REDUCING NITROGEN LOSSES DURING COMPOSTING OF POULTRY MANURE USING THE NATURAL ZEOLITE CLINOPTILOLITE

by

MUSSOLINI KITHOME

B.Sc., The University of Nairobi, Nairobi, Kenya, 1983
M.Sc., Wageningen Agricultural University, Wageningen, The Netherlands, 1987

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

(Department of Soil Science)

We accept this thesis as conforming to the required standard

Arthur A Bomke

L.M. Lavkulich

Robert Blair

THE UNIVERSITY OF BRITISH COLUMBIA

March, 1998

Reducing Nitrogen Losses During Composting of Poultry Manure Using the Natural Zeolite Clinoptilolite

ABSTRACT

Loss of N via NH_3 volatilization during composting of poultry manure reduces the agronomic value of the end-product and contributes to environmental pollution. The objectives of this study were to evaluate N losses via NH_3 volatilization during aerobic composting of poultry layer manure, examine the potential of natural zeolites to adsorb the volatilized NH_3 during composting, and evaluate the poultry manure-zeolite compost as a controlled-release N fertilizer. Eleven mineral samples were characterized for their physical properties, chemical composition, and NH_4^+ adsorption capacity. The effectiveness of a clinoptilolite zeolite Z1 as an NH_4^+ adsorbent at pH range 4 to 7 was tested. The kinetics of NH_4^+ exchange on the zeolite was evaluated at the pH range 4 to 7, initial NH_4^+ concentrations ranging from 70.1 to 1401 mg N L^{-1}, and a temperature range of 25 to 55 °C. Ammonia emissions were measured during composting of poultry manure with zeolites and other amendments in a laboratory composting simulator. The resulting composts were applied to a sand based medium planted with ryegrass (*Lolium multiflorum*) where growth, N uptake, and NH_4^+ and NO_3^- leaching were evaluated. The cation exchange capacity (CEC) and purity of the zeolites, with respect to mineralogy and constituent ions, influenced their affinity and adsorptive capacity for NH_4^+. The amount of NH_4^+ adsorbed increased with increasing pH and NH_4^+ concentration. The estimated NH_4^+ adsorption capacity increased linearly with pH ($r^2 = 0.994$), ranging from 9660 mg N L^{-1} at pH 4 to 13830 mg N L^{-1} at pH 7. Studies on thermodynamics of NH_4^+ exchange on the zeolite Z1 indicated a higher activation energy for desorption (5.65 kJ mol^{-1}) than for adsorption (2.32 kJ mol^{-1}). Composting poultry manure with 60% zeolite Z1 (weight basis) reduced NH_3 losses by 44.3%. The compost had total N concentration of 17.04 g N kg^{-1} and a high NH_4^+ concentration (52.8% of the total N). The 60% zeolite Z1-amended compost treatment produced the highest ryegrass dry matter, N accumulation and N use efficiency compared to the other composts evaluated. Nitrogen leaching losses were low. Although composting poultry manure amended with the natural zeolite clinoptilolite can reduce N losses to the atmosphere, recycling it for crop utilization, the cost of the high amount of zeolite required may be prohibitive.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

This research work was made possible by the support of various persons and institutions whom I have the pleasure to acknowledge. I am grateful to the Canadian International Development Agency (CIDA), University of British Columbia and University of Nairobi linkage program, and Matching Investment Initiative of Agriculture and Agri-Food Canada for financing this project. I am also grateful to Aberhill's Holdings Inc., Canmark International Resources Inc., and Western Industrial Clay Products Ltd. for partially funding this project and providing the zeolites Z1, Z2, and the clay product, respectively. The study leave granted by the University of Nairobi during the last four years is gratefully acknowledged.

I am indebted to the Associate Director of the Pacific Agri-Food Research Centre, Agassiz, for providing me with an absolutely splendid environment in which to conduct research. I would like to express my special thanks to my research supervisor Dr. John W. Paul for his excellent supervision, guidance and support throughout my research work. I greatly appreciate his valuable advice, ideas and help in preparing this thesis.

I express much gratitude to my academic supervisor Dr. Art. A. Bomke for making the entire research program possible. I deeply appreciate his advice, concern and the great efforts he made to find a suitable environment for me to conduct my proposed research in composting. I am very grateful to Dr. Les Lavkulich for accepting my request to be a member of my committee, and allowing me to work in his soils laboratory. I am thankful for the many hours he spent helping me interpret X-ray diffractograms, and I very much appreciate his technical advice and constructive criticisms in the course of my adsorption experiments. I am very grateful to Dr. R. Blair for accepting my request to be a member of my committee, and providing me with his research information on the use of zeolites as a feed supplement for chickens, which was of great help in formulating my research proposal.

The incredible technical support given to me by Tissa Kannangara throughout my research work is highly appreciated. I am extremely grateful for his tireless assistance, concern, and enthusiasm for my research work. I am also grateful to Shaobing Yu for his assistance at various times, and willingness to assist at short time notices.

Lastly, though not the least, I especially want to acknowledge the love, understanding, and encouragement of my dear wife Lucy Kasyoka, and children Malinda, Lula, and Mumo during my stay in Canada. You mean so much to me. My life in Canada was not the same without you. I greatly missed you. Only my Lord Jesus Christ understands the much agony, shame, and embarrassment I had to endure without you!

DEDICATION

I affectionately dedicate this thesis to my dear wife Lucy Kasyoka and children Malinda, Lula, and Mumo. Your fervent prayers, love and incredible support have brought me this far. May the Lord Jesus Christ richly bless you. I love you with the love of God - *Agape*!

CHAPTER 1

INTRODUCTION

Poultry production in the province of British Columbia, Canada, is one of the primary agricultural income generating activities. It is an impressive $244 million a year industry (Paulson, 1994). Most of the poultry production in British Columbia is concentrated on a small landbase overlying an unconfined aquifer in Abbotsford, within the Lower Fraser Valley. Intensification of poultry operations in the Lower Fraser Valley have created problems associated with the storage and disposal of large quantities of poultry manure. Although poultry manure is considered a valuable source of plant nutrients and organic matter, improper management of this waste can damage crops and pollute surface and groundwater resources. Not all protein fed to the birds is metabolized. Excess protein is excreted primarily as uric acid, which starts to decompose soon after excretion. Ammonium is a major product formed which converts to nitrate through the process of nitrification in soil. Nitrates originating from agricultural land use practices have been held responsible for groundwater pollution in the Abbotsford aquifer (Liebscher *et al.*, 1992). Farm practices identified as causes of groundwater pollution include exposed stockpiling, and overapplication of poultry manure for soil fertilization (Sustainable Poultry Farming Group, 1994).

Nitrates in drinking water pose a health risk to infants, particularly those under six months of age who are on a formula based diet, rather than breastmilk (Addiscott *et al.*, 1992). When infants consume too much NO_3^- they can develop a blood disorder called methaemoglobinaemia, also known as "blue-baby syndrome". The disease can be especially acute in those infants who already have a respiratory or intestinal infection (Muia and Thomas, 1990). Methaemoglobinaemia is not caused directly by NO_3^- but occurs when NO_3^- is reduced to nitrite (NO_2^-) by bacteria found in the digestive tract of human infants and animals. Nitrite can then oxidize the iron in the haemoglobin molecule from Fe^{2+} to Fe^{3+}, forming methaemoglobin, which cannot perform the essential oxygen transport functions of haemoglobin. This can result in a bluish coloration of the skin in infants, hence the origin of the term "blue-baby syndrome". Methaemoglobinaemia is a much more serious problem for very young infants than for adults, because after the age of 3 to 6 months the acidity in the human stomach increases to a level adequate to suppress the activity of the bacteria that reduce NO_3^- to NO_2^-. Although the majority of cases of blue baby syndrome have occurred when NO_3^- concentrations in drinking water exceeded 100 mg N L^{-1} (Addiscott, 1992), NO_3^- levels as low as 10 mg N L^{-1} in drinking water have been linked to methaemoglobinaemia (Cogger and MacConnell, 1991). Few cases of methaemoglobinaemia have been recorded in Canada and USA in recent years, but many are never reported (Cogger and MacConnell, 1991). The long-term effect of NO_3^- consumption in older infants, children and adults is not known for certain at this time. Ruminant animals such as cattle and sheep can also develop methaemoglobinaemia.

After many years of testing, Liebscher *et al.* (1992) reported that approximately 60% of the well samples collected from the south Matsqui study area had NO_3^- concentrations that exceeded the 10 mg N L^{-1} maximum acceptable concentration for drinking water (Federal-Provincial Working Group on Drinking Water, 1978). Environment Canada's 1989 sampling results found 46 out of 73 sample sites with NO_3^- concentrations greater than 10 mg N L^{-1} (Liebscher, 1992). Evaluation of annual mean NO_3^- levels shows that the trend is to progressively higher groundwater NO_3^- concentrations over time.

While a variety of human activities have had an impact on the groundwater quality of the Abbotsford aquifer, Liebscher *et al.*, (1992) identify storage and application practices of poultry manure, on both poultry and raspberry farms, as the primary source of contamination. Approximately 45 million birds in the Fraser Valley excrete 140,000 Mg of manure corresponding to about 7,000 Mg N annually (Ference & Associates, 1994). The moisture content of this manure can be as high as 70%, which limits its transport over long distances. As a result, much of this manure is applied to the soil in close proximity to the poultry farms. With time, this can lead to buildup of high concentrations of plant nutrients and toxic substances in the soil (Bomke and Lavkulich, 1975; Huneycutt *et al.*, 1988). There is therefore, need to refine the current use of poultry manure in order to address both agronomic and environmental concerns. Options that have been proposed include construction of more efficient storage facilities that enable poultry producers to store wastes until field crops are best able to utilize the manure nutrients, transportation of the manure away from the aquifer to places like Delta or other nearby areas that have N-deficient soils, feeding processed poultry manure to beef cattle, and composting with a view to producing a value-added product that can be exported from this small land base (Sustainable Poultry Farming Group, 1994).

Composting poultry manure to produce a value-added product has the advantage of producing a compost that can not only improve soil physical and chemical properties, but also provide plant available nutrients. The fertilizer value of poultry manure is often reduced by the loss of N through NH_3 volatilization and denitrification during composting (Kirchmann, 1985). Brinton (1985), Del Zan *et al.* (1987), Paul and Beauchamp (1993), and Brinton and Seekins (1994) compared N availability from fertilizer, fresh manure, and composts for silage and grain corn production. In those experiments where there was a yield response to treatments, the compost treatment was always lower in total N uptake compared with mineral fertilizers.

Aerobic composting of poultry manure amended with natural zeolites can be an effective means of conserving the N in the manure. The NH_4^+ ions can be adsorbed in the channels and central cavities of the zeolite, protecting the N from various loss pathways such as denitrification and leaching. With subsequent release, the N could possibly become available in closer synchrony with crop requirements. On coarse-textured soils, as found in sand-based golf greens, with high percolation rates, more efficient N management would occur since the bulk soil NO_3^- concentration is greatly reduced.

Objectives

The objectives of this thesis research work were:

(1) To evaluate N losses via NH_3 volatilization during aerobic composting of poultry manure.

(2) To examine the potential of natural zeolites as NH_3 adsorbents during composting of poultry manure.

(3) To evaluate poultry manure composted with natural zeolites as a controlled-release N fertilizer for plants.

Background Information

The Abbotsford Aquifer

The Abbotsford/Sumas Aquifer covers an area of approximately 100 km^2 in British Columbia, Canada and a similar area in Washington State, USA (Liebscher *et al.*, 1992). The aquifer is located south west of Abbotsford, British Columbia (49° 3' N 122° 17' W). The Abbotsford Aquifer is an important source of residential, industrial and agricultural water in the Lower Fraser Valley. In 1981, groundwater supplied 44% of the water used for domestic purposes for the area between Surrey and Chilliwack on the south side of the Fraser River, and from Maple Ridge to the district of Kent on the north side (Dorcey and Griggs, 1991). Groundwater provided almost all of the water requirements for the residents of Abbotsford, as well as a large portion of water for other uses.

Surficial deposits in the aquifer are of advance and recessional glaciofluvial, glaciolacustrine and ice-contact origins, collectively termed the Sumas Drift (Armstrong *et al.*, 1965; Easterbrook, 1976). The Sumas Drift is composed of tills, clays, and outwash materials that were deposited near the end of the Fraser Glaciation, approximately 10,000 years ago. The outwash materials are primarily unconfined sands and gravels believed to be up to 70 m thick in some locations (Dakin, 1993). Till inclusions within the outwash are of unknown continuity. The Sumas Drift is underlain by low permeability glaciomarine and marine sediments of the Fort Langley Formation (Halstead, 1986). The dominant soil types overlying the aquifer consist of 0 to 70 or more cm of silty eolian deposits over sandy and gravelly glaciofluvial deposits, and are generally classified as Haplorthods (Luttmerding, 1980). The soils are generally well drained. Organic matter contents in cultivated soils are commonly as high as 8% (Zebarth *et al.*, 1997). The aquifer is classified as being highly developed and highly vulnerable to contamination (Kreye and Wei, 1994).

The aquifer is recharged primarily by direct precipitation (Liebscher *et al.*, 1992). There is some recharge via overland flow from surrounding uplands, and groundwater is alternately recharged from and discharged to Fishtrap Creek depending on the season. The lakes located over the aquifer do not appear to have a direct hydrological connection to the aquifer. The water table in the aquifer ranges from less than 3 m at the west end of the aquifer to greater than 25 m close to the escarpment at the east end of the aquifer. Annual fluctuation of the water table is commonly as much as 3 m. Water flow within the Canadian portion of the aquifer is generally southward, tending toward south-easterly flow in the eastern portion of the aquifer, and south-westerly flow in the western portion of the aquifer. Land use on the Canadian side of the boundary influences water quality in the USA. Therefore, activities related to the aquifer are subject to the Boundary Waters Treaty of 1909. This treaty states that water flowing across the boundary "shall not be polluted on either side to the injury of health and property on the other side." Hence, water quality is an international concern.

Annual precipitation, based on the average of 1961 to 1990, is 1560 mm yr^{-1}, including 74 mm as snow (Environment Canada, unpublished data). Approximately 70% of the total precipitation occurs during the October to March period. In comparison, annual potential evaporation is 630 mm yr^{-1}. Horticultural crops in the area are irrigated in response to a water deficit during the growing season.

The dominant agricultural crop is red raspberry (*Rubus idaeus* L.) with significant areas in forage grass (*Dactylis glomerata* L.) and pasture. Other crops include strawberry (*Fragaria x ananassa*) and a variety of vegetable and nursery crops. A large number of poultry layer, broiler and turkey operations are located over the aquifer in addition to numerous greenhouses.

Poultry Farming in Abbotsford

The Abbotsford region has the highest concentration of poultry production in the province of British Columbia. Approximately 60% of the provincial poultry production is located on approximately 20% of the land above the aquifer (Sustainable Poultry Farming Group, 1994). Poultry producers specialize in one of the following products: eggs, broilers, or turkeys. The production and manure management practices of each farm type are different.

Laying hens are usually housed in cages that are suspended over deep (1.5 to 3.0 m) manure pits

(British Columbia Ministry of Agriculture, Fisheries and Food, 1992). Manure falls from the cages directly into the pits where it is dried using fans, and is stored there until the end of the one year bird rotation cycle. If farmers choose their rotation cycle appropriately, removal of manure will be at the environmentally-optimal time of the year, usually in the spring for application on nearby fields. In general, there are two problems that arise from this industry's manure management practices: (1) farmers' rotation cycles cannot be synchronized to end in spring because production needs to be consistent; and (2) poultry manure is low in nutrients relative to inorganic fertilizers and therefore costly to transport great distances. Layer operators must therefore, either stockpile manure or apply it to their land during rainy winter weather.

Broiler and turkey farms have much shorter rotation cycles of 6 and 13 weeks, respectively (the heavy turkey birds have 17 to 18 week cycles on average), than layer operations, and, hence, very different manure management problems. The birds are usually housed in barns with sawdust floors, which produces a dry litter. Barns are cleaned at the end of each cycle or after two cycles, so farmers must deal with a constant manure stream; however, the same problems exist with regards to stockpiling and field application as with egg producers, because virtually no broiler or turkey farmer in the region has "adequate" (i.e., covered) storage facilities.

Management of Poultry Manure

The management and disposal of poultry manure may become a limiting factor in the expansion of poultry industry in established areas of high poultry concentration such as the Fraser Valley. Recent studies by the Sustainable Poultry Farmer's Group (1994) revealed that there is a total of approximately 138,880 Mg of poultry manure produced in the Fraser Valley each year, and of that 66,603 Mg comes directly from broilers (an average of approximately 16,000 Mg every 6 weeks). Neither layer nor broiler producers tend to have acreage on which to apply the manure, and only 15,129 Mg year^{1} are kept in adequate storage facilities. Those farmers who do not have adequate storage facilities or acreage usually contract to have the manure taken off their farms, but the contractors often resell it to nearby raspberry growers. This may result in manure being applied on land at inappropriate times. Also, the poultry industry is based totally on imported feeds and therefore, expensive application of the N and P in the resulting manures. There is a lack of a local nutrient cycle through local feed grain production that causes the nitrate pollution problem to be as bad as it is. One possible solution to this problem would be to grow some feed grain locally in Delta and Sumas, for example, and use the poultry manure to fertilize the soils in these areas, thereby creating a local nutrient cycle.

Although raw poultry manure has long been valued for its ability to provide plant nutrients and improve soil physical and chemical properties (Vogtmann, 1984; Gao and Chang, 1996), its application to agricultural land may be discouraged because of the potential for introducing weed seeds, plant and human pathogens, and insect larvae (Taiganides, 1977; Pfirter *et al.*, 1981; Overcash *et al.*, 1983; Mawdsley *et al.*, 1995). Excessive applications of raw manure to agricultural fields can result in nutrient imbalances, N and P loading of surface waters, and NO_3^- and pathogen loading of groundwater (Swanson *et al.*, 1971; Overcash *et al.*, 1983; Keeney, 1989; National Research Council, 1993). Other undesirable characteristics of using raw poultry manure as a soil amendment include relatively low and variable nutrient content compared to inorganic fertilizers which limits economic hauling distances, and odor levels that can limit field applications near homes or communities (Overcash *et al.*, 1983).

The N content of poultry manure is greatest when it is fresh. It ranges from 3.7 to 8.8% for poultry layer manure, 2.9 to 6.1% for turkey manure, and 2.3 to 6.0% for broiler litter, on a weight basis (Overcash *et al.*, 1983). However, poultry manure is usually stockpiled for much of the year, because manure applications to cropland can only be made following harvest or prior to planting. Typically, manure is stockpiled on site, then removed from the confinement poultry houses and applied to nearby fields, prior to primary tillage operations. Nitrogen losses occur primarily via NH_3 volatilization (Sutton, 1994) during storage which reduces the value of the manure as a fertilizer. Phosphorus and K concentrations may also be reduced in storage primarily as a result of runoff and leaching. When applied to the soil surface, N loss from fresh manure can lower considerably its efficiency and potential use as a N fertilizer (Paul and Beauchamp, 1993). When stockpiled, manure represents a potential point source contaminant of surface and groundwater including N, P, bacteria, viruses, organic compounds, and total dissolved solids (Overcash *et al.*, 1983). Paul *et al.* (1994) also reported the highest soluble phenolic compound concentrations in stored manure compared with fresh or composted manure. Such compounds are thought to be phytotoxic to young plants or to inhibit seedling germination.

Composting as an Option in Poultry Manure Management

Poultry producers are faced with problems of a small land-base for manure disposal, compounded with major odor problems. On the other hand, these wastes also contain nutrients and organic matter which can be recycled to enhance the growth media for plants. In poultry manure, odor is caused largely by anaerobic microbial decomposition products such as ammonia, sulphide, mercaptans, amines, organic acids, and methane (Loehr, 1974). Some of these compounds can tenaciously cling to clothing and other articles, and persist for long periods. The fact that the odor-causing compounds are reduced organic compounds suggests that oxidative microbial processes, such as composting, are an option in odor control and manure stabilization.

Fundamentals of Composting

Haug (1993) defined composting as the biological decomposition and stabilization of organic substrates under conditions which allow development of thermophilic temperatures as a result of biologically produced heat, with a final product sufficiently stable for storage and application to land without adverse environmental effects. The composting process can be separated into two distinct stages: stabilization and maturation. During the stabilization stage, the temperature rises to a thermophilic level and is maintained. As the temperature increases, multiplication of bacteria occurs and the easily oxidised organic compounds are metabolized. Excess energy released results in a rapid rise in temperature, reducing or destroying pathogenic organisms.The maturation stage follows and it is characterized by a gradual decrease in temperature to ambient conditions. Because aerobic bacteria are important decomposers, the nature of the stabilization phase is influenced by oxygen availability. Composting processes, which are kept aerobic, reach and maintain higher temperatures than those allowed to become anaerobic. When the energy source is depleted, the temperature decreases gradually; allowing mesophilic bacteria to recolonize and aerobic fungi, such as actinomycetes, to become active (Loehr, 1974). The key to successful composting is to provide optimal starting conditions for the aerobic decomposers. Some important factors which affect starting conditions are moisture-content, aeration, C/N ratio, pH, and salinity. In general, the starting-moisture should be 45 to 60% , the C/N ratio should be 25 to 35, the pH should be 5.5 to 8.0, and the salinity should not exceed 2 g NaCl L^{-1} (Epstein, 1997).

The traditional goals of composting are basically to convert reactive organic wastes to a more stable form, and at the same time, reduce the bulk, conserve nutrients for recycling, and provide a soil amendment to improve conditions for plant growth. It is essentially a set of natural processes that are accelerated, and to some extent controlled. Micro-organisms are the agents of change, and conditions affecting the microbial populations will determine the nature and rate of biochemical changes occurring. The key conditions controlling the process include physical conditions like temperature, moisture, and ease of gas exchange, and chemical features like pH, redox conditions, and available nutrient supply. From the point of view of waste disposal, acceleration of the process is a key concern. In terms of resource utilization, nutrient conservation and product quality are more significant. In both cases, economic considerations are also critical.

In experimental studies of the composting process, it is important to recognize that the local environmental factors mentioned above do not operate independently. For example, elevated temperature will have different effects in aerobic versus anaerobic conditions. Another key consideration is the essential heterogeneity of conditions within a compost pile or experimental reactor. This variability is accentuated by decreased frequency of mixing or turning. Figure 1.1 shows the changes over time in

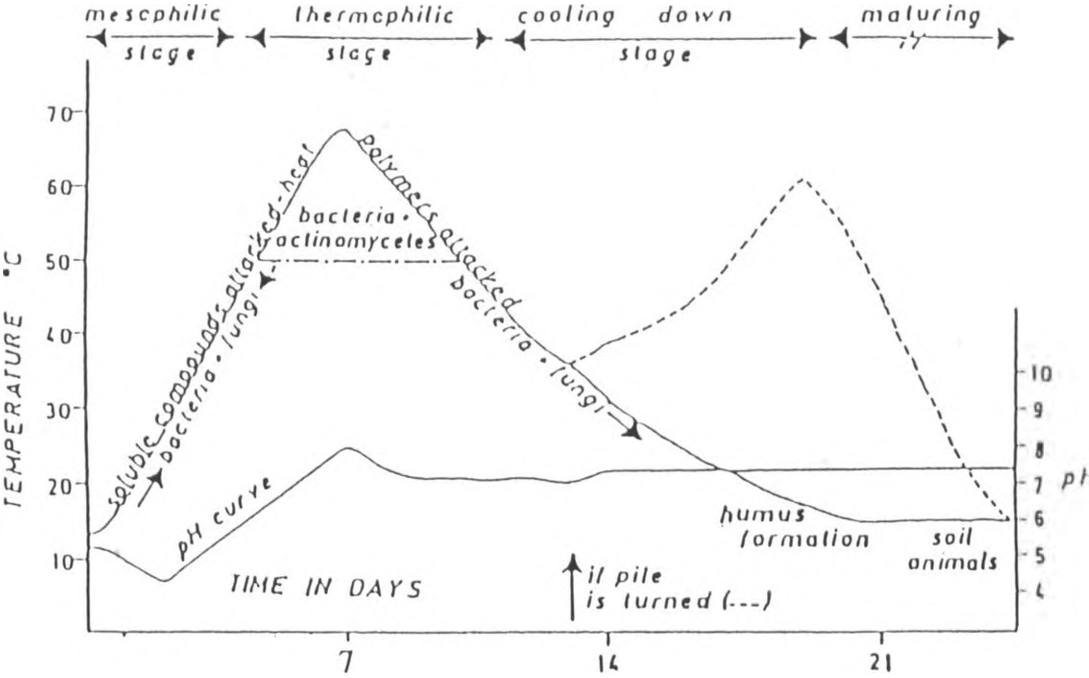


Figure 1.1. A generalized temperature curve of composting (Lowe, L.E., 1993).

microbial populations, temperature, and gross chemical characteristics; and indicates the complexity of the inter-relationships involved. It also emphasizes the significance of the thermophilic stage, which is very important for the elimination of pathogens and weed seeds, if present.

Composted Poultry Manure

Although most poultry farmers in the Fraser Valley are aware of composting, it was only recently that there has been a serious discussion of composting as a means of poultry manure management. Like raw manure, compost can improve soil physical and chemical properties by increasing organic matter while providing plant nutrients. During the composting process the C and N present in the manure are converted into more stable organic and humified forms, which allows compost to maintain greater nutrient content, and decreases pollution potential during storage and after application (Brinton, 1985;

Hervas *et al.*, 1989; Herbert *et al.*, 1991; Magdoff, 1992). Decomposition that occurs during composting also reduces total material mass and volume of the original compost mixture through CO_2 and H_2O loss. The low moisture content of the composted manure reduces handling and hauling costs. Additionally, the aerobic, thermophilic decomposition processes that occur during composting result in elevated temperatures that kill most pathogens, insect larvae, and weed seeds typically found in manure (Taiganides, 1977; Pfirter *et al.*, 1981; Chaney *et al.*, 1992). Composting has also been found to enhance breakdown of pesticide residues (Fogarty and Tuovinen, 1991), inhibit nitrification (Haug and Ellingsworth, 1991), and reduce levels of soluble phenolic compounds (Paul *et al.*, 1994). Applying mature compost to soil has also been reported to suppress the activity of some soil borne plant pathogens (Hoitink and Kuter, 1986; Schueler *et al.*, 1989). Finally, aerobic composting of poultry manure results in less offensive odors than raw manure and the finished compost is often odorless (Pfirter *et al.*, 1981).

Although composting poultry manure produces a stabilized product that can be stored or spread on land with little or no obnoxious odor, pathogens, weed seeds, or fly breeding potential, it results in a high potential for NH_3 volatilization during composting because nitrogen concentrations in poultry waste are generally higher and C/N ratios lower than those of other livestock wastes. Also, the initial stages of the bio-oxidation phase are characterized by unpleasant odor which can be quite offensive. However, the odor practically disappears by the end of the composting process.

Nitrogen Losses During Composting of Poultry Manure

Aerobic composting of poultry manure often leads to the formation, accumulation and consequential loss of N mostly via NH_3 volatilization. Different factors affect NH_3 volatilization during composting of poultry manure. During the first phase of the process, the combination of a high NH_3 concentration, high temperatures, and raised pH may lead to NH_3 losses (Witter, 1986). Also, high aeration of the composting piles increases the rate of NH_3 volatilization (Ashbolt and Line, 1982). Nitrogen losses via NH_3 volatilization have been evaluated during composting of poultry manure. Hansen *et al.* (1989)

reported N-losses of up to 33% of the initial total N during composting of poultry layer manure. In composting mixtures of fresh poultry layer manure and straw in rectangular reactors enclosed in hot-house sheds, Bonazzi *et al.* (1990) observed that 50 to 63% of the initial total N was lost, primarily via NH_3 volatilization. Hansen *et al.* (1990) found that N-losses could amount to 31% of the initial total N during composting of caged egg-layer poultry manure using reactor vessels. Mahimairaja *et al.* (1994) measured a 17% loss of N through NH_3 volatilization during composting of fresh chicken manure under aerobic conditions. High NH_3 losses reduce the agronomic value of the compost, contribute to the pollution of the atmosphere, and affect acid rain production. Due to its high solubility in water, NH_3 can return to soil and lakes via rain, thus, modifying the normal N cycle. Cost effective technologies which reduce NH_3 loss during composting of poultry manure would have positive economic and environmental benefits.

Ammonia volatilization can be reduced by temporary immobilization of NH_4^+ ions by composting poultry manure with carbon-rich organic waste materials such as paper waste (Mahimairaja *et al.*, 1994), and adsorption of NH_3 and/or NH_4^+ using adsorbents such as zeolite and peat (Witter and Kirchmann, 1989a). Inorganic chemicals have also been used to inhibit NH_3 volatilization during composting of poultry manure. These include pyrite (Bangar *et al.*, 1988), calcium and magnesium salts (Witter and Kirchmann, 1989b), sulfuric and phosphoric acids (Al-Kanani *et al.*, 1992), and alum and ferrous sulfate (Moore *et al.*, 1995). Although carbon-rich organic waste materials and a range of chemical amendments have been evaluated on NH_3 volatilization from manures, there is little information in the literature on the use of natural zeolites as NH_3 adsorbents during composting of poultry manure. This information would be of practical importance for improving the efficiency of N utilization in poultry manure.

Zeolites

Zeolites are hydrated aluminum-silicate minerals in which the Al and Si tetrahedra are connected by the sharing of oxygen atoms to form a three-dimensional framework structure. This framework structure has interconnecting channels through which alkali and alkaline cations (typically Na^+, K^+, Mg^{2+}, Sr^{2+}, and Ba^{2+}) and water molecules can pass. The cations neutralize the negative charge on the zeolite created by the substitution of Al^{3+} and Fe^{3+} for Si^{4+} in the tetrahedra. The amount of substitution in the tetrahedra determines the cation exchange capacity (CEC) of the zeolite. Presently, more than 50 species of natural zeolites have been identified (Tsitsishvili *et al.,* 1992).

Crystalline zeolites are unique adsorbent materials due to their large central cavities and entry channels. Most of the surface area is found within the zeolite structure and represents the inner surface of dehydrated channels and cavities. Molecules having diameters small enough to pass through the channels are readily adsorbed in the dehydrated channels and central cavities (Bernal and Lopez-Real, 1993). The unique geometries contained in zeolitic channels and cavities create selective sorption properties. The zeolite mineral clinoptilolite with the formula $(Na_4K_4)(Al_8Si_{40})O_{96}x24H_2O$ has a high CEC and affinity for NH_4^+. It is an abundant natural zeolite that is found in igneous, sedimentary, and metamorphic deposits. The framework structure of clinoptilolite consists of interlinked 4- and 5-tetrahedral rings, creating a layer. Between these layers are open 8- and 10-tetrahedral ring channels with approximate dimensions of 79 by 35 nm and 44 by 30 nm respectively (Vaughan, 1978). These rings form the ion sieving channels in clinoptilolite (Breck, 1974).

Natural Zeolites as Ammonium Adsorbents

Several cation selectivity series have been documented for clinoptilolite. Ames (1960, 1961), using a clinoptilolite from Hector, California, demonstrated a selectivity of Rb > K > Na > Mg and Ba > Sr > Ca > Li and Fe > Al in exchange for Cs and Cs > K > Ba = Sr > Ca > Na > Mg = Li in ion exchange experiments. Howery and Thomas (1965) found NaCl-treated clinoptilolite to have a Cs > NH_4^+ >> Na selectivity sequence.

As a result of its high affinity for NH_4^+, clinoptilolite has been evaluated for removal of this ion from waste waters. Mercer (1969) pumped waste water through a bed of clinoptilolite and found that the zeolite removed the NH_4^+. Ames (1967), in equilibrium experiments used simulated waste water to show that the removal of $K^+ > NH_4^+$ and $NH_4^+ > Na^+$, Ca^{2+}, and Mg^{2+} by clinoptilolite from Hector, California. Mumpton (1978) reported that Rosemont, Alexandria, Reston, and the North Lake Tahoe Sewage District of California were using clinoptilolite for removal of NH_4^+ from sewage effluent. Japan also uses waste water NH_4^+ removal units that contain clinoptilolite.

In agriculture, the nitrification of NH_4^+ to NO_3^- can result in loss of N through the leaching of NO_3^-. MacKown (1978) examined the effect of clinoptilolite from Texas on nitrification in the soil. He found through an incubation experiment that by using a rate equivalent to 30 Mg ha^{-1} of NH_4-exchanged clinoptilolite, nitrification decreased in the Gila silty clay loam (Arizona soils) and Rositas loamy sand by 4 to 11%, respectively. These decreases resulted from the retention of NH_4^+ by clinoptilolite in sites where the nitrifying bacteria could not oxidise the NH_4^+.

Lewis (1981) did a number of greenhouse experiments to evaluate the use of clinoptilolite as a plant nutrient carrier for N, K, and Zn. He found that NH_4-exchanged clinoptilolite (~ 75 mg kg^{-1}) from near Barstow, California produced a positive growth response in radishes (*Raphanus sativus* L.) when banded on 'light' (6% clay) and 'medium' (13% clay) textured soils. This NH_4^+-exchanged zeolite also decreased NO_3^- leaching losses in the 'light' soil. In controlled dissolution and greenhouse pot trial experiments using Princeton zeolite and Fernie phosphorite, Marcille-Kerslake (1991) showed that the zeolite enhanced the dissolution of apatite; and the effectiveness of the system was increased by using NH_4^+-saturated zeolite. Following some preliminary experiments with zeolite use in vegetable production, Johnson *et al.*, (1983) suggested that zeolites show promise as an adsorbent of NH_4^+ in composts, and as a slow release fertilizer.

In waste management practices, zeolites have been used to reduce odor and NH_3 volatilization from organic wastes. Pain *et al.* (1988) showed strong correlations between odor and NH_3 emissions from dairy and pig manure. Hence, if manure amendments reduce NH_3 volatilization, they may also be considered manure-odor suppressants. Witter and Lopez-Real (1988) found that ammonia loss from composting sewage sludge was minimal when the compost pile was covered with zeolite. Using an adiabatic laboratory composting simulator to compost pig slurry, Bernal *et al.* (1993) found that the zeolite clinoptilolite was very effective in trapping the ammonia lost during the composting process. Mahimairaja *et al.* (1994), working with poultry manure found that zeolite was an effective adsorbent for NH_3 and/or NH_4^+, and reduced NH_3 loss by 60%. These studies suggest that the natural zeolite clinoptilolite has the potential to adsorb NH_3 and reduce its loss through volatilization.

Zeolites differ in terms of their chemical and physical characteristics, both of which affect their ability to adsorb NH_3 and/or NH_4^+. In chapter 2 of this thesis, eleven zeolite and clay samples from different places, and a wide range of geological settings were characterized for their chemical and physical characteristics, and their NH_4^+ adsorption capacity evaluated. In chapter 3 the effect of pH on NH_4^+ adsorption by the natural zeolite clinoptilolite is examined because pH is the main factor that regulates the equilibrium between NH_4^+ ions and NH_3 gas during composting of manure. Also, the pH of minerals influences their ion sorption properties. Chapter 4 focusses on the kinetics of NH_4^+ adsorption and desorption by the natural zeolite clinoptilolite. The rate of NH_4^+ adsorption and subsequent release from this mineral will determine its potential to reduce NH_3 losses during composting of poultry manure, increase the nitrogen availability to crops, and minimize the potential for nitrogen leaching into surface and ground water. In chapter 5, the effect of temperature on NH_4^+ adsorption and desorption by the natural zeolite clinoptilolite is examined, because temperatures during composting range from 25 to 55 ^{0}C and even higher, and NH_3 emissions are enhanced at high temperatures. Therefore, studying the thermodynamics of NH_4^+ exchange on the zeolite mineral clinoptilolite will enable its efficient utilization as NH_3 and NH_4^+ adsorbents during composting of N-rich animal wastes such as poultry manure. In chapter 6, the potential of the natural zeolite clinoptilolite to reduce N losses via NH_3 volatilization during composting of poultry layer manure was examined. Finally, in chapter 7, poultry layer manure composted with the natural zeolite clinoptilolite was evaluated as a controlled-release N fertilizer for the growth of ryegrass (*Lolium multiflorum*).

CHAPTER 2

CHARACTERIZATION OF NATURAL ZEOLITES AND ASSESSMENT OF THEIR POTENTIAL AS AMMONIUM ADSORBENTS

INTRODUCTION

Losses of nitrogen via ammonia volatilization from nitrogenous fertilizers and animal wastes can be a serious environmental problem. One way to reduce these losses is to utilize amendments that can adsorb ammonium ion (NH_4^+) or ammonia gas (NH_3). Adding this amendment to soil could then result in timed release of the ammonium, providing a plant available form of nitrogen. One potential group of amendments that can be used are zeolites.

Zeolites are hydrated aluminum-silicate minerals in which the Al and Si tetrahedra are connected by shared oxygen atoms to form a three-dimensional framework structure. This framework structure has interconnecting channels through which alkali and alkaline earth cations (typically Na^+, K^+, Mg^{2+}, Sr^{2+}, and Ba^{2+}) and water molecules can pass. These cations neutralize the negative charge on the zeolite created by the substitution of Al^{3+} and Fe^{3+} for Si^{4+} in the tetrahedra. The amount of substitution in the tetrahedra determines the cation exchange capacity (CEC) of the zeolite. The greater the substitution the greater the charge deficiency, and number of cations required for electrical neutrality. In practice, however, the ion-exchange also depends on other factors, notably the nature of the cation species (size, charge, etc.), temperature, concentration of cation species in solution, and the structural characteristics of the zeolite.

Crystalline zeolites are unique adsorbent materials due to their large central cavities and entry channels. Most of the surface area is found within the zeolite structure and represents the inner surface of dehydrated channels and cavities. Molecules having diameters small enough to pass through the channels are readily adsorbed in the dehydrated channels and central cavities. The unique geometries contained in zeolite channels and cavities create selective sorption properties. Presently, more than 50 species of natural zeolites have been identified (Tsitsishvili *et al.*, 1992). Numerous studies have suggested that zeolites have a high affinity for NH_4^+ (Ames, 1960, 1961; Howery and Thomas, 1965). This has been successfully exploited to remove this cation from waste waters (Mercer, 1969), to retain it in soils (Lewis, 1981), and to reduce ammonia emissions from animal housings (Koelliker *et al.*, 1978) and during composting of nitrogen-rich wastes (Bernal *et al.*, 1993). Consequently, quantification of sorption properties of zeolites with respect to ammonium is necessary. The rate of ammonium adsorption and subsequent release from zeolites will determine their potential to reduce losses of ammonia in livestock enclosures and during composting of nitrogen-rich wastes, increase nitrogen availability to crops, and minimize the potential for nitrogen leaching into surface and groundwater.

Objectives

The objectives of this study were:

1. To characterize samples of natural zeolites for their physical properties and chemical composition.
2. To determine the ammonium adsorbing capacity of the zeolites.

MATERIALS AND METHODS

Eleven zeolite and clay samples from different places (mostly B.C. and North west U.S.A), and wide range of geological settings, were submitted for characterization and subsequent evaluation of ammonium adsorption.

Characterization study

All the samples were ground to < 2 mm.

(a) *X-Ray Diffraction analysis*

The clay fraction of these samples was separated using wet sieving, gravity sedimentation, and centrifugation techniques, after soluble salts were removed by repeated deionized water washing and decantation (Jackson, 1979). Subsamples were Ca and K saturated by repeated treatments with 1M solutions of the respective Cl^- salts, washed free of excess electrolyte, and made into oriented specimens for XRD analysis on glass slides using the paste method (Thiesen and Harward, 1962). Diffractograms of the oriented clay slides were obtained with an X-ray diffractometer using a step size of 1^0 2θ per minute with Cu-Kα radiation generated at 40 kV and 20 mA. Ca-saturated clays were analyzed at room temperature and after glycerol solvation. Diffractograms of K-saturated specimens were obtained after heating at 300 and 550 ^{0}C.

(b) *Chemical analyses*

The pH values were determined in 1:5 water and 1M KCl suspensions. Moisture content was determined by oven-drying the samples at 105 ^{0}C for 24 hours. Electrical conductivity was measured in 1:2 water extract. Total carbon was determined using Leco carbon analyzer. A simplified ethylene glycol monoethyl ether procedure was used for determining the specific surface area (Cihacek and Bremner, 1979). The ammonium acetate saturation method was used for determining the cation exchange capacity (Chapman, 1965). Exchangeable cations were analyzed from the ammonium acetate extract by means of atomic absorption spectrometry. Surface charge density (SCD) was calculated as CEC / Surface area.

