions repel one another. As H_3O^+ ions are consumed by OH^- ions and the above reaction proceeds, the positive charge on individual ions decreases (Black, 1968) and, like weak acids, they tend to con-

dense and share hydroxyls with the elimination of water (Jackson, 1963). So, as dilute, aqueous Al solutions are neutralized above pH 5.0, the Al ions tend to polymerize. But the tendency to polymerize decreases as the concentration of Al decreases.

Hydrolysis of Al in soil systems requires a higher pH than in solution. This occurs because the activity of Al in soil solution is reduced by adsorption to soil colloids and also because hydroxyls are repelled by the negatively charged soil particles (Dewan and Rich, 1970; Jackson, 1963). Clay minerals with a large surface charge, such as vermiculite, may hold Al so tightly that hydrolysis may be prevented (Hsu, 1977). Hodges and Zelazny (1983) report that kaolinite was able to dehydroxylate Al upon adsorption. The poorly crystalline Georgia kaolinite bound the Al so tightly that formation of Al precipitates was prevented until Al loading rates exceeded the CEC. Minerals such as montmorillonite not only have a lower surface charge than vermiculite but the charge is also more diffuse since it originates in the octahedral layer. Montmorillonite still attracts Al from solution but binds it less tightly, allowing hydrolysis. The attraction of Al to mineral surfaces increases the local concentration of Al atoms on the surface (at the expense of Ca, Mg and K) thus increasing the number of interactions leading to polymerization. Hsu (1977) has labeled this the template phenomenon. It has been used to explain chloritization and kaolinization of clay minerals which leads to the formation of hydroxy-interlayered vermiculite (Black, 1968; Jackson, 1963).

Kissel et al. (1971) suggested that hydroxy-Al interlayers increased structural stability and promoted aggregation of soils high in Al. This is not surprising since Al polymers increase their net positive charge as they grow, even though the charge per Al decreases. Aluminum polymers are often adsorbed between two or more clay platelets and are difficult or impossible to exchange with salt solutions because of the magnitude of their positive charge. This attribute tends to decrease soil CEC, increase the anion exchange capacity (Hsu, 1977) and bond clay particles together resulting in stronger, more stable structure.

Black (1968) stated that, "Polymeric hydroxy-aluminum interlayers appear to be, in effect, incompletely neutralized, hydrated-aluminum ions that are stabilized against further neutralization and against release by ion exchange by their polymerization, physical location, and chemical com-

ination with the adjacent layers of clay." He suggested that the occurrence of hydroxy-aluminum interlayers might explain why the pH drops with time when an acid soil is neutralized with a given quantity of alkali. Rich (1970) and Dewan and Rich (1970) showed that Al attracted to interlayer positions of vermiculite is very slow to exchange and is neutralized very slowly by hydrolysis and proton transfer. Speed of neutralization is limited by diffusion of cations into interlayers to balance valence charges. Jackson (1963) suggested that water is split by interlayer Al and that protons are transferred to solution by quantum mechanical tunneling. This may resemble exchangeable H_3O^+ in titrations but is due to hydrolysis of nonexchangeable Al. Kamprath (1970) stated that exchangeable Al was neutralized quickly, but the neutralization of nonexchangeable Al was much slower. Hodges and Zelazny (1983) observed that almost 60% of the exchange sites of poorly crystalline Georgia kaolinite had high affinity for hydrolyzed Al and that less than 2% of the added Al was exchangeable to $BaCl_2$ until added Al exceeded the CEC. Pleysier (1979) showed that Al activity remains very low when Al saturation is less than 40%. These observations suggest that significant amounts of Al may be unexchangeable while still contributing to soil acidity.

The fact that Al adsorbed to kaolinite may be partially neutralized adds to the error in estimating lime requirement by exchangeable Al. Hodges and Zelazny (1983) showed that kaolinite adsorbed hydrolyzed Al preferentially to trivalent Al. These observations suggest that it may be wise not to base lime recommendations on exchangeable Al but on titrations or buffer methods. However, even these methods will be in error if the soil contains significant quantities of interlayer Al.

Hydroxy-aluminum coatings on layer silicates are H^+ donors (OH^- acceptors) and are responsible for much of the apparent pH dependant charge of soils (Jackson, 1960). Another major source of pH dependant charge and acidity in soils is organic matter (Jackson, 1960). Carboxylic and phenolic groups on organic matter specifically adsorb H^+ and only release H^+ only at higher pH values (Jackson, 1963).

Hydroxy-aluminum compounds show a marked capacity to remove P from solution (Robarge and Corey, 1979). Soils high in hydroxy-aluminum coatings may require much more P fertilizer to produce a crop than soils low in hydroxy-aluminum.

Effects of Soil Acidity on Plant Growth

Hydronium ions in soils with pH above 4.0 are not generally thought to be an important limiting factor for crop growth (Moore, 1974). Using solution and sand cultures, Islam et al. (1980) showed that low pH (< pH 4.0) causes roots to be short, thick, dull grey or brown, and few in number. Lateral root growth was inhibited and plants wilted in warm sunny weather. Excess H^+ caused root membranes to leak resulting in the loss of K and organic substances and H_3O^+ was thought to be competing with other cations for uptake. In corn (*Zea mays* L.), Islam et al. (1980) observed low pH to induce suboptimal uptake of Mg and Mn.

In most acid soils, however, the pH is buffered between pH 4.0 and 5.6 by the hydrolysis of Al^{3+} (Coleman and Thomas, 1967). Below soil pH 5.5, the main limitations to crop growth are the high solubility of Al and Mn which may easily reach toxic levels while phosphate availability decreases with decreased pH (Foy, 1984). At low pH, legumes are often affected by the low solubility of molybdenum (Mo) which is part of the N reductase enzyme. Molybdenum deficiency in legumes manifests itself as N deficiency (Black, 1968; Foy, 1984). Munns (1978) has shown that in legumes it is the root infection process that is inhibited by acid soil, and not the survival of the rhizobia. The ability to nodulate at low pH varies with the species and strain of rhizobia. The low solubilities of micronutrient cations such as Fe, Mn, Cu and Zn and boron (B) compounds at high pH often induce deficiencies while Mo may accumulate in plant tissue grown on neutral to alkaline soil. Accumulation of Mo in forages may cause toxic quantities of Mo to be ingested by cattle (Bardshad, 1948).

Soil acidity is a major growth limiting factor in many parts of the world including the southeastern United States. Most research shows Al to be the major problem in strongly acidic soils. However, other factors are involved and vary with soil pH, mineralogy, amount of organic matter, presence and concentrations of ions, plant species and even cultivar within species (Foy, 1984). Kamprath and Foy (1972) have reported that the acid infertility complex includes toxicities of Al,

Mn and other metal ions (Cu, Zn, Cd, Ni, Pb), low pH and deficiency or unavailability of Ca, Mg, P and Mo.

Aluminum toxicity is common in soils with pH below 5.0. The critical pH for Al toxicity and the severity of toxicity varies with mineralogy, percent organic matter, concentration of cations and anions and the species and cultivar grown. Toxicity may occur in soils with pH values up to 5.5 if dominated by kaolinite (Foy, 1984). Bartlett and Riego (1972) and Hue et al. (1986) have shown that Al toxicity can be prevented by the presence of citrate, EDTA or soil organic matter extract. Hargrove and Thomas (1981) indicate that soil organic matter is very important in complexing Al. Mattson and Hester (1933) showed that Al toxicity occurred up to pH 4.8 in untreated soil while plants in soil treated with humic acid grew well at pH 4.4. Lance and Pearson (1969) concluded that reduced Ca uptake is probably the first externally observable sign of excess Al. Inhibition of Ca uptake in soybean roots by excess Al was suppressed by increasing the Ca concentration (Lund, 1970). The increased Ca reduced the activity of Al and suppressed its toxicity.

Symptoms of Al toxicity often include those of P deficiency (Foy, 1984) and some plants develop Fe or Ca deficiencies. Usually, roots are stubby and brittle with little branching and are inefficient in water and nutrient uptake (Foy, 1984). Hecht-Buchholtz and Foy (1981) report that Al^{3+} increases root membrane rigidity and reduces flow by binding with proteins and lipids. This would explain why plants sometimes wilt in nutrient culture solutions containing Al (Foy, 1984) and implicates Al in water stress of plants growing in surface soils which overlie acid subsoils (Black, 1968). Excess Al^{3+} is reported to interfere with root cell division, especially of root tips and laterals (Foy, 1984). This was related to increased rigidity of the cell walls due to cross linking of the pectins to Al and also to increased rigidity of the DNA molecules themselves which inhibits proper transcription. Aluminum has been reported to bind with nucleic acids (Trim, 1959) and the P in DNA (Matsumoto et al., 1979) and ATP (Trapp, 1980). Sugar metabolism was inhibited by Al^{3+} which prevented the formation of the Mg-ATP complex necessary for phosphorylation of glucose by hexokinase. Trapp (1980) observed that the affinity of Al for ATP is 40 times that of Mg, in agreement with Naidoo (1977) who observed the highest concentrations of Al in the nuclei of Al-injured snap beans.

Tolerance of Al in toxic concentrations has been noted to vary with species and cultivar (Foy, 1983 a,b; Kamprath and Foy, 1984). Many workers have noted superior Al tolerance in maize (McLean and Gilbert, 1927; Lignon and Pierre, 1932; Foy and Brown, 1964). It has been reported that citrate can prevent Al toxicity (Bartlett and Riego, 1972; Hue et al., 1986) and Small (1946) noted that acid tolerant plants generally have strong organic acid buffer systems in their cells but alkaline tolerant plants have phosphate buffer systems subject to complexation by Al. Klimashevskii and Chernysheva (1980) showed the roots of Al tolerant varieties of maize contained substantially higher concentrations of citric acid than those of Al sensitive varieties. Aluminum tolerance in maize has also been correlated with an increase in pH of nutrient solutions mediated by the plant (Foy et al., 1978) which may be due to preferential uptake of NO_3^- in the presence of NH_4^+ (DeWit et al., 1963; Foy et al., 1978). Foy and Fleming (1978) associated this with higher NO_3^- reductase levels in the leaves of Al tolerant wheat (Triticum aestivum L) varieties. Tolerance to Al in maize varieties has been related to greater Mg uptake and tolerance of low P levels (Foy et al., 1978).

Other limitations to plant growth arise when soil pH is low. Alexander (1977) indicates that Al toxicity limits the microbial decomposition of organic matter in some strongly acid soils. Although denitrification is inhibited below pH 5.5, the mineralization of N, P, S and micronutrients is much reduced (Hubbell, 1971). Manganese toxicities are common when pH falls below 5.5 (Foy, 1984). Toxicity is dependant on total Mn, aeration and availability of fresh organic matter (Foy, 1973). Manganese toxicity has frequently been induced by application of acid forming NH_4^+ fertilizers (Nelson, 1977). Normally, Al toxicity is the more important consideration but heavy metals applied to soils increase in solubility as the pH decreases and may reach toxic levels below pH 6.5 if the total quantity is high enough (Chaney, 1973).

Measurement of pH and Lime Requirement

Soil pH is a measure of the intensity of soil acidity. It does not measure the quantity of soil acidity, which may be vastly different for two soils of equal pH. Factors which affect the pH measured include non-soil measurement factors such as soil to solution ratio, temperature and the condition and type of equipment used (McLean, 1973) as well as soil related factors such as source of acidity, degree of H^+ dissociation, CO_2 content, salt or electrolyte content and liquid junction potential.

The type of soil acidity helps explain why soil pH may be the same for two soils with different quantities of acidity. Below pH 4.2, soils may contain some H_3O^+ (Black, 1968) from acid sulfate weathering or Al hydrolysis but above pH 4.2 to pH 5.2 soils are buffered by the hydrolysis of Al (Black, 1968). The quantity of Al in soils may vary while pH remains relatively constant. Above pH 5.2, pH is controlled by dissociation of H^+ ions held on sites which preferentially adsorb H^+ ions such as those on organic matter and hydroxy-aluminum polymers (Black, 1968). As pH rises, weaker and weaker acids dissociate and the exchange site becomes occupied by the basic cations while the H^+ is consumed by OH^- .

Liquid junction potential in soil pH measurements has been reviewed by Peech (1965). Since it is necessary for the reference electrode to leak small amounts of KCl to complete the electrical connection, the K^+ ion is subject to the attractive forces of the CEC and the Cl^- ion is repelled by the same forces. This causes the mobility of K^+ to differ from that of Cl^- which would ordinarily be almost equal to that of K^+ . The difference in mobility creates a potential which is reflected as a reduction in pH when the reference electrode is placed in the soil suspension rather than in the supernatant.

The pH of soils may be influenced by the formation of carbonic acid as discussed previously. The higher the content of CO_2 in soil the lower the pH. Salts held on the exchange complex and within the mineral lattice may be liberated by carbonic acid (McLean, 1973). The effect of increasing the salt or electrolyte content of a soil is to increase the hydrolysis of Al which will decrease

soil pH (Black, 1968; McLean, 1973). Salts may also occur as residues from microbial decomposition of organic matter.

Soil acidity may be easily and affordably reduced by the application of agricultural limestone but the problem is how much to add. To predict the lime requirement, the quantity of soil acidity must be quantified. This quantity is usually that amount of lime needed to raise soil pH to a desired level. The desired pH may vary with crop to be grown, effect of lime on soil structure (especially on Oxisols) or the solubility of toxic metals applied in sewage sludges.

Several methods have been developed which predict lime rates. Perhaps the most accurate methods are field studies of lime application rates. These are, however, the most time consuming methods. A similar, but quicker method is soil-lime incubations in which small quantities of soil are incubated with different rates of lime for a period of time. Soil pH is determined at the end of the incubation period, which may take four weeks (Adams and Evans, 1962) or longer, and a titration curve is generated by plotting the soil pH by the quantity of applied lime. The lime requirement is determined by obtaining the quantity of lime that corresponds to the desired pH. Since microbiological activity is intensified by liming (Hubbell, 1971) and incubation (McLean, 1973), NO_3^- and sulfate (SO_4^{2-}) salts of Ca, Mg and K accumulate in the incubated soil. The increase in salt concentration and the acidity produced by nitrification lowers the soil pH significantly over time (McLean, 1973; Peech, 1965).

Quicker laboratory methods of determining lime requirement of soils have been developed. Liming based on the quantity of exchangeable Al is a good method in theory but in practice is a poor index of lime requirement because lime is required in excess of the amount of Al present (Reeve and Sumner, 1970). The amount of the excess is somewhat unpredictable (Reeve and Sumner, 1970; Kamprath, 1970). Soil-base titrations are relatively quick and good indicators of lime requirement but tend to underestimate lime required due to the inability to detect slowly neutralized forms of acidity such as hydroxy-aluminum interlayers (Jackson, 1963). Soil-buffer methods are also good lime requirement predictors and are more rapid than the other procedures. However, they are still unable to detect slowly neutralized acidity.

The most commonly used lime requirement buffer was developed by Adams and Evans (1962). It was designed to predict small amounts of lime and to prevent over-liming of low CEC soils with only small amounts of 2:1 type clay minerals. Lime predictions using the buffer were correlated with soil-Ca(OH)₂ incubations and the buffer predictions were usually conservative. To counteract the conservative nature of the predictions and to correct for incomplete reaction of lime with soil acidity and incomplete mixing in the field, lime predictions were multiplied by 1.5.

Limestone is usually slower to react with soil acidity than Ca(OH)₂ is. It also reacts less completely. Therefore, it is necessary to determine the extent of the reaction with soil acidity and recalculate lime requirement using this information. This can be calculated as

$$Q = LR/CCE$$

where Q is the quantity of liming material needed, LR is the lime (pure CaCO₃) required to raise the soil pH to the desired level (6.5) and CCE is the calcium carbonate equivalence expressed as a fraction.

Chapter III

MATERIALS and METHODS

Sludge Characterization

Sampling

Samples of combined primary and waste-activated municipal sewage sludge, which had been coagulated with ferric chloride and stabilized with lime, were collected from the Blue Plains sewage treatment plant in Washington, DC before and after chemical-fixation by Chemfix Technologies, Inc. Samples were collected on seven days between September 2, 1982 and September 11, 1982 and analyzed for solids content, N, P, K, Ca, Mg, S, Cu, Fe, Mn, Zn, Na, pH and CCE to determine product variability. Ten samples were also collected between October, 1982 and August of 1983 and analyzed for solids content, total-N and CCE. The daily samples were large enough so that the excess materials when combined resulted in quantities suitable for other experiments. All samples were stored at 5°C (Sommers and Nelson, 1978).

Analysis

Solids

The chemical fixation process markedly changed the characteristics of the sludge. The most obvious change was the consistency of the sludge which changed from a thick liquid to a dense, clay like solid. With the thickening came an approximate twofold increase in the percent solids (Table 2 on page 31) which surely resulted from the addition of Portland cement and other additives involved in the chemical-fixation process.

Percent solids of the two materials (Table 2 on page 31) were measured by weight loss upon drying at 105°C until constant weight was achieved (Sommers and Nelson, 1978).

The chemically-fixed sludge was a well mixed solid but the lime stabilized sludge required homogenization before analysis.

Calcium Carbonate Equivalence and pH

The pH of the sludge was determined with a combination electrode using an Orion Research Microprocessor Ionalyzer/901 (Table 2 on page 31). A 1:5 sludge to water slurry was used in order to have enough solution to form a supernatant in which to place the reference electrode.

Calcium carbonate equivalence of the two sludges was determined by two methods. First, duplicate one gram samples of each material on an oven dry weight basis (ODWB) were boiled in 50 ml of 0.50 M HCl, cooled and titrated potentiometrically with 0.25 M NaOH to pH 7.0 (Horwitz, 1970). To characterize the response of the sludges to titration, a 0.3 g sample of the chemically-fixed sludge was titrated slowly with 0.1019 M HCl over a 20 to 30 minute period with a Radiometer Automatic Titration System from pH 10.8 to 4.5 (Figure 2 on page 33). The pen was left down at the end of the titration and the chart paper was fed at the rate of 1 cm/min

Table 2. Daily variation in pH, CCE and solids content for lime-stabilized and chemically-fixed sludges.

Day	Sludge Type					
	Lime Stabilized			Chemically Fixed		
	Solids (%)	pH	CCE (%)	Solids (%)	pH	CCE (%)
9/2/82	16.0	11.42	34.20	29.6	10.88	59.25
9/3/82	15.0	11.04	27.85	29.8	10.88	55.65
9/4/82	16.0	11.41	28.80	30.1	11.00	55.60
9/7/82	18.0	11.76	32.55	32.2	11.30	60.25
9/8/82	17.1	11.74	29.25	30.9	11.18	63.60
9/9/82	15.7	11.62	34.85	32.4	11.00	64.40
9/11/82	15.9	11.51	29.70	30.8	10.73	59.05
\bar{x}	16.24	11.50	31.03	30.83	11.00	59.69
SD	0.99	0.25	2.80	1.11	0.19	3.45

(Figure 3 on page 34) to characterize relaxation of the pH following titration of the chemically-fixed sludge with HCl.

A second method for determining CCE of the sludges was used in order to reduce inaccuracies due to buffering and high Ca levels. Sludge samples were oven dried and triplicate 1.5 g subsamples of lime-stabilized and chemically-fixed sludges were boiled for 5 minutes in 30 and 45 ml, respectively, of 0.4921 M HCl. Upon cooling, 50 ml of the Adams-Evans buffer (Adams and Evans, 1962) was added to each sludge-acid mixture, the mixtures were stirred occasionally for 20 minutes and analyzed for pH. A 50 ml sample of the buffer was titrated on the Radiometer Automatic Titration System with 0.1019 M HCl. The average pH values for the sludge-buffer mixtures were used with the buffer-HCl titration curve to determine the amount of unreacted acid in the sludge-acid mixtures prior to addition of the buffer. Subtraction of this value from the moles of HCl added to the sludge samples yielded the moles of base contained in each sludge.

The most significant chemical change resulting from the chemical-fixation process was a large increase in the CCE which paralleled that of Ca concentrations (Table 2 on page 31 and Table 5 on page 38). The lower pH observed in the chemically-fixed sludge may be due to a junction potential resulting from higher Ca concentrations (Coleman et al., 1950; Peech, 1965).

The analysis of CCE by potentiometric titration was time consuming and accurate values were difficult to obtain. After adding an aliquot of base, the pH would rise quickly and then slowly drift back close to the original pH. The reverse was observed when unacidified sludge was titrated with acid (Figure 2 on page 33 and Figure 3 on page 34). After the titration was complete, the pH increased rapidly in the first 2 minutes from 4.5 to above 5.5 and in the next 20 minutes increased to almost 7.0. The pH drift is probably due to a suspension effect. Suspension effects may be caused by junction potential due to high levels of salts such as those of Ca and large buffering capacities such as those of organic matter (Coleman et al., 1950; Peech, 1965).

The CCE of the chemically-fixed sludge was lower when determined with the Adams-Evans buffer while the CCE of the lime-stabilized sludge was practically unchanged (Table 3 on page 36). The standard deviation for this method was only .01 pH unit and the pH had no tendency to drift. Advantages to this method include ease, speed and accuracy of the determination while little

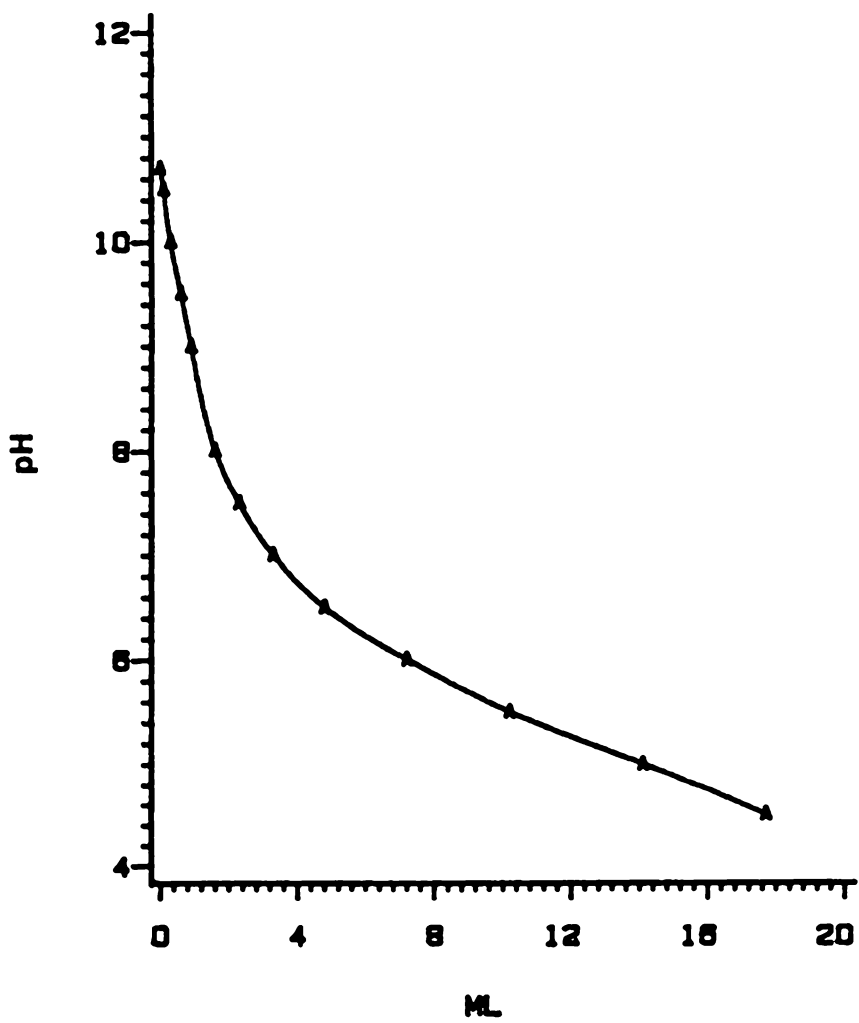


Figure 2. Titration of 0.28g of chemically-fixed sludge with 0.102 M HCl.

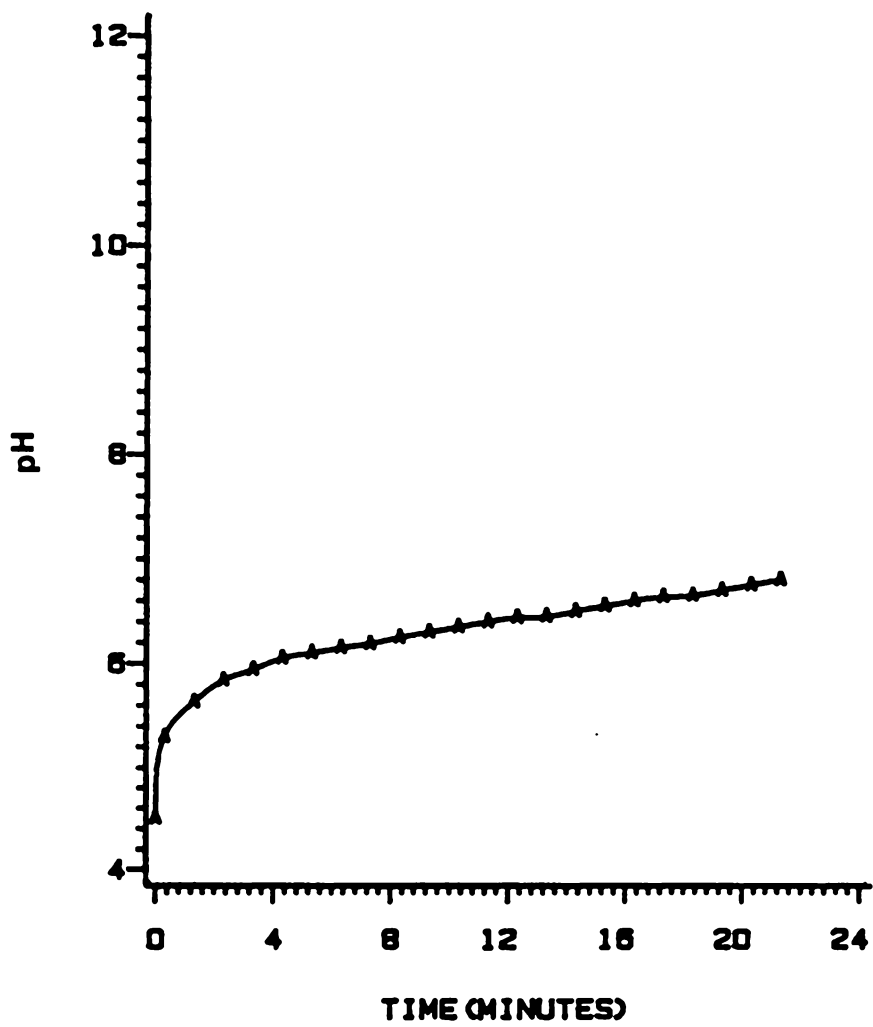


Figure 3. Relaxation of the pH of chemically-fixed sludge following titration with HCl.

extra effort is expended in determining CCE since a buffer will be employed to determine lime requirement for the soils.

