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THE EFFECT OF TEMPERATURE AND SOIL ACIDITY ON THE DECOMPOSITION RATE OF MANURE

By

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ABSTRACT

THE EFFECT OF TEMPERATURE AND SOIL ACIDITY ON THE DECOMPOSITION RATE OF MANURE

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Laboratory incubation studies were conducted to determine the effect of low temperature (3.5, 5.0, 10.0, 12.5°C) on NO_3^- transformations in a Spinks sandy loam soil (Psammentic Hapludalfo, sandy mixed, mesic) amended with fresh heifer or liquid beef manure. In addition, the effect of low pH, high Al on mineralization or nitrification processes in manure treated soil was evaluated. The surface charge of the low pH, high ex-Al amended with manure was also measured at two ionic strengths (0.02 and 0.005 mol kg^{-1}) and at pH values ranging from 3.5 to 6.5.

Ammonification was temperature dependent and increased with temperature up to 7 days. For fresh manure NH_4^+ concentration continued to increase up to 28 days at 3.5, and 5.0 °C. Nitrate level was low at all times, therefore this manure could be applied when soil temperature is <5 °C.

The concentration of NH_4^+ in soil amended with liquid beef manure reached a maximum in 7 days and was constant after that time. There was low or undetected NO_3^- concentration up to 28 days; thus, the application of liquid manure could be made with minimum loss of NO_3^- whenever soil temperature reaches 10 °C. At temperature 12.5 °C NO_3^- concentration in the control was higher than in fresh heifer or in liquid beef manure treated samples.

Manure addition significantly increased the pH of high ex-Al soils. At low, and medium concentration of ex-Al, NH_4^+ concentration increased with time before decreasing by the conclusion of the study. But NO_3^- level was lower whenever manure application was made and decreased with time. Manure application decreased the concentration of ex-Al with a more significant effect at lower Al concentrations.

The surface charge, and Ca adsorption of low pH, high Al soils increased with pH. At a given pH, manure application did not increase Ca adsorption or net charge. However the surface charge of manure treated soils was slightly higher than the control in the pH range of 4.5 to 5.0. Both Ca adsorption and surface charge were higher at high ionic strength. Ultimately the information obtain from this study can help in designing cropping systems where N may be efficiently used.

To my son Charles Christian and
my major advisor Dr. B. G. Ellis.

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CHAPTER I

INTRODUCTION AND REVIEW OF LITERATURE

INTRODUCTION

Organic matter and nitrogen (N) are important factors in cropping systems. Organic matter contributes a great deal to physical, chemical and biological properties of the soil. One of the most challenging problems facing farmers in developed or developing countries is to obtain maximum value of N and organic matter from organic wastes or natural organic materials. Thus, mineralization and nitrification have been the focus of considerable recent interest due to (1) the use of land for the disposal of large quantities of organic materials, either as digested sewage sludge from urban regions or as animal manure from feedlots containing thousands of cattle, chicken or pigs, in the temperate regions of the world, and (2) concerns of developing sustainable cropping systems which will cycle the available nutrients in the humid tropics.

When temperature, soil pH and moisture conditions are adequate for microbial growth, mineralization of organic matter and nitrification are often rapid, resulting in production of more nitrate than can be used immediately by

agronomic crops. Since nitrate partitions strongly to the water phase in many soils, it is susceptible to leaching. This leaching causes losses from soils of nitrogen which is essential for crop production. Nitrate, even though an important ion in plant nutrition, may be a significant environmental pollutant. Thus, N lost to the environment is undesirable because of its potential role in (1) eutrophication (enrichment of waters with nutrients which causes excessive growth of algae) and (2) infant and animal methemoglobinemia.

The rate of organic matter decomposition is governed by the soil forming factors climate, vegetation, relief or topography, parent material, and time.

Because of a faster growth rate of tropical forests, the annual amount of fresh organic matter, added to the tropical forest soil is 5 fold higher than that in temperate regions. Temperate prairies develop more abundant root systems; whereas, growth in tropical savannas is often limited by low nutrient availability (Sanchez, 1976).

In the tropical regions, temperature is seldom considered as an important factor limiting plant growth except for two instances in which soil temperatures can be limiting: (1) a very high temperature in the surface of certain sandy soils and (2) cool temperatures in the tropical highlands. Due to high temperature, the rate of decomposition of organic matter is higher (ranging from 2 to 5% per year) in tropical forests than in temperate forest

(ranging from 0.4 to 1% per year). The decomposition rate of tropical savannas averages 1.2% or 3 times that of temperate prairies (Sanchez, 1976).

Since there are beneficial effects of organic matter on physical, chemical and biological soil properties, organic wastes have been used on agricultural lands. Some sources of organic matter are: (1) farmyard manure from domestic animals containing partially decomposed straw mixed with urine and/or feces (Cooke, 1982), (2) green manure crops (legumes, grasses or pruned branches of trees), (3) plant residues, (4) composted materials, (5) sewage sludge (solid wastes generated by waste treatment plants), and (6) agro-industrial wastes (by-products of food processing industries, forest mills, tanneries, pharmaceutical plants, etc.).

The rate of release of nutrients present in organic wastes is controlled by: (1) environmental factors such as soil temperature, moisture, soil pH, nutrients, soil texture and structure, and oxygen, (2) carbon: nitrogen (C/N) ratio of the organic waste, and (3) the biochemical oxygen demand of the decomposer microbes (BOD=the amount of oxygen required by soil microorganisms to decompose organic wastes under standard conditions and during a specified period of incubation) (Paur, 1975).

When moisture is not limiting, factors that directly govern the formation of nitrate ions are temperature, pH or

Al activity, and nutrient deficiencies or toxicities. Temperature controls overall soil respiration, and the diffusion of NH_4^+ and O_2 to soil microorganisms. In the temperate areas, low (winter) temperature is considered as a constraint; however, its effect on the rate of nitrification causing groundwater pollution in winter has not been quantified.

Aluminum toxicity is recognized as a serious global problem because vast areas of the tropical and subtropical regions of the world possess highly weathered Oxisols and Ultisols. These soils combined cover 38% of the worlds land surface and are found mainly in tropical America and Africa (Sanchez, 1976). The aluminum ion and its hydroxides are common in these soils because of the low pH (less than 4.5). Previous studies have consistently shown that this low pH affects the amount of microorganism activity, particularly those responsible for nitrification. However, limited information is available concerning the importance of pH and Al in controlling nitrification rate.

Conservation of nutrients from the decomposition of organic matter is further complicated by the low net charge on acid, tropical soils. Thus, soils with low charge will allow nutrients to be lost from the root zone leading to further loss in productivity. Little is known about the effect of low levels of added organic matter on changing the charge of soil minerals.

The major objectives of this study were to quantify the interaction between acid soils and low levels of manure addition and to study manure decomposition at low temperatures. Specifically three areas were studied: (1) the effect of acidity and Al on decomposition of manures and N transformations, (2) the effect of low temperature on decomposition of manures and N transformations, and (3) the changes in charging of soil minerals with the addition of manures. This study is important in so far as its result will (1) contribute to our understanding of how the above factors control organic matter decomposition and N transformations in an organic waste-amended soil and (2) provide information useful in designing particular cropping systems for areas where heavy loads of organic waste are used, or where Al^{3+} is a dominant factor in the chemistry of the soil solution.

LITERATURE REVIEW

Effect of Temperature on Organic Matter Decomposition

Studies on two variables, temperature and carbon source, were conducted by Wood and Cooper, (1988). They reported that minimum temperatures (10.9 to 12.2 C) for multiplication were similar for strains of BEL 1214 at pH 4.2. The data obtained indicated that carbohydrate metabolism in R. trifolii is affected by the acidity of the growth medium. Wood and Cooper (1984) suggested that care should be taken when interpreting data from screening experiments for acid tolerance based solely on the appearance of visible turbidity.

From the above investigation, we conclude that little research has focused on the effects of temperature on nitrogen transformations that I consider important factors in mineralization and nitrate formation. Thus, a major objective of this study was to determine the effect of temperature on mineralization and nitrification rate in manure amended soils.

Effects of Acidity and Al on Organic Matter Decomposition and nitrogen transformations

The activity of H^+ and Al^{3+} ions in the soil solution are important because they influence roots, microbes and

soil reactions. As soils become acid, reaction rates of many biological processes may be greatly altered. Acid soils may have a negative effect on plants and plant growth: roots are short, thickened, and fewer in number (Arnon and Johnson, 1942; Islam et al., 1980). Excess H^+ ions may cause root membranes to become leaky. A solution pH <4 was found to enhance the loss of organic substances from cotton radicles and this effect was reversed by simply raising the pH (Christiansen et al., 1970). Pretreating barley roots with HCl at a pH <5 caused a pronounced loss of K (Hussain et al., 1954). Acid pretreatment at pH values <6 also significantly reduced the capacities of roots for subsequent uptake of K. Excess H^+ ions were also reported to decrease the uptake of Mg (Arnon and Johnson, 1942; Moore et al., 1961; Islam et al., 1980; Blamey et al., 1982), Mn (Robon and Loneragan, 1970), Zn (Rashid et al, 1976) and Cu (Bowen, 1969).

Soil reaction is an important constraint in limiting crop production through: (1) reduced nodulation and N_2 fixation by legumes in tropical soils; and (2) possible inhibition of nitrification by <u>Nitrosomonas</u> and <u>Nitrobacter</u>. To survive and grow in an acid, high Al soil, an organism needs to overcome various challenges: (1) toxicity from elements in excess (Mn and Al); and (2) deficiency of elements in short supply (Ca, Mg, and Mo).

Hydrogen ions also affect the mineralization of organic matter and subsequent availability of N, P, S, and

micronutrients to higher plants and to soil microorganisms. Soil pH is one of the important factors in determining the species, numbers and activities of microorganisms involved in organic matter decomposition (Sommers and Biederbeck, 1973; Alexander and Adams, 1980). Fungi are most active in this decomposition at pH values below 5.5. This is due to the absence of other micro-organisms which are more sensitive to acidity. Actinomycetes and other bacteria are particularly involved in organic matter transformation at pH values >6. Also, different optimum pH ranges for reproduction appear to exist for different bacteria including actinomycetes (Corke and Chase, 1964).

Ammonification can apparently take place over a wide range of soil pH's while nitrification is reduced at pH values <6 and >8 (Chase et al., 1968; Alexander and Adams, 1980). Alexander and Adams (1980) reported that nitrification rate decreases with decreasing pH and becomes undetectable at pH values below 4.5. But nitrification has been shown to occur in some acid soils of the southeast USA at pH values as low as 4 (Hiltbolt, 1962).

The activity of nitrifiers is known to be influenced by pH (Dancer et al., 1973; Laudelout et al., 1976). After using a wide range of soils in their studies, Morrill and Dawson (1967) found that pH (including its related factors) was the best indirect indicator of nitrification. Singh and Beauchamp (1986) provided evidence that during the first 14 days, nitrification of urea was correlated with initial

nitrifier activity which in turn related to the initial soil pH. These same researchers found that after 60 days, nitrifier activity in limed treatments increased by five-fold over the unlimed control. The relationship between pH and nitrification rate was investigated in a short term nitrification assay (Darrat et al., 1986; Schmidt and Belser, 1982). Based on these studies Darrat, et al. (1986) suggested that when modelling nitrification rate, the effect of pH on nitrifiers must be included or the predicted nitrate will be higher than actually measured.

Some research indicates that acid tolerant strains of nitrifying bacteria have developed in certain soils (Jackson, 1967; Brar and Giddens, 1968). However, fungi may carry out nitrification in strongly acid forest soils (Campbell and Lees, 1967, Dunkin et al., 1990).

In very acid soils, Al minerals may dissolve giving Al^{3+} ions which become a source of H^+ upon hydrolysis. Thus differentiating the effects of Al from those of H^+ has been difficult due to their interdependency. Foy (1984) reviewed studies on Al toxicity and reported that Al could be the most important growth-limiting factor for plants in most strongly acid soils and mine spoils. The problem is severe below pH 5.0 but it may occur as high as pH 5.5.

Evidence suggests that Al toxicity limits the microbial decomposition of organic matter in some strongly acid soils (Alexander and Adams, 1980). Mutaker and Pritchart (1966) found that the CO_2 production was greater in a Ca-muck than

in a Ca-Al-muck when both were maintained at pH 4. They reported that CO_2 production was markedly decreased with increasing concentrations of Al during incubation at pH 4.0 or below.

A low nitrification rate in a Bladen soil (Typic Albaqults) at pH 4.6 has been attributed to acidity and the resulting low population of nitrifiers (Brar and Giddens, 1968), but Al was probably a factor in limiting the nitrifier population. Soil factors (including the predominant clay minerals, organic matter levels, concentrations of the other cations, anions and total salts) and especially the plant species or cultivar, control the critical soil pH at which Al becomes soluble or exchangeable in toxic concentrations (Foy, 1974; Kamprath and Foy, 1972).

Aluminum effects on other organisms have also been investigated. There are different critical pH's for nodulation bacteria (Foy, 1984). Hydrogen ion is especially important in legumes grown without fertilizer N (Andrew, 1978). According to Munns (1978), H^+ affects rhizobial survival and multiplication in soils, root infection and nodule initiation, legume rhizobial efficiency, and nutrition of the host plant. He found that root infection is particularly sensitive to acidity. Reducing the solution pH from 5.5 to 5 decreased the number of nodules formed by beans, but increasing the pH from 4.5 to 5.5 did not affect nodule growth and nitrogenase activity (Franco and Munns, 1982) These results suggested that low pH could reduce

early nodulation of beans but when formed they will be active. The rhizobia of some legume species appear to be more sensitive to Al than their host plants. The nodulation of peanut was reduced when Al saturation of soil cation capacity (CEC) reached 30% in sandy soils of Senegal. Greater Al saturation was required for toxicity of the host plant (Pieri, 1974). Carvalho et al. (1981) reported that Al toxicity decreased the growth of Stylosanthes sp. more severely when plants were dependent on symbiotic N_2 fixation than when combined N was applied in fertilizer.

Some researchers (Carnalho et al., 1982) found that a 10 to 20-day exposure to Al concentration up to 2.7 mg L^{-1} in nutrient solutions did not affect the N_2 fixation of well-nodulated plants of S. homata, S. humilis, and Scabral.

Studies on shoot growth of soybean determined that as pH increased, nodule numbers and weights and N concentration and total N uptake by plants increased markedly (Mengel and Kamprath, 1978). The critical pH for nodule as well as for shoot and root growth was in the range of 4.6 to 4.8.

Cowpea, an important source of dietary protein in many parts of Africa, has been investigated to determine the effect of Al and low pH on its Rhizobia. Keyser and Munns (1979b) found that 1.34 mg L^{-1} of Al was more harmful to Rhizobia than low pH (4-5) or low P (0.3 mg L^{-1}). In another study Keyser and Munns, (1979a) concluded that cowpea Rhizobia contained a large and maybe continuous variation in symbiotic tolerance to soil acidity at pH 4.6.

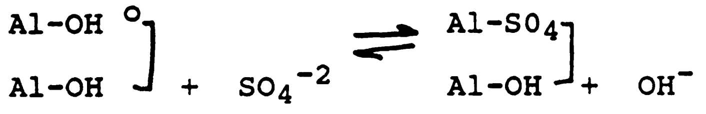
They identified 65% of the acid soil sensitive strains in nutrient solutions containing 1.35 mg L^{-1} of Al. Highly tolerant strains to acid soils were not sensitive to Al in solution.

Hartel and Alexander (1983) found no consistent relationship between the tolerance of three cowpea rhizobia under study and their growth and survival in four acid, Al-rich soils. Their data suggested that Al is of minor importance to growth and survival of cowpea rhizobium strains in acid soils. Soybean growth on acid soils has been suggested to be limited by factors other than nodulation failure (Munns et al. 1981). Plant symptoms indicated that soybeans grown on acid soils were limited by Al toxicity to the plant host. Munns et al. (1981) concluded that efforts to increase soybean production should be focused on developing acid-soil tolerant varieties, and not on rhizobia. Wood and Cooper (1988a) investigated the effects of initial inoculum density and growth phase on the response of <u>Rhizobium</u> <u>trifolii</u> to acidity and Al. They found that 50 uM Al caused a decrease in numbers of BEL 1192 (acid tolerant) at pH 4.5 and HP 3 (acid sensitive) at pH 5.5, irrespective of the initial cell densities. Their results suggested that cells in the log phase were more sensitive to Al than cells in the stationary phase. This was in agreement with data reported by Munns et al. (1981) that cells are more sensitive to Al in the tissue when cell division is occuring.

In studying the effects of Al on nitrifiers, it is essential to understand the chemical properties of the metal in soil solution since many different species of Al develop in solution after hydrolysis and polymerization. The distribution of different mononuclear species is dependent on pH and temperature. Smith (1971) postulated that the total concentration of Al, temperature, pH and anions present could control the reaction products that affect the toxicity level of Al.

Mehtods of Reducing Aluminum Toxicity

It has been observed that application of organic matter increases soil pH and reduces exchangeable Al in acid soils through formation of Al-organic matter complexes (Hargrove and Thomas, 1981). In addition, application of gypsum to topsoil has been found to increase the pH in the subsoil (Hammel et al. 1985; Sumner et al. 1986, Alva et al. 1990). This was done through an increase in surface negative charges of the soil due to specific sorption of SO_4^{-2} as shown in the following reaction:



$$\left.\begin{matrix}\text{Al-OH}^{\circ}\\ \text{Al-OH}\end{matrix}\right] + SO_4^{-2} \rightleftharpoons \left.\begin{matrix}\text{Al-SO}_4\\ \text{Al-OH}\end{matrix}\right] + OH^-$$

(Alva, et al., 1990)

Other researchers have also shown an increase in the sum of exchangeable cations with increasing SO_4 retention as a result of $CaSO_4$ application (Hue et al., 1985). They reported that at low pH's and low rates of $CaSO_4$ additions,

SO_4^{2-} sorption nearly doubled the increases of total exchangeable cations.