(c) *Ammonium-adsorption Isotherms*

The samples were treated with different solutions of NH_4Cl + NaCl (total 0.2M) in a sample:solution ratio of 1:10. Isonormal solutions were used in order to maintain a constant ionic strength in the sample-solution mixtures. The initial NH_4Cl concentration in the extracting solution was from 0.001 to 0.160M. Amounts of ammonium adsorbed by the samples were calculated from the reduction of ammonium in the solution after shaking for two hours, and centrifugation (Bernal and Real-Lopez, 1993).

RESULTS AND DISCUSSION

Identification of clay minerals

X-ray diffraction analysis of the clay fractions (which is the best means of identifying members of the zeolite group), revealed a mixed mineral composition for all the samples (Table 2.1). The zeolite species identified in this study were: clinoptilolite, heulandite, mordenite, phillipsite, and some traces of analcime. The non-zeolite minerals identified included; quartz, feldspar, montmorillonite, and amphibole. No zeolite minerals were identified in three of the samples, namely; 6, 7, and 9; whereas sample #5 contained only some traces of analcime.

Table 2.1. Mineralogy of the samples as revealed by X-ray diffraction.

Sample #	Source of Mineral	Minerals identified
1	Mountain Minerals Ltd., Vancouver, B.C.	Clinoptilolite, Heulandite, Mordenite, Quartz, and Feldspar
2	Mountain Minerals Ltd., Vancouver, B.C.	Clinoptilolite, Phillipsite, Quartz, and Feldspar
3	Industrial Minerals of North America, Surrey, B.C	Mordenite, Quartz, and Feldspar
4	Industrial Minerals of North America, Surrey, B.C.	Mordenite, Phillipsite, Quartz, and Feldspar
5	Kenya	Quartz, Feldspar, amphibole, and some traces of analcime
6	Western Industrial Clay Products Ltd. Kamloops, B.C.	Montmorillonite, Quartz, and Feldspar
7	Western Industrial Clay Products Ltd. Kamloops, B.C.	Montmorillonite, some illite, Quartz, and Feldspar
8	Western Industrial Clay Products Ltd. Kamloops, B.C.	Clinoptilolite, Heulandite, Mordenite, Quartz, and Feldspar
9	Faxton Resources Ltd. Coquitlam, B.C.	Montmorillonite, some Quartz and Feldspar
10	Aberhill's Holdings Inc., Abbotsford, B.C.	Heulandite-Clinoptilolite, very small amounts of feldspar (Na-Ca), and Quartz
11	Canmark International Resources Ltd., Vancouver, B.C.	Heulandite-Clinoptilolite, traces of mordernite, and feldspar (Na-Ca)

The XRD patterns of zeolites generally consist of sharp, narrow diffraction peaks suggesting materials with high degrees of crystallinity. Some samples, however, give rise to weak, broad peaks characteristic of poorly crystalline or very fine particles (< 1 μm). In addition, zeolites in geologic formations and soils are commonly associated with quartz, opal-CT, feldspars, smectite, illites, gypsum, halite, and unreacted volcanic glass (Ming and Mumpton, 1989). Of special concern is the overlap of the peaks of plagioclase and alkali feldspars with those of many zeolites. The XRD patterns of suspected

Table 2.2. Some chemical and physical characteristics of the samples.

	1	2	3	4	5	6	7	8	9	10	11
pH (H_2O)	8.95	4.77	9.91	9.49	8.80	5.75	5.89	7.25	7.30	7.87	9.06
pH (KCl)	7.70	4.28	9.48	8.28	7.74	5.27	5.07	6.81	7.02	5.84	7.39
Moisture (%)	2.7	3.8	7.1	8.9	1.7	5.6	5.7	6.4	5.8	4.52	2.73
EC (mmho)	0.44	3.38	1.55	0.45	0.25	0.98	0.51	5.49	3.96	1.72	0.37
Surface area (m^2g^{-1})	155.0	261.8	106.5	205.5	29.9	239.4	273.2	152.7	147.2	934.8	581.2
CEC (cmoles kg^{-1})	55.41	52.45	53.88	37.32	16.66	46.29	47.98	122.86	49.55	92.8	100.1
SCD (μem^{-2})	0.36	0.20	0.51	0.18	0.56	0.19	0.18	0.80	0.34	0.10	0.17
Total C (%)	0.17	0.81	3.11	0.13	0.36	2.97	2.66	0.04	0.12	0.00	0.00
Exchangeable cations											
Na (cmoles kg^{-1})	17.39	13.04	1.61	1.96	4.35	0.54	0.63	59.35	3.26	3.07	37.19
K(cmoles kg^{-1})	10.23	3.45	2.37	4.8	3.26	1.02	0.78	25.26	2.24	10.40	11.51
Ca (cmoles kg^{-1})	31.19	39.92	104.17	28.69	17.47	14.97	13.54	61.13	33.68	44.79	28.57
Mg (cmoles kg^{-1})	1.50	15.84	2.93	10.49	1.77	10.90	10.60	24.38	12.55	7.78	2.43
NH_4^+-N_{max} (mg g^{-1})	7.07	6.93	7.43	5.78	1.11	4.79	4.91	10.50	3.70	13.83	11.61

mixtures of zeolites and feldspars should therefore be examined carefully before positive identifications are made. Several zeolite minerals are characterized by strong peaks at 0.9 to 1 nm (e.g., chabazite, 0.928; clinoptilolite, 0.897; ferrierite, 0.951; laumonite, 0.943; mordenite, 0.908). For this reason, slow scans were carried out to resolve overlapping peaks in this region.

Chemical Analyses

Results for chemical analyses and specific surface area determination are shown in Table 2.2. The CEC, with the exception of samples No. 8, 10, and 11 were relatively low. Specific surface area was appreciably high except for sample #5. For most of the samples, Ca is the dominant exchangeable cation followed by K and Mg. Samples # 1, 8, 10, and 11 have relatively high levels of both K and Ca.

Ammonium Adsorption

Of special interest for environmental and animal waste management purposes is the high affinity of zeolites for ammonium and the ability to hold this cation in the internal channels. The Langmuir equation is often used to describe ammonium adsorption isotherms. A common form of this equation is

$$C / S = 1 / Kb + C / b \qquad [1]$$

Where:

C = equilibrium concentration of adsorbate in solution (mmol L^{-1}),

S = amount adsorbed per unit weight adsorbent (mmol kg^{-1} adsorbent),

K = empirical constant related to the bonding strength (L $mmol^{-1}$), and

b = empirical adsorption maximum (mmol kg^{-1} adsorbent).

Equation [1] can be used when comparing empirical adsorption maxima (b) between two or more adsorbents if the chemical nature of the added solutions and experimental conditions are identical (Bernal and Real-Lopez, 1993). This approach was, therefore, used to quantify the maximum amounts of NH_4^+-N, the various materials could adsorb from solution. The results are shown in the last row of Table 2.2. The ammonium adsorption capacities reflected the measured CEC and surface area values of the materials. This can be expected as the CEC was measured as adsorbed ammonium in an ammonium acetate solution. Samples # 8, 10, and 11 had both the highest ammonium affinity and adsorption capacity.

CONCLUSION

Cation exchange capacity, and purity of zeolites, with respect to mineralogy and constituent ions, influences their affinity and adsorptive capacity for ammonium. Some of the samples tested contained little or no zeolite minerals. This was reflected in their lower ammonium adsorption capacity. Further work is required on evaluating the effectiveness of high quality zeolites as ammonium and ammonia adsorbents in animal wastes.

CHAPTER 3

THE EFFECT OF pH ON AMMONIUM ADSORPTION BY THE NATURAL ZEOLITE CLINOPTILOLITE

ABSTRACT

Clinoptilolite, a zeolite mineral with a high cation exchange capacity and surface area, has ion-exchange properties that can be utilized to adsorb NH_4^+, protecting it from losses during composting of N-rich animal manures. Ammonium adsorption by the natural zeolite clinoptilolite was studied to ascertain the effectiveness of the zeolite as an NH_4^+ adsorbent at pH 4, 5, 6, and 7. The NH_4^+ adsorption data were fitted to the one- and two-surface Langmuir, Freundlich and Temkin isotherms. All models described the NH_4^+ adsorption data successfully ($r^2 \geq 0.939$). The one-surface Langmuir, Freundlich, and Temkin were converted to pH-dependent forms. The amount of NH_4^+ adsorbed increased as pH and initial NH_4^+ concentration increased. From the one-surface Langmuir isotherm, the NH_4^+ adsorption capacity (X_m) of the zeolite increased linearly with pH ($r^2 = 0.994$), and was estimated to be 9660 mg N kg^{-1} at pH 4, 11220 mg N kg^{-1} at pH 5, 12720 mg N kg^{-1} at pH 6, and 13830 mg N kg^{-1} at pH 7. The adsorption of higher amounts of NH_4^+ with increasing pH and initial NH_4^+ concentration is an important characteristic of the zeolite that can be beneficial to minimizing N-losses via NH_3 volatilization during composting of N-rich animal manures.

INTRODUCTION

Ammonia lost during composting of N-rich animal manures can adversely affect air quality for humans and animals (Peoples and Freney, 1995), and reduce the nutrient value of these wastes for land application. There is also increasing concern about the role of atmospheric NH_3 in enhancing acid deposition (ApSimon *et al.*, 1987) and increasing the nitrogen load of natural ecosystems (Roelfs *et al.*, 1985). Cost effective technologies which reduce NH_3 loss during composting of N-rich animal manures would have positive economic and environmental benefits.

Loss of NH_3 from manure is a function of total NH_4^+ content and pH of the manure, and the NH_3 concentration of the overlying atmosphere. Ammonia losses from decomposing manure can be reduced by decreasing manure pH or NH_4^+ concentration. One way of reducing the NH_4^+ concentration is by adsorption on suitable adsorbents such as zeolites. Zeolites are hydrated aluminum-silicate minerals in which the Al and Si tetrahedra are connected by shared oxygen atoms to form a three-dimensional framework structure. Zeolites have a high cation exchange capacity (CEC), mostly found on the inner surface of dehydrated channels and cavities within their structure. The unique geometries contained in zeolite channels and cavities create selective sorption properties. Presently, more than 50 species of natural zeolites have been identified (Tsitsishvili *et al;* 1992).

Numerous studies have suggested that zeolites have a high affinity for NH_4^+ (e.g., Ames, 1960; Breck, 1974; Blanchard *et al;* 1984; Barbarick and Pirella, 1984). As a result of their high affinity for NH_4^+, zeolites have been evaluated for removal of this ion from wastewaters (Ames, 1967; Mercer, 1969) and for improving nutrient use in agriculture (Allen, 1991). Mackown, (1978) found that NH_4^+ - exchanged clinoptilolite decreased nitrification of NH_4^+ to NO_3^- by 4 and 11% in two soil types. The decreases resulted from the retention of NH_4^+ by clinoptilolite in sites where the nitrifying bacteria could not oxidize the NH_4^+. These studies suggest that zeolites have the capacity to adsorb NH_4^+ and hence, reduce its losses.

Although much research has been conducted on adsorption of NH_4^+ by zeolites, the effect of pH on NH_4^+ adsorption by natural zeolites has not been addressed. pH is the main factor that regulates the equilibrium between NH_4^+ ions and NH_3 gas during composting of N-rich manure. The pH of minerals also influences their ion sorption properties. The objectives of this study were to determine the effect of pH on NH_4^+ adsorption by the natural zeolite clinoptilolite, and identify empirical models that best describe the adsorption process. Isotherms used in this study were: One- and two-surface Langmuir, Freundlich and Temkin.

MATERIALS AND METHODS

Zeolite Sample

A natural zeolite mined in Southwest USA and supplied by Aberhill's Holdings Inc., of 2838 Alice

St., Abbotsford, B.C. Canada V2T 3P1, was used in this study. The sample was air-dried and ground to < 2 mm. Mineral identification using X-ray diffraction technique showed that the zeolite consisted mainly of clinoptilolite, and traces of quartz and feldspars. Some of its physical and chemical characteristics are listed in Table 3.1. The pH was determined in 1:2 zeolite:water or 1M KCl suspensions. Electrical conductivity (EC) was measured in 1:2 zeolite:water extract. A simplified ethylene glycol monoethyl ether procedure was used to determine the specific surface area (Cihacek and Bremner, 1979). Ammonium nitrogen was extracted with 2M KCl and determined spectrophotometrically using an automated continuous flow injection analyzer. The neutral 1M ammonium acetate saturation procedure was used for determining cation exchange capacity (Chapman, 1965). Exchangeable cations were analyzed from the ammonium acetate extract by atomic absorption spectrometry. Total C was determined using Leco carbon analyzer (Leco Corporation, St. Joseph, MI).

Table 3.1. Some selected characteristics of the zeolite sample.

pH (H_2O)	7.87
pH (KCl)	5.84
Surface area (m^2 kg^{-1})	9.35×10^5
EC (S m^{-1})	0.17
Total C (%)	0.00
NH_4^+ (mg N kg^{-1})	12.30
CEC (cmol kg^{-1})	92.78
Exchangeable cations	
Na^+ (cmol kg^{-1})	3.07
K^+ (cmol kg^{-1})	10.40
Ca^{2+} (cmol kg^{-1})	44.79
Mg^{2+} (cmol kg^{-1})	7.78

Ammonium Adsorption Studies

Adsorption studies were carried out using triplicate 1 gram zeolite samples which were placed in 50-mL polypropylene centrifuge tubes. To each zeolite sample, 10 mL of acetic acid/sodium acetate buffer solution at pH 4, 5, 6, and 7 was added and the samples equilibrated with 20 mL of NH_4^+ solution at different concentrations. Isonormal solutions of $NH_4Cl + NaCl$ (total 0.2M) were used in order to maintain a constant ionic strength in the sample solution mixtures (Weber *et al.*, 1983; Bernal and Lopez-Real, 1993). The initial NH_4^+ concentration in the extracting solution varied from 70.1 to 2241.6 mg N L^{-1}. The centrifuge tubes were laid horizontally on a reciprocating shaker and agitated continuously at 22 ^{0}C for 2 h at 240 cycles min^{-1} with a throw distance of 5.2 cm, followed by centrifugation at 2000 x g RCF for 10 min. The supernatant was decanted and NH_4^+ determined spectrophotometrically in the equilibrium solution, using an automated continuous flow injection analyzer. Amounts of NH_4^+ adsorbed by the samples were calculated from the reduction of NH_4^+ in the solution.

Models

Different equilibrium-based models were used to describe NH_4^+ adsorption by the natural zeolite clinoptilolite. A relatively high r^2 value for the relationship between measured and predicted NH_4^+ adsorption data indicated that the model successfully described the NH_4^+ adsorption by the natural zeolite. It should be noted that a high r^2 value for a particular model does not necessarily mean that this model is the best (Sparks, 1989). A model also cannot be used to definitively determine the mechanisms of NH_4^+ adsorption.

One-Surface Langmuir

The one-surface Langmuir equation (Langmuir, 1918) is usually written in the form:

$$X = kX_mC/(1 + kC) \qquad [1]$$

Where X (mg kg^{-1}) is the amount of adsorbate sorbed per unit weight of adsorbent, X_m (mg kg^{-1}) is the maximum amount of adsorbate that can be sorbed in a monolayer by the specific type of adsorbent, k is an affinity constant, and C (mg L^{-1}) is the adsorbate concentration in the equilibrium solution.

Conformance to this equation was tested by using the linear form:

$$C/X = 1/kX_m + C/X_m \qquad [2]$$

If C_o (mg L^{-1}) is the initial adsorbate concentration, Eq. [2] can be transformed to:

$$(C_o - X)/X = a + b(C_o - X) \qquad [3]$$

where $a = 1/kX_m$, and $b = 1/X_m$. The constants a, b, k, and X_m were calculated from the intercepts and slopes of the plots C/X vs. C for all studied pH values. The slopes and intercepts of the plots of a, b, k, X_m vs. pH gave the pH-dependent equations of a, b, k and X_m. The linearity coefficient for each equation was determined by regression. The substitution of a, b, k and X_m pH-dependent equation to the Eq. [1], [2] or [3] gave the Langmuir pH-dependent isotherm.

Two-Surface Langmuir

Because soils are complex mixtures, Syers *et al.* (1973) proposed the following extension of the one-surface Langmuir model to two surfaces:

$$X = k_1b_1C/(1 + k_1C) + k_2b_2C/(1 + k_2C) + ... + k_nb_nC/(1 + k_nC) \qquad [4]$$

Where k_1, k_2, ... k_n are adsorption/desorption equilibrium constants related to the bonding energy for n energetically different categories of sorption sites, and b_1, b_2, ... b_n are constant parameters. Equation [4] is solved by plotting X/C versus X (also called a Scatchard plot) (Sposito, 1982; Klotz, 1982)

Freundlich

The Freundlich equation (Henry, 1922) can be written as:

$$X = KC^n \qquad [5]$$

or

$$\ln X = n \ln C + \ln K \qquad [6]$$

or

$$\ln X = a \ln C + b \qquad [7]$$

where K and n are constants ($n < 1$), $a = n$ and $b = \ln K$; and $n < 1$ assumes an exponential decrease of the bonding energy with coverage. The constant parameters K, a or n and b were calculated from the intercepts and slopes of the plots ln X vs. ln C for all studied pH values. The slopes and intercepts of the plots of K, a or n and b vs. pH gave the pH-dependent equations of K, a or n and b . The linearity coefficient for each equation of K, a or n and b was determined by regression. The substitution of the pH-dependent equation of K, a or n and b to Eq. [5], [6] or [7] gave the pH-dependent form of the Freundlich equation.

Temkin

The Temkin isotherm assumes that the fall in heat of adsorption is linear rather than logarithmic as implied in the Freundlich equation (Thomas and Thomas, 1967). The resulting equation is complex but by ignoring very high and very low values of adsorption, it can be reduced (Hayward and Trapnell, 1964) to:

$$X = (RTX_m/B) \ln (AC) = (RTX_m/B) (\ln A + \ln C) = a + b \ln C \qquad [8]$$

where $a = (RTX_m/B) \ln A$, $b = RTX_m/B$, R = the gas constant, T = the absolute temperature (°K), $A = e^{a/b}$ and B = constant. If equation (8) is obeyed, plots of adsorption (X) against logarithm of concentration (ln C) should yield a straight line. The values of A, B, a and b were calculated from the intercepts and slopes of the plots of X vs. ln C for all studied pH values. The slopes and intercepts of the plots of A, B, a and b vs. pH gave the pH-dependent equations of A, B, a and b. The linearity coefficient of each equation was determined by regression. The substitution of the pH-dependent equation of A and B to Eq. [8] gave the pH-dependent form of the Temkin isotherm.

RESULTS AND DISCUSSION

Increasing solution pH resulted in greater amounts of NH_4^+ being sorbed at any given solution concentration (Fig. 3.1). The probable cause for this may be the formation of new sorption sites together with decreased ionic competition for these sites (Garcia-Miragaya and Page, 1978). The zeolite was tested at pH range of 4 up to 7. Ammonia volatilization would occur at pH values above 7, whereas composting of wastes can result in pH of up to 8 or higher. The high pH would enhance NH_3 volatilization and lower the efficiency of the zeolite as an NH_3 and/or NH_4^+ adsorbent. The amount of NH_4^+ adsorbed also increased with increasing initial NH_4^+ concentration, as we observed in a separate study on the kinetics of NH_4^+ adsorption and desorption by this zeolite (Kithome et al., 1997e). This is

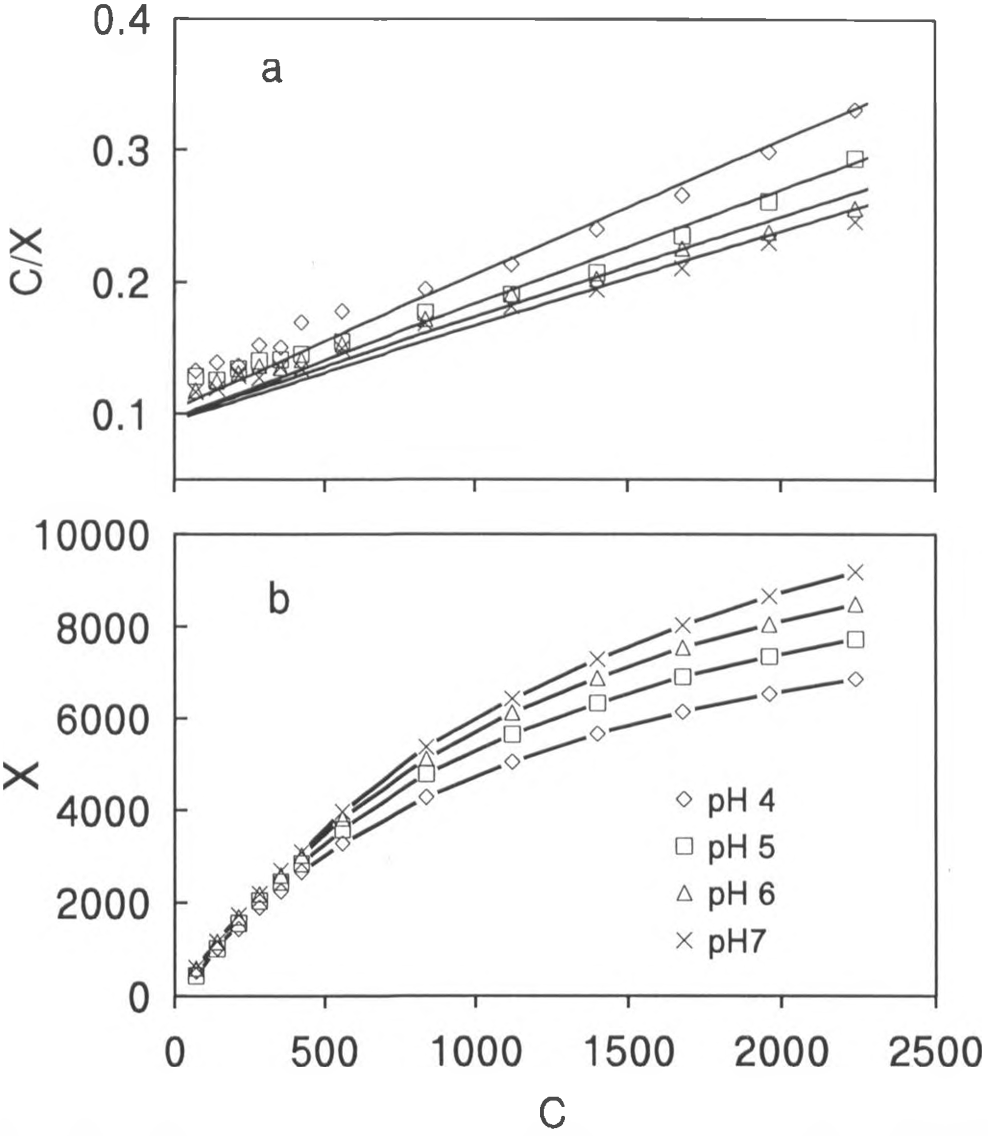


Figure 3.1. (a) One-Surface ; and (b) Two-Surface , Langmuir isotherms for NH_4^+-N adsorption on the natural zeolite at pH values 4, 5, 6, and 7. X = mg NH_4^+-N kg^{-1} zeolite and C = mg NH_4^+-N L^{-1} solution.

expected from a concentration standpoint (Kelly, 1948).

The one-surface Langmuir model fitted the experimental results slightly better than the Freundlich and Temkin models (Table 3.2). The NH_4^+ adsorption capacities (X_m) of the zeolite, calculated using the one-surface Langmuir model, increased linearly with pH (Fig. 3.2) and were 9660 mg N kg^1 at pH 4,

Table 3.2. Slopes (a), intersections (b), and estimated constants for One-Surface Langmuir, Freundlich and Temkin isotherms.

One-Surface Langmuir

pH	a	b	K	X_m	r^2
4	7.91×10^{-2}	1.04×10^{-4}	1.31×10^{-3}	9662	0.995
5	7.03×10^{-2}	8.91×10^{-5}	1.28×10^{-3}	11223	0.995
6	6.92×10^{-2}	7.86×10^{-5}	1.14×10^{-3}	12723	0.994
7	6.93×10^{-2}	7.23×10^{-5}	1.04×10^{-3}	13831	0.994

Freundlich

pH	a = n	b	K	n	r^2
4	0.664	3.995	54.32	0.664	0.979
5	0.687	3.984	53.71	0.687	0.976
6	0.693	4.002	54.72	0.693	0.988
7	0.698	4.019	55.67	0.698	0.988

Temkin

pH	a	b	A	B	r^2
4	-9122	2028	0.011	4.764RT	0.956
5	-10575	2331	0.011	4.815RT	0.954
6	-11592	2527	0.010	5.036RT	0.941
7	-12189	2650	0.010	5.220RT	0.939

11220 mg N kg^{-1} at pH 5, 12720 mg N kg^{-1} at pH 6, and 13830 mg N kg^{-1} at pH 7. A similar trend was observed by Mitsios *et al.*, (1994) for K (which is similar to NH_4^+) sorption in soils. The NH_4^+ adsorption capacities (X_m) were comparable to those obtained by Bernal and Lopez-Real, (1993) for four different zeolite samples at near neutral pH.

The experimental data were also successfully fitted to the two-surface Langmuir model (Fig. 3.1b). Holford *et al.*, (1974) used this model to account for the observed curvature of simple Langmuir plots. The physical model itself is no better than the one-site model. Considering the chemical and physical

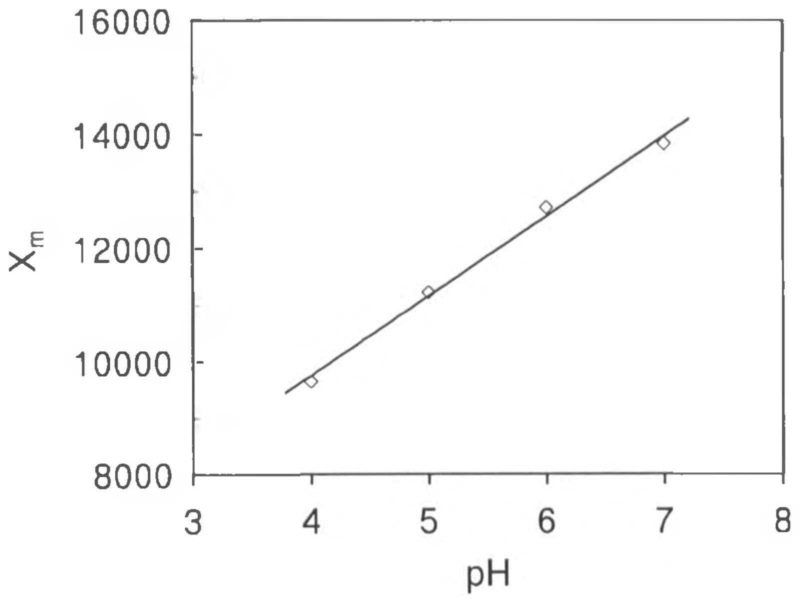


Figure 3.2. Maximum NH_4^+-N adsorption capacity (X_m) of the natural zeolite as a function of pH. X_m = mg NH_4^+-N kg^{-1} of zeolite.

complexity of the natural zeolite colloid surfaces, and on clay surfaces in soil, it is difficult to visualize sites at only two or even three discrete levels of sorption energy. It would be more natural to consider sorption energies as forming a continuum. Sposito (1982) claimed that this model is no more than an interpolation formula with four adjustable parameters.

The Freundlich isotherm also described the experimental data satisfactorily (r^2 values ranged from 0.976 to 0.988, Table 3.2; Fig. 3.3). However, when comparing the r^2 values of the Freundlich equation to that of Langmuir, one should remember that the logarithmically transformed Freundlich expression is less sensitive to changes in the variables.

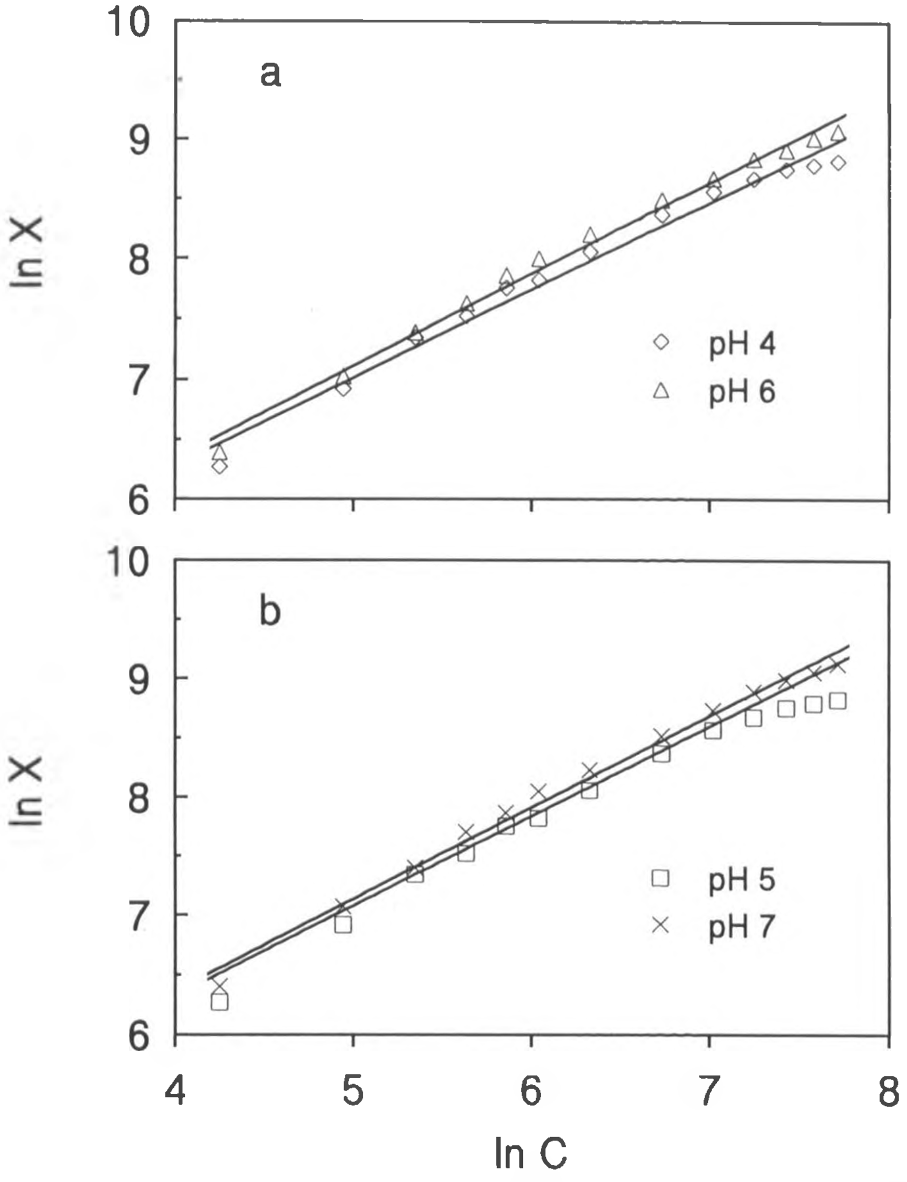


Figure 3.3. Freundlich isotherms for NH_4^+-N adsorption by the natural zeolite at (a) pH 4 and 6; and (b) pH 5 and 7. X = mg NH_4^+-N kg^{-1} zeolite and C = mg NH_4^+-N L^{-1} solution.

The Temkin isotherm also described the experimental data successfully with r^2 values ranging from 0.939 to 0.956 (Table 3.2). However, the plots of X vs. ln C remain most frequently curvilinear (Barrow, 1978). In the present case, the plots were found to be curvilinear in the pH range 6 to 7; whereas, for pH 4 and 5 they followed a sigmoidal trend (Fig. 3.4). The latter trend could possibly be attributed to the mechanism of ion-diffusion through the channels and central cavities of the zeolite. Despite the

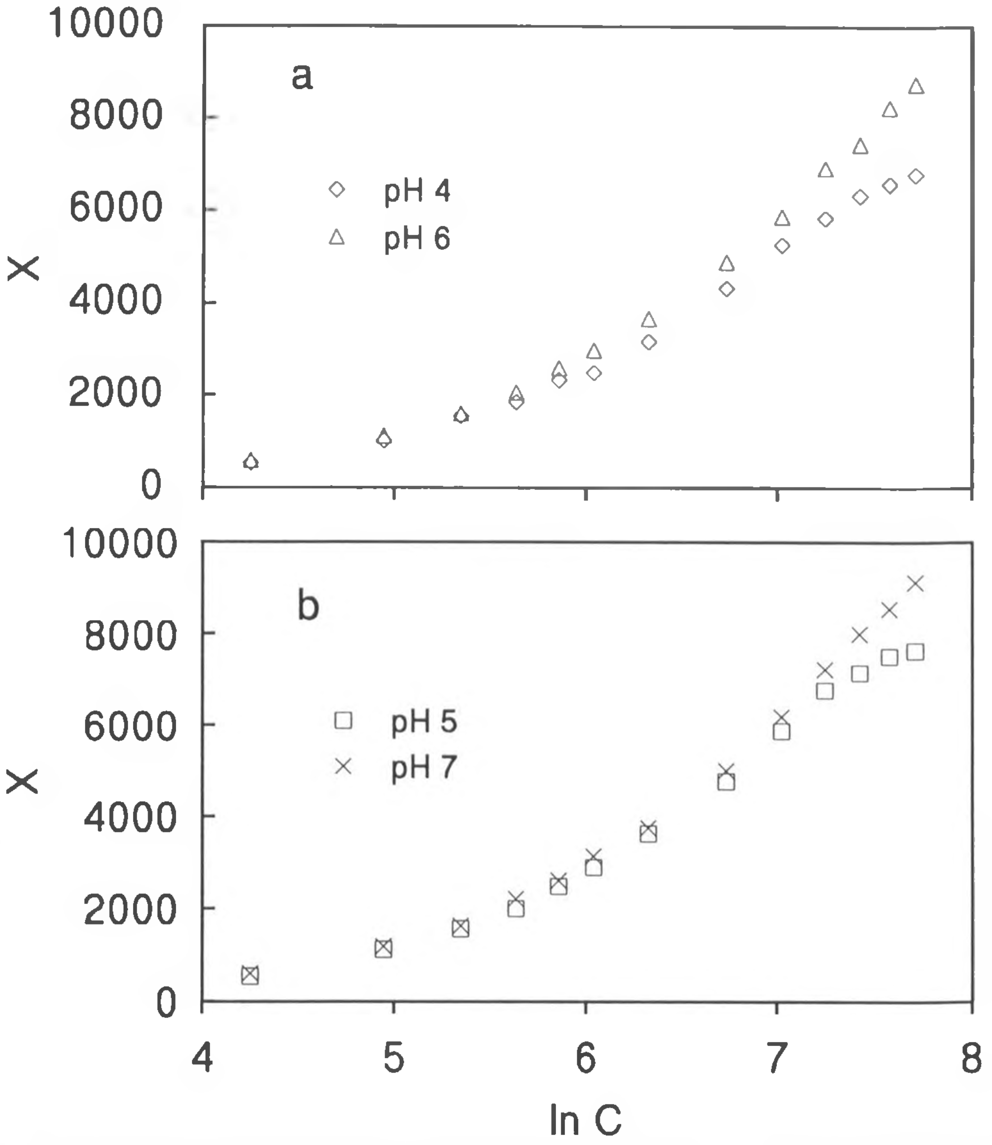


Figure 3.4. Temkin isotherms for NH_4^+-N adsorption by the natural zeolite at (a) pH 4 and 6; and (b) pH 5 and 7. X = mg NH_4^+-N kg^{-1} zeolite and C = mg NH_4^+-N L^{-1} solution.

nonlinearity of plots for P adsorption experiments, Bache and Williams (1971) considered this model to be convenient because the curves approach linearity over a wide concentration. In addition, the Temkin equation was believed to be advantageous for one point equilibration methods because the sorption isotherm itself is a characteristic of the soil, while the position of the point on the curve is a measure of the ion status of the soil (White and Zelazny, 1986).

Transformation of the Isotherms to pH-dependent Form

The one-surface Langmuir, Freundlich and Temkin isotherms were transformed to pH-dependent form.

One-Surface Langmuir

The pH-dependent equations for the Langmuir constants a, b, k, and maximum adsorption capacity (X_m), and coefficients of determination (r^2) are shown in Table 3.3. The Langmuir isotherm was transformed into the following form:

$$X = (-0.126pH^2 + 2.002pH + 7.14)C/(1 + (1.7x10^{-3}-9x10^{-5}pH)C) \quad [9]$$

Freundlich

The pH-dependent equations for the Freundlich's constants a = n, b and K, and coefficients of correlation (r^2) are shown in Table 3.3. The following pH-dependent form was derived:

$$X = (0.98pH + 48.82) \text{ x } C^{(0.006pH + 0.660)} \quad [10]$$

Temkin

Temkin's pH-dependent equations for the constant parameters, and their coefficients of determination (r^2) are shown in Table 3.3. The model was transformed to the following pH-dependent form:

$$X = 8811(pH + 3)/(pH + 25.7) \text{ x } \ln((1.26x10^{-2} - 4.0x10^{-4}pH)C) \quad [11]$$

All the tested pH-dependent isotherms described the NH_4^+ adsorption data ($r^2 \geq 0.887$, Table 3.3). However, none of the isotherms examined would be expected to perfectly represent NH_4^+ adsorption by the natural zeolite. This is because neither of them could simultaneously account for all factors involved in, and all changes taking place during NH_4^+ adsorption, such as: (i) sorption sites which are not energetically uniform; (ii) sorbed NH_4^+ ions which may interact laterally, their surface activity being thus lowered with coverage; (iii) a continuous increase in the positive charge of the surface with NH_4^+ sorption; (iv) a decrease in the number of vacant sites (especially two adjacent sites) as sorption progresses along with greater numbers of competing ions; and (v) changes in solution conditions such as

Table 3.3. Isotherm constants transformed to pH-dependent form

	r^2
Langmuir	
$a = 9.2 \times 10^{-2} - 3.5 \times 10^{-3} pH$	0.887
$b = 1.0 \times 10^{-4} - 1.0 \times 10^{-5} pH$	0.968
$k = 1.7 \times 10^{-3} - 9.0 \times 10^{-5} pH$	0.994
$X_m = 4.2 \times 10^{3} + 1.4 \times 10^{3} pH$	0.966
Freundlich	
$n = 0.660 + 5.63 \times 10^{-1} pH$	0.997
$b = 3.894 + 1.80 \times 10^{-2} pH$	0.999
$K = 48.82 + 9.80 \times 10^{-1} pH$	1.000
Temkin	
$a = -5250 - 1022 pH$	0.966
$b = 1251 + 206 pH$	0.963
$A = 1.26 \times 10^{-2} - 4 \times 10^{-4} pH$	0.951
$B = 4.085RT + 0.159 pH RT$	0.951

pH and ionic strength, which are known to influence the process. It is obvious that for a model to take into account all these changes, it must contain a large number of parameters. This would also explain the observation that a set of data can often be described successfully by more than one isotherm (Table 3.2). If it is not accepted *a priori* that one of these models is best, the simplest and most realistic one would be preferred. Such considerations imply that the Langmuir isotherm is preferable in this case. It fit the actual NH_4^+ adsorption data for the natural zeolite slightly better; and has the advantage that the adsorption maximum capacity can be calculated. It should be acknowledged that the Langmuir isotherm assumes no interaction between the adsorbed species, which is not realistic when the adsorbing species are charged and their adsorption changes the charge on the surface on which they adsorb. Except under very restricted circumstances, neither a one-surface nor a two-surface Langmuir isotherm, can give a realistic description of the adsorption process. Use of the Langmuir isotherm in this way can only be justified in pragmatic terms, but not mechanistically. For example, it can be used to give an approximate empirical description of the curves and so summarise them with two parameters, which then allow ready comparison of adsorption characteristics between adsorbents.

CONCLUSIONS

This study has demonstrated that pH and initial NH_4^+ concentration are significant factors that influence NH_4^+ adsorption by the natural zeolite clinoptilolite. Amounts of NH_4^+ sorbed increased with increasing pH and initial NH_4^+ concentrations. All the tested models adequately described the NH_4^+ sorption data ($r^2 \geq 0.939$). Three of the four models tested were transformed into their pH-dependent form. By doing so, a very significant factor of the adsorption process was introduced into the models. All the pH-dependent isotherms adequately described the dependence of NH_4^+ adsorption on pH as demonstrated by their r^2 values which ranged from 0.887 to 1.000. The estimated NH_4^+ adsorption capacity of this zeolite was reasonably high within the studied pH range, which attests to its potential use as an NH_4^+ adsorbent.

