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A SLOW-RELEASE NITROGEN FERTILIZER: AMMONIUM-LOADED

CLINOPTILOLITE

by

T. Scott Perrin

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Science

UTAH STATE UNIVERSITY
Logan, Utah

1997

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ABSTRACT

A Slow-Release Nitrogen Fertilizer: Ammonium-Loaded Clinoptilolite

by

T. Scott Perrin, Master of Science

Utah State University, 1997

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Department: Plants, Soils and Biometeorology

Crops grown in sandy soils require frequent irrigation. As a result, nitrogen (N) fertilizers, such as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), are leached from the rooting zone of crops. This loss of N increases N fertilizer use and the potential for nitrate (NO_3^-) contamination of water. Ammonium-loaded clinoptilolite (NH_4^+ -Cp) may reduce this N leaching, increase N fertilizer use-efficiency, and prevent NO_3^- contamination of water while sustaining normal crop growth.

The potential of NH_4^+ -Cp as a N fertilizer was assessed in three leaching experiments without plants and two leaching experiments with plants. Pots containing rounded quartz sand were amended with $(\text{NH}_4)_2\text{SO}_4$ and one of three NH_4^+ -Cp size fractions: small (<0.25 mm), medium (0.25 to 2 mm), large (2 to 4 mm). The pots were leached with a field irrigation water for 43 d. Results showed that NH_4^+ -Cp leaches N much slower than $(\text{NH}_4)_2\text{SO}_4$ and the rate of NH_4^+ release is affected by size fraction. The large size fraction leached less N (as NH_4^+ and NO_3^-) than the small or medium size fractions. The leaching experiment was then repeated twice in pots containing sandy soil. Results again indicated that NH_4^+ -Cp leaches N much slower than $(\text{NH}_4)_2\text{SO}_4$. No differences in N leaching were found among NH_4^+ -Cp size fractions. However, after extracting the NH_4^+ -Cp from the soil, the greatest concentration of N was recovered from the largest size fraction and the least concentration of N was recovered from the smallest size fraction.

Finally, in two leaching studies, pots containing the sandy soil were planted with sweet corn and grown for 35 d and 42 d, respectively. No differences were found among N sources in corn relative growth rates, leaf area ratios, and net assimilation rates, even though the corn plants that were fertilized with NH_4^+ -Cp assimilated significantly more N than the $(\text{NH}_4)_2\text{SO}_4$ -fertilized plants. The pots fertilized with NH_4^+ -Cp leached <4% of the added N, whereas the $(\text{NH}_4)_2\text{SO}_4$ treatments leached 18 to 47% of the added N, depending on the applied N rates.

In the greenhouse, NH_4^+ -Cp is a slow-release fertilizer that will reduce N leaching while maintaining normal plant growth. However, field studies are needed to confirm the suitability of NH_4^+ -Cp as a slow-release fertilizer under field conditions.

(110 pages)

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T. Scott Perrin

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CHAPTER 1
DEVELOPMENT OF CLINOPTILOLITE AS A SLOW-RELEASE
NITROGEN FERTILIZER

INTRODUCTION

Many farms in the arid West have areas of sandy soil. Although productive, the cultivation of these soils has two disadvantages. First, because of their low water-holding capacity, sandy soils require frequent irrigations to sustain plant growth. Consequently, a proportion of added fertilizers such as nitrogen (N) is leached from the rooting zones of the plants. These losses of leached N increase N fertilizer use for the farmer. Second, the leached N increases the potential to contaminate surface and ground water, which is especially important as population growth urbanizes agricultural lands. Therefore, farmers with sandy soils apply N in split applications, use slow-release fertilizers, and/or add soil conditioners such as organic matter to increase the soil's cation exchange capacity (CEC) and water holding capacity. Another possible solution for farmers is fertilizing with ammonium-loaded clinoptilolite (NH_4^+ -Cp). Ammonium-Cp may decrease N fertilizer use and reduce N leaching while sustaining plant growth.

Clinoptilolite (Cp) is a species of zeolite, a hydrated aluminosilicate mineral that has internal channels and a high CEC. The potential for Cp as an amendment for sandy soils is based on four mineralogical properties. First, Cp has a CEC of 125 to 200 $\text{cmol}_c \text{kg}^{-1}$, which is 30 to 50 times the native CEC of sandy soils. This high CEC is the result of the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedra of the Cp's structure, resulting in a Si/Al molar ratio of 4.3 to 5.3 (Ming and Mumpton, 1989). Second, due to its porous, channeled structure, Cp can increase the water holding capacity of a sandy soil. Tetrahedra, the Cp's primary building block, link to form rings or polyhedra, which further link to form an open, channeled framework. The channel dimensions in this framework are 0.41 x 0.47 nm, 0.44 x 0.72 nm, or 0.40 x 0.55 nm. As a result, Cp has about a 34% void volume and a density of 2.16 Mg m^{-3} (Ming and Mumpton, 1989). Third, due to channel angles, Cp has a

specific affinity for monovalent cations, particularly ammonium (NH_4^+) and potassium (K^+), two plant macronutrients. Finally, it is relatively abundant. Clinoptilolite is found in near-surface deposits in Texas, South Dakota, Idaho, New Mexico, California, Oregon, Wyoming, and Utah (Ming and Mumpton, 1989; Allen and Ming, 1995).

Clinoptilolite is initially identified by x-ray diffraction analysis, after which thermal analysis and various wet chemical methods are used to confirm its identity from other zeolite species (Ming and Mumpton, 1989; Boettinger and Graham, 1995). One important feature that distinguishes clinoptilolite from other zeolite species is its Si/Al molar ratio. Zeolite species with low Si/Al molar ratios (Si/Al = 1 to 2) are selective for divalent cations such as Ca^{2+} or Mg^{2+} , whereas zeolites with high Si/Al molar ratios (Si/Al = 4 to 6), such as clinoptilolite, are selective for monovalent cations like NH_4^+ and K^+ (Ming and Mumpton, 1989).

Early work with Cp and other zeolites began in the 1960s in Japan. Farmers would crush and apply the zeolite to control soil moisture content, reduce malodor from animal wastes, and to increase the pH of acidic volcanic soils (Mumpton, 1983). Hsu et al. (1967) reported that the addition of Cp to soils with low clay contents increased physio-chemical properties of the soil, such as CEC and water holding capacity. Minato (1968) supported these conclusions when he found that Cp additions to rice paddy soils with low CEC increased N use-efficiency.

In the U.S., preliminary work with Cp was done by Ames (1960). Using a clinoptilolite from Hector, California, he found that Cp had the following order of cation selectivity: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{2+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Li}^+$. He then demonstrated in simulated wastewater that Cp selectively exchanged K^+ over NH_4^+ , and NH_4^+ over either Na^+ , Ca^{++} , or Mg^{++} (Ames, 1967). Mercer et al. (1970) and Koon and Kauffman (1971, 1975) applied this research further by removing ammonium from secondary effluents of wastewater plants. By 1978, Mumpton (1978) reported the application of this technology at wastewater treatment facilities in Alexandria and Reston, Virginia, and the North Lake Tahoe Sewage District of California. Liberti et al. (1995) added to this waste treatment technology by creating a marketable by-product, struvite (MgNH_4PO_4), a slow-

release fertilizer. This patented procedure is called RIM-NUT, and is performed by simultaneously removing phosphate from the wastewater, raising the solution pH, and adding Mg.

Because $\text{NH}_3\text{-N}$ is toxic to fish, fisheries also grasped the potential benefits of using Cp to remove NH_4^+ from fishery water. In 1979, Bruin et al. successfully added Cp to raceways with coho salmon to maintain $\text{NH}_3\text{-N}$ levels below 0.005 mg L^{-1} . Smith et al. (1981) also reported success of maintaining low $\text{NH}_3\text{-N}$ levels in experiments that used Cp in leaching columns and in raceways with rainbow trout.

In the U.S., studies involving Cp in agriculture and horticulture were reported in the late 1970s and early 1980s. The following is a summary of these experiments from 1978 to 1996.

Early experiments were done by MacKown (1978) and Hershey et al. (1980). MacKown (1978), in laboratory and greenhouse studies, mixed Cp or erionite (another zeolite species), at rates of 45 to 450 metric tons ha^{-1} (0.3 m furrow slice) in two soils (a Torripsamment and Torrifluent). He found that increasing application rates of zeolite (Cp or erionite) increased the soil water-holding capacity, CEC, and NH_4^+ retention. Incubation experiments were conducted to evaluate the effect of zeolites on nitrification rates. Results suggested that only zeolites that were first loaded with NH_4^+ reduced nitrification rates. The influence of NH_4^+ -loaded, zeolite size fractions on nitrification was also evaluated. In general, nitrification rates decreased as the NH_4^+ -zeolite size fractions increased from the small (0.30 to 0.85 mm) to the large (1 to 2 mm) size fraction. In greenhouse studies with free-draining soils, sudangrass (*Sorghum vulgar sudanense* L.) was grown in soil amended with non-treated or NH_4^+ -loaded erionite. Only the additions of NH_4^+ -loaded erionite increase plant yield. The Cp and erionite used in the experiment were from Kuykendall, Texas, and Rome, Oregon, respectively. The watering solution for the leaching and plant growth experiments was distilled water (dH_2O). From MacKown's (1978) experiments, only the results from the NH_4^+ retention studies appear to have been published in any journals (MacKown and Tucker, 1985). Zeolites were not independently verified in either MacKown (1978) or MacKown and Tucker (1985).

Hershey et al. (1980) leached a modified Hoagland's solution (without K^+) through a potting mix amended with either KNO_3 or Cp high in native K^+ ($161 \text{ cmol}_c K^+ \text{ kg}^{-1}$). The potting mix consisted of silica sand, sphagnum peat moss, and composted redwood sawdust. Potassium quickly leached from the potting mix amended with KNO_3 , but slowly leached from the potting mix amended with Cp. Potting mix amended with 50 g of the Cp and irrigated with the modified Hoagland's solution sustained chrysanthemum (*Chrysanthemum morifolium*) growth for 3 mo. The Cp was received from the Anaconda Company, Denver, Colorado. Clinoptilolite's identity or characteristics were not independently verified. The size fraction was predominately 0.25 to 1 mm.

After these two experiments, the general study of Cp experiments was divided into two categories: 1) the use of untreated Cp as a soil amendment or 2) nutrient-loaded Cp as an amendment to natural or synthetic soils.

Untreated Cp

Weber et al. (1983) conducted two experiments to evaluate the retention of NH_4^+ in a clay loam soil (Aridic Argiustoll) amended with Cp. First, the NH_4^+ -adsorption capacities of Cp and clay loam soil were compared in a shaking (agitation) study with NH_4Cl . The Cp adsorbed 4.3 times more NH_4^+ than the clay loam soil. Second, increasing rates of Cp were mixed in the clay loam soil and leached with 2 M NH_4Cl . A 3 M KCl solution was then leached through the columns to determine which Cp rate retained the most NH_4^+ . Only the high (135 Mg ha^{-1}) rate of Cp reduced NH_4^+ leaching. Banding the 135 Mg ha^{-1} rate of Cp significantly increased the retention of NH_4^+ over the incorporated Cp rate. The Cp was from Washakie Basin, Wyoming. No Cp identification procedures were given. The Cp size fraction was 0.3 mm to 0.85 mm.

Ferguson et al. (1986) found that mortar sand mixed with Cp increased the growth and N use-efficiency of creeping bentgrass (*Agrostis palustris* Huds.). In the highest rates (10% by volume) of Cp, however, native exchangeable Na from the Cp was initially detrimental to plant growth. The origin and identification procedures for the Cp were not reported. The Cp size fraction was 0.5 to 2 mm. The composition of the watering solution was not given.

Ferguson and Pepper (1987) followed up on their 1986 experiment by performing an incubation experiment in mortar sand apparently amended with the same Cp. Loss of NH_4^+ decreased as the Cp amendment increased from 5% to 10% (by volume). A pronounced increase of NH_4^+ retention occurred when the initial NH_4^+ concentration was increased. Arizona tap water was used as the irrigation solution.

Nus and Brauen (1991) compared sand, a coarse Cp size fraction (55% > 4.7 mm), sphagnum peat moss, or saw dust as amendments for the establishment of creeping bentgrass in small soil plots. Cation exchange capacity and moisture retention of each amendment were compared. Clinoptilolite amendments had the highest volumetric CEC values. Although Cp increased the water holding capacity of the soil, the peat moss increased the water holding capacity the most. The CEC of untreated Cp size fractions ranged from 40 $\text{cmol}_c \text{ kg}^{-1}$ (for >5 mm size fractions) to 169 $\text{cmol}_c \text{ kg}^{-1}$ (for the <0.25 mm size fractions). This variability of CEC is probably due to a CEC analysis, which did not allow enough time for sufficient exchange in the larger Cp size fractions. The deposit and identification procedures for the Cp were not reported.

Finally, Huang and Petrovic (1994) found that a Cp amendment (10% by mass) to sand growing creeping bentgrass (*Agrostis stolonifera* L.) increased the CEC-200 fold, doubled the water holding capacity, decreased N loss due to leaching, and increased N use-efficiency. The Cp was from Teaque Mineral Products, Adrian, Oregon. No description of the Cp analysis was given. The Cp size fraction was 0.5 to 2 mm. The watering solution composition was not reported.

Nutrient-Loaded Cp

Lewis et al. (1983) performed a series of greenhouse experiments with NH_4^+ -Cp and Cp mixed with urea. Banding NH_4^+ -Cp in a medium sandy loam (13% clay) increased the N use-efficiency of radish (*Raphanus sativus* L., cv. Improved Scarlet Globe) compared to soil amended with $(\text{NH}_4)_2\text{SO}_4$. In a coarse loamy sand (6% clay), banding NH_4^+ -Cp decreased NO_3^- leaching compared to soil amended with $(\text{NH}_4)_2\text{SO}_4$. Radish growth was the same between N amendments. The Cp in the Cp + urea fertilizer prevented phytotoxic injury to radish plants, unlike the control, which was just

urea-amended. The Cp was supplied by Occidental Minerals Company from a deposit near Barstow, California. The composition and characteristics of the Cp were not independently verified. The procedure for loading and analyzing the Cp was insufficiently documented. The N content of the NH_4^+ -Cp in the experiment was claimed to be 2.99%, but the exchangeable NH_4^+ was reported as 128 meq/100 g, which results in only 1.79% N. The Cp size fraction was $< 44 \mu\text{m}$. The watering solution composition was not reported.

Bartz and Jones (1983) compared sudangrass (*Sorghum sudanese* cv. Trudan II) growth in two silt loam soils amended with either NH_4^+ -Cp or $(\text{NH}_4)_2\text{SO}_4$. In general, the sudangrass, watered with dH_2O , showed similar to better growth in the soils amended with NH_4^+ -Cp than in soils amended with $(\text{NH}_4)_2\text{SO}_4$. Nitrogen leaching was not monitored. The Cp, from Buckhorn, New Mexico, was identified by x-ray diffraction and thermal analysis. The procedure for loading the Cp and analyzing it for N was unclear. The NH_4^+ -Cp size fraction was $< 0.25 \text{ mm}$.

Lai and Eberl (1986) found that the P released into dH_2O increased when either NH_4^+ -Cp, Na^+ -Cp, or H^+ -Cp and phosphate rock were mixed, compared to P rock alone. They concluded that Cp and phosphate rock mixtures may supply sufficient plant nutrients such as N, K, Ca, and P. Their innovative idea was forwarded by Barbarick et al. (1990) and Allen et al. (1993) in an effort to create 1) a synthetic soil (Allen et al., 1993) and 2) a soil amendment (Barbarick et al., 1990; Allen et al., 1993).

Barbarick et al. (1990) mixed different ratios of NH_4^+ -Cp and phosphate rock in a sandy loam and a loam. They found that increasing the NH_4^+ -Cp/phosphate rock ratios generally increased P uptake by sorghum-sudangrass (*Sorghum bicolor* L., Moench-*S. sudanese* [Piper] Stapf, 'NB280S'). The NH_4^+ was released from the NH_4^+ -Cp from cation exchange reactions with Ca^{++} , from the dissolution of phosphate rock, and K^+ , which was added as a fertilizer. High NH_4^+ -Cp/phosphate rock ratios caused K^+ deficiency in the loamy sand because of the sequestering of the K^+ by the Cp. The Cp was from Washakie Basin, Wyoming. The procedure for loading the Cp and analyzing it for N was

not reported. Moisture levels in the soils were maintained by adding dH₂O about once a week. The NH₄⁺-Cp size fraction was 0.3 mm to 0.85 mm.

Allen et al. (1993) examined cation exchange relationships between combinations of NH₄⁺-Cp and K⁺-Cp, from San Miguel Cp in South Texas, and phosphate rocks from Tennessee and North Carolina. As Barbarick et al. (1990) found, the increase of NH₄⁺-Cp/phosphate rock ratios increased solution P concentrations. The same was true for increasing K⁺-Cp/phosphate rock ratios. In both mixtures, K⁺ and NH₄⁺ solution concentrations increased while Ca⁺⁺ concentrations decreased as Cp/phosphate rock ratios were increased. Higher phosphate rock reactivity (i.e., increased CO₃/PO₄ ratio) was found to increase the K⁺ and NH₄⁺ solution concentrations. Allen et al. (1993) concluded that sufficient levels of N, P, and K were released to maintain plant growth. Calcium levels were low due to the sequestering of Ca⁺⁺ by the Cp. A detailed analysis of the Cp was done by Senkayi et al. (1987). The NH₄⁺- and K⁺-Cp size fraction was 2 to 50 μm.