The toxicity of Al has been attributed to Al^{3+}, but recent investigations (Bertsch, 1987) have identified one polynuclear hydroxy-Al $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{+7}]$ called "Al_{13}" polymer which is more toxic to plants (Barlett and Riego, 1972; Wagatsuma and Ezoe, 1985; Wagatsuma and Kaneko, 1987; and Parker et al. 1989). Smith and Hem (1972) operationally defined three fractions Ala, Alb, and Alc corresponding to mononuclear Al, reactive polymers, and unreactive polymers or solid phase $Al(OH)_3$, respectively. Parker, et al., (1989) associated "Al_{13}" to Alb and Bertsch (1987) identified an OH/Al ratio of two, at which Al_{13} is formed which corresponded to a soil pH of 5.2.

In addition to experiments using a diverse number of plant species, (Barlett and Riego, 1972; Wagatsuma and Ezoe, 1985; Wagatsuma and Kaneko, 1987) polymer toxicity has been reported to occur in the symbiotic bacterium, Rizobium Tifolic (Wood and Cooper, 1984). The effects of those polymers on nitrifiers are unknown.

Charge Properties of Soils

The critical role of Al hydroxides in retaining nutrients and controlling pollutants has been investigated (Huang, 1975; Wada and Harvard, 1974). The aqueous chemistry of Al has illustrated the predominant influence of

ionic factors in governing the nature and properties of Al hydroxides. Studies on the influence of inorganic ligands on the hydrolytic products of Al have been carried out with chloride, sulfate, nitrate, and perchlorate (Hsu, 1967; Turner and Ross, 1970; and Ross and Turner, 1971), with organic anions of low molecular weight (Kwong and Huang, 1977; Violante and Huang, 1985; Violante and Jackson, 1981; and Violante and Violante,1980), and with fulvic acids (Kodama and Schnitzer, 1980).

Violante and Huang (1985) classified organic and inorganic ligands commonly found in nature according to their relative effectiveness in promoting the formation of noncrystalline products over crystalline Al(OH) polymorphes in the following order: pthalate = succinate < glutamate < aspartate < oxalate < silicate = fluoride < phosphate < salicylate = malate < tannate < citrate < tartrate. They found the lowest ligand/Al molar ratio at which the production of hydroxides or oxihydroxides was inhibited to be in the range 0.02 to 15. These authors reported that the polydentate and large ligands generally were more inhibitive than those with fewer functional groups or of smaller size. Organic acids enhanced the specific surface of the precipitation products of hydrolytic reactions through structural distortion. This development of surface charge and active sites in turn promote the retention of P and Ca (Kwong and Huang, 1979).

In the presence of 10^{-6} M organic acid and below pH 9.0, the Al hydroxides had a net positive charge higher than that of the corresponding products formed in the absence of organic acids (Kwong and Huang, 1979). They observed that the retention of phosphate by precipitation products of Al generally increased with concentration of organic acids present during precipitation. The capacities of organic acids to increase the retention of phosphate by the precipitation products were related to their ability to enhance specific surface. However, as the precipitation products of Al aged in the presence of organic acids, both the specific surface and the precipitation products ability to retain phosphate were reduced. In addition, adsorption of Ca by the reaction products of Al also increase with concentration of organic acids. Those authors suggested that organic acids, by promoting structural distortion, enhanced the specific surface of the reaction products and promoted the formation of active sites for sorption.

Parfitt et al. (1977) elucidated the mechanism of phosphate adsorption on gibbsite as involving ligand exchange of either H_2O at positive sites or OH^- at negative sites. The same authors also reported that fulvic acid (FA) and humic acid (HA) can also be adsorbed onto hydrous oxides. They provided infrared evidence for ligand exchange as a mechanism in adsorption. The process involved the release of OH^- which can increase the pH of the soil solution. Kurmert and Stumm (1980), studied the adsorption

of aromatic acids, catechol salicylic acid, and benzoic acid on y-Al_2O_3 and also proposed a ligand exchange model where anions of organic acid replace the hydroxo groups of the Al_2O_3 surface. Data obtained from adsorption isotherms and potentiometric titration curves allowed Kurmert and Stumm to speculate that salicylate binds to y-Al_2O_3 in 1:1 Al-salicylate complexes. Furthermore, their results support the formation of inner-sphere complexes. Yost et al. (1990) used cylindrical internal reflection Fourrier transform infrared spectroscopy and confirmed the 1:1 Fe-salicylate complex, but found that at higher concentrations of salicylates the inner sphere complexes coexist with weakly bound complexes.

Morrisson (1983) studying aqueous adsorption of anions (chloride, phosphate, acetate, citrate, succinate, and glycolate) onto oxides at different pH values above the oxide point of zero charge (6.5), concluded that the mechanism of adsorption involved a hydrogen bond to the surface oxide ion. He reported the adsorption envelop for citric acid to be significantly higher than that of acetic acid at pH 8. He suggested also that higher molecular weight compounds (phosphate esters, and polycarboxlates containing hydroxyls groups) are adsorbed at pH's significantly above the PZC, but through ligand exchange.

Some studies have demonstrated that organic anions such as citrate, succinate, HA, and FA compete with phosphate for adsorption sites on the surface of Al, thereby decreasing their capacity to retain phosphate (Nagarajah, et. al., 1970). Study by Sibande and Young (1986) showed that there is competitive adsorption between HA or FA and phosphate on synthetic oxides for two tropical soils from Zimbabwe. The effect of HA on phosphate adsorption on these soils was more pronounced in the soil with a lower pH (4.63). They suggested that the observed trend was probably due to the fact that relative positions of maximum buffer power of organic acids and phosphoric acid lie in different pH ranges.

Charlet and Sposito (1987) developed a method to simultaneously measure the net proton surface charge density and excesses of metal and ligand in a 1:1 electrolyte background. They found that a Brazilian oxisol has a point of zero net charge (PZNC) of 4.2, which was independent of the electrolyte and its ionic strength between 4 and 500 mol m^{-3}. They found that the PZNC of the Haplutox used had the same point of zero salt effect (PZSE) and the little dependence of the proton surface charge density on pH and ionic strength suggested the predominant role of kaolinitic and organic matter components in determining the surface chemistry of acid low charge soils.

It is expected that this study will provide information that may be useful in designing cropping systems where N can be efficiently used and recycled in the nitrification process.

CHAPTER II

LOW TEMPERATURE EFFECT ON NITROGEN TRANSFORMATIONS IN A MANURE AMENDED SOIL

Abstract

Farmers are faced with the problem of large quantities of manure produced each year in Michigan. Generally a portion of the manure is disposed of in the fall so that they may have the storage capacity to hold manure over the winter when land application is not advisable. When environmental conditions are favorable for nitrification, they further encounter the problem of groundwater pollution due to nitrate leaching. The effect of temperature on ammonification and nitrification is critical in reducing the loss of N through leaching. An incubation study was conducted to determine the effect of low soil temperatures (3.5, 5, 10 and 12.5 ^{o} C) on the rate of nitrogen (N) mineralization, and microbial immobilization in a manure amended soil. The long term goal is to develop N application programs which consider N transformations at low temperatures to reduce environmental degradation. Two cattle manures, fresh heifer manure and liquid beef manure from a holding lagoon, were used. One rate of manure application was used, 100 mg $N \cdot Kg^{-1}$ soil. Each manure was

mixed with Spink sandy loam (Psammentic Hapludalfo, sandy mixed, mesic).

Ammonification of fresh heifer manure occurred during the first 7 days at each of the four temperatures. At 14 days ammonification continued at 3.5 and 5 ° C. At 67 days ammonium concentration was higher in soils incubated at 3.5 than at 5 ° C. However, NO_3^- concentration decreased by 7 days and was nearly zero by 14 days. Concentration of NH_4^+ in liquid beef manure reached a maximum by 7 days and remained constant for the remainder of the incubation period. Nitrate concentration was again low in the incubated samples.

INTRODUCTION

Manure generated from cattle amounts to about 15 million tons ($13.6x10^9$ kg) a year in the state of Michigan (Jacobs1). Some of this manure is applied to land in the fall when farmers are emptying lagoons and holding pits so that they have storage capacity for the winter. The material is applied to land when a crop is not actively growing with the assumption that there will be little mineralization of organic N or nitrification during the winter. However, leaching of NO_3^- giving values exceeding 20 mg $N \cdot Kg^{-1}$ below the rooting zone has been found (B. G. Ellis, personal communication2) early in the spring following fall application of manure when temperature favored rapid transformation of NH_4^+ to NO_3^-. The optimum temperature for nitrification in pure culture has been reported to be in the range of 25-35 ° C (Focht and Verstraete, 1977), but this temperature varies widely among soils. For example, 20-25 ° C has been reported to be optimum for northwestern U.S. as compared to 30-40 ° C for some soils in the southwestern United States. Temperatures below 12-15 ° C, considered low, have been shown to drastically affect many biochemical processes including

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[1] L. Jacobs. 1991. Personal communication.
[2] B. G. Ellis. 1990. Personal communication.

nitrification. The minimum temperature for biological activity has been reported to be several degrees above the freezing point of water.

The limited information on temperature dependency of the nitrification rate would seem to indicate that the Arrhenius relation between temperature and rate would not hold at low temperature. The range of temperatures at which this transformation is effectively reduced has not yet been determined. Ingraham (1962), reporting on bacteria, stated that all biological systems cannot be well characterized by the Arrhenius equation at lower temperatures.

Soil temperature is one of the most important of many environmental factors affecting mineralization of organic N, nitrification, and immobilization of N into microbial tissue. Generally the lower the temperature, the slower is nitrification or immobilization of N. However, there is considerable difference of opinion relative to the precise relationship between temperature and these processes. The determination of the minimum range of temperatures for nitrification is particularly essential in areas where N fertilizers and organic materials are applied in the fall. Thus several investigations concerned with nitrification of N fertilizers at low temperatures have been conducted.

Studies have shown that nitrification of applied NH_4^+ occurs in some soils at lower temperatures than previously thought, and soils differed in their nitrifying characteristics at lower temperatures (Anderson and Purvis, 1955; Broadbent et al., 1958; Frederick, 1956; Justice and Smith 1962; Sabey et al., 1954; Sabey et al., 1959; Strojanovic and Broadbent, 1956). Anderson (1960) reported that nitrification was negligible in all samples incubated at 2.8 ° C. Other studies showed that nitrification of NH_4^+ in acid soils is influenced by the amount of NH_4NO_3 added and by the low soil temperature (Anderson and Boswell, 1964). These authors reported a depressive effect of both low temperature (2.7, 5.5, 8.3 ° C) and concentration of NH_4^+ on nitrification. The effect was most apparent in a loamy sand (Norfolk) and least in a clay loam (Hiwassee). They suggested an inhibitive influence of NH_3 on nitrifiers. Later, Singh and Beauchamp (1986) studying the effect of texture on nitrification also reported a possible NH_3 toxicity in coarser textured soils with a small amount of nitrifier activity.

Justice and Smith (1962) suggested that NH_4^+ oxidizers are less sensitive to low temperature than NO_2^- oxidizers. The evidence was nitrification at 2 ° C with production of NO_2^- which was not converted to NO_3^-. However, under favorable conditions the rate of nitrification at a temperature near freezing (2 ° C) was still appreciable, but when unfavorable conditions exist (e.g. low pH), nitrification was not significant below 7 ° C (Frederick, 1956). Frederick indicated that differences in the population of nitrifiers were the cause of differences in the temperature range of nitrification. He also reported that a low rate of nitrification in certain soils at low temperatures was probably due to the paucity of nitrifying microorganisms and a very slow rate of development rather than an inactivation of the nitrification process.

MATERIALS AND METHODS

Soil: A surface soil (0-20 cm) was sampled from a corn field experiment in 1991 located on the University Farms at Michigan State University. The soil was a Spinks sandy loam (Psammentic Hapludalfs, sandy, mixed, mesic) with a clay content of 12% and total C content of 1.43 %. The soil pH was 7.2 (1:1 soil to water) or 6.2 in 0.01 M $CaCl_2$ (1:1 soil to solution).

Manure: Fresh heifer and anaerobic liquid beef manures were used. The total and inorganic N for the fresh heifer manure was 4.09 and 0.86 mg N/g, respectively and for the liquid beef manure they were 3.76 and 1.88 mg N/kg, respectively The manure pH was determined on 1:2 manure:water slurry and was 7.1 for the fresh manure and 6.2 for the liquid manure.

Incubation method: The soil was screen to pass a 2mm sieve and stored at field moisture condition at 4 ^{o} C prior to use. Manure (100 mg TKN/kg) was added to the soil, mixed and incubated at field capacity (18%) with no further addition of water during the course of incubation. A split plot design was used with the main plot being temperatures (3.5, 5.0, 10.0, 12.5 ^{o} C), the subplots (manure type with two levels and sampling dates, 0, 7, 14, 28, 67, 150 days) were in a factorial arrangement (72 treatments). Each treatment was replicated three times. Thus, a total of 216 samples were prepared. Each individual treatment was added to a wide mouth square glass bottle, the soil packed to a bulk density of about 1.3 g cm^{-3}, brought to field capacity with deionized water and the bottles covered with polyethylene plastic attached with a rubber band. To allow gas exchange the polyethylene was punctured with a pin. At each sampling date, samples were sacrificed for NH_4^+, NO_3^-, and microbial N biomass analysis.

<u>Laboratory analysis</u>: Total Kjeldahl N was determined using Bremner and Mulvaney method (1982) and the determination of NH_4^+ was performed by Flow Injection Analysis (FIA) on Lachat Quikcalc II.

Inorganic N (NH_4^+ and NO_3^-) was extracted 1 hour with 1N KCl in 1:5 soil:solution ratio, filtered through Whatman No. 5 filter paper and the concentration of each ion determined colorimetrically by FIA. Nitrate and nitrite were analyzed together and will be referred to as nitrate in the text. Total C was determined by use of a Leco Carbon analyzer. The soil pH was determined on 1:1 (w/v) soil/water suspension.

Microbial biomass NO_3^- and NH_4^+ was extracted with 2N KCl after chloroform fumigation followed by incubation (Voroney and Paul, 1984), and samples analyzed by FIA.

Biomass N and C were calculated using the following formula (a modification of the origional formula):

Biomass-N = Nf/Kn

where: Nf = 2 N KCl extracted NH_4^+ after fumigation; Kn= $0.8(Cf/Nf)\wedge^{-.43}$; Cf=CO_2 evolved by fumigated samples. Biomass C = Cf/0.41. The CO_2 measurement was performed on a gas chromatograph (GC).

Statistical analysis: The experiment was analyzed for ANOVA as a split plot using Steel and Torrie procedure (1980) on MSTAT C.

RESULTS and DISCUSSION

Results presented in Figures II-1 and II-2 and Tables II-1 and II-2 show that most of NH_4^+ had been produced 7 days after incubation. For the fresh beef manure, even though NH_4^+ concentration reached a maximum at 7 to 14 days (except for 3.5 ^{o} C) ammonification may have continued but nitrification may have reduced the NH_4^+ concentration. At 14 days, NH_4^+ concentration continued to increase at temperatures of 5 and 3.5 ^{o} C while it decreases at 10, and 12.5 ^{o} C. As temperature increased from 5 to 12.5 ^{o} C there was a decrease in concentration with time (Fig. II-1). After 67 days of incubation, NH_4^+ concentration at 3.5 ^{o} C was significantly higher than at the higher temperatures. This suggests that the ammonification process takes place at low temperatures. However, by the end of the study there

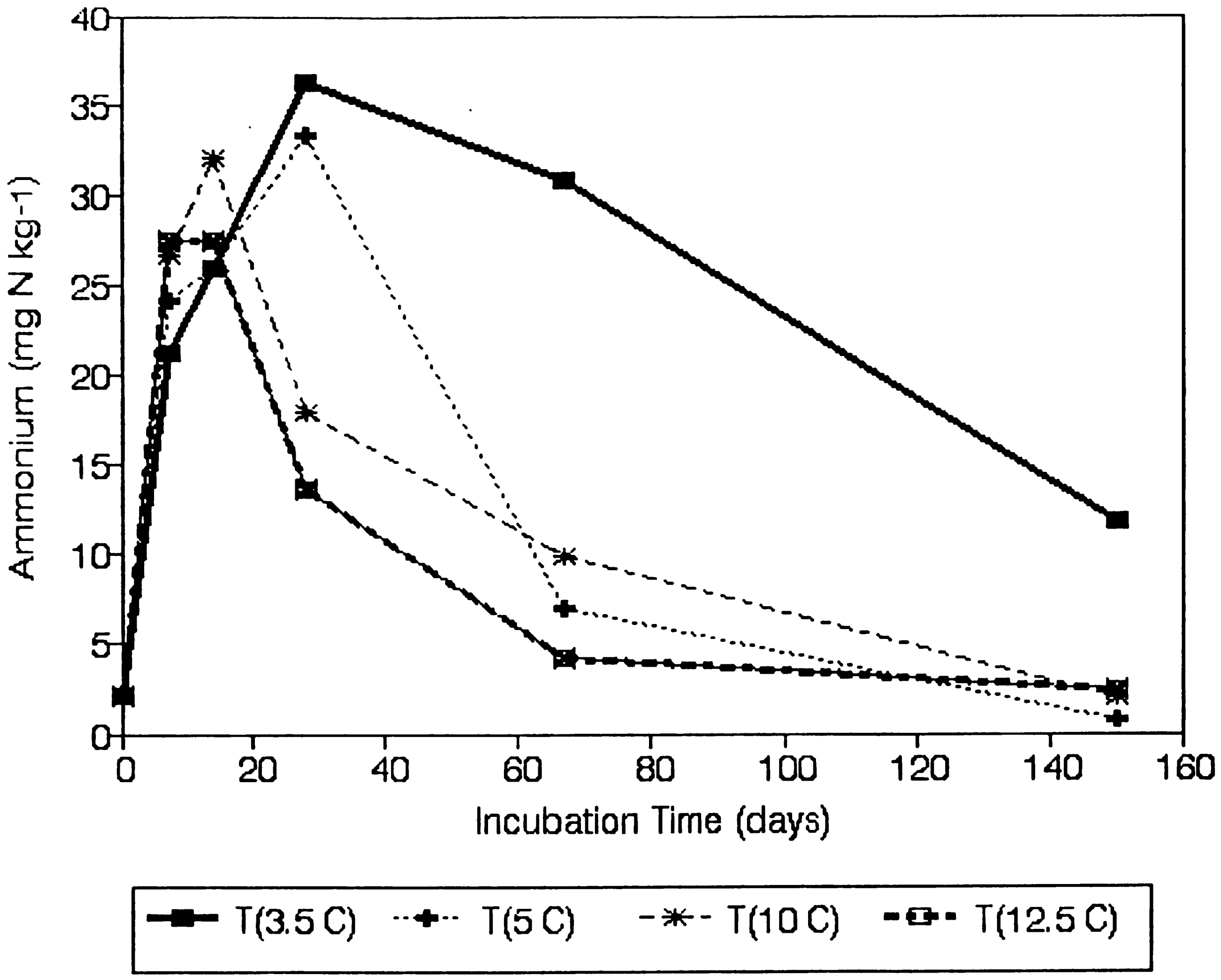

Figure II-1. Ammonium concentration in fresh heifer manure amended Spinks soil as affected by time and temperature.