CHAPTER 4

THE KINETICS OF AMMONIUM ADSORPTION AND DESORPTION BY THE NATURAL ZEOLITE CLINOPTILOLITE

ABSTRACT

The kinetics of NH_4^+ adsorption and desorption were investigated on the natural zeolite clinoptilolite to ascertain its ability to adsorb and release the important plant nutrient N in its NH_4^+ form at various pH values and initial NH_4^+ concentrations. Kinetics of NH_4^+ adsorption were evaluated on the samples using solutions containing 140.1, 280.2, 560.4 and 840.6 mg L^{-1} of NH_4^+-N at pH 4, 5, 6, and 7, equilibrated for 5, 10, 15, 20, 30, 45, 60, 75, 90 and 120 min. Samples for NH_4^+ desorption were equilibrated with 70.1, 280.2, 560.4, and 1401 mg L^{-1} NH_4^+-N solution at pH 4, 5, 6, and 7 for 2.5 h, and adsorbed NH_4^+ extracted with 2M KCl for 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, and 300 min. Equilibrium time for NH_4^+ adsorption ranged from 60 min for 140.1 mg L^{-1} initial NH_4^+-N concentration at pH 4 to 120 min for 840.6 mg L^{-1} initial NH_4^+-N concentration at pH 7. Desorption was nearly complete in 150 min for low initial NH_4^+ concentrations and 200 min for high initial NH_4^+ concentrations. Amounts of NH_4^+ sorbed increased with increasing pH and initial NH_4^+ concentrations. Models evaluated included the first-order kinetics, modified Freundlich, parabolic diffusion, Elovich, and heterogeneous diffusion. All the models adequately described the NH_4^+ adsorption process with r^2 values ranging from 0.955 to 0.999 and, with the exception of first-order kinetics, also described the desorption process well with r^2 values ranging from 0.897 to 0.999, for all pH and initial NH_4^+ concentrations. Reaction rate coefficients (k) were calculated from the modified Freundlich model and ranged from 0.134 to 0.193 min^{-1} for the adsorption process, and 0.129 to 0.226 min^{-1} for the desorption process. The models indicated that NH_4^+ adsorption and desorption by the zeolite were diffusion controlled. Data from this study indicated the potential use of the tested natural zeolite as an NH_4^+ adsorbent and a controlled-release NH_4^+ fertilizer.

INTRODUCTION

Zeolites are naturally occurring framework aluminosilicate minerals with high cation exchange capacity, ion adsorption, and high ammonium selective properties. More than 50 different species of this mineral group have been identified (Tsitsishvili *et al;* 1992), among them clinoptilolite with the formula

$$(Na_4K_4)(Al_8Si_{40})O_{96}.24H_2O$$

The zeolite mineral clinoptilolite is an abundant natural zeolite found in igneous, sedimentary, and metamorphic deposits, and has a high CEC and affinity for NH_4^+. The framework structure of clinoptilolite consists of interlinked 4- and 5-tetrahedral rings, creating a layer. Between these layers are open 8- and 10-tetrahedral ring channels having approximate dimensions of 7.9 x 10^{-8} by 3.5 x 10^{-8} m and 4.4 x 10^{-8} by 3.0 x 10^{-8} m, respectively (Vaughan, 1978). These rings form the ion sieving channels in clinoptilolite (Breck, 1974). Several cation selectivity series have been documented for clinoptilolite. Howery and Thomas (1965) found NaCl-treated clinoptilolite to have a Cs > NH_4^+ >> Na selectivity sequence. Ames (1967) reported the following selectivity sequence for the removal of ions from simulated wastewater by clinoptilolite: K > NH_4^+ > Na > Ca, Mg.

The high affinity of zeolites for NH_4^+, and the possibility of releasing it over time is of special interest for minimizing environmental pollution during animal waste management. The NH_4^+ adsorption properties of zeolites have enabled them to be used as NH_4^+ and/or NH_3 adsorbents during composting (Bernal *et al.*, 1993) and in poultry facilities (Koelliker, 1978), whereas their ability to desorb the adsorbed NH_4^+ ions gives them the potential to be used as controlled-release NH_4^+ fertilizers. For adsorbents to be effective in increasing N use efficiency they must be able to trap large amounts of NH_4^+, and release this N slowly over the growing season when applied to soil (Johnson *et al.*, 1983). Rapid release of the adsorbed NH_4^+ would increase the potential for N loss when applied to soil, and too slow a rate of release would limit the short-term benefits to the crop.

Equilibrium reactions between solution and exchangeable phases of zeolite-NH_4^+ profoundly influence the chemistry of NH_4^+ adsorption and desorption by zeolites. Understanding the kinetics of the adsorption and desorption process in natural zeolites is necessary for effective utilization of natural zeolites as NH_3 and/or NH_4^+ adsorbents, and consequently as controlled-release NH_4^+ fertilizers.

Several models have been used to describe adsorption and desorption of ions from soils and soil minerals. First-order kinetic models have been applied extensively to cation and anion sorption in soils. Sawhney (1966) described the uptake of Cs on vermiculitic clay minerals as a pseudo first-order rate reaction. Carski and Sparks (1987) described NH_4^+ release from soils using a first-order kinetic model. Kuo and Lotse (1974) proposed a modification of the Freundlich model to describe the kinetics of phosphate adsorption and desorption by hematite and gibbsite; and Sparks *et al.* (1980) used this model to study the kinetics of K adsorption from solution to exchangeable phases for two Dothan soils. The parabolic-diffusion model was used by many researchers to describe diffusion-controlled phenomena in soil constituents and release of ions in soils and soil minerals (Cooke, 1966; Evans and Jurinak, 1976; Feigenbaum *et al.*, 1981; Havlin *et al.*, 1985). The exponential Elovich model which has general application to chemisorption kinetics (Low, 1960) was used to describe the kinetics of ion adsorption and desorption on soils and soil minerals (Chien and Clayton, 1980; Sparks and Jardine, 1984; Peryea *et al.*, 1985). Recently, Steffens and Sparks (1997) used, among others, the heterogeneous diffusion model to describe the kinetics of nonexchangeable NH_4^+ release from soils.

Ammonium adsorption and desorption by zeolites in NH_4^+-aqueous systems is driven by cation exchange reactions. Equilibrium relationships in these systems have been investigated (Weber *et al.*, 1983; Bernal and Lopez-Real, 1993), but the kinetics of adsorption and desorption processes in these systems have not been studied. The objectives of this study were to determine the time, pH and initial concentration dependencies of NH_4^+ adsorption and desorption by the natural zeolite clinoptilolite, and identify empirical models that best describe the adsorption and desorption process.

MATERIALS AND METHODS

Zeolite Sample

A natural zeolite mined in Southwest USA and supplied by Aberhill's Holdings Inc., of 2838 Alice St., Abbotsford, B.C. Canada V2T 3P1, was used in this study. The sample was air-dried and ground to < 2 mm. Mineral identification using X-ray diffraction showed that the zeolite consisted mainly of

Table 4.1. Some characteristics of the zeolite sample.

pH (H_2O)	7.87
pH (KCl)	5.84
Surface area (m^2 kg^{-1})	9.35×10^5
EC (S m^{-1})	0.17
Total C (mg kg^{-1})	0.00
NH_4^+-N (mg kg^{-1})	12.30
CEC (cmol kg^{-1})	92.78
Exchangeable cations	
Na^+ (cmol kg^{-1})	3.07
K^+ (cmol kg^{-1})	10.40
Ca^{2+} (cmol kg^{-1})	44.79
Mg^{2+} (cmol kg^{-1})	7.78

clinoptilolite, with traces of quartz and feldspar. Some of its physical and chemical characteristics are listed in Table 4.1. The pH was determined in 1:2 zeolite:water or 1M KCl suspensions. Electrical conductivity (EC) was measured in 1:2 zeolite:water extract. A simplified ethylene glycol monoethyl ether procedure was used to determine the specific surface area (Cihacek and Bremner, 1979). Ammonium nitrogen was extracted with 2M KCl and determined spectrophotometrically using an automated continuous flow injection analyzer. The neutral 1M ammonium acetate saturation procedure was used for determining the cation exchange capacity (Chapman, 1965). Exchangeable cations were analyzed from the ammonium acetate extract by atomic absorption spectrometry. Total C was determined using Leco carbon analyzer (Leco Corporation, St. Joseph, Michigan, USA).

Kinetics of Ammonium Adsorption

We studied the kinetics of NH_4^+ adsorption at four pH levels, four initial NH_4^+-N concentrations, and ten agitation times with all the treatments replicated three times. We weighed 0.5 g of zeolite samples in 50-mL polypropylene centrifuge tubes, and added 5 mL of sodium acetate/acetic acid buffer solution at pH 4, 5, 6 and 7 followed by 10 mL of NH_4Cl solution containing 140.1, 280.2, 560.4, and 840.6 mg L^{-1} NH_4^+-N. We used isonormal solutions of NH_4Cl + NaCl (total 0.2M) to maintain a constant ionic strength in the sample solution mixtures and to provide competing ions for exchange sites (Weber *et al*., 1983; Bernal and Lopez-Real, 1993). The centrifuge tubes were laid horizontally on a reciprocating shaker and agitated continuously at 22 ^{0}C for 5, 10, 15, 20, 30, 45, 60, 75, 90 and 120 min at 240 cycles min^{-1} followed by centrifugation at 2000 x g RCF for 10 min. Ammonium in the supernatant was analyzed spectrophotometrically using an automated continuous flow injection analyzer. Amounts of NH_4^+ sorbed by the samples were calculated from the reduction of NH_4^+ in the solution.

Kinetics of Ammonium Desorption

We conducted desorption studies at four pH levels, four initial NH_4^+-N concentrations, and eleven agitation times with all the treatments replicated three times. We weighed 0.5 g of zeolite samples in 50 mL polypropylene centrifuge tubes, and added 5 mL of acetic acid/sodium acetate buffer solution at pH 4, 5, 6 and 7, followed by 10 mL of 70.1, 280.2, 560.4 and 1401 mg L^{-1} of NH_4^+-N solution. Isonormal solutions of NH_4Cl + NaCl (total 0.2M) were used. The centrifuge tubes were agitated continuously on a reciprocating shaker at 22 ^{0}C for 2.5 h, followed by centrifugation at 2000 x g RCF for 10 min. The supernatant was analyzed for NH_4^+ using an automated continuous flow injection analyzer. We calculated the amounts of NH_4^+ on the exchange sites of the zeolite samples at zero time of desorption from the reduction of NH_4^+ in the solution. We washed the samples remaining in the centrifuge tubes thoroughly with ethanol and deionized water, and extracted the adsorbed NH_4^+ with 10 mL portions of 2M KCl by agitating on a reciprocating shaker for 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, and 300 min, followed by centrifugation at 2000 x g RCF for 10 min. The supernatant was analyzed for desorbed NH_4^+ at each time of agitation using the automated continuous flow injection analyzer.

Kinetic Models

Different kinetic models described below were used to describe NH_4^+ adsorption and desorption by the natural zeolite clinoptilolite. The goodness of conformity between experimental data and the model-predicted values was expressed by the coefficient of determination (r^2). A relatively high r^2 value for the relationship between measured and predicted NH_4^+ adsorption or desorption data indicated that the model successfully described the kinetics of NH_4^+ adsorption and desorption by the natural zeolite. It should be noted that a high r^2 value for a particular kinetic model does not necessarily mean that this model is the best (Sparks, 1989). A model also cannot be used to definitively determine the mechanisms of NH_4^+ adsorption and/or desorption.

First-Order

The first-order rate model for the adsorption process can be expressed as (Sparks and Jardine, 1981)

$$\log_{10}(1 - F_a) = k't \qquad [1]$$

where F_a is fraction of NH_4^+ adsorbed (X_t/X_{eq}), X_t is the total amount of NH_4^+ adsorbed on the zeolite at time t, X_{eq} is total amount of NH_4^+ adsorbed on the zeolite at equilibrium, k' is the apparent adsorption rate coefficient defined as $kX_{eq}/2.303$, and k is the absolute velocity coefficient for the adsorption process. If the rate of NH_4^+ adsorption by the zeolite follows first-order kinetics, then a plot of $\log_{10}(1 - F_a)$ against the reaction time t should yield a linear relationship.

For the desoprtion process the first-order rate model is expressed as (Sparks and Jardine, 1981)

$$\log_{10}(X_t/X_0) = k'_d t \qquad [2]$$

where X_t is the amount of NH_4^+ on the exchange sites of the zeolite at time t of desorption, X_0 is the amount of NH_4^+ on the exchange sites of the zeolite at zero time of desorption, t is the reaction time in min, and k'_d is the apparent desorption rate coefficient in min^{-1}. This equation is valid if NH_4^+ adsorption is assumed to be negligible. The "$\log_{10}(X_t/X_0)$ vs t" relationship is linear if the rate of release of NH_4^+ follows first-order kinetics.

Modified Freundlich

The modified Freundlich model as proposed by Kuo and Lotse (1974), is

$$X_t = kC_0t^{1/m} \qquad [3]$$

or $$\log_{10} X_t = (\log_{10} k + \log_{10} C_o) + 1/m \log_{10} t \qquad [4]$$

where X_t is the amount of NH_4^+-N sorbed at time t per unit weight of zeolite, k is the adsorption or desorption rate coefficient, C_o is initial NH_4^+-N concentration, t is the reaction time, and m is a constant. A plot of $\log_{10} X_t$ versus $\log_{10}$ t should be linear if the NH_4^+ adsorption or desorption process conforms to the modified Freundlich model.

Parabolic Diffusion

The parabolic diffusion model may be stated as follows (Sivasubramaniam and Talibudeen, 1972)

$$F = Rt^{1/2} + \text{constant} \qquad [5]$$

where F is the fraction of NH_4^+ sorbed at time t and R is the overall diffusion constant. Plots of F or the amount of adsorbate (X_t) sorbed at time t against $t^{1/2}$ are often used to test a diffusion controlled reaction rate (Cooke, 1966; Vaidyanathan and Talibudeen, 1968; Sparks and Jardine, 1984).

Elovich

The Elovich equation as modified by Chien and Clayton (1980) was used to study the kinetics of NH_4^+ adsorption and desorption. It is expressed as

$$X_t = (1/\beta) \ln (\alpha\beta) + (1/\beta) \ln t \qquad [6]$$

where X_t is the amount of NH_4^+-N (mg kg^{-1}) sorbed at time t, and α and β are constants. If NH_4^+ adsorption or desorption conforms to the Elovich model, a plot of X_t versus ln t should yield a linear relationship with a slope of 1/β and an intercept of (1/β)ln (αβ). The chemical significance of these constants has not been clearly resolved (Sparks, 1989).

Hetereogeneous Diffusion

The heterogeneous diffusion model can be mathematically expressed as (Aharoni *et al.*, 1991; Aharoni and Sparks, 1991)

$$Z = (dq / dt)^{-1} = \rho t/q_\infty[1 - (4t/\pi_m)^{1/2} - 8/\pi^2\exp(-\pi^2 t/4\tau_i)]^{-1} \qquad [7]$$

where Z = the reciprocal of the rate of NH_4^+ adsorption or desorption; t = time; $\rho = \ln (\tau_m/\tau_i)$; τ_i = smallest τ, and τ_m = largest τ; $\tau = r^2/D$, where r = maximum length of the diffusion path; D = the diffusion coefficient; q_∞ = the amount of NH_4^+-N sorbed at 2 or 5 h; q = amount of NH_4^+-N sorbed at time t. In heterogeneous diffusion, a Z(t) plot is mainly linear because the negative terms in Eq. [7] are negligible. Hence Eq. [7] reduces to

$$d(q/q_\infty) / d\ln t = 1/\rho \qquad [8]$$

RESULTS AND DISCUSSION

Initial NH_4^+ concentration and pH significantly affected the amount of NH_4^+ adsorbed by the zeolite. An increase in pH resulted in greater amounts of NH_4^+ being adsorbed at any given solution concentration (Fig. 4.1), probably due to the formation of new sorption sites, together with a decrease of ionic competition for these sites (Garcia-Miragaya and Page, 1976). Also, the amount of NH_4^+ adsorbed increased as the initial NH_4^+ concentration increased, which is expected from a concentration standpoint (Kelly, 1948).

Increasing pH and initial NH_4^+ concentration resulted in greater amounts of NH_4^+ being desorbed, but the fraction of the total adsorbed NH_4^+ that was desorbed decreased. Total NH_4^+ desorbed ranged from 65.2% for high initial NH_4^+ concentration to 89.5% for low initial NH_4^+ concentration at all pH values.

Kinetics of Ammonium Exchange

Adsorption

The NH_4^+ adsorption process was virtually complete in the 140.1mg L^{-1} NH_4^+-N treated zeolite samples within 60 min at pH 4 and 80 min at pH 7. The 840.6 mg L^{-1} NH_4^+-N treated zeolite samples reached equilibrium in approximately 80 min at pH 4 while equilibrium was not reached at pH 7 until about 120 min. These findings are in agreement with those of Weber *et al.* (1983) and Bernal and Lopez-Real (1993) who observed that sorption of NH_4^+ by natural zeolites was essentially complete after shaking for 1-2 h.

Desorption

The kinetics of NH_4^+ desorption by the natural zeolite are shown in Fig. 4.2 for initial NH_4^+-N

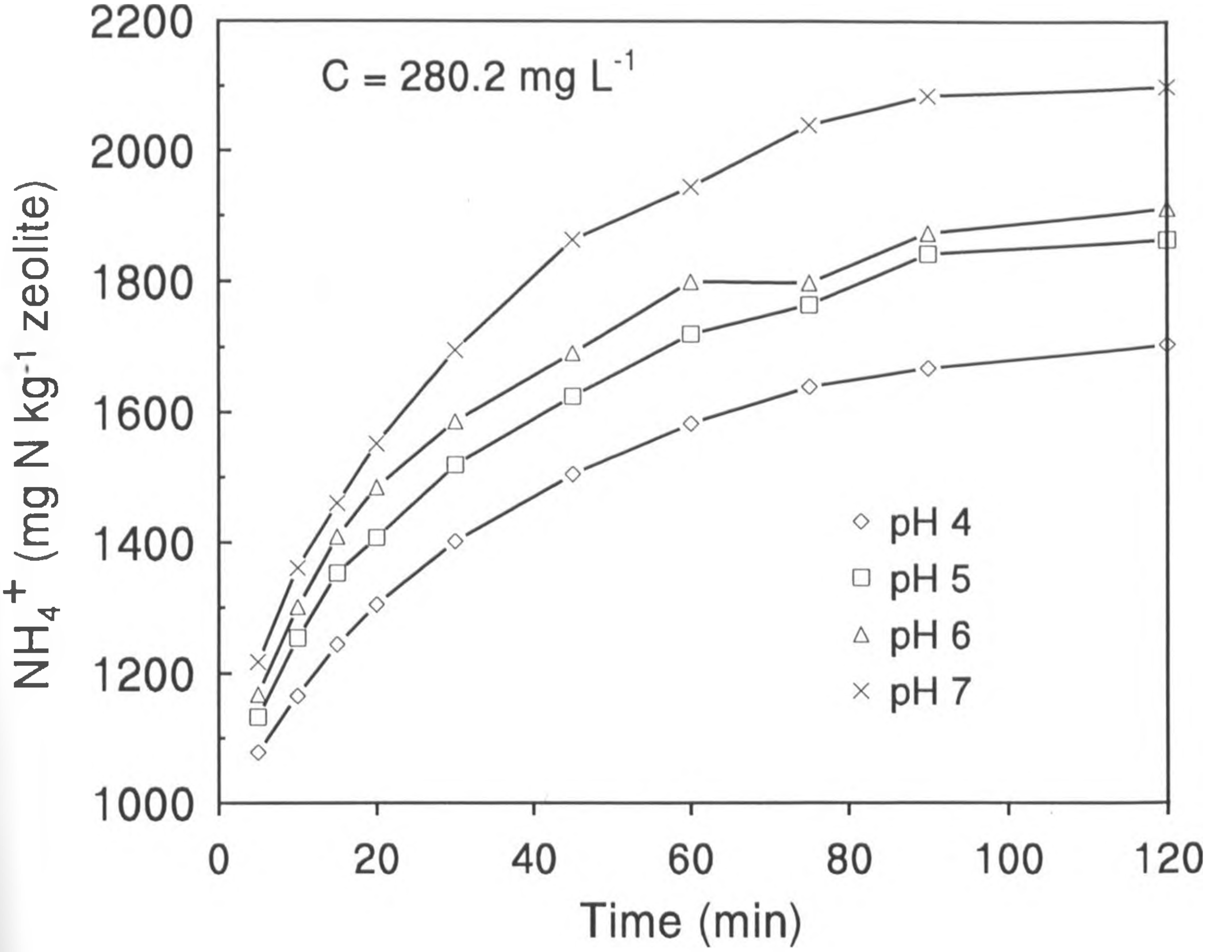


Figure 4.1. Ammonium adsorbed by zeolite over time at initial NH_4^+-N concentration of 280.2 mg L^{-1} and pH 4, 5, 6, and 7.

concentration of 280.2 mg L^{-1}, at all pH values. These plots are representative of those found for all the other treatments. The desorption process was nearly complete within 150-200 min for both low and high initial NH_4^+ concentrations. The desorption was rapid for the first 20 min then slower for the rest of the time at all pH values and initial NH_4^+ concentrations. This biphasic desorption is characteristic of a diffusion-controlled process and has previously been observed for NH_4^+ (Steffens and Sparks. 1997) and

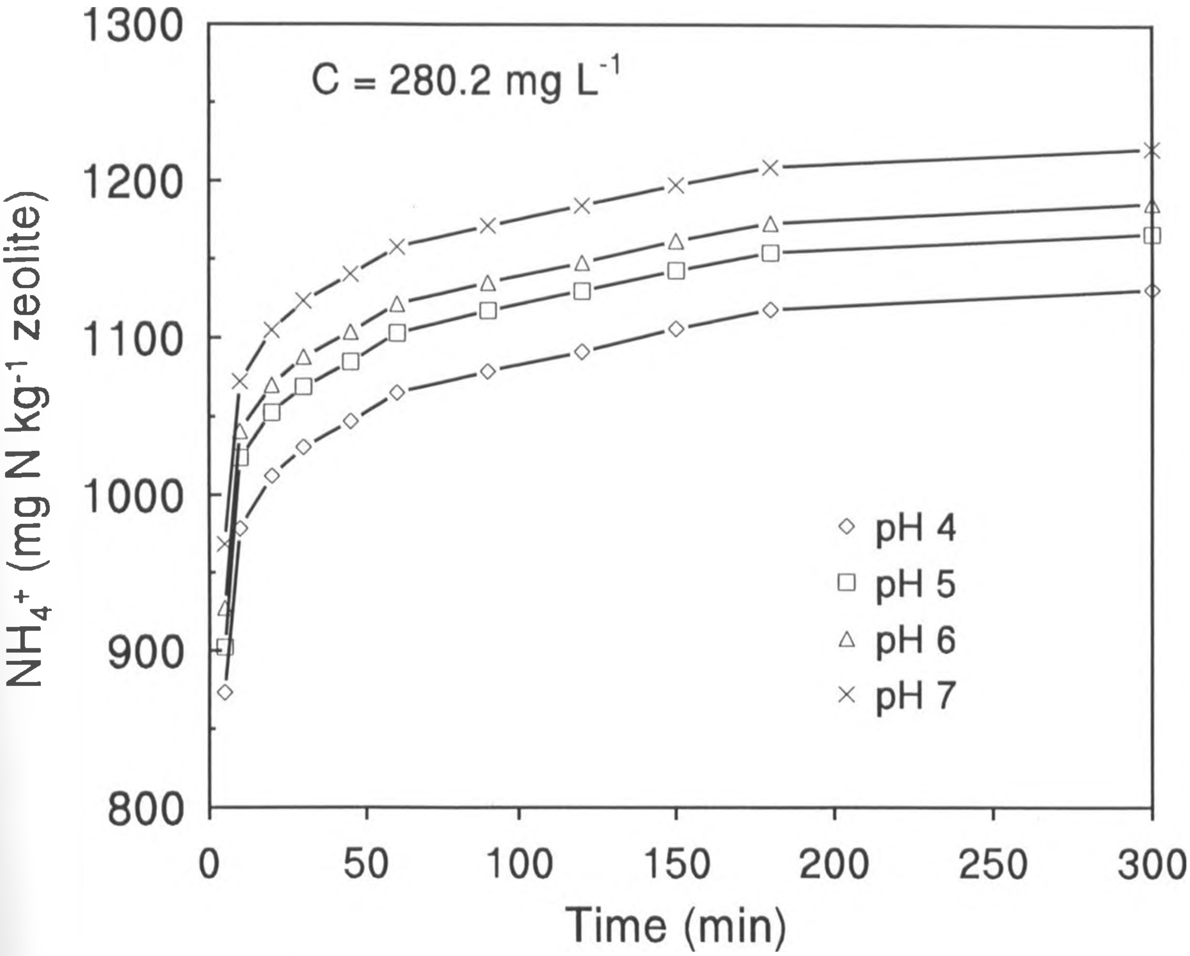


Figure 4.2. Cumulative NH_4^+-N desorbed by the zeolite over time at initial NH_4^+-N concentration of 280.2 mg L^{-1} and pH 4, 5, 6, and 7.

other similar ions, like K^+ (Feigenbaum *et al.*, 1981; Martin and Sparks, 1983).

Application of Data to Kinetic Models

Adsorption Process

The adsorption data were found to conform to the first-order kinetic model, with r^2 values ranging from 0.961 to 0.999 (Table 4.2). This was unexpected since several separate reactions may have taken

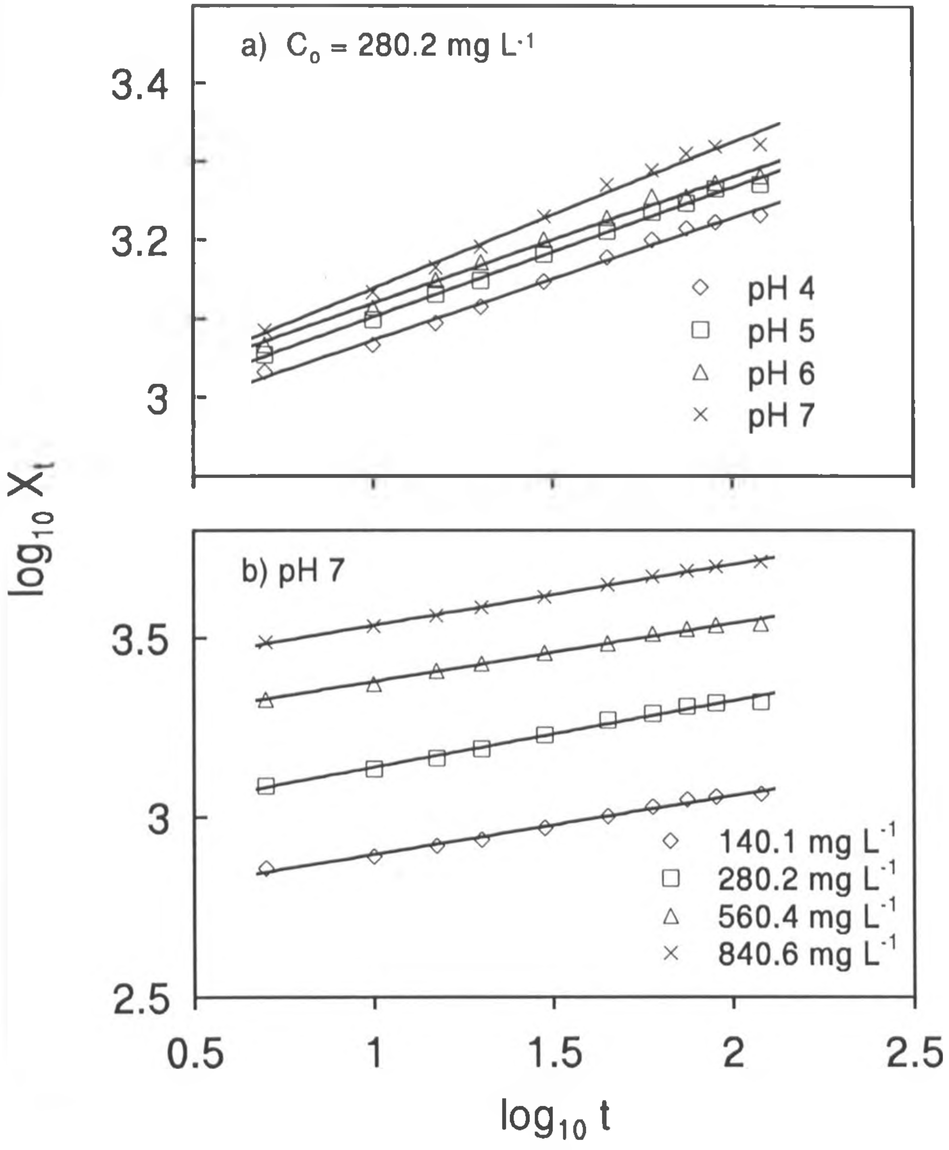


Figure 4.3. Relationship between NH_4^+-N adsorbed over time as described by the modified Freundlich model for (a) 280.2 mg L^{-1} initial added NH_4^+-N concentration for all tested pH values, and (b) all initially added NH_4^+-N concentrations at pH 7.

place. This indicated that all reactive sites had similar reaction rates, or offsetting errors resulted in a reasonable average fit of the data, or perhaps some other mechanism was operating that can coincidentally be described by the first-order rate equation. This same equation has been shown to describe both film diffusion controlled reactions and chemically controlled reactions for isotopic

Table 4.2. Regression equations for the first-order kinetic model and correlation coefficients (r^2) for NH_4^+ adsorption and desorption at various pH, initial NH_4^+-N concentrations (C_o), and adsorbed NH_4^+-N (C*).

	Adsorption			Desorption			
pH	C_o (mg L^{-1})	First-Order	r^2	C_o (mg L^{-1})	C* (mg kg^{-1})	First-Order	r^2
4	140.1	-0.3994-0.0087t	0.993	70.1	542	-0.4961-0.0020t	0.977
5		-0.3984-0.0087t	0.990		548	-0.4868-0.0020t	0.980
6		-0.3403-0.0100t	0.999		551	-0.4910-0.0019t	0.981
7		-0.3707-0.0094t	0.987		562	-0.5236-0.0022t	0.981
4	280.2	-0.3954-0.0093t	0.992	280.2	1733	-0.3746-0.0005t	0.903
5		-0.3666-0.0099t	0.988		1751	-0.3932-0.0005t	0.917
6		-0.3948-0.0097t	0.985		1831	-0.3761-0.0004t	0.912
7		-0.3560-0.0083t	0.961		1843	-0.3918-0.0004t	0.900
4	560.4	-0.3730-0.1170t	0.995	560.4	2946	-0.4874-0.0004t	0.801
5		-0.3638-0.0102t	0.996		3018	-0.5374-0.0003t	0.767
6		-0.3802-0.0101t	0.990		3092	-0.5328-0.0003t	0.728
7		-0.3614-0.0108t	0.997		3330	-0.4773-0.0002t	0.718
4	840.6	-0.4835-0.0098t	0.991	1401.0	5595	-0.5032-0.0002t	0.663
5		-0.4986-0.0101t	0.990		5728	-0.5189-0.0002t	0.733
6		-0.4355-0.0104t	0.998		5908	-0.4949-0.0002t	0.646
7		-0.3454-0.0100t	0.999		5946	-0.4972-0.0001t	0.734

C* amount of NH_4^+-N (mg kg^{-1}) on the exchange complex of the zeolite before desorption was initiated.

exchange conditions (Boyd *et al.*, 1947). Helfferich (1983) stated that other reactions known to be diffusion controlled can also be described using second-order chemical reactions through a mathematical coincidence. Other information must then be used to determine the rate limiting mechanism.

Plots of the measured NH_4^+ adsorption data versus the predicted adsorption data using the modified Freundlich model are shown in Fig. 4.3 for different pH and initial NH_4^+ concentrations. The r^2 values of this model ranged from 0.983 to 0.998 (Table 4.3a) therefore describing the NH_4^+ adsorption process well. Bache and Williams (1971) indicated that the energy of adsorption decreased exponentially with increasing surface saturation when the adsorption fitted the Freundlich equation. Interactions between the molecules may explain the decreasing energy of adsorption with increasing surface saturation. Everett (1965) suggested that for adsorbed gas molecules, a decrease in the distance between two adsorbed molecules will increase the perturbation potential. This interaction is also likely to exist between adsorbed NH_4^+ molecules. At low surface saturation, the adsorbed NH_4^+ molecules tend to locate

Table 4.3a. Regression equations and coefficients of determination for NH_4^+-N adsorption using the modified Freundlich and parabolic diffusion models at various pH, and initial NH_4^+-N concentrations (C_o).

C_o (mg L^{-1})	pH	Modified Freundlich	r^2	Parabolic	r^2
140.1	4	2.665+0.156log t	0.989	$516.3+46.5t^{1/2}$	0.967
	5	2.683+0.160log t	0.991	$539.3+50.2t^{1/2}$	0.966
	6	2.695+0.167log t	0.994	$550.5+55.9t^{1/2}$	0.994
	7	2.734+0.162log t	0.990	$597.8+59.0t^{1/2}$	0.995
280.2	4	2.917+0.155log t	0.993	$916.8+83.6t^{1/2}$	0.987
	5	2.937+0.165log t	0.996	$964.1+95.3t^{1/2}$	0.988
	6	2.959+0.160log t	0.992	$1023+94.7t^{1/2}$	0.966
	7	2.952+0.186log t	0.991	$989.4+121.7t^{1/2}$	0.986
560.4	4	3.177+0.157log t	0.983	$1615+168.5t^{1/2}$	0.972
	5	3.180+0.172log t	0.998	$1720+171.7t^{1/2}$	0.976
	6	3.200+0.165log t	0.996	$1794+169.2t^{1/2}$	0.975
	7	3.210+0.167log t	0.998	$1837+176.7t^{1/2}$	0.981
840.6	4	3.389+0.123log t	0.995	$2707+174.9t^{1/2}$	0.972
	5	3.400+0.123log t	0.991	$2789+177.7t^{1/2}$	0.955
	6	3.393+0.135log t	0.998	$2752+198.9t^{1/2}$	0.977
	7	3.365+0.170log t	0.998	$2593+265.8t^{1/2}$	0.988

themselves so that they obtain a minimum potential energy. With increasing NH_4^+ adsorption, the distance between the adsorbed NH_4^+ molecules decreases and the pertubation energy as well as the total potential energy of the adsorbed NH_4^+ molecules increases. Thus, the surfaces of the adsorbent may not necessarily contain sites of different energy levels as indicated by Muljadi *et al.* (1966a, b, c), but may hold the adsorbed molecules at different energy levels because of interactions between the adsorbed molecules. A clear distinction between the adsorbed molecules with respect to their potential energy is not possible.

The parabolic diffusion model also described the NH_4^+ adsorption process well, with r^2 values ranging from 0.955 to 0.995 (Table 4.3a). Conformity to the parabolic diffusion model suggested that the process of NH_4^+ adsorption by the natural zeolite was diffusion controlled; and either intra-particle diffusion or surface diffusion may be rate limiting (Helfferich, 1983; Crank, 1976). The former diffusional process is a transport of the adsorbing ion through the liquid associated with less accessible exchange sites of the adsorbent, whereas the latter involves the movement of the adsorbing ion along the walls of the less accessible spaces of the adsorbent. When particle resistance determines the adsorption velocity, surface diffusion is generally the rate controlling mechanism (Jardine and Sparks, 1984). Intra-particle surfaces in the natural zeolite clinoptilolite arise from intra-crystal spaces within the mineral assemblage and from the network of channels and cages within the crystal structure. Even though zeolites are tectosilicates, the exchange of one counter ion for another of different size could affect the ease of motion for adsorbing ions, and in so doing lead to variations of the diffusion coefficients as we observed in this study (Table 4.3a).

The experimental data fitted the Elovich model successfully with r^2 values ranging from 0.976 to 0.998 (Table 4.3b). The good fit of this model for the NH_4^+ adsorption data proves its utility for empirical prediction. As noted by Parravano and Boudant (1955), the Elovich model may describe a number of different processes, including bulk and surface diffusion, as well as activation and inactivation of catalytic surfaces. However, prediction is still marginal at very low and very high surface coverages

Table 4.3b. Regression equations and coefficients of determination for NH_4^+-N adsorption using the Elovich and heterogeneous diffusion models at various pH, and initial NH_4^+-N concentrations (C_o).

C_o (mg L^{-1})	pH	Elovich	r^2	Heterogeneous Diffusion	r^2
140.1	4	386.7+120.0ln t	0.989	0.927+0.128ln t	0.988
	5	399.5+129.3ln t	0.993	0.928+0.131ln t	0.993
	6	405.1+140.7ln t	0.976	0.902+0.132ln t	0.980
	7	439.6+150.6ln t	0.981	0.916+0.131ln t	0.976
280.2	4	688.1+214.5ln t	0.989	0.922+0.127ln t	0.987
	5	700.9+245.3ln t	0.992	0.917+0.133ln t	0.991
	6	754.3+245.5ln t	0.995	0.923+0.130ln t	0.994
	7	668.9+307.7ln t	0.987	0.925+0.151ln t	0.988
560.4	4	1197+415.3ln t	0.996	0.927+0.128ln t	0.987
	5	1222+449.9ln t	0.995	0.936+0.137ln t	0.995
	6	1188+473.6ln t	0.997	0.942+0.135ln t	0.989
	7	1227+488.6ln t	0.998	0.928+0.133ln t	0.994
840.6	4	2199+458.7ln t	0.994	0.937+0.106ln t	0.994
	5	2255+471.4ln t	0.998	0.944+0.106ln t	0.998
	6	2186+517.4ln t	0.997	0.928+0.112ln t	0.996
	7	1840+691.2ln t	0.992	0.906+0.134ln t	0.990

(Ungarish and Aharoni, 1981). Estimated α and β values of the Elovich equation for NH_4^+ sorption by the natural zeolite were found to vary with pH and initial NH_4^+ concentration. Some investigators have used Elovich parameters to estimate reaction rates. Chien and Clayton (1980) suggested that a decrease in β and/or an increase of α should enhance the reaction rate. This may be questionable because the slope of plots using an equation like Eq. [6] changes with the level of added ion, as was observed in this study, and with the solution to adsorbent ratio (Sharpley, 1983). Consequently, these slopes are not always characteristic of the adsorbent but depend on various experimental conditions (Sparks, 1986).

Desorption Process

Desorption data plotted according to the first-order kinetic model showed considerable deviation from linearity, with r^2 values ranging from 0.646 to 0.981 (Table 4.2). This was expected since several mass action rate processes may have been occurring independently. The possibility of multiple first-order reactions corresponding to multiple independent retention sites in the zeolite mineral, similar to the multiple reactions suggested by Griffin and Jurinak (1974) and Jardine and Sparks (1984), was not justified by the data. No distinct breaks in first-order plots were identified. Instead, a gradual change in slope from one time increment to the next was prevalent, indicating a continual change in the apparent rate constant (k_d') and precluding the operation of strictly first-order kinetics.

The modified Freundlich model provided a slightly better description of NH_4^+ desorption by the natural zeolite with r^2 values ranging from 0.977 to 0.999 (Table 4.4a). The parabolic diffusion model provided a satisfactory description of NH_4^+ desorption by the natural zeolite with r^2 values ranging from 0.897 to 0.992 (Table 4.4a). Conformity to this model suggested that NH_4^+ desorption was a diffusion-controlled process.

The Elovich model had r^2 values ranging from 0.965 to 0.996 and therefore provided a good description of the desorption process (Table 4.4b). Aharoni *et al.* (1991) and Aharoni and Sparks (1991) have noted that a conformity of experimental data to the Elovich equation indicated by a relatively high r^2 value during an entire experiment could suggest a heterogeneous diffusion process. Aharoni and Sparks (1991) predicted that a slope < 0.24 for the relationship $d(q/q_\infty)$ versus ln t would be expected for a heterogeneous diffusion. Figure 4.4 and 4.5 show plots of q/q_∞ versus ln t for adsorption and desorption process, respectively, which are linear (r^2 values ranged from 0.976 to 0.998 for the adsorption process, and 0.963 to 0.999 for the desorption process) across the entire reaction period for all pH and initial NH_4^+ concentrations (Table 4.3b, 4.4b). The slopes of these plots ranged from 0.106 to 0.151 for the adsorption process and 0.012 to 0.089 for the desorption process at all pH and initial NH_4^+ concentrations (Table 4.2b, 4.3b), suggesting heterogeneous diffusion (Aharoni and Sparks, 1991).

Table 4.4a. Regression equations and coefficients of determination (r^2) for NH_4^+-N desorption using the modified Freundlich and parabolic diffusion models, at various pH, initial NH_4^+-N concentrations (C_0), and adsorbed NH_4^+-N (C*).