Allen et al. (1995) modeled the transport kinetics of NH₄⁺- and K⁺-Cp/phosphate rock systems. They concluded that the power-function, Elovich, and parabolic-diffusion models adequately describe N, P, and K release into the "soil" solution. The power function model was preferred because of its simplicity. The models indicated that the nutrient release was diffusion controlled. The Cp used in the experiment was the same used by Allen et al. (1993). The preparation of the NH₄⁺- and K⁺-Cp was accomplished by washing the Cp four times with a 1 M chloride solution of the saturating cation. Interstitial salts were removed by dialyzing until the AgNO₃ test for Cl⁻ was negative, after which the samples were washed three times with acetone and oven dried.

Eberl et al. (1995) conducted an experiment similar to Barbarick et al. (1990) using the same soils, sorghum-sudangrass, and NH₄⁺-Cp. However, copper (Cu), manganese (Mn), Mg, and zinc (Zn) uptake in the plants were monitored. The addition of NH₄⁺-Cp increased plant yields and uptake of P, Cu, Mn, Mg, Ca, and Zn. They concluded that the low pH, as the result of nitrification of NH₄⁺, enhanced the uptake of these nutrients. Clinoptilolite was collected from two sites, Washakie Basin, Wyoming, and Pine Ridge Indian Reservation, South Dakota. Clinoptilolite appears to have been only

partially loaded because the Cp size fraction (<0.15 mm) was only soaked once with 0.5 M NH_4Cl before being washed with dH_2O . The watering solution composition was not reported.

Ming et al. (1995) grew wheat in a substrate that consisted of NH_4^+ -Cp and K^+ -Cp either synthetic or natural apatite (phosphate rock) for 90 d. Calcium, Mg, P, and micronutrients were made available to the plant through the dissolution of apatite. Potassium and N were supplied from Cp exchange sites via cation exchange reactions. Plant tissue tests indicated that the synthetic apatite/Cp substrate supplied sufficient levels of plant nutrients (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Mo, and Cl) for the vegetative growth of wheat. The natural apatite/Cp substrate supplied sufficient levels of plant nutrients, except Mg. The Cp was collected from the Washakie Basin, Fort LeClède deposit, Sweetwater County, Wyoming. Preparation of the loaded-Cp was done as explained by Allen et al. (1995). The wheat was watered with dH_2O .

Allen et al. (1996) used the power function model (Allen et al., 1995) to evaluate the factors that controlled the release of N, P, and K in Cp/phosphate rock systems. The model indicated that initial nutrient release rates were increased by increasing Cp/phosphate rock ratios and by using more reactive phosphate rock. Nutrient release rates, indicative of the cation selectivity of the Cp, were affected by the proportion of NH_4^+ and K^+ on the Cp's exchange sites. The Cp characteristics were the same as found by Allen et al. (1993) and Allen et al. (1995).

DISCUSSION

Untreated Cp amended to coarse soils 1) increases the CEC, 2) increases water holding capacity, and 3) if applied in high rates, decreases N leaching. Little value was placed on reporting which procedure(s), if any, was performed to identify the Cp, the Cp deposit, and the composition of water solutions used in the experiments. Consequently, the application of the results to the field from many of the experiments is questionable. First, other zeolite species such as heulandite (Ming and Mumpton, 1989) are similar to Cp and must be distinguished by x-ray diffraction and thermal analysis. If the identification of Cp is not correctly done, the experiment results may be about the

performance of a zeolite species other than Cp. Second, clinoptilolite deposits are not uniform, either within a state or from state to state. Each has varying CEC, impurities, and native exchangeable cations. Thus, reporting the Cp deposit and its characteristics is important. Third, the salinity of the irrigation water will presumably influence Cp's ability to minimize N leaching because cation exchange reactions govern NH_4^+ retention and release from Cp. Finally, the theory that Cp amendments to soil will decrease N leaching is reasonable, but maybe not practical unless the Cp is amended in large quantities to the soil (at least 10% w/w). On a farm, a 10% w/w amendment of Cp equals $450 \text{ Mg Cp ha}^{-1}$ (0.3 m slice), a huge amount of Cp to transport and add to a soil. However, when Cp is mixed into the soil and amended with NH_4^+ -based fertilizer, there is only a small chance (if NH_4^+ is not first nitrified to NO_3^-) of NH_4^+ coming in contact and being retained by a Cp particle.

Nutrient-loaded Cp are 1) slow-release fertilizers, 2) a part of a nutrient-rich substrate for synthetic soils when combined with a highly reactive phosphate rock, and 3) in the case of NH_4^+ -Cp, better at increasing N use-efficiency and decreasing nitrification compared to untreated Cp. However, like the experiments with untreated Cp, some researchers placed little value on reporting the procedure for confirming the identity of Cp, the procedures for loading and analyzing the Cp with K^+ or NH_4^+ , the potential influence of field irrigation water on nutrient release from Cp, and the effort to monitor N fate. As a result, the quality or usefulness of many of these experiments is questionable. For example, loading Cp with nutrients is different than loading common clays, such as smectite, because the cation exchange of the Cp is strongly influenced by diffusion in the rigid internal channels. Therefore, a single Cp loading event, as in (Eberl et al., 1995), may not be sufficient in saturating the Cp with K^+ or NH_4^+ . Also, cation exchange reactions are the mechanism by which NH_4^+ is released from NH_4^+ -Cp. Because all natural waters have varying concentrations and compositions of cations, not reporting the cations in irrigation water, or using dH_2O to irrigate a soil, neglects the role cations play in NH_4^+ release from NH_4^+ -Cp. The less cations in the irrigation solution, the slower NH_4^+ will probably be released from NH_4^+ -Cp. The influence of cations in field irrigation waters is a serious consideration if this technology is to be applied to the "real" world of agriculture or horticulture. The experiments that

used dH₂O in natural soils, though, demonstrated the influence of the soil's soluble cations on NH₄⁺ release from NH₄⁺-Cp (MacKown, 1978; Bartz and Jones, 1983; Eberl et al., 1995). Finally, NH₄⁺-Cp has low N concentrations. Economically, this will translate into high transportation costs. Because of these potential costs, understanding the N fate in a soil amended with NH₄⁺-Cp is crucial. Treating the soil amended with NH₄⁺-Cp as a "black box" is unacceptable if the NH₄⁺-Cp (or K⁺-Cp) fertilizer is to compete in the N fertilizer market.

PROPOSED EXPERIMENT

Green River, Utah, like many agricultural regions in the western U.S., has sandy soils (Swenson et al., 1970), which require high amounts of irrigation to sustain plant growth. As a result, a proportion of the added fertilizer N is leached from the rooting zones of crops. This N loss decreases N use-efficiency and increases the potential for N contamination of surface and groundwater.

At the northern end of Cache County, Utah, is a quality Cp deposit (Southard and Kolesar, 1978) that has been carefully characterized (MacQueen, 1996). I hypothesized that ammonium-Cp, prepared from this deposit, would increase N use-efficiency, and reduce N leaching while sustaining normal plant growth. Sweet corn (*Zea mays* L. cv. Incredible) was used in the experiment because of potential sweet corn production in the Green River area. Two leaching studies prefaced the plant growth study: one in rounded quartz sand and another in the Green River soil. The objective of these two leaching studies was to assess NH₄⁺ release from 3 NH₄⁺-Cp size fractions--small (<0.25 mm), medium (0.25 to 2 mm), and large (2 to 4 mm)--compared to (NH₄)₂SO₄. The soils were leached with field irrigation water because 1) dH₂O contains no cations to replace the NH₄⁺ on the NH₄⁺-Cp exchange site and 2) plants in Green River will never be irrigated with dH₂O. An effort was made to monitor the fate of the added N. The greenhouse growth experiment concluded the project. Sweet corn was planted in a sandy soil collected from Green River, Utah, and amended with one of the NH₄⁺-Cp size fractions or (NH₄)₂SO₄. Corn was grown in the greenhouse for approximately 6 wk. The fate of added N was monitored, and at the conclusion of the experiment an N budget was prepared.

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CHAPTER 2

DECREASED NITROGEN LEACHING WITH AMMONIUM-LOADED CLINOPTILOLITE

ABSTRACT

Clinoptilolite (Cp) is a zeolite mineral that has a high cation exchange capacity (CEC) and an affinity for ammonium (NH_4^+). Consequently, various size fractions of ammonium-loaded Cp (NH_4^+ -Cp) have been used in a nitrogen (N) fertilizer in leaching and plant growth studies. This study, as a preface to a plant growth study, evaluated NH_4^+ release from three NH_4^+ -Cp size fractions in two media: a rounded quartz sand and a sandy soil. Ammonium sulfate, or one of the three NH_4^+ -Cp size fractions, small (<0.25 mm), medium (0.25 to 2 mm), or large (2 to 4 mm), was banded at a depth of 5 cm in leaching columns at a rate of 112, 224, or 336 kg N ha⁻¹. The columns were leached for 40 d with a simulated irrigation water. The $(\text{NH}_4)_2\text{SO}_4$ fertilizer leached more N than the NH_4^+ -Cp fertilizer in the rounded quartz sand and sandy soil experiments. Results indicated that the larger the NH_4^+ -Cp size fraction, the slower NH_4^+ is released from NH_4^+ -Cp. Ammonium-Cp appears to be a slow-release (N) fertilizer that will minimize N leaching. The rate of NH_4^+ release may be manipulated by using different NH_4^+ -Cp size fractions.

INTRODUCTION

Clinoptilolite (Cp) is a species of the mineral zeolite, a hydrated aluminosilicate. It has a three-dimensional crystal structure having a high cation exchange capacity (CEC) and an affinity for ammonium (NH_4^+) and potassium (K^+) (Ming and Mumpton, 1989). Over the past 30 yr, researchers have amended soils (synthetic or natural) with varying size fractions of NH_4^+ - and K^+ -loaded Cp, or untreated Cp, in an effort to utilize the unique characteristics of Cp for plant nutrition and decreasing N leaching from soil. Ammonium-loaded Cp (NH_4^+ -Cp) or potassium-loaded Cp (K^+ -Cp) has been studied as a slow-release fertilizer alone (MacKown, 1978; Hershey et al., 1980; Bartz and Jones, 1983; Lewis et al., 1983) and in combination with phosphate rock (Lai and Eberl, 1986; Barbarick et

al., 1990; Allen et al., 1993; Allen et al., 1996). Allen et al. (1995), after modeling these reactions in a Cp/phosphate rock system, concluded that the transport kinetics of this system were controlled by diffusion. Part of this diffusion was intraparticle diffusion within the Cp, suggesting that larger Cp size fractions would release a pre-adsorbed nutrient slower than smaller Cp size fractions. MacKown (1978) observed this in nitrification studies where the larger (1- to 2-mm) NH_4^+ -Cp size fraction had lower nitrification rates than the smaller (0.30- to 0.85-mm) NH_4^+ -Cp size fraction; nitrification rates are dependent on NH_4^+ release rates.

Most studies, however, use only one Cp size fraction. Lewis et al. (1983) used a $< 44\text{-}\mu\text{m}$ NH_4^+ -Cp size fraction for growth studies with greenhouse grown radishes. Bartz and Jones (1983) used a $< 250\text{-}\mu\text{m}$ NH_4^+ -Cp size fraction for a plant growth study with sudangrass. In experiments with Cp/phosphate rock, NH_4^+ -Cp size fractions of 300 to 850 μm and $< 150 \mu\text{m}$ were used by Barbarick et al. (1990) and Eberl et al. (1995), respectively. Allen et al. (1993, 1995, 1996) in similar studies of Cp/phosphate rock systems used a NH_4^+ -Cp size fraction of 2 to 50 μm . An effort to correlate NH_4^+ release results with NH_4^+ -Cp size fractions from these studies is very difficult because of differing Cp deposits, unreported (Bartz and Jones, 1983; Lewis et al., 1983; Barbarick et al., 1990) or inadequate (Nus and Brauen, 1991; Eberl et al., 1995) NH_4^+ loading procedures and analysis of NH_4^+ -loaded Cp, and the different chemistries of the irrigation waters (Chapter 1).

The cations in irrigation water should play a significant role in the release of NH_4^+ from NH_4^+ -Cp because release of NH_4^+ is primarily driven by cation exchange reactions, which are dependent on the concentration and composition of the external solution. This important principle is not new to Cp or soil experiments. Using clinoptilolite from Hector, California, Ames (1960) found an order of cation selectivity: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{2+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Li}^+$. He then demonstrated in simulated wastewater that Cp selectively retained K^+ over NH_4^+ , and NH_4^+ over either Na^+ , Ca^{++} , or Mg^{++} (Ames, 1967). Mumpton (1978) reported the application of this technology at wastewater treatment facilities in Alexandria and Reston, Virginia, and the North Lake Tahoe Sewage District of California. The recharging of the Cp is performed by

purging the NH_4^+ -loaded Cp with Na^+ (Gunn, 1979). Although Cp is poorly selective for Na^+ , high concentrations of Na^+ can replace the highly selective ion, NH_4^+ , by the principle of mass action. In soils, the principle of mass action is used to analyze a soil's CEC (Peech et al., 1947).

In 1980, Hershey et al. observed that irrigation with a modified Hoagland's solution (minus K^+) caused K^+ release from a K-rich Cp. In 1986, Lai and Eberl expertly used the principles of cation exchange to suggest that nutrient-loaded Cp in combination with phosphate rock would supply nutrients such as N, K, Ca, and P. Their innovative idea was forwarded by Barbarick et al. (1990) and Allen et al. (1993) in an effort to make a synthetic soil (Allen et al., 1993; Ming et al., 1995) or a soil amendment (Barbarick et al., 1990; Allen et al., 1993).

Although the principle of cation exchange has been innovatively implemented in some experiments, it has also been forgotten or set aside in many others. Many researchers have made conclusions about Cp's ability to retain N, release N or K, and inhibit nitrification while only using deionized water in leaching (MacKown and Tucker, 1985) and plant growth studies (Bartz and Jones, 1983; Barbarick et al., 1990) without any preliminary experiments or discussion of the possible effects of field irrigation water on Cp (untreated or nutrient loaded). Other studies never reported water characteristics (Lewis et al., 1983; Ferguson et al., 1986; Huang and Petrovic, 1994). Consequently, some of these results may have limited interpretations. For example, the release rate of NH_4^+ from NH_4^+ -Cp may be much higher if irrigated with a saline irrigation water, or NH_4^+ retention in soils amended with Cp may be lower than claimed because other cations in solution will be competing for the Cp exchange sites. The effect of field irrigation water on Cp amendments is a weighty consideration if Cp/nutrient release technologies are to be applied in the "real world" of horticulture, floriculture, or agriculture, especially when all irrigation waters naturally contain exchangeable cations.

This study, as a preface to a greenhouse corn growth study, will compare the NH_4^+ release from three NH_4^+ -Cp size fractions and $(\text{NH}_4)_2\text{SO}_4$ in leaching studies without plants. The specific objectives were to: 1) determine whether fertilization with NH_4^+ -Cp in a rounded quartz sand or

sandy soil will reduce N leaching compared to $(\text{NH}_4)_2\text{SO}_4$ and 2) determine the effect of three NH_4^+ -Cp size fractions, small (<0.25 mm), medium (0.25 to 2 mm), or large (2 to 4 mm), on N leaching.

MATERIAL AND METHODS

Characterization of Soil

Two Mg of soil was collected from the upper 30 cm of an uncultivated sandy soil typical of the Green River area, Utah (39°00' N, 110°10' W). The climate in this area is arid and warm. Mean annual precipitation is about 165 mm and the mean annual air temperature is 11.1°C (Ashcroft et al., 1992). The soil was air-dried and sieved to <2 mm. The pipette method of particle size distribution (PSD) was performed according to the Soil Survey Laboratory Staff (1992), except that the organic matter was removed with 50 g NaOCl L^{-1} (buffered to pH 9.5) instead of H_2O_2 . Organic carbon (C) was analyzed via acid dichromate digestion (Soil Survey Laboratory Staff, 1992). Cations were extracted with 1 M NH_4OAc (Soil Survey Laboratory Staff, 1992) and analyzed by inductively coupled plasma spectroscopy (ICP). Soil CEC was determined using the NH_4OAc method (Soil Survey Laboratory Staff, 1992) except that exchangeable NH_4^+ was replaced with 2 M KCl . The NH_4^+ was determined using an automated ion analyzer (Quick Chem AE #202.AE, Milwaukee, WI). Soluble cations and anions were analyzed in a saturation paste extract (Soil Survey Laboratory Staff, 1992). The cations were analyzed by ICP and the anions were analyzed using an ion chromatograph (Dionex series 4500i, San Jose, CA). The pH and electrical conductivity (EC) of the saturation paste extract were also measured (Soil Survey Laboratory Staff, 1992). Mineralogy of the clay fraction separated after the PSD analysis was analyzed by x-ray diffraction (XRD) analysis following Mg and K saturation, glycerol solvation, and heating to 550 °C (Whittig and Allardice, 1986). Calcium carbonate (CaCO_3) equivalent was analyzed according to Bundy and Bremner (1972). Bulk density was calculated in the lab (Soil Survey Laboratory Staff, 1992). Gravimetric water content at -0.3 MPa and -1.5 MPa was analyzed according to the Soil Survey Laboratory Staff (1992).

Characterization and Preparation of NH_4^+ -Cp

A zeolite sample collected from Cache County, Utah, was confirmed as clinoptilolite using XRD analysis, differential scanning calorimetry, total elemental analysis, and ion exchange analysis (MacQueen, 1996). The Cp was crushed and sieved to three size fractions: small (0 to 0.25 mm), medium (0.25 to 2 mm), and large (2 to 4 mm). The Cp size fractions were loaded with NH_4^+ by soaking them in 1 M $(\text{NH}_4)_2\text{SO}_4$ for 10 d, changing the soaking solution every 2 to 3 d. The large size fraction required an extra 4 d of soaking in 1 M $(\text{NH}_4)_2\text{SO}_4$ to insure complete NH_4^+ saturation of exchange sites. The NH_4^+ -loaded Cp was rinsed with distilled water to remove excess salts. Rinsing continued until the EC of the supernatant was $< 5 \mu\text{S cm}^{-1}$. A sample of each NH_4^+ -Cp size fraction sample was collected, the large (2 to 4 mm) size fraction was crushed with a mortar and pestle to < 1 mm, and analyzed for N via Kjeldahl digestion (Bremner and Mulvaney, 1982; see Appendix A).