Elemental Analysis

Inorganic N was analyzed following extraction with 2 M KCl. Ammonium was determined on a Scientific Auto Analyzer using the indophenol blue method (Brown, 1973). Nitrate was reduced to NO_2^- with a cadmium-copper column and subsequently determined by the sulfanilamide method (Keeney and Nelson, 1982). Total N (Table 4 on page 37) was determined by the indophenol blue procedure following a Kjeldahl digestion (Bremner and Mulvaney, 1982).

Total K, Ca, Mg, Cu, Fe, Mn and Zn in duplicate daily samples of each material were determined with a Perkin Elmer Model 503 atomic absorption spectrophotometer (AAS) following digestion in nitric-perchloric acid (Lim and Jackson, 1982; Baker and Suhr, 1982). Total P was determined colorimetrically on a Hitachi Model 100-20 spectrophotometer using the ammonium molybdate and ascorbic acid procedure of Olsen and Sommers (1982). Sulfur (Table 5 on page 38) was determined colorimetrically with a Bausch & Lomb Spectronic 20 spectrophotometer using the method described by Tabatabai (1982).

Composite daily samples (1g) were also dry ashed in a muffle furnace at 450°C and the ash dissolved in 50 ml of 0.50 M HCl (Jones and Steyn, 1973). Copper, Zn, Cd, Ni, Cr, Al and Pb (Table 6 on page 39) were determined by AAS (Baker and Suhr, 1982). Organic C (Table 5 on page 38) was determined on composite samples following the Walkley-Black procedure (Walkley and Black, 1934).

Concentrations of most elements in the lime-stabilized and chemically-fixed sludges (Table 5 on page 38) were lower than in typical sludges (Sommers, 1977), however Ca concentrations were much higher. This was due to the addition of lime in the stabilization process. Total-N was < 3% and P was < 1% for both sludges. The content of most heavy metals in these two sludges (Table 6 on page 39) was below median sludge concentrations reported by Baker and

Table 3. Comparison of methods for determining CCE and quantity of charge contained in lime-stabilized and chemically-fixed sludges.

<u>Sludge Type</u>	<u>Unit</u>	<u>Method</u>	
		<u>Adams-Evans</u>	<u>Titration</u>
Chemically-fixed	cmoles (-) kg ⁻¹	11.62	11.94
	CCE (%)	58.1	59.7
Lime-stabilized	cmoles (-) kg ⁻¹	6.18	6.20
	CCE (%)	30.9	31.0

Table 4. Concentrations and variability of nitrogen components in lime-stabilized and chemically-fixed sludges.

Date	Sludge Type							
	Lime Stabilized				Chemically Fixed			
	TKN --%--	NH ₄ ⁺ ---mg kg ⁻¹ ---	NO ₃ ⁻ ---	Organic --%--	TKN --%--	NH ₄ ⁺ ---mg kg ⁻¹ ---	NO ₃ ⁻ ---	Organic --%--
9/2/82	2.69	485.0	10.1	2.64	0.97	580.0	7.6	0.91
9/3/82	2.94	253.0	10.0	2.91	1.04	577.0	6.9	0.98
9/4/82	2.88	413.0	8.7	2.84	1.00	699.0	5.0	0.93
9/7/82	2.77	698.0	13.3	2.70	0.84	479.0	4.0	0.79
9/8/82	2.78	807.0	13.9	2.70	0.95	524.0	6.7	0.90
9/9/82	2.72	1025.0	11.4	2.62	1.00	415.0	6.1	0.96
9/11/82	2.75	855.0	11.1	2.66	1.14	530.0	6.6	1.09
\bar{x}	2.79	648.0	11.2	2.72	0.99	543.0	6.1	0.94
SD	0.0891	274.0	1.9	0.110	0.091	89.0	1.2	0.090

Table 5. Elemental composition and variability of sludges. §

Element	Sludge Type			
	Lime Stabilized		Chemically Fixed	
	Mean (%)	SD	Mean (%)	SD
C ¶	35.1	.	19.3	.
N	2.79	0.089	0.99	0.091
P	0.844	0.096	0.45	0.054
K	0.07	0.005	0.30	0.019
Ca	13.49	0.74	25.41	1.82
Mg	0.34	0.20	0.95	0.058
S	0.52	0.028	0.61	0.045
Cu	0.0259	0.002	0.0142	0.002
Zn	0.0464	0.0024	0.0219	0.0019
Mn	0.2596	0.0147	0.1185	0.0087
Fe	6.22	0.622	3.56	0.295
Na	1.59	0.038	2.94	0.215

§ Sludges were analyzed from 7 samples taken between Sept 2, 1982 and Sept 11, 1982.

¶ Composite subsamples of the above 7 samples.

Table 6. Concentrations of metals in lime-stabilized and chemically-fixed sludges. §

Sludge Type	Element (mg kg ⁻¹)						
	Zn	Cu	Al	Cd	Cr	Pb	Ni
Lime-stabilized	500.0	260.0	7,100	2.8	199.8	194.0	45.7
Chemically-fixed	220.0	140.0	14,400	1.1	108.7	106.0	42.5

§Determined from a composite sample of the 7 daily samples collected in Sept., 1982.

Chesnin (1975) and Sommers (1977) and is undoubtedly due to the low level of industrial input to the Washington, D.C. area sewer system. Concentrations of Mn and Ni were somewhat higher, however. Limits to lifetime application of each sludge based on metal content, CEC and Virginia Sewerage Regulations (1977) are presented in Table 1 on page 10.

Concentrations of elements involved in the chemical-fixation process were increased in the chemically-fixed sludge and included Ca, Mg, Na, K, S and Al (Table 5 on page 38). Calcium was present at higher concentrations than C in the chemically-fixed sludge and was 188% higher than in the lime-stabilized sludge. Calcium oxide is the largest component of Portland cement which also contains large quantities of Fe and Al (Portland Cement Association, 1975). It is likely that the additional Mg originated as an impurity of the lime and the addition of sodium silicate explains the elevated levels of Na. Potassium is used in small quantities in Portland cement as a catalyst and may account for the small elevation in K concentration while gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added to control the setting time (Portland Cement Association, 1975) and could account for higher content of S in the chemically-fixed sludge.

The other components of the sludges were diluted by the addition of solids used in the chemical-fixation process. The concentration of C in the chemically-fixed sludge was only 55% of that in the lime-stabilized sludge. Likewise, P, Fe, Cu, Mn and Zn concentrations observed in perchloric-acid digests of the chemically-fixed sludge was 53, 57, 55, 46 and 47% respectively, of that in the lime-stabilized sludge (Table 5 on page 38). Non-nutrient heavy metal concentrations in the two sludges followed the same trend with Pb and Cr present in the chemically-fixed sludge at 54.6 and 54.5% of the lime-stabilized sludge levels, respectively (Table 6 on page 39). Nickel and Cd concentrations in the chemically-fixed sludge were 93 and 39.8%, respectively, of that observed in the lime-stabilized sludge. It is known that Ni occurs in limestone and may account for the lack of dilution (Lisk, 1972). The lifetime sludge loading rates were calculated (Table 7 on page 41) based on sludge metal content, soil CEC and the Virginia Sewerage Regulations (1977).

The lime-stabilized and chemically-fixed sludges contained relatively low concentrations of both total and inorganic-N (Table 4 on page 37). Low levels of NO_3^- are typical in sludges however, most sludges contain more NH_4^+ than the sludges used in this study (Sommers and Nelson,

Table 7. Maximum lifetime loading for the sludges based on soil CEC and sludge metal concentration.

Soil	Sludge §	Sludge-borne Metal				
		Zn	Cu	Ni	Cd	Pb
		-----Mg sludge ha ⁻¹ -----				
Glenelg	CF	2050	1790	2350	4550	9430
	LS	900	960	2190	1790	5150
State	CF	2050	1790	2350	4550	9430
	LS	900	960	2190	1790	5150
Tatum	CF	4550	3570	4710	9090	18,870
	LS	2000	1920	4380	3570	10,310

§ CF = Chemically-fixed, LS = Lime-stabilized

1978). These data are not unexpected when one considers that the effect of such large additions of lime is to dilute the sludge N contents and raise the sludge pH, thus promoting NH_3 volatilization.

Sludge Variability

The sludges varied surprisingly little with respect to percent solids, pH, CCE and elemental composition in the 7 daily samples collected in September, 1982 (Table 2 on page 31). The N components of the sludges were the most variable. The coefficients of variability for CCE by titration were 2.8 and 3.5% for the lime-stabilized and chemically-fixed sludges, respectively. The coefficient of variability for non-N nutrient elements for both sludges averaged 7.8%. The coefficient of variability for N components averaged 15% (Table 4 on page 37). More variability was associated with the inorganic-N components than with TKN or organic-N, but organic-N was more variable than the non-N sludge components.

The variability in CCE for the 10 samples collected over a 1-year period was greater than that of the 7 samples collected in September, 1982 (Table 8 on page 43). The mean CCE for both sludges was higher and probably reflects an increase in the level of lime added in the lime-stabilization process, especially in the June sample. Total-N in the monthly samples was higher than observed in the daily samples and the values were more variable (Table 9 on page 44).

Table 9 on page 44

Table 8. Monthly variation in CCE for lime-stabilized and chemically-fixed sludges.

Date	Sludge Type	
	Lime stabilized	Chemically fixed
10/18/82	30.78	61.43
11/30/82	31.62	61.51
12/19/82	27.94	66.47
1/28/83	40.86	60.17
2/27/83	31.70	58.90
3/22/83	35.79	55.79
4/29/83	36.56	58.45
6/27/83	54.19	71.40
7/29/83	29.00	63.39
8/9/83	34.78	63.50
\bar{x}	35.32	62.10
SD	7.678	4.436

Table 9. Monthly variation in TKN for lime-stabilized and chemically-fixed sludges.

<u>Date</u>	<u>Sludge Type</u>	
	<u>Lime stabilized</u>	<u>Chemically fixed</u>
10/18/82	2.37	1.13
11/30/82	3.13	1.25
12/19/82	3.16	1.28
2/27/83	3.57	1.63
3/22/83	3.20	1.45
4/29/83	3.36	1.44
6/27/83	2.20	0.98
\bar{x}	3.13	1.31
SD	0.40	0.22

Soils

Sampling and Analysis

Bulk soil samples were collected in October, 1982, air dried and ground to pass a 0.64 cm screen. After drying, soils were placed in plastic bags for storage. Air-dry moisture percentage was calculated from weight loss after drying to a constant weight at 105°C. Soil textures were determined by sieve and pipette procedures (Day, 1965). Soil pH levels were determined in 1:1 soil to water slurries with a combination electrode on an Orion Research Microprocessor Ionanalyzer/901. Lime requirement was determined by the Adams and Evans buffer technique (Adams and Evans, 1962). Nitrogen in soils was determined by the procedures discussed for liming amendments. Soil CEC was determined by the neutral, normal NH_4OAc procedure (Chapman, 1965). Samples for mineralogical analysis were pretreated with H_2O_2 buffered at pH 5.0 with NaOAc to remove organic matter and DCB to remove Fe oxides prior to clay separation by centrifugation and decantation (Jackson, 1979). Determination of clay mineralogy was by the method described by Wilson et al. (1983).

Field capacity moisture content was determined by a method similar to that described by Allen et al. (1976). Small plastic bags were filled with 100 g of soil (ODWB). Water was added to the estimated field capacity, and also to moisture percentages 1 and 2% above and below the estimated field capacity. The bags were sealed and allowed to equilibrate for 2 days. Then the bags were visually inspected for dryness or wetness. Signs of free water indicated that field capacity had been exceeded while signs of dryness indicated a moisture content lower than field capacity. Sub-samples were analyzed gravimetrically to determine the actual moisture percentage.

Characterization

Soils with varying physical and chemical properties (Table 11 on page 48) were selected for this study from an area within 160 km of Washington, DC. The soils used for these studies were the Glenclg loam (fine-loamy, mixed, mesic, Typic Hapludult), State fine sandy loam (fine-loamy, mixed, thermic, Typic Hapludult) and Tatum clay loam (clayey, mixed, thermic, Typic Hapludult). The Glenclg and State soils were sampled from the surface horizon while the Tatum soil was sampled from the B horizon. Typical pedons of the soils are described in detail in Appendix A. Although all three soils were acid, the Tatum cl was by far the most acid (Table 11 on page 48). The Tatum cl contained more exchangeable Al and required approximately three times as much lime to adequately neutralize acidity as the other soils. Lime requirements using the sludges and other lime sources are presented in Table 10 on page 47.

The State fine sandy loam was chosen because of its sandy texture which would be expected to possess a low CEC and buffering capacity. Plants grown on this soil would be expected to show micro-nutrient deficiencies if large quantities of lime were applied. It was low in total-N (Table 11 on page 48). The State sandy loam soil in Virginia is similar to the Sassafras series in Maryland and was classified as Sassafras in Virginia until recently. This sandy soil from the Coastal Plain comprises about 10% of St. Mary County, Maryland (Gibson, 1978) and Prince George County, Maryland (Kirby et al, 1967). Soils similar to State such as Mattapeake and Croom occupy about 50% of Prince George, St. Mary and Charles Counties, Maryland (Hall and Matthews, 1974).

The Tatum clay loam soil was chosen because of its extremely acidic nature and low organic matter content. Plants grown on this soil would be expected to show signs of Al toxicity and/or P deficiency when unamended but applications of lime or limed sludge should alleviate the toxicity/deficiency. This soil should require the highest rates of sludge application and should have the largest yield response to added sludge. Tatum clay loam and similar soils such as Nason are present in many areas of the Virginia Piedmont such as Orange County which is approximately 120

Table 10. Calcium carbonate, calcium hydroxide, lime-stabilized and chemically-fixed sludge required to raise soil pH to 6.5.§

Soil ¶	Liming Material			
	CaCO ₃	Ca(OH) ₂	Lime Stabilized Sludge	Chemically Fixed Sludge
	-----kg ha ⁻¹ -----			
Glenelg	2830	2096	9159	4871
State	3010	2230	9741	5181
Tatum	8735	6470	28,269	15,034

§ Based on the Adams and Evans buffer procedure for lime requirement and CCE values of 100, 135, 30.9 and 58.1%, respectively.

¶ Glenelg and State were sampled from the Ap horizon and Tatum from the B horizon.

Table 11. Physical and chemical characteristics of the Glenelg, State and Tatum soils.

Parameter	Soil Series ¶		
	Glenelg sil	State sl	Tatum cl
Texture			
Field Capacity			
Moisture (%)	26.0	12.0	30.0
pH	5.5	5.4	4.4
Exchangeable Al (mg kg ⁻¹)	3.0	11.0	371.0
Lime Requirement (kg ha ⁻¹) §	2830.0	3010.0	8735.0
CEC (cmol kg ⁻¹)	12.0	8.0	19.0
Nitrogen (mg kg ⁻¹)			
Total-N	1072.0	506.0	534.0
NH ₄ ⁺ -N	2.6	3.4	18.3
NO ₃ ⁻ -N	2.0	3.7	0.6
Organic-N	1067.4	498.9	515.1

§ Based on the Adams and Evans buffer procedure (1962) for pure CaCO₃.

¶ Glenelg and State soils were sampled from the Ap horizon and Tatum from the B horizon.

km from the Washington, DC area. Tatum covers approximately 13% and Nason approximately 24% of Orange county. These gently sloping to moderately steep soils of the Piedmont uplands are deep and well drained. They have formed from material weathered from fine grained sericite schist. Tatum soils are strongly to very strongly acidic (pH 4.0-5.5) and low in organic matter. Most of the soils are marginal for crops at present because of high levels of Al and subsequent acidity (Carter et al., 1967). Application of lime-stabilized sludges could possibly renovate these lands by reducing soil acidity and increasing soil organic matter content.

The Glenelg silt loam soil was chosen to represent a common production agricultural soil. It is a soil with few limitations to agricultural production. The Glenelg silt loam soil comprises approximately 18% of Fairfax County, Virginia (Porter et al., 1963) and 20% of Montgomery County, Maryland (Matthews et al., 1961). Glenelg soils are representative of soils that occupy much of the land adjacent to the DC area. Soils that are similar to Glenelg occupy approximately 75% of Montgomery County, Maryland and Fairfax County, Virginia. Glenelg soils with slopes less than 10% should be well suited for crops amended with municipal sewage sludge.

The texture of these soils is related to field moisture capacity and the CEC, which is also influenced by mineralogy (Table 11 on page 48 and Table 12 on page 50). The sandy textured State soil has a low field moisture capacity and CEC while the clayey textured Tatum has higher values for both parameters. The Glenelg soil has intermediate values for texture, field moisture capacity and CEC. The CEC of the Tatum B horizon is high enough that the regulatory agencies would permit larger lifetime loading rates of heavy metals on a surface soil with this CEC (Table 7 on page 41).

Table 12. Clay mineralogy of the Glenelg, State and Tatum soils. §

<u>Mineral (%)</u>	<u>Soil</u>		
	<u>Glenelg</u>	<u>State</u>	<u>Tatum</u>
Kaolinite	34.0	22.0	38.0
Montmorillonite	4.0	4.0	3.0
Vermiculite	2.0	N.D.	8.0
H.I.V. ¶	9.0	35.0	36.0
Mixed Interlayer †	5.0	1.0	9.0
Feldspars	1.0	4.0	1.0
Mica	36.0	15.0	4.0
Quartz	3.0	9.0	1.0
Gibbsite	1.0	1.0	Tr.
Chlorite	5.0	9.0	N.D.

§ Clay contents of 17.8, 7.6 and 32.7%, respectively.

¶ Hydroxy-interlayered vermiculite (intergrade).

† Regularly interstratified mineral with 24-28 Å d-spacing (Mg-glycerol, 25 °C).

N.D.-none detected.

Tr.-trace.

Lime Reaction

Design

An incubation experiment was designed to determine the effect of varying application rates of the lime-stabilized and chemically-fixed sludges on soil pH and exchangeable Al. Five rates of the two sludges were applied to the Glenelg, State and Tatum soils. A common control was included for each soil and the experiment was replicated three times. Five complete sets were prepared so that the reaction could be analyzed as a function of time since sampling was destructive. The application rates were based on lime requirement and CCE so rates were different across soils or materials. However, the five rates and the zero were sufficient to define the reaction up to the lime requirement and approximately four times that rate (Table 13 on page 52).

One hundred grams of soil (ODWB) were ground to pass a 10 mesh screen, mixed with the liming materials and placed in 500 ml plastic bags. Holes 0.64 cm in diameter were punched in the top of each bag to allow gas diffusion. Deionized water was added to bring soils to field capacity with a 50 ml syringe.

Samples were taken after 1, 21, 62, 142 and 203 days of equilibration. Data collected on these samples include soil pH and exchangeable Al. Exchangeable Al was displaced by shaking 2 g soil (ODWB) with 50 ml of 1 mol L⁻¹ KCl for 30 minutes (Bache and Sharp, 1976) in 100 ml plastic centrifuge tubes. The tubes were then centrifuged for 5 min, the solution decanted and filtered. Aluminum in the KCl extract was determined colorimetrically using the aluminon procedure (Jayman and Sivasubramaniam, 1974).

Table 13. Application rates used in the lime reaction experiment. §

<u>Sludge</u>	<u>Soil Series</u>		
	<u>Glenclg</u>	<u>State</u>	<u>Tatum</u>
	-----g-----		
Lime	0.00	0.00	0.00
Stabilized	0.10	0.15	0.50
	0.20	0.30	1.00
	0.30	0.45	1.50
	0.40	0.60	2.00
	0.80	1.20	4.00
Chemically	0.00	0.00	0.00
Fixed	0.05	0.05	0.15
	0.10	0.10	0.30
	0.15	0.15	0.45
	0.20	0.20	0.60
	0.40	0.40	1.20

§ Dry weights of soil used were 98.04, 99.01 and 90.09g for the Glenclg, State and Tatum soils, respectively.

Statistical Analysis

The lime reaction experiment was analyzed statistically as a nested factorial design using the statistical analysis system (SAS) available on the Virginia Tech mainframe computer (SAS Institute Inc., 1982). The rate of addition was nested within materials since the moles of base applied differed for each sludge. The analysis was performed on each soil separately. The factors included in the model were sludge type, time, moles of base added (nested within sludges), time by sludge interaction and time by moles (nested within sludges) interaction. The data was also analyzed by regression analysis in order to determine if the liming capabilities of the two sludge materials were significantly different based on moles of base applied. The pH values were averaged over replication and time before the regression. The values for moles of base applied per gram of sludge in each analysis were based on the Adams-Evans buffer procedure described earlier.

Nitrogen Mineralization

Design

A leaching tube experiment was designed to evaluate the N mineralization rate of soils amended with the two sludges. Three rates of the two sludges were added to the three soils and mixed with an equal weight of 20 mesh sand. These mixtures were added to 100 ml leaching tubes.

Soils were moistened to 0.033 MPa and then incubated using the method described by Stanford and Smith (1972). Samples were incubated in a polystyrene blood shipping box using heated water for temperature and humidity control. The temperature was maintained at 35°C.

The experiment was replicated three times. Deviations from the Stanford and Smith method (1972) include:

1. organic materials were added to the soil
2. twice the weight of sand and soil but the same volume of leaching solution was used
3. columns were moistened at day 1 instead of leached
4. the columns were leached at 2, 4, 6 and 10 weeks
5. the glass wool pad under the soil was covered with a glass fiber filter

Treatments

Sludge addition corresponding to field rates of 168 kg ha^{-1} of total N were designated 1x. This rate supplied 75 mg of organic N kg^{-1} to the soil. This level is equivalent to 17.0 and 6.2 Mg ha^{-1} (ODWB) of chemically-fixed and lime-stabilized sludges, respectively. Other treatments included 0x, 3x and 9x. Ammonium, NO_3^- and NO_2^- were determined colorimetrically as described earlier.

Statistical Analysis

This experiment was analyzed as a randomized complete block design with soils, sludge type and treatment level as the main effects to explain the variability in total cumulative inorganic N mineralized. Data was normalized by subtracting the mean N mineralized from the 0x treatments of each soil. Means across soils, sludges and treatments were compared with Fisher's protected LSD.

Greenhouse Experiments

Designs.

Two greenhouse experiments were conducted. The first experiment was designed to study the effect of increasing rates of sludge addition on the growth of corn. The treatments consisted of three liming materials applied at five rates to the Glenelg and Tatum soils and a control for each soil. The liming materials consisted of CaCO_3 and the two sludges. The rates were designed to raise soil pH to encompass 6.5 and to exceed the lime requirement by a factor of at least 3. The sludge rates were based on data averaged over the first three sampling dates of the lime reaction experiment. The CaCO_3 was applied at the rate obtained with the Adams-Evans buffer (Table 14 on page 56). The second experiment was designed to investigate the role of micronutrients on the growth of corn as sludge/lime rates were increased. This experiment used the Glenelg, State and Tatum soils and the above three liming materials at three rates. The rates were a zero rate of addition (0x), the rate expected to raise soil pH to 6.5 (1x) and four times that rate (4x) (Table 15 on page 57). One complete set as above received a suite of micronutrients and another did not. All experiments were replicated three times and arranged as a randomized complete block design.

Soil Preparation

Plastic pots with a plastic liner were filled with 2000 g (ODWB) of each soil. The soil, liming material, 1.7 g diammonium phosphate and 0.382 g potassium chloride were then mixed for five minutes in a V-shell mixer and returned to the pot (Allen et al.,1976). Micronutrient solutions, when added, were applied to the soil surface and allowed to dry overnight before mixing. The micronutrient pots received 10 ml per pot of a solution containing 1000 mg L^{-1} Cu, 3000 mg L^{-1}

Table 14. Application rates used in the lime rate greenhouse experiment (oven dry weight basis). §

<u>Liming Material</u>	<u>Treatment Level</u>	<u>Soil</u>	
		<u>Glenelg</u>	<u>Tatum</u>
		-----g-----	
CaCO ₃	0x	0.00	0.00
	1/4x	0.63	1.97
	1/2x	1.26	3.94
	1x	2.53	7.88
	2x	5.06	15.76
	4x	10.11	31.52
Lime Stabilized Sludge	0x	0.00	0.00
	1/4x	1.10	7.00
	1/2x	2.20	14.00
	1x	4.40	28.00
	2x	8.80	56.00
	4x	17.60	112.00
Chemically Fixed Sludge	0x	0.00	0.00
	1/4x	0.55	2.60
	1/2x	1.10	5.20
	1x	2.20	10.40
	2x	4.40	20.80
	4x	8.80	41.60

§ Dry weight of soil was 2 kg. Divide rates by 2 for rates in tons/A or multiply by 1.12 for rates in Mg ha⁻¹.

Table 15. Application rates used in the micronutrient by lime rate greenhouse experiment (oven dry weight basis). §

<u>Liming Material</u>	<u>Treatment Level</u>	<u>Soil</u>		
		<u>Glenelg</u>	<u>State</u>	<u>Tatum</u>
		-----g-----		
CaCO ₃	0x	0.00	0.00	0.00
	1x	2.53	2.69	7.88
	4x	10.11	10.76	31.52
Lime Stabilized Sludge	0x	0.00	0.00	0.00
	1x	4.40	7.20	28.00
	4x	17.60	28.80	112.00
Chemically Fixed Sludge	0x	0.00	0.00	0.00
	1x	2.20	2.20	10.40
	4x	8.80	8.80	41.60

§ Dry weight of soil was 2 kg. Divide rates by 2 for rates in tons/A or multiply by 1.12 for rates in N ha⁻¹.

Fe, 3000 mg L⁻¹ Mg, 3000 mg L⁻¹ Mn and 4000 mg L⁻¹ Zn; and 1 ml per pot of a solution containing 1000 mg L⁻¹ B. These solutions supplied 5 mg kg⁻¹ Cu, 15 mg kg⁻¹ Fe, 15 mg kg⁻¹ Mg, 15 mg kg⁻¹ Mn, 20 mg kg⁻¹ Zn, 0.5 mg kg⁻¹ B and 49 mg kg⁻¹ soil. The micronutrient cations were applied as sulfates and the B as sodium borate. These rates were the same as those used by Iyengar et al. (1981) but Fe was added and Zn concentration was 5 mg kg⁻¹ higher to ensure correction of the expected Zn deficiency without causing deficiency. Iron was added because Fe deficiencies frequently occur in calcareous soils. Pots were brought to 80% field capacity with distilled water and allowed to equilibrate for three days.