C_0 (mg L^{-1})	pH	C* (mg kg^{-1})	Modified Freundlich	r^2	Parabolic diffusion	r^2
70.1	4	542	2.459+0.092log t	0.997	$339.5+9.589t^{1/2}$	0.989
	5	548	2.458+0.095log t	0.996	$338.8+9.846t^{1/2}$	0.990
	6	551	2.472+0.090log t	0.995	$343.5+9.454t^{1/2}$	0.992
	7	562	2.501+0.086log t	0.996	$364.4+9.650t^{1/2}$	0.990
280.2	4	1733	2.943+0.047log t	0.999	$955.4+12.58t^{1/2}$	0.964
	5	1751	2.966+0.043log t	0.998	$999.1+12.00t^{1/2}$	0.974
	6	1831	2.974+0.042log t	0.998	$1016+12.11t^{1/2}$	0.972
	7	1843	2.988+0.042log t	0.999	$1050+12.38t^{1/2}$	0.964
560.4	4	2946	3.264+0.028log t	0.987	$1961+11.11t^{1/2}$	0.947
	5	3018	3.306+0.020log t	0.980	$2122+8.82t^{1/2}$	0.906
	6	3092	3.313+0.020log t	0.977	$2173+7.19t^{1/2}$	0.932
	7	3330	3.320+0.020log t	0.990	$2208+7.44t^{1/2}$	0.926
1401.0	4	5595	3.557+0.017log t	0.995	$3829+8.32t^{1/2}$	0.912
	5	5728	3.582+0.014log t	0.994	$3978+9.00t^{1/2}$	0.937
	6	5908	3.582+0.015log t	0.995	$4008+8.84t^{1/2}$	0.897
	7	5946	3.592+0.012log t	0.995	$4037+8.11t^{1/2}$	0.913

C* amount of NH_4^+-N (mg kg^{-1}) on the exchange complex of the zeolite before desorption is initiated.

Shell progressive film diffusion and shell progressive particle diffusion models were also evaluated but did not adequately describe NH_4^+ adsorption or desorption by the natural zeolite. The poor fit of these models indicated that liquid-filled micropore diffusion and particle film diffusion were not exclusive rate-controlling processes. It is likely that an activated transport process or a combination of several

Table 4.4b. Regression equations and coefficients of determination (r^2) for NH_4^+-N desorption using the Elovich and heterogeneous diffusion models, at various pH, initial NH_4^+-N concentrations (C_o), and adsorbed NH_4^+-N (C*).

C_o (mg L^{-1})	pH	C* (mg kg^{-1})	Elovich	r^2	Heterogeneous Diffusion	r^2
70.1	4	542	277.5+35.0ln t	0.991	0.892+0.089ln t	0.982
	5	548	271.1+36.8ln t	0.993	0.894+0.083ln t	0.994
	6	551	277.8+35.5ln t	0.991	0.895+0.080ln t	0.993
	7	562	296.0+36.6ln t	0.992	0.895+0.078ln t	0.994
280.2	4	1733	874.3+45.8ln t	0.996	0.942+0.045ln t	0.998
	5	1751	922.6+43.4ln t	0.996	0.946+0.040ln t	0.998
	6	1831	938.6+44.0ln t	0.996	0.946+0.040n t	0.997
	7	1843	970.5+44.8ln t	0.996	0.948+0.044ln t	0.999
560.4	4	2946	1836+52.4ln t	0.981	0.970+0.031ln t	0.963
	5	3018	2020+42.1ln t	0.972	0.980+0.022ln t	0.968
	6	3092	2108+30.5ln t	0.983	0.978+0.021ln t	0.983
	7	3330	2140+31.6ln t	0.980	0.977+0.021ln t	0.991
1401.0	4	5595	3752+35.4ln t	0.973	0.981+0.017ln t	0.997
	5	5728	3896+38.0ln t	0.984	0.985+0.013ln t	0.995
	6	5908	3926+37.8ln t	0.965	0.984+0.015ln t	0.996
	7	5946	3962+34.5ln t	0.973	0.987+0.012ln t	0.997

C* amount of NH_4^+-N (mg kg^{-1}) on the exchange complex of the zeolite before desorption was initiated.

interacting transport processes are rate controlling for the time span observed. Similar observations were made by Allen *et al.* (1995) while modeling nutrient release in clinoptilolite-phosphate rock systems.We could not find a rigorous solution for the general intermediate case in the literature, in which both particle and film diffusion affect the rate. The mathematical difficulty is that a nonlinear boundary

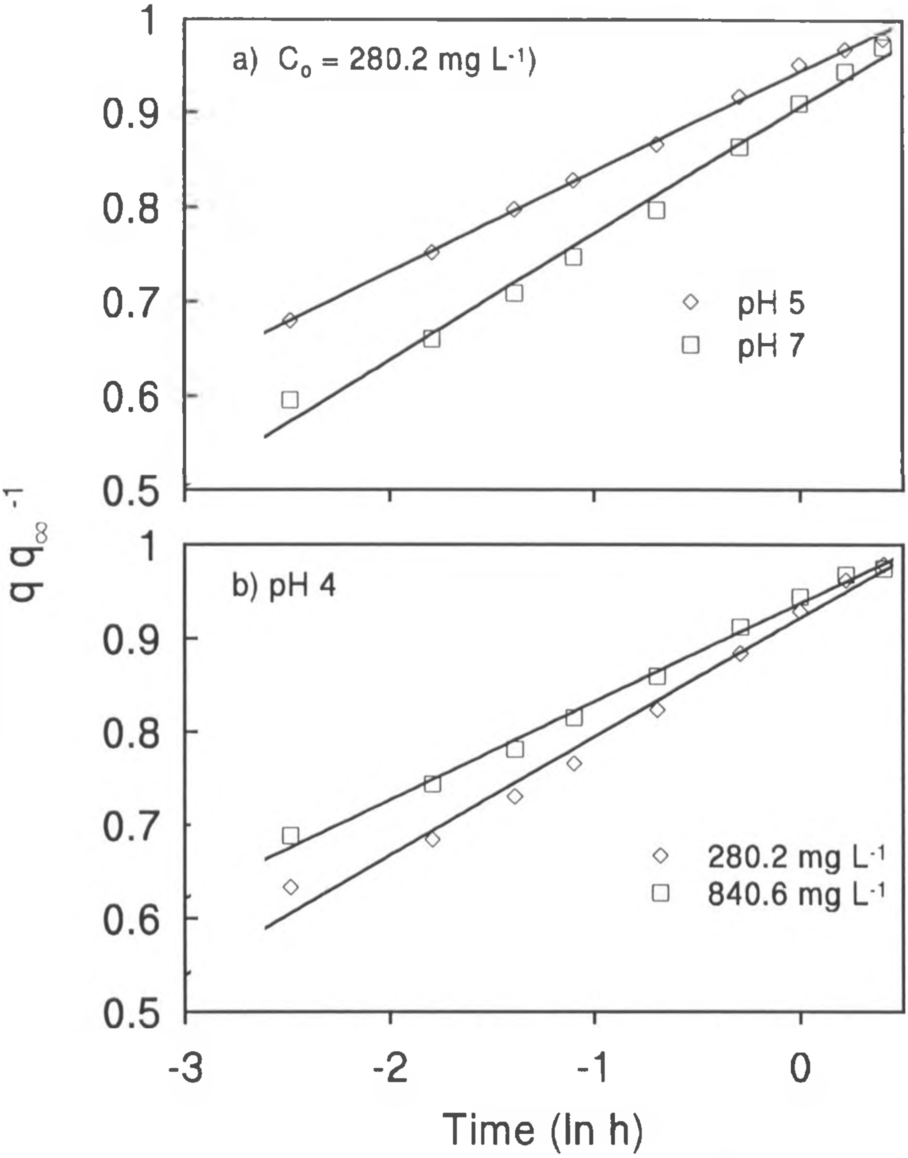


Figure 4.4. Ammonium adsorption data applied to a heterogeneous diffusion model at (a) initial NH_4 concentration of 280.2 mg L^{-1} at pH 5 and 7, and (b) initial NH_4^+-N concentrations of 28 and 840.6 mg L^{-1}, at pH 4, where q is the amount of NH_4^+-N adsorbed by the zeolite at ti and q_∞ is the amount of NH_4^+-N adsorbed at 2 h.

condition arises at the interface (Helfferich, 1983). The problem could probably become simpler if li concentration profiles in the film are postulated.

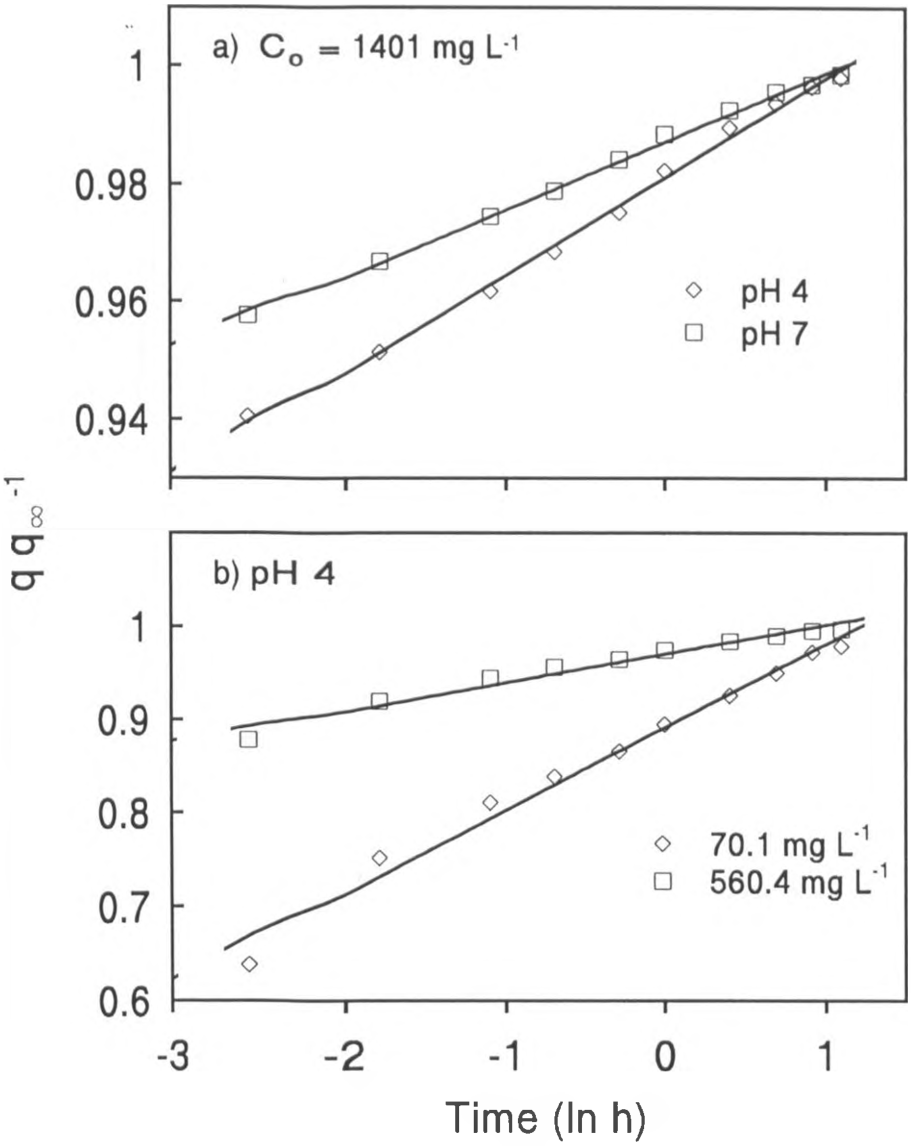


Figure 4.5. Ammonium desorption data applied to a heterogeneous diffusion model at (a) initial NH_4^+-N concentration of 1401.0 mg L^{-1} at pH 4 and 7, and (b) initial NH_4^+-N concentrations of 70.1 and 560.4 mg L^{-1}, at pH 4, where q is the amount of NH_4^+-N desorbed by the zeolite at time t, and q_∞ is the amount of NH_4^+-N desorbed at 5 h.

Reaction Rate Coefficients

The exchanging groups responsible for the adsorptive capacity of zeolites are known to be dispersed randomly in aqueous solution throughout the pores and capillaries of the zeolite. With NH_4^+ as the exchanging cation, the overall mass transport may be divided into five steps, apart from that effected by the moving liquid: (i) diffusion of NH_4^+ through the solution up to the zeolite particles, (ii) diffusion of NH_4^+ through the zeolite particles, accompanied by the anion in solution (two dimensional diffusion of the ion along the capillary walls of the zeolite must be considered as a possibility), (iii) chemical exchange between NH_4^+ and exchangeable cations at the exchange site in the interior of the zeolite minerals, (iv) diffusion of the displaced cation out of the interior of the mineral (reverse of step (ii)), and (v) diffusion of the displaced cation through the solution away from the zeolite mineral (reverse of step (i). The kinetics of the exchange will be governed either by a diffusion or by a mass action mechanism, depending on which of the above steps is the slowest.

We calculated the reaction rate coefficients (k) for NH_4^+ adsorption and desorption by the zeolite samples at different pH and initial NH_4^+ concentrations from the modified Freundlich model, and these k values ranged from 0.134 to 0.193 min^{-1} for the adsorption process, and 0.129 to 0.226 min^{-1} for the desorption process. Reaction rates are directly proportional to k values (Selim *et al.*, 1976). In this study, measured k values generally decreased with increasing ionic strength which conforms to Bronsted's activity rate theory (Moore, 1972). Similar observations were made by Doula *et al.* (1994) on studies of K^+, which behaves very similar to NH_4^+.

No previous reports on the rate constants for NH_4^+ adsorption or desorption by natural zeolites were found, hence, comparisons with similar work was not possible. However, our k_a values seemed to be relatively low compared to the k_a values (1 to 20 min^{-1}) obtained by Sparks *et al.*, (1980) for K^+ sorption in soils. This could possibly be due to slow movement of NH_4^+ ions along the walls of the negatively charged micropores, and to surface diffusion. To clearly visualize this, consider a model based upon a system of macropores plus micropores wherein the latter penetrate the walls and feed into the former. The major portion of the adsorptive capacity will be resident in the micropores. The macropores will merely serve as conduits for the transport of ions to and from the micropores. A practical aspect of these slow NH_4^+ sorption rates is that in situations where zeolites are used as NH_3 and/or NH_4^+ adsorbents, like during composting of N-rich wastes or in poultry facilities, high rates of NH_3 emissions could render the zeolite inefficient. Conversely, slowing the rate of NH_3 evolution from the system would allow prolonged time of contact between NH_3 and the zeolite. Hence, maximum NH_4^+ adsorption can be achieved with time, as a result of slow to moderate diffusion of the NH_4^+ ions into the channels and central cavities of the natural zeolite. One possible way of achieving this high efficiency is by covering the surface of the materials emitting NH_3 with a layer of the zeolite powder. In so doing, the rate of NH_3 escape as it passes through the covering layer of the zeolite will be slowed down, allowing a prolonged period of contact between NH_3 and the zeolite. We have observed this phenomenon in a previous study (unpublished report).

CONCLUSIONS

Initial NH_4^+ concentration and pH were significant factors that influenced the kinetics of NH_4^+ exchange on the natural zeolite. Increasing initial NH_4^+ concentration resulted in decreased NH_4^+ exchange rates. An increase in pH resulted in faster sorption and in greater amounts of NH_4^+ being sorbed. All the tested models provided an adequate description of the NH_4^+ adsorption and desorption processes in the natural zeolite. Conformity of data to the Elovich model and the excellent fit obtained for the heterogeneous diffusion model suggested that the rates of NH_4^+ exchange were governed by a heterogeneous diffusion process. However, the actual mechanism involved can only be determined by experiments designed to evaluate chemical and physical factors affecting the rate constants. The data presented here represent the first use of the first-order kinetics, modified Freundlich, parabolic diffusion, Elovich, and heterogeneous diffusion rate models to describe NH_4^+ adsorption kinetics in the natural zeolite clinoptilolite at different pH values and initial NH_4^+ concentrations, and indicates that the natural zeolite tested could be used as an NH_4^+ adsorbent and consequently as a controlled-release NH_4^+ fertilizer.

CHAPTER 5

THERMODYNAMICS OF AMMONIUM EXCHANGE ON THE NATURAL ZEOLITE CLINOPTILOLITE

ABSTRACT

Understanding the thermodynamics of NH_4^+ exchange on natural zeolites is important for efficient utilization of these minerals as NH_3 and/or NH_4^+ adsorbents, particularly in the process of composting which is characterized by temperature variation. The objective of this research was to study the effect of a temperature range of 25 to 55 °C on the kinetics of NH_4^+ exchange on the natural zeolite clinoptilolite, and to elucidate the exchange process using thermodynamic and pseudothermodynamic parameters formulated from the experimental data. Four kinetic models namely, modified Freundlich, Elovich, parabolic diffusion, and first-order were used to describe NH_4^+ exchange on the natural zeolite. All the models adequately described the NH_4^+ exchange process with r^2 values ranging from 0.9151 to 0.9990. The rate constants for both adsorption and desorption processes were calculated using the modified Freundlich model, and these rate constants increased with increasing temperature. Changes in rate constants with a 10 °C rise in temperature (Q_{10}) were slightly greater than 1, suggesting a diffusion-controlled process. Activation energies for adsorption (E_a) and desorption (E_d) were 2.32 and 5.65 kJ mol^{-1}, respectively. The higher E_d value indicated that more energy was needed to desorb NH_4^+ than to adsorb it. The standard enthalpy of exchange ($\Delta H°$) was negative, which indicated strong binding of NH_4^+ on the exchange sites of the zeolite. The free energy ($\Delta G°$) values for NH_4^+ exchange ranged from 50.58 to 269.27 J mol^{-1} and increased with increasing temperature. This implies that the driving force for the formation of an NH_4^+ charged zeolite from a predominantly Ca, Mg, and K zeolite was not favored, and that the latter ions became more preferred on the zeolite exchange sites as the temperature increased.

INTRODUCTION

The zeolite mineral clinoptilolite is a natural silicate mineral with internal channelling and a high cation exchange capacity. It has an affinity for NH_4^+ ions, and has been successfully exploited to remove these ions from wastewaters (Liberti *et al.*, 1981), to retain them in soils (Weber *et al.*, 1983), to reduce

NH_3 emissions from animal housing (Koelliker *et al*., 1978) and during composting of nitrogen-rich wastes (Witter and Lopez-Real, 1988).

Ammonium adsorption and desorption by clinoptilolite is driven by cation exchange reactions. Ion exchange equilibria on clays and on soils have been characterized using thermodynamic principles (Laudelout *et al*., 1968; Jensen, 1973; Sposito, 1981). These principles have been used to obtain exchange coefficients and thermodynamic parameters for various cation exchange systems (Hutcheon, 1966; Udo, 1978). Most thermodynamic studies on clays and soils have involved the calculation of the free energy of exchange (ΔG^o) from equilibrium constants (K) determined through the Gibbs-Duhem equation (Argersinger *et al*., 1950). Little can be deduced about the binding strengths of cations on negatively charged surfaces from ΔG^o values alone because these strengths are defined primarily in terms of enthalpy (Moore, 1972; Filep and Khargitan, 1977). Transition-state theory or absolute reaction-rate theory (Eyring, 1935a, b; Glasstone *et al*., 1941) has been used extensively to calculate pseudothermodynamic parameters and characterize reaction rates of chemical processes with respect to their potential energy barriers. This theory assumes that colliding molecules (e.g., reactions between solution ions and ions held by an exchange complex) must be in a high energy state before a reaction can occur. When these highly energized reactant molecules collide, they form an activated complex. It is a distinct chemical species in equilibrium with the reactants. The activated complex is highly unstable and rapidly dissociates to form the eventual product or to reform the original reactants (Sparks, 1989). Once the exchange reaction is complete, pseudothermodynamic parameters for the adsorption and the desorption process may be formulated. Griffin and Jurinak (1974) calculated pseudothermodynamic parameters for phosphate interactions with calcite using reaction rate theory. Gonzalez *et al*. (1982) applied reaction rate theory to a treatment of adsorption-desorption processes on a Fe-silica gel system. Sparks and Jardine (1981) successfully applied reaction rate theory to kinetics of K adsorption and desorption in soil systems for the first time.

Equilibrium relationships and kinetics of NH_4^+ adsorption and desorption by clinoptilolite have been investigated (Bernal and Lopez-Real, 1993; Kithome *et al.*, 1997a,b), but no information is available in the literature on the thermodynamics of NH_4^+ exchange on this mineral. Studying the thermodynamics of NH_4^+ exchange on the zeolite mineral clinoptilolite will enable its efficient utilization as NH_3 and NH_4^+ adsorbent in the composting process. This is particularly significant because temperatures during composting range from 25 to 55 °C or even higher and NH_3 emissions are enhanced at high temperatures.

Accordingly, the objective of this research was to study the effect of temperature on the kinetics of NH_4^+ exchange on the natural zeolite clinoptilolite, and elucidate the exchange process using thermodynamic and pseudothermodynamic parameters formulated from the experimental data.

MATERIALS AND METHODS

Experimental

The natural zeolite used in this study was mined in Southwest USA and supplied by Aberhill's Holdings Inc., of 2838 Alice St., Abbotsford, B.C. Canada V2T 3P1. It was air-dried and ground to pass through a 2-mm sieve. Mineralogical identification using XRD showed that the zeolite consisted mainly of clinoptilolite, and negligible amounts of feldspar and quartz. Some selected physical and chemical properties of the zeolite were analyzed using procedures described previously (Kithome *et al.* 1997a) and are provided in Table 5.1.

Thermodynamics of NH_4^+ *exchange on the zeolite*

Thermodynamic studies were carried out using triplicate 1 g zeolite samples which were weighed and placed in 250 mL centrifuge tubes. To each sample, 20 mL of a solution containing 840.6 mg L^{-1} NH_4^+-N was added. The samples were shaken at 200 rpm for 5, 10, 20, 30, 45, 60, 90, 120, 150, and 180 min under isobaric and isothermal conditions of 1 atmosphere and 25, 35, 45, and 55 °C on a Lab-Line's Environ-Shaker that combines a controlled temperature incubator with an orbital shaking mechanism in a bench top design (Lab-Line Instruments, Inc., Melrose Park, IL). After each shaking time, the samples were immediately centrifuged at 2000 x g RCF for 5 min, at approximately the same temperature as was

Table 5.1. Some characteristics of the zeolite sample.

pH (H_2O)	7.87
pH (KCl)	5.84
Surface area (m^2 kg^{-1})	$9.35x10^5$
EC (S m^{-1})	0.17
Total C (%)	0.00
NH_4^+-N (mg kg^{-1})	12.30
CEC (cmol kg^{-1})	92.78
Exchangeable cations	
Na^+ (cmol kg^{-1})	3.07
K^+ (cmol kg^{-1})	10.40
Ca^{2+} (cmol kg^{-1})	44.79
Mg^{2+} (cmol kg^{-1})	7.78

for the shaking. The supernatant was decanted and NH_4^+-N determined spectrophotometrically using an automated continuous flow injection analyzer. Amounts of NH_4^+-N adsorbed by the zeolite were calculated from the reduction of NH_4^+-N in solution. The samples remaining in the centrifuge tubes were washed with deionized water and a 1:1 acetone-to-water mixture until a negative test for Cl^- was obtained using $AgNO_3$. Adsorbed NH_4^+-N was then extracted with 20 mL portions of 1M KCl by shaking at 200 rpm for the same time, temperature and pressure as was for the adsorption, followed by centrifugation at 2000 x g RCF for 5 min. The supernatant was decanted and analyzed for NH_4^+-N as for the adsorption procedure. The amount of NH_4^+-N desorbed was calculated from the increased NH_4^+-N in solution.

Theoretical considerations

Kinetic models for NH_4^+ exchange on the zeolite

Four mathematical models (Table 5.2) were used to describe the kinetics of NH_4^+ exchange on the natural zeolite. The goodness of fit of each of these equations to the data was evaluated using the r^2

Table 5.2. Kinetic models used to describe NH_4^+ exchange on the natural zeolite clinoptilolite.

Model	Equation	Reference
1. Modified Freundlich	$\log_{10} X_t = \log_{10} kC_o + 1/m\log_{10} t$	Kuo and Lotse (1974)
2. Elovich	$X_t = 1/\beta\ln(\alpha\beta) + 1/\beta\ln t$	Chien and Clayton (1980)
3. First-order kinetic (adsorption)	$\log_{10}(1 - F_a) = k_a't$	Sparks and Jardine (1981)
4. First-order kinetic (desorption)	$\log_{10} F_d = k_d't$	Sparks and Jardine (1981)
5. Parabolic diffusion	$F_t = Rt^{1/2} + c$	Laidler (1965)

X_t is the amount of NH_4^+-N (mg/kg zeolite) adsorbed or desorbed by the zeolite at time t; C_o is the initial NH_4^+-N concentration (mg/kg zeolite); k is the adsorption or desorption rate coefficient; $F_a = NH_4^+\text{-}N_t / NH_4^+\text{-}N_{eq}$ where $NH_4^+\text{-}N_t$ is the amount of NH_4^+-N on the zeolite at time t, and $NH_4^+\text{-}N_{eq}$ is the amount of NH_4^+-N on the zeolite at equilibrium; $F_d = NH_4^+\text{-}N_t / NH_4^+\text{-}N_{t=0}$ where $NH_4^+\text{-}N_t$ is the amount of NH_4^+-N on the exchange sites of the zeolite at time t, and $NH_4^+\text{-}N_{t=0}$ is the amount of NH_4^+-N on the exchange sites of the zeolite at zero time of desorption; k_a' is the apparent adsorption rate coefficient; k_d' is the apparent desorption rate coefficient; $F_t = NH_4^+\text{-}N_t / NH_4^+\text{-}N_{eq}$ where $NH_4^+\text{-}N_t$ is the amount of NH_4^+-N adsorbed or desorbed by the zeolite at time t, and $NH_4^+\text{-}N_{eq}$ is the amount of NH_4^+-N on the zeolite at equilibrium; R, overall diffusion coefficient; m,α, β, and c are constants.

values to determine which best described the NH_4^+ exchange process.

Calculation of thermodynamic parameters for NH_4^+ exchange using Gibbs' theory

Because 94.1 to 98.3% of all adsorbed NH_4^+ was subsequently desorbed, it implies that the kinetics of NH_4^+ adsorption and desorption were reversible on the zeolite. This justifies the application of thermodynamic principles to the zeolite mineral.

Assuming that the ion-exchange is analogous to an ordinary metathesis reaction, and that the Mass Law applies to the heterogeneous system: zeolite + aqueous solution at equilibrium, the exchange reaction involving two cations, A^+ and B^+ may be written as

$$A^+ + BZ \rightleftharpoons AZ + B^+ \qquad [1]$$

where Z has been taken to designate the insoluble structurally bound anionic part of the zeolite. If k_a and k_d are the adsorption and desorption rate coefficients for the forward and reverse directions, respectively, one can calculate the thermodynamic equilibrium constant K_{eq} using the principle of detailed balancing (Lasaga, 1983a), by the equation:

$$K_{eq} = (AZ)(B') / (A')(BZ) = k_a/k_d \qquad [2]$$

The Mass Law is obeyed if the appropriate activity values when substituted into Eq. [2] lead to a constant value of K_{eq} independent of the composition for a variety of compositions of the system containing the exchanging ions plus adsorbent. Equation [2] forms a link between kinetics and thermodynamics, and allows us, for example, to obtain a value for k_d from only a kinetic measurement of k_a and knowledge of thermodynamics (e.g., K_{eq}).

The free energy for NH_4^+ exchange on the zeolite can be obtained from classical thermodynamics using the relationship:

$$\Delta G^o = -RT \ln K_{eq} \qquad [3]$$

or

$$\Delta G^o = -RT \ln k_a/k_d \qquad [4]$$

Using the Arrhenius and van't Hoff equations (Moore and Pearson, 1981), energies of activation for NH_4^+ adsorption (E_a) and desorption (E_d) can be determined as follows:

$$d \ln k_a / dT = E_a / RT^2 \qquad [5]$$

for the adsorption kinetic reaction, and

$$d \ln k_d / dT = E_d / RT^2 \qquad [6]$$

for the desorption kinetic reaction.

Substituting,

$$d \ln k_a / dT - d \ln k_d / dT = d \ln K_{eq} / dT \qquad [7]$$

and from the van't Hoff equation, the enthalpy (ΔH^o) for NH_4^+ exchange on the zeolite can be calculated as:

$$d \ln K_{eq} / dT = \Delta H^o / RT^2 \qquad [8]$$

or

$$E_a - E_d = \Delta H^o \qquad [9]$$

The entropy (ΔS^o) for NH_4^+ exchange on the zeolite can be computed from the third law of thermodynamics as:

$$\Delta S^o = (\Delta H^o - \Delta G^o) / T \qquad [10]$$

Calculation of pseudothermodynamic parameters for NH_4^+ exchange using the Reaction-Rate Theory

The reaction-rate theory can be used as a model to substantiate the thermodynamic parameters calculated by Gibbs' theory (Sparks and Jardine, 1981). Pseudothermodynamic parameters obtained using this theory can be expressed as (Moore and Pearson, 1981):

$$\Delta G^{o\ddagger} = -RT \ln K_{eq}^{\ddagger} = \Delta H^{o\ddagger} - T\Delta S^{o\ddagger} \qquad [11]$$

where $\Delta G^{o\ddagger}$ is the free energy of activation, $\Delta H^{o\ddagger}$ is the enthalpy of activation, $\Delta S^{o\ddagger}$ is the entropy of activation, R is the universal gas constant, T is the absolute temperature, and $K_{eq}^{\ddagger}$ is the pseudothermodynamic equilibrium constant of the activated complex.

From the laws of thermodynamics, the adsorption rate coefficient can also be found as:

$$k_a = (K_B T/h) \exp(-\Delta G_a^{o\ddagger}/RT) \qquad [12]$$

where K_B is the Boltzmann's constant, h is the Planck's constant, and subscript a denotes the adsorption reaction. From the reaction rate theory (Moore and Pearson, 1981), the $\Delta G_a^{o\ddagger}$ can be calculated using the expression:

$$\Delta G_a^{o\ddagger} = \Delta H_a^{o\ddagger} - T\Delta S_a^{o\ddagger} \qquad [13]$$

Manipulation of Eq. [13] and substitution into Eq. [12] yields:

$$k_a = (K_B T/h) \exp(\Delta S_a^{o\ddagger}/R) \exp(-\Delta H_a^{o\ddagger}/RT) \qquad [14]$$

Equation [14] can be used to calculate $\Delta S_a^{o\ddagger}$ because the following relationship for a unimolecular reaction is true:

$$\Delta H_a^{o\ddagger} = E_a - RT \qquad [15]$$

Analogous expressions can be obtained in the same manner for the desorption reaction through the use of E_d and k_d calculated for the reverse process.

RESULTS AND DISCUSSION

Kinetic Models for NH_4^+ Exchange on Zeolite

Conformity of the data to the linear form of each kinetic model was tested using linear regression analysis. All four models satisfactorily described the kinetics of NH_4^+ exchange on the natural zeolite clinoptilolite at the four temperatures studied ($r^2 \geq 0.9151$, Table 5.3). Similar results were obtained previously (Kithome *et al.*, 1997b) for kinetics of NH_4^+ exchange on the same zeolite.

The modified Freundlich and Elovich models had the highest coefficients of determination (r^2) ranging from 0.9878 to 0.9990. This observation conforms to the findings of others (Kuo and Lotse, 1974; Sparks *et al.*, 1980; Havlin *et al.*, 1985; and Allen *et al.*, 1995). The first-order kinetic model described the adsorption process well up to 120 min after which there was a distinct break from linearity (Fig. 5.1). Similar deviations were noted by Boyd *et al.* (1947) and Sivasubramaniam and Talibudeen (1972) when a relatively long time of contact was employed. Boyd *et al.* (1947) suggested that deviation from first-order kinetics as the equilibrium point is approached may be related to irregularities in particle size of the solid exchanger. However, Jardine and Sparks (1984a) attributed this phenomenon to the existence of multiple first-order kinetics. Only the linear portion of the regression equations and coefficients of determination for the first-order kinetic model are given in Table 5.3. It should be noted that these values would change significantly if all data points were included. Using the linear portion only, the r^2 values for the first-order kinetic model are very close to those of modified Freundlich and Elovich models. Ammonium adsorption and desorption data also conformed reasonably well to the parabolic diffusion model as evidenced by r^2 values of 0.9492 to 0.9831 (Table 5.3), suggesting that intraparticle diffusion or surface diffusion may be rate limiting (Helfferich, 1969; Crank, 1976). The intraparticle diffusional process is a transport of the adsorbing ion through the liquid associated with less accessible exchange sites of the mineral and is characterized by

Table 5.3. Regression equations and coefficients of determination for NH_4^+ exchange on the natural zeolite clinoptilolite using modified Freundlich, Elovich, first-order kinetic, and parabolic diffusion models at four temperatures.

	Temperature °C	Modified Freundlich	r^2	Elovich	r^2
Adsorption	25	3.6437+0.0556log t	0.9974	4322+295.7ln t	0.9948
	35	3.6566+0.0811log t	0.9974	4352+484.5ln t	0.9946
	45	3.6688+0.1091log t	0.9970	4304+737.1ln t	0.9949
	55	3.6809+0.1148log t	0.9931	4392+809.8ln t	0.9949
Desorption	25	3.6524+0.0017log t	0.9878	4491+7.502ln t	0.9878
	35	3.6828+0.0832log t	0.9954	4726+484.5ln t	0.9974
	45	3.7118+0.0997log t	0.9941	5005+644.1ln t	0.9967
	55	3.7436+0.1133log t	0.9971	5333+813.6ln t	0.9990

	Temperature °C	First-order kinetic[†]	r^2	Parabolic diffusion	r^2
Adsorption	25	-0.7460-0.0090t	0.9936	$0.8085+0.0165t^{1/2}$	0.9669
	35	-0.6155-0.0084t	0.9898	$0.7316+0.0231t^{1/2}$	0.9646
	45	-0.5068-0.0084t	0.9910	$0.6547+0.0296t^{1/2}$	0.9597
	55	-0.4976-0.0083t	0.9771	$0.6438+0.0307t^{1/2}$	0.9492
Desorption	25	-1.2122-0.0010t	0.9151	$0.9371+0.0009t^{1/2}$	0.9568
	35	-0.6706-0.0339t	0.9943	$0.7533+0.0458t^{1/2}$	0.9777
	45	-0.5228-0.0620t	0.9994	$0.7379+0.0559t^{1/2}$	0.9759
	55	-0.4876-0.0570t	0.9992	$0.7008+0.0627t^{1/2}$	0.9831

[†] Only regression equations and coefficients of determination for the linear portion (5 to 120 min) are shown.

activation energies of 21 to 42 kJ mol^{-1} (Reichenberg, 1957). The surface diffusional process, on the other hand, involves the movement of the adsorbing ion along the walls of the less accessible spaces and is characterized by an activation energy roughly equal to the heat of adsorption, ΔH^0 (Boyd *et al.*, 1947).

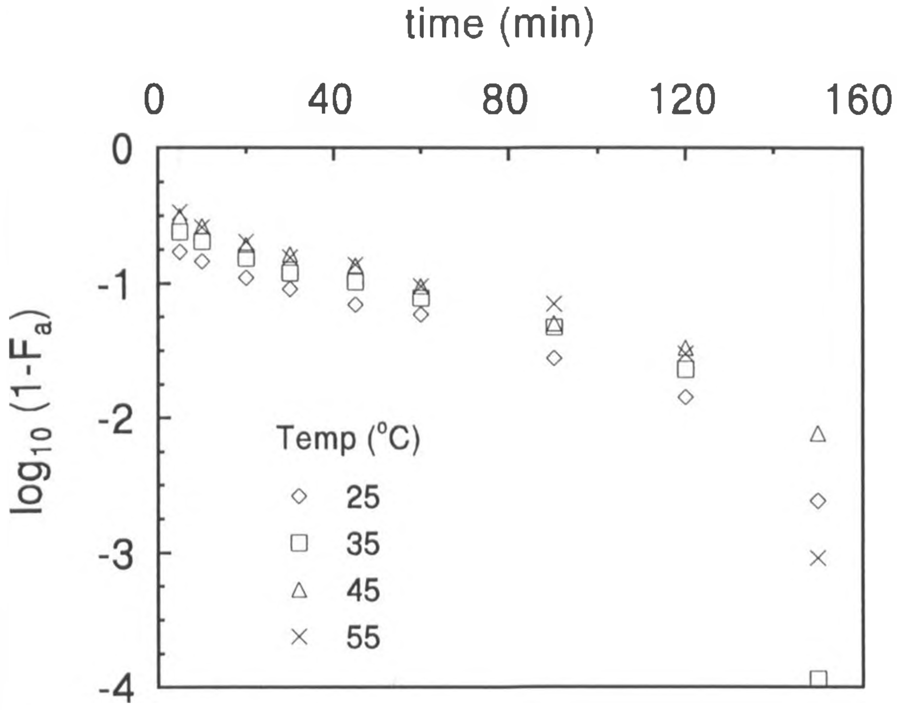


Figure 5.1. Plot of the first-order kinetic model for NH_4^+-N adsorption by the natural zeolite at 25, 35, 45, and 55 °C, where F_a was the fraction adsorbed at time t of the total amount of NH_4^+-N on the exchange complex of the zeolite at equilibrium.

Temperature Effects on the Kinetics of NH_4^+ Exchange

The k_a and k_d values (Table 5.4) calculated using the modified Freundlich model increased with increasing temperature, indicating faster NH_4^+ exchange at higher temperatures as predicted from Bronsted's reaction rate theory (Adamson, 1973). The k_d values were slightly higher than the k_a values.

Table 5.4. Reaction-rate constants (k) of the modified Freundlich model and Q_{10} values (Q_{10}-I, Q_{10}-II, and Q_{10}-III)[†] for NH_4^+ exchange on the natural zeolite clinoptilolite as influenced by temperature.

	25 °C	35 °C	45 °C	55 °C	Q_{10}-I	Q_{10}-II	Q_{10}-III
			k min^{-1}				
Adsorption	0.2618	0.2698	0.2775	0.2853	1.031	1.029	1.028
Desorption	0.2672	0.2865	0.3063	0.3296	1.072	1.069	1.076

[†] Temperature quotient $(Q_{10}) = (k_2/k_1)^{10/(T2-T1)}$; Q_{10}-I = (k_{35}/k_{25}), Q_{10}-II = (k_{45}/k_{35}), and Q_{10} -III = (k_{55}/k_{45}) where k_{25}, k_{35}, k_{45}, and k_{55} are rate constants at 25, 35, 45, and 55 °C, respectively.

This was expected because the desorption studies were carried out using 1M KCl as the extractant. This high salt concentration provided tremendous desorption energy, whereas 0.06M NH_4Cl was used for the reverse process of adsorption. Changes in rate constants with a 10°C rise in temperature (Q_{10}; Q_{10}-I from 25 to 35 °C, Q_{10}-II from 35 to 45 °C, and Q_{10}-III from 45 to 55 °C) are also shown in Table 5.4. Values of Q_{10} for NH_4^+ exchange on the zeolite were slightly greater than 1 at all four temperatures studied. Most chemical and biological reactions have Q_{10}s between 2 and 3, while physical processes such as diffusion have Q_{10}s slightly greater than 1 (Salisbury and Ross, 1969). This is further evidence that diffusion is the rate-determining step for NH_4^+ exchange on the zeolite. All Q_{10} values for the desorption process were higher than for the adsorption process (Table 5.4), which implies higher net reaction energies for the desorption process. These results support the statement by Salisbury and Ross (1969) that reactions having greater Q_{10} values have higher activation energies.