Characterization of Irrigation Water

Irrigation water similar to that at Green River, Utah, was used in the experiment because 1) dH_2O has no cations to replace the NH_4^+ on the NH_4^+ -Cp, 2) preliminary lab work showed that dH_2O has no effect on NH_4^+ release from NH_4^+ -Cp, and 3) plants *in situ* never see dH_2O . The use of dH_2O is probably the reason (Bartz and Jones, 1983) concluded that NH_4^+ -Cp (< 0.25 mm) may supply N to sudangrass for 242 d. The ion concentrations for the irrigation water from Green River, Utah were derived from a five year summer average (Table 1) of water analyses done each month by the United States Geological Service (ReMillard et al., 1990, 1991, 1992, 1993, 1994). In the lab, this solution was made by dissolving 5.89 g CaSO_4 , 3.56 g MgSO_4 , 1.77 g MgCl_2 , 0.129g KCl , 0.186 g NaCl , and 4.06 g NaHCO_3 in 27 L of dH_2O .

N Leaching from Quartz Sand Amended with NH_4^+ -Cp

Rounded quartz sand was washed in 1 M HCl , rinsed with dH_2O , and placed in 70-ml syringes. One of the four N amendments was banded at a 5-cm depth in each syringe. Each N

amendment, small, medium, and large NH_4^+ -Cp, and $(\text{NH}_4)_2\text{SO}_4$, was applied at 112, 224, or 336 kg N ha^{-1} (calculated as a proportion of soil mass found in a ha of soil) and replicated three times. An additional no-N treatment, to determine background N levels, was included for a total of 13 treatments.

Table 1. Typical composition of irrigation water in Green River, UT.

Cations		Anions		pH	EC
mg L ⁻¹		mg L ⁻¹			dS m ⁻¹
Ca ⁺⁺	51	SO ₄ ⁻⁻	170	8.12	0.675
Mg ⁺⁺	20	Cl ⁻	18		
K ⁺	3				
Na ⁺	53				

Before beginning the leaching experiment, each syringe was inoculated with soil bacteria. Two parts distilled water and one part of the sandy soil sampled from Green River, Utah, was shaken for 1 min and then allowed to settle for 1 min. Ten ml of the solution was pipetted into each syringe. Temperatures in the lab were maintained from 18 to 23° C.

Twenty ml of irrigation water, which represents an excessive irrigation volume (2/3 pore volume), was added to each syringe every 3 d for a period of 24 d. At 24 d, irrigation water was added every 7 d for 3 more weeks to estimate the influence of nitrifying bacteria. Leachate was collected and immediately frozen. Leachate was later analyzed for NH_4^+ and NO_3^- colorimetrically on the Lachat Quik Chem AE (QuickChem Method 10-107-06-1-A and Method 10-107-06-1-A for NH_4^+ -N and NO_3^- -N, respectively). Total leachate collected for the experiment was approximately seven pore volumes. After the experiment, the residual N was extracted from the quartz sand via a 2 M KCl extraction in which the quartz sand and NH_4^+ -Cp were placed in a container and shaken for 1 h. The 2 M KCl extract was analyzed on the Lachat (Quick Chem AE #202.AE, Milwaukee, WI) for NH_4^+ -N and NO_3^- -N (QuickChem Method 12-107-06-1-B and QuickChem Method 12-107-04-1-B for NH_4^+ -N and NO_3^- -N, respectively).

Statistical Design

The background N levels were subtracted from all the treatments, making the statistical design a 4 (N fertilizers) X 3 (N rates) factorial with three replicates. Analysis was performed on SAS (6.10) using the general linear model (GLM). Data were analyzed by date and by all dates combined.

N Leaching from the Soil Amended with NH_4^+ -Cp

The N leaching experiment with sandy soil and NH_4^+ -Cp was conducted twice, once in the lab and once in the greenhouse. The lab experiment was repeated by replacing the rounded quartz sand with sieved soil from Green River, Utah. Irrigation timing, amounts, and data collection were the same as the quartz sand leaching experiment.

A greenhouse leaching experiment was conducted so that containers, soil, and temperature conditions would be similar to the containers, soil, and temperature used for the corn growth experiment. Sandy soil (6.5 kg) was placed in 6-L pots. One of the four N fertilizers was banded at a depth of 5 cm in each pot. The banded fertilizer was located just off center and was about 2 to 3 cm wide and 10 to 12 cm long. Each N amendment was applied at 112 and 224 kg N ha⁻¹ for a total of eight treatments. The 336 kg N ha⁻¹ rate was dropped because of limited greenhouse space. Each treatment was replicated three times.

After initially wetting the soil in each pot with 1500 ml of irrigation water, approximately 500 ml of irrigation water was added to each container every 4 d for a period of 40 d. Leachate was collected and immediately frozen. Leachate was later analyzed for NH_4^+ and NO_3^- colorimetrically as previously described. Temperatures in the greenhouse were approximately 16°C during the night and 30°C during the day. Total leachate collected for the experiment was about one pore volume. After the experiment, the NH_4^+ -Cp was extracted from the soil, and a representative portion was analyzed for residual NH_4^+ via Kjeldahl digestion (Bremner and Mulvaney, 1982). The soil below the fertilizer band of each treatment was homogenized, and a sample of the soil was analyzed for residual N via Kjeldahl digestion (Bremner and Mulvaney, 1982).

Statistical Analysis

The background N levels were subtracted from each treatment making the statistical design a 4 (N fertilizers) x 2 (N rate) factorial with three replicates. Analysis was performed on SAS (6.10) using the general linear model (GLM). Data were analyzed by date and by all dates combined.

RESULTS AND DISCUSSION

Soil Analysis

The soil was classified as sandy over loamy, mixed, mesic Ustic Hapocalcid. The clay mineralogy consisted of mica, chlorite, and kaolinite. Specific physical and chemical characteristics are listed in Table 2.

Clinoptilolite Analysis

The clinoptilolite had a silicon/aluminum molar ratio of 5.38:1, and was stable at 600°C. The proportions of exchangeable cations on the native exchange complex were 52% Ca, 36% K, 6% Mg, and 6% Na (MacQueen, 1996).

The NH_4^+ -saturated CEC was about 165 $\text{cmol}_c \text{ kg}^{-1}$. The N concentrations of the small, medium, and large NH_4^+ -Cp size fractions were 2.28%, 2.22%, and 2.24%, by weight, respectively.

N leaching from Rounded Quartz Sand Amended with NH_4^+ -Cp

Ammonium and Nitrate Leaching

More N was leached from the quartz sand amended with $(\text{NH}_4)_2\text{SO}_4$ than the quartz sand amended with any size fraction of NH_4^+ -Cp. For all N amendments, as N rates increased, the amount of N that leached also increased.

The added $(\text{NH}_4)_2\text{SO}_4$ -N leached almost exclusively as NH_4^+ . After two irrigations (6 d), the quartz sand amended with $(\text{NH}_4)_2\text{SO}_4$ leached almost all of the applied N, 95%, 91%, and 98% kg

$\text{NH}_4^+\text{-N ha}^{-1}$ of the 112 (Fig. 1), 224 (Fig. 2), and 336 (Fig. 3) kg N ha^{-1} , respectively. In contrast, for the same period the quartz sand amended with the 1) small $\text{NH}_4^+\text{-Cp}$ leached 16%, 10%, and 7%, 2) medium $\text{NH}_4^+\text{-Cp}$ leached 13%, 12%, and 10%, and 3) large $\text{NH}_4^+\text{-Cp}$ leached 2%, 3%, and 3% from the 112, 224, and 336 kg N ha^{-1} , respectively. This slow release of NH_4^+ from the $\text{NH}_4^+\text{-Cp}$ sizes continued for the 43 d. By 43 d, the quartz sand amended with the 1) small $\text{NH}_4^+\text{-Cp}$ leached 44%, 34%, and 26%, 2) medium $\text{NH}_4^+\text{-Cp}$ leached 48%, 41%, and 40%, and 3) large $\text{NH}_4^+\text{-Cp}$ leached 18%, 19%, and 16% from the 112, 224, and 336 kg N ha^{-1} , respectively. The lack of NH_4^+ in the leachate after 24 d (Fig. 1b, 2b, and 3b) was related to decreasing the irrigating frequency from every 3 d to 7 d. This increased irrigation interval apparently allowed more NH_4^+ to be nitrified. As a result, NO_3^- was predominately leached from the quartz sand amended with the $\text{NH}_4^+\text{-Cp}$ sizes after 24 d.

Negligible NO_3^- was leached from the $(\text{NH}_4)_2\text{SO}_4$ amendments because the $(\text{NH}_4)_2\text{SO}_4\text{-N}$ leached almost exclusively as NH_4^+ . However, a substantial amount of $\text{NO}_3^-\text{-N}$ leached from the $\text{NH}_4^+\text{-Cp}$ sizes (Fig. 4, 5, 6). As the N rate increased from 112 to 336 kg N ha^{-1} , more $\text{NO}_3^-\text{-N}$ leached from the quartz sand amended with $\text{NH}_4^+\text{-Cp}$. The leached $\text{NO}_3^-\text{-N}$ decreased as the $\text{NH}_4^+\text{-Cp}$ size fraction increased from small to large: 1) the small $\text{NH}_4^+\text{-Cp}$ leached 28%, 18%, and 18%, 2) the medium $\text{NH}_4^+\text{-Cp}$ leached 19%, 12%, and 16%, and 3) the large $\text{NH}_4^+\text{-Cp}$ leached 14%, 12%, and 9% from the 112 (Fig. 4), 224 (Fig. 5), and 336 (Fig. 6) kg N ha^{-1} , respectively. Although these trends are identical for all rates and N fertilizers, not all differences are significant according to Tukey's test ($p < 0.05$). One reason less $\text{NO}_3^-\text{-N}$ leached from the larger $\text{NH}_4^+\text{-Cp}$ size fraction is probably because the larger size has a lower external surface-area-to-mass ratio than the small or medium sizes. This would decrease the relative number of attachment sites for nitrifying bacteria and the surface area contacted by the irrigation water. Another reason is the larger $\text{NH}_4^+\text{-Cp}$ size fraction has longer diffusion channels than the medium or small $\text{NH}_4^+\text{-Cp}$ size fractions. Nitrate began leaching around 10 d, probably due to the lag phase of bacterial growth in the new, $\text{NH}_4^+\text{-rich}$ environment. Had this soil been under cultivation with high populations of nitrifying bacteria, NO_3^- leaching would have probably started sooner. Nitrate leaching increased from 10 d to 16 d regardless of the rate applied

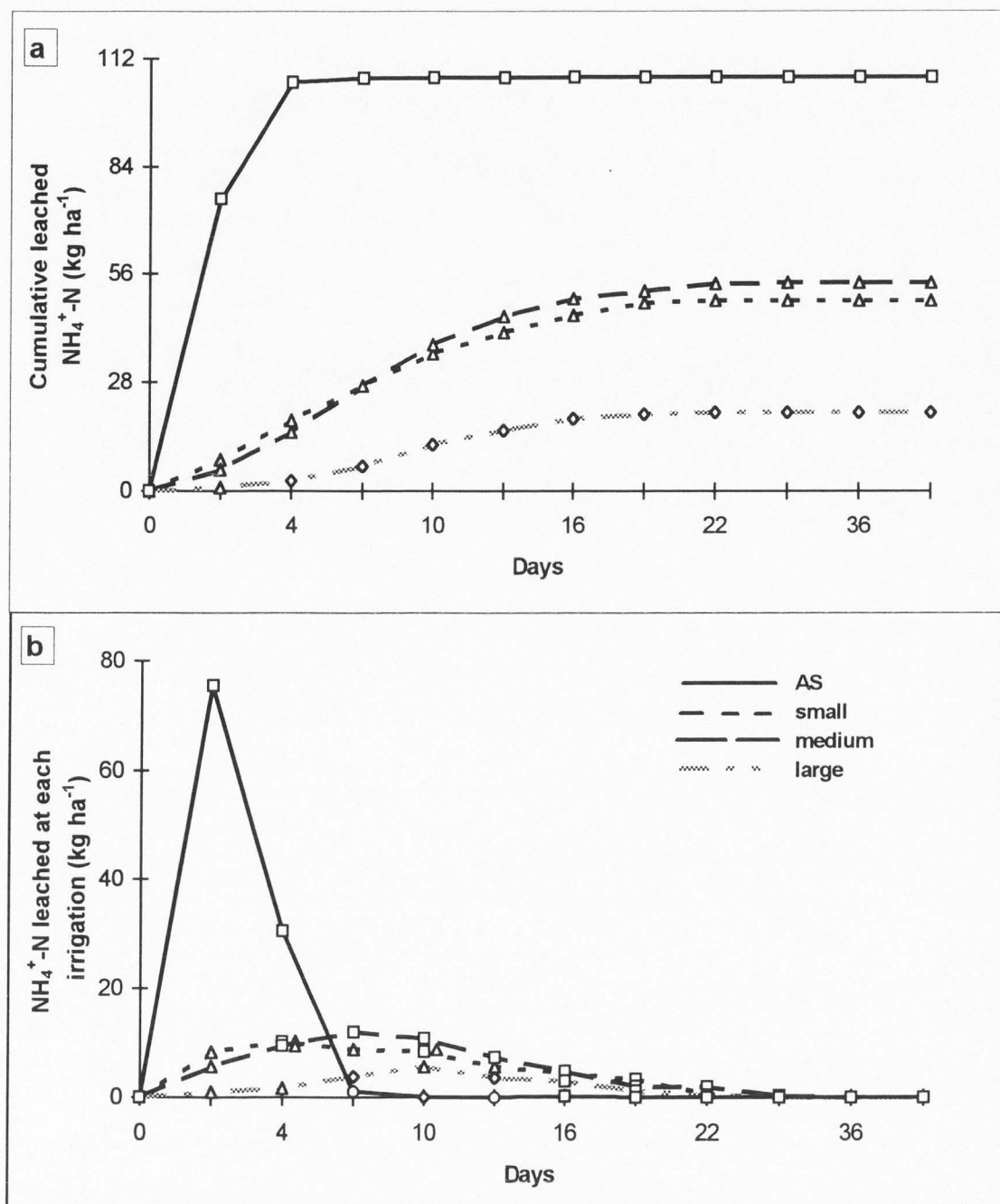


Fig. 1. Cumulative (a) and actual (b) kilograms of NH_4^+ -N that leached at each irrigation from the quartz sand amended with 112 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and NH_4^+ -Cp (small, medium, or large). Different symbols (\square \triangle \diamond \circ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix B for ANOVA tables.

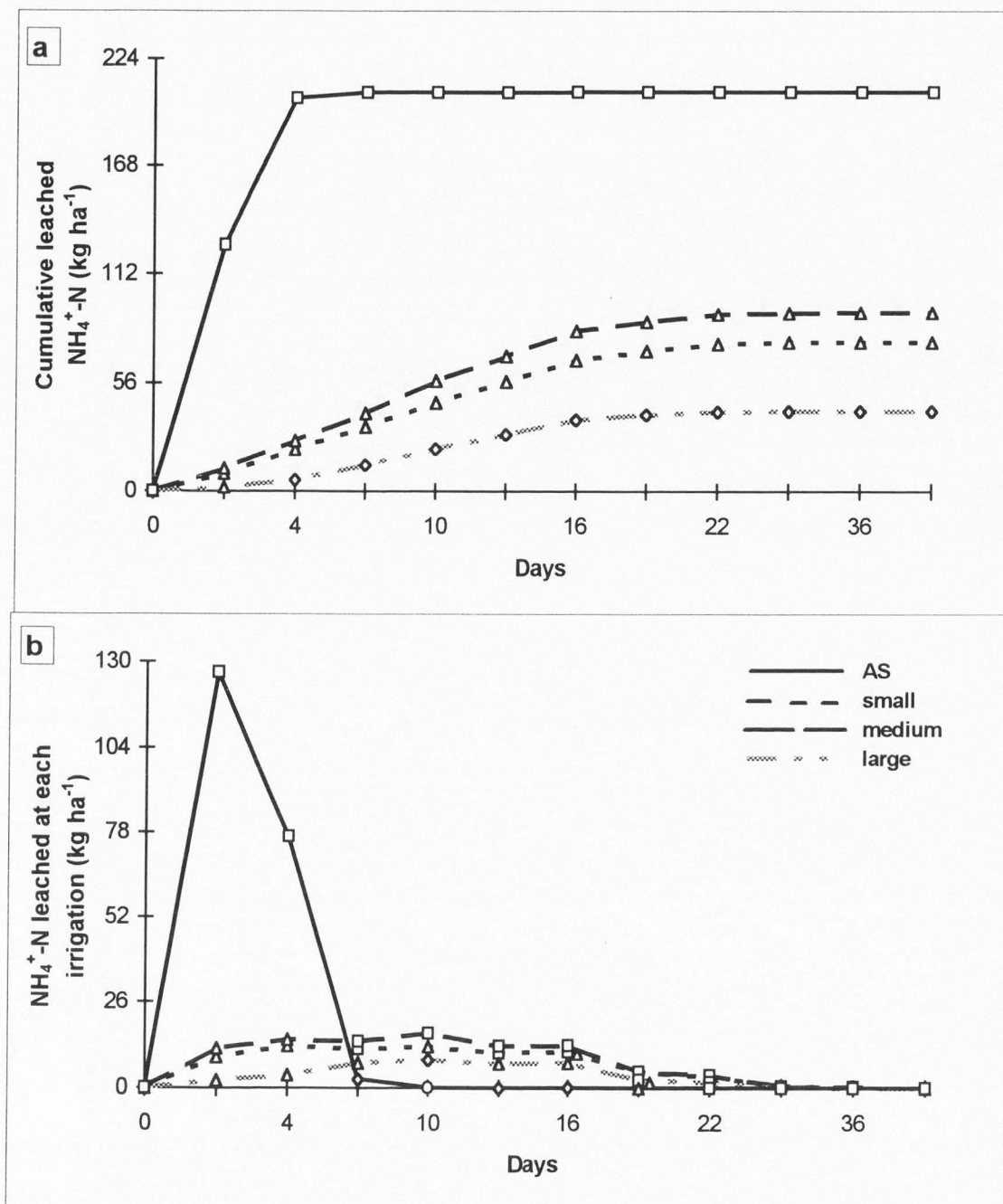


Fig. 2. Cumulative (a) and actual (b) kilograms of $\text{NH}_4^+\text{-N}$ that leached at each irrigation from the quartz sand amended with 224 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4^+\text{-Cp}$ (small, medium, or large). Different symbols (\square \triangle \diamond \circ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix B for ANOVA tables.