Culture

Five Pioneer 3369A corn seeds were planted 1.27 cm deep in each pot. The soil surface was covered with filter paper and brought to field capacity with deionized water. Plants were thinned to 3 per pot 7 days after germination. Pot positions were rotated in the greenhouse and on the bench when water was applied each day. Nitrogen and K were applied to each pot 20 days after germination at a rate of 100 mg kg⁻¹ with KNO₃ and Ca(NO₃)₂•4H₂O. Seven days later, 110 mg L⁻¹ of N was applied as Ca(NO₃)₂•4H₂O.

Harvest

The plants were harvested after five weeks when most plants were between 50 and 100 cm tall. Plants were placed in paper bags and dried in a forced air drier at 70°C. When dry, the tissue was weighed and ground to pass a 40-mesh screen and thoroughly mixed. After the plots were harvested, the soil was air-dried, the roots were separated from the soil by gentle crushing and the soil was passed through a 10 mesh screen.

Plant Tissue Analysis

Nitrogen in plant tissue was determined as described for sludges following Kjeldahl digestion. Samples were digested in nitric-perchloric acid prior to analysis of K, S, Ca and Mg (Lim and Jackson, 1982). Samples were dry-ashed as described earlier for the analysis of P, Zn, Cu, Mn and Fe. Phosphorous was determined by the ammonium molybdate method described earlier. Sulfur was determined colorimetrically as described previously. Potassium, Ca, Mg, Mn, Cu, Fe and Zn were determined by AAS.

Statistical Analysis

The first greenhouse experiment (without micronutrients) was analyzed as a nested factorial using SAS. Main effects were liming materials and moles of base nested within liming material. Mean values of yield were compared across materials using Fisher's protected LSD. The second greenhouse experiment was also analyzed as a nested factorial with liming materials, moles of base applied and micronutrient addition as the main effects. Interpretation of the tissue analysis was facilitated with the use of Diagnosis and Recommendations Integrated System (DRIS) developed by Beaufils (1971 and 1973) using the data base of Letzsch and Sumner (1983). DRIS was used to rank nutrients in order of the degree to which they limited growth. This was useful in determining the effect of lime rates and micronutrient applications. Nutrient sufficiency ranges reported by Bates (1984) and Jones and Eck (1973) were also used to interpret the plant tissue data.

Chapter IV

RESULTS and DISCUSSION

Lime Reaction Experiment

Main Effects

Soil pH increased with sludge addition (Figure 4 on page 63 - Figure 6 on page 65) and exchangeable Al levels were reduced (Figure 7 on page 66 and Figure 8 on page 67). In fact, the rate of sludge addition explained most of the variability on all soils (Appendix B). At the high rates of sludge addition the pH appeared to approach a maximum between 7.0 and 8.0 which was probably due to the formation of CaCO_3 , which buffers soil pH below about 7.7 (Jenny, 1980).

The rates of lime-stabilized and chemically-fixed sludges calculated to raise soil pH to 6.5 caused soil pH values to exceed 6.5 initially. After 203 days of incubation, soil pH values at the same levels of addition had fallen below 6.5. The dashed vertical lines in Figure 9 on page 68

through Figure 11 on page 70 represent the calculated rates that should have raised soil pH to 6.5.

The reaction of the lime component of the sludges with soil acidity was rapid, being complete within 24 hours. Soil pH for all rates, sludges and soils decreased with time (Figure 12 on page 71 - Figure 17 on page 76). The decrease in pH with time accounted for much of the remaining variability but did not appear to be related to the addition of sludge, since the pH of the unamended soils also decreased with time. Instead the pH reduction appeared to be influenced by greenhouse incubation and fall collection of soils. Soils collected in the fall tend to have elevated levels of plant residues and, when incubated in the warm temperatures present in the greenhouse, microbiological activity is increased (Alexander, 1977). The decrease in soil pH over time may have been associated with acidity produced by nitrification and organic acids liberated by microbial metabolism. It is not known whether the pH depression would occur under field conditions so direct use of these results in the field would not be advisable until field studies have been conducted.

The chemically-fixed sludge appeared to raise soil pH more per mole of base applied than the lime-stabilized sludge (Figure 4 on page 63 - Figure 6 on page 65). This conclusion was supported by regression analysis which indicated that the difference in sludges was significant at the .007 level of probability. Evidently, not all of the potential liming capacity of the lime-stabilized sludge was realized when applied to soils. This may be due to the method of determining CCE in which the sludges were boiled in acid. Jackson (1963) and Black (1968) suggested that sites exist on organic matter which specifically adsorb H^+ ions and only release these ions at higher pH values (pH dependent charge). These sites would be occupied by Ca on lime-stabilized sludge and would probably be the first to adsorb H^+ ions from soils. These would correspond to Jackson's 3rd range acidity (Jackson, 1963). Some COOH groups which tend to be more strongly dissociated correlate to Jackson's 2nd range acidity (Jackson, 1963) and are common in organic matter. These sites would be saturated by H^+ when boiled in acid but would not necessarily react with soil acidity because of their tendency to remain dissociated between pH 5.6 and 7.6 (Jackson, 1963). These 2nd range sites would probably be neutralized in a titration with NaOH which would tend to result in an over-estimation of CCE. This over-estimation would probably be more pronounced for the

lime-stabilized sludge since it contains three or four times the amount of organic matter per unit of base than the chemically-fixed sludge. So, the superiority of the chemically-fixed sludge on a molar basis may be an artifact of the method of determining CCE.

Interactions

The interaction between time and rate of sludge addition was significant at the .05 level of probability for the State and Tatum soils (Figure 14 on page 73 - Figure 17 on page 76). This interaction may be due largely to soil and sludge heterogeneity, since experimental units were not reused for later sampling dates. Another factor which may have contributed to the time by rate interaction is the formation of CaCO_3 at the highest rate of addition. This may have buffered soil pH so that it did not drop as much over time as the other rates.

There was a significant time by sludge interaction for the State and Tatum soils. Differential complexation of Al by degradation products of added organic matter may have contributed to the interaction. The State and Tatum soils contained substantial amounts of hydroxy-interlayer vermiculite in the clay fraction while the Glenelg contained limited quantities of this mineral. This mineral may allow Al to slowly diffuse into solution over time which would lower pH in the State and Tatum soils more than in the Glenelg soil.

Nitrogen Mineralization

The cumulative N mineralized over 20 weeks was not linearly related to time (Figure 18 on page 80 - Figure 20 on page 82) or the square root of time (Figure 21 on page 83 - Figure 23 on page 85) but revealed a rapid initial phase and a later, more stable, constant phase, each of which appeared to be linear but with different slopes. This trend was observed on all soils. These data

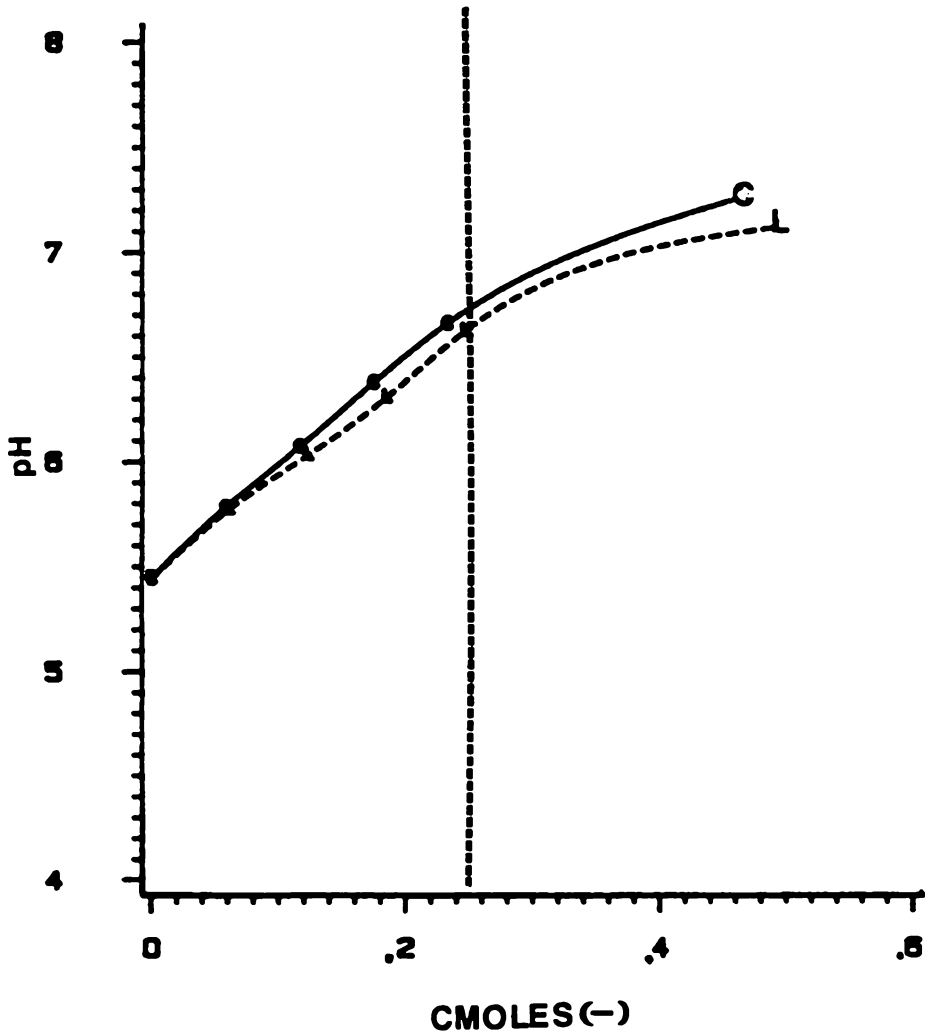


Figure 4. Effect of sludge application rate on pH of the Glenelg soil: pH averaged over time. Dashed vertical line represents the rate calculated to raise soil pH to 6.5, L = Lime-stabilized and C = Chemically-fixed sludge.

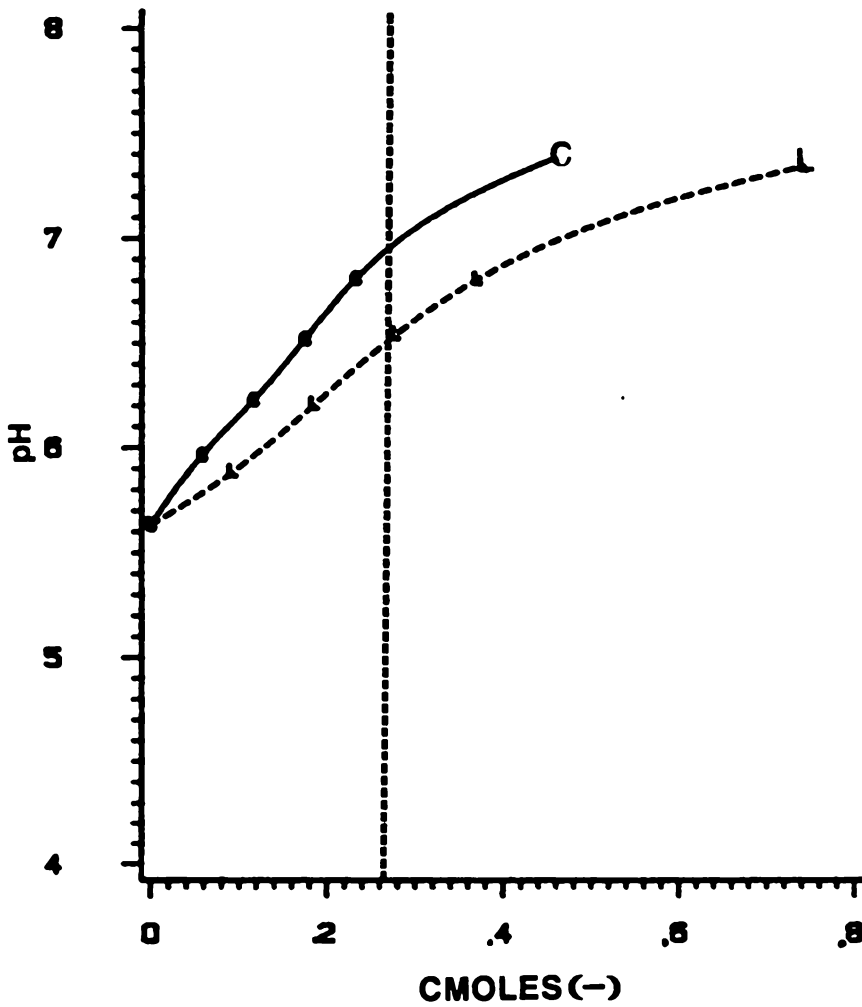


Figure 5. Effect of sludge application rate on pH of the State soil: pH averaged over time. Dashed vertical line represents the rate calculated to raise soil pH to 6.5, L = Lime-stabilized and C = Chemically-fixed sludge.

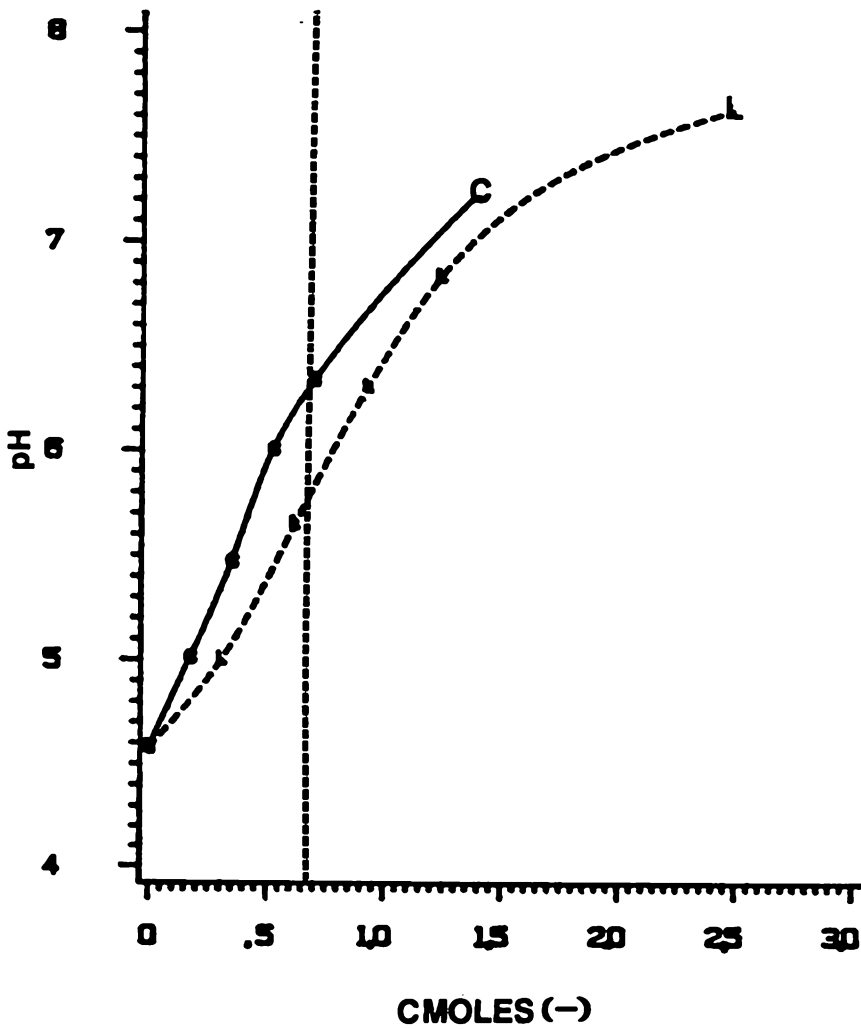


Figure 6. Effect of sludge application rate on pH of the Tatum soil: pH averaged over time. Dashed vertical line represents the rate calculated to raise soil pH to 6.5, L = Lime-stabilized and C = Chemically-fixed sludge.

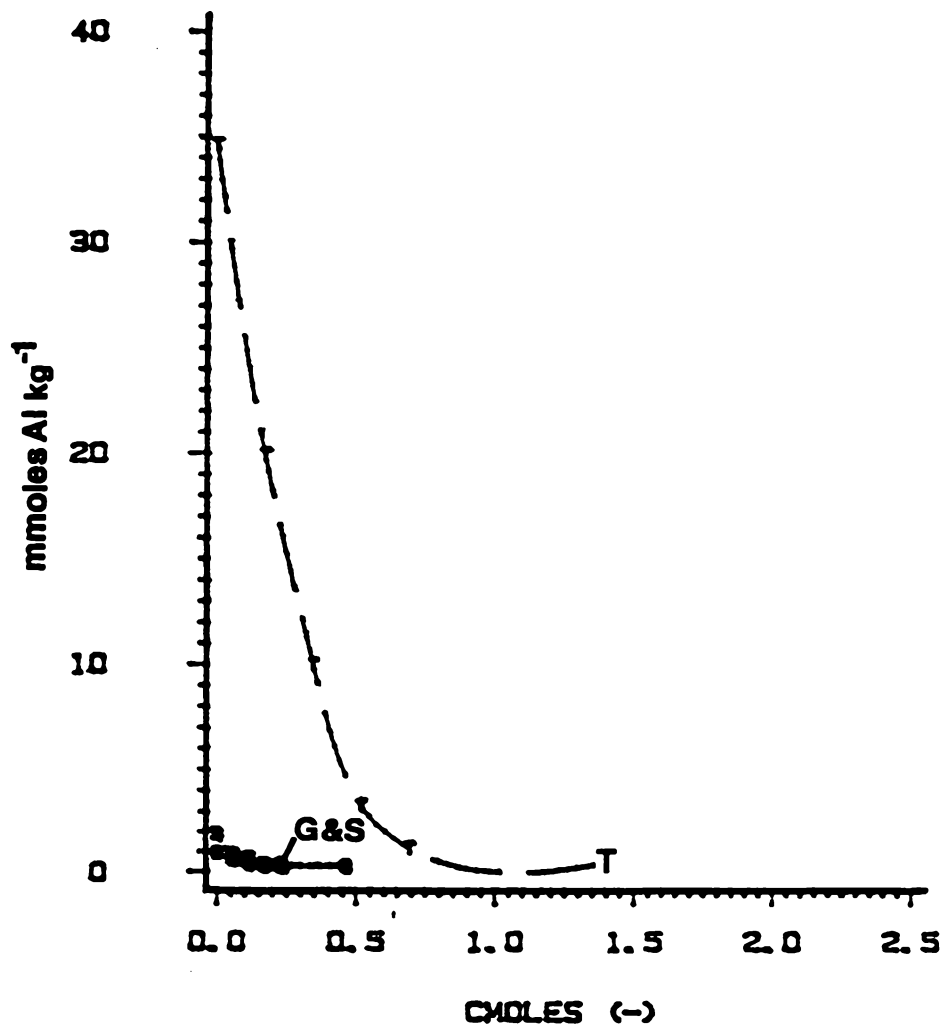


Figure 7. Effect of adding chemically-fixed sludge at different rates on exchangeable soil Al. G = Glenelg, S = State and T = Tatum.

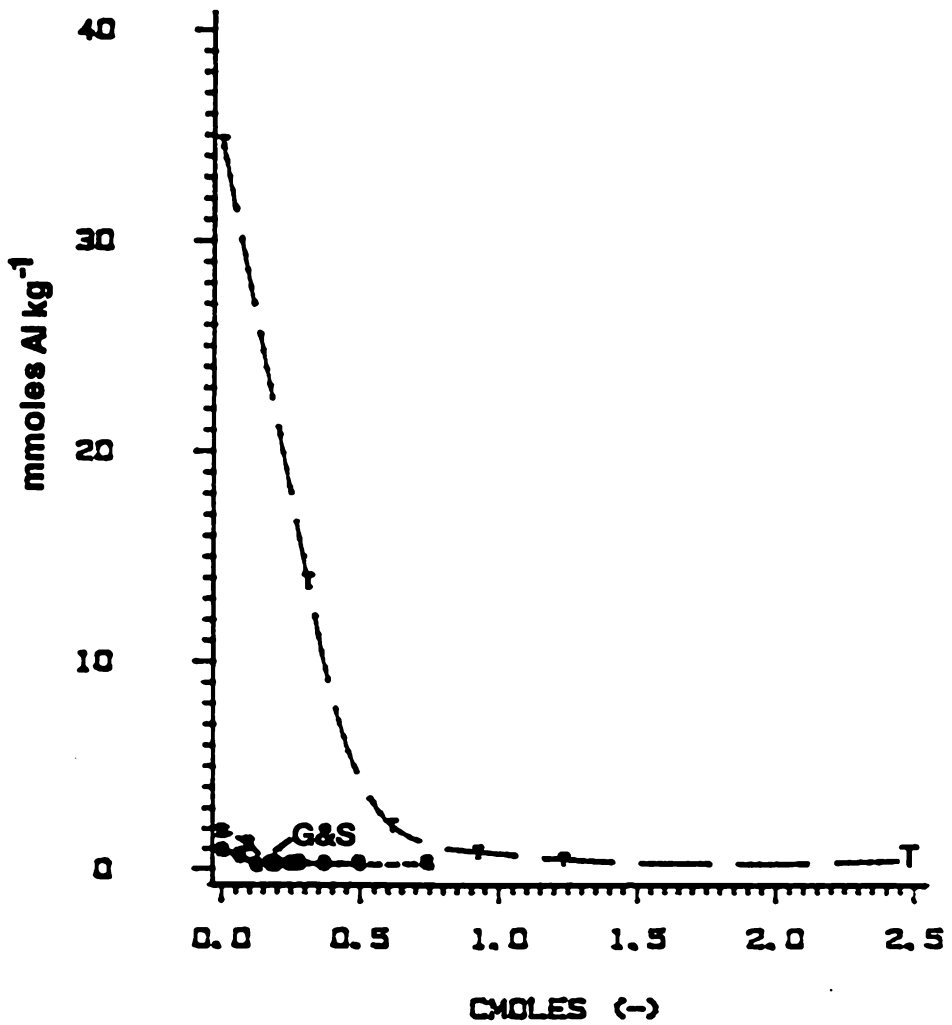


Figure 8. Effect of adding lime-stabilized sludge at different rates on exchangeable soil Al: G = Glencelg, S = State and T = Tatum.

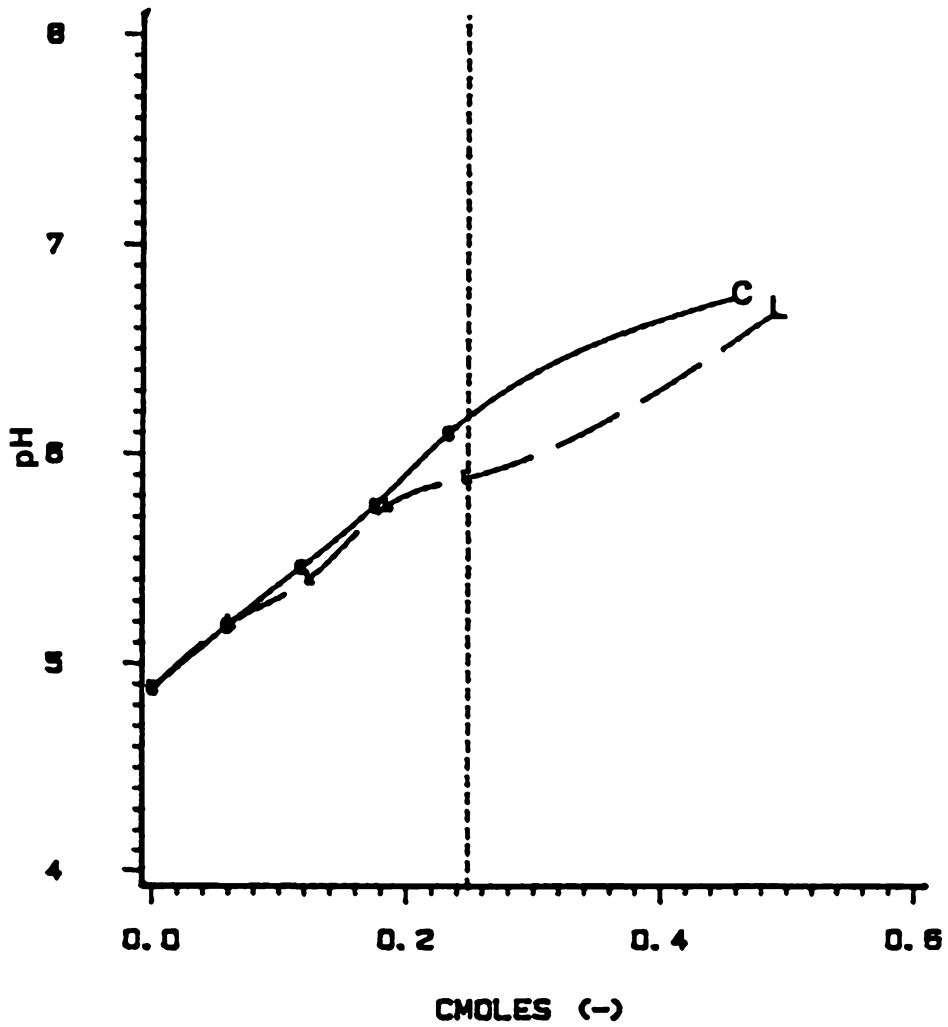


Figure 9. Effect of sludge rate on the Glenelg soil pH after 203 days of incubation.: Dashed vertical line represents the rate calculated to raise soil pH to 6.5, L=Lime-stabilized and C= Chemically-fixed sludge.