Activation Energies for NH_4^+ Adsorption and Desorption Processes

The energy of activation measures the magnitude of the forces to be overcome during the process of ionic exchange (Sparks, 1986). The activation energy of adsorption and desorption were determined from the Arrhenius equation using four temperatures with r^2 values of 0.9998 and 0.9983 for adsorption and desorption respectively (Fig. 5.2). The energy of activation for desorption (E_d) was greater than for adsorption (E_a) (Table 5.5). This indicates that the energy needed to desorb NH_4^+ was greater than that to

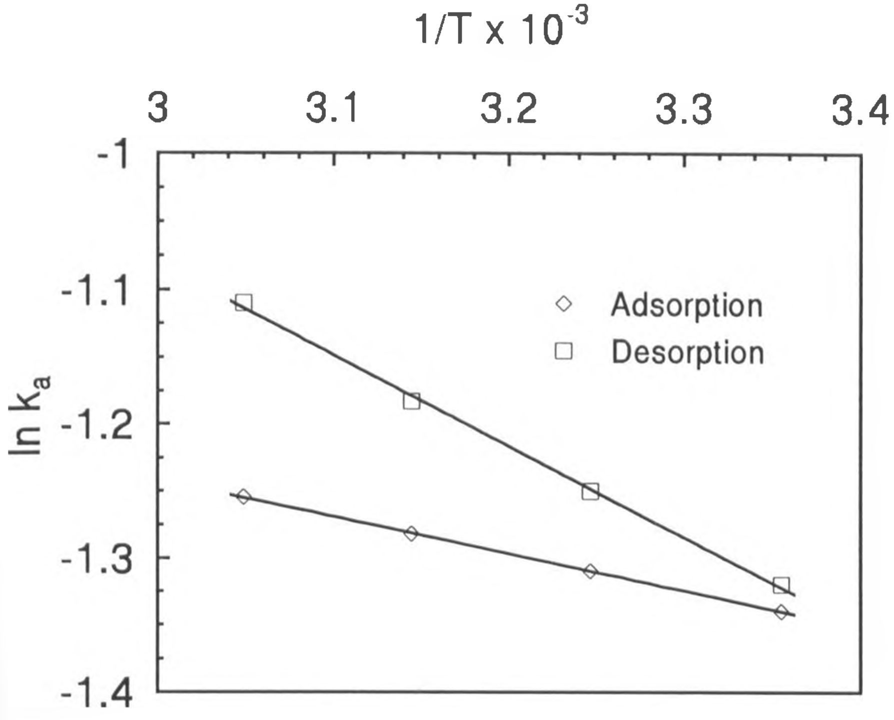


Figure 5.2. Arrhenius plot of the adsorption and desorption rate constants for NH_4^+ exchange on the natural zeolite at 25, 35, 45 and 55 °C.

adsorb it, which is probably due to strong adsorption of the NH_4^+ in the internal channels and central cavities of the zeolite. This is an important property if the NH_4^+ charged zeolite is to be used as a controlled-release fertilizer. Release of NH_4^+ may be slower because a significant amount of energy is required for desorption. Preliminary results from a greenhouse trial where the NH_4^+ charged zeolite was used as a controlled-release fertilizer for ryegrass in a sand based medium supported this view (unpublished data). The magnitude of the activation energy, in addition to providing the temperature dependency of the reaction rate, offers a clue to the reaction mechanism. Surface-controlled reactions have higher activation energy values than do diffusion-controlled reactions (Lasaga, 1983a, b). The low E_a (2.32 kJ mol^{-1}) and E_d (5.65 kJ mol^{-1}) values suggest a diffusion-controlled exchange because purely surface-confined reactions have energies of activation > 42 kJ mol^{-1} (Sparks, 1986). This observation

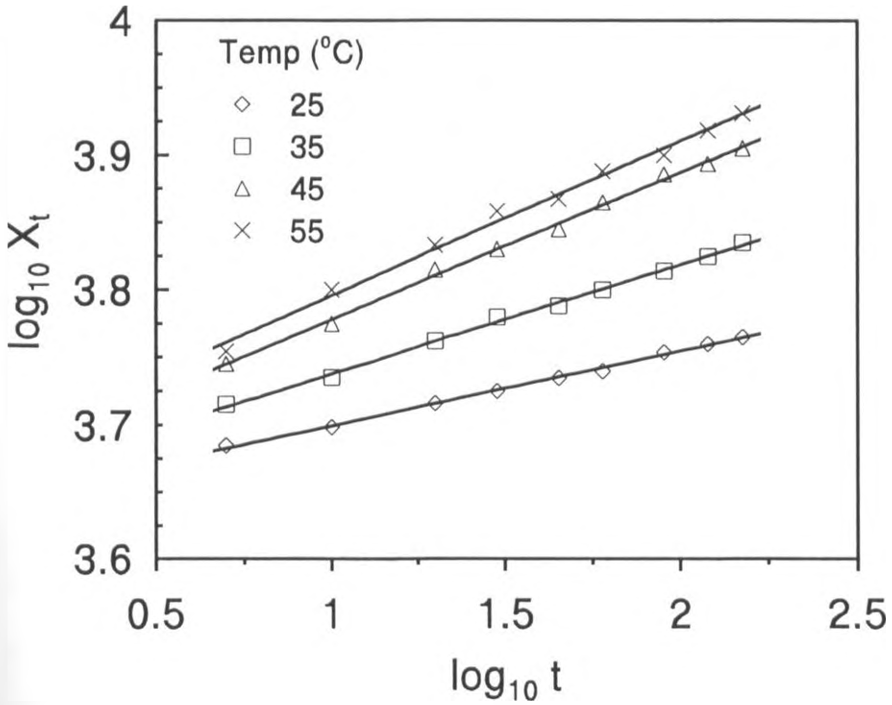


Figure 5.3. Plot of the modified Freundlich model for NH_4^+-N adsorption by the natural zeolite at 25, 35, 45, and 55 °C, where X_t is the amount of NH_4^+-N (mg/kg) adsorbed by the zeolite at time t.

Table 5.5. Calculated rate constants, energies of activation, and thermodynamic parameters for NH_4^+ exchange on the natural zeolite clinoptilolite at four temperatures.

Temperature	k_a	k_d	E_a	E_d	ΔG^o	ΔH^o	ΔS^o
°C	min^{-1}		$kJ\ mol^{-1}$		$J\ mol^{-1}$	$kJ\ mol^{-1}$	$J\ mol^{-1}\ {}^oK^{-1}$
25	0.2618	0.2672	-	-	50.58	-	-11.36
35	0.2698	0.2865	-	-	153.79	-	-11.33
45	0.2775	0.3063	-	-	261.06	-	-11.31
55	0.2853	0.3296	2.32	5.65	269.27	-3.34	-11.37

correlates well with our previous findings (Kithome *et al.*, 1997b) that the kinetics of NH_4^+ exchange in this zeolite was diffusion controlled. No reports on the activation energies of NH_4^+ exchange on natural zeolites were found in the literature for comparison.

Thermodynamic Parameters for NH_4^+ Exchange Calculated Using Gibbs' Theory

Although the amount of NH_4^+ adsorbed increased with increasing temperature (Fig. 5.3), the zeolite exhibited preference for the cations already adsorbed at its exchange complex (43% Ca, 11.2% K, and 8.4% Mg) at all temperatures. This is evidenced by the positive standard free energy (ΔG^o) values (Table 5.5). The positive ΔG^o values implied that the driving force for the formation of an NH_4^+ charged zeolite from a predominantly Ca, Mg, and K zeolite was not favored. The overall Ca and Mg preference may possibly be attributed to strong adsorption due to their double charge, whereas K has been observed to be selectively bound by zeolites compared to NH_4^+ (Ames, 1967). The ΔG^o values became increasingly positive as temperature increased (Table 5.5) implying that Ca, Mg, and K ions became increasingly preferred on the zeolite exchange sites with increasing temperature. This conforms with the Le-Chatelier-Bran principle (Dickerson, 1969) which states that exothermic reactions are impeded with additions of heat and endothermic reactions are enhanced by heat additions. Because heats of exchange for adsorption of the preferred cations are generally exothermic, a decrease of NH_4^+ adsorption with increasing temperature can be expected. This is one possible explanation for the observed decrease in NH_3 and/or

NH_4^+ adsorption by zeolites with time during the composting process (Weber *et al.*, 1983; Witter and Lopez-Real, 1988; and Bernal *et al.*, 1993). The zeolite exchange complex often becomes saturated with the favored cations such as Ca^{2+}, Mg^{2+}, and K^+ which are increasingly preferred as the temperature rises. In such situations large amounts of the zeolite are required to adsorb significant amounts of NH_4^+.

The standard enthalpy of exchange (ΔH^o) in Table 5.5. was determined from the van't Hoff equation, and provides information about the binding strength of NH_4^+ to the zeolite. The ΔH^o value for the zeolite was negative, which indicated strong bonding of NH_4^+ with exchange sites of the zeolite. Also, the negative ΔH^o is related to the heat release associated with the changing hydration status of the cations as they are adsorbed and desorbed from the zeolite surface (Jardine and Sparks, 1984b). The ΔH^o value was several orders of magnitude larger than the ΔG^o values, suggesting that the bonding of NH_4^+ ions in the channels and central cavities of this zeolite was very strong. The low ΔG^o values imply that a small amount of heat in the standard state was left for the system to do useful work; thus, NH_4^+ ions have a limited molecular motion once adsorbed in the channels and central cavities of the zeolite. This restriction suggests formation of strong bonds between NH_4^+ ions and the exchange sites of the zeolite. This is an important property of the zeolite that can be manipulated to develop a controlled-release NH_4^+ fertilizer.

The standard entropy (ΔS^o) values were negative (Table 5.5), indicating that NH_4^+ sorption by the zeolite produced a condition that was more ordered in its molecular arrangement. This would be expected for the formation of an NH_4^+ charged zeolite from that of a predominantly Ca^{2+} and Mg^{2+} saturated zeolite because the total entropy change of an aqueous zeolite system may be regarded as the sum of two terms: a configurational entropy term and a term encompassing the entropy of ion hydration. The adsorption of a monovalent ion and subsequent desorption of a divalent ion would both result in an entropy decrease (Jardine and Sparks, 1984b). The adsorption of NH_4^+ ions onto the exchanger would cause a decrease in the configurational entropy of the zeolite because monovalent ions have fewer ways in which to arrange themselves on a given quantity of exchange sites compared with divalent ions (Laudelout *et al.*, 1968).

The desorption of Ca^{2+} and Mg^{2+} ions into the bulk solution would in turn cause a decrease in the entropy of hydration, because these divalent ions structurally order water molecules (Hutcheon, 1966; Sparks and Jardine, 1981). The sum of these two factors would result in a net negative ΔS^o value (Table 5.5). No literature data was found to compare with the magnitude of ΔG^o, ΔH^o, and ΔS^o values obtained in this study for NH_4^+ exchange on natural zeolites.

Pseudothermodynamic Parameters Derived from the Reaction-Rate Theory

The $\Delta G^{o\ddagger}$ value may be considered as the free energy change between the activated complex and the reactants from which it was formed, with all substances in reference to their standard states (Laidler, 1965). The $\Delta G^{o\ddagger}$ value determines the rate of reaction (Glasstone *et al.*, 1941), and increased with temperature (Table 5.6), as was also observed by Frost and Pearson (1961). The $\Delta G^{o\ddagger}$ values were higher for adsorption than for desorption, suggesting a slower reaction for the adsorption process, due to the difficulty of NH_4^+ in displacing Ca^{2+}, Mg^{2+}, and K^+ ions from the zeolite exchange complex. A positive standard free energy (ΔG^o) was calculated from the differences of $\Delta G^{o\ddagger}$ for adsorption and desorption

Table 5.6. Pseudothermodynamic parameters calculated using reaction-rate theory for NH_4^+ exchange on the natural zeolite at four temperatures.

	Temperature	$\Delta G^{o\ddagger}$	$\Delta H^{o\ddagger}$	$\Delta S^{o\ddagger}$
	°C	kJ mol^{-1}	J mol^{-1}	J mol^{-1} °K^{-1}
Adsorption	25	86.45	-158.57	-290.62
	35	89.35	-241.71	-290.90
	45	92.27	-324.85	-291.17
	55	95.18	-407.99	-291.41
Desorption	25	86.40	3176.43	-279.26
	35	89.20	3093.29	-279.57
	45	92.00	3010.15	-279.85
	55	94.78	2927.01	-280.04

(Frost and Pearson, 1961; Laidler, 1965), which implies that NH_4^+ release by the zeolite is not spontaneous. A practical aspect of this unspontaneous release is that NH_4^+ could be made available to plants slowly and over a longer period of time after application of the NH_4^+-charged zeolite to soil. Table 5.7 shows results of a correlation between the pseudothermodynamic parameters as established by the reaction-rate theory, and those established by Gibbs' theory. The $\Delta G_a^{o\ddagger}$ is the change in free energy required for NH_4^+ to cross the barrier of adsorption at a rate of k_a. The $\Delta G_d^{o\ddagger}$ represents the change in free energy needed by the reverse reaction of desorption at a rate of k_d. The difference between these two parameters yields ΔG^o, the thermodynamic parameter established from Gibbs' theory.

The enthalpy of activation ($\Delta H^{o\ddagger}$) is a measure of the energy barrier that must be overcome by reacting molecules (Jencks, 1969). The $\Delta H^{o\ddagger}$ values were higher for desorption than for adsorption (Table 5.6), suggesting that the heat energy required to overcome the NH_4^+ desorption barrier was greater than that for NH_4^+ adsorption. This was also seen in the magnitude of the E_a and E_d values (Table 5.5). A comparison between ΔH^o and $\Delta H^{o\ddagger}$ is shown in Table 5.7. The $\Delta H_a^{o\ddagger}$ represents the change in heat energy needed for NH_4^+ to go from the solution phase to the solid phase, whereas $\Delta H_d^{o\ddagger}$ is the heat energy requirement for the reverse reaction. The difference in these two parameters represents ΔH^o (Table 5.7). The adsorption process is an exothermic process where heat is liberated, and the desorption process is an endothermic reaction where heat is adsorbed (Table 5.6). This concurs with the findings of Moreale and van Bladel (1979) who theorized that solute adsorption was clearly exothermic while desorption was often endothermic. However, variations in $\Delta H^{o\ddagger}$ with temperature are not the result of energy changes involved in making or breaking bonds, but rather are due to alterations in the heat-capacity behavior of the ions involved in the exchange reaction (Moore and Pearson, 1981). Because the overall ΔH^o of the reaction was negative (Table 5.5), NH_4^+ exchange on the zeolite mineral clinoptilolite is not an energy-consuming process.

Table 5.7. Comparison of Gibbs' theory and reaction-rate theory in the calculation of some thermodynamic parameters for NH_4^+ exchange on the natural zeolite clinoptilolite at four temperatures.

	Gibbs' theory	Reaction-rate theory	Gibbs' theory	Reaction-rate theory
Temperature	$\Delta G^o = -RT \ln k_a/k_d$	$\Delta G^o = \Delta G_a^{o\ddagger} - \Delta G_d^{o\ddagger}$	$\Delta H^o = E_a - E_d$	$\Delta H^o = \Delta H_a^{o\ddagger} - \Delta H_d^{o\ddagger}$
°C	J mol^{-1}		kJ mol^{-1}	
25	50.6	51.0		-3.34
35	153.8	154.0		-3.34
45	261.1	261.0		-3.34
55	393.6	393.0	-3.34	-3.34

Jencks (1969) noted that entropy of activation ($\Delta S^{o\ddagger}$) could be regarded as a measure of the width of the "saddle point of energy" over which reactant molecules must pass as activated complexes. The $\Delta S_a^{o\ddagger}$ values were smaller than $\Delta S_d^{o\ddagger}$ values (Table 5.6) suggesting that a more ordered system would be obtained with adsorption than with desorption. The smaller $\Delta S_a^{o\ddagger}$ values would be expected because there is an ionic exchange of predominantly Ca^{2+} and Mg^{2+} from the solid to the solution phase and movement of NH_4^+ from the solution to the solid phase, both of which decrease entropy due to an alteration of their hydrated radii. Again, we did not find values of $\Delta G^{o\ddagger}$, $\Delta H^{o\ddagger}$, and $\Delta S^{o\ddagger}$ for NH_4^+ exchange on natural zeolites reported in the literature for comparison.

CONCLUSIONS

The amount of NH_4^+ adsorbed by the zeolite increased with increasing temperature. All four tested models described the NH_4^+ adsorption process ($r^2 \geq 0.9151$), with the modified Freundlich and Elovich being slightly superior ($r^2 \geq 0.9878$). Both the k_a and k_d values as calculated by the modified Freundlich model increased with increasing temperature, indicating faster NH_4^+ exchange at higher temperatures as predicted from Bronsted's reaction rate theory. Changes in the rate constants with a 10 °C rise in temperature (Q_{10}) were slightly greater than 1 at the temperature range of 25 to 55 ^{0}C, suggesting that diffusion was the rate determining step for NH_4^+ exchange on the zeolite. The activation energy for desorption (E_d) was greater than that of adsorption (E_a), indicating a greater energy requirement for NH_4^+ desorption than for adsorption. The increasingly positive ΔG^o values obtained in this work implied that the driving force for the formation of an NH_4^+ charged zeolite from a predominantly Ca, Mg, and K zeolite was not favored, and that the latter ions became more preferred on the zeolite exchange sites as the temperature increased. The thermodynamic parameters calculated using Gibbs' theory compared very well with the pseudothermodynamic parameters derived from the reaction-rate theory, which indicated that thermodynamic parameters can be calculated using a kinetics approach.

CHAPTER 6

REDUCING NITROGEN LOSSES DURING COMPOSTING OF POULTRY MANURE USING NATURAL ZEOLITES, CLAY, COIR, AND CHEMICAL AMENDMENTS

ABSTRACT

Ammonia emissions during composting of poultry manure can be significant, representing increased environmental pollution and decreased fertilizer value of manure. The objectives of this study were to measure NH_3 volatilization losses during composting of poultry layer manure, and to evaluate the potential of different amendments to reduce NH_3 losses using a laboratory composting simulator. The poultry manure was treated with various amendments which included three natural zeolites, clay, coir, $CaCl_2$ (calcium chloride), $CaSO_4$ (calcium sulfate), $MgCl_2$ (magnesium chloride), $MgSO_4$ (magnesium sulfate), and $Al_2(SO_4)_3$ (alum). The manure was composted for 49 to 56 d. Ammonia volatilized from the manure was trapped in a 0.3M H_2SO_4 solution, which was titrated for NH_3 content. The composts were weighed and analyzed for moisture content, pH, electrical conductivity (EC), total C, and soluble and total N. The NH_3 volatilization loss for the unamended manures ranged from 47.1 to 62.5% of the total manure N. A layer of 60% zeolite placed on the surface of the manure reduced NH_3 losses by 44.3%, whereas 50% coir placed on the surface of the manure reduced NH_3 losses by 48.5%. The 25% alum treatment reduced NH_3 losses by 27.7%. Composting poultry manure with zeolites, coir, and alum produced composts with high NH_4^+ concentrations ranging from 15 to 55% of total N. The addition of 25% $CaCl_2$ to poultry manure decreased NH_3 volatilization but did not result in increased NH_4^+ or NO_3^- concentrations. The 60% zeolite Z1 and 50% coir -treated composts had total N concentrations of 17.04 and 31.03 g kg^{-1} respectively. The zeolite and coir amendments were proposed to be most suitable for reducing NH_3 losses during composting of poultry manure.

INTRODUCTION

Composting poultry manure produces a stabilized product that can be stored or spread on land with little or no obnoxious odor, pathogens, weed seeds, or fly breeding potential. Poultry manure composting results in a high potential for NH_3 volatilization because nitrogen concentrations in poultry waste are generally higher and C/N ratios lower than those of other livestock wastes. Nitrogen losses via NH_3 volatilization have been evaluated during composting of poultry manure. Hansen *et al.* (1989) reported N-losses of up to 33% of the initial total N during composting of poultry layer manure. In composting mixtures of fresh poultry layer manure and straw in rectangular reactors enclosed in hot-house sheds, Bonazzi *et al.* (1990) observed that 50 to 63% of the initial total N was lost, primarily via NH_3 volatilization. Hansen *et al.* (1990) found that N-losses could amount to 31% of the initial total N during composting of caged egg-layer poultry manure using reactor vessels. Mahimairaja *et al.* (1994) measured a 17% loss of N through NH_3 volatilization during composting of fresh chicken manure under aerobic conditions.

Loss of NH_3 during composting of poultry manure not only reduces the agronomic value of the end-product, but also contributes to pollution of the environment. ApSimon *et al.* (1987) indicated that atmospheric NH_3 pollution plays an important role in acid rain. They suggested that the dominant source of NH_3 in Europe was livestock wastes, with long-term trends showing a 50% increase in NH_3 emissions in Europe from 1950 to 1980. Ammonia raises the pH of rain water, which allows more SO_2 to dissolve in it forming ammonium sulfate. The ammonium ions can undergo nitrification in the soil, resulting in soil acidification (van Breemen *et al.*, 1982). This can result in decreased soil pH (pH 2.8 to 3.5) and high levels of dissolved aluminum in noncalcareous soils (van Breemen *et al.*, 1982, 1989). Ammonia volatilization can also contribute to eutrophication. Nitrogen deposited via wet fallout tripled in Denmark from 1955 to 1980 and corresponded to N losses from agriculture during this period (Schroder, 1985). The increased N in the fallout was correlated with increased NO_3^- content in Danish streams (Schroder, 1985). Thus, cost effective technologies which reduce NH_3 loss during composting of poultry manure would have positive economic and environmental benefits.

Most of the N (approximately 60 to 70%) excreted in poultry manure is in the form of uric acid and urea (Shuler *et al.*, 1979). The uric acid and urea are rapidly hydrolyzed to NH_3 and CO_2 by the enzymes urease and uricase if temperature, pH, and moisture are adequate for microbial activity (Bachrach, 1957;

Rouf and Lomprey, 1968; Siegel *et al*; 1975). The hydrolysis reactions result in elevated pH levels that facilitate NH_3 volatilization (Reynolds and Wolf, 1987). The N in poultry manure can be conserved by either inhibiting the hydrolysis of uric acid to NH_3 or by reducing the NH_3 volatilization.

Various organic chemicals such as formaldehyde and yucca saponin have been used to reduce uric acid hydrolysis in poultry manure (Carlile, 1984). These chemicals have been found to have a negative effect and render the manure unsuitable for composting. Ammonia volatilization can be reduced by temporary immobilization of NH_4^+ ions by composting poultry manure with carbon-rich organic waste materials (Mahimairaja *et al.*, 1994), and adsorption of NH_3 and/or NH_4^+ using adsorbents such as zeolite and peat (Witter and Kirchmann, 1989a). Inorganic chemicals that have been used to inhibit NH_3 volatilization during composting of poultry manure include pyrite (Bangar *et al.*, 1988), calcium and magnesium salts (Witter and Kirchmann, 1989b), sulfuric and phosphoric acids (Al-Kanani *et al.*, 1992), and alum and ferrous sulfate (Moore *et al.*, 1995).

Although a range of chemical amendments have been evaluated on NH_3 volatilization from manures, there is little information in the literature on the use of inert adsorbents to minimize NH_3 emission during composting of poultry manure. This information would be of practical importance for improving the efficiency of N utilization in poultry manure. The objectives of this study were (i) to quantify N losses through NH_3 volatilization during composting of poultry manure under aerobic conditions using a laboratory composting simulator, and (ii) to evaluate the effectiveness of different amendments in reducing N losses.

MATERIALS AND METHODS

Poultry Manure and Amendments

Poultry layer manure (7.3% moisture) used for this study was collected from a poultry layer farm in Abbotsford, British Columbia, Canada. This farm utilized fans to dry the manure in a deep pit manure collection area under the cages. The characteristics of the manure are given in Table 6.1. The amendments

Table 6.1. Characteristics of the poultry layer manure.

Characteristic[†]		SD[‡]
Moisture (g kg^{-1})	73.40	0.06
pH (H_2O) at 1:5	7.50	0.01
pH (KCl) at 1:5	7.33	0.02
EC (S m^{-1}) at 1:5	0.69	0.03
CEC (cmol kg^{-1})	50.60	1.04
NH_4^+-N (g kg^{-1})	3.42	0.11
NO_3^--N (g kg^{-1})	0.02	0.00
Total C (g kg^{-1})	389.80	2.52
Total N (g kg^{-1})	68.00	2.92
Total C/$N_{organic}$	5.73	0.25
Total P (g kg^{-1})	24.50	0.10
Total S (g kg^{-1})	4.97	0.06
Total Na (g kg^{-1})	3.11	0.01
Total K (g kg^{-1})	18.23	0.40
Total Ca (g kg^{-1})	86.93	1.50
Total Mg (g kg^{-1})	5.55	0.36
Total Fe (g kg^{-1})	0.99	0.10
Total Mn (g kg^{-1})	0.47	0.01
Total Cu (g kg^{-1})	0.06	0.00
Total Zn (g kg^{-1})	0.51	0.01
Total B (g kg^{-1})	0.02	0.00
Total Al (g kg^{-1})	1.89	0.19

[†] Characteristics are reported on an air dry basis.
[‡] Standard Deviation; n = 3.

used in this study can be grouped into (i) adsorbents, and (ii) chemical amendments. The adsorbents consisted of three natural zeolites Z1, Z2, AcZ1 (zeolite Z1 acidified to pH 5), clay, and coir pith. Coir is the name given to the fibrous material that constitutes the thick mesocarp (middle layer) of the coconut fruit (*Cocos nucifera* L.). This material is replacing peat moss as a potting mix in some countries (Handreck, 1993; Meerow, 1994). In a separate experiment to evaluate its NH_4^+ adsorption capability, the coir showed a high pH buffering capacity and affinity for NH_4^+ (Kithome *et al.*, 1997d), so we included it as an NH_3 adsorbent during composting of poultry manure. The zeolites and the clay consisted of clinoptilolite and montmorillonite, respectively as the dominant minerals. Characteristics of these adsorbents are provided in Table 6.2. The chemical amendments used for this study were $CaCl_2.2H_2O$

Table 6.2. Some selected characteristics of the adsorbent materials used to amend the poultry layer manure.

	Z1	AcZ1	Z2	Clay	Coir
Moisture (g kg^{-1})	45.00	-	27.00	56.00	83.30
pH (H_2O)	7.90	5.09	9.10	5.80	5.16
pH (KCl)	5.80	4.88	7.40	5.30	4.09
EC (S m^{-1})	0.17	5.14	0.04	0.10	0.04
Surface area (m^2 kg^{-1})	9.35×10^5	-	5.81×10^5	2.39×10^5	5.95×10^5
Total C (g kg^{-1})	0	-	0	30.00	230.10
Total N (g kg^{-1})	0.10	-	0.15	1.57	5.25
CEC (cmol kg^{-1})	92.80	41.90	100.00	46.00	77.60
SCD[†] (µmol m^{-2})	0.99	-	1.72	1.92	1.30
Exchangeable cations					
Na (cmol kg^{-1})	3.10	3.01	37.20	0.54	4.57
K (cmol kg^{-1})	10.00	6.91	11.50	1.02	5.11
Ca (cmol kg^{-1})	45.00	22.83	28.60	15.00	3.63
Mg (cmol kg^{-1})	7.80	3.50	2.43	10.90	4.11
Ammonium Adsorption Capacity					
NH_4^+-N[‡] (g kg^{-1})	14.00	-	11.60	4.80	7.30

[†] Surface charge density, calculated as CEC divided by the surface area.

[‡] Ammonium adsorption capacity was determined using uniform-surface Langmuir adsorption isotherms.

(calcium chloride), $CaSO_4.2H_2O$ (calcium sulfate), $MgCl_2.6H_2O$ (magnesium chloride), $MgSO_4.7H_2O$ (magnesium sulfate), and $Al_2(SO_4)_3.18H_2O$ (alum). Seventeen treatments were utilized in this study (Table 6.3).

Laboratory Composting Simulator

The laboratory composting simulator consisted of a waterbath with a platform that held twenty four 250-mL Erlenmeyer flasks. Poultry manure was placed in the flasks together with the appropriate chemical amendments. Water was added to increase the moisture content to 45%. The flasks were closed and the contents of the flasks mixed thoroughly using a high speed electric mixer. The adsorbents, unlike the chemical amendments, were applied as a layer on the surface of the poultry manure because a preliminary experiment showed that surface application was more effective in reducing NH_3 losses than mixing. The flasks were then clamped onto the waterbath platform. Each flask was provided with an air inlet and outlet tube. The air inlet tube provided a continuous stream of pre-moistened air to the poultry manure in the flask which ensured adequate oxygen for the micro-organisms and prevented drying of the manure. The air outlet tube was connected to a 100-mL Taylor tube containing 50 mL of 0.3M H_2SO_4. The air passed through these acid traps via a pasteur pipette which created small bubbles to capture the NH_3 in 0.3M H_2SO_4 by conversion to NH_4^+. A vacuum-pressure pump (Barnant Co., Barrington, IL) was used to provide a constant and continuous flow of 1.1 L of air min^{-1}, as measured using a Gilmont flow meter (Gilmont Instrument, Inc., Great Neck, NY). The following controlled temperature cycle was used to simulate temperatures in a compost pile: 1 day at 25 ^{0}C, 2 days at 35 ^{0}C, 3 days at 45 ^{0}C, 4 days at 55 ^{0}C, 3 days at 45 ^{0}C, 14 days at 35 ^{0}C, and 22 days at 25 ^{0}C. A preliminary experiment indicated that this temperature pattern coupled with the selected air-flow rate induced maximum loss of NH_3. The acid traps were sampled and replenished at measured time intervals. Water was added at regular intervals to maintain adequate moisture during composting. The NH_4^+ in the sulfuric acid was determined by steam distillation using a Kjeltec Auto 1030 Analyzer (Tecator Inc., Herndon, VA). Three separate laboratory composting experiments were conducted at different time periods. Each

Table 6.3. Effect of different treatments on some selected poultry layer manure characteristics at the end of composting period.

Treatment	Moisture (g kg^{-1})	Wt. loss[‡] (g kg^{-1})	pH$_{(H2O)}$	pH$_{(KCl)}$	EC (S m^{-1})	NH_4^+-N (g kg^{-1})	Total N (g kg^{-1})	Total C (g kg^{-1})	C/N$_{org}$[†]
				Experiment 1					
Control	51.2	444.5	7.80	7.44	0.85	0.67	26.21	294.1	11.52
40% Z_1	40.6	247.7	7.46	7.31	0.35	5.73	17.33	138.5	11.95
60% Z_1	34.4	151.0	7.90	7.55	0.24	8.99	17.04	76.4	9.50
40% AcZ_1	41.6	250.6	7.49	7.33	0.38	5.66	17.76	146.1	12.08
60% AcZ_1	34.5	145.8	7.92	7.60	0.24	9.15	16.67	75.8	10.10
10% $CaCl_2$	54.2	290.3	6.88	7.00	2.52	9.68	37.08	309.3	13.06
25% $CaCl_2$	200.6	126.5	6.68	6.79	3.51	4.05	67.13	265.2	6.29
25% Alum	50.2	360.8	6.62	6.45	2.03	10.12	51.20	238.0	9.47
LSD (0.05)	9.4	28.3	0.2	0.2	0.3	0.9	5.0	27.8	1.1
				Experiment 2					
Control	65.0	399.0	7.98	7.69	0.85	0.58	26.79	300.9	11.50
40% Z_2	56.6	247.7	7.61	7.26	0.35	2.36	15.84	131.8	9.78
60% Z_2	40.5	177.4	8.06	7.48	0.22	3.94	12.38	71.80	8.50
40% Clay	70.5	262.3	7.60	7.29	0.47	1.05	15.51	157.4	10.89
60% Clay	61.9	190.8	7.66	7.30	0.36	1.68	11.35	98.0	10.14
25% Coir	69.5	346.9	7.54	6.95	0.59	2.95	29.16	418.9	15.98
50% Coir	155.0	170.1	8.41	7.53	0.44	5.18	31.03	620.6	17.72
25% $MgSO_4$	106.0	339.9	7.86	7.82	1.81	0.78	29.46	257.4	12.08
LSD (0.05)	15.4	40.7	0.2	0.2	0.1	0.2	1.4	37.2	1.0
				Experiment 3					
Control	65.4	275.0	7.11	7.02	0.71	1.58	27.65	387.8	14.89
40% Clay	54.4	190.1	7.38	7.15	0.45	1.36	14.77	217.0	16.19
25% $CaCl_2$	321.0	80.0	6.43	6.51	0.33	3.06	62.37	301.1	6.57
25% $CaSO_4$	40.5	201.7	6.68	6.57	1.08	3.03	30.77	275.8	14.56
25% $MgCl_2$	335.0	122.2	7.11	7.21	2.71	4.59	68.05	317.6	7.06
25% $MgSO_4$	98.5	245.2	7.51	7.57	1.52	1.42	43.39	330.7	10.92
LSD (0.05)	17.9	20.1	0.2	0.2	0.3	0.5	6.1	59.1	1.6

[†] The C/N ratio was computed from the total C and organic N for the compost.

[‡] Organic matter loss per kg of initial composting material.

experiment consisted of a randomized complete block design with three replicates. There were eight treatments for experiments 1 and 2, and six treatments for experiment 3.

Experiment 1

The eight treatments consisted of the control (unamended poultry manure), 40 and 60% zeolite Z1, 40 and 60% acidified zeolite (AcZ1), 10 and 25% $CaCl_2.2H_2O$, and 25% $Al_2(SO_4)_3.18H_2O$. Forty grams of poultry manure were weighed for each of the flasks. All amendments were applied on a weight to weight basis. Acid traps were sampled and replenished after 3, 6, 8, 10, 12, 14, 16, 18, 20, 22, 25, 28, 31, 35, 40, 45, 50, and 56 days.

Experiment 2

The eight treatments included a control (unamended poultry manure), 40 and 60% zeolite Z2, 40 and 60% clay, 25 and 50% coir pith, and 25% $MgSO_4.7H_2O$. Thirty grams of poultry manure were weighed for each of the flasks. The acid traps were sampled and replenished after 1, 3, 5, 7, 9, 11, 14, 17, 20, 23, 26, 30, 34, 38, 42, 46, and 50 days.

Experiment 3

The six treatments included a control (unamended poultry manure), 40% clay, 25% $CaCl_2.2H_2O$, 25% $CaSO_4.2H_2O$, 25% $MgCl_2.6H_2O$, and 25% $MgSO_4.7H_2O$. Thirty grams of poultry manure were weighed for each of the flasks. The acid traps were sampled and replenished after 1, 3, 5, 7, 9, 11, 14, 17, 22, 25, 28, 31, 34, 37, 40, 43, 46, and 49 days.

Compost Characterization

After composting, the materials were weighed and homogenized. Subsamples were analyzed for moisture, pH (H_2O), pH (KCl), electrical conductivity (EC), extractable NH_4^+ and NO_3^-, total N, and total C. Moisture was determined by drying at 60 °C for 3 days. The pH was determined in 1:5 compost:H_2O or KCl suspension. Subsamples were extracted with deionized H_2O at a compost:H_2O ratio of 1:5 and EC determined in the water extract using an electrical conductivity meter. Exchangeable NH_4^+ and NO_3^- was determined after extracting subsamples with 2M KCl at a compost:KCl ratio of 1:10. Ammonium was determined using an automated continuous flow injection analyzer, whereas NO_3^- and NO_2^- were determined using the Cd reduction method (APHA, 1992). The NO_3^- and NO_2^- levels were very low (< 2% of the total inorganic N) and were therefore not reported. Total N was determined by distillation after using the salicylic acid modification of the Kjeldahl digestion to include NO_3^- (Walinga *et al.*, 1995). To avoid N losses during drying, the total N analysis was carried out using moist samples, and values corrected for water content. Total C was determined using a Leco carbon analyzer (Leco Corporation, St. Joseph, MI). Differences between treatment means were tested for significance using analysis of variance (SAS, 1990).

RESULTS AND DISCUSSION

Some selected characteristics of the amended poultry manure after a composting period ranging from 49 to 56 days are provided in Table 6.3. Organic matter loss during composting ranged from 80 to 444.5 g kg^{-1} (Table 6.3). The organic matter loss for the controls averaged 37% which is consistent with the normal range of 35 to 50% (Eghball *et al.*, 1997). The treatments that had a low organic matter reduction either composted partially or did not compost at all.

Total Nitrogen Losses via Ammonia Volatilization

Ammonia volatilization from the composting manure was initially high but decreased with time (Fig. 6.1). Cumulative NH_3 losses from the controls (unamended manure) in experiments 1, 2, and 3 were 42.5, 38.3, and 32.1 g N kg^{-1} of manure, respectively for the entire composting period. More than 50% of the NH_3 loss occurred in the first 3 to 6 days. Ammonia loss from the controls (unamended manure) was 14 to 29% of the initial total N after the first 3 days of composting and increased slowly to 47 to 62% after 25 days of composting, after which NH_3 losses were minimal (Fig.6.1). The high NH_3 losses measured in this study were due in part to the optimum environmental conditions for NH_3 volatilization (temperature evolution, adequate air-flow rate), high initial total N content, and low C/N ratio of the manure (Table 6.1). Hansen *et al.* (1989) measured N losses of up to 33% of the initial total N during aerobic composting of poultry layer manure. Kirchmann and Witter (1989) observed that up to 44% of the initial total N was

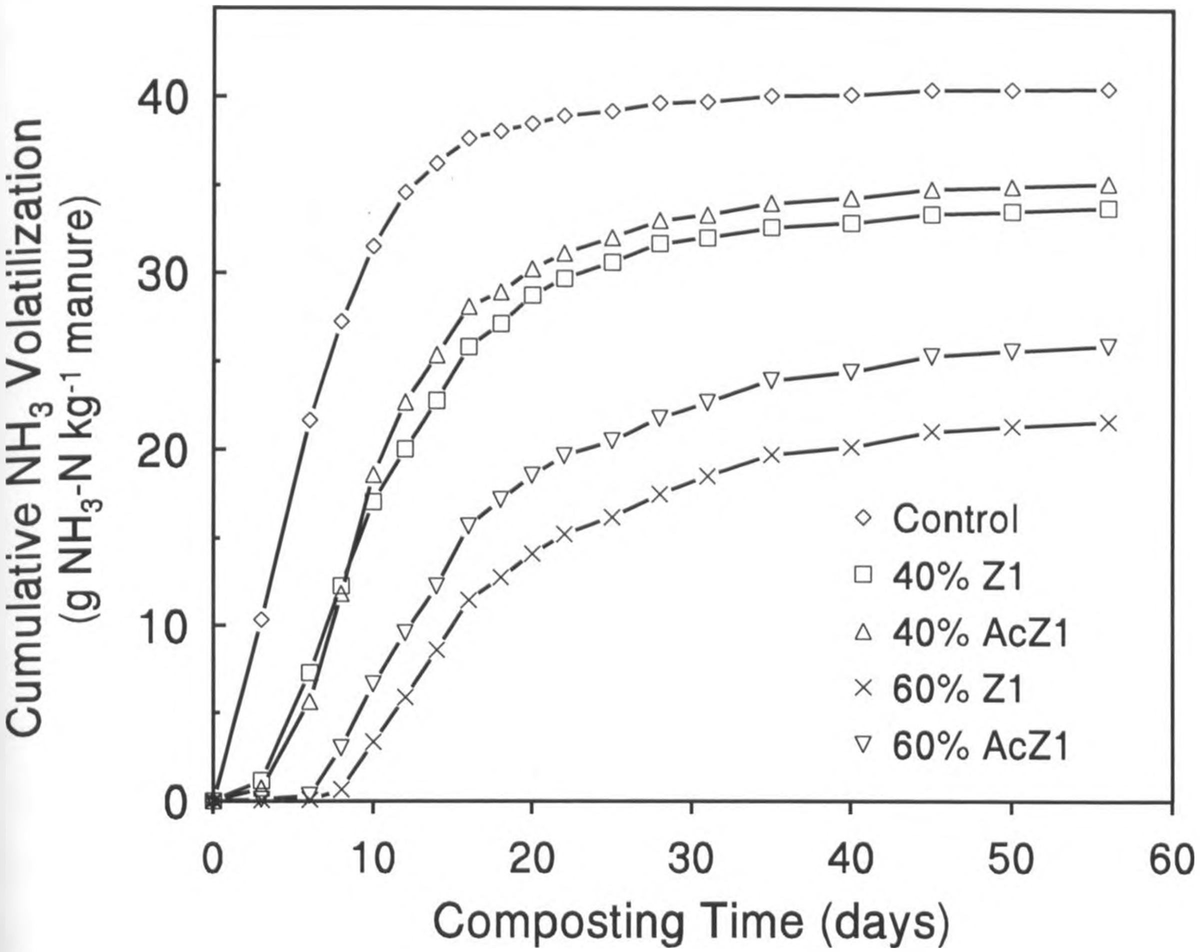


Figure 6.1. Cumulative NH_3 volatilization from poultry layer manure without amendment and amended with 40 and 60% of each of the zeolites Z1 and the acidified zeolite AcZ1 (Exp. 1), LSD (0.05) at Day 3, and 56 = 0.18 and 0.08, respectively.

lost through NH_3 volatilization during aerobic composting of fresh chicken manure. Recently, Mahimairaja *et al.* (1994) reported that 17% of the total manure N was lost through NH_3 volatilization during aerobic composting of fresh chicken manure.