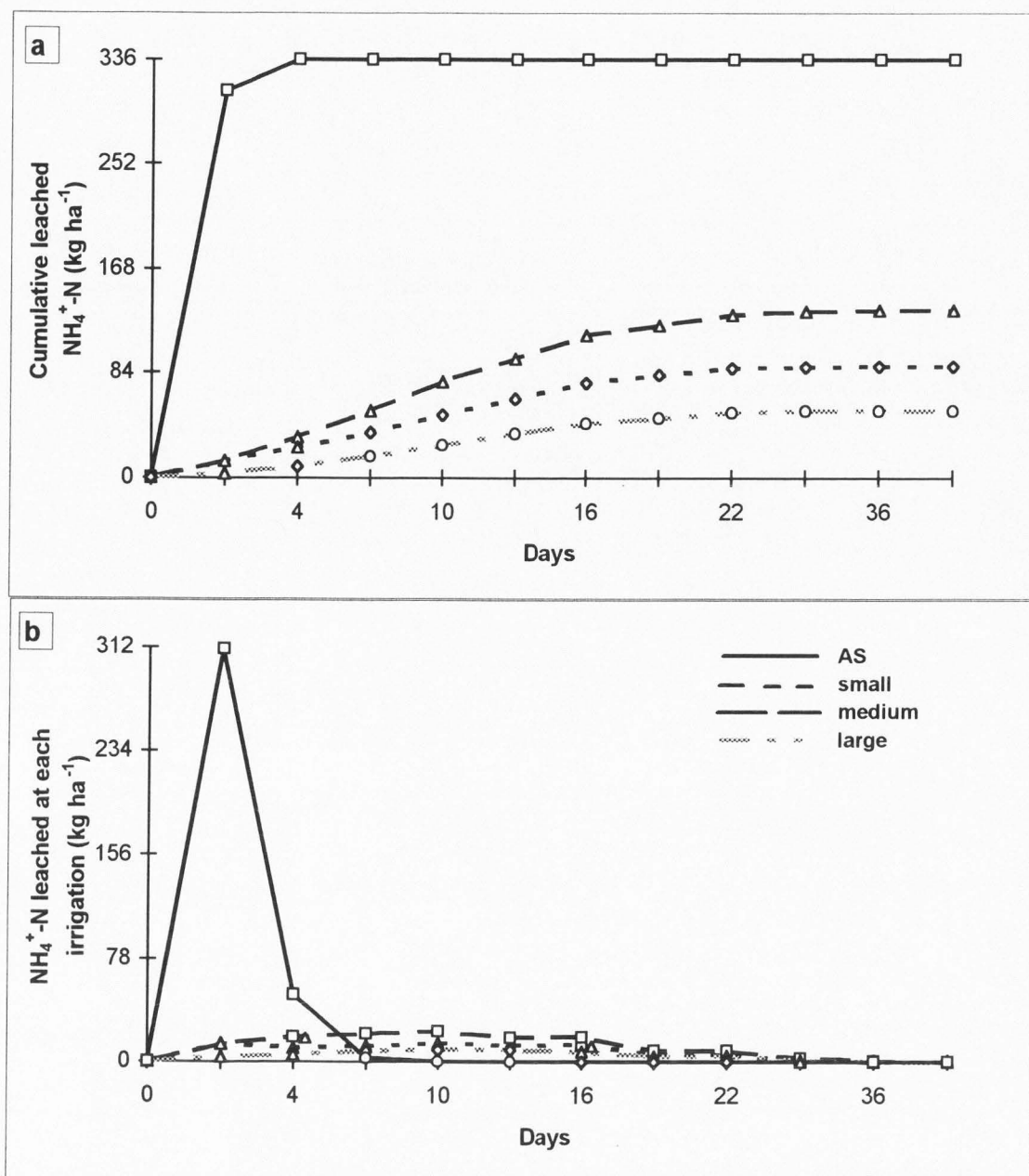


Fig. 3. Cumulative (a) and actual (b) kilograms of NH_4^+ -N that leached at each irrigation from the quartz sand amended with 336 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and NH_4^+ -Cp (small, medium, or large). Different symbols (\square \triangle \diamond \circ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix B for ANOVA tables.

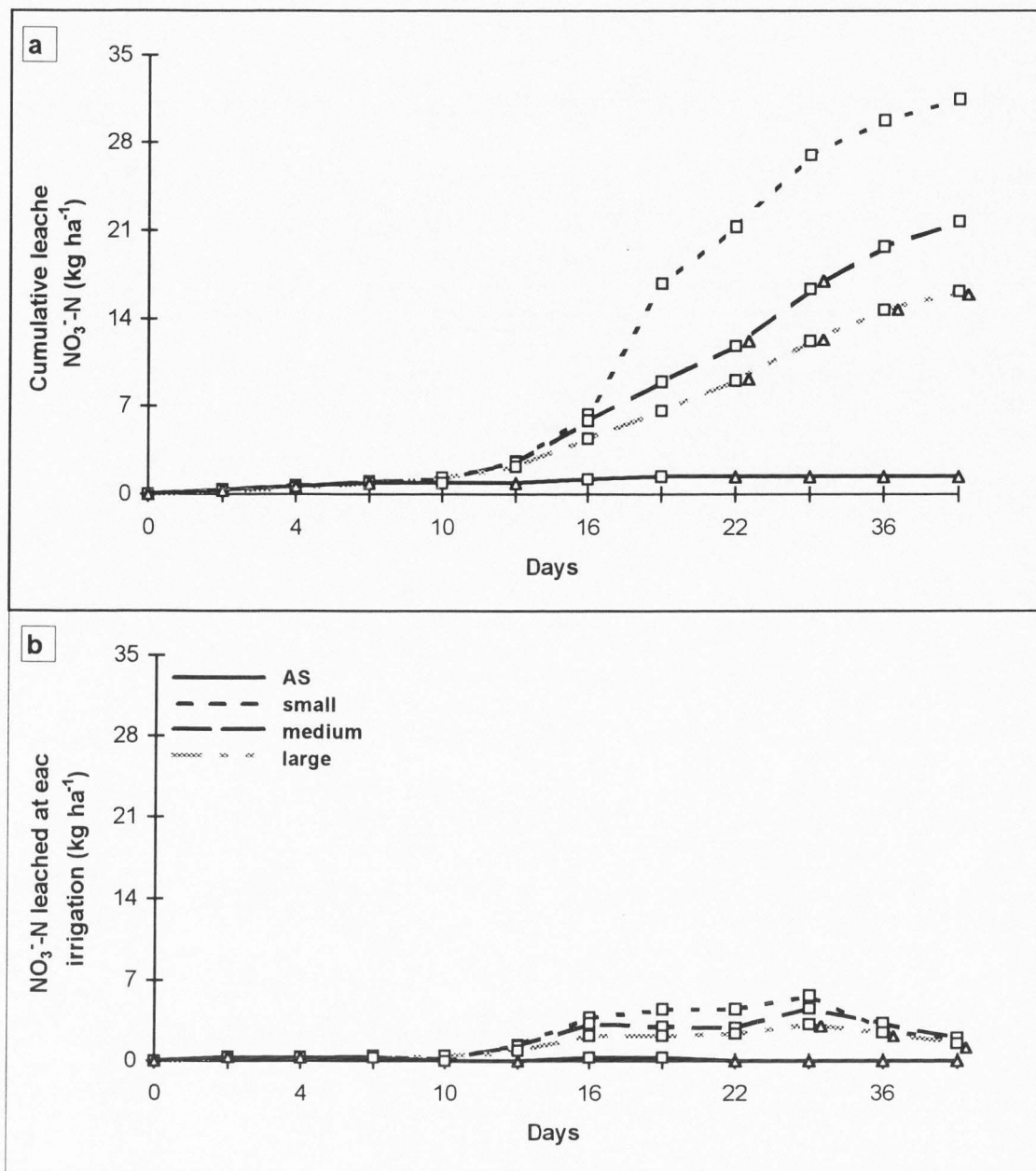


Fig. 4. Cumulative (a) and actual (b) kilograms of $\text{NO}_3^- \text{-N}$ that leached at each irrigation from the quartz sand amended with 112 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4^+ \text{-Cp}$ (small, medium, or large). Different symbols (\square Δ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix C for ANOVA tables.

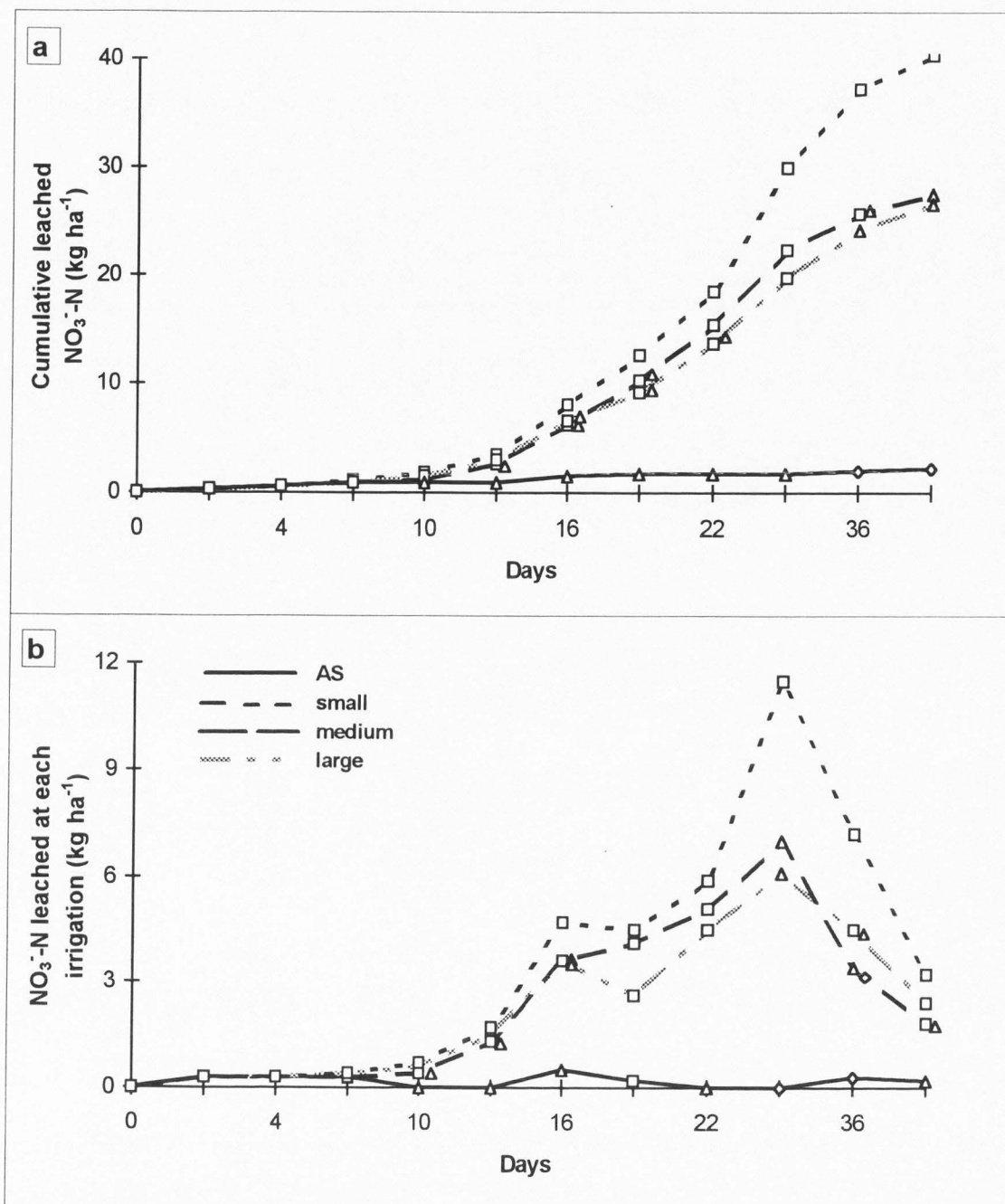


Fig. 5. Cumulative (a) and actual (b) kilograms of $\text{NO}_3\text{-N}$ that leached at each irrigation from the quartz sand amended with 224 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4\text{-Cp}$ (small, medium, or large). Different symbols (\square \triangle \diamond) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix C for ANOVA tables.

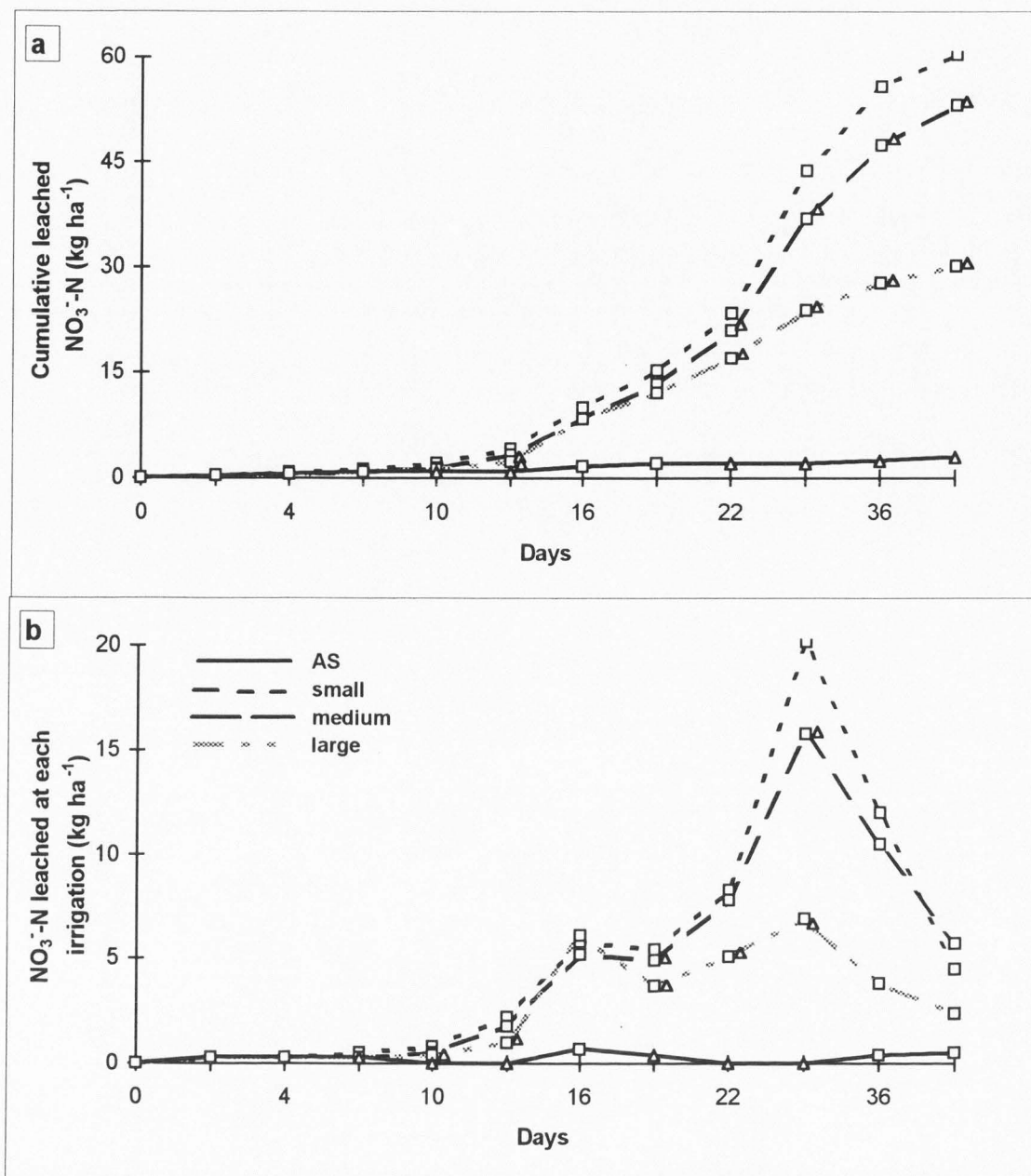


Fig. 6. Cumulative (a) and actual (b) kilograms of $\text{NO}_3^- \text{-N}$ that leached at each irrigation from the quartz sand amended with 336 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4^+ \text{-Cp}$ (small, medium, or large). Different symbols (\square Δ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix C for ANOVA tables.

and then leveled until 22 d before increasing again. (The NO_3^- leaching rates probably leveled as the kinetics of nitrification and the irrigation interval equilibrated, i.e., the bacteria could only nitrify so much NH_4^+ before it was leached by the next irrigation.) The increase of NO_3^- -N leaching after 22 d coincided with the irrigation interval change from 3 d to 7 d. With more time between irrigations, the nitrifying bacteria were able to nitrify more of the NH_4^+ that diffused to the Cp's external surface (Allen et al., 1995). The decreased rate of NO_3^- -N leaching after 29 d is probably due to the lower amount of water leached through the quartz sand. These speculations, though, are based on the assumption that the nitrifying bacteria have colonized on the Cp surface. This would indicate that nitrifying bacteria, even though they do not have access to the internal channels of Cp, can influence the form of N released from NH_4^+ -Cp to the soil solution. J.M. Norton (unpublished data from pure culture experiments, personal communication, 1996) supports the plausibility of nitrifying bacteria colonizing on the Cp's external surface.