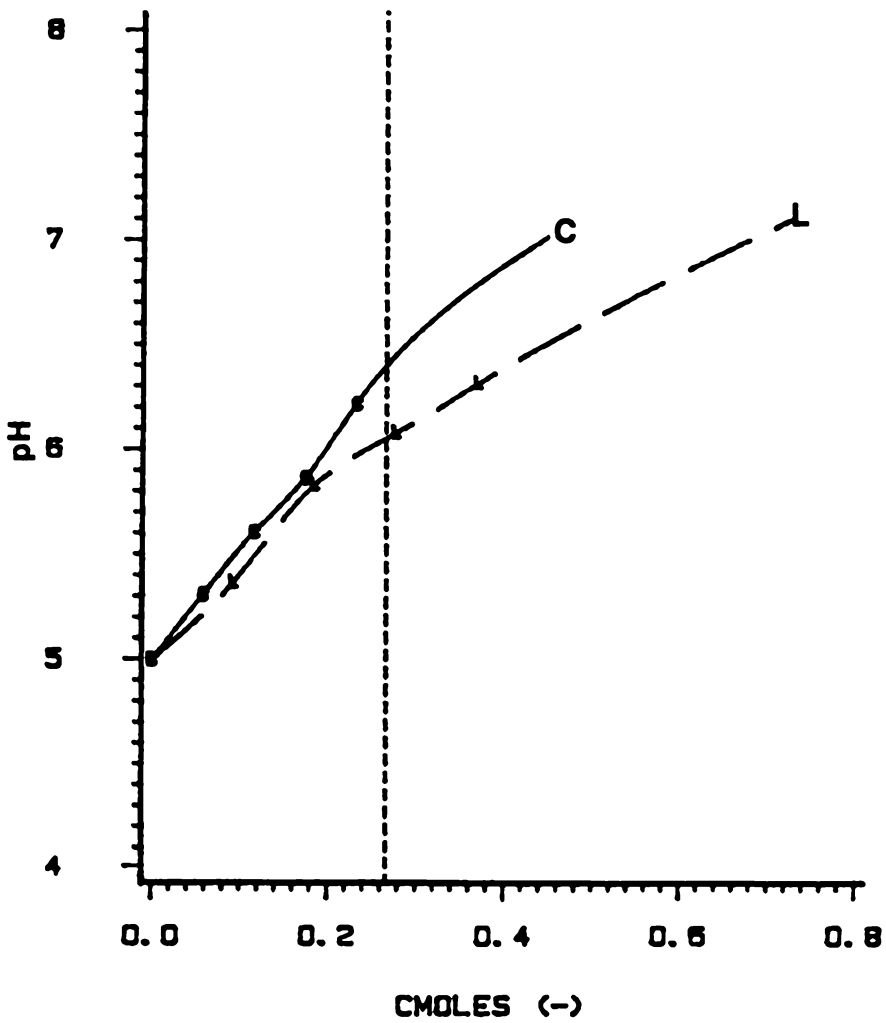


Figure 10. Effect of sludge rate on the State soil pH after 203 days of incubation.: Dashed vertical line represents the rate calculated to raise soil pH to 6.5, L = Lime-stabilized and C = Chemically-fixed sludge.

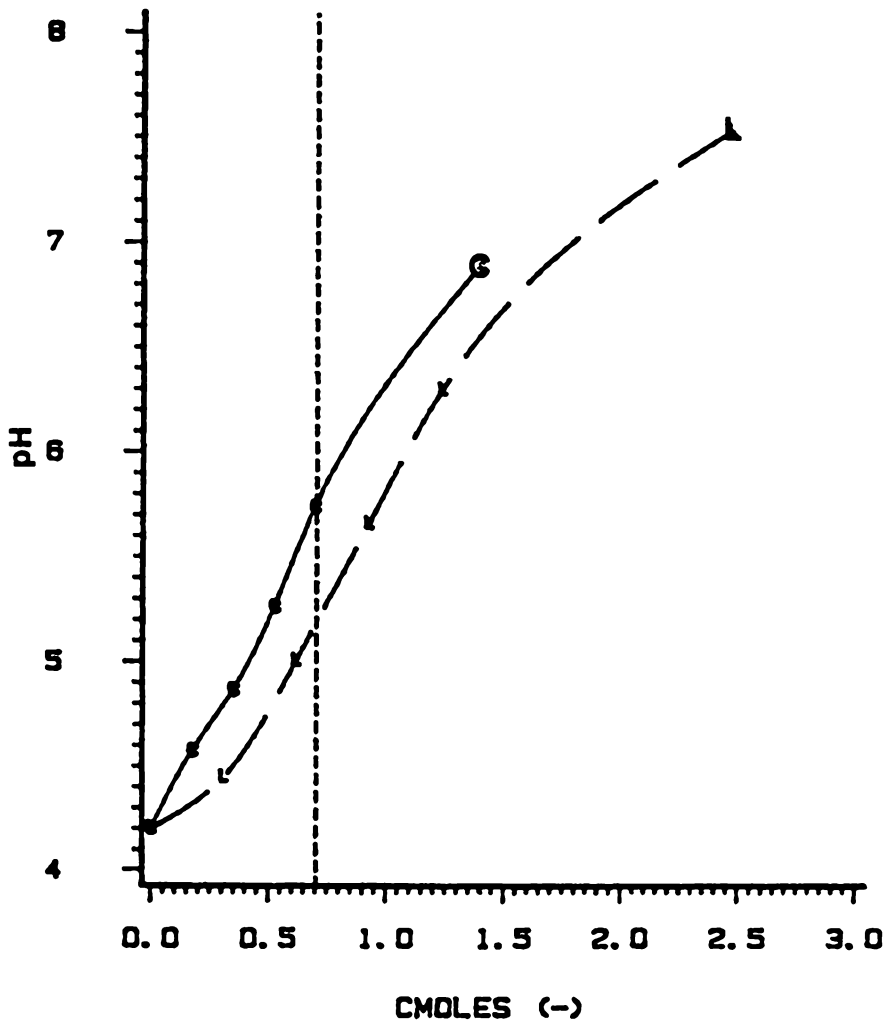


Figure 11. Effect of sludge rate on the Tatum soil pH after 203 days of incubation.: Dashed vertical line represents the rate calculated to raise soil pH to 6.5, L = Lime-stabilized and C = Chemically-fixed sludge.

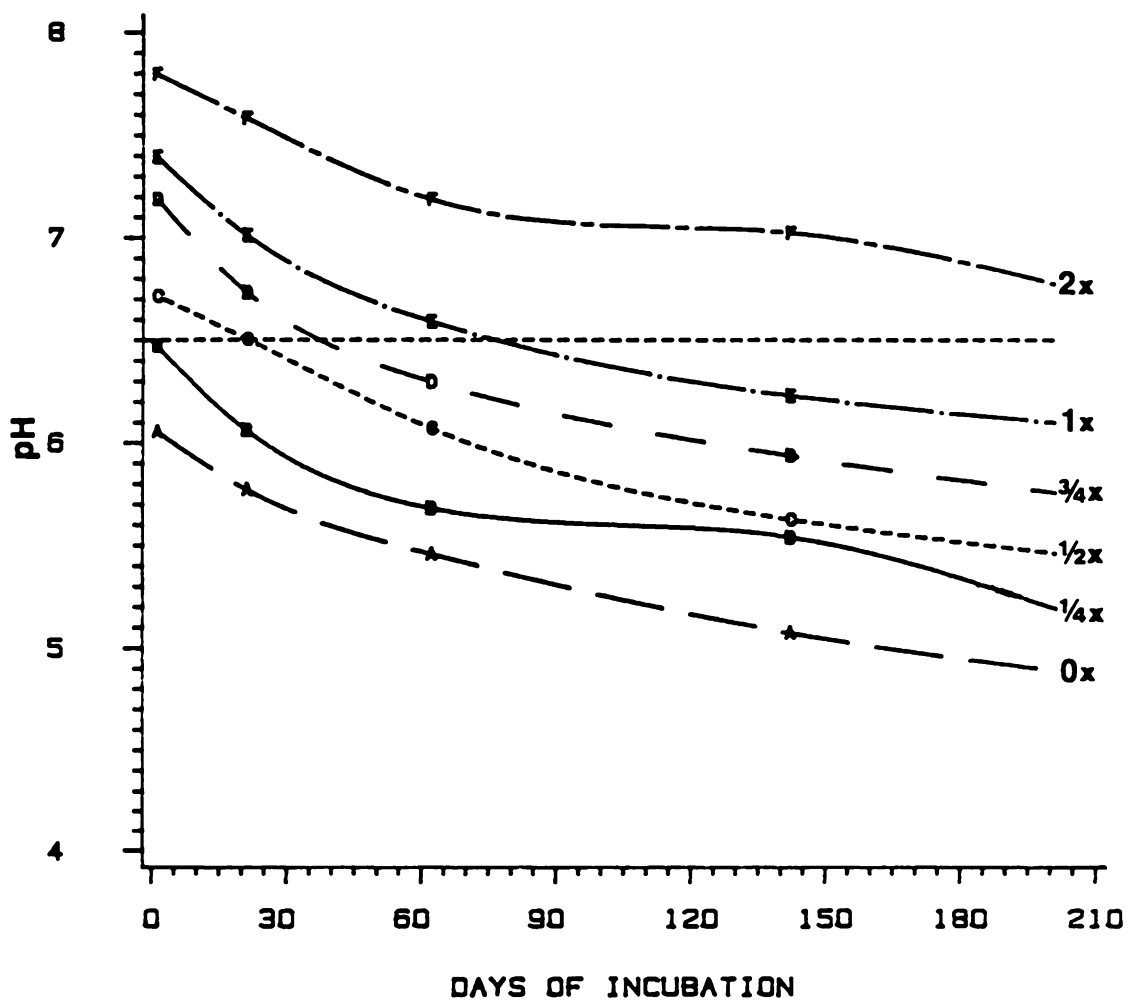


Figure 12. Effect of incubation time on the pH of the Glenelg soil amended with chemically-fixed sludge.

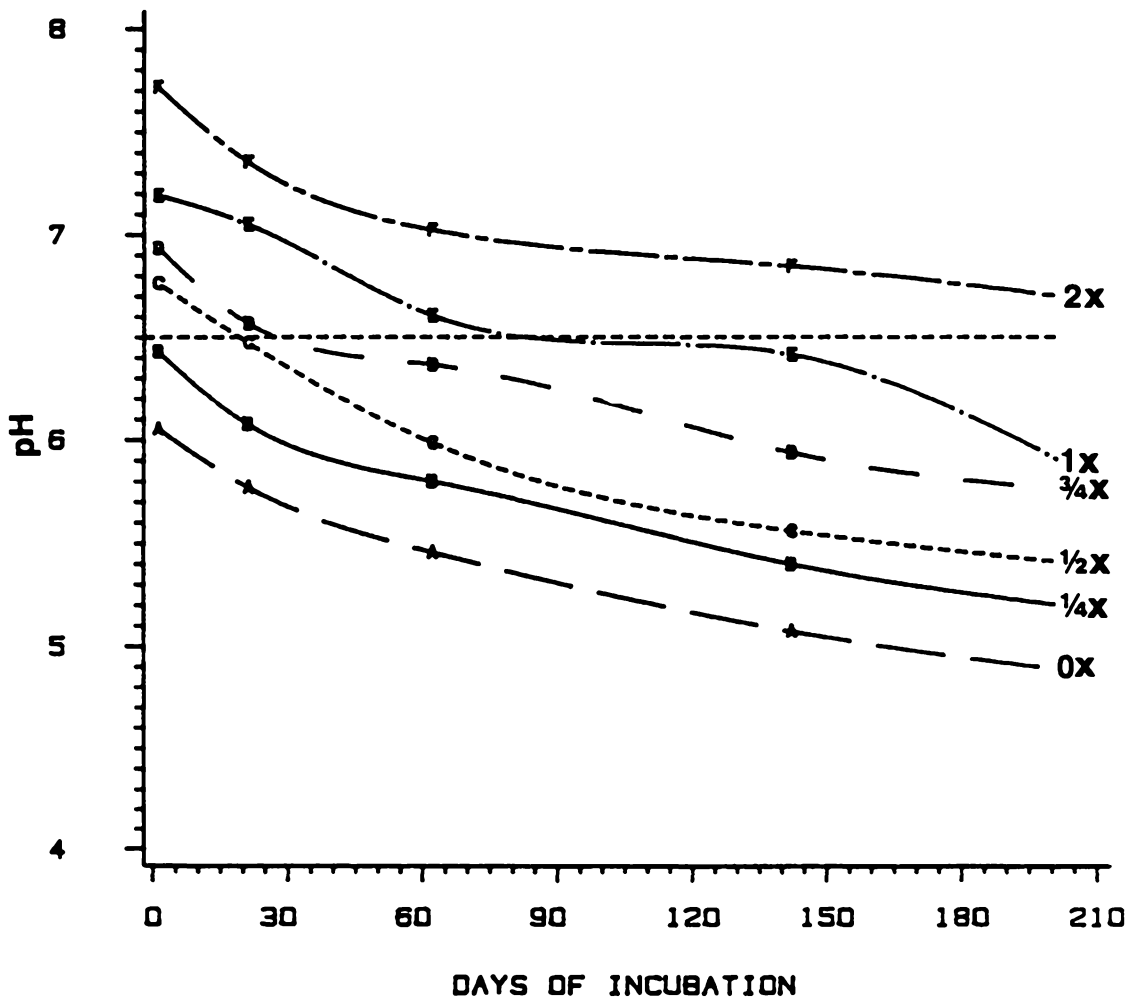


Figure 13. Effect of incubation time on the pH of the Glenelg soil amended with lime-stabilized sludge.

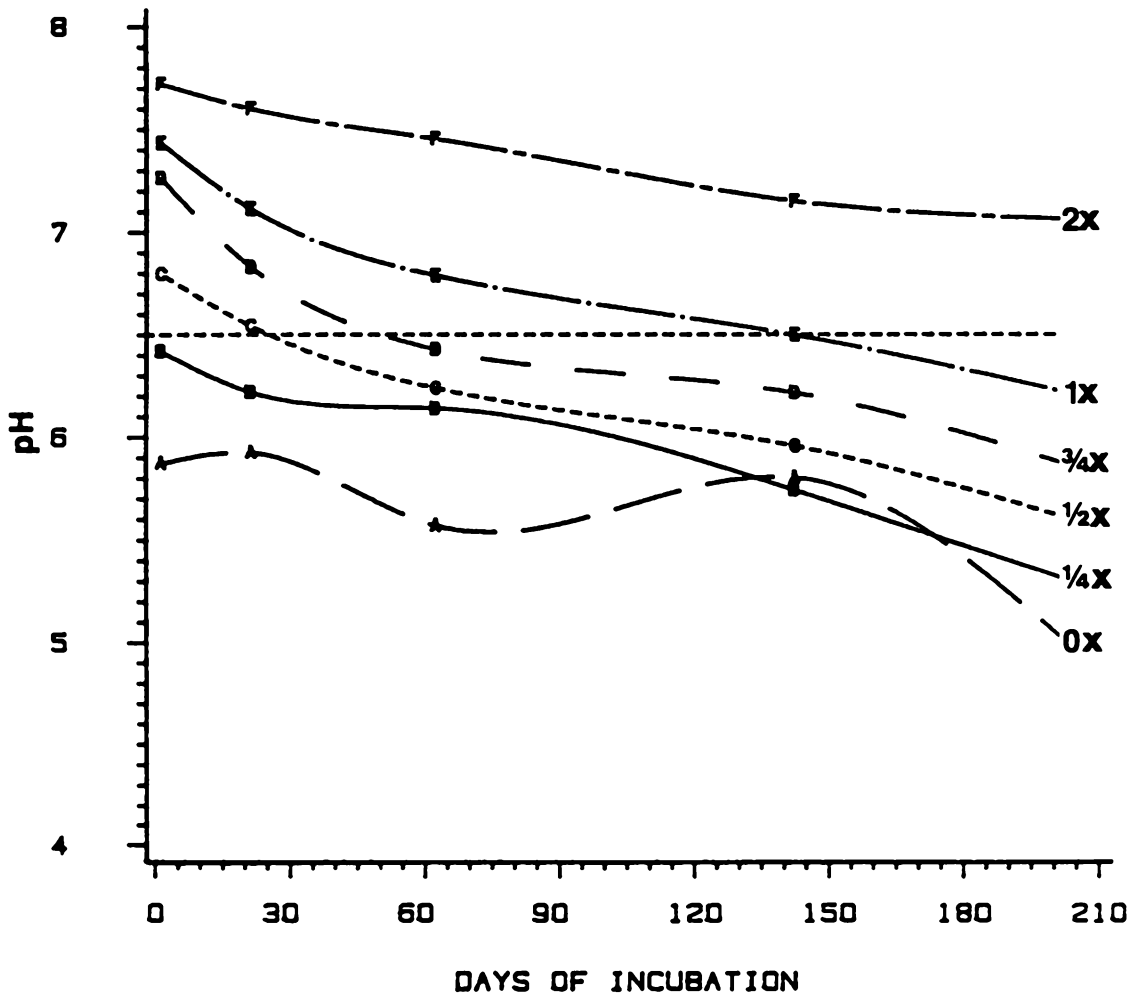


Figure 14. Effect of incubation time on the pH of the State soil amended with chemically-fixed sludge.

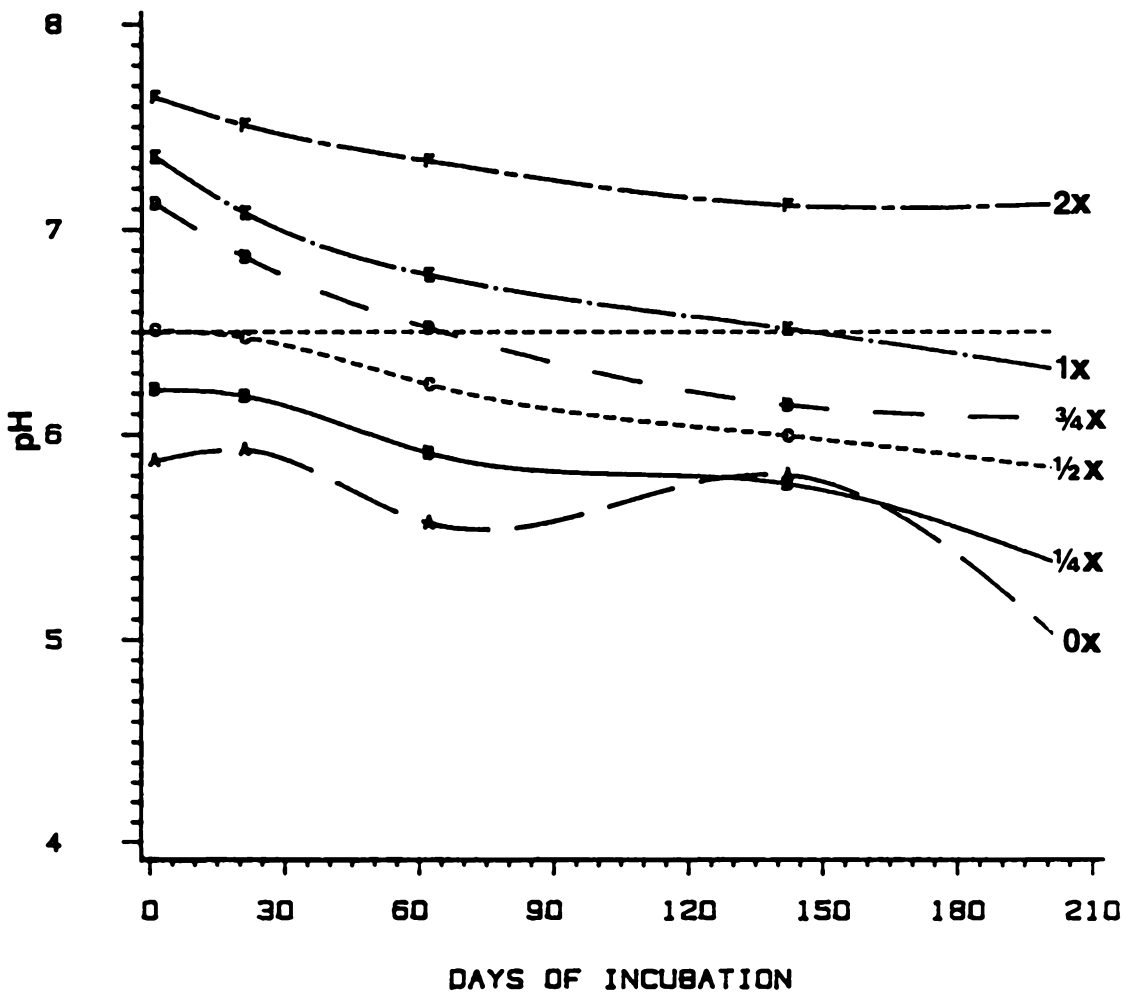


Figure 15. Effect of incubation time on the pH of the State soil amended with lime-stabilized sludge.

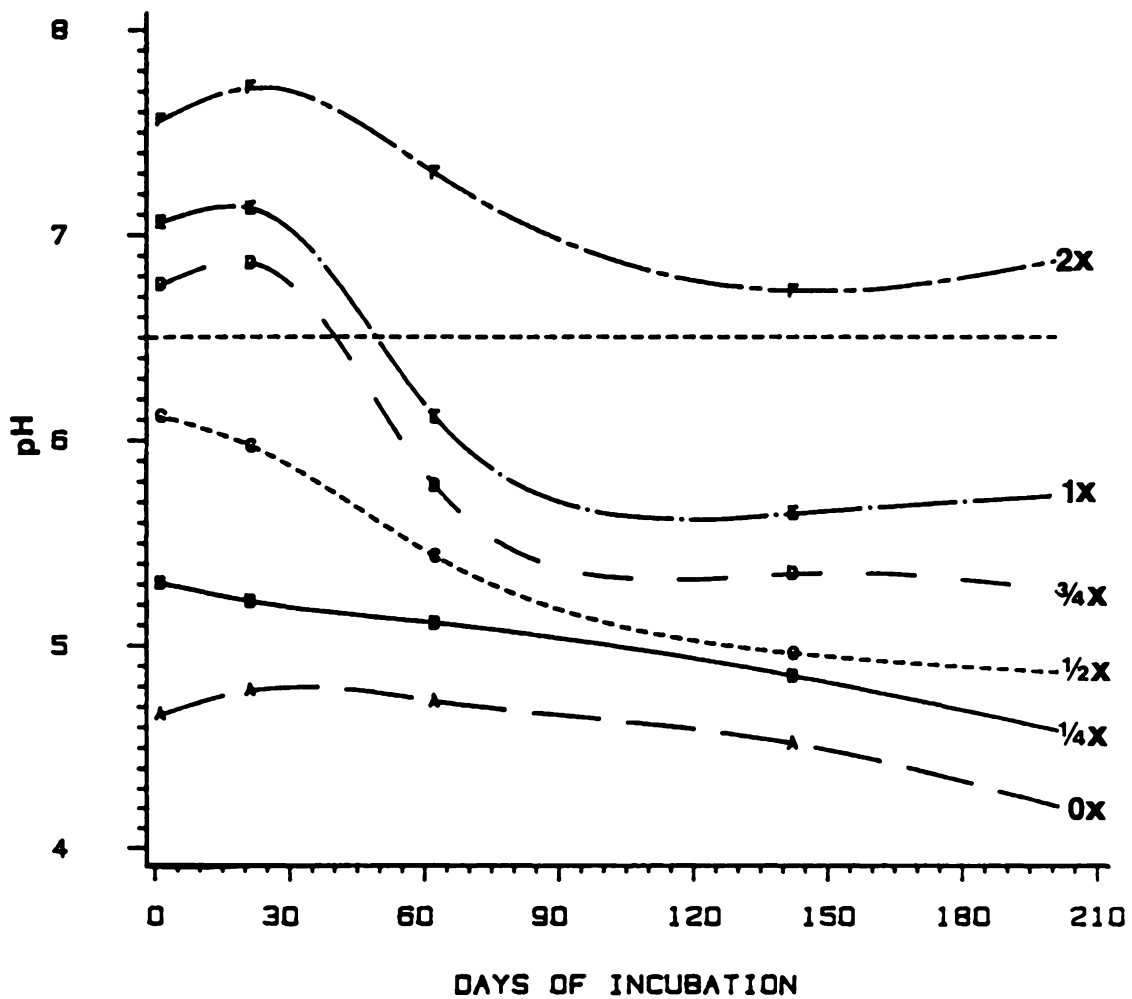


Figure 16. Effect of incubation time on the pH of the Tatum soil amended with chemically-fixed sludge.

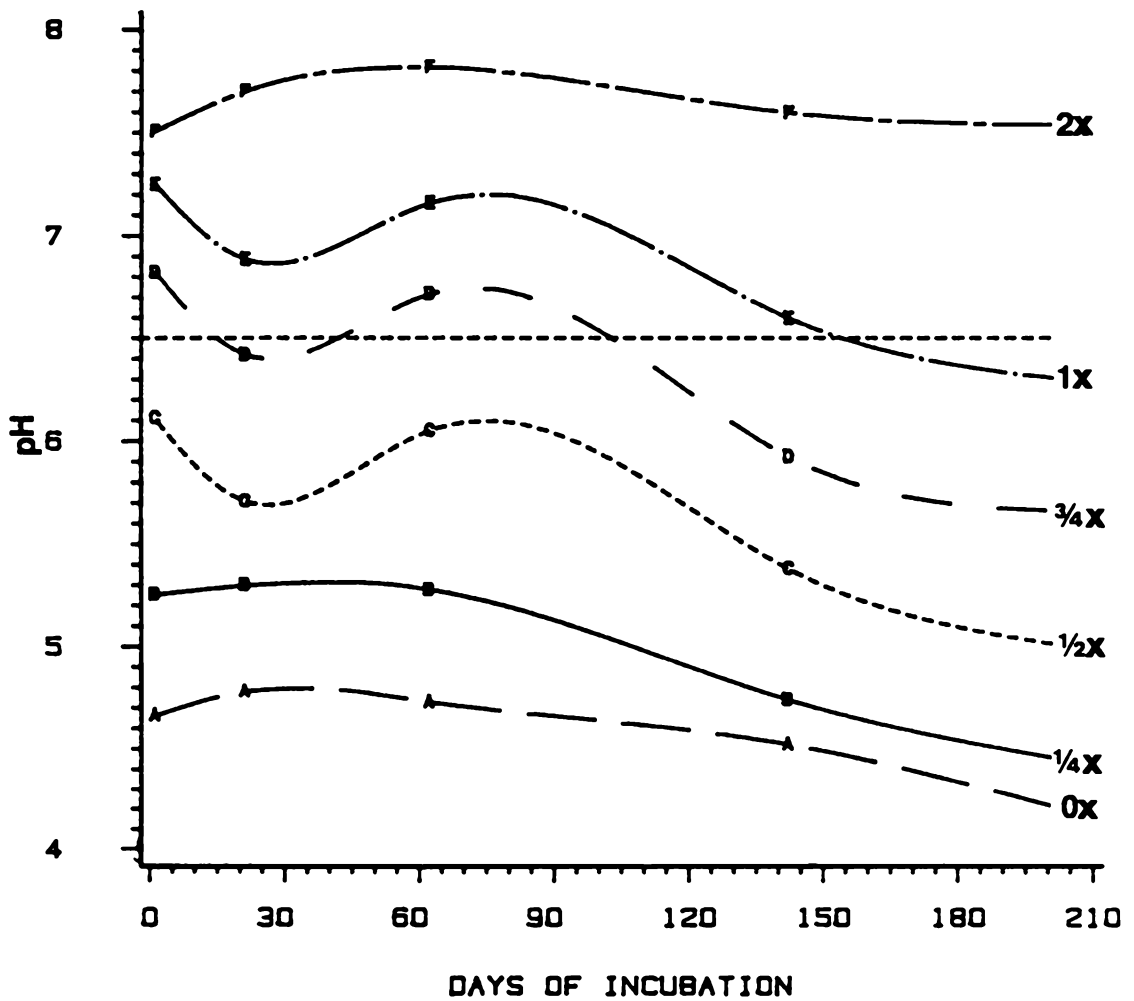


Figure 17. Effect of incubation time on the pH of the Tatum soil amended with lime-stabilized sludge.

are in agreement with O'Keefe et al. (1986) and Hadas et al. (1986). Part of the rapid initial phase may be attributed to the collection of soils in the fall when the content of easily decomposable organic components was relatively high. The rapid initial phase was extended by the addition of the sludges. Increasing the rate of addition increased the duration of the rapid initial phase on all soils.