Effect of Adsorbents on Ammonia Volatilization

A layer of zeolite Z1 placed on top of the poultry manure proved to be effective in adsorbing NH_3 during the composting process. A 44.3% reduction in NH_3 loss was recorded in the manure treated with 60% zeolite Z1 as compared to a 15.8% reduction in the 40% zeolite Z1 treated manure at the end of the 56 d composting period (Fig. 6.1; Table 6.4, Exp. 1). The 60% zeolite Z1 showed a high affinity for NH_3 in the first 6 d of composting, adsorbing almost all volatilized NH_3 (Fig. 6.2). However, after 12 d of composting, NH_3 emissions were higher from the 60% zeolite Z1 treatment than from the unamended manure (Fig. 6.2). The zeolite probably became fully saturated after 12 d of composting and started to release some of the NH_3 initially adsorbed. This may have been caused by the decreased NH_3 concentration of the effluent air from the compost passsing through the zeolite, resulting in the establishment of new equilibria between gaseous, soluble, and NH_3 sorbed as NH_4^+ on the zeolite. This is consistent with what we observed during kinetic studies using the same zeolite, where NH_4^+ adsorption decreased with decreasing initial NH_4^+ concentration (Kithome *et al.*, 1997b). At the end of the 56 d composting period, the difference between total NH_3 volatilized from the control and that from the 60% zeolite Z1 treatment was 18.8 g N kg^{-1} manure which is equivalent to 12.4 g N kg^{-1} zeolite or 88.4 cmol N kg^{-1} zeolite. This suggests full saturation of the zeolite sites responsible for cation exchange with NH_4^+, because the CEC of the zeolite was 93 cmol kg^{-1} (Table 6.2). This was in agreement with our estimation of the NH_4^+ empirical adsorption maximum for the zeolite which ranged from 69 to 99 cmol N kg^{1} at pH 4 to 7 (Kithome *et al.*, 1997a).

There was no difference in NH_3 adsorption between 40% zeolite Z1 acidified to pH 5 (AcZ1) and the 40% unacidified zeolite Z1. The 60% AcZ1 was less effective in adsorbing the volatilized NH_3 compared to the 60% Z1 (Fig. 6.1). This was expected because the CEC of the zeolite Z1 decreased from 92.8 to 41.9 cmol kg^{-1} after acidification (Table 6.2). The decrease in CEC of the zeolite following acidification is consistent with the observations of Curtin *et al.* (1996) that during soil acidification, titratable acidity

Table 6.4. Nitrogen mass balance calculated from the amounts of total N remaining and total NH_3-N volatilized at the end of composting period.

Treatment	Initial total N (g kg^{-1})	NH_3-N volatilization (g kg^{-1})	Final total N (g kg^{-1})	Unaccounted N loss (g kg^{-1})
		Experiment 1		
Control	68.00	42.49	26.21	-0.70
40% Z_1	68.07	35.77	28.89	3.41
60% Z_1	68.15	23.66	42.61	1.88
40% AcZ_1	68.07	37.15	29.60	1.32
60% AcZ_1	68.15	27.91	41.67	-1.43
10% $CaCl_2$	68.00	34.95	37.08	-4.03
25% $CaCl_2$	68.00	4.41	67.13	-3.54
25% Alum	68.00	30.72	51.20	-13.92
LSD (0.05)		2.83	2.36	
		Experiment 2		
Control	68.00	38.32	26.79	2.89
40% Z_2	68.10	40.60	26.40	1.10
60% Z_2	68.23	34.09	30.96	3.18
40% Clay	69.05	47.54	25.86	-4.35
60% Clay	70.36	42.66	28.38	-0.68
25% Coir	69.75	41.34	38.88	-10.47
50% Coir	73.25	19.73	62.06	-8.54
25% $MgSO_4$	68.00	40.82	29.46	-2.28
LSD (0.05)		4.08	2.85	
		Experiment 3		
Control	68.00	32.01	27.65	8.34
40% Clay	69.05	35.32	24.61	9.12
25% $CaCl_2$	68.00	2.38	62.37	3.25
25% $CaSO_4$	68.00	33.00	30.77	4.23
25% $MgCl_2$	68.00	9.03	68.05	-9.08
25% $MgSO_4$	68.00	23.30	43.39	1.31
LSD (0.05)		2.11	4.33	

increases and effective CEC decreases by an equivalent amount. Bernal and Lopez-Real (1993) postulated that acid pre-treatment of the zeolite could stimulate NH_4^+ adsorption by zeolites because of increased hydrogen ions (protons) on the exchange sites. Protonation of NH_3 would then occur on these acid exchange-sites prior to the actual ion-exchange process. In contrast, we found that acidification of the zeolite resulted in slightly lower NH_4^+ adsorption compared to the unacidified zeolite because of a

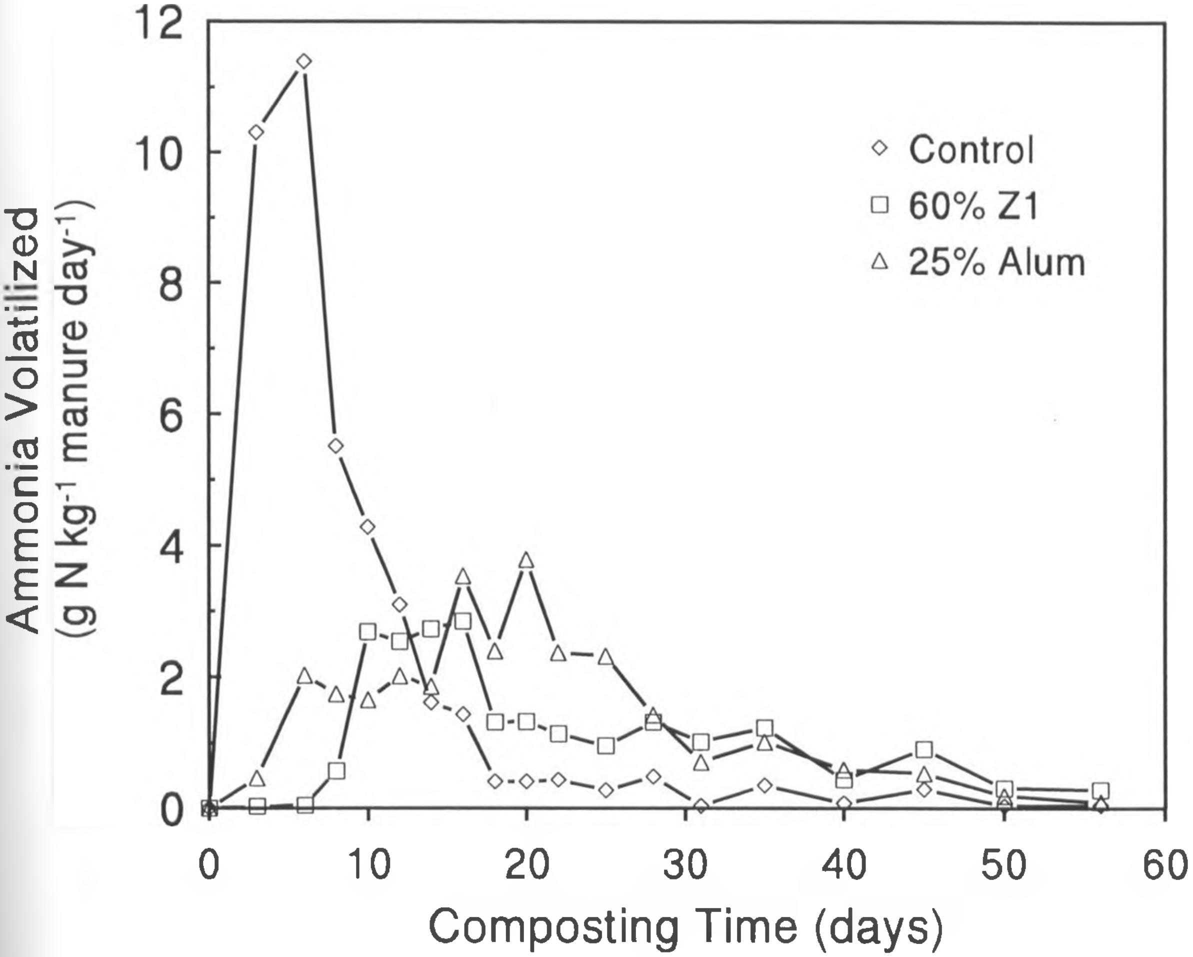


Figure 6.2. Ammonia losses as affected by a layer of 60% of the zeolite Z1 placed on the composting poultry layer manure, and 25% of alum mixed with poultry layer manure (Exp. 1), LSD (0.05) at Day 3, and 56 = 0.18 and 0.08, respectively.

decrease in CEC. We also observed that NH_4^+ adsorption by this zeolite decreased with decreasing pH (Kithome *et al.*, 1997a).

The 40% zeolite Z2 application increased NH_3 volatilization by 6%, whereas application of 60% of zeolite Z2 to the poultry manure reduced NH_3 emission by only 11% (Fig. 6.3a). The poor performance of this zeolite can be explained by its high pH of 9.1 (Table 6.2), which promoted increased NH_3 emission.

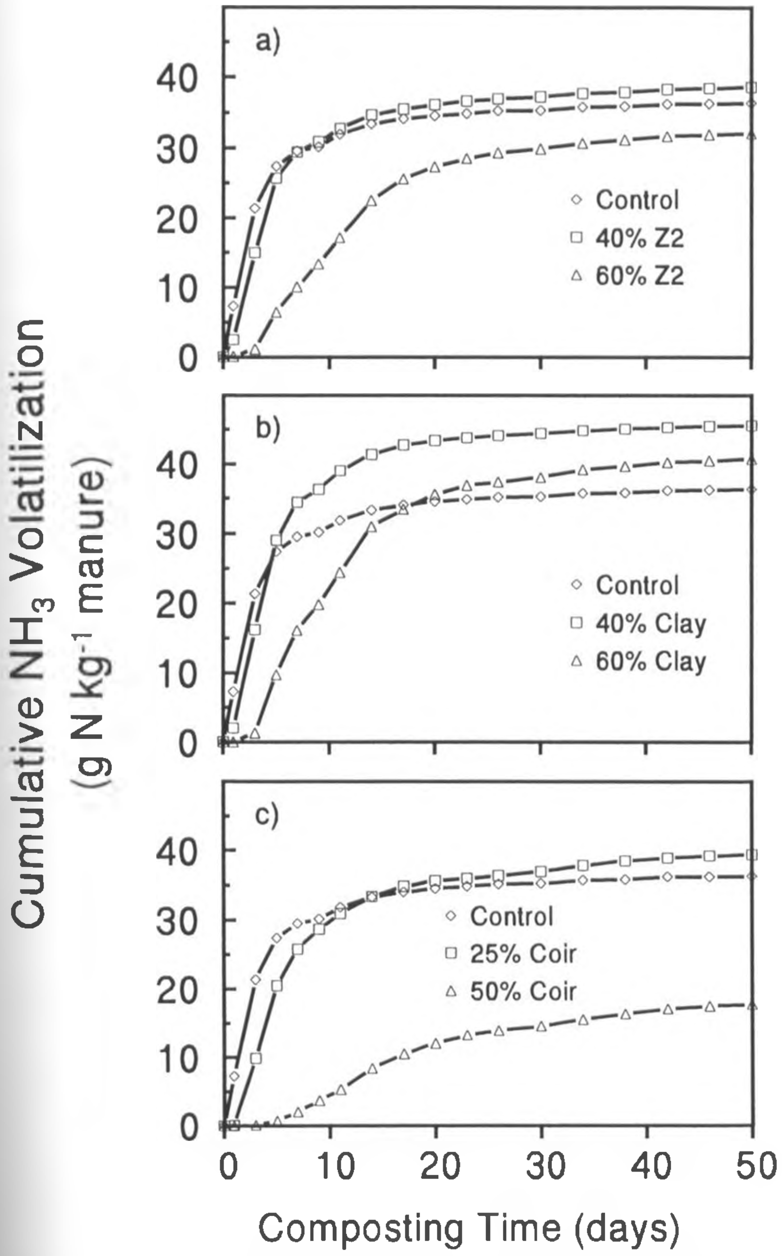


Figure 6.3. Cumulative NH_3 volatilization from poultry layer manure without amendment and amended with (a) 40 and 60% of the zeolite Z2, (b) 40 and 60% of the clay product, and (c) 25 and 50% of the coir (Exp. 2), LSD (0.05) at Day 3, and 49 = 1.03 and 0.05, respectively.

Ammonia emission from the 40% clay treatment was 24% greater than the control (Fig. 6.3b). The 60% clay treatment reduced NH_3 losses by 65% for the first 5 d of composting. Losses were higher than the control between 5 and 24 d, after which there were no significant losses of NH_3. This implies that the clay exchange-sites were saturated by day 5, then released adsorbed NH_4^+ as the NH_3 concentration of the air decreased.

The 25% coir treatment reduced NH_3 losses by 53% during the first 4 d (Fig. 6.3c). The 50% coir treatment adsorbed almost all NH_3 for the first 3 d, and continued to adsorb until 12 d. Thereafter, differences in NH_3 losses from both 50% coir-treated manure and the control were not significant. At the end of the 50 d composting period, the 50% coir had reduced NH_3 volatilization by 48.5% and had adsorbed 18 g N kg^{-1} coir as calculated from the differences in NH_3 loss. This amount of adsorbed N is high in relation to the CEC of the coir, and may include physically adsorbed NH_3 and/or NH_4^+ facilitated by the large surface area of the coir (Table 6.2). The mechanism by which the coir reduced NH_3 loss was not clear. Analysis of KCl extractable NH_4^+ (Table 6.3, Exp. 2) showed that 56% of the NH_3 adsorbed was recoverable as exchangeable NH_4^+. This indicates a possibility of NH_3 also being adsorbed as 'fixed' NH_3 by the coir, probably prior to adsorption onto sites of cation exchange. Nõmmik and Vahtras (1982) relying largely on earlier literature reviewed by Mortland and Walcott (1965) suggested that this 'fixed' NH_3 is formed from reactions with carbonyl, phenolic or enolic hydroxyls, or unsaturated carbon groupings leading to the formation of covalent compounds.

Effect of Chemical Amendments on Ammonia Volatilization

Application of 10 and 25% $CaCl_2$ to the poultry manure decreased NH_3 volatilization by 17.7 and 89.6%, respectively, compared to the controls (Table 6.4, Fig 6.4, Exp. 1). It appears that the 10% $CaCl_2$ reduced NH_3 emission primarily by decreasing pH, but the 25% $CaCl_2$ reduced NH_3 emission primarily by microbial inhibition due to high salt concentration (Allison, 1973). The organic matter loss was 290 and 127 g kg^{-1} for 10 and 25% $CaCl_2$ amended poultry manure, respectively, compared with 445 g kg^{-1} for the control (Table 6.3, Exp. 1). This suggested greater inhibition of microbial activity by addition of the 25%

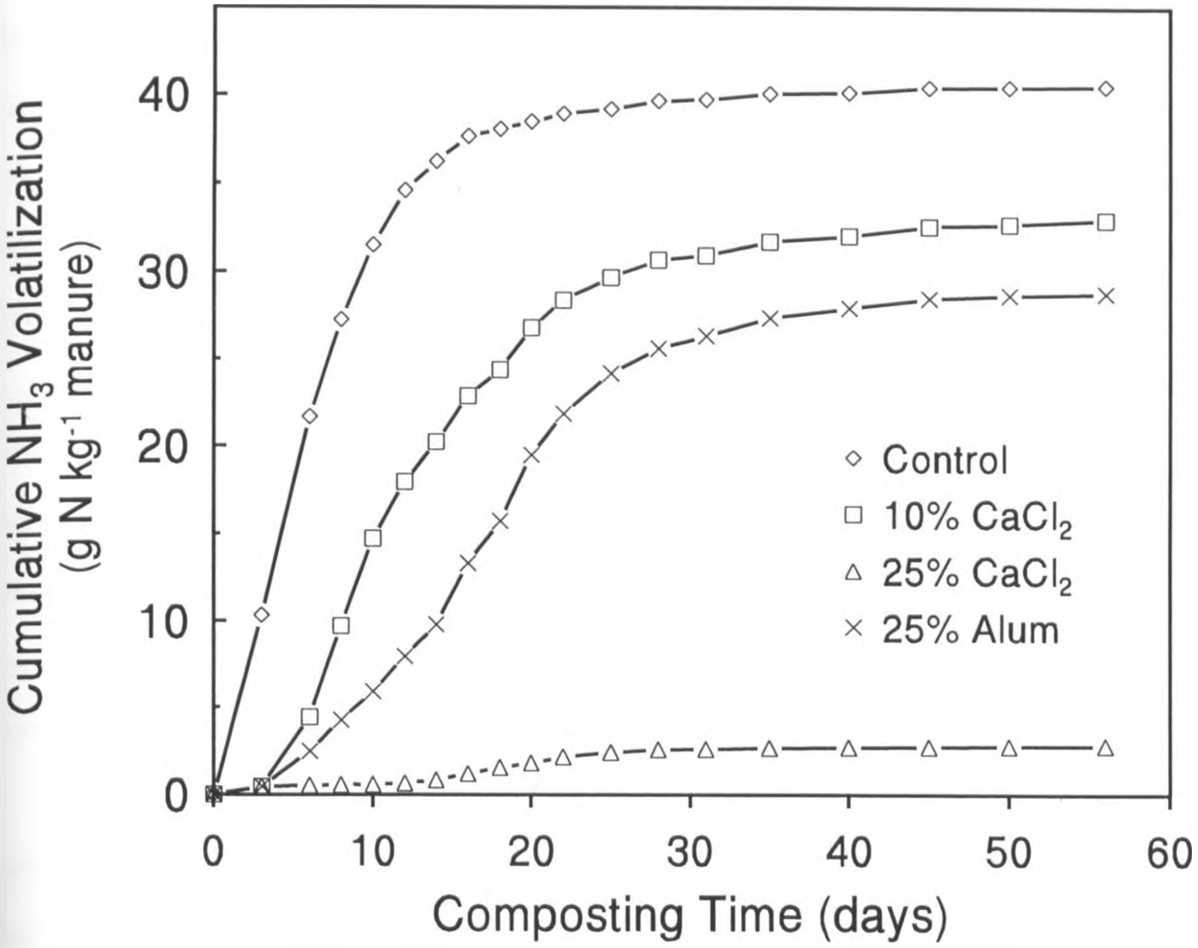


Figure 6.4. Cumulative NH_3 volatilization from poultry layer manure without amendment and amended with 10 and 25% $CaCl_2$, and 25% alum (Exp. 1), LSD (0.05) at Day 3, and 56 = 0.18 and 0.08, respectively.

$CaCl_2$ than by 10% $CaCl_2$. The 10% $CaCl_2$ amended poultry manure had an increased NH_4^+ concentration, compared to the uncomposted poultry manure, suggesting some decomposition of organic N. The 25% $CaCl_2$ amended manure, however, had a similar NH_4^+ concentration as the uncomposted poultry manure (Table 6.1; Table 6.3, Exp. 1). The lack of NH_4^+ accumulation and the small organic matter weight reduction suggests that microbial activity was inhibited in the 25% $CaCl_2$ treatment.

Molloy and Tunney (1983) made use of the acidic nature of $CaCl_2$ and $MgCl_2$ to reduce NH_3 losses during drying of cattle and pig slurry at 90°C, and reported up to 50% reduction in NH_3 loss. Witter (1991) reported that the addition of $CaCl_2$ to fresh chicken slurry decreased peak rates of NH_3 volatilization by 73% and total NH_3 losses by 37%. He attributed the reduction in NH_3 volatilization by $CaCl_2$ to a reaction mechanism first proposed by Egner (1932) and later advanced by Fenn *et al.* (1981). This hypothetical reaction mechanism assumes that the addition of soluble Ca to aerobically decomposing manure will result in the precipitation of CO_3^{2-} (formed as a result of urea hydrolysis) as $CaCO_3$, thereby reducing the pH.

There was an effect of cation (Ca^{2+} or Mg^{2+}) on NH_3 volatilization, but it was strongly interdependent on the type of anion. The 25% $CaCl_2$ treatment was more effective than either 25% $MgCl_2$, 25% $MgSO_4$, and 25% $CaSO_4$ treatments at reducing NH_3 losses over the entire composting period (Fig. 6.5). The $CaCl_2$ retained 21% more NH_3 than $MgCl_2$, whereas, 25% $CaSO_4$ did not conserve any NH_3 throughout the composting period, as was also reported by Termeer and Warman (1993) in an aerobic decomposition of manure amended with $CaSO_4$.

The type of anion (Cl^- or SO_4^{2-}) had a very significant effect on NH_3 volatilization. The Cl^- salts were more effective in conserving NH_3 than the SO_4^{2-} salts (Fig. 6.5). This was attributed to the toxic effect of the Cl^- ions on microbes. The manure amended with the Cl^- salts either composted partially or did not compost at all, as evidenced by the smaller organic matter loss compared to the control (Table 6.3). The greater NH_3 losses with SO_4^{2-} salts compared with Cl^- salts was also reported by Fenn *et al.* (1981), and Witter and Kirchmann (1989b).

Addition of 25% $Al_2(SO_4)_3$ (alum) to the poultry manure resulted in a 27.7% reduction of NH_3 losses (Table 6.4, Exp. 1). The alum-treated manure composted well as was evidenced by its physical and chemical characteristics. The alum reduced NH_3 emissions by 73% in the first 14 d but emissions increased during day 14 up to day 27, after which emissions were not significantly different from the control (Fig. 6.2, 6.4). The increased NH_3 emissions after 14 d were probably due to a decrease in the

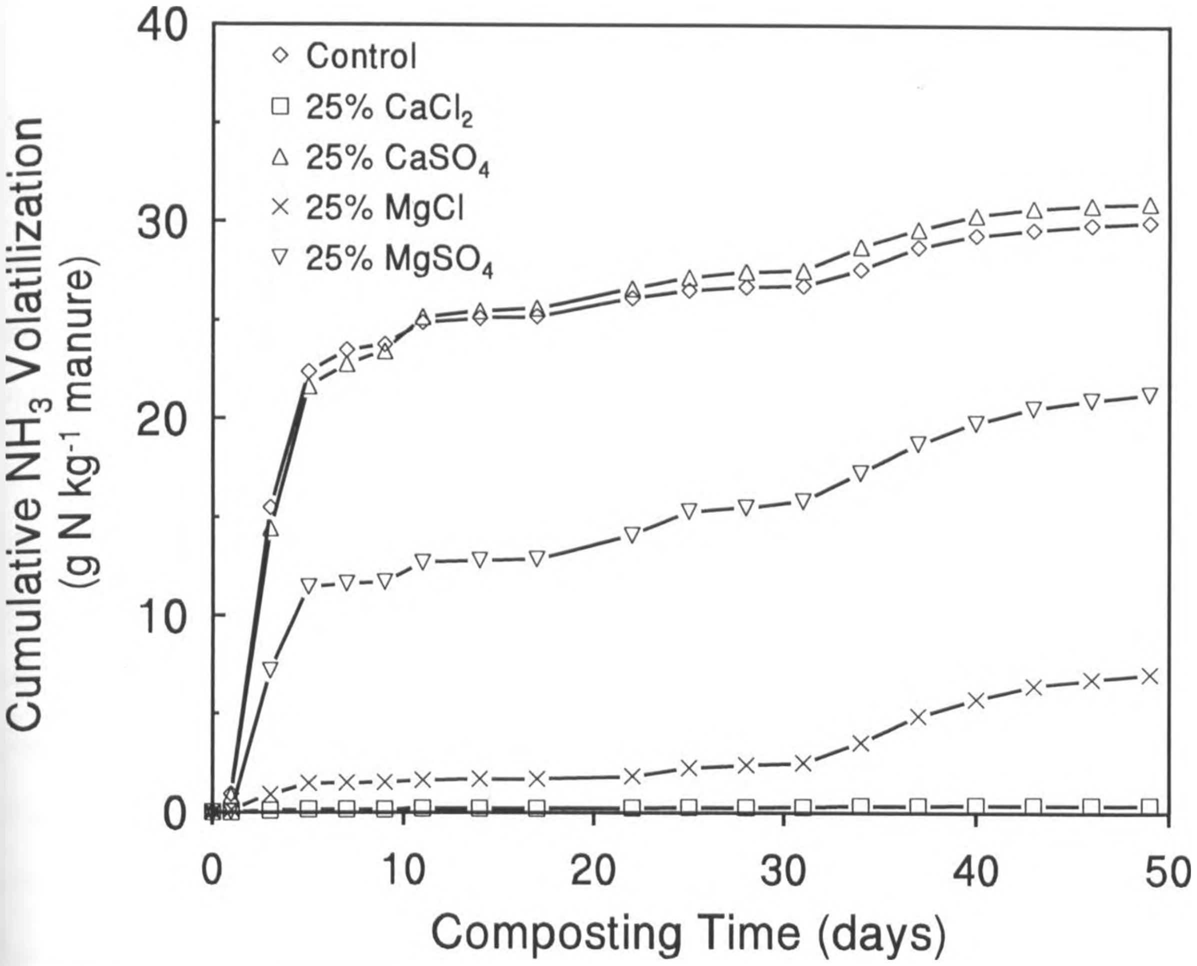


Figure 6.5. Cumulative NH_3 volatilization from poultry layer manure without amendment and amended with 25% of each of the $CaCl_2$, $CaSO_4$, $MgCl_2$, and $MgSO_4$ (Exp. 3), LSD (0.05) at Day 3, and 49 = 0.68 and 0.07, respectively.

hydrolysis of alum with time. Recently, Moore *et al.* (1995) reported that application of alum to poultry litter at 200 g kg^{-1} of poultry litter reduced NH_3 losses by 99% during composting. The mechanism by which alum reduces NH_3 losses involves its hydrolysis according to the following overall equation: $Al_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Al(OH)_3 + 3H_2SO_4$. The acid generated decreases NH_3 volatilization by reducing the pH.

Ammoniacal-N Contents in the Composts

The uncomposted poultry manure contained 5% (3.42 g N kg^{-1}) of total N in the form of NH_4^+, whereas at the end of 49 to 56 d of composting the NH_4^+ concentrations in the composts ranged from 6 to 55% of the total N (Tables 6.1 and 6.3). Less than 2% of the inorganic N was present as NO_3^- (data not shown). Nitrification during composting may have been minimal due to the presence of a high density of ammonifiers (Nodar *et al.*, 1990). Nitrification is affected by high concentration of NH_3 (Bramley and White, 1990).

The clay treatments did not adsorb significant amounts of NH_3, hence, had very low amounts of KCl extractable NH_4^+ compared to zeolite treatments (Table 6.3, Exp. 2). Addition of 40 and 60% of zeolite Z1 to the manure increased the proportion of NH_4^+ in the composts to 33.1 and 52.8% of the total N, respectively. Application of 40 and 60% of the acidified zeolite AcZ1 to the manure increased the proportion of exchangeable NH_4^+ in the composts to 31.9 and 54.9% of the total N, respectively. All of the NH_4^+ was recovered through extraction with 2M KCl. This is consistent with the results of a previous study (Kithome *et al.*, 1997c) on the thermodynamics of NH_4^+ exchange on the same zeolite, where more than 93% of the adsorbed NH_4^+ was recovered using 1M KCl as the extractant. The ability of the zeolites to release the adsorbed NH_4^+ attests to their potential use as fertilizers. However, because the NH_4^+ extraction was achieved using a much higher salt concentration than found in most soils, we would expect slower release kinetics in soils. In this case the zeolite may serve well as a controlled-release NH_4^+ fertilizer. With larger scale composting, 60% zeolite Z1 amended poultry manure composts generated using 224-L vessel reactors had similar characteristics as the one generated in this study, and showed high N use and agronomic efficiency as a controlled-release N fertilizer for the growth of ryegrass (*Lolium multiflorum*) in a greenhouse experiment (Kithome *et al.*, 1997f).

Although the 50% coir treatment adsorbed more NH_3 than all the other adsorbents (Table 6.4, Exp.

2), only 56% of the NH_4^+ was KCl extractable. This indicates that the rest of the adsorbed N was probably `fixed' and/or held strongly in a form that was not easily extractable with 2M KCl. Noren (1986) and Mathur *et al.* (1990) hypothesized that sphagnum peat moss could retain urea and other NH_3 producing compounds within its structures, rendering these compounds partially unavailable to chemical and/or biological hydrolysis. This type of NH_3 retention could be beneficial if coir is used as a controlled-release fertilizer where there would be a controlled release of NH_4^+ to the soil for plant uptake.

Poultry manure composted with alum had the highest NH_4^+ concentration of 10.1 g N kg^{-1} (Table 6.3, Exp. 1), which was attributed to its acidifying effect. Acidic compounds have previously been used to reduce NH_3 volatilization from animal manures and slurries. For example, Stevens *et al.* (1989) used 5M H_2SO_4 to reduce and virtually eliminate NH_3 volatilization from cow and pig slurries surface-applied to soil. However, their use has never become popular because of high cost, hazards associated with the acid, and their acidifying effect on the soil.

Total Nitrogen in the Composts

The total N contents of all the composts were lower than that of the uncomposted poultry manure. The 60% zeolite Z1 and 50% coir -treated composts had total N concentrations of 17.04 and 31.03 g kg^{-1} compost, respectively. The controls contained total N concentrations of 26.2 to 27.7 g kg^{-1} compost at the end of the study. Although N is conserved in the composting process with zeolites and coir, the N is diluted by the high amounts of these amendments in the final products, resulting in low N in the composts. However, addition of 60% zeolite Z1 and 50% coir to the poultry manure resulted in a considerably high plant available N in the composts, which would greatly increase their fertilizing value. The alum-treated composts had high total N and NH_4^+ concentrations (Table 6.3, Exp. 1). Environmental and any health risk consequences that may be associated with aluminum must be considered before applying the alum treated composts to agricultural land.

Nitrogen Mass Balance

Nitrogen mass balances were computed from the amounts of N initially present in the poultry manure treated with the various amendments before composting, NH_3 volatilized, and total N in the generated composts at the end of the experiments. The unaccounted N losses were significant with some of the treatments (Table 6.4). These differences were attributed to variability in NH_3 losses and compost N measurements.

CONCLUSIONS

Composting of poultry manure amended with zeolites and coir is an effective means of conserving the N which enhances the plant available N of the manure and reduces the potential for NH_3 to contribute to environmental pollution. Addition of 60% zeolite Z1 and 50% coir to the manure reduced NH_3 losses by 44.3 and 48.5%, respectively. Decreases in NH_3 volatilization resulted in higher soluble N in the zeolite and coir-treated composts, which enhanced their N fertilizing value. Addition of adsorbents diluted the conserved N, such that the composts had lower total N contents than the raw poultry litter or poultry manure composted without amendments. The alum was also effective in reducing NH_3 losses, and the resulting compost had a higher total N concentration than the control. Potential environmental and health risk consequences that may be associated with aluminum must, however, be considered before applying the alum-treated composts to agricultural land. Finally, as these composting experiments were carried out under controlled laboratory conditions, appropriate caution should be taken while extrapolating the results to a large scale composting process.

CHAPTER 7

THE EFFECT OF COMPOST FERTILIZATION ON YIELD AND NITROGEN UPTAKE BY ITALIAN RYEGRASS (*LOLIUM MULTIFLORUM*)

ABSTRACT

Composting poultry manure amended with the natural zeolite clinoptilolite shows promise in reducing NH_3 loss during composting and producing a controlled-release organic fertilizer. The objectives of this study were to determine the availability of the N in the poultry manure composted with the natural zeolite clinoptilolite to established Italian ryegrass (*Lolium multiflorum*) in a sand based media in the greenhouse; and evaluate the leaching of NH_4^+ and NO_3^- from the media following twice weekly watering. The treatments included uncomposted poultry manure (UM); poultry manure composted alone (MA); poultry manure composted with: 35% zeolite (35% ZM), 60% zeolite (60% ZM), and 25% $CaCl_2$ (CA), on a weight basis; vermicompost (VC); and Sustane (SU), a commercial composted poultry manure product blended with inorganic fertilizer. The treatments were applied at two rates; 250 and 500 mg of total N per pot, except SU which was applied at the high rate only. High compost application rate increased yield and N accumulation. The 60% ZM_H had the highest dry matter production, N accumulation and N use efficiency. Nitrogen leaching losses were low with all treatments except SU_H which had NH_4^+ and NO_3^- concentrations of up to 9 and 11mg N L^{-1}, respectively, in leachates. The role of the natural zeolite clinoptilolite in NH_4^+ retention and subsequent higher plant N recovery accounted for the major reduction in NH_4^+ and NO_3^- concentrations in leachates.

INTRODUCTION

Waste management in areas dominated by animal-based agriculture can be a major cause of non-point source pollution. In the province of British Columbia, Canada, most of the poultry production occurs on a small landbase overlying an unconfined aquifer. Poultry production has been identified as a source of high nitrate concentrations in the aquifer (Liebscher *et al.*, 1992). Alternatives to local land application of poultry manure are needed to reduce the likelihood of nonpoint source pollution of ground and surface waters by N.

Options that have been proposed include construction of facilities that enable poultry producers to store wastes until field crops are best able to handle the manure, transportation of the manure to other areas, feeding processed poultry manure to beef cattle, and composting with a view to producing a value-added product that can be exported from this small land base (Liebscher, 1992). Composting poultry manure to produce a value-added product has the advantage of producing a compost that can improve soil properties, and provide plant available nutrients, with little or no harmful effects to the plants and environment.

Although poultry manure is rich in the plant nutrient N (Bomke and Lavkulich, 1975), its fertilizer value is often reduced by the loss of N through NH_3 volatilization and denitrification during composting (Kirchmann, 1985). Brinton (1985), Del Zan *et al.* (1987), Paul and Beauchamp (1993), and Brinton and Seekins (1994) compared N availability from fertilizer, fresh manure, and composts for silage and grain corn production. In those experiments where there was a yield response to treatments, the compost treatment was always lower in total N uptake compared with mineral fertilizers.

Aerobic composting of poultry manure amended with the natural zeolite clinoptilolite has been found to be effective in conserving the N in the manure (Kithome *et al.*, 1997e). The NH_4^+ ions are tightly held in the channels and central cavities of the zeolite, protecting the N from various loss pathways such as denitrification and leaching. With subsequent release, the N could become available in closer synchrony with crop requirements. On coarse-textured soils with high percolation rates, more efficient N management would occur because the readily leachable N concentration is greatly reduced.

Although several studies have examined the agronomic value of poultry manure on its own (Adolph *et a*l., 1969; Kirchmann, 1985; Bitzer and Sims, 1988), there have been no reports examining the effect of soil fertilization with poultry manure composted with zeolites on yield and N uptake by crops. The objectives of this study were to determine the availability of the N in the poultry manure composted with the natural zeolite clinoptilolite to established Italian ryegrass (*Lolium multiflorum*) in a sand based media in the greenhouse; and evaluate the leaching of NH_4^+ and NO_3^- from the compost-amended media following twice weekly watering.

MATERIALS AND METHODS

Poultry Manure and Compost Materials

The poultry layer manure used for this study was collected from a poultry layer farm in Abbotsford, British Columbia, Canada. This farm utilized fans in deep pit manure collection area to dry the manure. Poultry manure without amendment (MA), poultry manure amended with: 35% natural zeolite clinoptilolite (35% ZM), 60% natural zeolite clinoptilolite (60% ZM), and 25% $CaCl_2.2H_2O$ (CA), on a weight basis, were composted for eight weeks in 224-L in-vessel reactors. Each reactor was partially submerged in a large insulated waterbath. The temperature of the waterbath was gradually increased from 25 to 55 °C and decreased slowly to 25 °C during the eight week composting period. The material was turned twice a week by rotating the reactors. The characteristics of the zeolite used to amend the poultry manure are found in Table 7.1.

The composts had a characteristic earthy smell which is produced by actinomycetes during the maturation phase of composts (De Bertoldi and Zucconi, 1980). Total inorganic N in the MA, 35% ZM, and 60% ZM increased to 58, 305, and 551 g N kg^{-1} of the total N, respectively compared with 47 g N kg^{-1} of the total N in the uncomposted manure (Table 7.2). The total P content of the composted waste also increased during composting (Table 7.2). Total N contents were lower with the zeolite-amended composts than with the control because of dilution by the large amount of zeolite used for amendment. The 25% $CaCl_2$ amended poultry manure (CA) did not compost. It had a characteristic foul smell similar to that of uncomposted manure, high total N of 59 g N kg^{-1} manure, and low inorganic N of 2 g N kg^{-1}manure (Table 7.2). We made similar observations with the same treatment in a previous experiment using a small scale composting simulator (Kithome *et al.*, 1997e). We attributed this to Cl^- toxicity on microorganisms.

A vermicompost (VC) was produced over a period of sixteen weeks in a stationary, nonheating windrow primarily via the feeding activities of the manure worms *Eisenia foetida* on household refuse (vegetable and food wastes). The vermicompost composted well as was evidenced by its uniform texture,

Table 7.1. Characteristics of the natural zeolite used to amend poultry layer manure.

Characteristic	
Moisture (g kg^{-1})	45.00
pH (H_2O) at 1:2	7.90
pH (KCl) at 1:2	5.80
EC (Sm^{-1}) at 1:2	0.17
Surface area (m^2 kg^{-1})	9.35×10^4
Total C (g kg^{-1})	0
Total N (g kg^{-1})	0.10
Total P (g kg^{-1})	0.23
Total S (g kg^{-1})	0.09
Total Fe (g kg^{-1})	8.47
Total Mn (g kg^{-1})	5.94
Total Cu (g kg^{-1})	0
Total Zn (g kg^{-1})	0.06
Total B (g kg^{-1})	0
Total Al (g kg^{-1})	38.87
CEC (cmol kg^{-1})	92.80
[a] SCD (µmol m^{-2})	0.99
Exchangeable Cations	
Na (cmol kg^{-1})	3.10
K (cmol kg^{-1})	10.00
Ca (cmol kg^{-1})	45.00
Mg (cmol kg^{-1})	7.80
Ammonium Adsorption Capacity	
[b] NH_4^+-N (g kg^{-1})	14.00

[a] Surface charge density, calculated as CEC divided by the surface area.

[b] Ammonium adsorption capacity was determined using uniform-surface Langmuir adsoprtion isotherms.

Table 7.2. Chemical properties of the poultry layer manure and composts used in the greenhouse plant growth experiment (all values are on a dry matter basis).

Characteristic	UM	MA	35% ZM	60% ZM	CA	VC	SU
Moisture (g kg^{-1})	73.43 (0.06)†	289.82 (14.12)	224.21 (9.38)	350.46 (4.40)	379.01 (5.47)	666.95 (10.04)	59.07 (0.78)
pH (H_2O) at 1:2	7.5 (0.02)	8.01 (0.01)	7.85 (0.03)	7.89 (0.02)	6.43 (0.01)	7.06 (0.02)	7.19 (0.12)
pH (KCl) at 1:2	7.33 (0.02)	7.95 (0.04)	7.77 (0.02)	7.66 (0.01)	6.46 (0.05)	6.53 (0.04)	7.50 (0.02)
EC (S m^{-1}) at 1:2	0.67 (0.03)	0.89 (0.01)	0.48 (0.03)	0.24 (0.08)	6.21 (0.16)	0.32 (0.01)	6.39 (0.32)
CEC (cmol kg^{-1})	50.60 (1.04)	62.87 (2.85)	109.33 (8.50)	117.20 (5.19)	49.98 (2.77)	60.18 (2.23)	29.13 (0.87)
NH_4^+-N (g kg^{-1})	3.17 (0.10)	1.19 (0.12)	5.64 (0.77)	6.40 (0.20)	1.99 (0.06)	0.07 (0.01)	17.67 (2.90)
NO_3^--N (g kg^{-1})	0.02 (0)	0.02 (0)	0.02 (0)	1.21 (0.03)	0 (0)	0.17 (0.01)	0.82 (0.03)
Total C (g kg^{-1})	389.83 (2.52)	256.60 (14.50)	130.17 (4.42)	59.70 (3.27)	285.83 (7.70)	188.29 (12.49)	185 (4.58)
Total N (g kg^{-1})	68.00 (2.92)	20.77 (0.47)	18.55 (0.1)	13.80 (0.72)	59.0 (2.53)	4.08 (0.36)	82.43 (0.09)
Total C/N$_{org}$	6.02 (0.26)	13.12 (0.79)	10.14 (0.94)	9.69 (0.69)	6.77 (0.30)	49.53 (7.37)	6.02 (0.19)
Total P (g kg^{-1})	24.50 (0.10)	39.37 (1.22)	20.10 (0.26)	10.90 (0.56)	12.23 (0.45)	1.97 (0.37)	14.63 (0.25)
Total S (g kg^{-1})	4.97 (0.06)	8.56 (0.14)	4.70 (0.1)	2.40 (0.53)	2.77 (0.06)	1.97 (0.40)	0.06 (0.00)
Total Na (g kg^{-1})	3.11 (0.01)	5.56 (0.13)	3.54 (0.19)	2.89 (0.13)	6.08 (0.20)	6.33 (0.94)	3.62 (0.14)
Total K (g kg^{-1})	18.23 (0.40)	31.83 (0.64)	22.17 (1.45)	19.30 (0.87)	9.73 (0.04)	12.00 (1.90)	62.32 (1.80)
Total Ca (g kg^{-1})	90.27 (6.02)	162.67 (6.81)	85.53 (0.51)	55.67 (3.45)	163.67 (2.08)	15.07 (2.70)	39.53 (1.41)
Total Mg (g kg^{-1})	5.55 (0.36)	9.46 (0.12)	8.31 (0.10)	7.53 (0.47)	2.74 (0.06)	4.14 (0.80)	5.4 (0.22)
Total Fe (g kg^{-1})	0.99 (0.10)	12.77 (1.18)	7.67 (0.58)	6.67 (0.58)	4.23 (0.45)	8.67 (2.08)	27.5 (0.82)
Total Mn (g kg^{-1})	0.47 (0.01)	0.84 (0.02)	0.59 (0.01)	0.48 (0.03)	0.26 (0.01)	0.29 (0.05)	0.50 (0.01)
Total Cu (g kg^{-1})	0.06 (0)	0.12 (0)	0.07 (0)	0.03 (0)	0.03 (0)	0.03 (0.01)	0.17 (0.01)
Total Zn (g kg^{-1})	0.51 (0.01)	1.00 (0.03)	0.54 (0.01)	0.29 (0.02)	0.28 (0)	0.10 (0.02)	0.36 (0.01)
Total B (g kg^{-1})	0.02 (0)	0.04 (0)	0.02 (0)	0.01 (0)	0.02 (0)	0.02 (0)	0.01 (0.00)
Total Al (g kg^{-1})	1.89 (0.19)	4.10 (0.65)	17.63 (0.98)	26.27 (1.17)	1.30 (0.09)	16.83 (2.83)	1.42 (0.17)

† Sample standard deviation in parentheses; n = 3.

and dark humus-like, fluffy material. The source-separated organics used to feed the worms were virtually not recognizable, as they had completely been transformed to humus-like materials by the feeding activities of the manure worms. However, this compost had very low nutrient concentrations (Table 7.2).