In terms of total inorganic N ($\text{NH}_4^+ + \text{NO}_3^-$), 97%, 93%, and 102% of the added $(\text{NH}_4)_2\text{SO}_4$ -N leached from the quartz sand amended with 112 (Fig. 7), 224 (Fig. 8), and 336 (Fig. 9) kg N ha^{-1} , respectively. The overestimation for N leached from the 336 kg N ha^{-1} is likely due to a dilution error because several dilutions were required for the NH_4^+ analysis. In contrast, the NH_4^+ -Cp size fractions leached significantly less N (Fig. 7, 8, and 9). The quartz sand amended with the 1) small NH_4^+ -Cp leached 72%, 52%, and 44%, 2) medium NH_4^+ -Cp leached 68%, 54%, and 56%, and 3) large NH_4^+ -Cp leached 32%, 30%, and 25% from the 112, 224, and 336 kg N ha^{-1} , respectively. Although the N release curves (Fig. 7b, 8b, and 9b) for the NH_4^+ -Cp size fractions appear fairly uniform, based on the leached NH_4^+ and NO_3^- , a plant root in this system would be exposed to final $\text{NH}_4^+/\text{NO}_3^-$ ratios of 1.6:1, 2.7:1, and 1.5:1 for the small, medium, and large NH_4^+ -Cp sizes, respectively. In reality the plants would be primarily exposed to NH_4^+ for the first 22 d and then NO_3^- for the next 16 d. However, longer irrigation intervals and smaller water volumes applied at each irrigation may have decreased this $\text{NH}_4^+/\text{NO}_3^-$ ratio. Longer irrigation intervals would probably allow nitrifying bacteria more time to nitrify NH_4^+ before it is leached. Irrigation with a smaller water volume would probably

decrease the amount of NH_4^+ leached. Consequently, nitrifying bacteria, upon colonizing on the NH_4^+ -Cp surface, will potentially nitrify more of the remaining NH_4^+ as it is released from the NH_4^+ -Cp. The $\text{NH}_4^+/\text{NO}_3^-$ ratio that plant roots are exposed to is important for three reasons. First, plants adapted to acidic soils appear to have a preference for NH_4^+ (Ismunadji and Dijkshoorn, 1971). In contrast, plants adapted to calcareous soil utilize NO_3^- well (Kirby, 1967). As a rule, highest growth rates and yield are achieved via a combination of NH_4^+ and NO_3^- (Marschner, 1995). Second, the $\text{NH}_4^+/\text{NO}_3^-$ ratio can influence plant nutrition because the uptake of NH_4^+ will decrease the rhizosphere's pH and the uptake of NO_3^- will increase the rhizosphere's pH (Marschner, 1995). In calcareous soils, the supply of NH_4^+ can increase the plant's uptake of phosphorus (Gahoonia et al., 1992), as well as boron (Reynolds et al., 1987), iron, manganese, and zinc (Marschner, 1995). Conversely, phosphorus uptake can be enhanced in acid soils by NO_3^- uptake (Gahoonia et al., 1992). Third, high NH_4^+ concentrations can inhibit the uptake of K^+ , and, more particularly, Ca^{++} and Mg^{++} due to competition (Marschner, 1995). For carefully fertilized horticulture systems, this discussion of the $\text{NH}_4^+/\text{NO}_3^-$ ratio has practical application (Rupp, 1989) and emphasizes the need for more research on the primary location of nitrification in Cp systems. If nitrification primarily takes place on the NH_4^+ -Cp, the $\text{NH}_4^+/\text{NO}_3^-$ ratio may be somewhat manipulated by adjusting water volume, irrigation frequency, and the water chemistry. In a sense, this would give a horticulturist some control over how much NH_4^+ the nitrifying bacteria may metabolize. As a result, a preferential $\text{NH}_4^+/\text{NO}_3^-$ ratio for a certain crop may be applied, optimizing yield. However, if nitrification takes place primarily within the soil, then the amount of NH_4^+ released can be controlled by adjusting water volume, irrigation frequency, and, potentially, the water chemistry (which would be an asset by itself because plants take up N at different rates depending upon their phase of growth). This influence of water volume (which is most likely directly related to the watering solution composition) and irrigation frequency on the $\text{NH}_4^+/\text{NO}_3^-$ ratio is an area that needs more study. And although possible, the practicality and application of this technology would have to outweigh the convenience and ease of applying a preferred, pre-mixed $\text{NH}_4^+/\text{NO}_3^-$ ratio in the irrigation water.

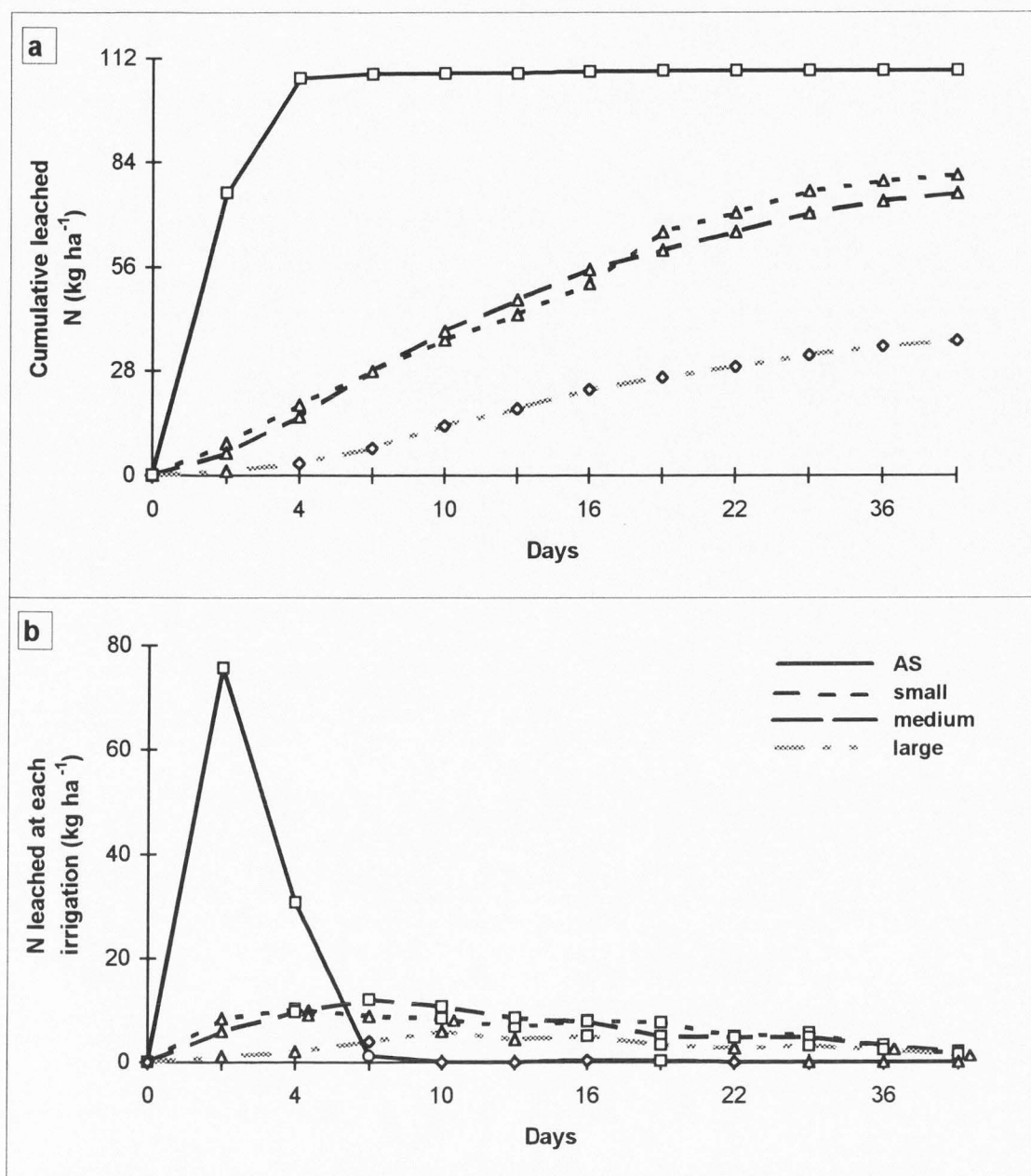


Fig. 7. Cumulative (a) and actual (b) kilograms of the total N ($\text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$) that leached at each irrigation from the quartz sand amended with 112 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4^+\text{-Cp}$ (small, medium, or large). Different symbols (\square \triangle \diamond \circ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix D for ANOVA tables.

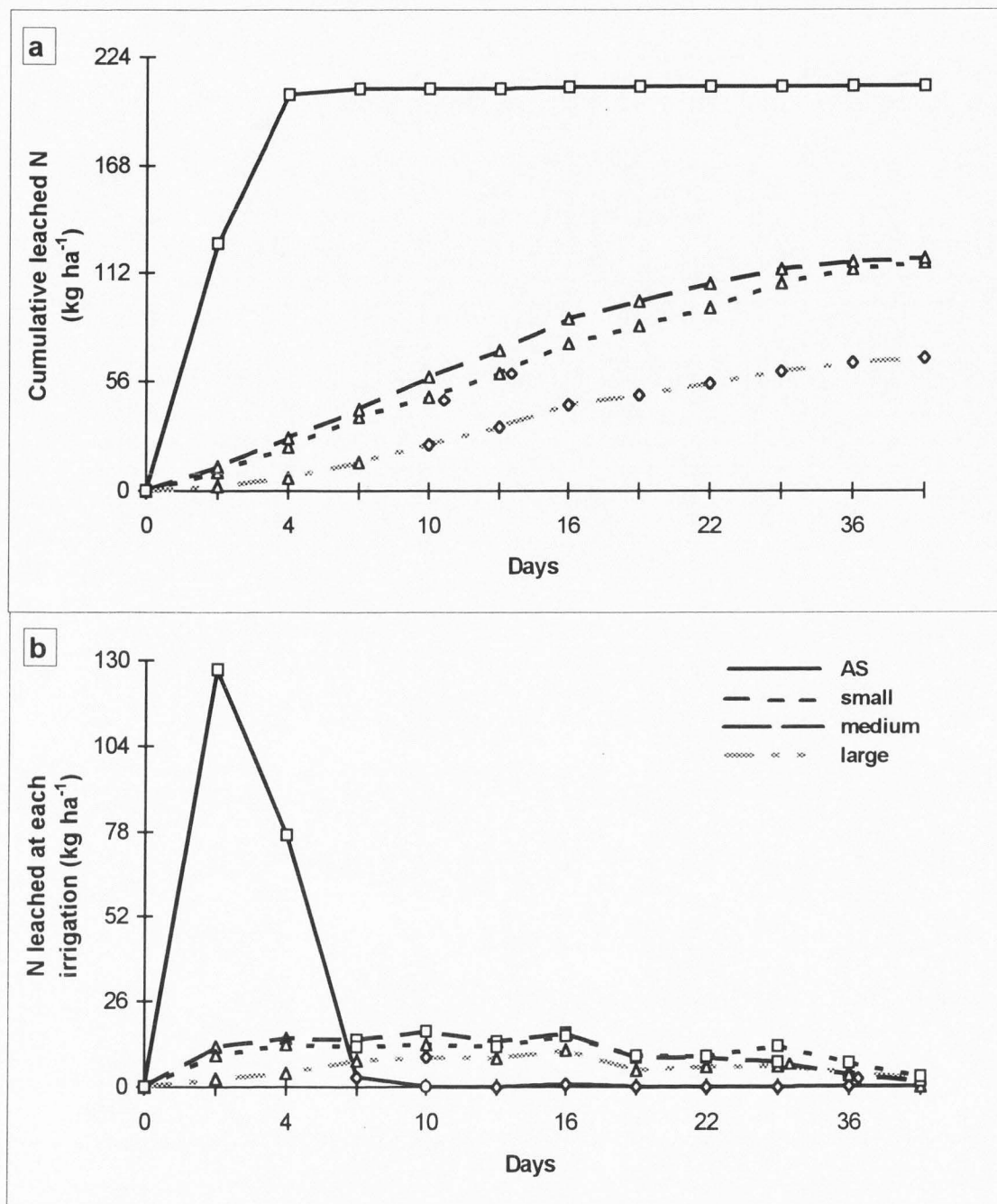


Fig. 8. Cumulative (a) and actual (b) kilograms of the total N ($\text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$) that leached at each irrigation from the quartz sand amended with 224 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4^+\text{-Cp}$ (small, medium, or large). Different symbols (\square \triangle \diamond \circ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix D for ANOVA tables.

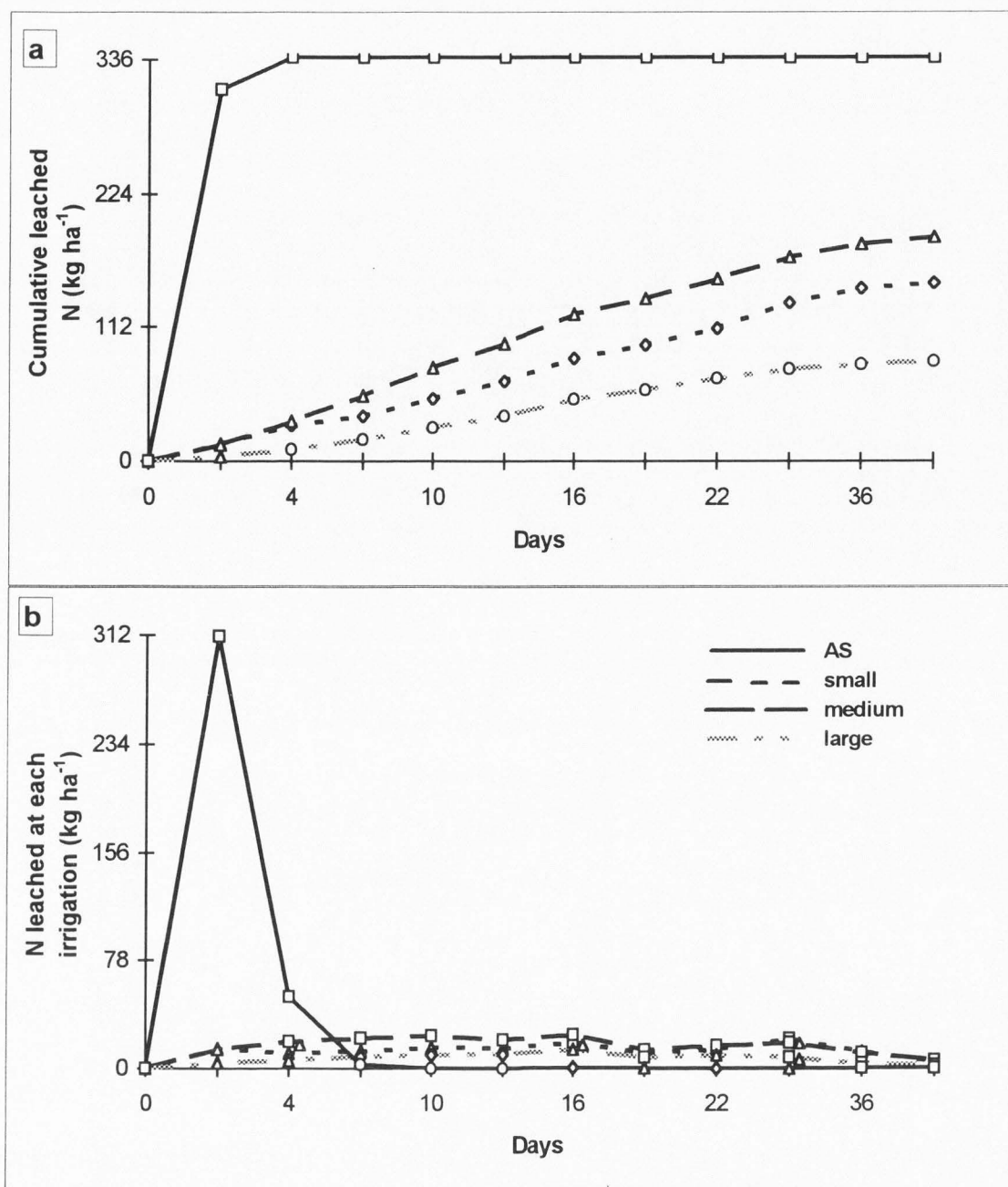


Fig. 9. Cumulative (a) and actual (b) kilograms of the total N ($\text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$) that leached at each irrigation from the quartz sand amended with 336 kg N ha^{-1} . Nitrogen fertilizers were $(\text{NH}_4)_2\text{SO}_4$ (AS) and $\text{NH}_4^+\text{-Cp}$ (small, medium, or large). Different symbols (\square \triangle \diamond \circ) at each irrigation date are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix D for ANOVA tables.