Nitrogen was mineralized in larger quantities in the Glenelg soil (Figure 24 on page 86) while the State and Tatum soils appeared to mineralize N at similar rates. But when the data was normalized by subtracting N-mineralized in the unamended control sample from sludge treated samples, statistical analysis indicated that the Tatum soil mineralized added N at a lower rate than the Glenelg and State soils. The N-mineralization rates on the Glenelg and State soils were not different. Nitrogen mineralization after 20 weeks on the Tatum soil was only 11.25%. The lower mineralization rate on the Tatum soil is probably related to the fact that it is a B horizon soil high in clay, with large contents of 2:1 type clay minerals such as mica, vermiculite and hydroxy-interlayer vermiculite. These minerals are capable of "fixing" NH_4^+ between clay platelets and in wedge-sites which may account for the lower apparent rates of mineralization especially in the higher pH treatments on the Tatum soil (Nommik and Vahtras, 1982). The Glenelg and State soils had mineralized 33.8 and 31.5%, respectively, of the added organic N within 20 weeks. The percentages of N mineralized by the Glenelg and State soils were not statistically different at the .05 level of probability.

The cumulative N mineralized on the State and Tatum soils was slightly larger when amended with the chemically-fixed sludge compared with the lime-stabilized sludge (Figure 18 on page 80 and Figure 19 on page 81) although this difference was not statistically significant. The increase in mineralization was probably related to soil acidity and the greater liming potential of the chemically fixed sludge per unit of N added. Soil pH was higher in the chemically fixed treatments (Table 16 on page 78).

The effect of treatments was to increase the cumulative N mineralized (Figure 25 on page 87 - Figure 30 on page 92). However, when the data was normalized, the percent of added N was not significantly different across treatments. Figures 20 and 23 illustrate the interesting but statistically insignificant process of immobilization on the lowest treatment levels on the Tatum soil. The N

Table 16. Mean soil pH values after 20 weeks of mineralization.

<u>Soil</u>	<u>Treatment</u>	<u>Sludge Type</u>	
		<u>Chemically Fixed</u>	<u>Lime Stabilized</u>
Glenelg	0x	5.8	5.8
	1x	7.0	6.1
	3x	7.5	6.6
	9x	7.7	7.4
State	0x	5.3	5.3
	1x	7.0	5.8
	3x	7.4	6.5
	9x	7.6	7.3
Tatum	0x	4.3	4.3
	1x	5.4	4.5
	3x	7.2	4.9
	9x	7.5	6.4

is probably liberated at the same rate as the other treatments but microbial growth is stimulated by the addition of sludge and the N is assimilated into their cells. The effect is probably a response to the increase in pH which stimulates growth. The increase in pH could also promote increased NH_4^+ "fixation" and result in lower apparent mineralization.

Nitrification was generally delayed until after the second week although this varied with soil and treatment level. The most notable exception was on the State soil which produced NO_3^- in the initial leachate. The Glenelg soil began producing NO_3^- after 2-4 weeks while the Tatum took 6-10 weeks when amended with sludge but produced limited NO_3^- when unamended. This was probably due to the high level of soil acidity in the Tatum soil which inhibits nitrification. The general effect of increasing rates of sludge addition was to delay nitrification. This was true for all treatments except the low rates on the State soil.

Nitrate production after 20 weeks on the Glenelg and State soils ranged from 75 to 200 mg kg^{-1} . Because the nitrification process produces acidity, this could help explain the reduction in soil pH with time experienced in the lime reaction experiment.

As a N fertilizer, the lime-stabilized and chemically-fixed sludges could provide 9.4 and 3.6 Kg of N Mg^{-1} (18.8 and 7.1 lb ton^{-1}), respectively. This calculation assumes a 32% N mineralization factor which was the average rate of mineralization observed in this experiment after 20 weeks on the two surface soils (Glenelg and State). If a corn crop requires between 179.2 and 201.6 Kg N ha^{-1} (160 to 180 lbs A^{-1}), (Follette et al., 1981), then 19.1 to 21.5 Mg ha^{-1} (8.5 to 9.6 tons A^{-1}) of lime-stabilized sludge or 50.4 to 56.7 Mg ha^{-1} (22.5 to 25.4 tons A^{-1}) of chemically-fixed sludge, respectively, would be needed to supply the N.

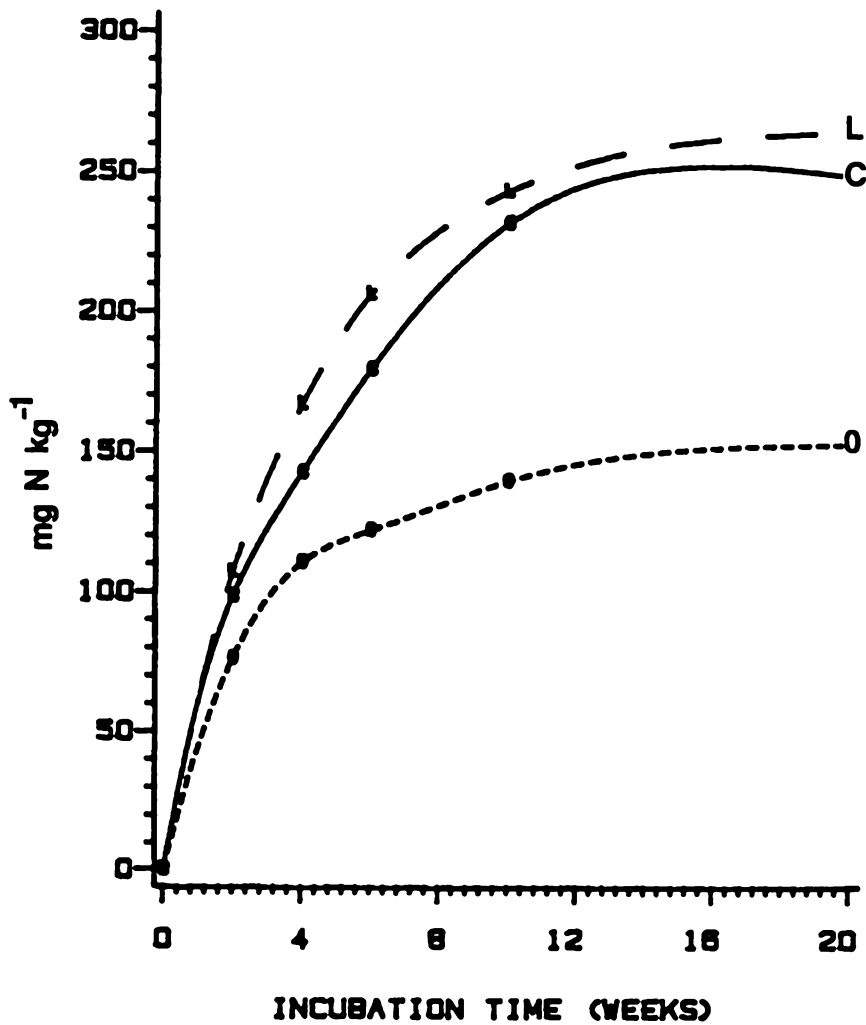


Figure 18. Nitrogen mineralized on the Glenelg soil as a function of time and sludge addition.: C = Chemically-fixed, L = Lime-stabilized sludge and 0 = unamended.

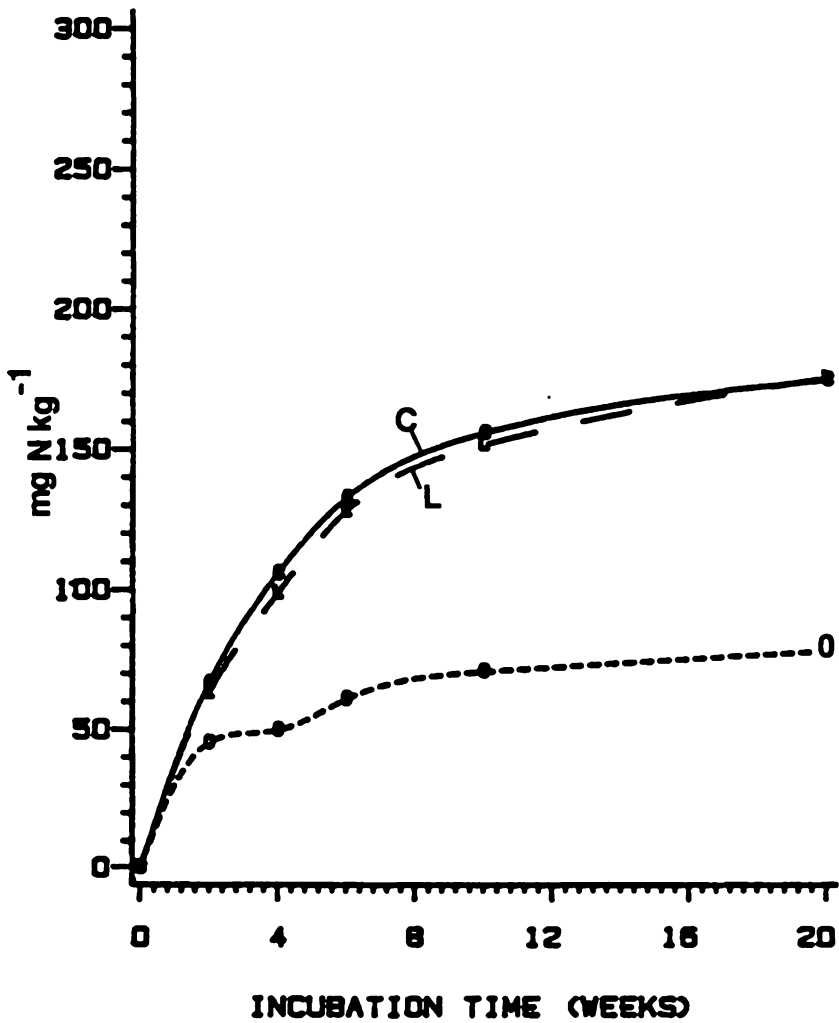


Figure 19. Nitrogen mineralized on the State soil as a function of time and sludge addition.: C = Chemically-fixed, L = Lime-stabilized sludge and 0 = unamended.

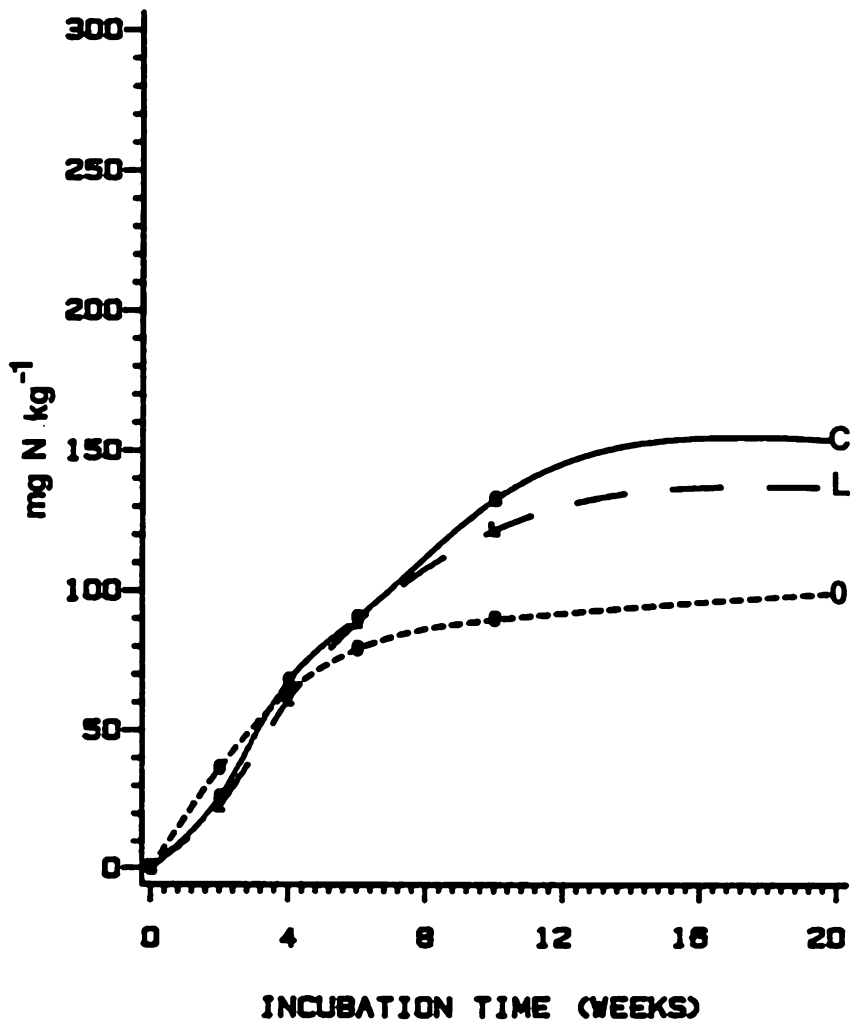


Figure 20. Nitrogen mineralized on the Tatum soil as a function of time and sludge addition.: C = Chemically-fixed, L = Lime-stabilized sludge and 0 = unamended.

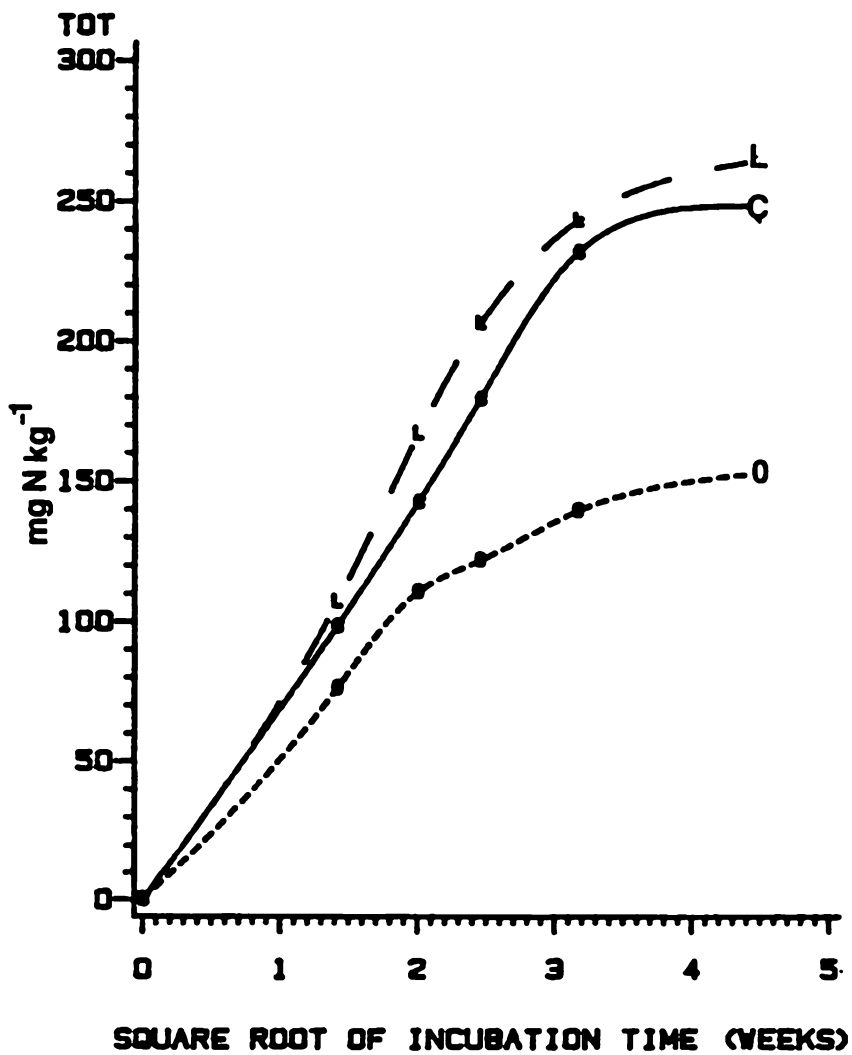


Figure 21. Nitrogen mineralized on the Glenelg soil as a function of the square root of time and sludge addition.: C = Chemically-fixed, L = Lime-stabilized sludge and 0 = unamended.

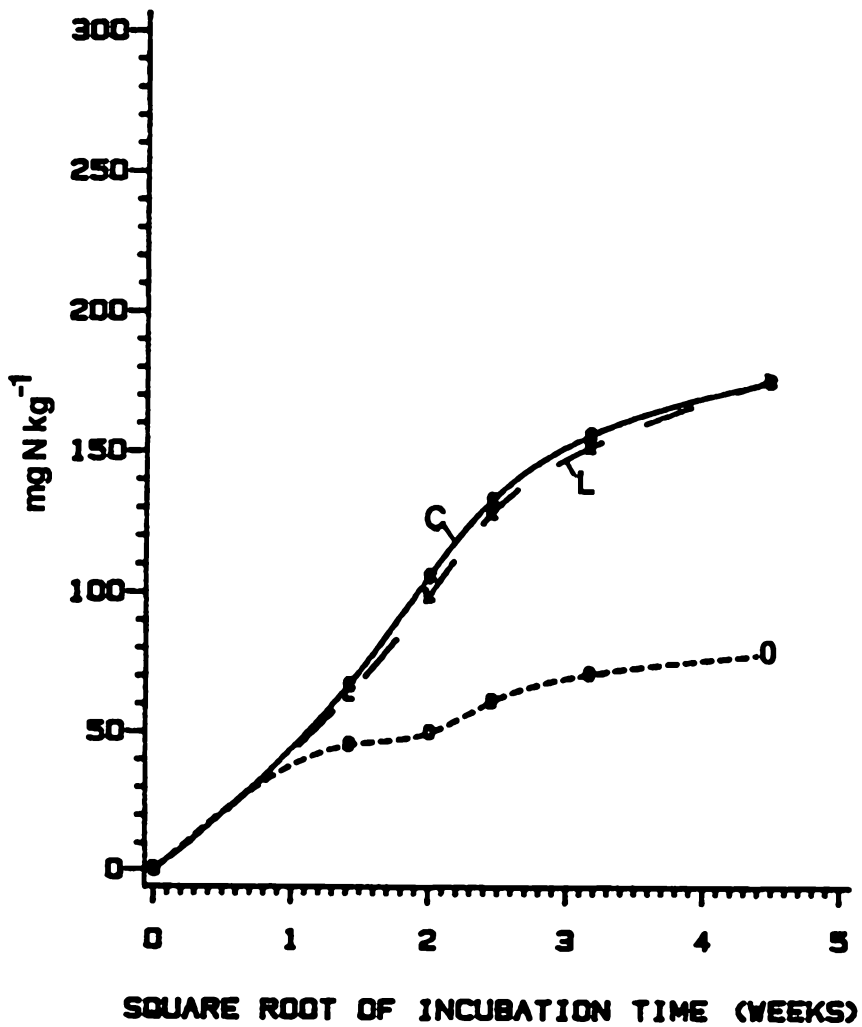


Figure 22. Nitrogen mineralized on the State soil as a function of the square root of time and sludge addition.: C = Chemically-fixed, L = Lime-stabilized sludge and 0 = unamended.

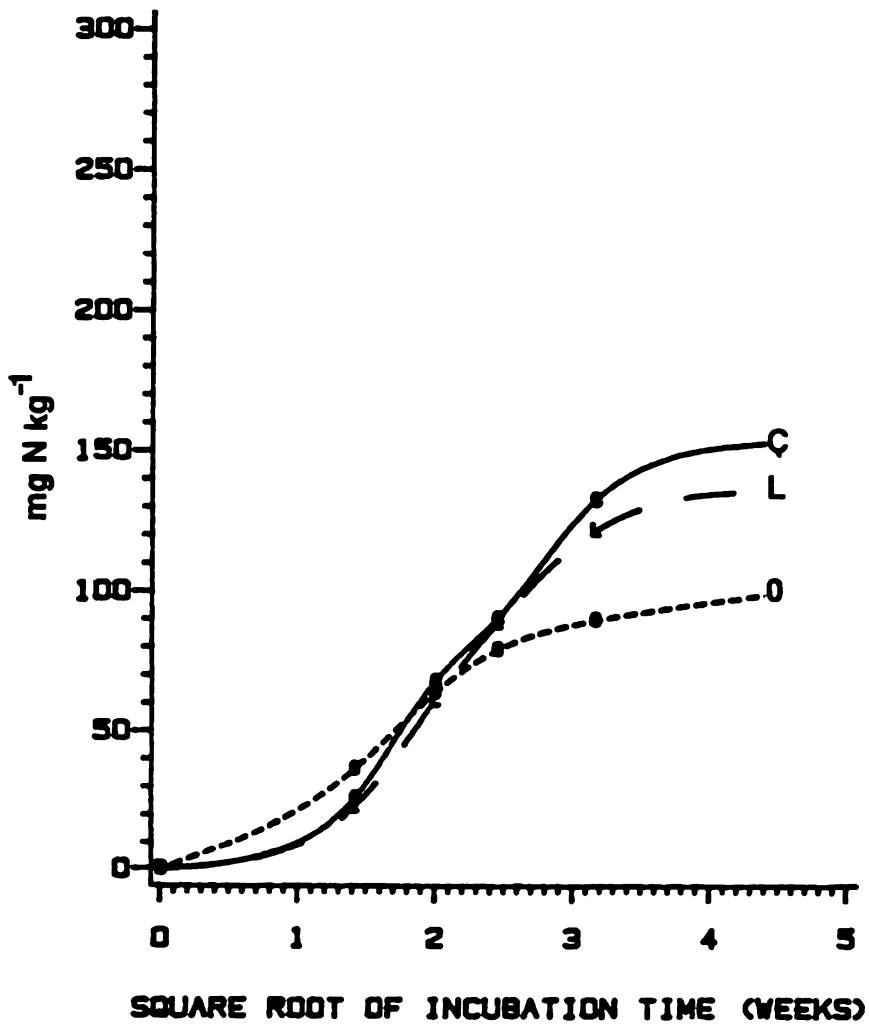


Figure 23. Nitrogen mineralized on the Tatum soil as a function of the square root of time and sludge addition.: C=Chemically-fixed, L= Lime-stabilized sludge and 0=unamended.

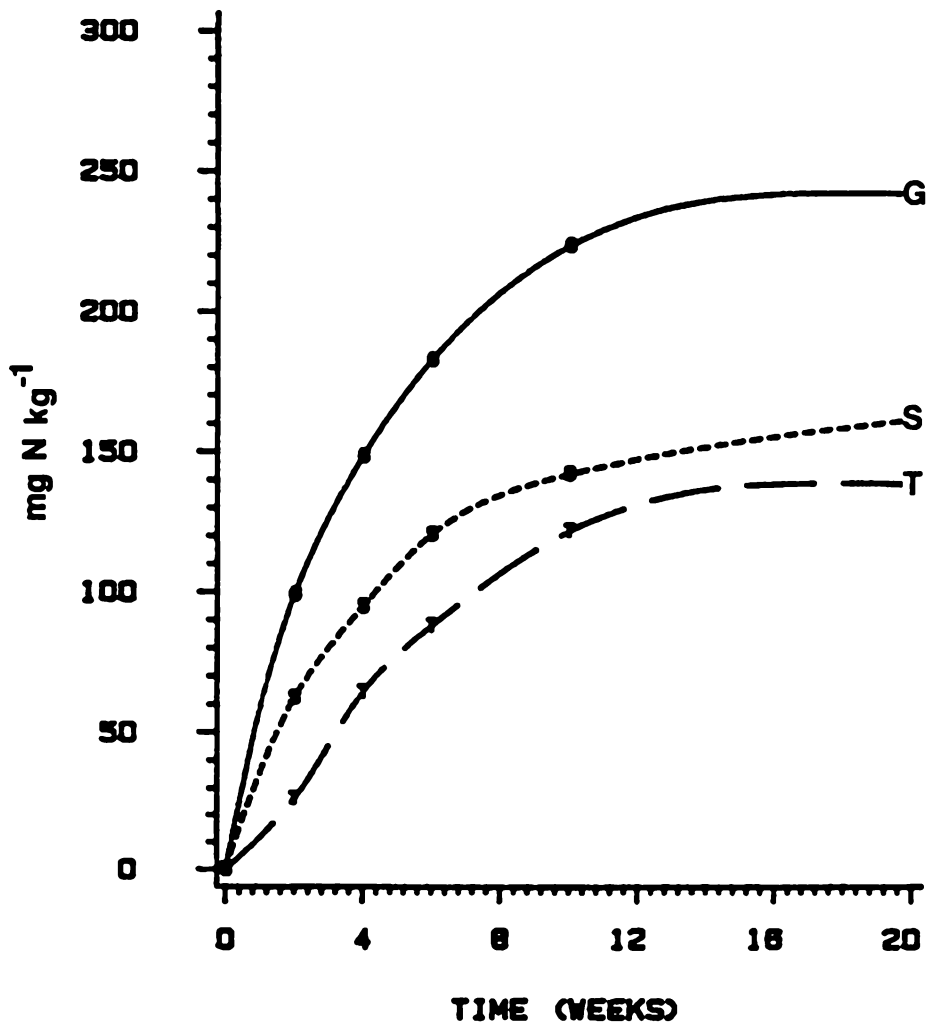


Figure 24. Nitrogen mineralized on the Glenelg (G), State (S) and Tatum (T) soils as a function of sludge addition.