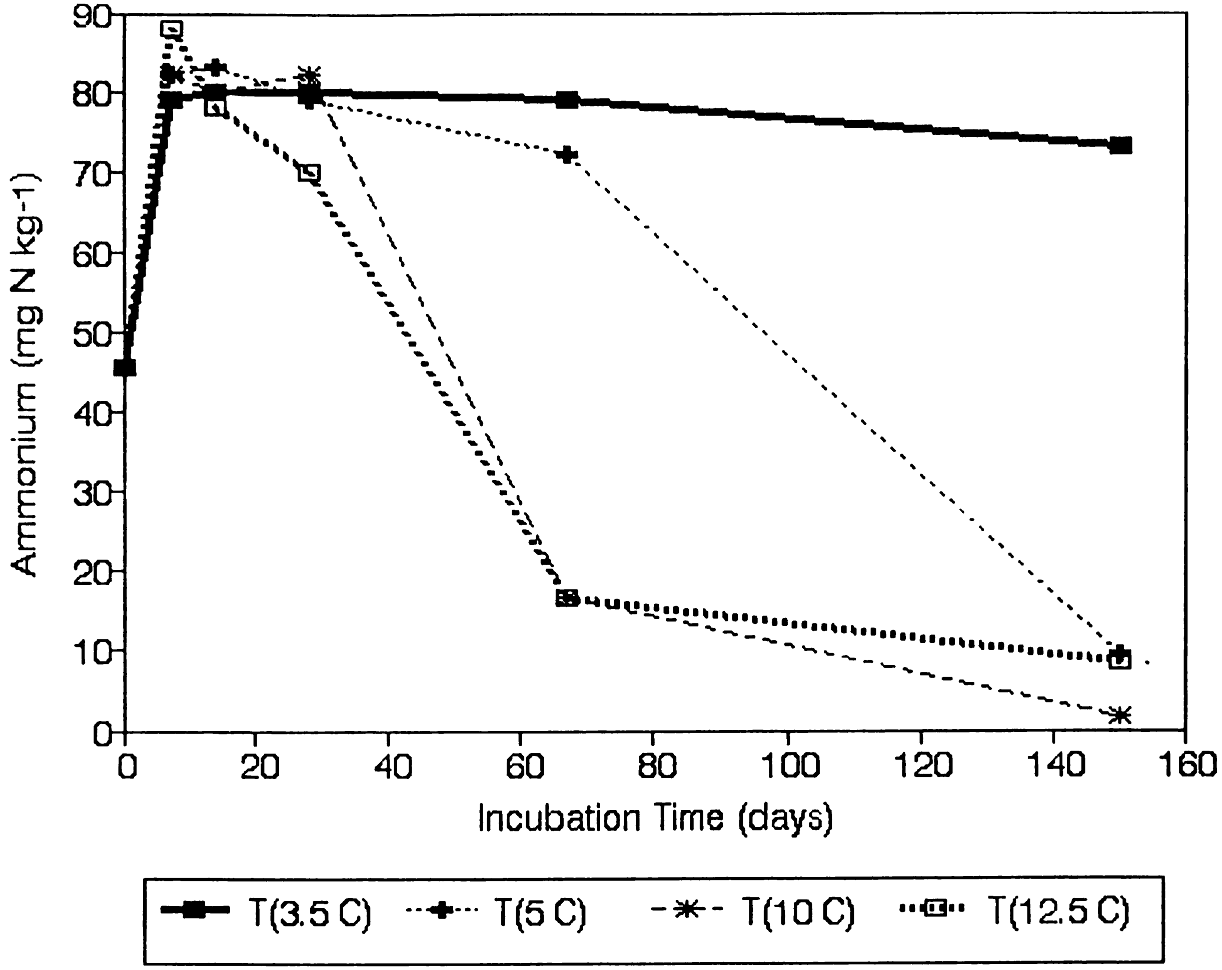

Figure II-2. Ammonium concentration in liquid beef manure amended Spinks soil as affected by time and temperature.

Table II-1 Effect of incubation time, manure and temperature on soil nitrate level

Temp	Manure Treat[1]	Incubation time					
		0	7	14	28	67	150
°C		mg N/kg soil as nitrate[2]					
3.5	1	1.21	0.87	0.6	0.06	0.60	0.29
	2	5.79	0.26	0.06	20.1	1.74	10.2
	3	3.95	0.64	0.06	0.06	0.60	0.54
5	1	1.21	7.66	10.3	14.8	31.0	43.7
	2	5.79	0.54	0.06	0.06	39.4	6.39
	3	3.95	0.54	10.36	0 06	3.71	9.54
10	1	1.21	3.11	2.92	8.03	5.57	0.32
	2	5.79	0.42	0.06	14.5	0.60	17.4
	3	3.95	0.32	0.06	0.06	3.61	34.9
12.5	1	1.21	12.5	15.3	20.4	35.3	50.8
	2	5.79	0.36	0.52	1.41	6.6	0.42
	3	3.95	0.56	0.06	1.72	2.86	0.75

LSD (0.01 between temperatures) = 4.9
LSD (0.01 between 2 dates) = 2

[1] 1= no manure; 2=100 mg TKN/kg as fresh heifer manure.
3=100 mg TKN/kg as liquid beef manure.

[2] Each value reported is a mean of three replications.

Table II-2 Effect of incubation time, manure and temperature on soil ammonium level

Temp	Manure Treat[1]	Incubation time 0	7	14	28	67	150
°C		---mg N/kg soil as ammonium[2]---					
3.5	1	15.4	10.3	10.0	6.8	9.0	11.7
	2	2.16	21.3	25.9	36.2	30.8	11.8
	3	45.5	79	80	80	79	73
5	1	15.4	7.5	4.2	5.5	5.6	1.6
	2	2.16	24.1	25.9	33.3	6.9	0.79
	3	45.6	82	83	79	72	9.5
10	1	15.4	8.0	6.33	6.13	9.2	5.24
	2	2.16	26.7	32.0	17.9	9.9	2.00
	3	45.6	82	80	82	16.5	1.73
12.5	1	15.4	3.13	1.23	3.75	5.79	0.50
	2	2.16	27.5	27.5	13.6	4.18	2.44
	3	45.6	88	78	70	16.5	8.53

LSD (0.01 between temperatures) = 3.27
LSD (0.01 between 2 dates) = 1.8

[1] 1= no manure; 2=100 mg TKN/kg as fresh heifer manure. 3=100 mg TKN/kg as liquid beef manure.

[2] Each value reported is a mean of three replications.

was no significant difference in NH_4^+ concentration at temperature 5, 10, and 12.5 ° C. Examination of data in Figure I-1 shows that there was a significant increase in NH_4^+ concentration at temperature 3.5, and 5.0 after 28 days of incubation followed by slow decrease at temperature 3.5 C and rapid decrease at temperature 5 ° C. On the other hand, there was an observed linear decrease in NH_4^+ concentration until the termination of the experiment for temperature 10 and 12.5 ° C.

Results show that NO_3^- concentration decreased 7 days after incubation of applied fresh or in liquid manure and was constant or approximately zero by 14 days (Fig.II-3 and II-4). Sporadic increases in NO_3^- were observed at later incubation times. The great variability in those data suggest that denitrification was occurring.

Data for liquid beef manure indicated that at temperature 3.5 ° C, the NH_4^+ concentration was the same throughout the duration of the experiment (150 days). Approximately 80 percent of the applied N was in the NH_4^+ form during this period. At 5 ° C the NH_4^+ level decreased slowly up to 67 days and then decreased more rapidly. At 10 ° C the decrease in NH_4^+ was more rapid after 28 days. Finally, at 12.5 ° C the decline in NH_4^+ was continuous after 7 day.

Loss of NH_4^+ could be explained by increases in microbial biomass, conversion to NO_3^- or by gaseous loss. Immobilization of N-NH_4^+ increased significantly for all

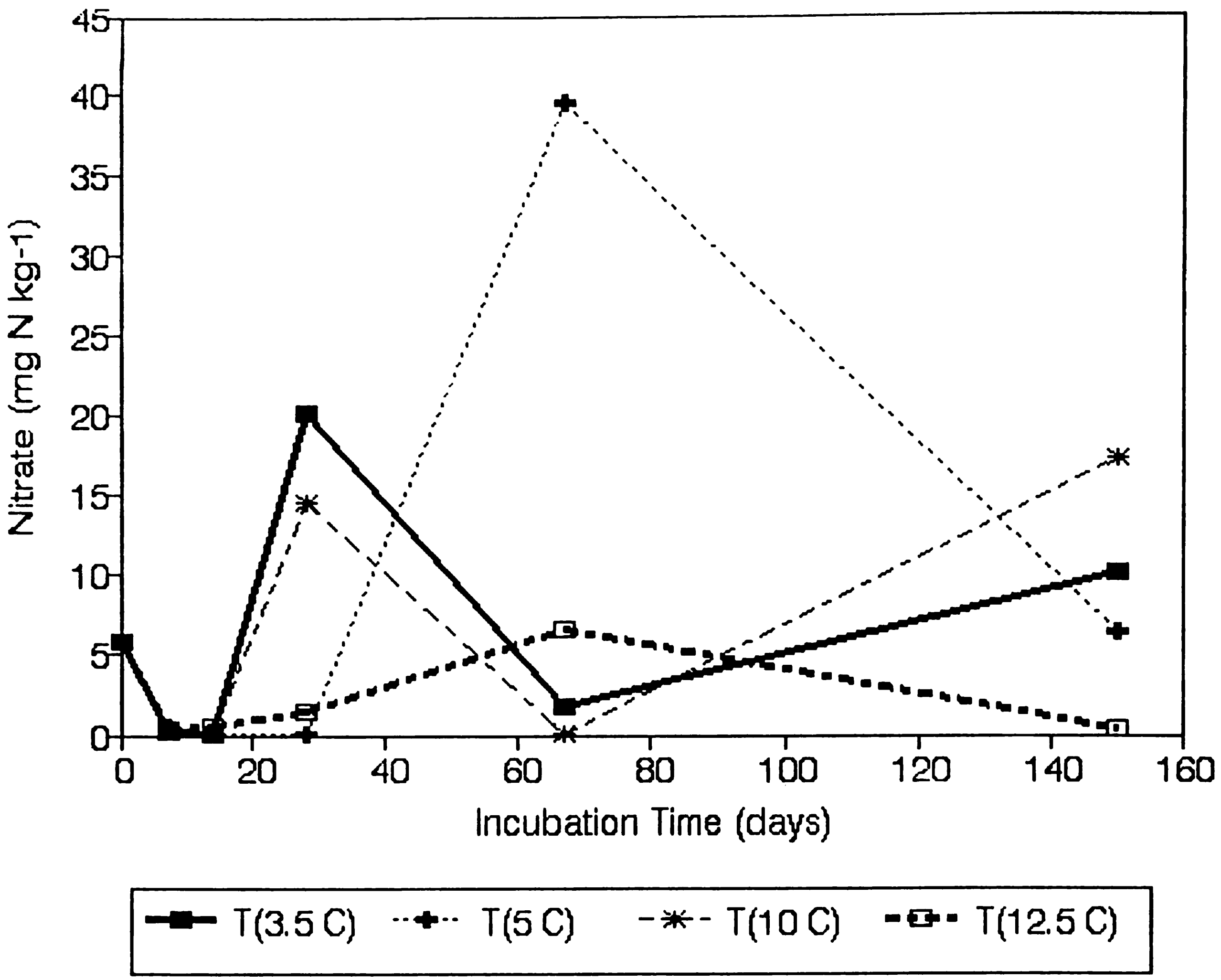

Figure II-3. Nitrate concentration in fresh heifer manure amended Spinks soil as affected by time and temperature.

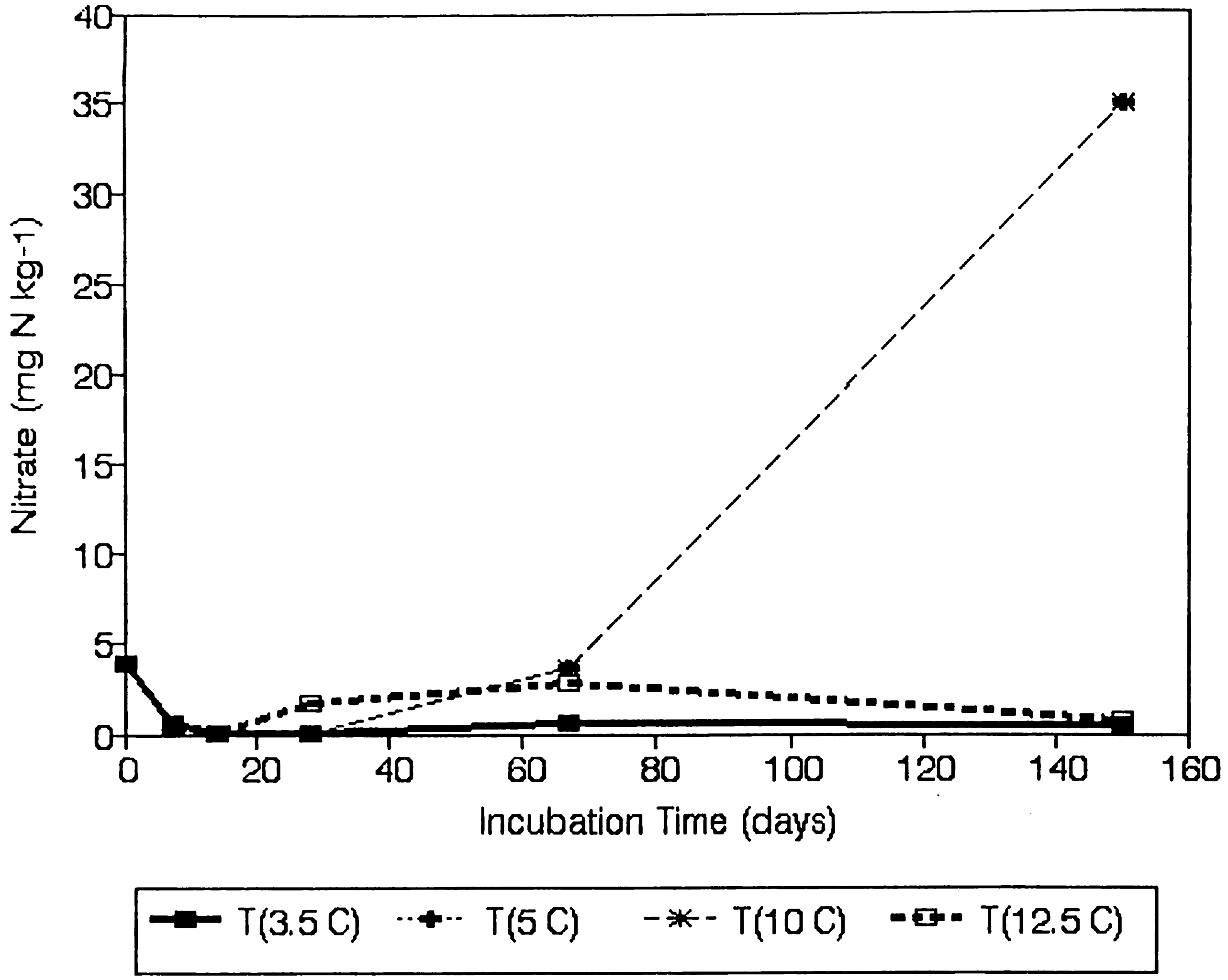

Figure II-4. Nitrate concentration in liquid beef manure amended Spinks soil as affected by time and temperature.

temperatures after 7 days of incubation. However, it was higher with liquid manure than for fresh heifer manure (Table II-3). At a temperature of 3.5 ° C and after 7 days there was no further incorporation of NH_4^+ into microbial biomass. The concentration of NH_4^+ in microbial biomass continuously increased up to 28 days for fresh manure-treated samples at 5 ° C. At 10 ° C, microbial biomass NH_4^+ gradually decreased for fresh and liquid manure treated soils. At 3.5 and 10 ° C where fresh manure had been applied the microbial biomass NH_4^+ decreased between 14 and 28 days. This corresponded to an increase in soil NO_3^- concentration. This suggest that there was denitrification at 3.5 ° C which is in agreement with Cho et al. (1979).

Nitrate levels were low with the exception of the 10 ° C, 150 day sample. Nitrate concentration in soil amended with liquid manure and incubated at 3.5 ° C remained low during the study. As would be expected after 28 days NO_3^- production was observed at 12.5 C, since the activity of nitrifiers increases with temperature. There were no significant differences in the NO_3^- concentration between the different temperatures up to 67 days.