NH₄⁺-Cp Size Fractions

The NH₄⁺ leached differently from the NH₄⁺-Cp size fractions than hypothesized. The smallest size fraction was expected to leach more NH₄⁺ than the medium or large size fraction due to 1) a higher external surface area:mass ratio and 2) shorter diffusion channels. Banding instead of mixing the NH₄⁺-Cp throughout the quartz sand may explain this discrepancy. The aggregate nature of the banded small NH₄⁺-Cp size fraction resulted in greater tortuosity (compared to the medium and large sizes), which increased the chance for released NH₄⁺ to re-adsorb to Cp. However, this is only speculative. Another possible reason is water flow restrictions through the banded NH₄⁺-Cp size fractions. The small size fraction contained clay- and silt-sized NH₄⁺-Cp while the medium and large NH₄⁺-Cp did not have any clay- or silt-sized particles. As a result, less water probably passed through the small size fraction, leaching less NH₄⁺. Had the NH₄⁺-Cp been mixed throughout the quartz sand instead of banded, more NH₄⁺ may have leached from the smallest NH₄⁺-Cp size fraction than the medium or large NH₄⁺-Cp size fractions.

The increased tortuosity of the small NH₄⁺-Cp size fraction did not appear to affect the NO₃⁻ leaching. This is because NO₃⁻ is an anion and will not re-adsorb to Cp. Consequently, the smaller the size fraction, the more NO₃⁻-N that was leached. Because the small size fraction had greater external surface-area-to-mass ratio, it could support more nitrifying bacteria per gram of Cp than the medium or large size fraction. Thus more NH₄⁺ could be nitrified. Also, because the small size fraction had shorter diffusion channels, more NH₄⁺ could diffuse to the Cp's surface where it was available to the nitrifying bacteria. MacKown (1978) noted this trend in leaching experiments where nitrification rates increased as the NH₄⁺-Cp size fractions decreased from the large (1 to 2 mm) to the small (0.30 to 0.85 mm) size fraction.

N Budget

The N recovered from the KCl extraction of the quartz sand was added to the N collected from the leachate in an effort to account for all the added N. The N recovered from the NH₄⁺-Cp strongly correlated ($r^2=0.97$) to size fractions: More N was recovered from the NH₄⁺-Cp as the size

increased (Fig. 10). This supports the hypothesis that the smaller NH_4^+ -Cp size fractions release N faster than larger NH_4^+ -Cp size fractions. Nitrogen recovered from NH_4^+ -Cp also increased as the N rate increased.

Almost all of the added N was recovered from the $(\text{NH}_4)_2\text{SO}_4$ amendments. The total N recovered from the NH_4^+ -Cp fertilizer however were lower than expected (Table 3). The total N recovered from the small, medium, and large NH_4^+ -Cp amendments averaged from 60 to 80%, depending on the size and N rate.

One reason for the low recovery of the added N via NH_4^+ -Cp is NH_3 volatilization. The irrigation water had a pH of 8.1. At this pH, about 15% of the NH_4^+ exists in solution as NH_3 , and is susceptible to volatilization (Tisdale et al., 1993). And, because Ca^{++} , HCO_3^- , and SO_4^{--} were present in the irrigation water, the potential for volatilization was high. Ammonium in the soil solution associates with SO_4^{--} or HCO_3^- . Because this soil solution contained Ca^{++} , ammonium's association was primarily limited to HCO_3^- because Ca^{++} and SO_4^{--} forms a relatively insoluble precipitate called gypsum (CaSO_4), and a white precipitate assumed to be gypsum was found in the leachate containers.

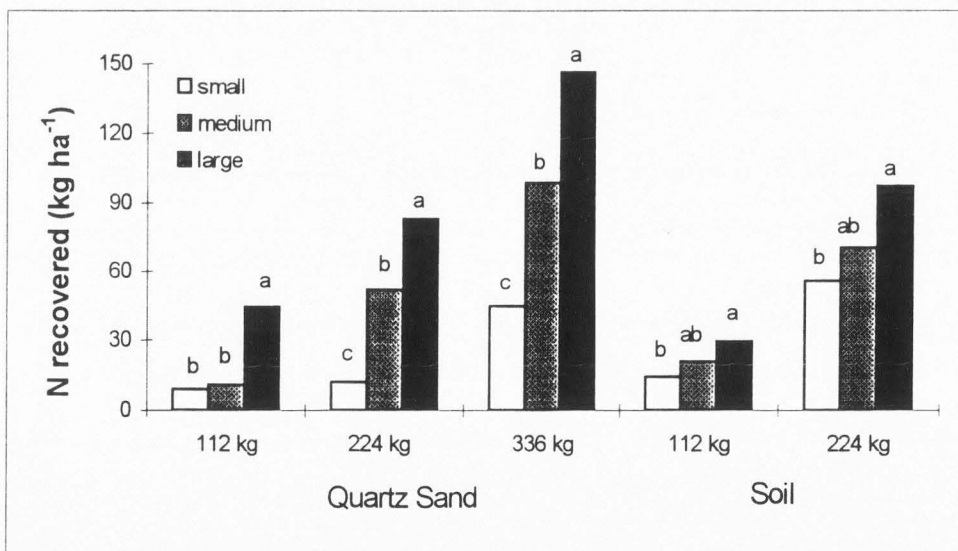


Fig. 10. Kilograms of N recovered from the small, medium, and large NH_4^+ -Cp size fractions which were extracted from the quartz sand and soil. Different letters within each experiment and each rate are significant ($p < 0.05$) according to Tukey's test. Refer to Appendix E for ANOVA tables.

Table 3. Kilograms of N recovered from the quartz sand and field soil leaching experiments. Refer to Appendix E for ANOVA tables.

experiment	fertilizer	rate	Cp N	leached N	soil N	total N	total N
			kg N				%
quartz sand	small NH ₄ -Cp	112	9.2 b [†]	80.7 b	nd [‡]	89.9 ab	80.3
	medium NH ₄ -Cp	112	11.1 b	75.6 b	nd	86.7 ab	77.4
	large NH ₄ -Cp	112	44.4 a	36.4 c	nd	80.8 b	72.1
	(NH ₄) ₂ SO ₄	112	na [§]	108.6 a	nd	108.6 a	97.0
	small NH ₄ -Cp	224	12.2 c	117.3 b	nd	129.6 b	57.8
	medium NH ₄ -Cp	224	51.9 b	119.7 b	nd	171.6 ab	76.6
	large NH ₄ -Cp	224	83.1 a	68.4 c	nd	151.5 b	67.6
	(NH ₄) ₂ SO ₄	224	na	209.1 a	nd	209.0 a	93.3
	small NH ₄ -Cp	336	44.7 c	149.1 b	nd	193.7 c	57.6
	medium NH ₄ -Cp	336	98.9 b	187.9 b	nd	286.7 b	85.3
	large NH ₄ -Cp	336	146.3 a	83.7 c	nd	229.9 bc	68.4
	(NH ₄) ₂ SO ₄	336	na	345.0 a	nd	345.0 a	100.0
soil	small NH ₄ -Cp	112	14.5 b	13.4 a	1.8 a	29.7 a	26.5
	medium NH ₄ -Cp	112	20.8 ab	11.9 a	3.1 a	34.7 a	30.1
	large NH ₄ -Cp	112	29.7 a	19.4 a	2.4 a	51.4 a	45.9
	(NH ₄) ₂ SO ₄	112	na	48.3 a	3.1 a	51.4 a	45.9
	small NH ₄ -Cp	224	55.9 b	24.0 b	2.9 a	82.8 c	37.0
	medium NH ₄ -Cp	224	70.2 ab	25.4 b	2.7 a	98.3 bc	43.9
	large NH ₄ -Cp	224	97.3 a	19.8 b	3.9 a	121.0 ab	54.0
	(NH ₄) ₂ SO ₄	224	na	145.0 a	4.5 a	139.1 a	62.1

† Different letters after each number within each column and each rate are significant according to Tukey's test (p<0.05).

‡ nd=not determined.

§ na=not applicable.

As a result, NH_4^+ associates with HCO_3^- and the products NH_3 , CO_2 , and H_2O are formed. Loss of any NH_3 will result in the production of more NH_3 until the system is in equilibrium again. Over time, this can result in N loss of 10 to 70% (Ismail et al., 1991; Tisdale et al., 1993). Besides the potential of NH_3 volatilization during the experiment, some NH_3 volatilization was expected in the 2M KCl extraction procedure, which was performed to recover NH_4^+ from the NH_4^+ -Cp at the end of the experiment. Instead of freezing the samples after the extraction, the samples were erroneously left in the lab for 10 d at room temperature. During this period, the 2M KCl solution's pH changed from approximately 5.3 to 8.8. However, the NH_3 volatilized from this procedure was probably not as great as the NH_3 volatilized during the experiment because 1) no insoluble Ca^{++} precipitates were formed in the extracts and 2) unlike the leaching columns, the containers of the extracts were closed, preventing high losses of NH_3 . The $(\text{NH}_4)_2\text{SO}_4$ fertilizer was not as affected by NH_3 volatilization because all the added N was essentially leached from the $(\text{NH}_4)_2\text{SO}_4$ fertilizer after two irrigations.

Another possible reason for low N recovery is denitrification because NO_3^- was measured in the leachate. This is most applicable for the small NH_4^+ -Cp size fraction, which had banded silt- and clay-sized particles. At each irrigation, these particles would re-wet, creating potential anaerobic zones in or next to the banded fertilizer. Nitrate, an electron acceptor for some anaerobic bacteria, would be reduced to a gas such as N_2 or N_2O and lost to the atmosphere.

N Leaching from Soil Amended with NH_4^+ -Cp

The leaching study with the syringes containing Green River soil had unexpected poor drainage and water logging because of small drain holes. The results are therefore uncertain and are placed in Appendix I. Only the data from the 6-L pots will be discussed here.

Ammonium and Nitrate Leaching

More N was leached from the soil amended with $(\text{NH}_4)_2\text{SO}_4$ than the soil amended with NH_4^+ -Cp. For all N amendments, as N rates increased, the kilograms of N leached also increased.

Three and 18% of the added $(\text{NH}_4)_2\text{SO}_4$ -N leached as NH_4^+ -N from the 112 and 224 kg N ha^{-1} , respectively. Most of the NH_4^+ leached from the $(\text{NH}_4)_2\text{SO}_4$ fertilizer by 20 d, suggesting that NH_4^+ , although a cation, was mobile in this sandy soil. In contrast, <0.7% of the added N leached as NH_4^+ -N from the NH_4^+ -Cp size fractions for the 112 and 224 kg ha^{-1} (Fig. 11a and 11b). Also, differences in NH_4^+ leaching between size fractions were not significantly different. This indicates that NH_4^+ -Cp reduces NH_4^+ leaching better than the $(\text{NH}_4)_2\text{SO}_4$ treatments. It also suggests that NH_4^+ -Cp size fractions may not be an important factor in NH_4^+ leaching in this soil. This contrasts the previous quartz sand leaching experiment and is probably due to the increased CEC of the soil, which reduced and masked any leaching differences between the NH_4^+ -Cp sizes.

Significantly more NO_3^- -N was leached from the $(\text{NH}_4)_2\text{SO}_4$ fertilizer than from the NH_4^+ -Cp fertilizers (Fig. 12). Forty-one and 46% of the added $(\text{NH}_4)_2\text{SO}_4$ -N leached as NO_3^- -N for the 112 and 224 kg N ha^{-1} , respectively. In contrast, <18 and <11% of the added N leached as NO_3^- -N from all the NH_4^+ -Cp size fractions for the 112 and 224 kg N ha^{-1} , respectively. No significant differences were found between the NH_4^+ -Cp size fractions, suggesting that Cp particle size did not influence NO_3^- -N leaching from this soil. Nitrate began leaching around 17 d (Fig. 12b), 7 d later than quartz sand experiment and probably due to the increased leaching depth of the soil. Had this soil been under cultivation with high populations of nitrifying bacteria, NO_3^- leaching would have probably started sooner.

The low amount of NO_3^- that leached from the NH_4^+ -Cp size fractions indicates that food and fiber producers will decrease N lost via NO_3^- leaching with NH_4^+ -Cp instead of using $(\text{NH}_4)_2\text{SO}_4$. Many farmers, because of NO_3^- leaching, try to apply an NH_4^+ -based fertilizer to reduce N loss. They also try to incorporate the NH_4^+ -based fertilizer to decrease volatilization (Ismail et al., 1991). Because NH_4^+ is primarily found on the internal exchange sites of the NH_4^+ -Cp, NH_4^+ -Cp may increase N use-efficiency because 1) NH_4^+ is protected from nitrifying bacteria and 2) until the NH_4^+ is released into the soil solution via a cation exchange reaction, the NH_4^+ is not susceptible to volatilization reactions found in alkaline environments.

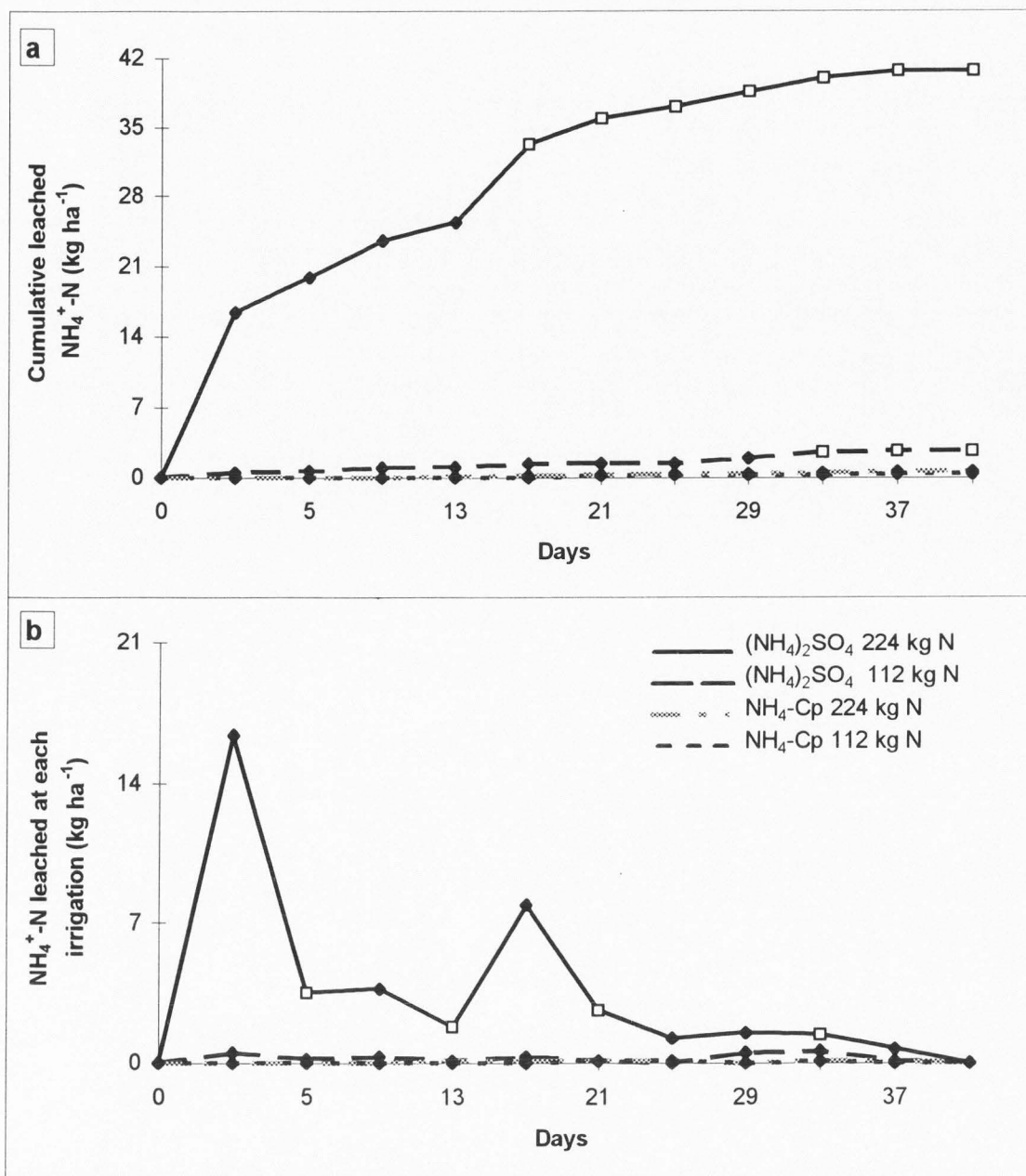


Fig. 11. Cumulative (a) and actual (b) kilograms of $\text{NH}_4^+\text{-N}$ that leached at each irrigation from the soil amended with 112 and 224 kg N ha^{-1} . The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the $\text{NH}_4^+\text{-Cp}$ size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix F for ANOVA tables.