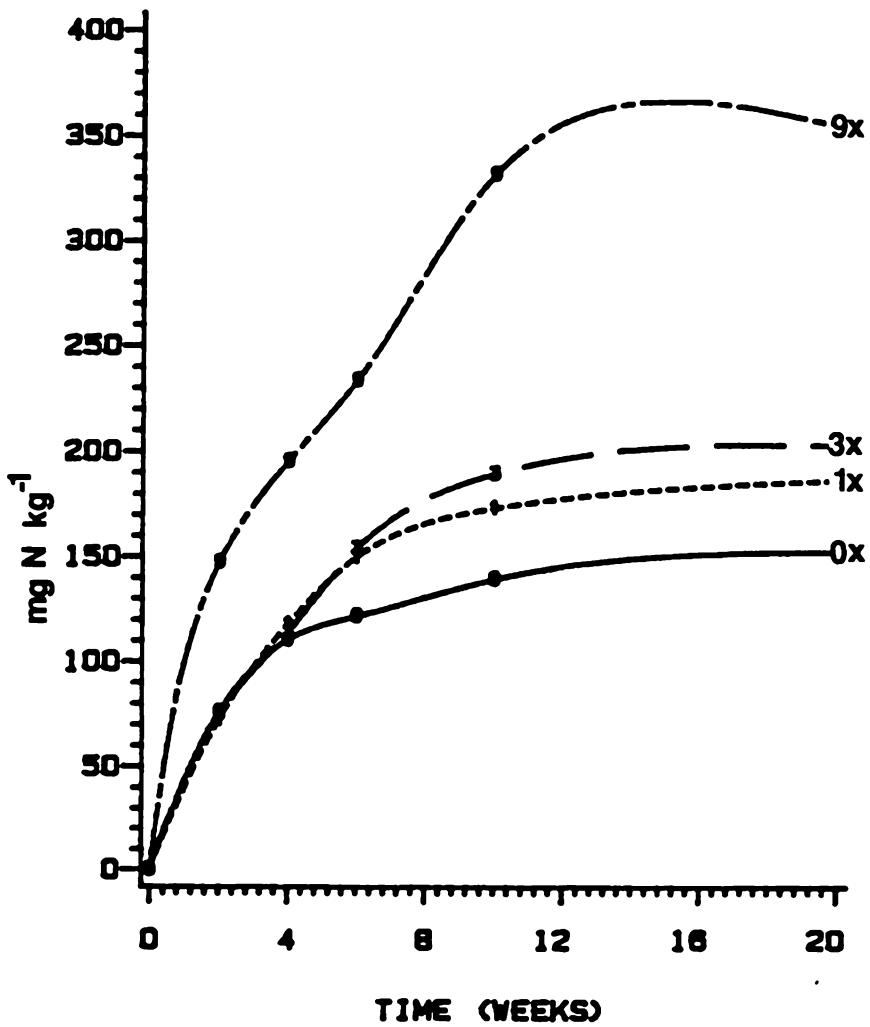


Figure 25. Total N mineralized on the Glenelg soil as a function of time and rate of chemically-fixed sludge applied.

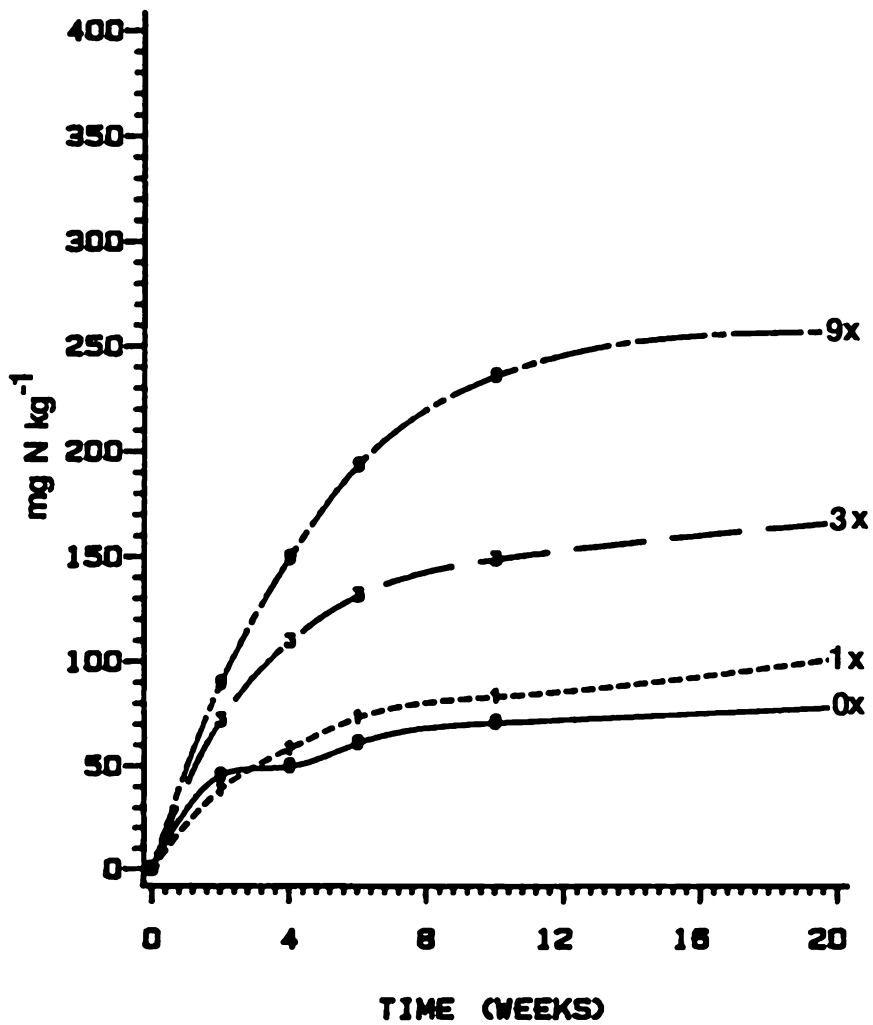


Figure 26. Total N mineralized on the State soil as a function of time and rate of chemically-fixed sludge applied.

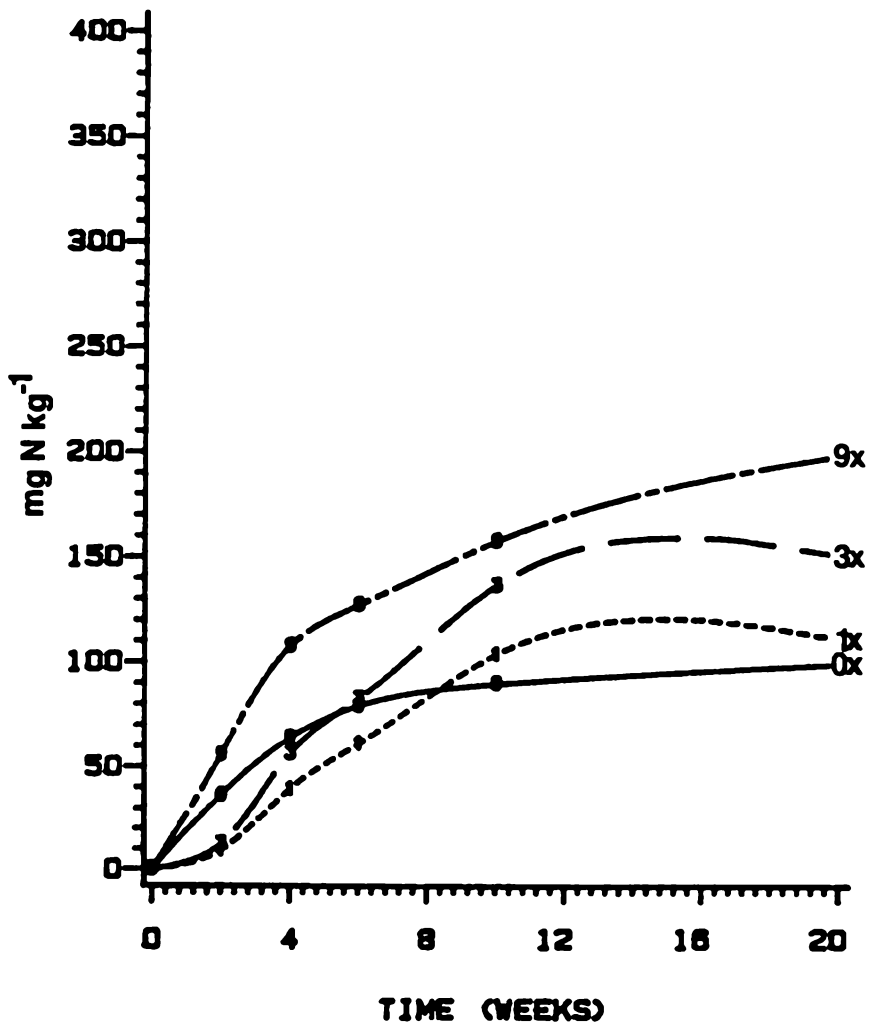


Figure 27. Total N mineralized on the Tatum soil as a function of time and rate of chemically-fixed sludge applied.

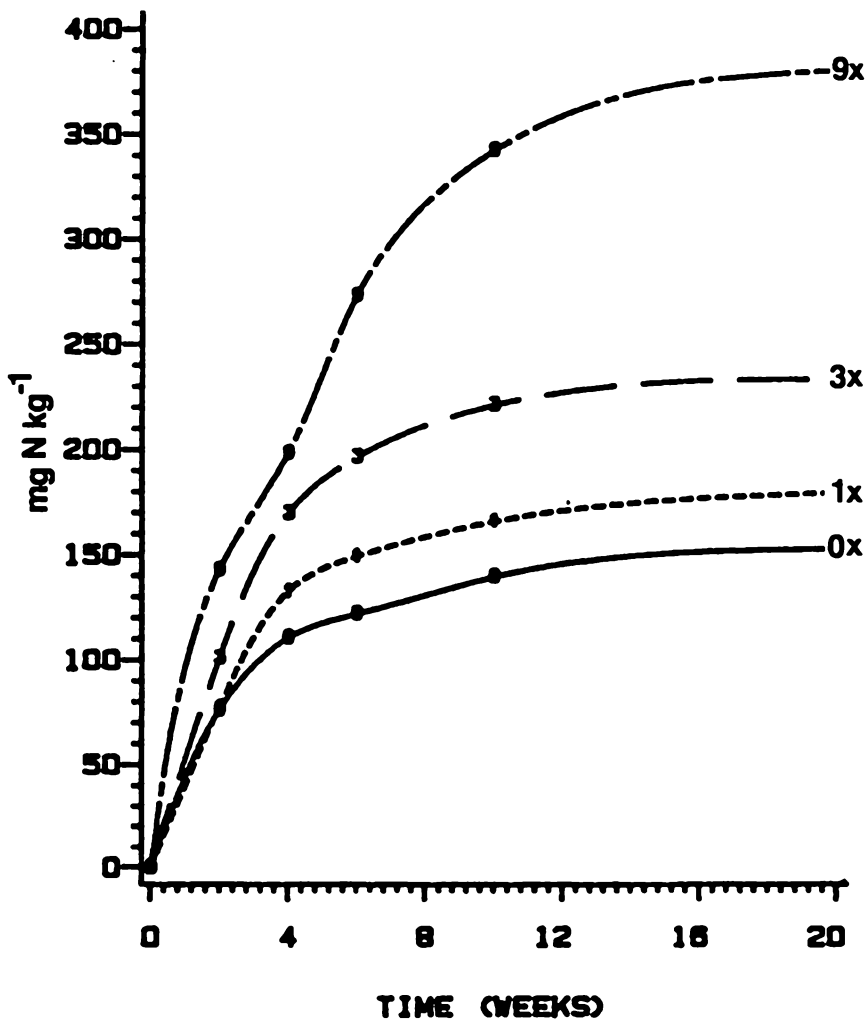


Figure 28. Total N mineralized on the Glenelg soil as a function of time and rate of lime-stabilized sludge applied.

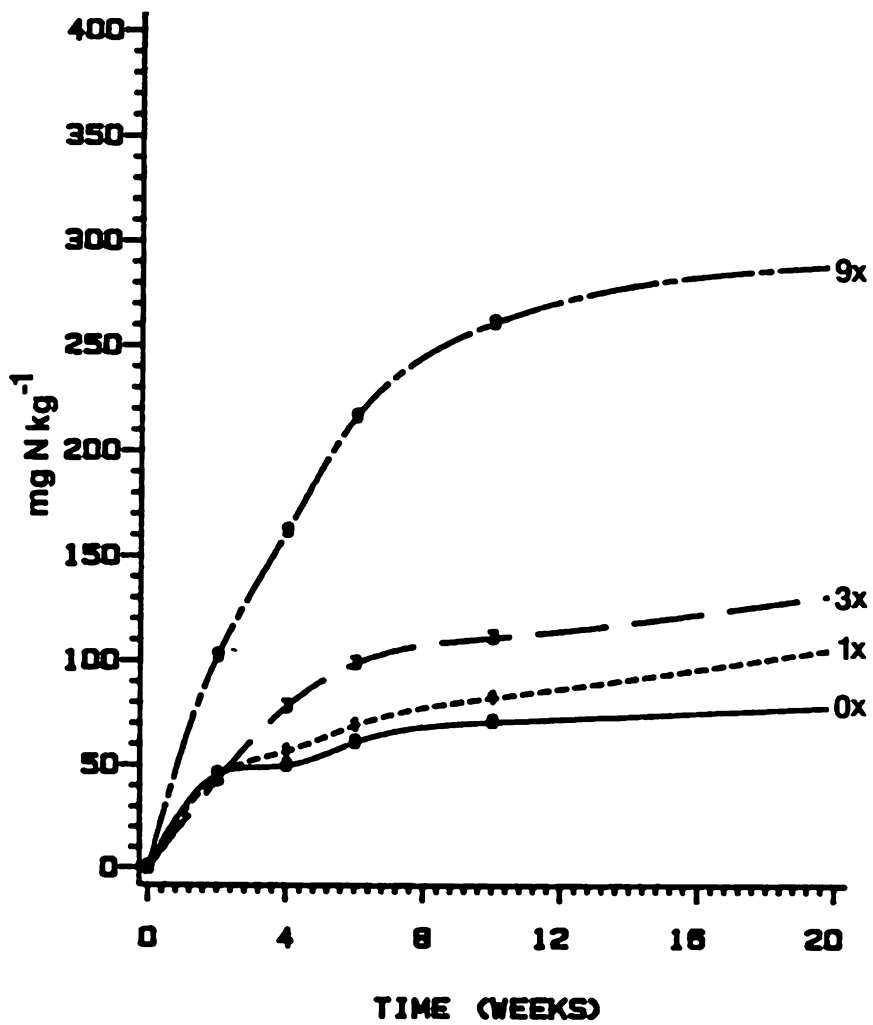


Figure 29. Total N mineralized on the State soil as a function of time and rate of lime-stabilized sludge applied.

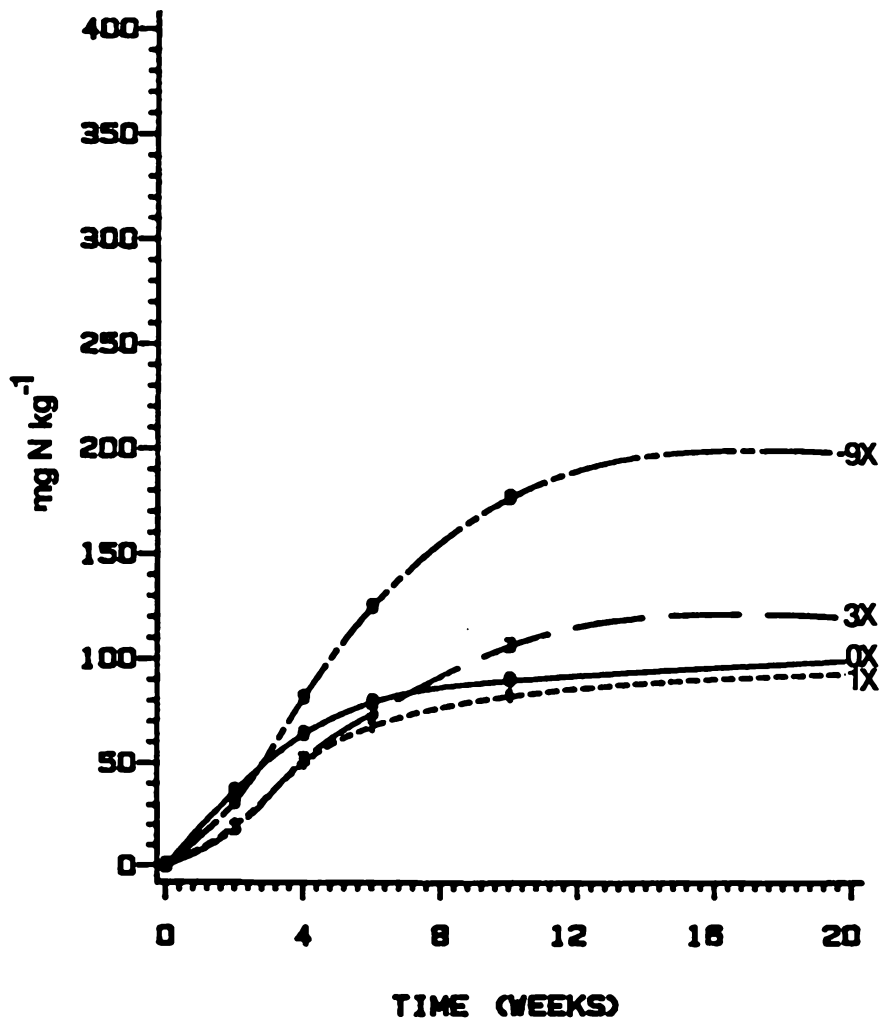


Figure 30. Total N mineralized on the Tatum soil as a function of time and rate of lime-stabilized sludge applied.

Greenhouse Experiments

Effect of Sludge Rate on Corn Growth

The first greenhouse experiment was designed to study the effects of increasing rate of lime-stabilized and chemically-fixed sludges on the growth of corn and to compare their influence on corn growth to that of CaCO_3 . The model which included the factors of rate and sludge type explained 76 and 94% of the yield variation on the Glenelg and Tatum soils, respectively (Appendix C). Coefficients of variability were 9.7 and 13.0%, respectively.

The variable which accounted for most of the variability was the quantity of lime or sludge applied. This variable was significant at the .0001 level of probability on both soils. Yields on the Glenelg soil generally decreased after a slight yield increase at the lowest levels of application (Figure 31 on page 95). Analysis of the concentrations of nutrients in the plant tissue (Table 17 on page 94) by DRIS indicated that decreased yields on the Glenelg soil were associated with inadequate concentrations of Zn.

Yields on the Tatum soil increased with increased sludge addition up to the lime requirement and then decreased with further addition (Figure 32 on page 96). Yield increases were probably in response to neutralization of acidity and increased availability of P. Analysis by DRIS showed that yield increases on the Tatum soil were due to increased availability of P while yield decreases at the higher application rates were associated with lower Zn availability. Decreased concentrations of Zn in the plant tissue could have been related to decreased availability of Zn caused by lower solubility when soil pH was raised. Lower tissue Zn concentrations may also have been associated with the high levels of P applied to the soils in this experiment. High levels of P fertilization have been shown to induce Zn deficiency (Stukenholtz et al., 1966) although the relationship between Zn and P is not fully understood.

Table 17. Effect of varying lime rate and source on elemental composition of corn.

Soil §	Lime Source ¶	Treatment Level	Element										
			N	P	K	Ca	Mg	S	Mn	Fe	Zn	Cu	
			%						mg kg ⁻¹				
G	NONE	0X	2.17	0.19	0.66	0.83	0.38	.254	209	61	12	6	
G	CF	0.25X	2.20	0.15	0.64	0.81	0.38	.315	176	63	12	4	
G	CF	0.50X	2.13	0.18	0.64	0.85	0.38	.260	150	63	12	4	
G	CF	1X	2.13	0.17	0.66	0.86	0.40	.204	108	58	9	5	
G	CF	2X	2.40	0.15	0.91	0.87	0.45	.254	93	66	8	7	
G	CF	4X	2.50	0.12	0.97	0.98	0.48	.303	84	79	15	10	
G	LIME	0.25X	2.00	0.21	0.77	0.90	0.40	.181	155	51	12	5	
G	LIME	0.50X	1.97	0.20	0.71	0.85	0.38	.175	119	65	7	6	
G	LIME	1X	2.17	0.20	0.93	0.93	0.40	.208	122	123	7	8	
G	LIME	2X	2.73	0.26	1.76	1.16	0.47	.299	148	209	17	9	
G	LIME	4X	2.90	0.38	2.31	1.34	0.45	.331	158	203	8	13	
G	LS	0.25X	2.27	0.19	0.73	0.89	0.39	.164	167	71	11	6	
G	LS	0.50X	2.27	0.16	0.68	0.95	0.40	.197	158	68	12	8	
G	LS	1X	2.13	0.17	0.68	0.84	0.40	.214	120	63	18	6	
G	LS	2X	2.40	0.12	0.68	0.90	0.42	.206	86	67	14	7	
G	LS	4X	2.50	0.12	1.00	1.15	0.46	.219	88	69	25	7	
T	NONE	0X	2.33	0.08	2.49	0.61	0.26	.274	138	57	49	3	
T	CF	0.25X	2.37	0.13	2.12	0.73	0.33	.388	135	65	70	6	
T	CF	0.50X	2.27	0.12	1.91	0.69	0.38	.348	132	71	54	5	
T	CF	1X	2.27	0.13	1.79	0.75	0.45	.317	109	75	33	7	
T	CF	2X	2.10	0.12	1.57	0.83	0.46	.241	62	72	10	4	
T	CF	4X	2.30	0.13	2.02	0.88	0.45	.388	84	71	9	5	
T	LIME	0.25X	2.50	0.10	1.88	0.70	0.29	.308	115	90	73	5	
T	LIME	0.50X	2.43	0.13	1.76	0.79	0.33	.338	90	82	39	6	
T	LIME	1X	2.20	0.10	1.52	0.88	0.32	.367	44	91	7	7	
T	LIME	2X	2.93	0.26	3.31	1.21	0.33	.630	71	429	6	13	
T	LIME	4X	2.97	0.22	3.18	1.08	0.31	.722	64	398	6	14	
T	LS	0.25X	2.40	0.13	1.77	0.77	0.33	.304	200	72	66	5	
T	LS	0.50X	2.47	0.14	1.65	0.95	0.42	.190	167	96	39	7	
T	LS	1X	2.57	0.16	1.47	1.04	0.48	.276	100	83	21	7	
T	LS	2X	2.93	0.14	1.85	1.15	0.45	.373	123	81	19	6	
T	LS	4X	4.43	0.13	2.38	1.43	0.43	.581	123	75	33	10	

§ G = Glenelg, S = State and T = Tatum.

¶ CF = Chemically-fixed sludge, Lime = CaCO₃ and LS = Lime-stabilized sludge.

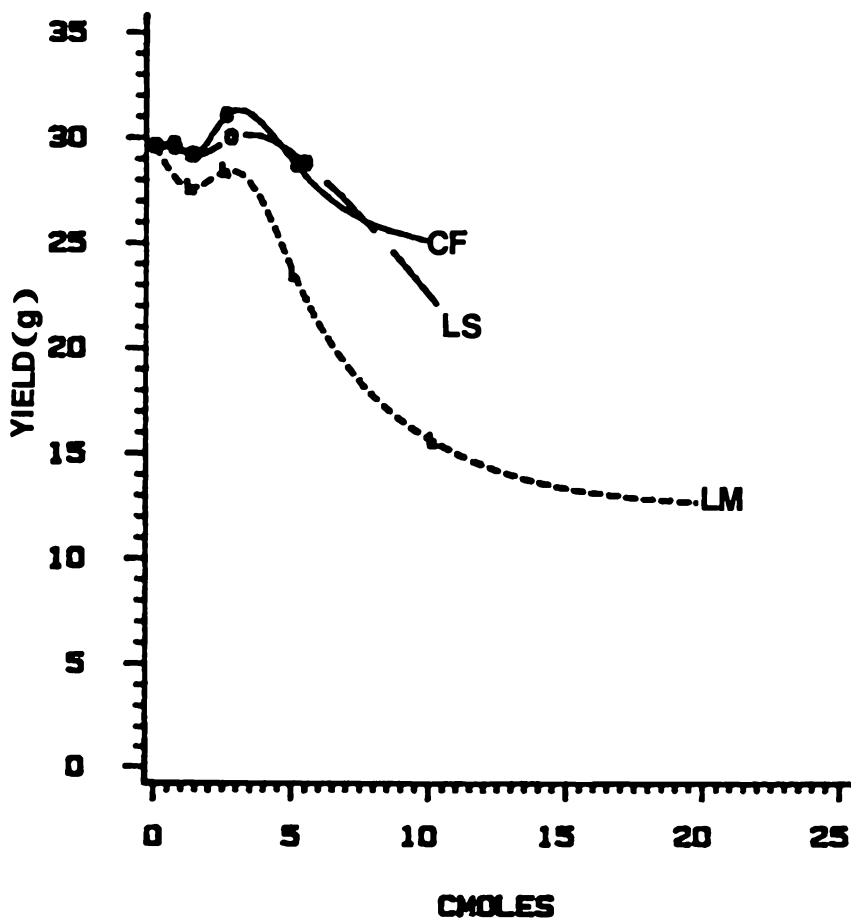


Figure 31. Influence of lime source and rate on corn dry weight on the Glencg soil.: CF = Chemically-fixed, LS = Lime-stabilized sludge and LM = CaCO_3 .

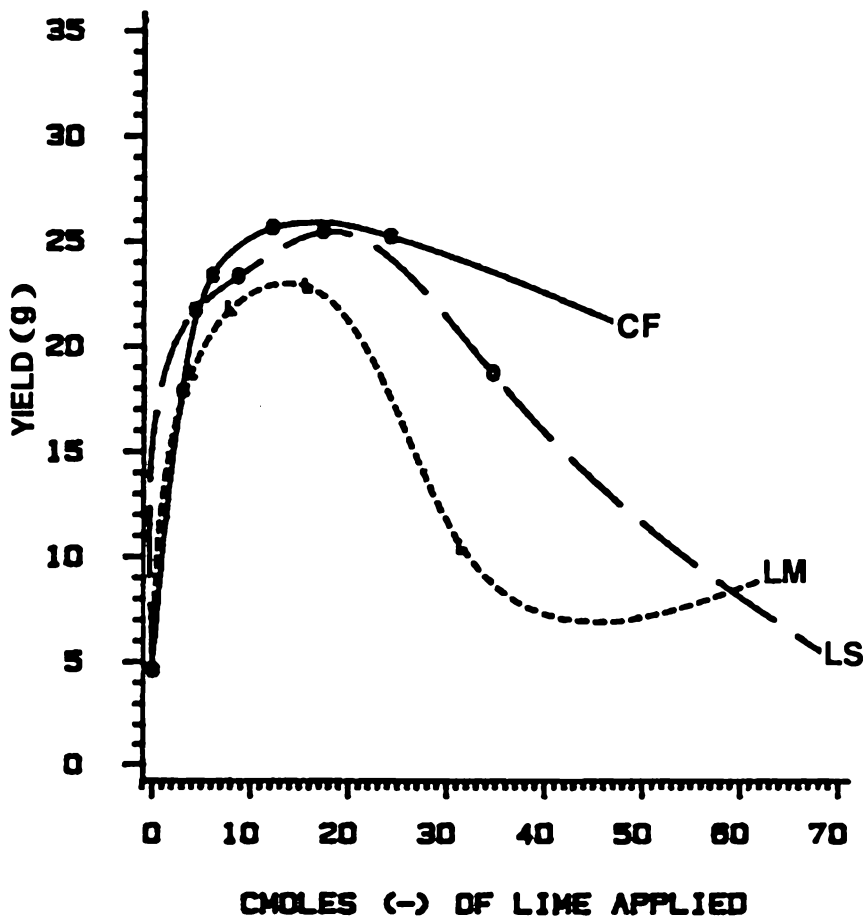


Figure 32. Influence of lime source and rate on corn dry weight on the Tatum soil.: CF = Chemically-fixed, LS = Lime-stabilized sludge and LM = CaCO₃.