The NH_4^+ that disappeared during the course of incubation was not recovered as NO_3^+ at 5, 10, and 12.5 ° C. This could probably be accounted by these possible mechanisms. First, the denitrification process which has been reported to occur at temperature as low as 2.7 ° C (Cho et al. 1979). However, there was significant accumulation

Table II-3. Effect of incubation time, manure an
temperature on soil microbial biomas

Temp-	Manure Treat[1]	Incubation time		
		0	7	14
°C		--------mg N/kg soil as ammonium[2]		
3.5	1	4.1	46.4	41.4
	2	16.9	62.5	60.4
	3	47.4	97.7	102
5	1	4.1	42.8	41.7
	2	16.9	64.0	61.8
	3	47.4	91.1	84.7
10	1	4.1	47.7	41.8
	2	16.9	55.5	58.9
	3	47.4	102	97.3
12.5	1	4.1	37.9	61.2
	2	16.9	57.7	41.8
	3	47.4	71.9	96.1

LSD (0.01 between temperatures) =
LSD (0.01 between 2 dates) =

[1] 1= no manure; 2=100 mg TKN/kg as fresh heifer
3=100 mg TKN/kg as liquid beef manure.

[2] Each value reported is a mean of three replica

of NO_3^- at 10, but not at 12.5 ° C after 150 days of incubation. This lack of accumulation of NO_3^- could be explained by formation of NO_2^- or NO_3^- followed denitrification which linear between 2.7 and 20 ° C (Cho et al., 1979). Second, decomposition of manure may occur in microsites that may contain a high concentration of manure and may give a high pH due to consumption of H^+ leading to formation of NH_3 and subsequent loss of gaseous NH_3. Third, immobilization of soluble N by microorganisms may occur which will incorporate the N into the microbial biomass. Finally, it is possible to fix NH_4^{+Y}in interlayer positions of weathered illite or vermiculite clays.

The decomposition of beef manure was affected by temperature, handling and time of incubation (Fig II-7 and II-8). At 3.5 ° C the concentration of NH_4^+ in both manure was fairly constant, but decreased after 67 days. Figure II-8 suggests that independent of handling, beef manure can be applied when soil temperature reaches 3.5 ° C, whereas at 12.5 ° C liquid manure application might result in significant loss of NH_4^+ after 28 days (Fig II-7 and II-8).

Nitrate concentration in the soil decreased to near zero amounts within 7 days for both manure sources and remained fairly constant throughout the incubation period for the 12.5 ° C treatment (Fig. II-5). Conversely, NO_3^+ concentration in the control increased with incubation (Fig. II-6).

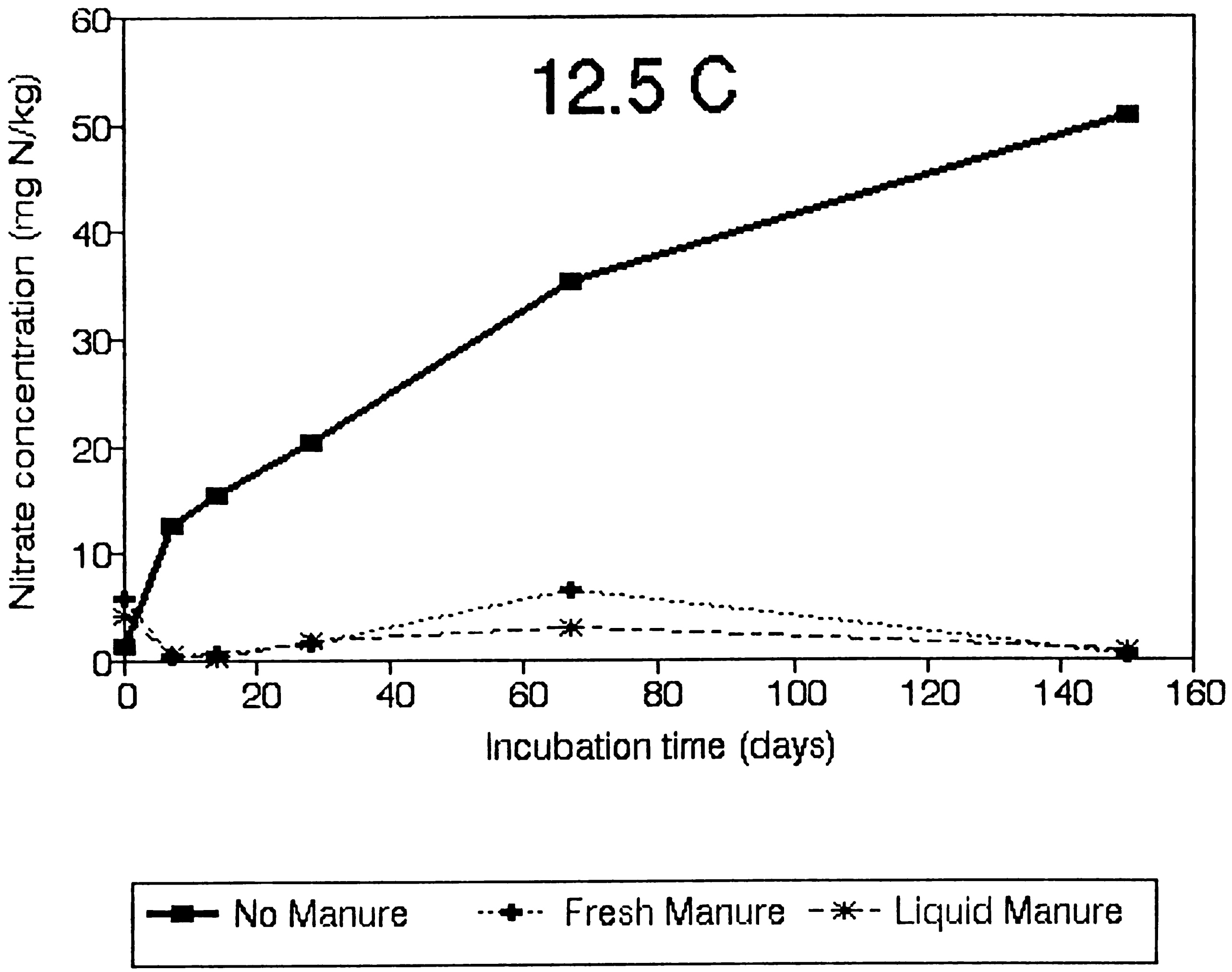

Figure II-5. Concentration of nitrate in Spinks soil as affected by handling of manure and time of incubation at 12.5 ° C.

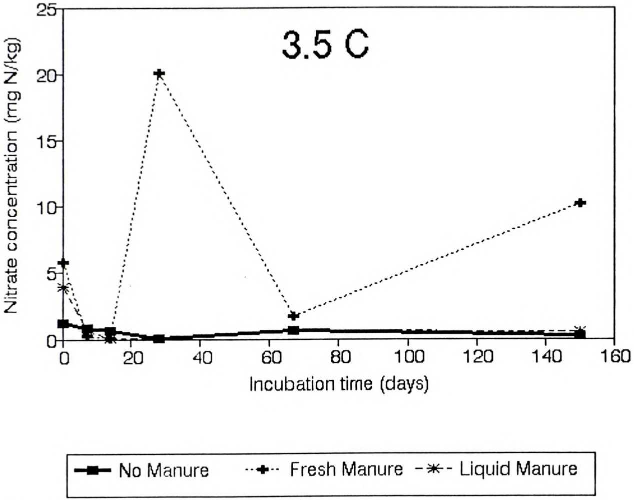

Figure II-6. Concentration of nitrate in Spinks soil as affected by handling of manure and time of incubation at 3.5 ^{o} C.

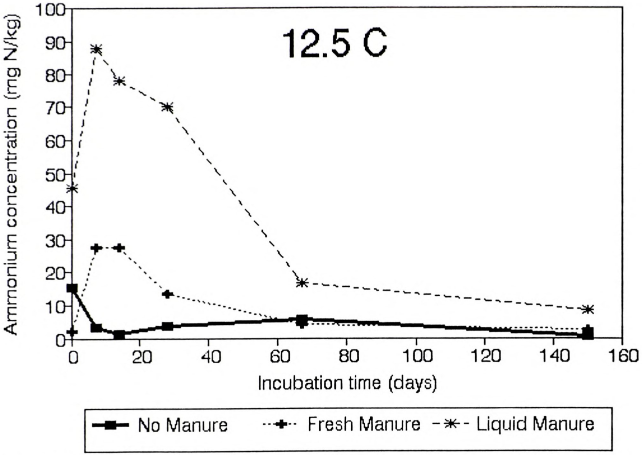

Figure II-7. Concentration of ammonium in Spinks soil as affected by handling of manure and time of incubation at 3.5 ° C.

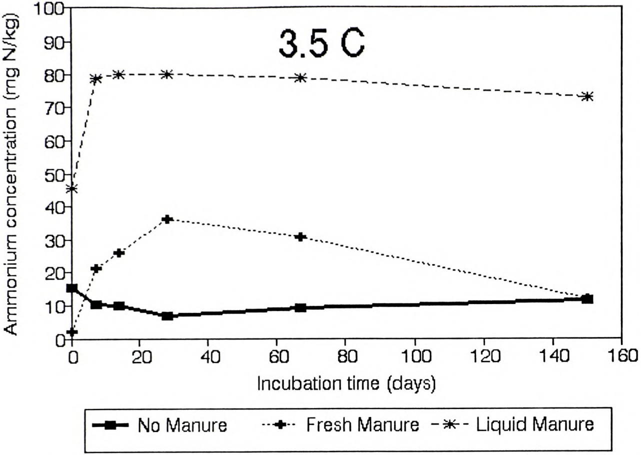

Figure II-8. Concentration of ammonium in Spinks soil as affected by handling of manure and time of incubation at 3.5 ° C.

During this first period ammonification of both types of manure is obviously temperature dependent with ammonium production increasing with temperature. The rate of NH_4^+ production for fresh manure amended soil increased with temperature (Figure II-9a). However, the increase failed to fit an Arrhenius plot (Figure II-9b). Since other reactions are removing NH_4^+, particularly evident at 10 and 12.5 $^{\circ}$ C, the calculated "rate" would be an under-estimate at those temperatures.

SUMMARY AND CONCLUSIONS

It was surprising that in most treatments with fresh or liquid manure there was little NO_3^- production. This suggests that the contribution of NO_3^- to the pool of potential pollution for NO_3^- would be negligible for soils amended with manure compared to the control if temperature is low.

Due to the linear increase and persistence of NH_4^+ for 28 days at 3.5 and 5 $^{\circ}$ C, the practical implication of this result is that fresh manure could be applied when soil temperature is 5 $^{\circ}$ C or below. On the other hand, a farmer producing beef liquid manure could incorporated it whenever soil temperature reaches 10 $_{o}$ C with minimum risk of loosing a significant amount of NO_3^-. Generally, the soil would be frozen within 30 days of reaching 10 $^{\circ}$ C in Michigan.

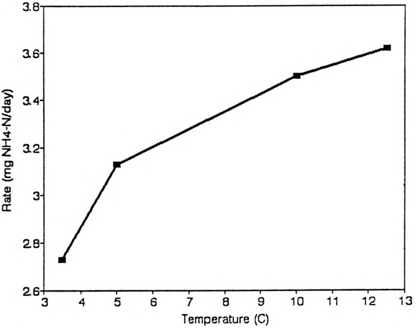

Figure II-9a. Effect of temperature on rate of ammonium production from fresh manure amended soil.

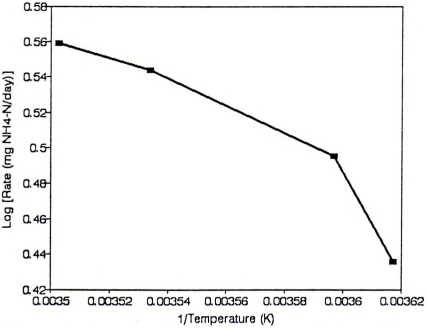

Figure II-9b. Arrhenius plot for reaction rate of ammonium production from fresh manure amended soil.

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CHAPTER III

EFFECT OF SOIL ACIDITY AND ALUMINUM CONTENT ON NITROGEN TRANSFORMATIONS IN A MANURE AMENDED SOIL

ABSTRACT

Low pH, high Al soils are known to often be low in nutrient availability and productivity. Sustaining food production is the ultimate goal of any cropping system in areas where those soils prevail. Liming is commonly used to solve the problem. The observation that additions of organic material to these soils often improves productivity suggest that their incorporation may sustain the productivity of those soils. Thus a series of laboratory incubation studies were conducted to determine the effect of manure from two sources, fresh heifer manure and liquid beef manure stored in a lagoon, on soil pH, Al level, nitrogen mineralization, and nitrification processes. The data showed that 100 mg TKN kg^{-1} from fresh or liquid beef manure was sufficient to significantly increase the pH of all soils studied. The pH increase was greatest for a low Al soil (pH 4.1 to 5.0) and least for a high Al soil (pH 3.7 to 3.9) when measured 63 days after application. Simultaneously, the concentration of exchangeable Al was reduced from 92 to 28.5 mg kg^{-1} for the low Al soil and from 335 to 208 for the

high Al soil. On-the-other hand, ammonium concentration was relatively constant for all levels of Al. Application of beef manure, whether fresh or liquid, reduced the level of nitrate in the soil in low pH, high Al soils.

INTRODUCTION

Soil microorganisms are considered as facilators of nutrient flow and decomposition of organic residues. In a search of ways to sustain cropping systems in areas where high aluminum (Al) and low nutrient soils prevail, researchers have proposed the incorporation of organic materials to reduce the concentration of exchangeable Al, and to increase or to maintain the fertility level of those soils. The effect of high Al on some soil microorganisms (N fixing bacteria) has been extensively investigated but limited information is available on its effects on nitrifying bacteria. Nitrogen is one of the limiting factors in sustaining most crop production systems, especially in high Al soils. Currently there is a need to efficiently use the available organic materials. The objective of this study was to determine by soil incubation studies whether or not Al and/or pH influences the rate of transformation of N from manures. The specific objectives were to measure the effect of Al on: 1) inorganic N accumulation (net mineralization); and 2) the interaction of manure and exchangeable Al.

LITERATURE REVIEW

Aluminum ion and its different hydroxides are common in highly weathered Oxisols and Ultisols and present a serious global problem because of their toxicity to plants and other biological organisms. When the soil pH is <4.5 Al ions are dominant in soil solution and they affect the activity of many microorganisms. Limited information is available on the importance of Al^{3+}, or other Al forms in controlling the rate of nitrification.

As soils become acid, reaction rates of many biological processes may be greatly altered. Soil reaction is an important constraint in limiting crop production through: a) nodulation and N_2 fixation by legumes in tropical soil; and b) possible inhibition of nitrification by nitrosomonas and nitrobacter. To survive and grow in an acid, high Al soil, an organism needs to overcome both toxicity from elements in excess (Mn and Al) and deficiency of elements in short supply (Ca, Mg, Mo).

Hydrogen ions affect not only Rhizobial survival (Munns, 1978) but also the mineralization of organic matter and subsequent availabilities of N, P, S, and micronutrients to higher plants and to organisms responsible for soil biomass accumulation. In addition, soil pH is one of the factors which determines the species, numbers and activities of microorganisms involved in organic matter decomposition (Sommers and Biederbeck, 1973; Alexander and Adams, 1980).

Fungi are most active in this decomposition at pH values below 5.5. Actinomycetes and other bacteria are involved in organic matter transformation at pH values >6.

Ammonification can apparently take place over a wide range of soil pH's while nitrification is reduced at pH values <6 and >8 (Chase et al., 1968; Alexander, 1980). But, nitrification has been shown to occur in some acid soils of the southeastern USA at pH values as low as 4 (Hiltbolt and Adams, 1960). Soil pH and its related factors was the best indirect indicator of nitrification (Morrill and Dawson, 1967) and evidence shows that up to 14 days nitrification of urea was correlated with initial nitrifier activity which was related to the initial soil pH (Singh and Beauchamp, 1986). The activity of nitrifiers is known to be influenced by pH (Dancer et al., 1973; Laudelout, 1976). Studies by Darrat et al. (1986) and Schmidt and Belser (1982) suggested that when modelling nitrification rate, the effect of pH on nitrifiers must be included or the predicted NO_3^- will be higher than actually measured.

Aluminum is one of many sources of acidity in the soil. Thus differentiating the effects of Al from those of H^+ has been difficult due to their interdependence. However, Foy (1984) reviewed studies on Al toxicity and reported that Al could be the most important growth-limiting factor for plant and microorganisms in most strongly acid soils and mine spoils. The problem is severe below soil pH 5.0 but it may occur in soils with a pH as high as 5.5.

Low nitrification rate in a Bladen soil (Typic Albaqults) at pH 4.6 has been attributed to acidity and Al was probably a factor in limiting the nitrifier population (Brar and Biddens, 1968). Soil factors, including the predominant clay minerals, organic matter content, concentrations of the other cations and anions, and total salts and especially the plant species or cultivar, control the critical soil pH at which Al become soluble or exchangeable in toxic concentrations (Foy, 1974; Kramprath and Foy, 1972). Aluminum effects on other organism have been investigated [i.e., Rhizobia of peanut (Pieri, 1974), Stylosanthes species (Carvalho et al., 1981)]. Some researchers (Carvalho et al., 1982) found that a 10 to 20-day exposure to Al concentration up to 2.7 mg L^{-1} in nutrient solutions did not affect the N_2 fixation of well-modulated plants of S. homata, S. humilis, and Scabral.