Sustane (SU) (Sustane Corporation, Canon Falls, MI) a commercially available organic based fertilizer with a $N:P_2O_5:K_2O$ content of 10:10:10 was also included for comparison.

Greenhouse Experiment

A greenhouse experiment was conducted from July through November 1996. The growing medium consisted of clean, silica sand less than 1 mm in diameter. Plastic pots (top diameter = 0.155 m, volume 3.0 L) were filled with 2.5 kg of the sand medium. The inside of the containers was lined with a spun bonded polyester fabric barrier to avoid sand losses through the drainage holes. Twelve Italian ryegrass (*Lolium multiflorum*) seeds were planted in each pot. All the seeds germinated after 4 d. The seedlings were watered twice a week with 300 mL of a nutrient solution containing 0.5 g of the $N:P_2O_5:K_2O$ fertilizer 20:20:20 per liter. In addition to N, P, and K, the fertilizer also contained 0.1, 0.05, 0.05, 0.05, 0.02, and 0.0005% of the micronutrients Fe, Mn, Cu, Zn, B, and Mo, respectively, in a chelated form. The minimum EDTA content was 1%. After 4 weeks, the plants were trimmed to a height of 0.025 m from the sand surface and allowed to grow again. After 3 weeks of re-growth, the plants were thinned to 7 uniform plants and trimmed to a height of 0.025 m from the sand surface. At this time, the sand was thoroughly leached with deionized water to wash out any remaining nutrient solution.

In order to compare the treatments on a N equal basis, we weighed 7.36, 24.08, 26.96, 36.22, 8.47, 122.62, and 5.00 g of UM, MA, 35% ZM, 60% ZM, CA, VC, and SU, respectively per pot, to yield a high N rate (H) of 500 mg N per pot or 500 kg ha^{-1}. Half the amounts were weighed for a low N rate (L) of 250 mg N per pot or 250 kg ha^{-1}, except for SU which was applied at the high rate only. The manure and composts were evenly distributed (topdressed) over the sand surface. Although the treatments were evaluated on an equal N basis, the different amounts of material weighed created a disparity in the micro- and other macro-nutrients among treatments. This may have had an effect on plant growth, and N uptake, but this was not evaluated. The pots were arranged on a greenhouse bench in a completely randomized design with 4 replicates per treatment. The temperature in the greenhouse was maintained at approximately 25 °C, under natural lighting conditions. All pots were irrigated with 500 mL of deionized water twice a week. Leachate from each container was captured in plastic saucer trays. To avoid contamination of the leachate with the medium, the bottom of the container was placed on top of a smaller, inverted container placed in the middle of the saucer tray. Leachate volume was determined 30 min after irrigation and a 10-mL sample was retained for analysis. The samples were then analyzed for NH_4^+ and NO_3^-, or frozen for later analysis. Ammonium was determined using an automated continuous flow injection analyzer, whereas NO_3^- and NO_2^- were determined using the cadmium reduction method (APHA, 1992).

The ryegrass was harvested four times at three week intervals. Each harvest consisted of cuttings made at 0.025 m above the sand surface. Fresh plant tissue was dried at 60 °C for 72 h, weighed for yield determination, and ground in a Wiley stainless steel micromill to pass a 1-mm screen. The grass root biomass was sampled and estimated, because it represented an additional source of labile N. The roots were carefully extracted from the sand and from the fabric lining inside the pot. The roots were washed, dried at 60 °C for 72 h, weighed, and ground in a Wiley stainless steel micromill to pass a 1-mm screen. The harvested material and the roots were analyzed for total N using a Leco nitrogen analyzer (Leco Corporation, St. Joseph, MI). Differences between treatment means were tested for significance using analysis of variance (SAS, 1990)

Models

We evaluated N use efficiency using two quantitative relationships. The first calculation defined as nitrogen use efficiency (NUE), or apparent nitrogen recovery, relates N accumulation by the crop to the amount applied to soil (Harmsen, 1984):

$$NUE = (N_{fc} - N_{uc}) / N_T \qquad [1]$$

where N_{fc} is the N accumulation by the above ground dry matter for the four harvests of the fertilized crop;

N_{uc} is the N accumulation by an unfertilized crop; and N_T is the total N applied to soil. Because we used clean silica sand as the growth medium, we did not include unfertilized crop. The parameter N_{uc} was therefore zero.

The second calculation defined as physiological efficiency (PE) relates yield to total plant N accumulation (Harmsen, 1984):

$$PE = Y_{dw} / N_{acc} \qquad [2]$$

where Y_{dw} is the dry weight yield, and N_{acc} is the total plant N accumulation.

RESULTS AND DISCUSSION

Crop Response and N Accumulation

Both compost type and rate significantly affected ryegrass yields and N uptake, however, compost rate varied with compost type. The data for above-ground dry matter production, roots, total biomass, and N accumulation are provided in Tables 7.3 and 7.4 for both the high (H) and low (L) rates.

Cumulative above ground dry weight yields for the four harvests were greatest in the 60% ZM_H, 35% ZM_H, SU_H, 60% ZM_L, and MA_H treatments (Table 7.3). Application of vermicompost resulted in the lowest dry matter yields for both high and low rates compared to all the other treatments (Table 7.3). This may have been due to the low levels of nutrients in this compost (Table 7.2). Also, the high C/N ratio of this compost (Table 2) may have caused N immobilization, a possible factor in the yield depression.

The use of UM, regardless of the rate, resulted in a significantly lower cumulative above ground dry matter, root, and total biomass production for all the four harvests compared to the MA treatment (Table 7.3). This was probably due to the fact that higher amounts of MA were used because of its lower total N content compared to the UM, which may have resulted in higher amounts of micro- and other macro-nutrients being applied in the MA treatment than UM treatment. The decreased yields in the UM treatment may also be attributed to toxic concentrations of NH_3, NO_2^-, soluble salts, and/or soluble phenolic compounds emanating from the manure as it decomposes. Weil *et al.* (1979) found NH_3 concentrations as great as 800 mg kg^{-1} soil and NO_2^- concentrations exceeding 60 mg kg^{-1}, levels which were toxic to corn,

Table 7.3. Above ground dry matter yield from four harvests, and root dry weight, for the ryegrass as influenced by different compost and poultry layer manure applications.

	Dry weight (g per pot)						
Treatment	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Total	Roots	TBM[†]
UM_H	1.94 c[‡]	0.98 e	0.49 ef	0.34 fg	3.75 fg	3.53 cd	7.28 efg
UM_L	1.88 c	0.88 e	0.42 f	0.23 g	3.41 g	2.79 cde	6.20 g
MA_H	2.05 c	1.99 bc	1.11 c	0.60 bc	5.74 cd	4.82 b	10.57 b
MA_L	2.50 abc	1.34 d	0.73 d	0.45 cdef	5.02 de	3.67 bc	8.69 cde
35% ZM_H	2.12 bc	2.60 a	1.42 b	0.72 b	6.86 b	2.84 cde	9.70 bc
35% ZM_L	2.00 c	1.73 c	0.75 d	0.37 efg	4.85 e	3.07 cde	7.92 def
60% ZM_H	2.16 bc	2.52 a	1.72 a	1.40 a	7.80 a	6.11 a	13.91 a
60% ZM_L	2.04 c	2.04 b	1.11 c	0.70 b	5.89 c	2.96 cde	8.85 cde
CA_H	2.43 abc	1.36 d	0.66 de	0.41 def	4.86 e	2.73 cde	7.59 defg
CA_L	2.14 bc	1.01 e	0.37 f	0.34 fg	3.84 fg	3.51 cd	7.37 efg
VC_H	2.92 a	0.90 e	0.38 f	0.38 efg	4.58 ef	1.94 e	6.52 fg
VC_L	1.90 c	0.96 e	0.48 f	0.50 cde	3.84 fg	2.36 de	6.20 g
SU_H	2.69 ab	2.18 b	1.08 c	0.55 cd	6.50 bc	2.65 cde	9.15 bcd
LSD (0.05)	0.64	0.30	0.19	0.15	0.83	1.23	1.66

[†] Total biomass weight.

[‡] Means with different letters in the same column indicate significant differences at $p < 0.05$. Values in parentheses represent the standard deviation; n = 4.

shortly following application of up to 110 Mg ha^{-1} poultry manure. Paul *et al.* (1994) reported high soluble phenolic compound concentrations in stored manure compared with fresh or composted manure. Such compounds are thought to be phytotoxic to young plants or to inhibit seedling germination (Edwards and Daniel, 1992; Gupta *et al.*, 1997). The low dry matter yields and total biomass production in the CA treatment (Table 7.3) could also be explained similarly as for the UM treatment, although the high EC (Table 7.2) may also have contributed to yield depression.

Table 7.4. Total N content of the above ground dry matter in different harvests and roots of ryegrass as influenced by different compost and poultry layer manure applications.

	N (mg per pot)						
Treatment	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Total	Roots	TBM[†]
UM_H	83.45 cde[‡]	30.56 gh	14.97 e	7.90 fg	136.88 fg	13.78 e	150.66 f
UM_L	78.80 de	26.24 g	12.50 e	5.62 g	123.16 g	14.78 de	137.94 f
MA_H	83.50 cde	63.12 de	35.45 c	15.22 cd	197.29 cd	30.20 b	227.49 cd
MA_L	98.37 bcde	40.98 fg	21.63 d	11.19 def	172.17 def	25.08 bc	197.25 de
35% ZM_H	106.58 bcd	96.32 b	49.22 b	19.04 bc	271.16 b	19.39 cde	290.55 b
35% ZM_L	95.58 bcde	55.92 e	22.56 d	9.85 efg	183.91 de	13.23 e	197.14 de
60% ZM_H	111.62 bc	109.54 a	75.42 a	41.32 a	337.90 a	45.19 a	383.09 a
60% ZM_L	91.01 cde	73.64 d	39.68 c	19.76 b	224.09 c	19.89 cde	243.98 c
CA_H	122.87 b	42.15 f	21.84 d	9.99 efg	196.85 cd	17.50 de	214.35 cd
CA_L	91.84 bcde	30.68 gh	11.81 e	8.40 fg	142.73 fg	15.78 de	158.51 ef
VC_H	109.53 bcd	25.14 h	11.35 e	10.18 ef	156.20 efg	13.35 e	169.55 ef
VC_L	73.96 e	27.62 g	14.96 e	13.55 de	130.09 g	16.27 de	146.36 f
SU_H	158.73 a	84.77 c	38.83 c	15.15 cd	297.48 b	21.60 cd	319.08 b
LSD (0.05)	31.79	10.96	6.04	4.43	36.24	7.20	39.62

[†] Total biomass N.

[‡] Means with different letters in the same column indicate significant differences at $p < 0.05$. Values in parentheses represent the standard deviation; n = 4.

Crop N accumulation was correlated with the above ground dry matter yield ($r^2 = 0.94$). The root yield of all treatments was also correlated with N accumulation in roots ($r^2 = 0.76$), as was the relationship between yield and root N concentration ($r^2 = 0.78$).

Ryegrass yield and N uptake correlated with the inorganic N content of the composts before application. The total inorganic N added in the composts correlated much better with N uptake by the above ground dry matter yield in the first harvest and cumulative harvests ($r^2 = 0.93$ and 0.87, respectively), and dry matter yield for the first harvest and cumulative harvests ($r^2 = 0.87$ and 0.78, respectively) than did the amount of total N added (no correlation for both N uptake and dry matter yield was found). The amount of inorganic N added has been found to be a suitable predictor of the availability of N in manures and composts in the application year (Paul and Beauchamp, 1993). The C/N ratio was not significantly correlated with dry matter yield or N uptake. Failure of the C/N ratio to predict N availability or crop yield response to organic materials or composts added to soils has been reported previously (Allison *et al.*, 1963; Sabey *et al.*, 1975; Brinton and Seekins, 1994).

Nitrogen Use Efficiency

The NUE was correlated with the inorganic N in the composts ($r^2 = 0.96$). The generally high NUE with the composts containing zeolite reflected the increased inorganic N contents of the composts (Table 7.5). Total N for the cumulative above ground dry matter yield of the ryegrass was generally high in the zeolite amended compost treatments, for both rates (Table 7.4), which was attributed to the initial high inorganic N content of the composts at the time of application (Table 7.2). Similar observations were made by Huang and Petrovic (1992) who reported enhanced N uptake by bentgrass in zeolite amended sand regardless of N level used. The zeolite used in our study was found to adsorb 12.4 g NH_3-N kg^{-1} zeolite during composting of the same poultry layer manure using a laboratory composting simulator (Kithome *et al.*, 1997e). This is equivalent to 88.4 cmol kg^{-1} zeolite expressed as NH_4^+-N, indicating possible full saturation of the zeolite sites responsible for cation exchange with NH_4^+, because the CEC of the zeolite was 93 cmol kg^{-1} (Table 7.1). This was in agreement with our previous estimation of the NH_4^+ empirical adsorption maximum for this zeolite which ranged from 69 to 99 cmol N kg^1 at the pH range 4 to 7 (Kithome *et al.*, 1997a). The high NUE computed for the 60% ZM_H treatment was not surprising because the process of NH_4^+ adsorption by the zeolite was also shown to be reversible (Kithome *et al.*, 1997b), implying that the zeolite had the potential to release the adsorbed NH_4^+ after application, making it available for plant uptake. Though not quantified, ryegrass visual quality closely paralleled shoot growth and high root density. Similar observations were made by Lewis (1981) who reported a positive growth response in radishes (*Raphanus sativus* L.) using NH_4^+-exchanged clinoptilolite as a slow release fertilizer. Following some preliminary experiments with zeolite use in vegetable production, Johnson *et al.*

Table 7.5. Calculated values for nitrogen use efficiency (NUE) and physiological efficiency (PE) by ryegrass (*Lolium multiflorum*) in response to different compost and manure treatments.

Treatment	NUE	PE
UM_H	0.27	27.40
UM_L	0.25	27.69
MA_H	0.39	29.09
MA_L	0.34	29.16
35% ZM_H	0.54	25.30
35% ZM_L	0.37	26.37
60% ZM_H	0.68	23.08
60% ZM_L	0.45	26.28
CA_H	0.39	24.69
CA_L	0.29	26.90
VC_H	0.26	35.21
VC_L	0.31	24.58
SU_H	0.59	21.85

(1983) reported that zeolites had a potential to be used as an adsorbent of NH_4^+ in composts, and as a slow release fertilizer.

It is interesting to note that the yield and crop N use efficiency in the pots that received SU_H treatment were inferior to that of the 60% ZM_H treatment. This occurred despite the higher inorganic N content of the SU_H compost compared to that of the 60% ZM_H (Table 7.2). This is because much of the soluble N in the SU_H compost was leached during irrigation and therefore, not available for plant uptake. The MA treatment surpassed the UM and CA treatments in every evaluation method for both rates. The crop in the pots supplied with the MA treatment had a higher yield and produced greater yield per unit of total plant dry matter and per unit of total N accumulated than the crop in the pots that received the UM and CA treatments (Table 7.5).

Although the VC_H treatment had the highest PE than all the other treatments, it had a low NUE (Table 7.5), suggesting that parameters other than the inorganic N content may have contributed to the high PE. This may be a very important characteristic of vermicomposts. They may have plant growth regulation qualities (Buchanan and Gliessman, 1990).

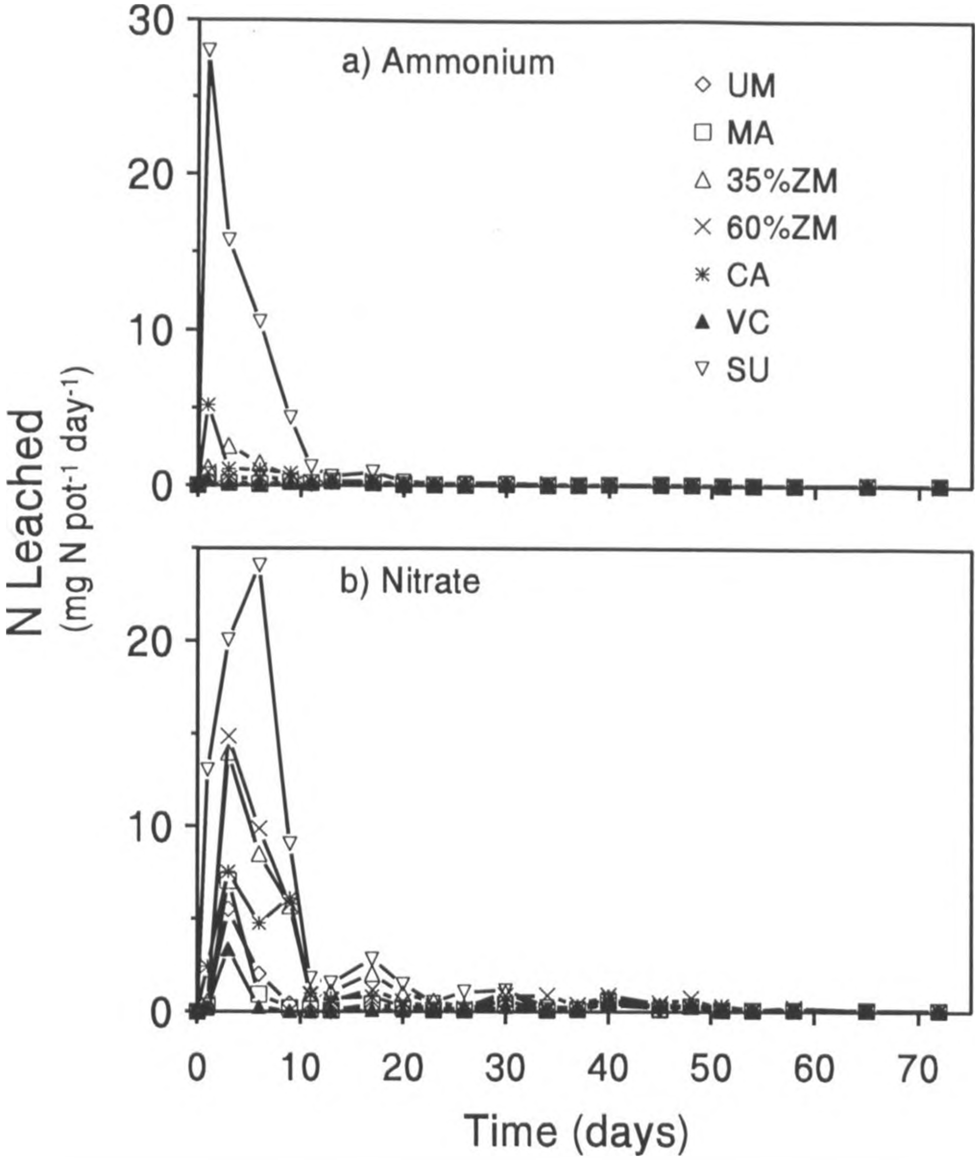
Nitrogen Leaching

The quantities of NH_4^+ and NO_3^- leached following each application of 500 mL (equivalent to 2.6 cm of rainfall) of water from seven compost and manure amended soils are shown in Fig. 7.1 for the high rate. The elution curves for the low rate treatments followed a similar pattern and are therefore not shown. The cumulative NH_4^+ recovered in 21 leachate fractions accounted for 0.4, 0.5, 1.4, 0.8, 1.9, 0.4, and 10.0% of the total N applied as UM_H, MA_H, 35% ZM_H, 60% ZM_H, CA_H, VC_H, and SU_H, respectively (Table 7.6). The concentrations of NH_4^+ in the individual leachate fractions were less than 11.1 mg N L^{-1} for all the treatments except SU_H. The concentration of NH_4^+ in leachate from the pots amended with SU_H peaked at 59 mg N L^{-1} in the first leachate and then decreased gradually to 0.5 mg N L^{-1} within 23 d after which there were no significant amounts of NH_4^+ leached (Fig. 7.1a). The high amounts of NH_4^+ leached from this treatment were attributed to high soluble inorganic N blended with the compost to enhance its fertilizer value. Concentrations of NH_4^+ were substantially lower in the leachate from soil amended with UM, MA, VC, and 60% ZM treatments than the other treatments, for both rates (Fig. 7.1a). The 60% ZM_H treatment significantly decreased the amount of NH_4^+ in the leachates compared to SU_H treatment (Table 7.6), despite its high initial NH_4^+ concentration (Table 7.2). This was attributed to the high retention of NH_4^+ in the channels and central cavities of the zeolite clinoptilolite. The higher zeolite concentration reduced N loss more than the low zeolite concentration, at both rates (Table 7.6). MacKown and Tucker (1985) observed that clinoptilolite zeolite effectively enhanced the retention of NH_4^+ resulting in less NH_4^+ leaching from a coarse-textured soil. The cumulative NH_4^+ leached from the 35% ZM_H and 60% ZM_H was total plant dry matter and per unit of total N accumulated than the crop in the pots that received the UM and CA treatments (Table 7.5).

Although the VC_H treatment had the highest PE than all the other treatments, it had a low NUE (Table 7.5), suggesting that parameters other than the inorganic N content may have contributed to the high PE. This may be a very important characteristic of vermicomposts. They may have plant growth regulation qualities (Buchanan and Gliessman, 1990).

Nitrogen Leaching

The quantities of NH_4^+ and NO_3^- leached following each application of 500 mL (equivalent to 2.6 cm of rainfall) of water from seven compost and manure amended soils are shown in Fig. 7.1 for the high rate. The elution curves for the low rate treatments followed a similar pattern and are therefore not shown. The cumulative NH_4^+ recovered in 21 leachate fractions accounted for 0.4, 0.5, 1.4, 0.8, 1.9, 0.4, and 10.0% of the total N applied as UM_H, MA_H, 35% ZM_H, 60% ZM_H, CA_H, VC_H, and SU_H, respectively (Table 7.6). The concentrations of NH_4^+ in the individual leachate fractions were less than 11.1 mg N L^{-1} for all the treatments except SU_H. The concentration of NH_4^+ in leachate from the pots amended with SU_H peaked at 59 mg N L^{-1} in the first leachate and then decreased gradually to 0.5 mg N L^{-1} within 23 d after which there were no significant amounts of NH_4^+ leached (Fig. 7.1a). The high amounts of NH_4^+ leached from this treatment were attributed to high soluble inorganic N blended with the compost to enhance its fertilizer value. Concentrations of NH_4^+ were substantially lower in the leachate from soil amended with UM, MA, VC, and 60% ZM treatments than the other treatments, for both rates (Fig. 7.1a). The 60% ZM_H treatment significantly decreased the amount of NH_4^+ in the leachates compared to SU_H treatment (Table 7.6), despite its high initial NH_4^+ concentration (Table 7.2). This was attributed to the high retention of NH_4^+ in the channels and central cavities of the zeolite clinoptilolite. The higher zeolite concentration reduced N loss more than the low zeolite concentration, at both rates (Table 7.6). MacKown and Tucker (1985) observed that clinoptilolite zeolite effectively enhanced the retention of NH_4^+ resulting in less NH_4^+ leaching from a coarse-textured soil. The cumulative NH_4^+ leached from the 35% ZM_H and 60% ZM_H was



ure 7.1. (a) Ammonium and (b) Nitrate elution curves for sand amended with uncomposted poultry layer manure (UM); poultry layer manure composted alone (MA); poultry layer manure composted with: 35% zeolite (35% ZM), 60% zeolite (60% ZM), and 25% $CaCl_2.2H_2O$ (CA), on a weight basis; vermicompost (VC); and Sustane (SU); LSD (0.05) at Day 3, and 72 = 2.87 and 0.02, respectively.

d 0.8%, respectively; and from the 35% ZM_L and 60% ZM_L was 0.77 and 0.47% of the total ost N applied, respectively. At present, there are no critical limits with respect to concentration of for drinking water standard. The proposed maximum contamination level (MCL) for groundwater is

Table 7.6. Total amounts of NH_4^+, NO_3^-, and inorganic N ($NH_4^+ + NO_3^-$) in 21 leachates from different compost and manure treatments used to amend sand for growth of ryegrass.

	Inorganic N (mg N pot^{-1})		
Treatment	NH_4^+	NO_3^-	Total
UM_H	2.10 d[†]	10.33 d	12.43 d
UM_L	2.19 d	10.79 cd	12.97 d
MA_H	2.26 d	11.48 cd	13.75 d
MA_L	2.12 d	5.81 cd	7.93 d
35% ZM_H	7.05 bc	37.67 b	44.72 b
35% ZM_L	3.84 cd	20.21 cd	24.05 cd
60% ZM_H	3.82 cd	39.13 b	42.95 b
60% ZM_L	2.36 d	14.37 cd	16.73 d
CA_H	9.62 b	26.64 bc	36.26 bc
CA_L	4.74 cd	11.58 cd	16.32 d
VC_H	1.99 d	6.11 d	8.10 d
VC_L	1.82 d	4.98 d	6.79 d
SU_H	62.56 a	78.66 a	141.21 a
LSD (0.05)	4.57	15.87	17.62

[†] Means with different letters in the same column indicate significant differences at $p < 0.05$. Values in parentheses represent the standard deviation; n = 4.

1.5 mg NH_4^+-N L^{-1} (Li *et al.*, 1997). Ammonium in groundwater may eventually transform into NO_3^- and result in elevated NO_3^- levels. All treatments had cumulative NH_4^+ concentrations of less than 1.2 mg N L^{-1} in leachates, with the exception of SU_H which had 8.7 mg N L^{-1}.

The NO_3^- concentrations were higher in the leachate fractions compared to NH_4^+ concentrations for all the treatments, as was also reported by Morton *et al.* (1988). These observations indicate that nitrification did occur in the containers. Furthermore, long residence times of NH_4^+ due to the irrigation intervals used, conceivably allowed for near complete conversion to NO_3^-. Niemiera (1985) found that NH_4^+ in a bark medium underwent a complete conversion to NO_3^- over 2 d. The total NO_3^- recovered in 21 leachate fractions was significantly different among all the treatments and accounted for 2.1, 2.3, 7.5, 7.8, 5.3, 1.2, and 15.7% of the total N applied as UM_H, MA_H, 35% ZM_H, 60% ZM_H, CA_H, VC_H, and SU_H, respectively (Table 7.6). The peak elution of NO_3^- was highest for SU_H, followed by 60% ZM_H and 35% ZM_H, and occurred in the third day after treatment application for all the treatments except SU_H which occurred in the sixth day (Fig. 7.1b). After the peak elution the NO_3^- levels in the leachates gradually decreased, and after 48 d the concentrations of NO_3^- in the leachates from the various treatments were not significantly different ($p < 0.05$). The period for which the NO_3^- concentrations in the various leachate fractions were high coincided with a rapid decrease in NH_4^+ concentrations in the leachate (Fig. 7.1a). This demonstrates the effect of nitrification. Following this lag phase, the release of NO_3^- for an extended period of time was evident. The pattern of NO_3^- in the leachate could be attributed to differential behavior of the composts and manure with respect to their ability to release nutrients. Recently, Paramasivan and Alva (1997) reported similar observations while evaluating nitrogen recovery from controlled-release fertilizers under intermittent leaching and dry cycles. The NO_3^- so released is at risk of contaminating groundwaters. Except for the SU_H treatment which had a cumulative NO_3^- concentration of 10.9 mg N L^{-1}, non of the other treatments exceeded the federal drinking water standard of 10 mg N L^{-1}. We suggest that leaching of NO_3^- should be considered when fertilizers and compost application rates and frequencies are determined, particularly on coarse-textured soils with high infiltration rates, as found in sand-based golf courses, which are vulnerable to nutrient leaching. The total inorganic N (NH_4^+ + NO_3^-) leached throughout the experimental period were 2.5, 2.8, 8.9, 8.6, 7.3, 2.7, and 22.6% of the total N applied as UM_H, MA_H, 35% ZM_H, 60% ZM_H, CA_H, VC_H, and SU_H, respectively (Table 7.6). Besides water contamination, high losses of N via leaching could seriously reduce the available N content and hence, the agronomic value of composts. Although the total recovery of N from SU_H was very close to that from 60% ZM_H (Table 7.4), the leaching losses of various forms of N were significantly greater for the former compared with the latter product (Table 7.6). Therefore, the longevity of N release in the soil was much greater for 60% ZM_H than for SU_H, which attests to the potential use of poultry manure composted with zeolite as controlled-release fertilizer.

CONCLUSIONS

Nitrogen accumulation and N use efficiency by ryegrass was largely affected by the source and amount of N supplied by the composts. High compost application rate increased yield and N accumulation. The 60% ZM_H had the highest dry matter production, N accumulation and N use efficiency. Nitrogen leaching losses were low in all the treatments except SU_H which had NH_4^+ and NO_3^- concentrations of up to 9 and 11mg N L^{-1} in leachates, which were above the 1.5 mg N L^{-1} maximum contamination level and 10 mg N L^{-1} federal drinking water safety standards for NH_4^+ and NO_3^-, respectively. We suggest that leaching of both NH_4^+ and NO_3^- be considered when compost and fertilization application rates and frequencies are determined, particularly on coarse-textured soils vulnerable to nutrient leaching. Composted poultry manure provided plant available N, however, the rate of mineralization may not have been rapid enough to provide all of the N requirements of plants during their rapid growth period. Although uncomposted poultry manure had high total N, phytotoxic compounds in the manure may have inhibited optimal plant growth. From the standpoint of fertilizer management and water quality, composting of poultry manure amended with the natural zeolite clinoptilolite can widen the range of NH_4^+ rates used without jeopardizing water quality through excessive N leaching.

CHAPTER 8

GENERAL CONCLUSIONS

It was observed in this study that cation exchange capacity (CEC) and purity of zeolites with respect to mineralogy and constituent ions, influences their affinity and adsorptive capacity for NH_4^+. Some of the samples tested either had a very low CEC, and/or contained little or no zeolite minerals. This was reflected in their lower NH_4^+ adsorption capacity. The amount of NH_4^+ adsorbed by the zeolite increased as pH and initial NH_4^+ concentration increased. From the one-surface Langmuir isotherm, the NH_4^+ adsorption capacity (X_m) of the zeolite increased linearly with pH ($r^2 = 0.994$), and was estimated to be 9660 mg N kg^{-1} at pH 4, 11220 mg N kg^{-1} at pH 5, 12720 mg N kg^{-1} at pH 6, and 13830 mg N kg^{-1} at pH 7. The adsorption of higher amounts of NH_4^+ with increasing pH and initial NH_4^+ concentration is an important characteristic of the zeolite that can be beneficial to minimizing N-losses via NH_3 volatilization during composting of poultry manure.

The kinetics of NH_4^+ adsorption and desorption by the zeolite indicated that pH and initial NH_4^+ concentration were significant factors influencing the rate of exchange and amount of NH_4^+ sorbed with time. Increasing the initial NH_4^+ concentration resulted in decreased NH_4^+ exchange rates, whereas an increase in pH resulted in faster sorption and in greater amounts of NH_4^+ being sorbed. Conformity of data to the Elovich model and the excellent fit obtained for the heterogeneous diffusion model suggested that the rates of NH_4^+ exchange were governed by a heterogeneous diffusion process. The adsorption (k_a) and desorption (k_d) rate constants, as calculated using the modified Freundlich model, increased with increasing temperature, indicating faster NH_4^+ exchange at high temperatures. This is particularly significant because temperatures during composting range from 30 to 70°C and NH_3 emissions are enhanced at high temperatures. The activation energy (E_d) for the desorption process was greater than for the adsorption (E_a) process, which indicated that the energy needed to desorb NH_4^+ was greater than the energy needed for adsorption. This was probably due to strong adsorption of NH_4^+ in the internal channels and central cavities of the zeolite. This is an important property if the NH_4^+-zeolite is to be used as a controlled-release fertilizer. Release of NH_4^+ may be slower because a significant amount of energy is required for desorption. For the zeolite to be effective in increasing N use efficiency it must be able to trap large amounts of NH_4^+, and release this N slowly over the growing season when applied to soil. Rapid release of the adsorbed NH_4^+ would increase the potential for N loss when applied to soil, and too slow a rate of release would limit the short-term benefits to the crop. Although the amount of NH_4^+ adsorbed increased with increasing temperature, the zeolite exhibited preference for the ions already adsorbed at the exchange complex (Ca^{2+}, Mg^{2+}, and K^+). The overall Ca^{2+} and Mg^{2+} preference may possibly be attributed to strong adsorption due to their double charge, whereas K^+ has been observed to be selectively bound by zeolites compared to NH_4^+. This explains why NH_3 and/or NH_4^+ adsorption by zeolites decreases with time during composting. The zeolite exchange complex becomes saturated with the favored cations which are increasingly preferred as the temperature increases. In such situations large amounts of the zeolite are required to adsorb significant amounts of NH_4^+, as was observed in this study.

Evaluation of the potential of natural zeolite, coir, clay, and chemical amendments to reduce NH_3 losses during composting of poultry manure showed that composting of poultry manure amended with the natural zeolite clinoptilolite is an effective means of conserving the N which not only enhances the plant available N of the manure, but also reduces the potential for NH_3 to contribute to environmental pollution. Addition of 60% zeolite (on a weight basis) to the manure reduced NH_3 losses by 44.3%. Decreases in NH_3 volatilization resulted in high soluble N in the zeolite-treated composts. The N in the 60% zeolite-treated compost was available to the Italian ryegrass (*Lolium multiflorum*), as indicated by the much higher dry matter production, N accumulation, and all measures of N use efficiency examined, compared to the other composts tested. Evaluation of N release from the composts following twice weekly watering showed that N leaching losses were very low in the zeolite-treated composts. Leaching of NH_4^+ and NO_3^- should be considered when compost application rates and frequencies are determined, particularly on coarse-textured soils vulnerable to nutrient leaching. The role of zeolite in NH_4^+ retention and subsequent higher plant N recovery appeared to account for the major reduction in NH_4^+ and NO_3^- concentrations in leachates. Results of the greenhouse experiment indicated that poultry manure composted alone does provide plant available N, but the rate of mineralization may not be rapid enough to provide all of the N requirements of plants during their rapid growth period. Although uncomposted poultry manure provided N for the ryegrass growth, phytotoxic compounds may have inhibited optimal plant growth.

From the standpoint of fertilizer management and water quality, composting of poultry manure amended with the natural zeolite clinoptilolite can widen the range of NH_4^+ rates used without jeopardizing water quality through excessive NH_4^+ and NO_3^- leaching.

Economic Considerations

The study showed that relatively high rates of the zeolite clinoptilolite (60% on a weight basis) were needed to significantly retain NH_4^+ during composting of poultry manure. For practical purposes, use of such a large amount of zeolite may not be economical. Even if this zeolite could be applied for about $ 100 Mg^{-1}, the cost for 18.3 $Mg\ ha^{-1}$ used for this study would be prohibitive unless the amendment was effective for a long time. Also, composting can be a labor intensive and costly process. Livestock producers are unlikely to implement costly practices unless they are induced to do so for example, via economic incentives or regulation. While regulation appears to be currently the preferred choice of decision makers, there appear to be incentives and means to avoid compliance. This is not meant to suggest that livestock producers are not concerned about their impact on others, only that the costs they incur are often borne solely by those producers or might be perceived as a threat to their farm enterprise. In addition, the Agricultural Waste Control regulation might be viewed as a shift in property rights from the livestock producers to urbanites who are encroaching upon farmland as a result of rapidly increasing populations in the region.

It has been indicated by various researchers and consulting agencies (e.g., Ference Weicker & Co., 1994) that no alternatives to current livestock waste disposal practices are preferred by the farmers on economic grounds. Composting manure with a view to producing a value-added product (e.g., poultry manure composted with zeolite) may be the best option for disposal of livestock wastes, at least from an environmental point of view, but may not be economical. For composting to be considered a viable alternative to current livestock waste disposal practices in the Lower Fraser Valley, one needs to justify composting on the basis of its social costs and benefits. The social costs of composting are equal to the production, handling, transportation and marketing costs of compost. The social benefits include the revenue obtained from the sales of compost plus benefits to water users of improvements in water quality brought about as a result of composting.

Whether composting is economically viable from a private perspective depends on the availability of markets for the product and the price that is received (i.e., revenue). It was estimated that, in the Fraser Valley, approximately 27.8 million litres of product could be sold by 1997 (Ference Weicker & Co., 1989), but such a market is inadequate to absorb all of the compost that could be generated from livestock wastes in the Valley; nor is it known whether this amount of compost from livestock wastes could be sold in the valley if competing sources of compost are available. Competing sources include backyard and municipal composting facilities. Other markets include the states of Washington and Oregon in the USA. However, as an import into the USA, manure is treated the same as sewage sludge and requires an import permit as a controlled material; a permit is required for each shipment, with restrictions on packaging and pathogen control having to be met (Ference Weicker & Co., 1989). Because of these regulations, it is unlikely that much compost will be sold across the border. Further, exported compost will need to compete with that produced in the USA, which is also moving toward the construction of more compost facilities. Alberta has been considered another market for composted material, but the size of that market is limited and transportation costs are likely to pose an obstacle to economic viability. Also, as composting of livestock wastes, household wastes and other wastes in both Canada and the USA becomes more popular, especially at the municipal level, the supply of bulk compost will increase, thereby reducing price. While prices for bagged compost will be high, costs are also increased and market saturation continues to be a problem.

Composting could be economically viable for some private composters if they are able to charge tipping fees that cover losses in the production and sale of the compost. However, tipping fees can only be charged if livestock producers are required by law to dispose of their manure in a manner that makes this a competitive alternative to other methods of disposal, and on-farm composting is more expensive for the individual than transporting manure to a regional facility and paying tipping fees. Although tipping fees may make composting profitable from a private perspective, this does not also mean it is economically efficient from the standpoint of society. Tipping fees simply constitute a redistribution of income against the livestock producer, but any requirements that change the "rules of the game" and increase costs to livestock producers have a negative impact on their incomes.

My view of the available evidence regarding the costs and benefits of composting in the Lower Fraser Valley, indicates that composting is not generally viable from a private perspective and constitutes a risky investment at best. Although there will undoubtedly be exceptions, it is unlikely that on-farm composting or large, commercial-scale composting will develop without some form of government intervention either via regulations or financial incentives (subsidies, taxes, etc.). Public intervention to bring about composting of livestock wastes can be justified only if the on-farm plus off-farm (or external) benefits of composting exceed the costs. Otherwise, public subsidies to reduce livestock pollution are not worth undertaking. Public subsidies to agricultural producers will simply encourage an activity (composting) which probably costs more than it benefits society. Subsidies would simply result in increased inefficiency and a waste of taxpayer money. The same can be said about taxes or regulations that force producers to compost their wastes. These will encourage economic inefficiency from a social standpoint and have the effect of driving some producers to bankruptcy. This will be aggravated in some sectors if, and when, marketing boards no longer provide them with the protection they would otherwise have.