Most of the remaining variability was associated with the use of different liming materials. This variable was also significant at the .0001 level of probability. On the Glenelg soil, the use of CaCO_3 produced significantly lower yields than the sludge treatments (Figure 31 on page 95). This was probably due to the low initial availability of Zn in the Glenelg soil which was indicated by DRIS. The fact that the sludges contained considerable quantities of Zn might explain why yields were higher when sludge was used as the lime source on the Glenelg soil than when CaCO_3 was used. The yields were highest at all rates on the Glenelg soil when the chemically-fixed sludge was applied although this was not a statistically significant increase. On the Tatum soil, the use of chemically-fixed sludge produced yields which were higher than when lime-stabilized sludge or CaCO_3 was applied (Figure 32 on page 96).

The use of all liming materials increased yields when compared to the zero rate of addition except for CaCO_3 on the Glenelg soil. Yields reached a maximum at 3 cmoles of lime addition on the Glenelg soil and about 15 cmoles on the Tatum soil and remained within 95% of maximum up to 6 and 25 cmoles, respectively, for both sludges but yields decreased with further amendment addition. This indicates that more sludge can be applied than predicted by CCE and lime requirement and still maintain yields within 95% of maximum (Table 18 on page 98). The application rates based on corn yield are close to those based on CCE and do not exceed application rates based on N. DRIS indicated that yields on the Glenelg soil were limited initially by Zn and the availability of Zn was reduced even further by the application of liming materials. Plants grown at the 4x rates, especially of CaCO_3 , on the Glenelg exhibited strong interveinal chlorosis and appeared stunted in growth. DRIS indicated that P availability was also reduced at the higher rates of addition. On the Tatum soil, DRIS indicated that P was the most limiting nutrient until lime rates became so high as to limit the availability of Zn which then became the most limiting factor to yields. Plants grown on the unamended Tatum soil exhibited stunted growth and purple coloring of the leaves and stems. The P deficiency was alleviated by liming but overliming created a Zn deficiency.

Table 18. Limits to yearly sludge application based on nitrogen, corn yield, lime or cadmium levels.

Soil	Sludge §	Limiting Factor			
		Nitrogen ¶	Yield ξ	Lime †	Cd
		-----Mg ha ⁻¹ -----			
Glenelg	CF	56.7	5.8	4.9	409.1
	LS	21.5	10.9	9.2	160.7
State	CF	56.7	---	5.2	409.1
	LS	21.5	---	9.7	160.7
Tatum	CF	56.7	24.1	15.0	409.1
	LS	21.5	45.3	28.3	160.7

§ CF = Chemically-fixed, LS = Lime-stabilized.

¶ Assumes a 49.28 Mg ha⁻¹ corn silage crop requiring 201.6 kg-N ha⁻¹; no previous sludge application and a N-mineralization factor of 0.32.

ξ Based on the greenhouse rate study with corn (State soil not included).

† Based on the Adams and Evans buffer procedure for lime requirement and CCE values of 30.9 and 58.1% for the lime-stabilized and chemically-fixed sludges, respectively.

Effect of Micronutrient and Sludge Addition on the Growth of Corn

The second greenhouse experiment was designed to investigate the role of micronutrients in the growth of corn as liming rates increase. The model which was described earlier explained nearly all of the variability in yield (Appendix D) with R^2 values exceeding .89 for all soils. The coefficients of variability ranged from 5.0% for the Glenelg soil to 13.5% for the State soil.

The most influential factor in this experiment was, again, the quantity of base applied. This factor was significant at the .0001 level of probability for all three soils despite a highly significant interaction with micronutrient application. Yield increases on the State soil at the 1x rate were apparently related to neutralization of exchangeable Al and increased availability of P and S.

Micronutrient application improved yields but could not compensate for overapplication of sludge or CaCO_3 (Figure 33 on page 101 - Figure 41 on page 109). This factor was significant at the .0001 level of probability on all soils despite the above mentioned interaction with rate and an interaction with liming materials on the Glenelg soil. The effect of micronutrient addition was to shift the yield limiting factor from a micronutrient to P (Table 19 on page 100).

Yield differences between liming materials were highly significant on all soils. Mean separation using Fishers LSD indicated that the chemically-fixed sludge produced the highest yields while lime-stabilized sludge and CaCO_3 did not produce different yields.

The interaction between micronutrient application and quantity of base applied was highly significant for all soils. This interaction indicates that the yield response due to the application of micronutrients was different at different amendment rates. This was expected since the solubilities of micronutrient cations, especially Mn and Zn, decrease with increasing pH. The largest yield increases due to the addition of micronutrients to the Glenelg and Tatum soils occurred at the 4x rate, especially when treated with CaCO_3 as was expected considering the effect of soil pH on the availability of micronutrient cations. However, the yield increases due to micronutrient addition on these two soils were not as great when sludges were applied because the sludges contained Zn. On the State soil, however, the largest yield increases from micronutrient addition occurred at the zero

Table 19. Effect of micronutrient addition and lime rate on the nutrient predicted by DRIS to limit corn yields in the micronutrient by lime rate greenhouse experiment.

Liming Material	Treatment Level	Micronutrient Addition	Soil		
			Glenelg	State	Tatum
Chemically Fixed Sludge	0x	no	Zn	Cu	P
		yes	P	P	P
	1x	no	Zn	Cu	P
		yes	P	P	P
4x	no	Zn	Zn	Zn	
	yes	P	P	P	
Lime Stabilized Sludge	0x	no	Zn	Cu	P
		yes	P	P	P
	1x	no	Zn	Cu	Zn
		yes	P	P	P
4x	no	Zn	Zn	P	
	yes	P	P	P	
CaCO ₃	0x	no	Zn	Cu	P
		yes	P	P	P
	1x	no	Zn	P	Zn
		yes	Cu	P	P
	4x	no	Zn	Zn	Zn
		yes	P	P	P

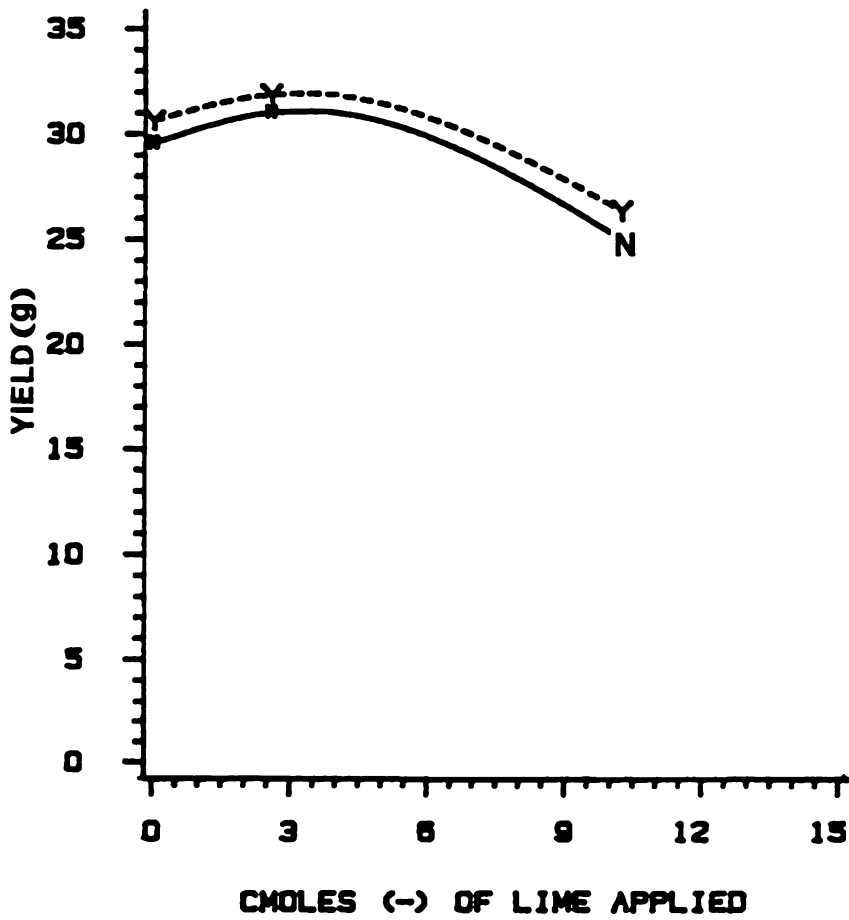


Figure 33. Influence of micronutrient addition on corn yields from the Glenelg soil amended with chemically-fixed sludge: Y = micronutrients added, N = no micronutrients added.

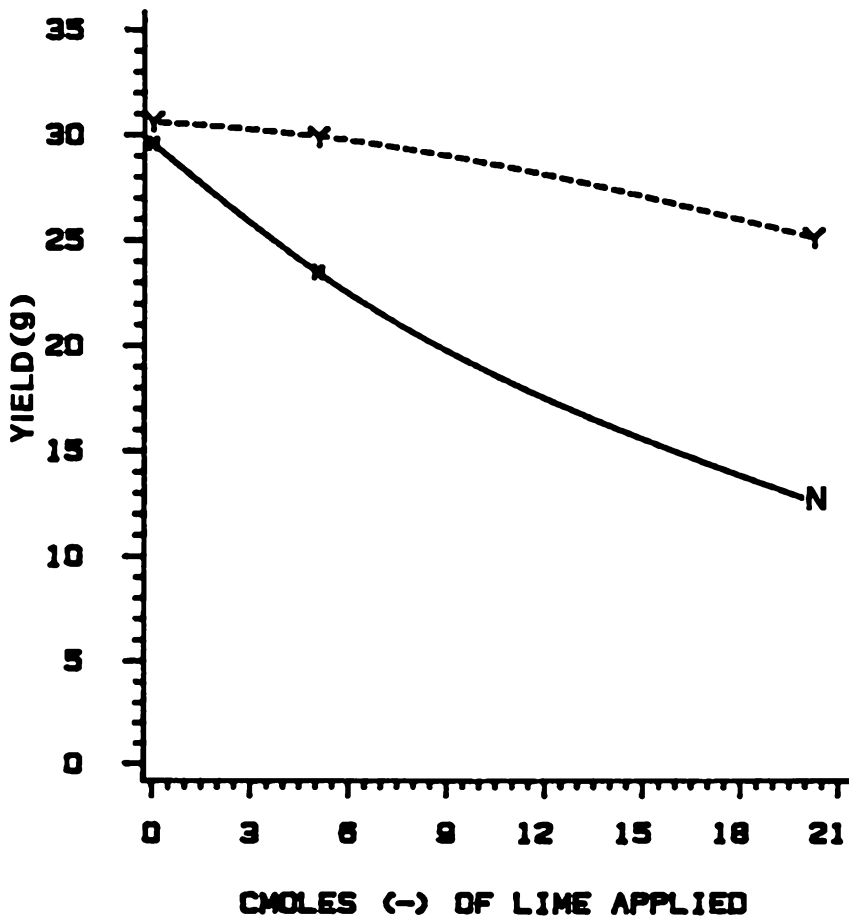


Figure 34. Influence of micronutrient addition on corn yields from the Glenelg soil amended with calcium carbonate.: Y = micronutrients added, N = no micronutrients added.

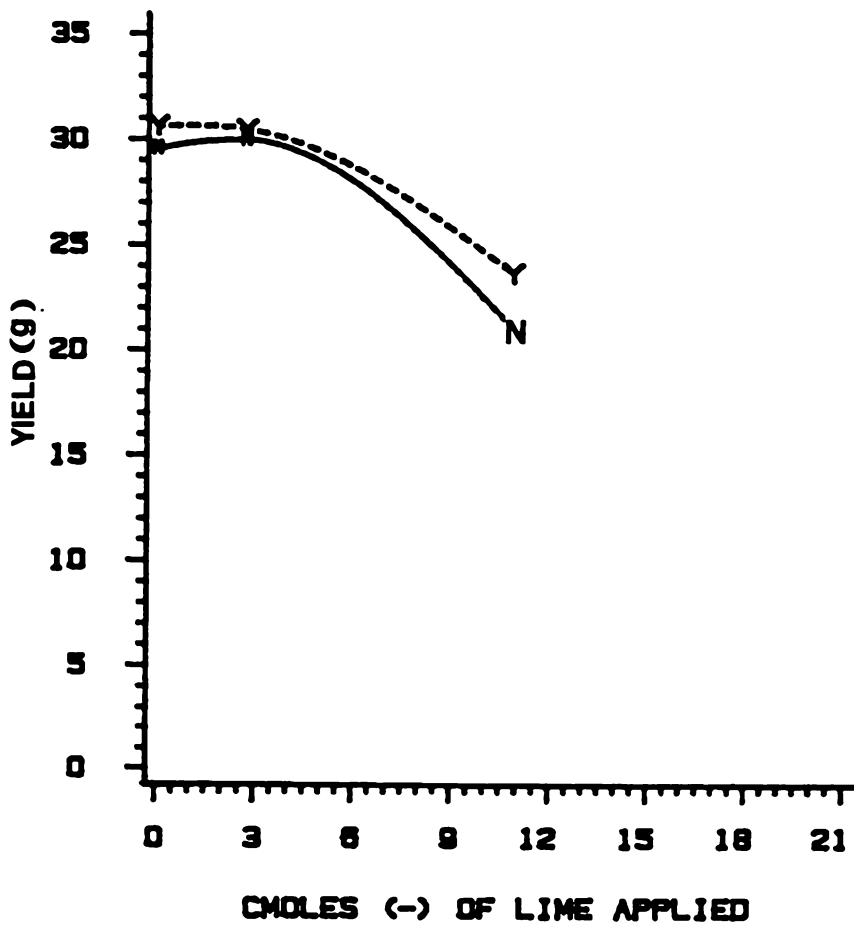


Figure 35. Influence of micronutrient addition on corn yields from the Glenelg soil amended with lime-stabilized sludge.: Y = micronutrients added, N = no micronutrients added.

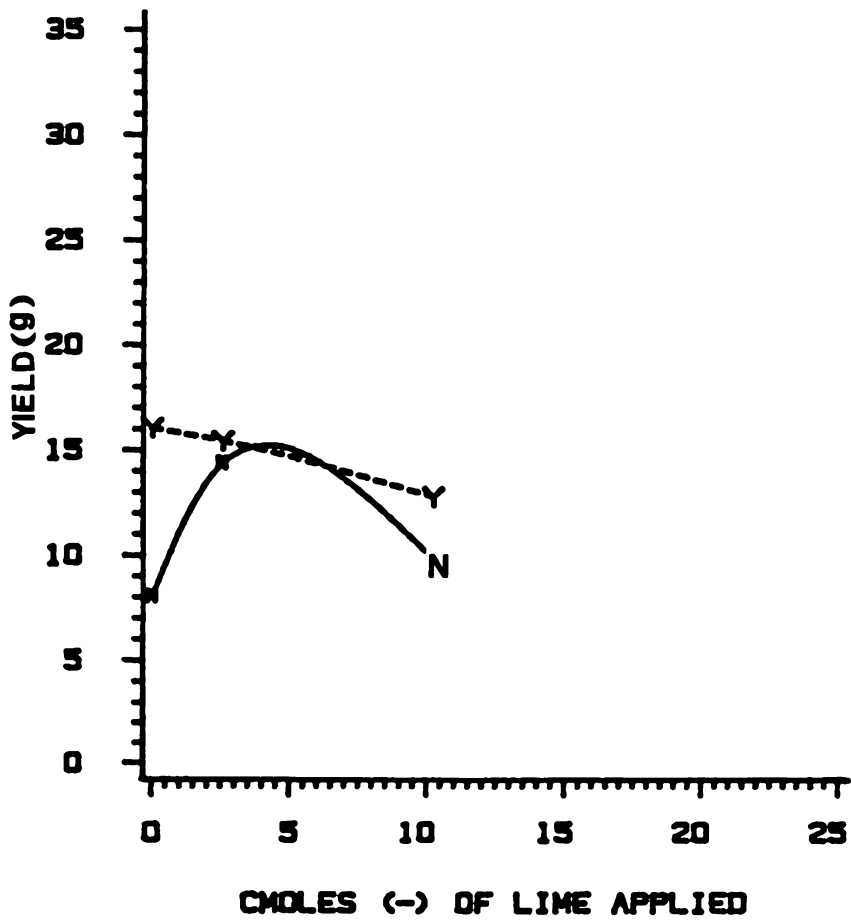


Figure 36. Influence of micronutrient addition on corn yields from the State soil amended with chemically-fixed sludge.: Y = micronutrients added, N = no micronutrients added.

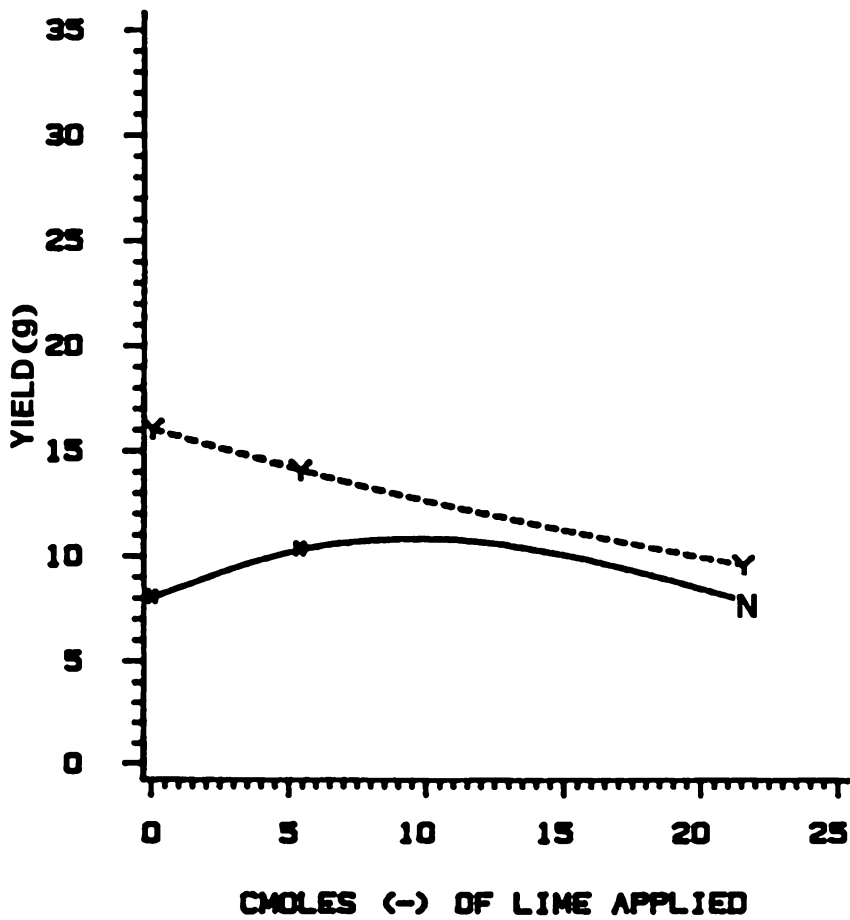


Figure 37. Influence of micronutrient addition on corn yields from the State soil amended with calcium carbonate.: Y = micronutrients added, N = no micronutrients added.

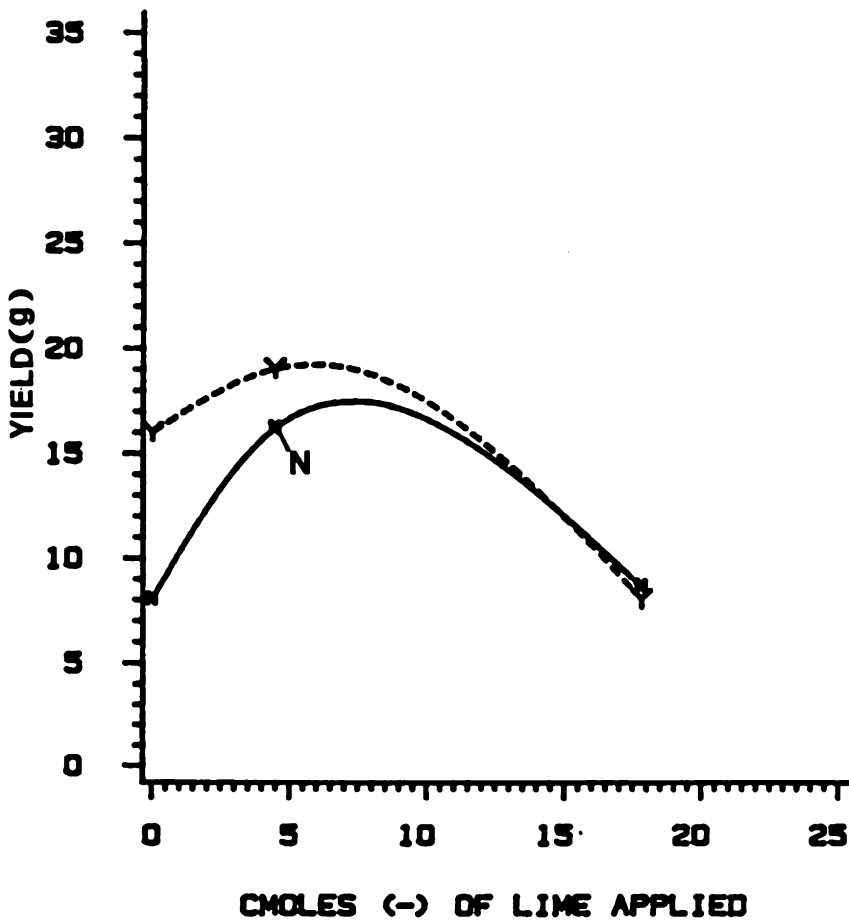


Figure 38. Influence of micronutrient addition on corn yields from the State soil amended with lime-stabilized sludge.: Y = micronutrients added, N = no micronutrients added.

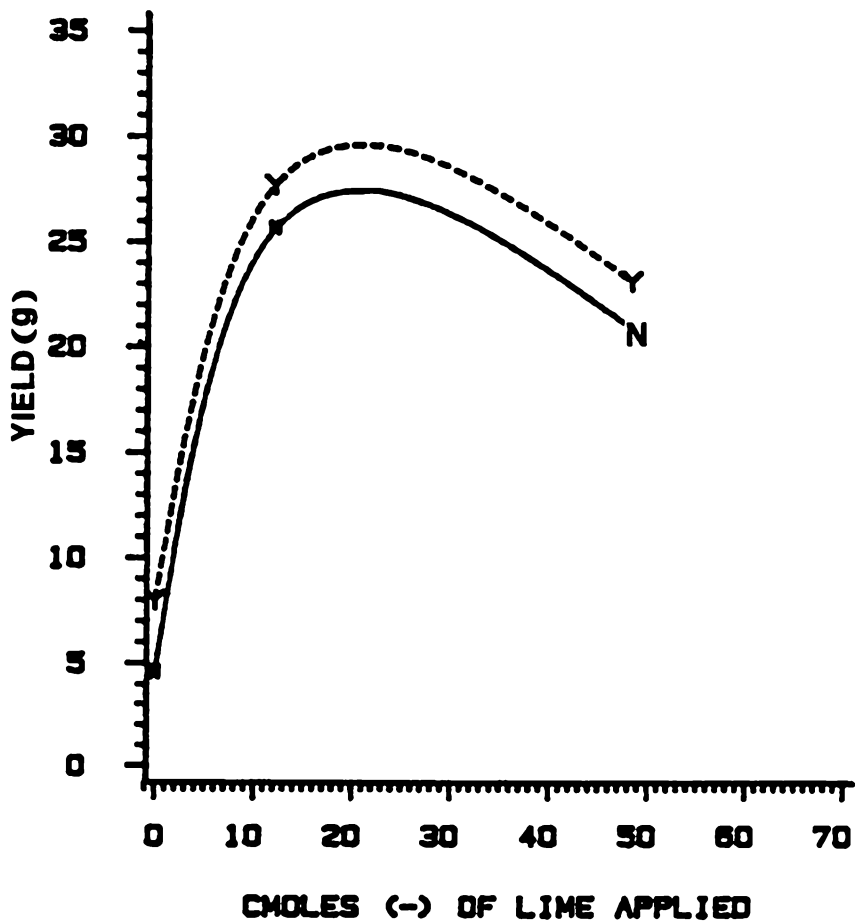


Figure 39. Influence of micronutrient addition on corn yields from the Tatum soil amended with chemically-fixed sludge.: Y = micronutrients added, N = no micronutrients added.