The critical pH for nodule growth of soybean was in the range of 4.6 to 4.8 (Mengel and Kamprath, 1978). Keyser and Munns (1979) found that 1.34 mg L^{-1} of Al was more harmful to rhizobia of cowpea than low pH (4-5) or low P (0.3 mg L^{-1}). Hartel and Alexander (1983) found no consistent relationship between the tolerance of three cowpea rhizobia under study and their growth and survival in four acid, Al-rich soils. Their data suggested that Al is of minor importance to growth and survival of cowpea Rhizobium strains in acid soils. On the other hand, Munns et al., (1981) concluded that efforts to increase soybean

production should be focused in developing acid tolerant varieties, and not on <u>Rhizobia</u>. Wood and Cooper (1988a) found that 50 uM (micro M) Al caused a decrease in numbers BEL 1192 (acid tolerant) at pH 4.5 and HP 3 (acid sensitive) at pH 5.5 irrespective of the initial cell densities. Their results suggested that cells in the log or cell division phase were more sensitive to Al than cells in stationary phase.

From the above investigation, I conclude that little research has focussed on the effects of low pH and high Al on the nitrifiers that I consider important factors in NO_3^- formation. In studying the effects of Al on nitrifiers, it is essential to understand the chemical properties of the metal in soil solution. There are various species of Al in solution after hydrolysis and polymerization. The distribution of different mononuclear species is dependent on pH and temperature. Smith (1971) postulated that total concentration of Al, temperature, pH and anions present could affect the reaction products which could affect the toxicity level of Al. It has been observed that application of organic matter increases soil pH and reduces exchangeable Al in acid soils through formation of Al-organic matter complexes (Hargrove and Thomas, 1981).

In addition to experiments using a diverse number of plant species (Barlett and Riego, 1972; Wagatsuma and Ezoe, 1985; Wagatsuma and Kaneko, 1987) polymer toxicity has been

reported to occur in the symbiotic bacterium Rhizobium Trifoliac (Wood and Cooper, 1984). The effects of those polymers on nitrifiers are unknown.

It is expected that this study will provide information, hopefully useful in designing a cropping system where nitrogen can be efficiently used and recycled in the mineralization or nitrification process.

MATERIALS AND METHODS

Experiment 1.

Three bulk samples were collected from Kalamazoo subsoils at the Kellogg Biological Station, Michigan State University. Samples were air dried, screened to pass a 2mm sieve, and stored in plastic bags at 4 C before analysis for soil characterization and the beginning of the experiment. Selected chemical properties of the soils used are in table III-1. The exchangeable Al (ex-Al) concentration was 39.2, 82.9 and 266 mg Al kg^{-1} for low (Al1), medium (Al2), and high (Al3) soil, respectively.

Soil pH (H_2O) was measured on a 1:1 soil/water suspension using a glass electrode, and a pH in 1N KCl was also measured in a 1:2.5 soil/solution suspension. The ex-Al (1N KCl) concentration was determined using IC plasma after extraction with a 1:5 soil to solution ratio. Total C was determine by dry combustion on a Leco carbon analyzer.

Table III-1. Selected physico-chemical properties of the soils used in low pH, high aluminun studies

Soil	pH(Water)	pH(KCl)	Ex-Al mg/kg	C %	Sand	Silt -------%--------	Clay
			Experiment I				
1.	6.30	4.39	39.2	1.72	48	39	13
2.	6.44	4.55	82.9	0.8	51	31	18
3.	4.97	3.91	266	0.4	50	22	28
			Experiment II.				
Al-1	5.99	5.06	0	1.51	51	35	14
Al-2	5.62	4.61	10	1.10	51	30	19
Al-3	5.57	4.42	45	1.34	51	29	20
Al-4	5.33	3.97	92	0.78	51	27	22
Al-5	5.16	3.79	193	0.69	48	26	26
Al-6	5.16	3.70	335	0.41	50	22	28

Beef liquid manure was carefully sampled from a lagoon located on MSU farms at East Lansing, MI. Dry matter content of the manure, total Kjedalhl N, NO_3^- and NH_4^+ content were determined by standard methods (Agronomy No. 9, Part II, 1982).

An incubation experiment was established with each treatment in triplicate and arranged in a completely randomized block design. Each individual treatment was 100 g of soil placed in a wide mouth, 8 oz. square bottle. The soil was packed to a bulk density of about 1.3 g cm^{-3} and brought to field capacity with DI water. Total weight of the bottle and mixture was recorded. The bottles were covered with polyethylene plastic attached with a rubber band. Each sample was weighed every three days and if necessary DI water added to return the soil to field capacity. Samples were expended after 0, 1,5, 9 and 13 weeks and the NO_3^-, NH_4^+, pH and exchangeable Al determined by standard methods. The data was analyzed for ANOVA using MSTAT-C (Freed and Eisensmith, 1991).

Experiment 2.

Soils: Both surface soil (0-8 cm) and subsoil (30-45 cm) were collected from an area (under grass) at the Kellogg Biological Station where the soil was known to be high in exchangeable Al. The soils were screened to pass a 2 mm sieve and stored in the field moist condition at 4 C prior to use. To obtain soil samples with different Al levels the soils were mixed as follows:

A = 100% low Al surface soil.
B = 100% high Al surface soil
C = 75% low Al surface soil and 25% high Al subsoil.
D = 50% low Al surface soil and 50% high Al subsoil.
E = 25% low Al surface soil and 75% high Al subsoil.
F = 100% high Al subsoil.

Some selected physio-chemical and mineralogical characteristics of these soil samples are in Table III-1. Total Kjeldahl N was determined by digestion of the sample by semi-microKjeldahl method (Bremner and Mulvaney (1984) with NH_4^+ determined by Flow Injection Analysis (FIA). Total carbon was determined by dry combustion on a Leco carbon analyzer. The C/N ratio was calculated as the ratio of TKN/Total C.

These soils were mixed and incubated at field capacity at room temperature (25 °C) for 2 weeks to obtain equilibrium. Then manure was added to obtain the following treatments.

1. Soil Mix A (No manure) Al-1, 0 mg Al/kg
2. Soil Mix A (+ 100 mg N/kg as manure) Al-1, 0 mg Al/kg
3. Soil Mix B (No Manure) Al-3, 45 mg Al/kg
4. Soil Mix B (+100 mg N/kg as manure) Al-3, 45 mg Al/kg
5. Soil Mix C (No Manure) Al-2, 10 mg Al/kg
6. Soil Mix C (+100 mg N/kg as manure) Al-2, 10 mg Al/kg
7. Soil Mix D (No Manure) Al-4, 92 mg Al/kg
8. Soil Mix D (+100 mg N/kg as manure) Al-4, 92 mg Al/kg
9. Soil Mix E (No Manure) Al-5, 193 mg Al/kg

10.Soil Mix E (+100 mg N/kg as manure) Al-5, 193 mg Al/kg
11.Soil Mix F (No Manure) Al-6, 335 mg Al/kg
12.Soil Mix F (+100 mg N/kg as manure) Al-6, 335 mg Al/kg

Each treatment was replicated three times and arranged in a completely randomized block. The incubation experiment was conducted with the same methods given for experiment 1 except that treatments 5 and 6 were inadvertently brought to twice field capacity with DI water. A total of 144 samples were prepared and samples sacrificed at 7, 14, 28, 42 and 63 days. Nitrate and ammonium were extracted by 1 N KCl by shaking 5 grams of soil with 50 mls of 1 M KCl for one hour, filtering through Whatman No. 5 filter paper and determining NO_3^- and NH_4^+ by Flow Injection Analysis (FIA). Aluminum extracted by 1 M KCl was determined by ICP and pH of the soil samples was measured by glass electrode.

RESULTS AND DISCUSSION

Experiment 1:

Prior to incubation the pH of the three soils were approximately the same without manure incorporation. Table III-2 shows that soil pH of the control samples decreased with time, but remained relatively similar for each sampling period. On the other hand the pH of manure amended samples was immediately increased and in one week the increases over controls was significant for all Al levels. At 5 weeks the pH had decreased to a level lower than the initial values of

Table III-2. The effect of incubation time, exchangeable Al and liquid beef manure on soil pH.

Al[1] Conc.	Incubation Time	Control	Plus Manure
	weeks	Soil pH	Soil pH
Low	0	4.89	5.93
Medium	0	4.84	5.53
High	0	4.71	5.25
Low	1	4.28	6.53
Medium	1	4.13	6.00
High	1	4.25	5.68
Low	5	4.10	5.75
Medium	5	3.94	5.37
High	5	3.79	4.28
Low	9	3.95	6.55
Medium	9	3.78	5.33
High	9	3.70	4.10
Low	13	3.90	6.90
Medium	13	3.83	5.90
High	13	3.70	4.28

LSD (0.05) (3-way interaction) = 0.94

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[1] Low Al = 39 mg Al kg^{-1}; Med Al = 83 mg Al kg^{-1}; High Al = 266 mg Al kg^{-1}.

manure amended soil but was higher than the controls. From 5 weeks to the conclusion of the experiment, there was no significant difference between the pH of the treated and the control samples of high Al soil. However, there was a significant difference in pH for low and medium Al content soils. This change in pH was probably due to the change in the chemistry of Al compounds in the soil solution. The rapid pH increase observed immediately after manure incorporation and one week after incubation indicated the presence of OH^- with the NH_4^+ in the manure or that there was a release of OH^- from Al oxides involving the exchange of organic anions (i.e, different organic acids resulting from the decomposition of manure). The plausible explanation for the subsequent decreased pH is the nitrification of NH_4^+ to NO_3^- and hydrolysis of Al^{3+} with the release of H^+ into soil solution. The pH for the control stabilized in 5 weeks to a value slightly less than 4 with the high Al soil lower in pH than the low Al soil. At 13 weeks the pH of the high Al soil has been relatively stabilized to approximately 3.70 for the control and to 4.28 for the manure samples in high Al samples.

Observation of the 1 N extractable Al (Ex-Al) data helps clarify the nature of Al compounds formed during incubation. As would be expected the Ex-Al concentration of treated samples was significantly reduced through the duration of the study (Table III-3). Examination of the data of the control reflects the instability of the Al

Table III-3. The effect of liquid beef manure, incubation time and initial Al level on 1 N KCl extractable aluminum.

Al[1] Level	Incubation Time	Control	Plus Manure
	weeks	--extractable Al	(mg Al/kg soil)--
Low	0	64.5	1.25
Medium	0	132	15.1
High	0	288	96
Low	1	42.5	0.35
Medium	1	129	1.30
High	1	358	40.1
Low	5	85	0.75
Medium	5	146	0.90
High	5	312	0.75
Low	9	86	2.20
Medium	9	173	0.95
High	9	296	57.5
Low	13	122	2.50
Medium	13	131	52.5
High	13	146	56.0

LSD (0.05) (3-way interaction) = 83

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[1] Low Al = 39 mg Al kg^{-1}; Med Al = 83 mg Al kg^{-1}; High Al = 266 mg Al kg^{-1}.

compounds after a long incubation period probably due to aging/polymerization of Al hydroxides (Sims, 1981). The concentration of Ex-Al for the manure amended samples decreases to reach a minimum of about 0.75 mg kg^{-1} and then slightly increases, but the increase was higher with the high Al soil. The rapid reduction in extracted Al after manure application indicates precipitation or complex formation. The further reduction of extractable Al by five weeks may suggest the formation of Al complexes. Spectroscopic (Sikora and McBride, 1990) and titration (Hargrove and Thomas, 1981) methods provided evidence for formation of Al complexes in the presence of phenolic acids or organic matter. Sikora and McBride (1990) showed that Al readily formed complexes with phenolic acids such as protocatachuic, caffeic acids. Even though the analysis of the manure for detection of those acids was not performed, it is documented that the decomposition of organic residues release the above acids (Stevenson,1982). Similarly, during beef manure mineralization there was probably the release of the phenolic acids leading to the formation stable Al complexes.

There was little or no detection of NO_3^- in medium and high Al soils throughout the study where manure was added except for the high Al soil at the termination of the experiment (Table III-4). There was more nitrification in soils without manure application, although nitrate levels were not significantly different from the manure treated

Table III-4. The effect of soil aluminum content on the rate of nitrification of added liquid beef manure.

Al^1 Level	Incbation Time	Control		Plus Manure	
		NO_3	NH_4	NO_3	NH_4
	weeks	mg N/kg soil			
Low	0	11.1	5.90	3.32	427
Medium	0	2.30	7.64	0.03	314
High	0	2.13	2.24	0.33	412
Low	1	1.54	0.99	1.19	396
Medium	1	6.89	4.24	n.d.	399
High	1	0.22	0.34	0.09	423
Low	5	2.66	3.94	1.54	435
Medium	5	9.45	1.10	n.d.	415
High	5	0.45	4.20	n.d.	426
Low	9	9.20	1.16	1.68	427
Medium	9	2.96	3.62	0.22	396
High	9	3.74	3.92	0.09	400
Low	13	16.1	9.50	0.63	418
Medium	13	0.79	54.9	0.17	397
High	13	0.28	1.39	2.60	401

LSD (0.05) (3-way interaction for nitrate) = 10.6

[1] Low Al = 39 mg Al kg^{-1}; Med Al = 83 mg Al kg^{-1}; High Al = 266 mg Al kg^{-1}.

samples. There was a slight increase in NH_4^+ concentration suggesting that nitrifiers are more sensitive to Al levels than microorganisms responsible for NH_4^+ production.

Examination of KCl pH and ex-Al data suggested the possibility to significantly alter those parameters in low pH high Al soil by incorporating small, practical quantities of organic matter such as animal manure.

Experiment 2.

The treatments developed by mixing soils gave a range in soil pH at all sampling periods measured either in water or 1 N KCl (Table III-5). As would be expected soil pH fluctuated during incubation but when controls and treated samples were averaged, only the high Al soil (Al-6) showed a significant decrease in pH from the beginning to end of the incubation period.

Manure incorporation had a significant effect on both H_2O and KCl pH (Table III-6). Water pH of manured samples was higher than the control except for the highest Al level (335 mg kg-1) where the quantity of manure applied probably was too small to significantly affect the H_2O pH. However, KCl pH of the treated samples was significantly higher than controls for all the soils used in this experiment. Initial Al x Manure x Date interaction was significant. At any sampling date the KCl pH of the treated samples was significantly higher than the control for most treatments (Table III-6).

Table III-5. The effect of initial exchangeable Al and incubation time on soil pH[1]

Sampling time	Initial Al level					
	Al-1	Al-2	Al-3	Al-4	Al-5	Al-6
Days	pH (in Water)					
0	6.19	5.80	5.39	5.42	5.15	4.98
7	5.98	6.02	5.88	5.61	5.27	5.04
14	6.08	5.95	5.93	5.43	4.87	4.61
28	6.23	6.10	6.05	5.71	5.40	4.96
63	5.89	5.39	5.77	5.69	5.03	4.74
LSD (0.01) = 0.21						
	pH (in 1 N KCl)					
0	5.28	4.77	4.68	4.38	4.13	3.94
7	5.10	4.84	4.56	4.23	3.86	3.68
14	5.34	5.03	4.87	4.39	4.08	3.92
28	5.60	5.18	5.03	4.58	4.10	3.90
63	5.37	5.33	4.86	4.72	4.09	3.86
LSD (0.01) = 0.12						

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[1] Each value reported is a mean of three replications and two treatments (control and manure added).

Table III-6 The effect of incubation time, fresh heifer manure and initial exchangeable Al on soil pH.

Al level[1]	Incubation time (days)									
	0		7		14		28		63	
	0	100[2]	0	100	0	100	0	100	0	100
	---pH (in water)[3]---									
Al-1	5.94	6.44	5.97	6.00	5.58	6.58	5.72	6.84	5.28	6.49
Al-2	5.65	5.95	5.81	6.23	5.56	6.34	5.78	6.43	6.05	6.22
Al-3	5.27	5.51	5.83	5.94	5.71	6.18	5.91	6.20	5.81	5.74
Al-4	5.34	5.53	5.53	5.69	5.24	5.62	5.51	5.92	5.48	5.89
Al-5	5.12	5.19	5.28	5.26	4.76	4.99	5.28	5.52	4.99	5.08
Al-6	4.93	5.04	5.13	4.96	4.67	4.55	5.03	4.90	4.73	4.76

LSD (0.01 for 3 way interaction) = 0.29

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[1] Al-0= 0; Al-2= 10; Al-3= 45; Al-4=92; Al-5= 193; Al-6=335 mg Al/kg.

[2] 0 = control; 100 = 100 mg TKN kg^{-1}.

[3] Each value reported is a mean of three replications.

Table 6. (cont.)

Al level[1]	Incubation time (days)									
	0		7		14		28		63	
	0	100[2]	0	100	0	100	0	100	0	100
	pH (in 1 N KCl)[3]									
Al-1	5.01	5.55	4.96	5.24	5.04	5.65	5.01	6.19	4.88	5.86
Al-2	4.56	5.00	4.49	5.12	4.68	5.34	4.82	5.54	5.21	5.54
Al-3	4.19	5.16	4.40	4.71	4.56	5.18	4.86	5.21	4.84	4.88
Al-4	4.10	4.66	4.02	4.42	4.19	4.59	4.29	4.88	4.41	5.04
Al-5	3.93	4.23	3.79	3.93	3.99	4.17	4.02	4.19	3.99	4.18
Al-6	3.78	4.12	3.63	3.74	3.88	3.96	3.86	3.95	3.83	3.89

LSD (0.01 for 3 way interaction) = 0.17

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[1] Al-0= 0; Al-2= 10; Al-3= 45; Al-4=92; Al-5= 193; Al-6=335 mg Al/kg.

[2] 0 = control; 100 = 100 mg TKN kg^{-1}.

[3] Each value reported is a mean of three replications.

The pH in water of the control treatment decreased 7 days after incubation for most treatments while KCl pH for all soils was at a minimum after 7 days of incubation (Table III-6). This apparently reflects that nitrification had occurred depleting NH_4^+ from the soil. After this period, KCl pH increased significantly for all treatments. It reached a maximum after 28 days for the surface soil Al-1, Al-3, and Al-5. It increased continuously for Al-2 and Al-4 while in Al-6 it became steady after 14 days. This result indicates that the ammonification was the dominating process in those soils.