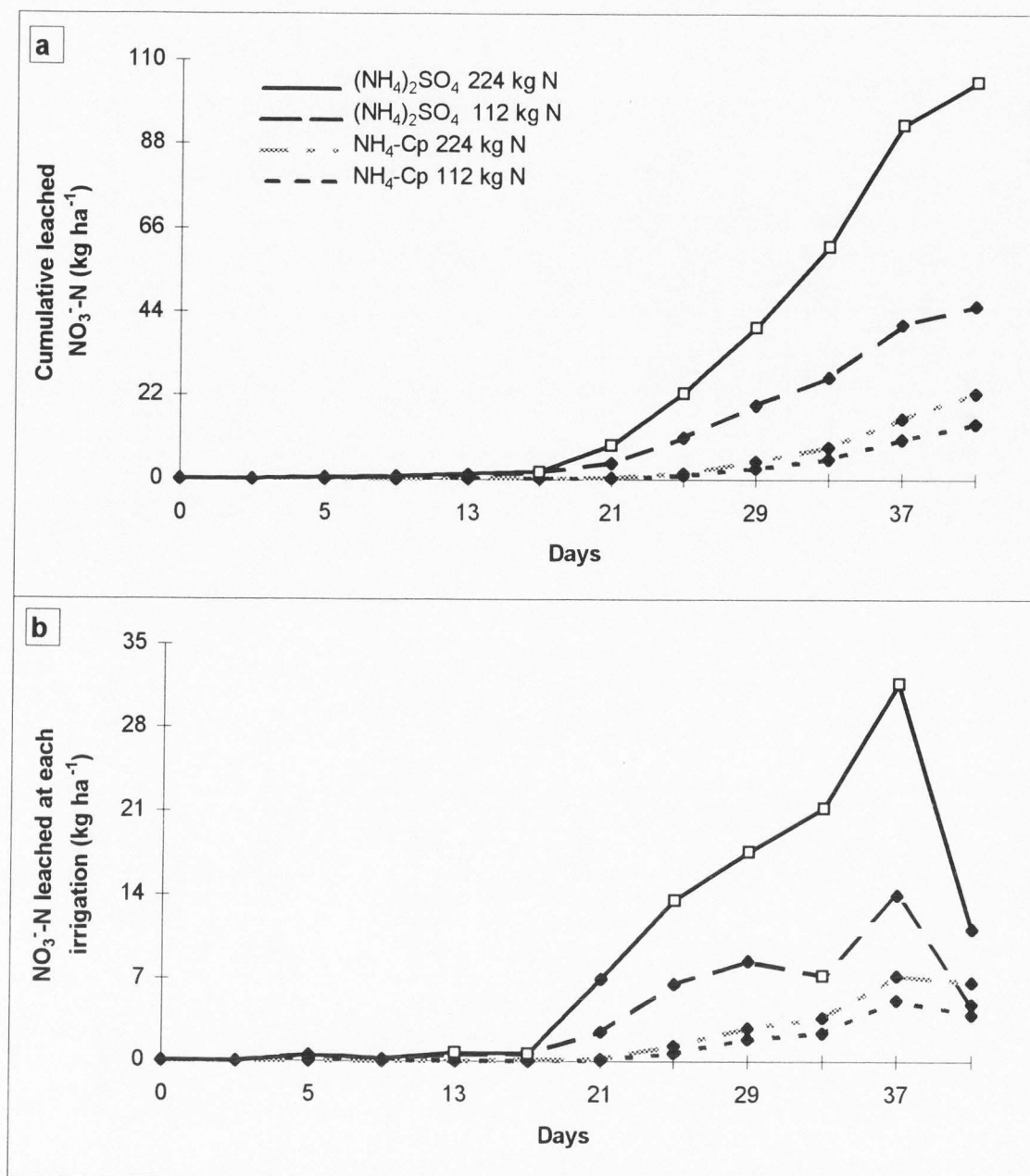


Fig. 12. Cumulative (a) and actual (b) kilograms of $\text{NO}_3\text{-N}$ that leached at each irrigation from the soil amended with 112 and 224 kg N ha^{-1} . The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the $\text{NH}_4\text{-Cp}$ size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix G for ANOVA tables.

In terms of the total N (NH_4^+ and NO_3^-), 43 and 65% of the added $(\text{NH}_4)_2\text{SO}_4$ -N leached from the 112 and 224 kg N ha^{-1} , respectively (Fig. 13). On the other hand, 18 and 11% of the added N leached from the NH_4^+ -Cp fertilizers for the 112 and 224 kg N ha^{-1} , respectively. This indicates that NH_4^+ -Cp reduces N losses due to leaching better than the $(\text{NH}_4)_2\text{SO}_4$. The N that leached from the soil amended with NH_4^+ -Cp started at 24 d, whereas the soil amended with $(\text{NH}_4)_2\text{SO}_4$ began leaching N almost immediately. Apparently the NH_4^+ -Cp released NH_4^+ slowly enough that it was retained on exchange sites until it was nitrified and leached.

Because most of the N leached as NO_3^- from the soil amended with NH_4^+ -Cp, it appears that a plant in this soil would primarily be exposed to NO_3^- ($\text{NH}_4^+/\text{NO}_3^-$ ratio was greater than 1:20). This contrasts the quartz sand experiment that leached a $\text{NH}_4^+/\text{NO}_3^-$ ratio of roughly 2:1. This difference in $\text{NH}_4^+/\text{NO}_3^-$ ratios indicates that increasing the irrigation volume may increase the $\text{NH}_4^+/\text{NO}_3^-$ ratio. (In the quartz sand experiment, 7 pore volumes were leached through the quartz sand whereas only 1 pore volume was leached through the soil). Fertilizer placement, although not studied here, is another factor that may influence the $\text{NH}_4^+/\text{NO}_3^-$ ratio. For example, broadcasting the NH_4^+ -Cp would appear to encourage a low $\text{NH}_4^+/\text{NO}_3^-$ ratio because nitrifying bacteria will probably nitrify the NH_4^+ before the plant root may incorporate it, whereas banding NH_4^+ -Cp may encourage a higher $\text{NH}_4^+/\text{NO}_3^-$ ratio because the fertilizer is placed next to the plant roots, and the plant may take up NH_4^+ before it is nitrified. Although not directly studied in these experiments, field irrigation water has a strong effect on the release of NH_4^+ from NH_4^+ -Cp. Hershey et al. (1980) observed this when cations from a modified Hoagland's solution appeared to exchange and release K^+ from a K^+ -rich Cp. This implies that the salinity or chemistry of the irrigation water will influence the release of NH_4^+ from NH_4^+ -Cp due to the cation exchange reactions that drive the release of NH_4^+ from NH_4^+ -Cp. The more saline the irrigation water, the greater the probability that NH_4^+ will be released from NH_4^+ -Cp. On the other hand, if the water's salinity is low, there is less chance that NH_4^+ will be released from NH_4^+ -Cp. For example, in the quartz sand experiment the small NH_4^+ -Cp size fraction released about 90% of the pre-

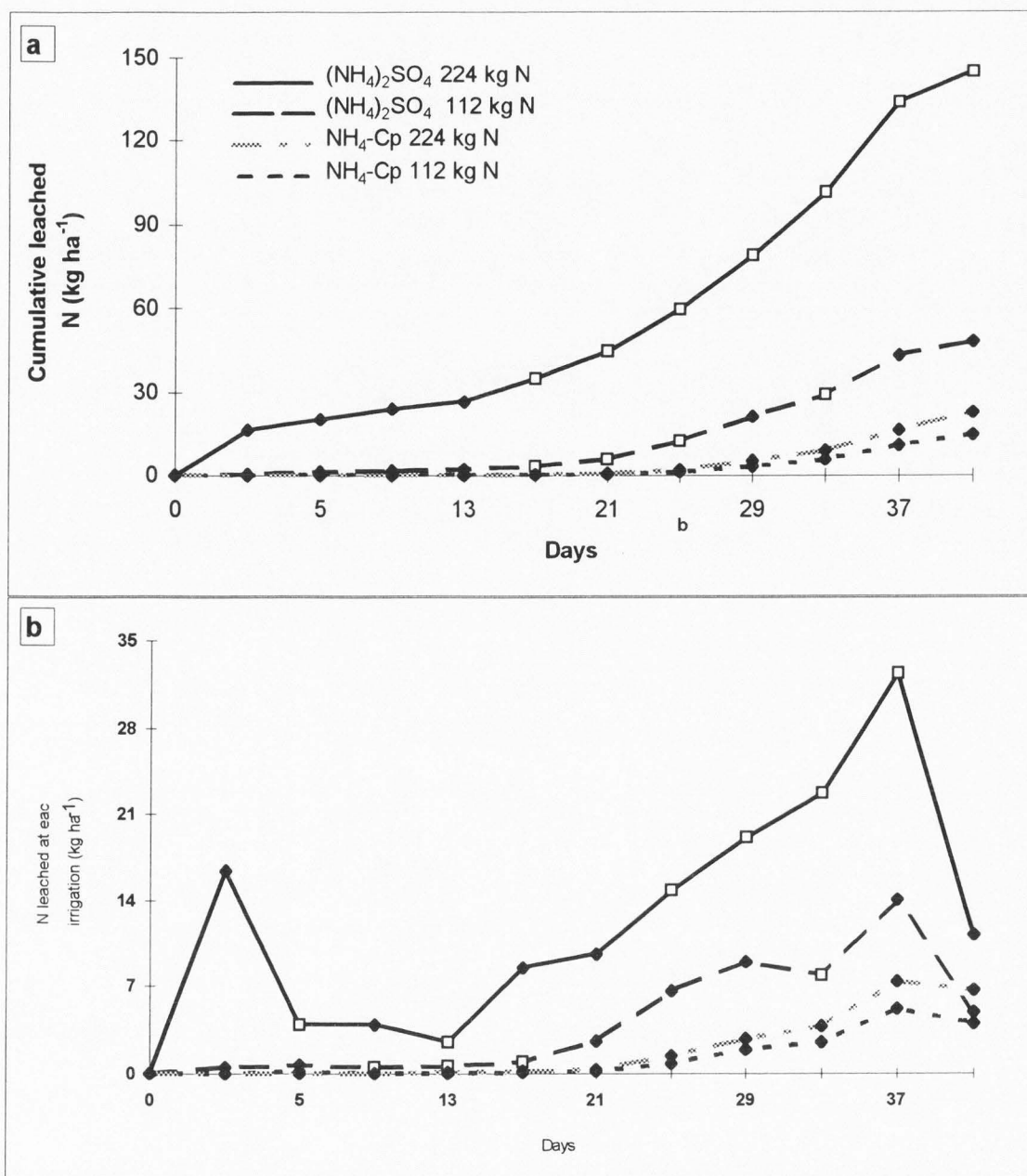


Fig. 13. Cumulative (a) and actual (b) kilograms of N ($\text{NH}_4^+ + \text{NO}_3^-$ -N) that leached at each irrigation from the soil amended with 112 and 224 kg N ha⁻¹. The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the NH_4^+ -Cp size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix H for ANOVA tables.

sorbed NH_4^+ in 43d, whereas Bartz and Jones (1983), irrigating with dH_2O on soil fertilized with the same NH_4^+ -Cp size fraction (<0.25 mm), suggested that NH_4^+ from NH_4^+ -Cp was available for 242 d. The type of cations that are in the irrigation water is also important because the cation selectivity of Cp is greater for monovalent cations than divalent cations (Ames, 1960; Goto and Ninaki, 1980; Ming and Mumpton, 1989). Consequently, irrigation water high in Na^+ or K^+ will probably replace NH_4^+ faster than an irrigation water whose primary cations are Ca^{++} or Mg^{++} .

NH_4^+ -Cp Size Fractions

No statistical differences in N leaching were found among the three NH_4^+ -Cp size fractions in the soil. These results contrast with the results in the rounded quartz sand leaching experiment, in which NH_4^+ -Cp size fractions influenced NH_4^+ and NO_3^- leaching ($p < 0.0001$). However, the soil's increased CEC; water holding capacity; increased soil depth; and potential immobilization, NH_3 volatilization, and denitrification probably masked any NH_4^+ and NO_3^- leaching differences between NH_4^+ -Cp size fractions.

N Budget

After the experiment, the remaining N found in the soil and NH_4^+ -Cp was estimated from each pot via Kjeldahl digestion. After subtracting the control soil values, the excess N was added to the leached N values of each pot and totaled for a N budget for all N amendments (Table 3). The soil N averaged about 2 to 4.5 kg of the added N for both rates. No statistical differences were observed among the four N fertilizers.

The remaining N on the NH_4^+ -Cp increased as the size and rate increased (Fig. 10). These values follow the same trend of N recovered from the NH_4^+ -Cp in the quartz sand leaching experiment.

The totaled recovered N was very low for all N amendments. The N recovered ranged from 27 to 45% of the 112 kg N ha^{-1} and 36 to 62% of the 224 kg N ha^{-1} . Incomplete N recovery was expected due to NH_3 volatilization because the soil solution had Ca^{++} and SO_4^{--} and the soil and irrigation water had a pH of 8.5 and 8.1, respectively. This large loss of N, though, was unexpected.

One reason for the large loss of N appears to be that ideal conditions existed for volatilization during the leaching study: warm soil temperatures and soil water content near field capacity (Tisdale et al., 1993). Under these conditions, N losses of 50 to 70% have been observed (Tisdale et al., 1993). Another reason is that any NO_3^- formed may have been denitrified under the moist, warm conditions, especially because the soils were near or above field capacity during the experiment. This may explain why the small NH_4^+ -Cp size (which contained banded silt and clay particles) had lower N recovery at the 112 kg N ha^{-1} and significantly lower N recovery at the 224 kg N ha^{-1} . The influence of N immobilization was probably minor, compared to volatilization and denitrification, because soil organic carbon levels were low (0.34%). Future experiments measuring gaseous losses of N could be helpful for establishing a more accurate N budget.

CONCLUSIONS

The quartz sand and soil amended with NH_4^+ -Cp leached less NH_4^+ -N and NO_3^- -N than did the quartz sand and soil amended with $(\text{NH}_4)_2\text{SO}_4$. In the quartz sand experiment, the quartz sand amended with NH_4^+ -Cp had a $\text{NH}_4^+/\text{NO}_3^-$ ratio of roughly 2:1, with the NH_4^+ -N primarily leaching during the first 22 d and the NO_3^- -N primarily leaching during the remaining 21 d. Although the final $\text{NH}_4^+/\text{NO}_3^-$ ratio was high, nitrifying bacteria appeared to colonize on the NH_4^+ -Cp and thereby strongly influenced the form of N released from NH_4^+ -Cp. In contrast, the soil leached (about 1 pore volume in 40 d) a $\text{NH}_4^+/\text{NO}_3^-$ ratio greater than 1:20. This suggests that in cultivated soils, especially those with high populations of nitrifying bacteria, the primary N form taken up by plant roots would be NO_3^- . The results also suggest that irrigation volume and irrigation intervals may influence the $\text{NH}_4^+/\text{NO}_3^-$ ratio.

The NH_4^+ -Cp size fractions influenced the rate of N released. This influence was best observed in the leachate from the syringes containing inert quartz sand: The larger the NH_4^+ -Cp size fraction, the slower N was released. Although the influence of different NH_4^+ -Cp size fractions on N release rates was not detected in the leachate from the soil, more N was recovered from the NH_4^+ -Cp

fertilizers as the size fractions became larger. This suggests that a combination of NH_4^+ -Cp size fractions should be applied in plant systems to ensure that N is available for an extended period.

Ammonium-Cp may be a slow-release N fertilizer if amended to soils with plants.

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CHAPTER 3

AMMONIUM-LOADED CLINOPTILOLITE: A SLOW-RELEASE NITROGEN FERTILIZER FOR SWEET CORN

ABSTRACT

Frequent water application is required for normal plant growth in sandy soils. Consequently, a portion of nitrogen (N) fertilizers is leached from the rooting zones of plants. This leaching increases N needs and the chance for nitrate (NO_3^-) contamination of water. Ammonium-loaded clinoptilolite (NH_4^+ -Cp) may reduce N leaching, increase N use-efficiency, and prevent NO_3^- contamination of water while supporting normal plant growth. Ammonium sulfate or one of three NH_4^+ -Cp size fractions, small (<0.25 mm), medium (0.25 to 2 mm), or large (2 to 4 mm), was banded in pots containing a sandy soil planted with 'Incredible' sweet corn. Relative growth rate (RGR), leaf area ratio (LAR), and net assimilation rates (NAR) were measured every week until 42 d. The $(\text{NH}_4)_2\text{SO}_4$ -N leached 18 to 48% of the added N (depending on N rate), whereas <3% of the added N leached from the NH_4^+ -Cp fertilizers. Although negligible differences between N fertilizers were observed in RGR, LAR, and NAR, the plants fertilized with NH_4^+ -Cp assimilated significantly more N than the plants fertilized with $(\text{NH}_4)_2\text{SO}_4$. Results indicate that NH_4^+ -Cp will decrease N leaching, and increase N use-efficiency while sustaining plant growth.

INTRODUCTION

The arid West has large areas of young, coarse-textured soils that require high amounts of irrigation water to sustain crop growth. Consequently, a large proportion of traditional nitrogen (N) fertilizer, such as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), is washed from the rooting zone of crops, especially after being nitrified. High losses of N due to leaching increases N fertilizer use and the potential for nitrate (NO_3^-) contamination of surface and groundwater, which is a growing concern, especially as population growth urbanizes agricultural lands. In order to save money from N loss due to leaching

and prevent NO_3^- contamination of water, farmers with sandy soils apply N in split applications, use slow-release fertilizers, and/or add soil conditioners such as organic matter to increase the soil's cation exchange capacity (CEC) and water holding capacity.

Ammonium-loaded clinoptilolite (NH_4^+ -Cp) may reduce the loss of nitrogen from the rooting zones of crops, decrease N fertilizer use, and reduce NO_3^- contamination of groundwater and surface water. Clinoptilolite (Cp) is a relatively abundant zeolite mineral that has a high cation exchange capacity (CEC), and an affinity for ammonium (NH_4^+) and potassium (K^+) (Ming and Mumpton, 1989). It is found in Texas, South Dakota, New Mexico, Wyoming, Idaho, California, Oregon, and Utah. As a soil conditioner, Cp can increase soil CEC, increase the water holding capacity of a sandy soil, and, to some degree, increase the retention of NH_4^+ from N fertilizers (Weber et al., 1983; MacKown and Tucker, 1985; Nus and Brauen, 1991; Huang and Petrovic, 1994). As a slow-release N fertilizer, NH_4^+ -Cp can increase N use-efficiency and meet the N needs of plants (Bartz and Jones, 1983; Barbarick et al., 1990; Allen et al., 1993). However, the degree to which NH_4^+ -Cp increases N use-efficiency, meets the N needs of plants, and decreases NO_3^- leaching is uncertain. Some studies of NH_4^+ -Cp effectiveness have limited application because NH_4^+ loading and analysis were not adequately reported (Lewis et al., 1983) or because leachate was not monitored (Bartz and Jones, 1983).