Finally, it should be noted that these conclusions are based on an "all-or-nothing" scenario, where all or none of the livestock wastes are composted. There may well be some benefits from providing subsidies to producers to enable them to clean up the worst cases of pollution. There may be benefits to research that aims to optimize the rates and timing of manure applications so that less nitrates enter the aquifer. Indeed, research and extension efforts that change management practices at low cost may do more to reduce pollution than large investment schemes that seek to establish regional manure storage and/or composting facilities. It is my recommendation that more effort be directed at improving on-farm management practices, both for livestock and field crops.

Recommendations for Further Research Work

(1) Further research work is needed to examine adsorption by zeolites of other essential plant nutrients such as Ca^{2+}, Mg^{2+}, and K^{+} present during composting of poultry manure, and the extent of their availability to plants.

(2) At present there is no information in the literature on anion adsorption by zeolites. Phosphorus is an essential plant nutrient which is organically bound in manures. During composting of manure, P mineralizes as an anion. Its adsorption by zeolites would enhance the fertilizing value of the manure.

(3) Information about the actual costs of composting, potential markets for compost and composting techniques is sparse; further research into any of these areas is certainly warranted.

REFERENCES

Adamson, A.W. 1973. A Textbook of Physical Chemistry. Academic Press, New York.

Addiscott, T.M., A.P. Whitmore, and D.S. Powlson, 1992. Farming, Fertilizers, and the Nitrate Problem. Wallingford, UK, CAB International.

Adolph, R.H., V. Brown, and C.M. McKell. 1969. Poultry manure as a rangeland fertilizer. Poul. Sci. 48:1778-1782.

Aharoni, C., and D.L. Sparks. 1991. Kinetics of soil chemical processes - A theoretical treatment. p. 1-18. *In* D.L. Sparks and D.L. Suarez (ed.) Rates of Soil Chemical Processes. SSSA Spec. Publ. 27. SSSA, Madison, WI.

Aharoni, C., D.L. Sparks, S. Levinson, and I. Ravina. 1991. Kinetics of soil chemical reactions: Relationships between empirical equations and diffusion models. Soil Sci. Soc. Am. J. 55:1307-1313.

Al-Kanani, T., E. Akochi, A.F. MacKenzie, I. Alli, and S. Barrington. 1992. Organic and inorganic amendments to reduce ammonia losses from liquid hog manure. J. Environ. Qual. 21:709-715.

Allen, E.R. 1991. Supplying nitrogen, phosphorus, and potassium to plants through dissolution and ion exchange using a zeolite-based substrate. Ph.D. Diss. Texas A & M Univ. College Station, TX (Diss. Abstr. 92 - 06456).

Allen, E.R., D.W. Ming, L.R. Hossner, and D.L. Henninger. 1995. Modeling transport kinetics in clinoptilolite-phosphate rock systems. Soil Sci. Soc. Am. J. 59:248-255.

Allison, F.E., R.M. Murphy, and C.J. Klein. 1963. Nitrogen requirements for the decomposition of various kinds of finely ground woods in soil. Soil Sci. Soc. Am. Proc. 27:187-190.

Allison, F.E. 1973. Soil Organic Matter and its Role in Crop Production. Developments in Soil Science. Vol. 3. Elsevier Press, New York.

Ames, L.L., Jr. 1960: The cation sieve properties of clinoptilolite. Am. Mineral. 45:689-701.

Ames, L.L., Jr. 1961: Cation sieve properties of the open zeolites chabazite, mordenite, erionite, and clinoptilolite. Am. Mineral. 46:1120-1131.

Ames, L.L. Jr. 1967. Zeolite removal of ammonium ions from agricultural and other wastewaters. 13th Pacific Northwest Industrial Waste Conference Proceedings, Washington State University; Pullman.

APHA (American Public Health Association). 1992. Standard methods for the examination of water and wastewater. 18th ed. APHA, Washington, DC.

ApSimon, H.M., M. Kruse, and J.N.B. Bell. 1987. Ammonia emissions and their role in acid deposition. Atmospheric Environ. 21:1939-1945.

Argersinger, W.J., A.W. Davidson, and O.D. Bonner. 1950. Thermodynamics and ion exchange phenomena. Trans. Kan. Acad. Sci. 53:404-410.

Armstrong, J.E., D.R. Crandell, D.J. Easterbrook, and J.B. Noble. 1965. Late Pleistocene stratigraphy and chronology in south west British Columbia and north west Washington. Geological Society of America Bulletin, 76:321-330.

Ashbolt, N.J., and M.A. Line. 1982: A bench-scale system to study the composting of organic wastes. J. Environ. Qual. 11:405-408.

Bache, B.W., and E.G. Williams. 1971. A phosphate sorption index for soils. J. Soil Sci. 22:289-301.

Bachrach, U. 1957. The aerobic breakdown of uric acid by certain pseudomonads. J. Gen. Microbiol. 17:1-11.

Bangar, K.C., K.K Kapoor, and M.M. Mishra. 1988. Effect of pyrite on conservation of nitrogen during composting. Biol. Wastes 25:227-231.

Barbarick, K.A., and H.J. Pirella. 1984. Agronomic and horticultural uses of zeolites: A review. pp. 93-104. In: W.G. Pond and F.A. Mumpton (eds.), Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture. Westview Press, Boulder, Colorado.

Barrow, N.J. 1978. The description of phosphate adsorption curves. J. Soil Sci. 29:447-462.

Bernal, M.P., and J.M. Lopez-Real. 1993. Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. Bioresource Technology 43:27-33.

Bernal, M.P., J.M. Lopez-Real, and K.M. Scott. 1993. Application of natural zeolites for the reduction of ammonia emissions during the composting of organic wastes in a laboratory composting simulator. Biores. Tech. 43:35-39.

Bitzer, C.C., and J.T. Sims. 1988. Estimating the availability of nitrogen in poultry manure through laboratory and field studies. J. Environ. Qual. 17:47-54.

Blanchard, G., M. Maunage, and G. Martin. 1984. Removal of heavy metals from waters by means of natural zeolites. Water Res., 18:1501-1507.

Bomke, A.A., and L.M. Lavkulich. 1975. Composition of poultry manure and effect of heavy application on soil chemical properties and plant nutrition in British Columbia, Canada. p. 614-617. *In* Managing Livestock Wastes. Proc. 3 rd Int. Symp. on Livestock Wastes. ASAE, St. Joseph, MI.

Bonazzi, G., L. Vialli, and S. Piccinini. 1990. Controlling ammonia emission at composting plants. BioCycle 31:68-71.

Boyd, G.E., A.W. Adamson, and L.S. Myers, Jr. 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites: II. Kinetics. J. Am. Chem. Soc. 69:2836-2848.

Bramley, R.V., and R.E. White. 1990. The variability of nitrifying activity in field soils. Plant and Soil 126:203-208.

Breck, D.W., 1974. Zeolite Molecular Sieves: structure, chemistry, and use. John Wiley & Sons, Inc., New York.

Brinton, W.F., Jr. 1985. Nitrogen response of maize to fresh and composted manure. Biol. Agric. Hort. 3:55-64.

Brinton, W.F., Jr., and M.D. Seekins. 1994. Evaluation of farm plot conditions and effects of fish scrap compost on yield and mineral composition of field grown maize. Compost Sci. & Utiliz. 2:10-16.

British Columbia Ministry of Agriculture, Fisheries and Food. 1992. Environmental Guidelines for Poultry Producers in British Columbia. B.C. Ministry of Agriculture, Fisheries and Food, Soils and Engineering Branch, Abbotsford, B.C.

Buchanan, M.A., and S.R. Gliessman. 1990. The influence of conventional and compost fertilization on phosphorus use efficiency by broccoli in a phosphorus deficient soil. Am. J. Altern. Agric. 5:38-46.

Carlile, F.S. 1984. Ammonia in poultry houses: A literature review. World's Poult. Sci. J. 40:99-113.

Carski, T.H., and D.L. Sparks. 1987. Differentiation of soil nitrogen fractions using a kinetic approach. Soil Sci. Soc. Am. J. 51:314-317.

Chaney, D.E., L.E. Drinkwater, and G.S. Pettygrove. 1992. Organic soil amendments and fertilizers. Univ. of California Sustainable Agric. Res. Ed. Prog. Publ. 21505, Davis, CA.

Chapman, H.D. 1965. Cation-exchange capacity. p. 891-901. *In* C.A. Black (ed.) Methods of Soil Analysis. Part 2. Agronomy 9. American Society of Agronomy, Madison, Wisconsin.

Chien, S.H., and W.R. Clayton 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci. Soc. Am. J. 44:265-268.

Cihacek, L. J. and J. M. Bremner. 1979: A simplified ethylene glycol monoethyl ether procedure for assessment of soil surface area. Soil Sci. Soc. Am. J. **43**, 821-822.

Cogger, C.G., and C. MacConnell, 1991. Clean Water for Washington: Why the Concern about Agricultural Contamination in Groundwater? Washington State University, Cooperative Extension Publication # EB1632. August.

Cooke, I.J. 1966. A kinetic approach to the description of soil phosphate status. J. Soil Sci. 17:56-64.

Crank, J. 1976. The Mathematics of Diffusion. Oxford Press, New York.

Curtin, D., C.A. Campbell, and D. Messer. 1996. Prediction of titratable acidity and soil sensitivity to pH change. J. Environ. Qual. 25:1280-1284.

Dakin, A. 1993. Groundwater resources of the basins, lowlands and plains: Fraser lowland. pp. 9.1-9.27. *In* Groundwater Resources of British Columbia. B.C. Environment, Victoria, B.C.

De Bertoldi, M., and F. Zucconi. 1980. Microbiologia della transformazione dei rifiuti solidi urbani in compost e loro utilizzazione in agricoltura. Ingegneria ambientale 9:209-216.

Del Zan, F., L. Baruzzini, M. Candotti, I. Tonetti, and G. Murgot. 1987. Manuring a maize crop with composts obtained from different technological processes: short-term effects on soil-plant system. p. 546-555. *In* De Bertoldi, M., M.P. Ferranti, P.L' Hermite, and F. Zucconi (ed.). Compost Production, Quality and Use. Elsevier Applied Science, London, UK.

Dickerson, R.E. 1969. Molecular Thermodynamics. W.A. Benjamin, Inc., New York.

Dorcey, A.H.J., and J.R. Griggs. 1991. Water in Sustainable Development. Exploring our Common Future in the Fraser River Basin. Vancouver: Westwater Research Institute, University of British Columbia.

Doula, M., A. Ioannou, A. Dimirkon, and J. Mitsios. 1994. Potassium sorption by calcium-bentonite (Ca-b). Commun. Soil Sci. & Plant Anal. 25:1387-1400.

Easterbrook, D.J. 1976. Geologic Map of Western Whatcom County, Washington. USA. Geological Survey Map I-854-B.

Edwards, D.R., and T.C. Daniel. 1992. Environmental impacts of on-farm poultry waste disposal - a review. Biores. Technol. 41:9-33.

Eghball, B., J.F. Power, J.E. Gilley, and J.W. Doran. 1997. Nutrient, carbon, and mass loss during composting of beef cattle feedlot manure. J. Environ. Qual. 26:189-193.

Egnér, H. 1932. Nitrogen losses from stable manure through ammonia volatilization. Meddalande Nr 409 Från Centralanstalten försöksväsendet på jordbruksområdet, Avdeling för lantbrukskemi Nr 48.

Epstein, E. 1997. The Science of Composting. Technomic Publ. Co., Inc., Lancaster, PA, USA.

Evans, R.L., and J.J. Jurinak. 1976. Kinetics of phosphate release from a desert soil. Soil Sci. 121:205-1208.

Everett, D.H. 1965. Interactions between adsorbed molecules. Discussions Faraday Soc. 40:177-187.

Eyring, H. 1935a. The activated complex in chemical reactions. J. Chem. Phys. 3:107-120.

Eyring, H. 1935b. The activated complex and the absolute rate of chemical reactions. Chem. Rev. 17:65-82.

Federal-Provincial Working Group on Drinking Water. 1978. Guidelines for Canadian Drinking Water Quality. Hull, PQ: Canadian Government Publishing Centre.

Feigenbaum, S., R. Edelstein, and I. Shainberg. 1981. Release rate of potassium and structural cations from micas to ion exchangers in dilute solutions. Soil Sci. Soc. Am. J. 45:501-506.

Fenn, L.B., R.M. Taylor, and J.E. Matocha. 1981. Ammonia losses from surface applied nitrogen as controlled by soluble calcium and magnesium: general theory. Soil Sci. Soc. Am. J. 45:777-781.

Ference Weicker & Co., 1989. Hog Market Study and Strategic Plan for Composted Hog Manure. B.C. Ministry of Agriculture, Fisheries, and Food. September.

Ference Weicker & Co., 1994. Options to Remove Poultry Manure from the Fraser Valley: The Canada-BC Green Plan for Agriculture. August.

Filep, D., and I. Khargitan. 1977. Thermodynamic analysis of cation exchange processes in the soil-solution system. Sov. Soil Sci. 9:599-609.

Forgaty, A.M., and O.H. Tuovinen. 1991. Microbial degradation in yard waste composting. Microbiol. Rev. 55:225-233.

Frost, A.A., and R.G. Pearson. 1961. Kinetics and Mechanism. John Wiley & Sons, New York.

Gao, G., and C. Chang. 1996. Changes in CEC and particle size distribution of soils associated with long-term annual applications of cattle feedlot manure. Soil Sci. 161:115-120.

Garcia-Miragaya, J., and A.L. Page. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. Soil Sci. Soc. Am. J. 40:658-663.

Gilmour, J.T., D.C. Wolf, and P.M. Gale. 1987. Estimating Potential Ground and Surfacewater Pollution from Land Application of Poultry Litter. Arkansas Water Resources research Centre, Publication No. 128.

Glasstone, S., K. Laidler, and H. Eyring. 1941. The Theory of Rate Processes. McGraw-Hill, New York.

Gonzalez, J.L., M.A. Herraez, and S. Rodriquez. 1982. Kinetic treatment of adsorption-desorption processes of Fe (III)-silica gel system by a theoretical generalized model. J. Colloid Interface Sci. 88:313.

Griffin, R.A., and J.J. Jurinak. 1974. Kinetics of the phosphate interaction with calcite. Soil Sci. Soc. Am. Proc. 38:75-79

Gupta, G., J. Borowiec, and J. Okoh. 1997. Toxicity identification of poultry litter aqueous leachate. Poultry Science. 76:1364-1367.

Halstead, E.C. 1986. Ground Water Supply - Fraser Lowland, British Columbia. National Hydrology Research Institute Paper No. 26, Environment Canada, Saskatoon.

Handreck, K.A. 1993. Properties of coir dust, and its use in the formulation of soilless potting media. Commun. Soil Sci. Plant Anal. 24:349-363.

Hansen, R.C., H.M. Keener, H.A.J. Hoitink. 1989. Poultry manure composting - an exploratory study. Trans. ASAE 36:2151-2157.

Hansen, R.C., H.M. Keener, W.A. Dick, C. Marugg, and H.A.J. Hoitink. 1990. Poultry manure composting: ammonia capture and aeration control. Paper No. 90-4062, ASAE, St. Joseph, MI.

Harmsen, K. 1984. Nitrogen fertilizer use in rainfed agriculture. Fert. Res. 5:371-382.

Haug, J.T. 1993. Compost Engineering. Lewis Publishers, Ann Arbor, MI.

Haug, J.T., and W.F. Ellingsworth. 1991. Measuring compost substrate degradability. BioCycle 32:56-61.

Havlin, J.L., D.G. Westfall, and R.S. Olsen. 1985. Mathematical models for potassium release kinetics in calcareous soils. Soil Sci. Soc. Am. J. 49:366-370.

Hayward, D.O., and B.M.W. Trapnell. 1964. Chemisorption. 2nd ed. London: Butterworth and Co. Ltd.

Hébert, M., A. Karam, and L.E. Parent. 1991. Mineralization of nitrogen and carbon in soils amended with composted manure. Biol. Agric. Hortic. 7:349-361.

Helfferich, F. 1969. Ion exchange kinetics. p. 65-79. *In* J.A. Marinsky (ed.) Ion Exchange and Solvent Extraction, Vol. I. Marcel Dekker, Inc., New York.

Helfferich, F.G. 1983. Ion exchange kinetics - evolution of a theory. p. 157-159. *In* L. Liberti and F.G. Helfferich (ed.) Mass Transfer and Kinetics of Ion Exchange. Martinus Nijhoff Pub., Boston.

Henry, D.C. 1922. A kinetic theory of adsorption. Phil. Mag. (Series 6) 44:689-705.

Hervas, L., N. Mazuelos, N. Senesi, and C. Saiz-jimenez. 1989. Chemical and physico-chemical characterization of vermicomposts and their humic acid fractions. Sci. Tot. Environ. 81/82:543-550.

Hileman, L.H. 1965. Broiler litter as a fertilizer. Ark. Farm Res.16:6.

Hoitink, H.A.J., and G.A. Kuter. 1986. Basis for the control of soil-borne pathogens with composts. Annu. Rev. Phytopath. 24:93-124.

Holford, I.C.R., R.W.M. Wedderburn, and G.E.G. Mattingly. 1974. A Langmuir two-surface equation as a model for phosphate adsorption by soils. J. Soil Sci. 25:242-255.

Howery, D.G., and H.C. Thomas. 1965: Ion exchange on the mineral clinoptilolite. J. Phys. Chem. 69:531-537.

Huang, Z.T., and A.M. Petrovic. 1994. Clinoptilolite zeolite influence on nitrate leaching and nitrogen use efficiency in simulated sand based golf greens. J. Environ. Qual. 23:1190-1194.

Huneycutt, H.G., C.P. West, and J.M. Phillips. 1988: Responses of bermudagrass, tall fescue and tall fescue-clover to broiler litter and commercial fertilizer. Bull. 913, Arkansas Agricultural Experiment Station, University of Arkansas, Fayetteville, AR.

Hutcheon, A.T. 1966. Thermodynamics of cation exchange on clay: Ca-K montmorillonite. J. Soil Sci. 17:339-355.

Jackson, M. L. 1979: Soil Chemical Analysis - Advanced course. 2nd edition. M. L. Jackson, Madison, WI.

Jardine, P.M., and D.L. Sparks. 1984a. Potassium-calcium exchange in a multireactive soil system: I. Kinetics. Soil Sci. Soc. Am. J. 48:39-45.

Jardine, P.M., and D.L. Sparks. 1984b. Potassium-calcium exchange in a multireactive soil system: II. Thermodynamics. Soil Sci. Soc. Am. J. 48:45-50.

Jencks, W.P. 1969. Catalysis in Chemistry and Enzymology. McGraw-Hill, New York.

Jensen, H.E. 1973. Potassium-calcium exchange on a montmorillonite and a kaolinite clay: I. A test on the Argersinger thermodynamics approach. Agrochimica 17:181-189.

Johnson, P.A., R.P. Hiron, and A. Pemberton. 1983. The use of zeolite as an additive for composts for vegetable transplant production and pot plants. J. Sci. Food Agric. 34:267-268.

Keeney, D.R. 1989. Sources of nitrate to groundwater. p. 23-33. *In* R.F. Follet (ed.) Nitrogen Management and Groundwater Protection. Elsevier Press, New York.

Kelly, W.P. 1948. Cation Exchange in Soils. Am. Chem. Soc. Monograph 109. Rheinhold Publ. Corp., New York

Kirchmann, H. 1985. Losses, plant uptake and utilization of manure-nitrogen during a production cycle. Acta Agric. Scand. 24:1-77.

Kirchmann, H., and E. Witter. 1989. Ammonia volatilization during aerobic and anaerobic manure decomposition. Plant and Soil 115:35-41.

Kithome, M., J.W. Paul, L.M. Lavkulich, and A.A. Bomke. 1997a. The effect of pH on ammonium adsorption by the natural zeolite clinoptilolite. Commun. Soil Sci. & Plant Anal. (submitted).

Kithome, M., J.W. Paul, L.M. Lavkulich, and A.A. Bomke. 1997b. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. Soil Sci. Soc. Am. J. (in press).

Kithome, M., J.W. Paul, L.M. Lavkulich, and A.A. Bomke. 1997c. Thermodynamics of ammonium exchange on the natural zeolite clinoptilolite. Commun. Soil Sci. & Plant Anal. (submitted).

Kithome, M., J.W. Paul, and T. Kannangara. 1997d. Adsorption isotherms of ammonium on coir pith. Commun. Soil Sci. & Plant Anal. (submitted).

Kithome, M., J.W. Paul, and A.A. Bomke. 1997e. Reducing nitrogen losses during composting of poultry manure using different amendments. J. Environ. Qual. (submitted).

Kithome, M., J.W. Paul, and A.A. Bomke. 1997f. The effect of compost fertilization on yield and nitrogen uptake by Italian ryegrass (*Lolium multiflorum*). J. Environ. Qual. (submitted).

Klotz, I.M. 1982. Number of receptor sites from Scatchard graphs: Facts and fantasies. Science 217:1247-1249.

Koelliker, J.K., H.S. Nakaue, M.L. Hellickson, and J.R. Miner. 1978. Improving poultry house environment with zeolite. American Society of Agricultural Engineering, Technical Paper No. 78, p. 4044.

Kreye, R., and M. Wei. 1994. A proposed Aquifer Classification System for Groundwater Management in British Columbia. B.C. Ministry of Environment, Lands and Parks, Victoria, B.C.

Kuo, S., and G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by hematite and gibbsite. Soil Sci. 116:400-406.

Laidler, K.J. 1965. Chemical Kinetics. 2nd ed. McGraw-Hill, New York.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum, J. Amer. Chem. Soc. 40:1361-1403.

Lasaga, A.C. 1983a. Rate laws of chemical reactions. p. 1-68. *In* A.C. Lasaga *et al.* (ed.) Kinetics of Geochemical Processes. Mineral. Soc. Am., Washington, DC.

Lasaga, A.C. 1983b. Transition state theory. p. 135-169. *In* A.C. Lasaga *et al.* (ed.) Kinetics of Geochemical Processes. Mineral. Soc. Am., Washington, DC.

Laudelout, H., R. van Badel, G.H. Bolt, and A.L. Page. 1968. Thermodynamics of heterovalent cation exchange reactions in a montmorillonite clay. Trans. Faraday Soc. 64:1477-1488.

Lewis, M.D. 1981. Clinoptilolite as a N, K, and Zn source for plants. M.Sc. Thesis. Dept. of Horticulture, Colorado State University, Fort Collins.

Li, Y.C., P.J. Stoffella, A.K. Alva, D.V. Calvert, and D.A. Graetz. 1997. Leaching of nitrate, ammonium, and phosphate from compost amended soil columns. Comp. Sci. & Utiliz. 5:63-67.

Liberti, L., G. Boari, and D. Petruzelli. 1981. Nutrient removal and recovery from wastewater by ion exchange. Water Research 15:337-342.

Liebscher, H., B. Hii, and D. McNaughton. 1992: Nitrates and Pesticides in the Abbotsford Aquifer, Southwestern British Columbia. Inland Waters Directorate, Environment Canada, North Vancouver, B.C.

Loehr, R.C. 1974. Agricultural Waste management: Problems, Processes, and Approaches. Academic Press, New York. Processes.

Low, M.J.D. 1960. Kinetics of chemisorption of gases on solids. Chem. Rev. 60:267-312.

Lowe, L.E. 1993. Introduction to chemical and microbiological studies. p. 70-73. *In* Integrated Management of Agricultural Wastes. Final Report on Hazardous, Toxic and Special Wastes Project. April 1991-October 1993.

Luttmerding, H.A. 1980. Soils of the Langley-Vancouver Map Area. B.C. Soil Survey Report No. 15.

MacKown, C.T. 1978: Role of mineral zeolites as soil amendments. PhD. Dissertation, Dept. of Soils, Water, and Engineering, University of Arizona, Tucson.

MacKown, C.T., and T.C. Tucker. 1985. Ammonium nitrogen movement in coarse-textured soil amended with zeolite. Soil Sci. Soc. Am. J. 49:235-238.

Magdoff, F. 1992. Building Soils for Better Crops. Univ. of Nebraska Press, Lincoln.

Mahimairaja, S., N.S. Bolan, M.J. Hedley, and A.N. Macgregor. 1994. Losses and transformation of nitrogen during composting of poultry manure with different amendments: an incubation experiment. Biores. Technol. 47:265-273.

Marcille-Kerslake, V. 1991. Evaluation of the Fernie phosphorite and Princeton Zeolites: Potential for rock phosphate-zeolite fertilizer use. M.Sc. Thesis, Dept. of Land Resources, University of Guelph.

Martin, H.W., and D.L. Sparks. 1983. Kinetics of non-exchangeable potassium release from two coastal plain soils. Soil Sci. Soc. Am. J. 47:883-887.

Mathur, S.P., N.K. Patni, and M.P. Levesque. 1990. Static pile, passive aeration composting of manure slurries using peat as a bulking agent. Biol. Wastes 30:323-333.

Mawdsley, J.L., R.D. Bardgett, R.J. Merry, B.F. Pain, and M.F. Theodorou. 1995. Pathogens in livestock waste, their potential for movement through soil and environmental pollution. Appl. Soil Ecol. 2:1-25.

Maynard, D.G., and A.A. Bomke. 1980. The response of grass-legume sward to poultry manure. Can. J. Soil Sci. 60:451-459.

Meerow, A.W. 1994. Growth of two subtropical ornamentals using coir (coconut mesocarp pith) as a peat substitute. HortScience 29:1484-1486.

Mercer, B.W. 1969. Clinoptilolite in water pollution control. The Ore Bin. 31:209-213.

Ming, D. W. and F. A. Mumpton. 1989: Zeolites in Soils. In *Minerals in Soil environment*: SSSA Book series #1. Madison, WI, pp. 873-911.

Mitsios, J., A. Dimirkou, A. Ioannou, Ch. Paschalidis, and M. Doula. 1994. The sorption isotherms of potassium. Commun. Soil. Sci. Plant Anal. 25:1373-1386.

Molloy, S.P., and H. Tunney. 1983. A laboratory study of ammonia volatilization from cattle and pig slurry. Irish J. Agric. Res. 22:37-45.

Moore, W.J. 1972. Physical Chemistry. 2nd ed. Prentice-Hall, Englewood Cliffs, N.J.

Moore, J.W., and R.G. Pearson. 1981. Kinetics and Mechanism. 3rd ed. John Wiley & Sons, New York.

Moore, P.A., Jr., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Effect of chemical amendments on ammonia volatilization from poultry litter. J. Environ. Qual. 24:293-300.

Moreale, A., and R. van Bladel. 1979. Soil interactions of herbicide-derived aniline residues: a thermodynamic approach. Soil Sci. 127:1-9.

Mortland, M.M., and A.R. Walcott. 1965. Sorption of inorganic nitrogen compounds by soil materials. p. 150-197. *In* W.V. Bartholomew and F.E. Clark (ed.) Soil Nitrogen. Agronomy 10. Madison, Wisconsin, American Society of Agronomy.

Morton, T.J., A.J. Gold, and W.M. Sullivan. 1988. Influence of overwatering and fertilization on nitrogen losses from home lawns. J. Environ. Qual. 17:124-130.

Muia, M.J., and M.P. Thomas, 1990. "A Question of Nitrates", Environmental Education and Information. 9:91-100.

Muljadi, D., A.M. Posner, and J.P. Quirk. 1966a. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. Part I. The isotherms and the effect of pH on adsorption. J. Soil Sc. 17:212-229.

Muljadi, D., A.M. Posner, and J.P. Quirk. 1966b. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. Part II. The location of the adsorption sites. J. Soil Sc. 17:230-237.

Muljadi, D., A.M. Posner, and J.P. Quirk. 1966c. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. Part III. The effect of temperature on adsorption. J. Soil Sc. 17:238-247.

Mumpton, F.A. 1978: Natural zeolites: a new Industrial mineral commodity. p. 3-27. *In* L.B. Sand and F.A. Mumpton (ed.). Natural Zeolites: occurrence, properties, use. Pergamon Press, New York, NY, USA.

Niemiera, A.X. 1985. Nitrification in a pine bark medium. Ph.D. dissertation, Virginia Polytechnic Inst. and State Univ., Blacksburg.

Nodar, R., M.J. Acea, and T. Carballas. 1990. Microbial composition of poultry excreta. Biol. Wastes 33:95-105.

Nömmik, H., and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. p. 123-252. *In* F.J. Stevenson (ed.) Nitrogen in Agricultural Soils. Agronomy Monograph 22. Madison, Wisconsin.

Noren, O. 1986. Design and use of biofilters for livestock buildings. p. 234-237. *In* V.C. Nielsen *et al.* (ed.) Odor Prevention and Control of Organic Sludge and Livestock Farming. Elsevier Appl. Sci. Publ. London.

Overcash, M.R., F.J. Humenik, and J.R. Miner. 1983. Livestock Waste Management. Vol. I and II. CRC Press, Boca Raton, FL.

Pain, B.F., Y.J. Rees, and D.R. Lockyer. 1988. Odor and ammonia emissions following the application of pig or cattle slurry to land. p. 2-11. *In* V.C. Nielsen, J.H. Voorburg, and P.L'Hermite (ed.), Volatile Emissions from Livestock Farming and Sewage operations. Elsevier Applied Science, NY, USA,

Paramasivan, S., and A.K. Alva. 1997. Nitrogen recovery from controlled-release fertilizers under intermittent leaching and dry cycles. Soil Sci. 162:447-453.

Parravano, G., and M. Boudant. 1955. Chemisorption and catalysis on oxide semiconductors. p. 47. *In* W.G. Frankenburg *et al.* (ed.) Advances in Catalysis. Academic Press, New York.

Paul, J.W., and E.G. Beauchamp. 1993. Nitrogen availability for corn in soils amended with urea, cattle slurry, and solid and composted manures. Can. J. Soil Sci. 73:253-266.

Paul, J.W., J.A. Covert, and E.G. Beauchamp. 1994. Influence of soil temperature and moisture on water-soluble phenolic compounds in manured soil. Can. J. Soil Sci. 74:111-114.

Paulson, S. 1994. Poultry Industry Specialist, British Columbia, Ministry of Agriculture, Fisheries and

Food, South Coastal region. Presentation to British Columbia Institute of Agrologists, Vancouver Branch. January 25.

Peoples, M.B., and J.R. Freney. 1995. Minimizing gaseous losses of nitrogen. pp. 565-602. In: P.E. Bacon (eds.), Nitrogen Fertilization in the Environment. Marcel Dekker, Inc., New York, NY.

Peryea, F.J., F.T. Bingham, and J.D. Rhoades. 1985. Kinetics of post-reclamation boron dissolution. Soil Sci. Soc. Am. J. 49:836-839.

Pfirter, A., A. von Hirschheydt, P. Ott, and H. Vogtmann. 1981. Composting. Cooperative Migros Aargau/Solothurn, Switzerland.

Reichenberg, D. 1957. Properties and behavior: Kinetics, electrolyte penetration, and absorption of nonelectrolytes. p. 66-85. *In* C. Calmon and T.R.E. Kressman (ed.) Ion Exchange in Organic and Biochemistry. Interscience, New York.

Reynolds, C.M., and D.C. Wolf. 1987. Influence of urease activity and soil properties on ammonia volatilization from urea. Soil Sci. 143:418-425.

Roelfs, J.G.M., A.J. Kempers, A.L.F.M. Houdijk, and J. Jansen. 1985. The effect of airbone ammonium sulphate on P*inusnigra var. maritima* in the Netherlands. Plant and Soil 84:45-56.

Roig, A., A. Lax, J. Cegarra, F. Costa, and T. Hernández. 1988. Cation exchange capacity as a parameter for measuring the humification degree of manures. Soil Sci. 146:311-316.

Rouf, M.A., and R.F. Lomprey, Jr. 1968. Degradation of uric acid by certain aerobic bacteria. J. Bacteriol. 96:617-622.

Sabey, B.R., N.N. Agbim, and D.C. Markstrom. 1975. Land application of sewage sludge: III. Nitrate accumulation and wheat growth resulting from addition of sewage sludge and wood waste to soils. J. Environ. Qual. 4:388-393.

Salisbury, F.B., and C. Ross. 1969. Plant Physiology. Wadsworth Publ. Co., Belmont, CA.

SAS (Statistical Analysis Systems) Institute. 1990. Procedures guide for personal computers, Version 6, 4th Ed. SAS Institute, Cary, NC.

Sawhney, B.L. 1966. Kinetics of cesium sorption by clay minerals. Soil Sci. Soc. Am. Proc. 30:565-569.

Schroder, H. 1985. Nitrogen losses from Danish agriculture-trends and consequences. Agric. Ecosyst.Environ. 14:279-289.

Schueler, C., J. Biala, and H. Vogtmann. 1989. Anti-phytopathogenic properties of biogenic waste compost. Agric. Ecosyst. Environ. 27:477-482.

Selim, H.M., R.S. Mansell, and L.W. Zelazny. 1976. Modeling reactions and transport of potassium in soils. Soil Sci. 122:77-84.

Sharpley, A.N. 1983. Effect of soil properties on the kinetics of phosphorus desorption. Soil Sci. Soc. Am.

J. 47:462-467.

Shuler, M.L., E.D. Roberts, D.W. Mitchell, and F. Kargi. 1979. Process for the aerobic conversion of poultry manure into high-protein feedstuff. Biotechn. & Bioeng. 21:19-38.

Siegel, R.S., A.A.R. Hafez, J. Azevebo, and P.R. Stout. 1975. Management procedures for effective fertilization with poultry manure. Compost Sci. 16:5-9.

Sivasubramaniam, S., and O. Talibudeen. 1972. Potassium-aluminum exchange in acid soils. I. Kinetics. J. Soil Sci. 23:163-176.

Sparks, D.L. 1986. Kinetics of reactions in pure and in mixed systems. p. 83-145. *In* D.L. Sparks (ed.) Soil Physical Chemistry. CRC Press, Boca Raton, FL.

Sparks, D.L. 1989. Kinetics of Soil Chemical Processes. Academic Press, San Diego, CA.

Sparks, D.L., and P.M. Jardine. 1981. Thermodynamics of potassium exchange in soil using a kinetics approach. Soil Sci. Soc. Am. J. 45:1094-1099.

Sparks, D.L., and P.M. Jardine. 1984. Comparison of kinetic equations to describe K-Ca exchange in pure and in mixed systems. Soil Sci. 138:115-122.

Sparks, D.L., L.W. Zelazny, and D.C. Martens. 1980. Kinetics of potassium exchange in a paleudult from the Coastal Plain of Virginia. Soil Sci. Soc. Am. J. 44:37-40.

Sposito, G. 1981. Cation exchange in soils: A historical and theoretical perspective. p. 13-30. *In* D.E. Baker *et al.* (ed.) Chemistry in the Soil Environment. ASA Spec. Pub. No. 40, Am. Soc. of Agron., and Soil Sci. Soc. of Am., Madison, Wis.

Sposito, G. 1982. On the use of the Langmuir Equation in the interpretation of "Adsorption" phenomena: II. The "Two-Surface" Langmuir Equation. Soil Sci. Soc. Am. J. 46:1147-1152.

Steffens, D., and D.L. Sparks. 1997. Kinetics of nonexchangeable ammonium release from soils. Soil Sci. Soc. Am. J. 61, 455-462.

Stevens, R.J., R.J. Laughlin, and J.P. Frost. 1989. Effect of acidification with sulfuric acid on the volatilization of ammonia from cow and pig slurries. J. Agric. Sci. Camb. 113:389-395.

Sustainable Poultry Farming Group, 1994. Final Report and Resource Binder. Canada-British Columbia Soils & Water Conservation Program. Project No. SCP1109. March.

Sutton, A.L. 1994. Proper animal manure utilization. J. Soil Water Conserv. 50:65-70.

Swanson, N.P., L.N. Mielke, J.C. Lorimor, T.M. McCalla, and J.R. Ellis. 1971. Transport of pollutants from sloping cattle feedlots as affected by rainfall intensity, duration, and recurrence. *In* Livestock Waste Management and Pollution Abatement. ASAE, St. Joseph, MI.

Syers, J.K., M.G. Browman, G.W. Smillie, and R.B. Corey. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. Soil Sci. Soc. Proc. 37:358-363.

Taiganides, E.P. 1977. Composting of feedlot wastes. p. 241-251. *In* E.P. Taiganides (ed.) Animal Wastes. Appl. Sci. Publ., London.

Termeer, W.C., and P.R. Warman. 1993. Use of mineral amendments to reduce ammonia losses from dairy-cattle and chicken-manure slurries. Biores. Technol. 44:217-222.

Thiesen, A. A. and M. E. Harward. 1962. A paste method for preparation of slides for clay mineral identification by X-ray diffraction. Soil Sci. Soc. Am. Proc. **26**, 90-91.

Thomas, J.M., and W.J. Thomas. 1967. Introduction to the Principles of Heterogeneous Catalysis. Academic Press, New York, NY.

Tsitsishvili, G. V., T. G. Andronikashvili, G. N. Kirov, L. D. Filizova. 1992: Natural Zeolites. Ellis Horwood, New York.

Udo, E.J. 1978. Thermodynamics of potassium-calcium and magnesium-calcium exchange reactions on a kaolinitic soil clay. Soil Sci. Soc. Am. J. 42:556-560.

Ungarish, M., and C. Aharoni. 1981. Kinetics of Chemisorption: Deducing kinetic laws from experimental data. J. Chem. Soc. Faraday Trans. 77:975-979.

Vaidyanathan, L.V., and O. Talibudeen. 1968. Rate-controlling processes in the release of soil phosphate. J. Soil Sci. 19:342-353.

van Breemen, N., P.A. Borrough, E.J. Velthorst, H.F. van Dobben, T. de Wit, T.B. Ridder, and H.F.R. Reijinders. 1982. Soil acidification from atmospheric ammonium sulfate in forest canopy throughfall. Nature (London) 299:548-550.

van Breemen, N., P.M.A. Boderie, and H.G.W. Booltink. 1989. Influence of airborne ammonium sulfate on soils of an oak woodland ecosystem in the Netherlands: Seasonal dynamics of solute fluxes. p. 211-236. *In* D.C. Adriano and M. Havas (ed.) Acid precipitation. Vol. 1. Case Studies. Springer-Verlag, New York.

Vaughan, D.E.W. 1978. Properties of natural zeolites. p. 353-372. *In* L.B. Sand and F.A. Mumpton (ed.), Natural Zeolites: Occurrence, Properties, Use. Pergamon Press, NY, USA.

Vogtmann, H. 1984. Organic farming practices research in Europe. p. 19-36. *In* D.F. Bezdicek (ed.) Organic farming: Current technology and its role in sustainable agriculture. ASA Spec. Publ. 46. ASA, CSSA, and SSSA, Madison, WI.

Walinga, I., J.J. van der Lee, V.J.G. Houba, W. van Vark, and I. Novozamsky. 1995. Plant Analysis Manual. Kluwer Academic Publishers, Dordrecht.

Weber, M.A., K.A. Barbarick, and D.G. Westfall. 1983. Ammonium adsorption by a zeolite in a static and a dynamic system. J. Environ. Qual. 12:549-552.

Weil, R.R., W. Kroontje, and G.D. Jones. 1979. Inorganic nitrogen and soluble salts in a Davidson clay loam used for poultry manure disposal. J. Environ. Qual. 8:86-91.

White, G.N., and L.W. Zelazny. 1986. Charge properties of soil colloids. pp. 39-81. In: D.L. Sparks (ed.) Soil Physical Chemistry. CRC Press, Boca Raton, FL.

Witter, E. 1986. The fate of nitrogen during high temperature composting of sewage sludge-straw mixtures. PhD Thesis, Wye College, University of London.

Witter, E. 1991. Use of $CaCl_2$ to decrease ammonia volatilization after application of fresh and anaerobic chicken slurry to soil. J. Soil Sci. 42:369-380.

Witter, E., and J. Lopez-Real. 1988. Nitrogen losses during composting of sewage sludge and the effectiveness of clay soil, zeolite and compost in adsorbing the volatilized ammonia. Bio. Wastes 23:279-294.

Witter, E., and H. Kirchmann. 1989a. Peat, zeolite and basalt as adsorbents of ammoniacal nitrogen during manure decomposition. Plant and Soil 115:43-52.

Witter, E., and H. Kirchmann. 1989b. Effects of addition of calcium and magnesium salts on ammonia volatilization during manure decomposition. Plant and Soil 115:53-58.

Zebarth, B.J., C.G. Kowalenko, B. Harding, and D. Chapple. 1997. Development of a test-based nitrogen recommendation system for raspberries to reduce nitrate leaching to the Abbotsford Aquifer. Pacific Agri-Food Research Centre (Summerland) Technical Report No. 97-01.