Nitrate production was consistently lower in manure amended soils than in the control for experiment 2 as well as for experiment 1, but when averaging all sampling periods, the differences were not significant in experiment 2 except for Al-1 (Figure III-1). It should be noted that the Al-3 treatment that was incubated at a higher water content did not follow this trend. Surprisingly, nitrification was also low in the treated surface soil. Considering the pH of the surface soil (5.94 in water and 5.01 in KCl) one might expect nitrification to be higher for soils treated with manure. The lower nitrification observed may be explained by denitrification process which was not measured. The nitrate concentration when control samples and manure treated samples were averaged decreased with time except for the soil with the lowest Al level (Figure III-2). By 14 days, little NO_3^- was found in either the control or

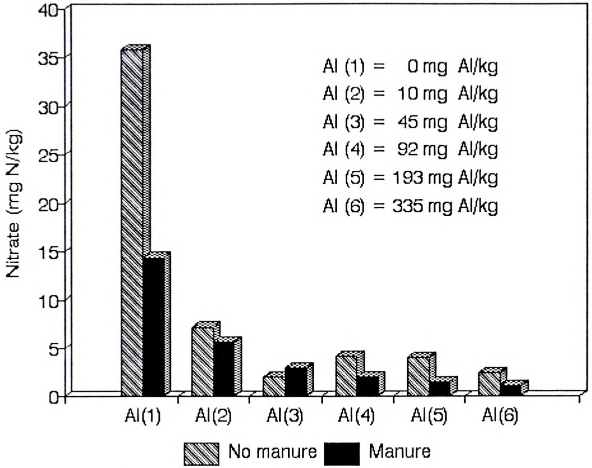

Figure III-1. Effect of initial exchangeable Al and manure on nitrate concentration after 63 days incubation (each data point is a mean of 5 incubation times).

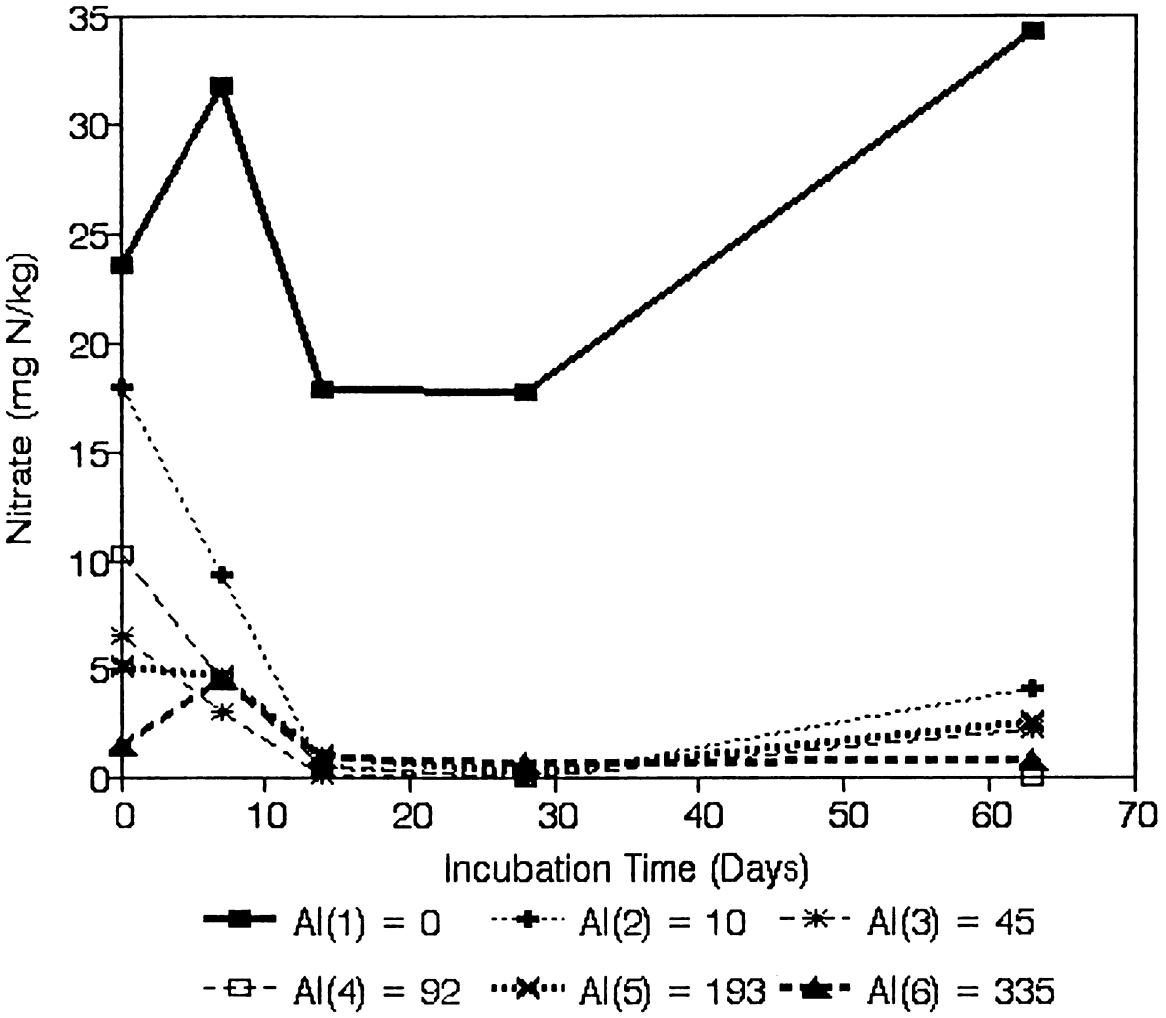

Figure III-2. Nitrate concentration as affected by initial extractable Al (each point is a mean of control and manure treated soil).

manure treated soils except for the low Al soil without manure addition. After 28 days some nitrate increases were observed, particularly in soil Al-1, Al-2, Al-3 and A-5. Little change occurred in soil Al-4 and Al-6. Examination of data in Table III-7 suggest that nitrifiers can tolerate low concentration of exchangeable Al because after 63 days of incubation the nitrate concentration in manure amended treated Al-2 (10 mg Al kg-1) and Al-3 (45 mg Al kg-1) were approximately the same as in Al-1 (0 mg Al kg-1). A low concentration of exchangeable Al (10 mg Al kg^{-1}) was toxic to nitrifiers (see Table III-7). Since this occurred at pH 5.6, it would appear that Al is more toxic to nitrifiers than is low pH. Treatment Al-1 at 7 days has a KCl pH value of 5.1 and nitrate concentration of 31 mg kg^{-1} compared to 5.3 and 4.1 at 63 days in Al-2. In addition, at 63 days the pH of Al-1 is similar to that of Al-2 while the nitrate concentration is 34.4 and 4.1 mg kg^{-1}, respectively (Figure III-2 and Table III-6). Furthermore, it appears that the concentration of Al in Al-4, Al-5, and Al-6 was too high for nitrifiers to carry out the oxidation of NH_4^+ and one might be tempted to conclude that after 63 days the population of nitrifiers has been eliminated because of the toxic concentration of exchangeable Al (92, 193, and 335 mg kg^{-1}. This result is supported by the work of Keyser and Munns (1979) on <u>Rhizobium</u> of cowpea and contradicted by that of Hartel and Alexander (1983).

Table III-7. The effect of incubation time, fresh heifer manure and initial exchangeable Al on soil nitrate level.

Al level[1]	Incubation time									
	0		7		14		28		63	
	0	100[2]	0	100	0	100	0	100	0	100
	--------------------mg N/kg soil as nitrate[3]--------------------									
Al-1	24.7	22.5	32.9	30.7	27.1	8.8	35.2	0.33	59.0	9.8
Al-2	18.7	17.2	15.8	2.9	0.87	0.13	0.10	0.002	0.23	8.0
Al-3	6.8	6.4	3.0	3.2	0.10	0.23	0.002	0.002	0.05	5.38
Al-4	10.8	9.8	9.0	0.002	1.18	0.04	0.07	0.002	0.05	0.05
Al-5	5.32	4.95	7.2	2.12	2.20	0.002	0.55	0.002	4.95	0.17
Al-6	1.53	1.47	5.48	3.68	1.85	0.002	1.40	0.04	1.70	0.05

LSD (0.01 for 3 way interaction) = 7.58

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[1] Al-0= 0; Al-2= 10; Al-3= 45; Al-4=92; Al-5= 193; Al-6=335 mg Al/kg.

[2] 0 = control; 100 = 100 mg TKN kg^{-1}.

[3] Each value reported is a mean of three replications.

Results for NH_4^+ concentration are presented in Figure III-3 and III-4, and Table III-8. Ammonia concentration was greater in Al-3 (Figure III-4) and increased with time reaching a maximum at 28 days and decreasing rapidly after that date (Figure III-4). This may correspond to the higher moisture level in Al-3. This is seen in the production of NH_4^+ in the control sample during the first week of incubation which shows that ammonification of the organic matter in the soil as well as ammonification of the added manure was occurring. In addition, there may have more denitrification in treatments Al-1 and Al-2 than other soil mixes since NH_4^+ disappeared in this treatment with incubation time but NO_3^- did not increase by the same quantity. By 14 days after the incubation the concentration of NO_3^- is almost undetectable while that of NH_4^+ increased slightly before becoming steady (Figure III-2 and III-4). Thus, it appears that the process of nitrification was more sensitive to Al concentration than was the process of ammonification, whereas, the process of ammonification is sensitive to moisture content if we consider Al-3.

The persistence of NH_4^+ in the soils with exchangeable Al may be beneficial to crops if there is a well planned coordination between planting and manure application. If nitrification does not occur, N loss by leaching may be controlled. This implies more efficient use of crop production inputs (N) leading to a more sustainable cropping system.

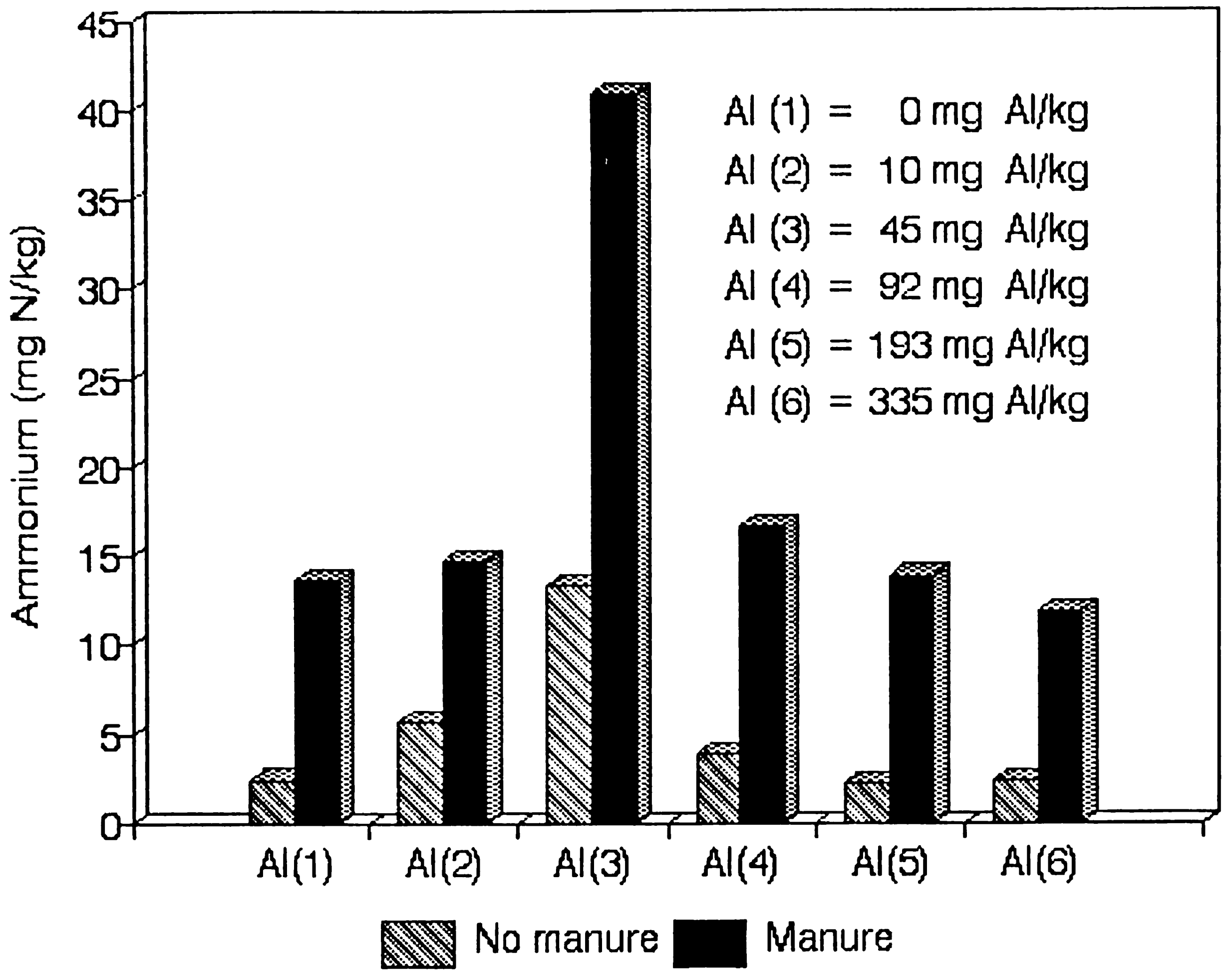

Figure III-3. Effect of initial exchangeable Al and manure on ammonium concentration after 63 days incubation (each data point is a mean of 5 incubation times).

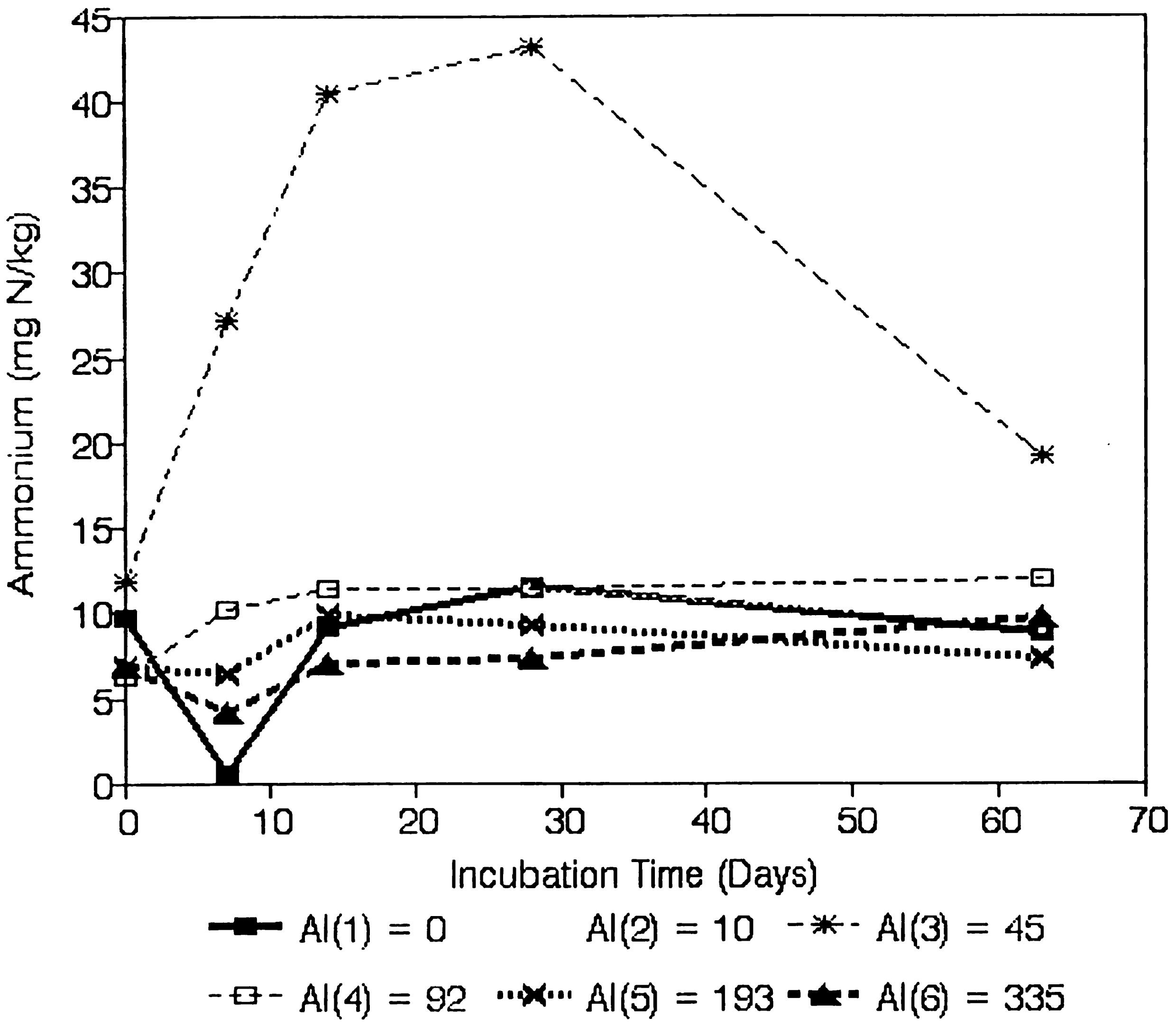

Figure III-4. Ammonium concentration as affected by initial exchangeable Al (each point is a mean of control and manure treated soil).

Table III-8. The effect of incubation time, fresh heifer manure and initial exchangeable Al on soil ammonium level.