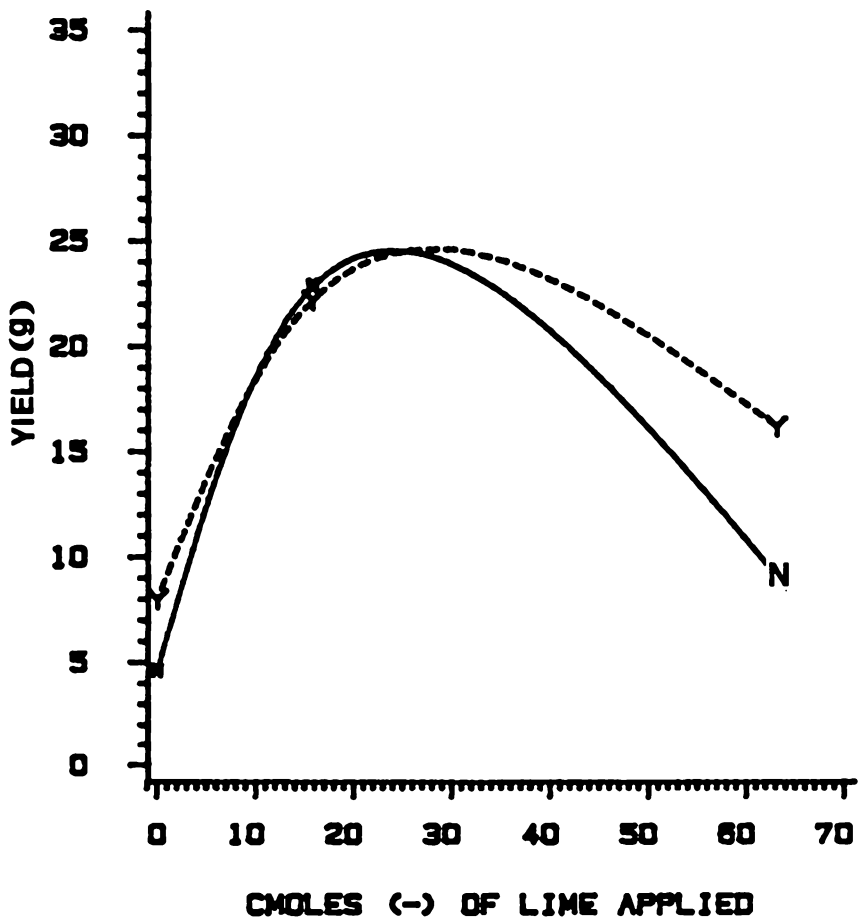


Figure 40. Influence of micronutrient addition on corn yields from the Tatum soil amended with calcium carbonate.: Y = micronutrients added, N = no micronutrients added.

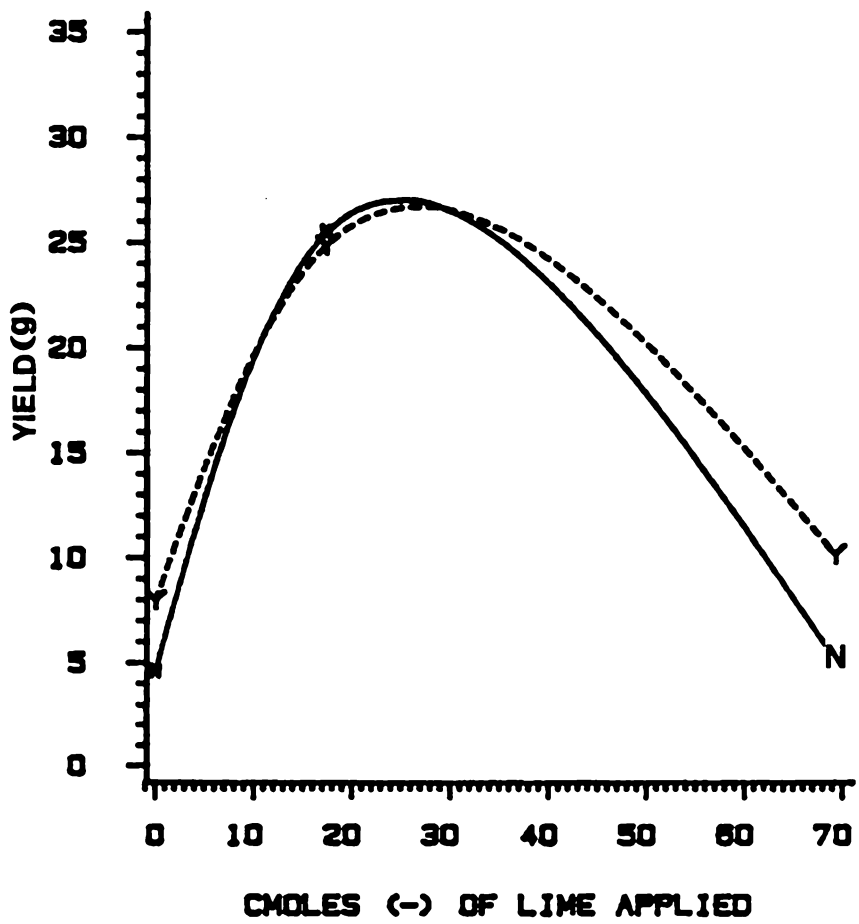


Figure 41. Influence of micronutrient addition on corn yields from the Tatum soil amended with lime-stabilized sludge.: Y = micronutrients added, N = no micronutrients added.

rate of addition. DRIS indicated that Cu was the yield limiting factor in the unamended State soil. It has been shown that the affinity of organic ligands for Cu decreases as soil pH increases toward 7.0 (Bohn et al., 1979). The decreased affinity may have made Cu more available and helped reduce the yield differences at higher rates. However, experimentation of Lucas and Knezek (1972) indicates that soil pH does not greatly affect Cu uptake. DRIS did not take into consideration the tissue concentrations of S. Although soil S was not analyzed, it is likely that levels of soil S were low in the State soil as is often the case in leached sandy soils low in organic matter (Reneau, 1983). The concentrations of S in the corn tissue grown in the unamended State soil (Table 20 on page 111) were very close to the sufficiency level of 0.2% reported by Bates (1984) and Jones and Eck (1973) but the ratios of N to S were greater than 16 in the unamended State soil indicating that yields probably would be increased by the addition of S (Reneau, 1983) and plants grown on the unamended State soil were light green and stunted with striping of the upper leaves. These are symptoms of S deficiency (Follett et al., 1981). As soil pH is increased, SO_4^{2-} is desorbed from soil surfaces (Elkins and Ensminger, 1971). The addition of micronutrient cations as SO_4^{2-} would add enough S to correct a S deficiency and promote a yield increase. Raising the pH of an acid soil would cause SO_4^{2-} to be desorbed and decrease the deficiency, thus reducing the influence of micronutrient addition as SO_4^{2-} . The use of the sludges as lime sources reduced the yield advantage due to micronutrient addition because the sludges contained SO_4^{2-} . Plants grown with sludges were much greener than those plants amended with CaCO_3 .

The interaction between liming materials and micronutrient addition was only significant for the Glenelg soil. The interaction was highly significant and can be explained using Table 21 on page 113. More moles of CaCO_3 were applied to the Glenelg soil than lime-stabilized or chemically-fixed sludge because the rates of CaCO_3 were derived from the Adams and Evans buffer recommendation instead of from the incubation study. Consequently, when the lime source was CaCO_3 , the pH was higher than when the sludges were used. This caused the solubility of Zn in the Glenelg soil to be reduced more at the higher rates and the response to added Zn increased. This conclusion was supported by DRIS. The differences in yield due to adding micronutrients to

Table 20. Effect of micronutrient addition, lime source and lime rate on elemental composition of corn.

Soil §	Lime Source ¶	Treatment Level	Element										
			N	P	K	Ca	Mg	S	Mn	Fe	Zn	Cu	
			%						mg kg ⁻¹				
G	NONE	0X	2.17	0.19	0.66	0.83	0.38	.254	209	61	12	6	
G	NONE	0X ξ	2.53	0.19	0.93	0.81	0.42	.259	188	86	135	8	
G	CF	1X	2.13	0.17	0.66	0.86	0.40	.204	108	58	9	5	
G	CF	1X ξ	2.57	0.17	0.97	0.96	0.47	.288	102	71	69	6	
G	CF	4X	2.50	0.12	0.97	0.98	0.48	.303	84	79	15	10	
G	CF	4X ξ	2.50	0.13	0.85	0.96	0.53	.345	70	70	39	11	
G	LIME	1X	2.17	0.20	0.93	0.93	0.40	.208	122	123	7	8	
G	LIME	1X ξ	2.30	0.14	0.62	0.86	0.42	.318	67	58	52	4	
G	LIME	4X	2.90	0.38	2.31	1.34	0.45	.331	158	203	8	13	
G	LIME	4X ξ	2.20	0.12	0.81	0.99	0.40	.279	53	70	33	5	
G	LS	1X	2.13	0.17	0.68	0.84	0.40	.214	120	63	18	6	
G	LS	1X ξ	2.47	0.19	1.09	1.00	0.51	.494	114	66	80	9	
G	LS	4X	2.50	0.12	1.00	1.15	0.46	.219	88	69	25	7	
G	LS	4X ξ	2.53	0.12	1.11	1.08	0.52	.359	91	69	51	8	
S	NONE	0X	4.30	0.61	3.62	1.05	0.47	.274	398	51	102	5	
S	NONE	0X ξ	3.57	0.27	2.81	0.85	0.48	.540	557	89	272	10	
S	CF	1X	3.37	0.33	3.17	1.02	0.43	.347	234	63	56	4	
S	CF	1X ξ	.	0.30	2.94	0.97	0.51	.536	355	73	160	9	
S	CF	4X	3.25	0.22	3.98	1.13	0.50	.481	73	84	19	7	
S	CF	4X ξ	3.53	0.21	3.22	1.05	0.50	.503	100	81	53	8	
S	LIME	1X	3.10	0.25	3.42	1.20	0.41	.285	116	50	34	4	
S	LIME	1X ξ	3.43	0.22	2.73	1.16	0.49	.395	188	103	90	8	
S	LIME	4X	3.13	0.22	3.82	1.34	0.40	.325	53	64	14	4	
S	LIME	4X ξ	3.37	0.21	4.34	1.20	0.43	.502	91	80	47	7	
S	LS	1X	3.00	0.19	2.58	1.06	0.46	.382	204	134	52	6	
S	LS	1X ξ	3.37	0.23	2.28	1.03	0.54	.489	242	98	115	9	
S	LS	4X	3.43	0.22	4.02	1.58	0.42	.578	84	80	24	10	
S	LS	4X ξ	3.37	0.21	4.29	1.61	0.44	.436	109	74	47	9	
T	NONE	0X	2.33	0.08	2.49	0.61	0.26	.274	138	57	49	3	
T	NONE	0X ξ	2.53	0.10	2.29	0.57	0.30	.468	357	73	312	10	
T	CF	1X	2.27	0.13	1.79	0.75	0.45	.317	109	75	33	7	
T	CF	1X ξ	2.43	0.15	1.38	0.76	0.46	.391	167	91	76	8	
T	CF	4X	2.30	0.13	2.02	0.88	0.45	.388	84	71	9	5	
T	CF	4X ξ	2.17	0.12	1.73	0.86	0.46	.329	93	70	23	5	
T	LIME	1X	2.20	0.10	1.52	0.88	0.32	.367	44	91	7	7	
T	LIME	1X ξ	2.07	0.20	2.13	1.16	0.46	.522	66	77	33	8	
T	LIME	4X	2.97	0.22	3.18	1.08	0.31	.722	64	398	6	14	
T	LIME	4X ξ	1.87	0.08	1.86	0.90	0.31	.253	47	65	16	8	
T	LS	1X	2.57	0.16	1.47	1.04	0.48	.276	100	83	21	7	
T	LS	1X ξ	2.53	0.14	1.33	0.91	0.49	.319	150	79	49	8	
T	LS	4X	4.43	0.13	2.38	1.43	0.43	.581	123	75	33	10	
T	LS	4X ξ	3.90	0.15	2.49	1.38	0.50	.566	146	88	50	12	

§ G = Glenelg, S = State and T = Tatum.

¶ CF = Chemically-fixed sludge, Lime = CaCO₃ and LS = Lime-stabilized sludge.

ξ Micronutrients added.

the Glenelg soil amended with CaCO_3 was greater than with the other liming amendments because the rates were larger for CaCO_3 .

Table 21. Quantities of base applied in the micronutrient by lime rate greenhouse experiment at the 1x level.

Liming Material	Soil		
	<u>Glenn</u>	<u>State</u>	<u>Tatum</u>
	-----cmoles-----		
CaCO ₃	5.1	5.4	15.8
LS §	2.7	4.4	17.3
CF ¶	2.6	2.6	12.4

§ Lime-stabilized sludge.

¶ Chemically-fixed sludge.

Chapter V

SUMMARY

Lime Reaction.

The lime component of the sludges reacted very quickly with soil acidity. Rates predicted to raise soil pH to 6.5 using the Adams and Evans buffer and sludge CCE raised pH above 6.5 in the incubation studies. The cause of overestimation of rates may have been the correction factor of 1.5 employed by Adams and Evans (1962) to correct for incomplete mixing of lime with soil and slow reaction of CaCO_3 with soil acidity. It is not known if lime rates would be overestimated under field conditions. The pH of all treatments including the control decreased with increased incubation time. This decrease in soil pH may or may not occur under field conditions so field studies are needed to determine the effect of application rate on soil pH in the field. The CCE of lime-stabilized and chemically-fixed sludges was the factor which limited application rates in all cases except application of the lime-stabilized sludge to the acid Tatum B horizon.

Nitrogen mineralization.

Organic-N applied to the Glenelg and State soils mineralized at an average rate of 32%. This mineralization rate is higher than has been reported for most biologically stabilized sludges. Easily decomposable N containing organic compounds were probably still present after stabilization. Organic-N appeared to mineralize at a much lower rate on the Tatum B horizon soil. Organic-N was mineralized at only 11.25% after 20 weeks of incubation in the Tatum soil. The lower mineralization rates in the Tatum soil may have been lowered artificially by NH_4^+ "fixation". In only one case in this study would sludge application be limited by N application. This occurred when the lime-stabilized sludge was applied to the acid Tatum B horizon.

Greenhouse Studies.

The use of lime-stabilized and chemically-fixed sludges as lime sources on acid soils for the growth of corn resulted in yield increases up to the 1x rate and yields remained within 95% of maximum yield at application rates of up to 118% of the 1x rate on the Glenelg soil and 160% of the 1x rate on the Tatum soil. When sludges or CaCO_3 were applied in larger quantities yield decreases resulted from decreased availability of Zn and P. Yields were depressed less when the sludges were applied than when CaCO_3 was applied due to the content of nutrients in the sludges.

The application of micronutrients to the soil improved yields in most cases but never compensated for the reduction in yields which occurred at the 4x rates of sludge addition. Application rates of lime-stabilized and chemically-fixed sludges greater than those designed to neutralize soil acidity cannot be justified by the application of micronutrients to the soil.

Lime-stabilized and chemically-fixed sludges are superior lime sources and contribute to the fertility requirements of the crop. Field studies are needed to determine true field application rates since greenhouse results are not always directly applicable to field conditions.

Chapter VI

CONCLUSIONS

1. Lime-stabilized and chemically-fixed sludge addition raised soil pH and neutralized exchangeable Al very rapidly.
2. The chemically-fixed sludge was a more effective liming agent than the lime-stabilized sludge.
3. Rates designed to raise soil pH to 6.5 increased soil pH above the desired level initially but pH declined with increased incubation time. It is not known whether the decline in soil pH will occur under field conditions.
4. The method for determining sludge CCE needs to be improved, possibly by using an acidic buffer.
5. Nitrogen was mineralized at equal rates for both the lime-stabilized and chemically-fixed sludges. The mineralization rate was relatively high when sludges were mixed with surface soils (approximately 32% of added organic-N).

6. The factor which would limit application rates of lime-stabilized and chemically-fixed sludges is the CCE and lime requirement based on the Adams-Evans buffer. The lime requirement becomes rate limiting before N or Cd. Even though field data is not available, it appears that sludge CCE would limit application rates of lime-stabilized and chemically-fixed sludges except in very acid soils such as the Tatum cl used in the present study. Nitrogen would limit application rates of lime-stabilized sludge on the acid Tatum B horizon.
7. Moderate sludge and lime additions improved yields on the acid State and Tatum soils. Yield increases were probably attributable to neutralization of acidity and increased availability of S for the State and P for the Tatum soils.
8. Yields on the Glenelg soil were limited by the availability of Zn at all levels of sludge application. The addition of sludges and especially lime decreased the availability of Zn which resulted in yield reductions.
9. At the high rates of CaCO_3 addition to the Glenelg soil yields were reduced more than with sludge application. This is attributed to the fact that the sludges contained plant nutrients, especially Zn and P.
10. Yields on all soils were reduced at the 4x levels of sludge or lime addition. These reductions were associated with reduced availability of Zn and P.
11. Yields on the Glenelg and Tatum soils remained within 95% of maximum at sludge application rates up to 118 and 160%, respectively, of the 1x greenhouse rates. The higher rates were still lower than the N requirement of a corn crop except on the Tatum B horizon using lime-stabilized sludge.
12. Yields were higher when micronutrients were applied. Although micronutrients reduced the effect of overliming, yields at the high rates of addition were still depressed below those at the 1x level. Micronutrient addition would not allow for increased sludge application.

13. Annual sludge application rates for corn on all but the most acid soils would be limited by the CCE of these sludges. Application of these sludges to supply the N requirements of a corn crop would exceed the lime requirement and result in a Zn deficiency on most soils. Application rates might be higher for a crop which grows well at higher soil pH values.

14. Lime-stabilized and chemically-fixed sludges are effective liming agents. Additional field research correlating lime addition with pH and yield would allow refinement of current recommendations.

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Appendix A

Descriptions of soils.

Gleneig Description

Surface soil -

Ap 0 to 8 inches, dark brown channery silt loam; weak, fine, subangular blocky to coarse crumb structure; friable when moist; roots plentiful; mica flakes common; about 20 percent fragments of channery phyllite; strongly acid; abrupt, smooth boundary.

Subsoil -

B2 8 to 20 inches, yellowish red channery silty clay loam; moderate, fine subangular blocky structure; friable when moist, and plastic when wet. Roots fairly common; continuous clay strong of yellowish red; mica flakes plentiful; about 15% fragments of channery phyllite strongly acid; gradual, smooth to wavy boundary.

B3C 20 to 37 inches; partly weathered phyllite in a matrix of yellowish red, micaceous silt loam; matrix has a moderate, fine, subangular blocky structure; friable when moist; a few roots; some discontinuous, yellowish red clay skins and a few, irregular, dark, reddish brown stains on structural faces; about 50% partly weathered fragments of channery phyllite, many very small; very strongly acid; clear to abrupt, wavy to irregular boundary.

Substratum -

C 37 to 62 inches, weathered, and partially weathered phyllitic schist.

D 62 inches, hard, unweathered phyllite.

State Description

Surface soil -

- Ap 0 to 9 inches, grayish brown, sandy loam; weak, fine granular structure; moist friable, roots plentiful; abrupt, smooth boundary.
- Bt1 9 to 23 inches, strong brown, loamy; weak medium subangular blocky structure; moist friable; many fine roots; clear smooth boundary.
- Bt2 23-30 inches, strong brown, sandy loam texture, weak medium subangular blocky structure; moist friable consistence; few fine roots; few fine mica flakes; clear smooth boundary.
- BCt 30 to 39 inches, variegated, yellowish brown, and brownish yellow loamy coarse sand; coarse subangular blocky structure; moist very friable consistence; few fine roots; discontinuous smooth boundary.
- Ct 39 to 70 inches, yellowish brown, very pale brown variegated, loamy coarse sand; massive structure; moist loose consistence.

Tatum Description

Surface soil -

- Ap 0-8 inches, yellowish brown silt loam; moderate, fine, granular structure; moist, friable consistence; many fine and medium roots; common small quartz pebbles; strongly acid; clear, smooth boundary.
- B1t 8 to 13 inches, yellowish red, silty clay loam; weak, fine, and medium; subangular blocky structure; moist-friable consistence; few clay films; many medium and coarse roots; many fine and medium pores; few small quartz pebbles; very strongly acid; clear, smooth boundary.
- B21t 13 to 18 inches, red silty clay; moderate, medium, subangular blocky structure; moist friable, common patchy clay films; common medium and coarse roots; few small fragments of quartz; very strongly acid, gradual boundary.
- B22t 18 to 30 inches, red silty clay; strong, medium and fine subangular blocky structure; moist friable to moist firm consistence; common, distinct, continuous clay films; common medium and fine pores; few weathered fragments of schist; and few small fragments of quartz; few very fine mica flakes; very strongly acid; gradual, smooth boundary.
- B3t 30 to 45 inches, red silty clay loam streaked with yellowish red and strong brown; moderate to weak, fine subangular blocky structure; moist friable; common, thin, patchy clay films; many fragments of weathered schist; few quartz pebbles; very strongly acid; irregular, wavy boundary.
- R 47 inches to hard multicolored, fine grained schist.

Appendix B

Analyses of variance for the lime reaction experiments.

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: PHM

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	51	67.44662933	1.32248293	45.71	0.0001	0.959660	2.6565
ERROR	98	2.83519467	0.02893056		ROOT MSE		PHM MEAN
CORRECTED TOTAL	149	70.28182400			0.17008985		6.40280000

SOURCE	DF	ANOVA SS	F VALUE	PR > F
REP	2	0.02107200	0.36	0.6957
MAT	1	0.11985067	4.14	0.0445
TIME	4	30.34039067	262.18	0.0001
MAT*TIME	4	0.03896933	0.34	0.8526
MEQ(MAT)	8	36.08513333	155.91	0.0001
TIME*MEQ(MAT)	32	0.84121333	0.91	0.6101

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = MOLES OF SLUDGE APPLIED

SOIL=STATE
ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: PHH

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	51	57.29683667	1.12346739	58.61	0.0001	0.968255	2.1076
ERROR	98	1.87855067	0.01916888		ROOT MSE		PHH MEAN
CORRECTED TOTAL	149	59.17538733			0.13845174		6.56913333

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SOURCE	DF	ANOVA SS	F VALUE	PR > F
REP	2	0.08304933	2.17	0.1201
MAT	1	0.02136067	1.11	0.2937
TIME	4	18.39326400	239.88	0.0001
MAT*TIME	4	0.33282933	4.34	0.0028
MEQ(MAT)	8	37.17552000	242.42	0.0001
TIME*MEQ(MAT)	32	1.29081333	2.10	0.0028

REP = REPLICATION
MAT = SLUDGE TYPE
MEQ = CHOLS OF SLUDGE APPLIED

SAS
SOIL=TATUM

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ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: PHM

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	51	138.59161200	2.71748259	43.50	0.0001	0.957691	4.0655
ERROR	98	6.12266533	0.06247618			ROOT MSE	PHM MEAN
CORRECTED TOTAL	149	144.71427733				0.24995235	6.14813333

SOURCE	DF	ANOVA SS	F VALUE	PR > F
REP	2	0.05540133	0.44	0.6431
MAT	1	2.81809067	45.11	0.0001
TIME	4	21.71383733	86.89	0.0001
MAT*TIME	4	3.62369600	14.50	0.0001
MEQ(MAT)	8	105.98774667	212.06	0.0001
TIME*MEQ(MAT)	32	4.39284000	2.20	0.0017

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = CHOLS OF SLUDGE APPLIED

Appendix C

Analyses of variance for the greenhouse lime rate experiments.

SAS
SOIL = GLENELG

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GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YLD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	19	1382.63025449	72.77001339	10.30	0.0001	0.762421	9.7327
ERROR	61	430.84214190	7.06298593			ROOT MSE	YLD MEAN
CORRECTED TOTAL	80	1813.47239640				2.65762788	27.30608642

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
MAT	2	279.85909847	19.81	0.0001	2	290.28124070	20.55	0.0001
REP	2	12.40654077	0.88	0.4207	2	12.40654077	0.88	0.4207
MEQ(MAT)	15	1090.36461526	10.29	0.0001	15	1090.36461526	10.29	0.0001

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = CHOLES OF SLUDGE APPLIED

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YLD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	19	4695.35270374	247.12382651	51.98	0.0001	0.942726	12.9725
ERROR	60	285.25972365	4.75432873			ROOT MSE	YLD MEAN
CORRECTED TOTAL	79	4980.61242739			2.18044232		16.80821250

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
MAT	2	330.41413235	34.75	0.0001	2	291.26556182	30.63	0.0001
REP	2	2.34378717	0.25	0.7823	2	6.19774789	0.65	0.5248
MEQ(MAT)	15	4362.59478422	61.17	0.0001	15	4362.59478422	61.17	0.0001

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = CHOLS OF SLUDGE APPLIED

Appendix D

**Analyses of variance for the greenhouse lime rate by
micronutrient experiments.**

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YLD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	19	1209.20176063	63.64219793	33.06	0.0001	0.948656	5.0865
ERROR	34	65.44568352	1.92487304			ROOT MSE	YLD MEAN
CORRECTED TOTAL	53	1274.64744415			1.38739794		27.27581481

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
MAT	2	137.32679915	35.67	0.0001	2	137.32679915	35.67	0.0001
REP	2	2.62259848	0.68	0.5128	2	2.62259848	0.68	0.5128
MIC	1	126.43308119	65.68	0.0001	1	126.43308119	65.68	0.0001
MAT*MIC	2	89.50030781	23.25	0.0001	2	89.50030781	23.25	0.0001
MIC*MEQ(MAT)	12	853.31897400	36.94	0.0001	6	102.49162767	8.87	0.0001
MEQ(MAT)	0	0.00000000			6	750.82734633	65.01	0.0001

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = CMOLLES OF SLUDGE APPLIED
 MIC = MICRONUTRIENTS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YLD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	19	732.97284946	38.57751839	14.40	0.0001	0.889486	13.5189
ERROR	34	91.06801752	2.67847110			ROOT MSE	YLD MEAN
CORRECTED TOTAL	53	824.04086698				1.63660353	12.10601852

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
MAT	2	35.54951659	6.64	0.0037	2	35.54951659	6.64	0.0037
REP	2	6.62039715	1.24	0.3033	2	6.62039715	1.24	0.3033
HIC	1	211.44427824	78.94	0.0001	1	211.44427824	78.94	0.0001
MAT*MIC	2	2.46787748	0.46	0.6347	2	2.46787748	0.46	0.6347
HIC*MEQ(MAT)	12	476.89078000	14.84	0.0001	6	125.98803344	7.84	0.0001
MEQ(MAT)	0	0.00000000	.	.	6	350.90274656	21.83	0.0001

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = MOLES OF SLUDGE
 MIC = MICRONUTRIENTS

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: YLD

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	19	3957.06137426	208.26638812	111.16	0.0001	0.984616	9.0467
ERROR	33	61.82800891	1.87357603			ROOT MSE	YLD MEAN
CORRECTED TOTAL	52	4018.88938317				1.36878633	15.13030189

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
MAT	2	278.70155118	74.38	0.0001	2	289.39333009	77.23	0.0001
REP	2	0.20510839	0.05	0.9468	2	1.09828226	0.29	0.7479
HIC	1	118.76254798	63.39	0.0001	1	103.92955891	55.47	0.0001
MAT*MIC	2	1.17823674	0.31	0.7324	2	1.46176535	0.39	0.6801
HIC*HEQ(MAT)	12	3558.21392998	158.26	0.0001	6	69.12006127	6.15	0.0002
HEQ(MAT)	8	0.00000000	.	.	6	3468.91441794	308.58	0.0001

REP = REPLICATION
 MAT = SLUDGE TYPE
 MEQ = CMOLS OF SLUDGE APPLIED
 MIC = MICRONUTRIENTS

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