Al level[1]	Incubation time									
	0		7		14		28		63	
	0	100[2]	0	100	0	100	0	100	0	100
	--------------------mg N/kg soil as ammonium[3]------------------									
Al-1	3.18	16.6	1.20	0.24	2.86	15.5	1.55	21.7	3.52	14.3
Al-2	2.07	11.9	3.53	15.1	6.15	21.9	5.28	17.7	11.6	7.1
Al-3	4.62	18.9	15.8	38.6	21.9	59.1	17.71	68.5	7.1	19.3
Al-4	1.51	11.2	2.63	17.9	4.50	18.4	4.67	18.2	6.3	17.8
Al-5	0.72	13.0	0.62	12.5	3.68	16.2	3.35	15.3	2.53	12.3
Al-6	1.02	12.9	0.002	8.6	3.65	10.5	3.15	11.6	4.28	15.3

LSD (0.01 for 3 way interaction) = 7.64

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[1] Al-0= 0; Al-2= 10; Al-3= 45; Al-4=92; Al-5= 193; Al-6=335 mg Al/kg.

[2] 0 = control; 100 = 100 mg TKN kg^{-1}.

[3] Each value reported is a mean of three replications.

Table III-10 indicated that the small quantity of manure applied was sufficient to substantially reduce the Al concentration in different soils. This was particularly true for the moderately high Al soils (Al-4 and Al-5). Although reductions did occur with the highest Al treatment the percentage reduction was less than for the intermediate Al treatment. Little change produced by addition of manure was seen in the ammonium acetate extractable Al (Table III-9) suggesting that the reduction was associated with increasing pH caused by the addition of manure. Ammonium acetate, pH 4.8, generally extracted much larger amounts of Al than did KCl. The ammonium acetate extractable Al should include the ex-Al and the amorphous fractions, especially at high pH in Al1 to Al3. As pH decreases the ex-Al extracted with 1 N KCl is approximately the same as ammonium acetate extractable Al. Figure III-5, illustrates the effect of manure on exchangeable Al after 28 days incubation again showing the reduction with manure application. The level of ex-Al in both treated and control generally decreases with time (Figures III-6 and III-7). This is probably due to polymerization or to crystallization of Al compounds.

These experiments consistently show that manure (i.e organic matter) application can simultaneously modify the pH (KCl) and ex-Al in high Al soils. The practical implication of these results is the increase in soil pH and N content of the soils with addition of manure. In addition, the indirect effect of increasing the pH of these soils is to

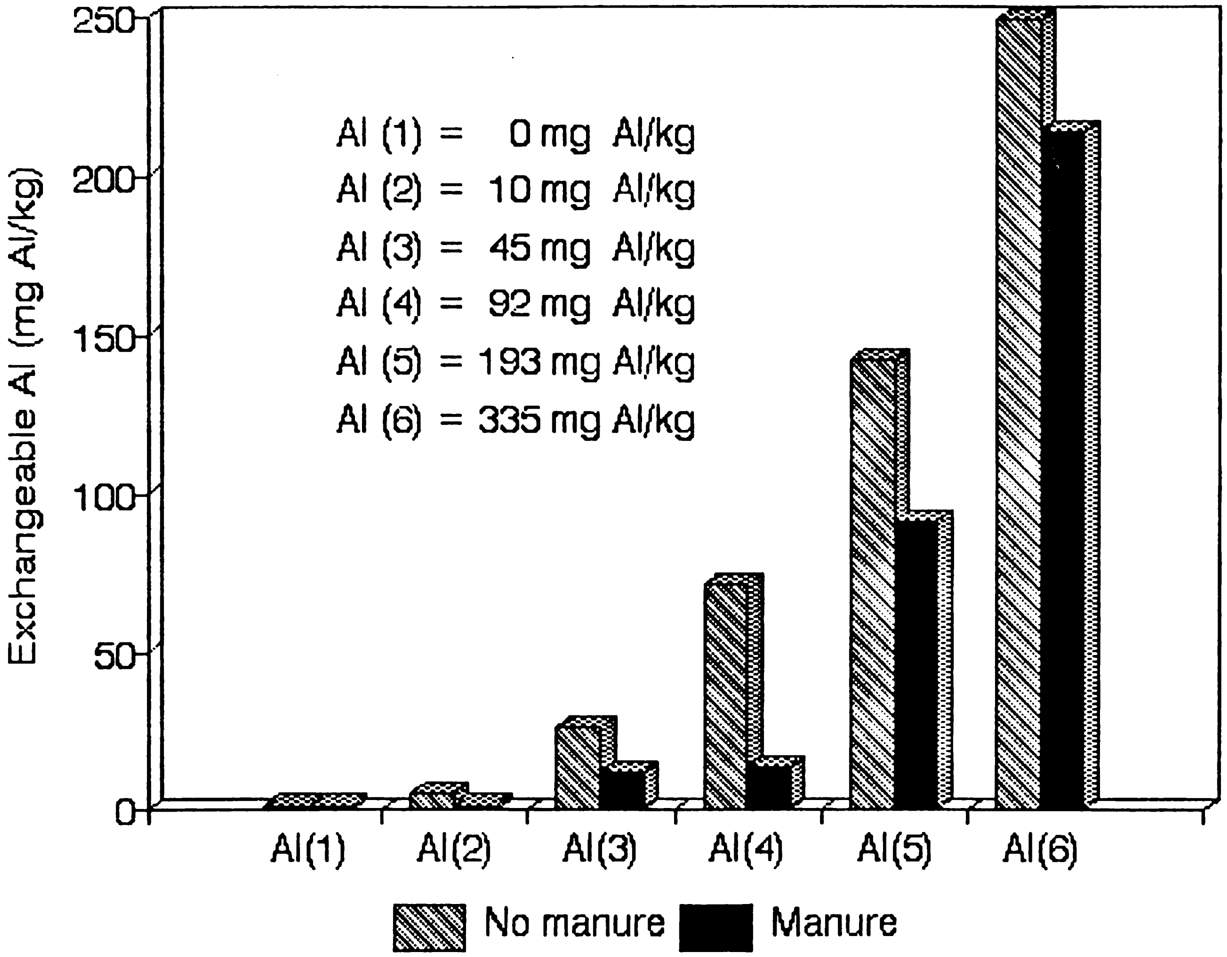

Figure III-5. Effect of initial exchangeable Al and manure on exchangeable Al after 28 days of incubation (each data point is a mean of 4 incubation times).

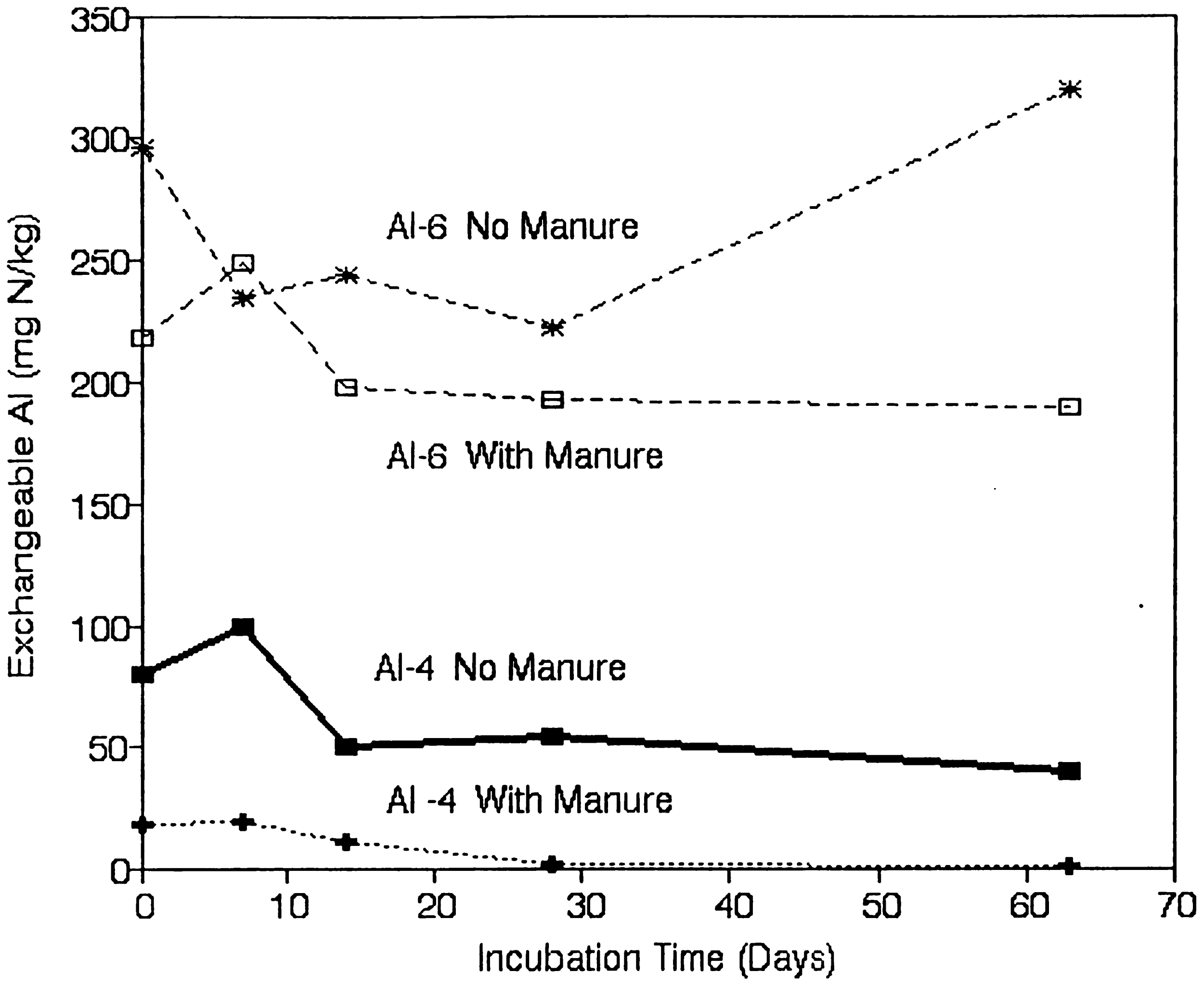

Figure III-6. Effect of initial exchangeable Al, manure, and incubation time on exchangeable Al.

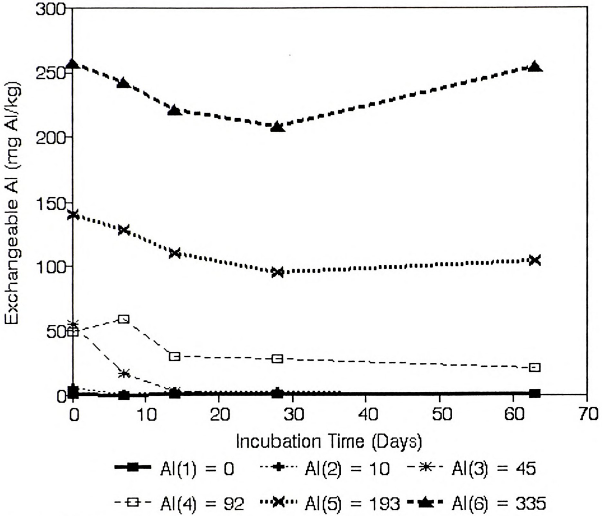

Figure III-7. Effect of initial exchangeable Al and incubation time on exchangeable Al.

Table III-9. The effect of incubation time, fresh heifer manure and initial exchangeable Al on Ammonium Acetate Extractable Al.

Al level[1]	Incubation time									
	0		7		14		28		63	
	0	100[2]	0	100	0	100	0	100	0	100
	----------mg Al/kg soil[3]----------									
Al-1	25.0	20.4	22.7	20.0	48.8	80.0	30.3	74.6	29.2	53.4
Al-2	57.0	45.0	54.0	48.6	88	107	66.1	81	66.5	61.5
Al-3	92	84	87	77	144	129	107	94	80	72
Al-4	117	96	112	92	150	148	129	114	96	104
Al-5	188	166	185	162	226	216	204	174	206	167
Al-6	282	249	299	250	328	303	282	262	298	265

LSD (0.01 for 3 way interaction) = 16.28

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[1] Al-0= 0; Al-2= 10; Al-3= 45; Al-4=92; Al-5= 193; Al-6=335 mg Al/kg.
[2] 0 = control; 100 = 100 mg TKN kg^{-1}.
[3] Each value reported is a mean of three replications.

Table III-10. The effect of incubation time, fresh heifer manure and initial exchangeable Al on KCL extractable Al.

Al level[1]	Incubation time									
	0		7		14		28		63	
	0	100[2]	0	100	0	100	0	100	0	100
	mg Al/kg soil[3]									
Al-1	1.6	0.75	0.53	0.57	1.39	0.91	0.55	2.3	1.41	1.16
Al-2	9.3	2.2	3.0	0.08	4.1	0.89	3.4	2.5	1.4[4]	0.6[4]
Al-3	66.6	42.8	33.5	0.36	4.3	2.2	1.7	1.8	1.1[4]	2.4[4]
Al-4	80	18.8	100	20.1	50	11.5	55	2.3	40[4]	1.2[4]
Al-5	179	102	156	102	132	90	102	72	130[4]	77[4]
Al-6	296	218	235	249	244	198	222	193	320[4]	190[4]

LSD (0.01 for 3 way interaction) = 27.07

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[1] Al-0= 0; Al-2= 10; Al-3= 45; Al-4=92; Al-5= 193; Al-6=335 mg Al/kg.

[2] 0 = control; 100 = 100 mg TKN kg^{-1}.

[3] Each value reported is a mean of three replications.

[4] Values were corrected for instrument drift.

increase the surface charge of high Al soils and thus promote cation retention. It has been shown that as pH increases the surface charge and cation adsorption increases (i.e see Chap. IV of this dissertation). This result can be helpful in planning low input, sustainable cropping systems that are essential to feed the people in high populated, developing countries located on acid, tropical soils.

SUMMARY AND CONCLUSIONS

Results from this study showed that even low exchangeable Al concentration (10 mg Al kg^{-1}) in soils reduced nitrification. Further more, this study showed that application of either liquid (anaerobic) or fresh heifer manure did not result in accumulation of NO_3^- in low pH, high Al soils but did show loss of NO_3^- with time. This would indicate that denitrification progresses more rapidly than nitrification under these conditions.

The results presented indicate that manure amendments significantly increase the pH, and simultaneously decrease the exchangeable fraction of Al in those soils. Changes in pH will bring about changes in surface charge, subsequently increase in CEC or cation adsorption (Chap. IV of this dissertation).

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CHAPTER IV

EFFECT OF LOW LEVEL OF MANURE APPLICATION ON THE SURFACE CHARGE PROPERTIES OF SOIL MATERIALS

ABSTRACT

Organic matter depletion under intensive cropping of tropical soils, the presence of Oxisols and Ultisols, and the growing area of the temperate-zone soils with low pH and high exchangeable Al are very challenging in sustaining food crop production to feed the expanding population. Increasing the charge on soil minerals would be very beneficial in improving the productivity of soils in tropical areas. A $Ca(NO_3)_2$ adsorption study was carried out to determine the effect of a practical rate of beef manure application (100 mg N kg^{-1}) on the surface charge of a low pH, high Al subsoil of the Kalamazoo series as a function of pH and ionic strength (I). Results showed that Ca adsorption increased as pH increased from 3.1 to 5.4 and was independent of I. Nitrate adsorption was not observed at any pH or I. Calcium adsorption was lower in the manure-treated soil at a given pH which may be due to a long incubation time of the soil with manure before the equilibration of samples for the study. However the CEC of the manure-amended soil was higher than the control in the range of pH 4.5 and 5.5.

INTRODUCTION

Managing acid, tropical soils to maintain crop productivity and to feed an expanding population is very challenging. One of the fundamental problems is the lack of charge on sites on mineral surfaces to retain cations or anions under conditions of severe leaching. In fact, G. Gillman (personal communication[1]) has considered the lack of surface charge to be the most severe problem in acid, low pH soils of the tropics.

Depletion of organic matter under intensive cropping in tropical soils has increased the problems of low charge on the mineral fraction of soils, because organic matter is responsible for a large fraction of the total charge in soils. Measures to prevent the depletion of organic carbon are being studied. In addition amendments that change both the pH and the ionic strength of the soil solution have been used to increase the surface charge of soils in tropical areas where Oxisols and Ultisols prevail, or in temperate areas with low pH and high Al. Examples of such amendments are lime, gypsum or phosphogypsum, or organic materials.

Aluminum hydroxides are known to retain nutrients (Huang, 1975; Wada and Harvard, 1974). But the aqueous chemistry of Al also influences the nature and properties of Al hydroxides by controlling ionic factors that influence the hydroxide surface chemistry. The speciation of aqueous

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[1] Gillman, G. 1990. Personal communication with B. Ellis.

Al and Al hydroxide surfaces is affected by inorganic anions (Cl, SO_4, NO_3, and ClO_4) (Hsu, 1967; Turner and Ross, 1970; Ross and Turner, 1971), low molecular weight organic anions (Kwong and Huang, 1977; Violante and Huang, 1985; Violante and Jackson, 1981; and Violante and Violante, 1980), and fulvic acids (Kodama and Schnitzer, 1980). Organic acids increased the surface area of Al hydroxides formed by precipitation through structural distortion which resulted in increased retention of P and Ca (Kwong and Huang, 1979). However, as the precipitation products of Al aged in the presence of organic acids, the specific surface was reduced and their power to retain P was also reduced.

Parfitt et al. (1977) elucidated the mechanism of P adsorption on gibbsite as involving ligand exchange of either H_2O at positive sites or OH^- at negative sites. They also showed that fulvic acid and humic acid can be adsorbed onto hydrous oxide surfaces by ligand exchange. The process involved the release of OH^-, which resulted in an increase in the pH of the soil solution. Their results support the formation of inner-sphere complexes.

Using cylindrical, internal reflection Fourrier transform infrared spectroscopy, Yost et al. (1990), confirmed the 1:1 Fe-salicylate complexes and reported that at higher concentrations of salicylates, the inner sphere complexes coexist with weakly bound complexes.

Morrisson (1983) studyed the adsorption of anions (chloride, phosphate, acetate, citrate, succinate, and

glycolate) onto oxides at different pH values above the oxide point of zero charge (6.5). He concluded that the mechanism involved bonding through a hydroxyl to the surface oxide ion. He reported the adsorption envelope for citric acid to be significantly higher than that of acetic acid at pH 8. He also suggested that higher molecular weight compounds (phosphate esters or polycarboxlates containing hydroxyls groups) are adsorbed at pH's significantly above the PZC, but through ligand exchange. Some studies have demonstrated that organic anions such as citrate, succinate, HA, and FA compete with P for adsorption sites on the surface of Al, thereby decreasing their capacity to retain P (Nagarajah et al. 1970; Siband and Young 1986).

Charlet and Sposito (1987) developed a method to simultaneously measure the net proton surface charge density and surface excesses of metal and ligand in a 1:1 background electrolyte. They found that the point of zero net charge (PZNC) of a Brazilian Oxisol was 4.2 and independent of the electrolyte (KNO_3 or NaCl) and ionic strength between 4 and 500 mol m^{-3}. In addition, the PZNC was not significantly different from the point of zero salt effect (PZSE). The low value of the PZNC suggested a predominant role of kaolinitic and organic matter components in determining the surface chemistry the Haplustox they studied.

In a spearate study, the adsorption of Ca was independent of ionic strength in the range of 2 to 67 mol

m^{-3} (Charlet and Sposito, 1989). This result suggested that Ca formed inner sphere surface complexes with this soil. The methods of Charlet and Sposito, 1987, give promise of determining effects of added amendments upon charging of acid, high Al soils.

A question remains, "will agronomic rates of animal manures affect the charging of soil materials from acid, high Al, low organic soils?" The objective of this study was to answer this question through incubation of an acid, low organic matter Kalamazoo subsoil with fresh heifer manure. I expect the data obtained from this study to significantly improve the understanding of the surface chemistry in high Al soils, and subsequent surface reactivities in relation to the accumulation of nutrients.

MATERIALS AND METHODS

Soil Characteristics

A bulk sample for this study was collected from the B horizon of a Kalamazoo sandy loam (Kellogg Biological Station of Michigan State University). The soil was screened to pass a 2mm sieve and stored in a field moist condition at 4 ° C. The soil is classified as a Kalamazoo sandy loam (Typic Hapludalfs, fine-loamy, mixed mesic). Some selected physical-chemical properties of the soil and manure characteristics are in Table IV-1.

Table IV-1. Selected physico-chemical properties of the soil used in charging studies

pH(Water)	pH(KCl)	Ex-Al	C	Sand	Silt	Clay
			mg/kg	%	------%--------	
5.16	3.70	335	0.41	50	22	28

Note: Methods were standard methods from Agronomy 9, Part 1 (1965) and Part 2 (1982)except for C which was total C determined with a Leco C analyzer.

The soil was divided into two subsamples and fresh heifer manure was added to one portion at a rate of 100 mg N Kg^{-1}. Both amended and unamended soils were incubated at field capacity (19% moisture on an oven dry basis) in triplicate. One hundred grams of soil was added to a preweighed, wide mouth square glass bottle. The soil was packed to a bulk density of about 1.3 g cm^{-3} and total weight of the mixture recorded. The bottles were covered with polyethylene plastic perferated with pin holes and attached with a rubber band. Samples were weighed every week and returned to field capacity with deionized water if needed. After 10 weeks of incubation at room temperature (24.5 ± 05 ° C), samples were air dried. Each replicate was mixed separately and a representative 20 g subsample was taken for characterization of surface charge properties.

The surface charge and Ca^{2+} and NO_3^- adsorption of the two soils were determined using a discontinuous proton titration and ion adsorption procedure (Charlet and Sposito, 1987). The soils were placed in 250-ml centrifuge bottles and were saturated with $Ca(NO_3)_2$ by suspending them in 200 ml of 0.5 mol kg^{-1} of $Ca(NO_3)_2$ solution and shaking at low speed for one hour on a Eberbach tray shaker. The suspensions were centrifuged at 6000 rpm for 10 min on a Sorvall RC 5B Refrigerated Superspeed centrifuge at 25 °C. The supernatant solutions were discarded. This equilibration and centrifugation procedure was repeated until the pH of supernatant was equal to that of the $Ca(NO_3)_2$ solution (pH 6.5). Then the samples were washed repeatedly with 0.1 mol kg^{-1} of $Ca(NO_3)_2$ until the pH of the supernatant was 6.5. The final resuspension was accomplished using 200ml of 0.02 mol kg^{-1} of $Ca(NO_3)_2$, and the supernatant solution discarded. The soil paste remaining in the centrifuge tube was then mixed thoroughly and transferred to small vials. A subsample of the paste was used for moisture determination. The saturated soil pastes were stored at 4 °C and used for the Ca and NO_3 adsorption and titration experiments.

Triplicate subsamples of $Ca(NO_3)_2$-saturated soil pastes containing 300 mg of soil (dry soil basis) were added to preweighed 40-ml polyallomer centrifuge tubes. The soils were suspended in 0.030 kg of $Ca(NO_3)_2$ solution containing HNO_3 to adjust to a desired pH value between 3.5 to 6.5. The ionic strength was either 0.005 or 0.02 mol kg^{-1}. For each I, six pure $Ca(NO_3)_2$ solutions with the same initial HNO_3 concentrations used for the soil suspensions were included as blanks. The soil suspensions and electrolyte blanks were equilibrated at room temperature (24 ± 0.5 °C)

by shaking for 2 hours on an Eberbach tray shaker. The samples were centrifuged for 15 min at 12000 rpm. The supernatant liquid was transferred into small plastic vials for immediate pH measurement with a combination pH electrode on an Orion 811 meter. To determine the mass of entrained solution, each centrifuge tube was weighed with its content. To estimate the amount of H^+ consumed during the experiment, the difference between the pH of the blank solution (no soil added) and the supernatant solution of the same initial pH and ionic strength was calculated and converted to H^+ concentration. Samples were then stored at 4 $^{\circ}$ C for later Ca^{2+} and NO_3^- determination.

The adsorbed Ca^{2+} and NO_3^- were then displaced by shaking overnight with 0.030 kg of 0.2 mol kg^{-1} of $MgCl_2$. The supernatant was transferred into plastic vials. The total concentration of Ca in the supernatant and extractant solution was determined using a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer. The analysis of NO_3 was performed by Flow injection with a Lachat Quikchem.

The relative surface excess of Ca^{2+} and NO_3^- was calculated using the following equation:

$n_i = n_{itot(MG)} - M_{entr}(m_i)$ (Sposito, 1984, Ch. 4)

where: n_i = relative surface excess; i = Ca or NO_3; $n_{itot(MG)}$ is the total number of moles of Ca or NO_3 extracted by $MgCl_2$ from the soil per unit mass of soil; M_{entr} is the mass of entrained $Ca(NO_3)_2$ solution per unit

mass of soil; and m_i is the concentration of Ca or NO_3 (mol kg solution^{-1}) in the supernatant solution.

Statistical Analysis

The statistical analysis ANOVA was performed with MSTAT C (Freed and Eisensmith, 1986). The experiment was treated as factorial arrangement in a completely randomized design. Factors were: a) manure with two levels (0, 100 mg N TKN kg^{-1}), b) ionic strength (0.02 mol kg^{-1}, 0.005 mol kg^{-1}), c) equilibrium supernatant solution pH (3.5, 4.0, 4.5, 5.0, 5.5, 6.0). Treatments were in triplicates. A total of 72 samples were analyzed.

RESULTS AND DISCUSSION

Surface charge determination by Ca adsorption

The experimental data as function of manure (Man), ionic strength (I), and pH are shown in Tables IV-2 and IV-3. The main effects of manure and pH on the Ca adsorption of a Kalamazoo subsoil with high Al and low pH (Table IV-4) were statistically significant, ($P<0.05$ and 0.01 respectively). The only exception was the ionic strength. It is apparent that Ca adsorption increases with pH in both treated and non-treated soils. Surprisingly, there was no NO_3^- adsorption at any pH except at low I and at pH 3.11 where there was an anion exchange capacity (AEC) of 1.9 mmol$_c$ kg^{-1}. This result suggests that even though the soil was high in exchangeable Al (Ex-Al), it was not comparable to most Oxisols or Ultisols. There was a higher net charge

Table IV-2. The effect of manure and pH on the adsorption of calcium, nitrate and net charge of an acid Kalamazoo sandy loam subsoil at high ionic strength.

Treatment	pH	Exchangeable Ca	Exchangeable NO_3	Net Charge
		$mmol_c/kg$	$mmol_c/kg$	$mmol_c/kg$
		Ionic Strength = 0.02 mol L^{-1}		
Control	3.07±0.03	46±6	-3±4	50±2
Manure	2.91±0.01	44±2	-3±2	46±0
Control	3.54±0.01	58±3	-3±1	60±2
Manure	3.38±0.01	48±3	-7±2	55±1
Control	3.89±0.02	64±2	-6±2	69±4
Manure	4.06±0.02	56±7	-15±8	70±1
Control	4.27±0.02	68±1	-3±2	71±2
Manure	4.51±0.02	70±3	-5±1	75±3
Control	4.81±0.02	72±2	-4±1	75±1
Manure	4.89±0.02	72±2	-5±1	76±1
Control	5.35±0.03	72±4	-2±0.4	74±4
Manure	5.32±0.02	64±2	-2±0.7	66±2

Table IV-3. The effect of manure and pH on the adsorption of calcium, nitrate and net charge of an acid Kalamazoo sandy loam subsoil at low ionic strength.

Treatment	pH	Exchangeable Ca	Exchangeable NO_3	Net Charge
		$mmol_c/kg$	$mmol_c/kg$	$mmol_c/kg$
		Ionic Strength = 0.005 mol L^{-1}		
Control	3.11±0.01	21 (1.4)	+2±1	40±4
Manure	3.13±0.01	22 (5.7)	-1±1	45±13
Control	3.54±0.01	25 (1.1)	-2±0	52±2
Manure	3.48±0.00	24 (0.6)	-1.9±0.2	51±1
Control	4.03±0.02	30 (0.2)	-1.8±0.2	62±0
Manure	4.21±0.03	31 (0.9)	-2.1±0.2	63±2
Control	4.64±0.04	34 (1.2)	-1±1	69±4
Manure	4.68±0.01	33 (1.4)	-2±0.1	68±2
Control	5.12±0.01	34 (1.1)	-1±2	69±1
Manure	5.20±0.01	37 (1.3)	-0.5±0.5	74±2
Control	5.76±0.02	47 (9.4)	-0.5±0.8	93±19
Manure	5.67±0.02	40 (1.2)	-0.5 (0.0)	80±2

Table IV-4. Source of variance and level of significance for analyses of adsorbed calcium and net surface charge.

Variable	Source of Variation						
	Man 36	I 36	pH 12	ManxI 18	ManxpH 6	IxpH 6	ManxIxpH 3
Calcium	*	n.s.	**	n.s.	n.s.	**	n.s.
Net Charge	n.s.	*	**	n.s.	*	**	n.s.

Note: n.s.= not significant; *, and ** indicate signifiance at the 0.05 and 0.01 levels of probability, respectively.

at a given pH with the higher ionic strength (Tables IV-2 and IV-3). Ca adsorption was independent of I between 0.02 and 0.005 mol kg^{-1} and increased with pH in the range 3.0 to 5.5. This result is in agreement with Charlet and Sposito's (1989). However, a significant (IxpH) interaction was apparent probably reflecting the difference in Ca adsorption at the same pH. The Ca adsorption was 38.6 $mmol_c$ kg^{-1} at pH value of 3.5 for low I and 45 for high I. Calcium adsorption averaged across all pH's was 59.8 $mmol_c$ kg^{-1} for manure amended and 62.2 $mmol_c$ kg^{-1} for the control. Apparently the hypothesized positive effect of beef manure on high Al, low pH subsoil of the Kalamazoo series is not correct. At low pH's addition of manure decreased the Ca adsorption slightly (Tables IV-2 and IV-3). Between pH's 4.5 and 5.5 there was a slight increase in Ca adsorption after manure addition. But, on the other hand, manure application caused soil pH to increase significantly (Chapter III of this thesis). The practical implication of this study is that the application of manure will increase the pH of the soil to a certain level at which Ca retention will be higher than for the soil without manure treatment. The observation that at the same pH the application of manure has lead to the reduction of ion adsorption, is probably explained by the blocking of exchange sites of the soil by manure undergoing decomposition, and whose sites in turn were blocked by Al ions. This suggests that the ionic strength of the solution electrolyte was insufficient to

displace the Al complexed with organic matter. This could be explained by the higher concentration of Al removed by NH_4OAc at pH 4.8 (Table IV-1) which may come from the fraction representing the exchangeable and the amorphous Al (organically bound Al in this study). Marcano-Martinez and McBride (1989) also found that the high concentration of organically bound Al reduced the CEC of an A horizon to a value approximately equal to that of the B horizon (Dark Red Acrustox in Brazil). Another explanation is that the Al organo complex formed might have reduced their surface reactivity with aging during soil incubation. Kwong and Huang (1979) showed a decrease with aging in surface reactivity of aluminum hydroxides precipitated in the presence of low molecular weight organic acids. Because we wanted to reflect what the farmer does we did not want to evaluate the surface charge of the soil immediately after application. Results from Ca adsorption suggest that during the 12 week incubation period much of the effect of manure application disappears. Thus, one might assume that the incorporation of organic materials will not have a long term effect on the retention of Ca^{2+} in soil like the one used in this study.

Surface Charge

The ion adsorption data show that Ca adsorption increased significantly as either pH or I increased. But manure amendements did not affect total net charge. ManxpH

and IxpH interactions were also significant (Table VI-2). The manure amended-soil constantly had a low CEC, but at pH 4.0 there was a rapid increase, followed by a near steady state. However, in the range of pH 4.5 and 5.5, the CEC of the treated soil was higher than that of the non-treated soil.

There was no nitrate adsorption at any pH studies therefore, the PZNC for this soil was below pH 3.0 (Table IV-2 and IV-3).

CONCLUSIONS

The adsorption of Ca^{2+} by a low pH, high Al Kalamazoo subsoil as function of pH and I was negatively affected by amendment with heifer manure. The net charge did increase with increasing pH. The lack of anion exchange capacity suggests that even though the soil was high in exchangeable Al, the permanent surface charge was not negligible. The effect of organic matter on Ca^{2+} adsorption could be more appropriately evaluated with an Oxisol having a small amount of permanent charge (van Raij and Peech, 1972).

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CHAPTER V

SUMMARY AND CONCLUSIONS

Because of the critical role of N, and the importance of utilizing the available organic wastes to sustain food crop production, a series of laboratory incubation studies were conducted to determine the effects of low pH and high Al on mineralization, nitrification, and immobilization processes in soils. In addition, studies were conducted to determine the effect of agronomic rates of fresh heifer manure on the surface charge of high Al soil.

Since the rate of conversion of NH_4^+ from animal waste is so critical to loss of N from soils during the fall of the year, studies were conducted to determine the effect of temperature in the range of 3.5 to 12.5 C on transformation of N from animal waste.

For the experiment with temperatures, 100 g samples were equilibrated with no manure added, and with 100 mg TKN/kg soil with fresh heifer manure or liquid beef manure. Temperatures used were 3.5, 5, 10 and 12.5 $^{\circ}$ C. Results from this low temperature incubation study show that application of fresh manure to a Spinks soil increased the NH_4^+ concentration after 7 days and that ammonification was temperature dependent. Ammonium concentration continued to

increase for temperature of 3.5 and 5 C up to 28 days before a decline in NH_4^+ content occurred with time.

Nitrate production in soil amended with fresh manure decreased by 7 days, and was low or undetected up to 14 days, and irregular for the remainder of the incubation for most temperatures. This suggests that beef manure or partially decomposed organic wastes applied in the fall when soil temperature reaches 3.5 C will dissipate NO_3^-, perhaps through denitrification, thereby reducing the risk of loosing it by leaching.

For liquid beef manure at a temperature of 3.5 $^\circ$ C, NH_4^+ was at a maximum by 7 days and remained in the NH_4^+ form for the remainder of the incubation; thus, application of liquid beef manure to a soil with 3.5 $^\circ$ C temperature will have little risk of N loss due to leaching. At higher temperatures, NH_4^+ concentration reached a maximum in 7 to 14 days but decreased with incubation time. The data suggest that application when the soil reachs 10 $^\circ$ C would be satisfactory providing the soil temperature was reduced within 4 weeks.

At 10 and 12.5 $^\circ$ C there was little recovery of the disappeared NH_4^+ as NO_3^-. This could be explained by nitrification followed by denitrification, by microbial immobilization, by gaseous NH_3 loss, or by clay fixation of NH_4^+.

Incubation studies were done varying exchangeable Al (ex-Al) by mixing soils low in ex-Al with a subsoil high in

ex-Al to obtain 6 levels of ex-Al. Both fresh heifer and liquid beef manure was used. At each sampling time, soil pH, ex-Al, NO_3^-, and NH_4^+ were determined.

The pH of high ex-Al, low pH soil was significantly increased by addition of fresh or liquid manure, and simultaneously the ex-Al level decreased. However, the nitrate level was lower than in the control soils with no manure added. Results suggested that a low concentration of ex-Al may be more toxic to nitrifiers than to denitrifiers so higher Al level may favor a net loss of nitrate.

The surface charge of high ex-Al soil was found to increase with pH, however, at the same ionic strength it was lower where amended with manure than in the control. Calcium adsorption was also increased with pH but not with addition of manure at a constant pH. Since a small amount of beef manure increased the soil pH, the Ca adsorption and consequently the surface charge of high Al soils was also increased. The practical implication of this is that timely application of organic waste in acid, high Al soils will increase the pH and consequently their surface charge which is generally low.

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