I hypothesized that N added as NH_4^+ -Cp will act as a slow-release nitrogen fertilizer and reduce the potential for NO_3^- contamination of water in a sandy soil. The specific objectives of this study were to:

- 1) Determine whether fertilization with NH_4^+ -Cp reduces N leaching compared to $(\text{NH}_4)_2\text{SO}_4$.
- 2) Determine whether NH_4^+ -Cp will meet the N needs of a corn plant compared to $(\text{NH}_4)_2\text{SO}_4$ by measuring relative growth rates (RGR), leaf area ratio (LAR), and net assimilation rate (NAR), and
- 3) Determine the effect of three size fractions of NH_4^+ -Cp, small (0 to 0.25 mm), medium (0.25 to 2 mm), and large (2 to 4 mm), on N leaching and corn growth.

MATERIAL AND METHODS

Characterization of Soil

The soil, a Ustic Haplocalcid, was analyzed for particle size distribution, organic carbon, CaCO_3 , pH, bulk density, water content as field capacity, CEC, exchangeable cations, and soluble anions and cations. Refer to Chapter 2, Characterization of Soil, for details.

Soil Fertility

Soil was analyzed for the macronutrients N, phosphorus (P), K, sulfur (S), and the micronutrients zinc (Zn), iron (Fe), copper (Cu), and manganese (Mn). Nitrogen was extracted via a 30-min 2 M KCl extraction and analyzed on the Lachat (Quick Chem AE #202.AE, Milwaukee, WI) for NH_4^+ -N and NO_3^- -N (QuikChem Method 12-107-06-1-B and QuikChem Method 12-107-04-1-B for NH_4^+ -N and NO_3^- -N, respectively). Phosphorus was analyzed by a NaHCO_3 extraction according to Olsen and Sommers (1982). Exchangeable K was determined by NH_4OAc extraction (see Chapter 2, Characterization of Soil). Sulfate-S was determined by a Ca_2PO_4 extraction according to Tabatabai (1982). A DTPA extraction (Lindsay and Norvell, 1978) was performed to assess available micronutrients. Fertilizer recommendations were based on the Utah Fertilizer Guide by Topper et al. (1989).

Characterization and Preparation of NH_4^+ -Cp

A sample of clinoptilolite was collected from Cache County, Utah, and crushed to three size fractions: small (<0.25 mm), medium (0.25 to 2 mm), and large (2 to 4 mm). The NH_4^+ -Cp was loaded with NH_4^+ via $(\text{NH}_4)_2\text{SO}_4$. For details refer to Chapter 2, Characterization and Preparation of NH_4^+ -Cp.

Characterization of Irrigation Water

A simulated irrigation water was applied to the soils because distilled water does not have cations to replace the NH_4^+ from the NH_4^+ -Cp and field plants are never irrigated with distilled water. For details on the characteristics of the irrigation water, refer to Chapter 2, Characterization of Irrigation Water.

Experiment #1

Three kg of soil was placed in 4-L pots. Each fertilizer, $(\text{NH}_4)_2\text{SO}_4$ or one of three NH_4^+ -Cp size fractions, small (<0.25 mm), medium (0.25 to 2 mm), or large (2 to 4 mm), was banded at a 5-cm depth, just off the center of the pot, at rates of 112, 224, and 336 kg N ha^{-1} . The banded fertilizers were covered with 1.5 kg of soil (about 5 cm deep) and two seeds of sweet corn (*Zea mays* L., variety 'Incredible') were planted 2 to 3 cm deep. A control with no N fertilizer was also planted with sweet corn to assess background N levels in leachate and corn plant tissue. Each treatment was replicated three times. After 2 wk, corn in each container was thinned to 1 plant. Natural greenhouse light was supplemented with high pressure Na light at about 500 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (16 h photoperiod). Daytime temperatures were about 30°C and nighttime temperatures were about 16°C.

Three plants were harvested from each treatment at 23 d and 35 d. At harvest, the leaf area of each plant was measured (Licor, model Li 3000, Lambda Instruments Corp., U.S.A), and the stalks and leaves were dried at 78°C for 24 h and weighed. The stalk mass, leaf mass, and leaf area of the plant were used to calculate relative growth rate (RGR), leaf area ratio (LAR), and net assimilation rate (NAR) (Leopold and Kriedemann, 1975). These growth indices were used because RGR measures how fast a plant is growing, LAR indicates if the plant is partitioning the carbon to the leaves or to the stalk, and NAR measures how efficiently the plant can photosynthesize given the plant's leaf area. RGR, LAR, and NAR were calculated by equations 1, 2, and 3, respectively:

$$(1) \quad \text{RGR} = (\ln \text{mass}_2 - \ln \text{mass}_1) / (\text{time}_2 - \text{time}_1)$$

$$(2) \quad \text{LAR} = [(\text{leaf area}_1/\text{leaf mass}_1) + (\text{leaf area}_2/\text{leaf mass}_2)] / 2$$

$$(3) \quad \text{NAR} = (\text{mass}_2 - \text{mass}_1) / (\text{time}_2 - \text{time}_1) * (\ln \text{ leaf area}_2 - \ln \text{ leaf area}_1) / (\text{leaf area}_2 - \text{leaf area}_1)$$

The stalk and leaves from each plant were ground (Thomas Wiley Laboratory Mill, model 4, Philadelphia, PA.) and analyzed for N via Kjeldahl digestion (Bremner and Mulvaney, 1982).

Plants were irrigated every 4 d and the leachate was collected and immediately frozen until it was analyzed on the Lachat (Quick Chem AE #202.AE, Milwaukee, WI) for NH_4^+ -N and NO_3^- -N (Quick Chem Method 10-107-06-1-A and Method 10-107-06-1-A for NH_4^+ -N and NO_3^- -N, respectively). Total leachate collected for the experiment was approximately 1 pore volume.

At the end of the experiment, a portion of the clinoptilolite from the soils amended with NH_4^+ -Cp was extracted and analyzed for remaining N by a Kjeldahl digestion and a 2 M KCl extraction, in which a representative sample of the NH_4^+ -Cp was placed in a container with 2 M KCl and shaken for 1 h. The 2 M KCl extract was analyzed on the Lachat (Quick Chem AE #202.AE, Milwaukee, WI) for NH_4^+ -N and NO_3^- -N (QuikChem Method 12-107-06-1-B and QuikChem Method 12-107-04-1-B for NH_4^+ -N and NO_3^- -N, respectively).

A N budget was prepared for each treatment by adding the added N recovered from the leachate, corn tissue, soil, and Cp (for the pots amended with NH_4^+ -Cp).

A modified N use-efficiency was used to calculate the N use-efficiency (equation 4):

$$(4) \quad \text{N use-efficiency} = \text{plant tissue N} / (\text{total added N} - \text{soil N} - \text{remaining N on } \text{NH}_4^+\text{-Cp})$$

This modified N use-efficiency calculation was used because the recovered N from the soil or NH_4^+ -Cp was still potentially available to the plant.

Statistical Analysis

The statistical design was a completely randomized 4 (N sources) x 3 (rates) factorial and analyzed on SAS (6.10) using the general linear model (the background N measured in the controls were averaged and subtracted from each treatment). Data were analyzed by date and by all dates combined.

Experiment #2

A second leaching experiment with corn was conducted because of limited corn growth data in experiment #1.

Six-liter pots were filled with 6.5 kg of soil. Each fertilizer, $(\text{NH}_4)_2\text{SO}_4$ or one of three NH_4^+ -Cp size fractions, small (<0.25 mm), medium (0.25 to 2 mm), or large (2 to 4 mm), was banded at a 5-cm depth, just off the center of the pot, at rates of 112 and 224 kg N ha^{-1} . The banded fertilizers were covered with 1.5 kg of soil (about 5 cm deep) and planted with 4 seeds of sweet corn 2 to 3 cm deep. A control with no N fertilizer was also planted with sweet corn to assess background N levels in leachate and corn plant tissue. Each treatment was replicated 6 times. The same greenhouse lighting and temperature conditions were used as in experiment #1.

Seven days after emergence, corn plants were thinned to one plant in each pot. At 14, 21, 28, 35, and 42 d, stalk height, stalk diameter, leaf length, and leaf width of each plant were measured with a ruler. The measurements were used to estimate stalk mass, leaf mass, and leaf area to calculate RGR, LAR, and NAR.

At 42 d, the stalk, leaves, and roots of each plant were harvested and dried at 78°C for 24 h before weighing. Roots were collected by washing the soil from each root system through a fiberglass screen with 6 L of dH_2O . The stalk and leaves from each plant were ground (Thomas Wiley Laboratory Mill, model 4, Philadelphia, PA) and analyzed for N via Kjeldahl digestion. The roots were ground (Arthur H. Thomas, Scientific Apparatus, Philadelphia, PA) and analyzed for N via Kjeldahl digestion.

Plants were irrigated every 4 d and the leachate was collected and immediately frozen until it was analyzed on the Lachat (Quick Chem AE #202.AE, Milwaukee, WI) for NH_4^+ -N and NO_3^- -N (as previously described). Leachate collected was approximately 1 pore volume. At the end of the experiment, soil and Cp (from pots amended with NH_4^+ -Cp) were extracted, cleaned from root tissue, and analyzed for N via Kjeldahl digestion. A N budget was prepared for each treatment by adding the added N recovered from the leachate, corn tissue, Cp (for the pots amended with NH_4^+ -Cp), and

residual soil N (which included N found in the root washing water). For calculating the N use-efficiency, the modified N use-efficiency calculation was used as explained in experiment #1, Material and Methods.

Statistical Analysis

The statistical design was a completely randomized 4 (N sources) \times 2 (rates) factorial and analyzed on SAS (6.10) using the general linear model (the background N measured from the controls were averaged and subtracted from each treatment). Data were analyzed by date and by all dates combined.

RESULTS AND DISCUSSION

Soil Analysis

The soil classified as a sandy over loamy, mixed, mesic Ustic Haplocalcid. Refer to Chapter 2, Results and Discussion, for specific physical and chemical characteristics.

Soil Fertility

The soil was deficient in N, P, S, Zn, and Mn. Phosphorus, Zn, and Mn were mixed in the soil as 50 kg P ha⁻¹ of Ca(H₂PO₄)₂, 20 kg Zn ha⁻¹ of ZnSO₄, and 5 kg Mn ha⁻¹ of MnSO₄, respectively. No sulfur was added because SO₄²⁻ was added via the Zn and Mn fertilizers and the irrigation water, which contained 170 mg L⁻¹ SO₄²⁻-S.

Clinoptilolite Analysis

The zeolite sample was confirmed as clinoptilolite. The NH₄⁺-saturated CEC was 165 cmol_c kg⁻¹. For details about the specific results of the Cp analysis, refer to Chapter 2, Results and Discussion.

Ammonium and Nitrate Leaching

More of the added N was leached as NH_4^+ from the $(\text{NH}_4)_2\text{SO}_4$ amendments than from the NH_4^+ -Cp size fractions in both experiments. The $(\text{NH}_4)_2\text{SO}_4$ -N in experiment #1 leached 1, 13, and 28% of the added N as NH_4^+ -N from the soil containing 112, 224, and 336 kg N ha^{-1} , respectively (Fig. 14), and the $(\text{NH}_4)_2\text{SO}_4$ -N in experiment #2 leached 5 and 17% of the added N as NH_4^+ -N from the soil containing 112 and 224 kg N ha^{-1} , respectively (Fig. 15). In contrast, <1% of the added N leached as NH_4^+ -N from any of the NH_4^+ -Cp size fractions in both experiments and size fractions were not significantly different. These results indicate that the application of NH_4^+ -Cp fertilizer reduced NH_4^+ leaching compared to the application of $(\text{NH}_4)_2\text{SO}_4$ fertilizer. This is due to the slow release of NH_4^+ from the NH_4^+ -Cp to the soil solution. Based on the soil leaching study without plants (Chapter 2), the corn plant also had little effect on the NH_4^+ leaching. This is probably due to the NH_4^+ leaching before the corn plant was large enough to take up a large amount because almost all of the leached NH_4^+ was leached by 2 wk (Fig 14b and 15b).

More of the added N was leached as NO_3^- from the $(\text{NH}_4)_2\text{SO}_4$ amendments than from the NH_4^+ -Cp size fractions in both experiments. The $(\text{NH}_4)_2\text{SO}_4$ -N in experiment #1 leached 20, 33, and 45% of the added N as NO_3^- -N from the soil containing 112, 224, and 336 kg N ha^{-1} , respectively (Fig. 16), and the $(\text{NH}_4)_2\text{SO}_4$ -N in experiment #2 leached 4 and 11% of the added N as NO_3^- -N from the soil containing 112 and 224 kg N ha^{-1} , respectively (Fig. 17). In contrast, in experiment #1, the N leached as NO_3^- -N (all rates) from the 1) small NH_4^+ -Cp size was <3% of the added N, 2) medium NH_4^+ -Cp size was < 4% of the added N, and 3) large NH_4^+ -Cp size was <4% of the added N. In experiment #2, <2% of the added N leached as NO_3^- -N (both rates) from the small, medium, and large NH_4^+ -Cp (Fig. 16 and 17). These results indicate that application of NH_4^+ -Cp reduces NO_3^- leaching compared to the application of $(\text{NH}_4)_2\text{SO}_4$. More NO_3^- -N was leached from the soil in experiment #1 than experiment #2, because 75% more soil was used in the experiment #2 which increased the chance for corn to take up NO_3^- before it leached. The soil amended with $(\text{NH}_4)_2\text{SO}_4$ and NH_4^+ -Cp began leaching NO_3^- near 17 d (Fig. 16b and 17b). Had this soil been farmed for a few years, NO_3^- leaching would probably

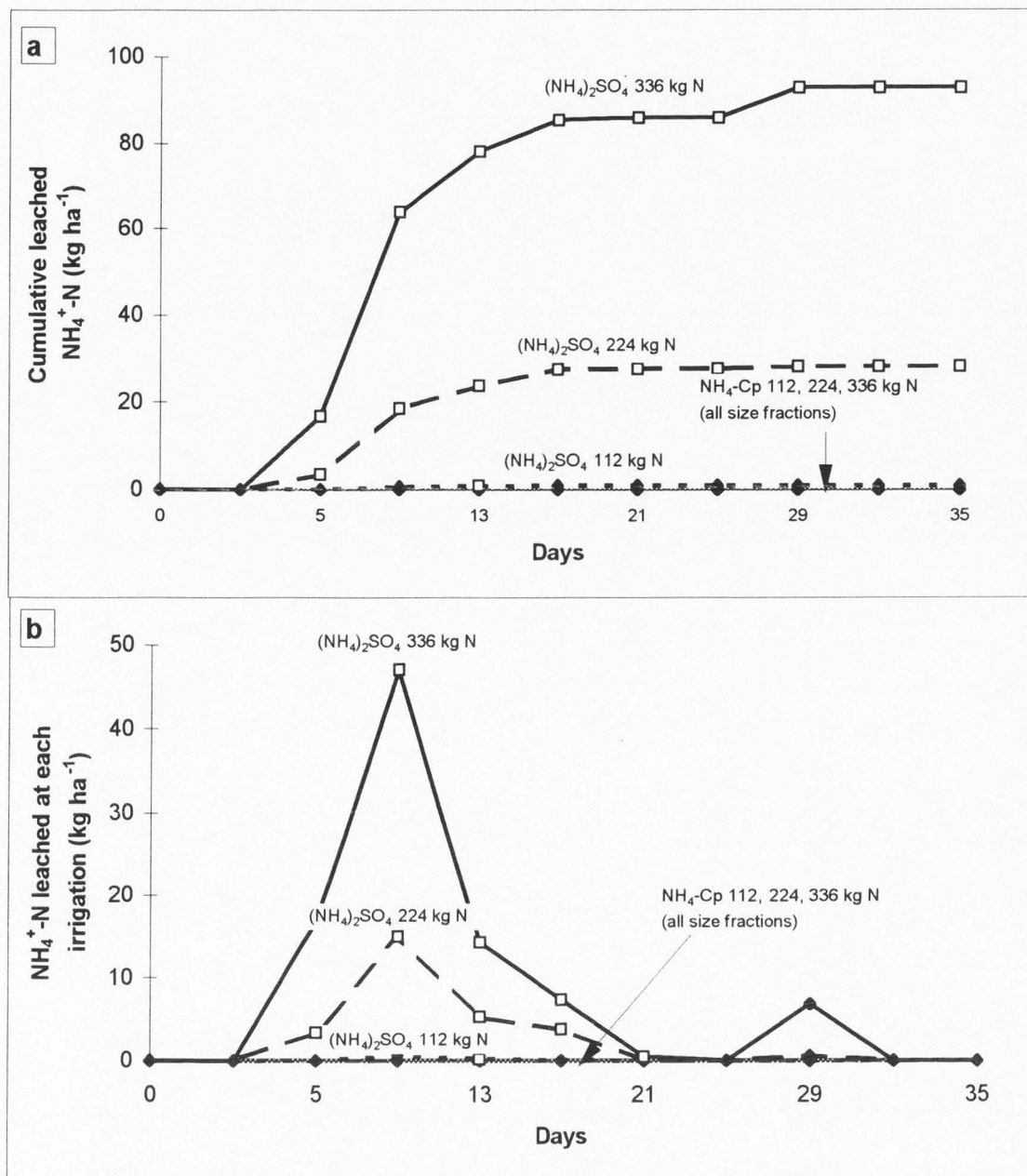


Fig. 14. Cumulative (a) and actual (b) kilograms of NH_4^+ -N that leached at each irrigation from the soil of experiment #1 amended with 112, 224, and 336 kg N ha^{-1} . The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the NH_4^+ -Cp size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix J for ANOVA tables.

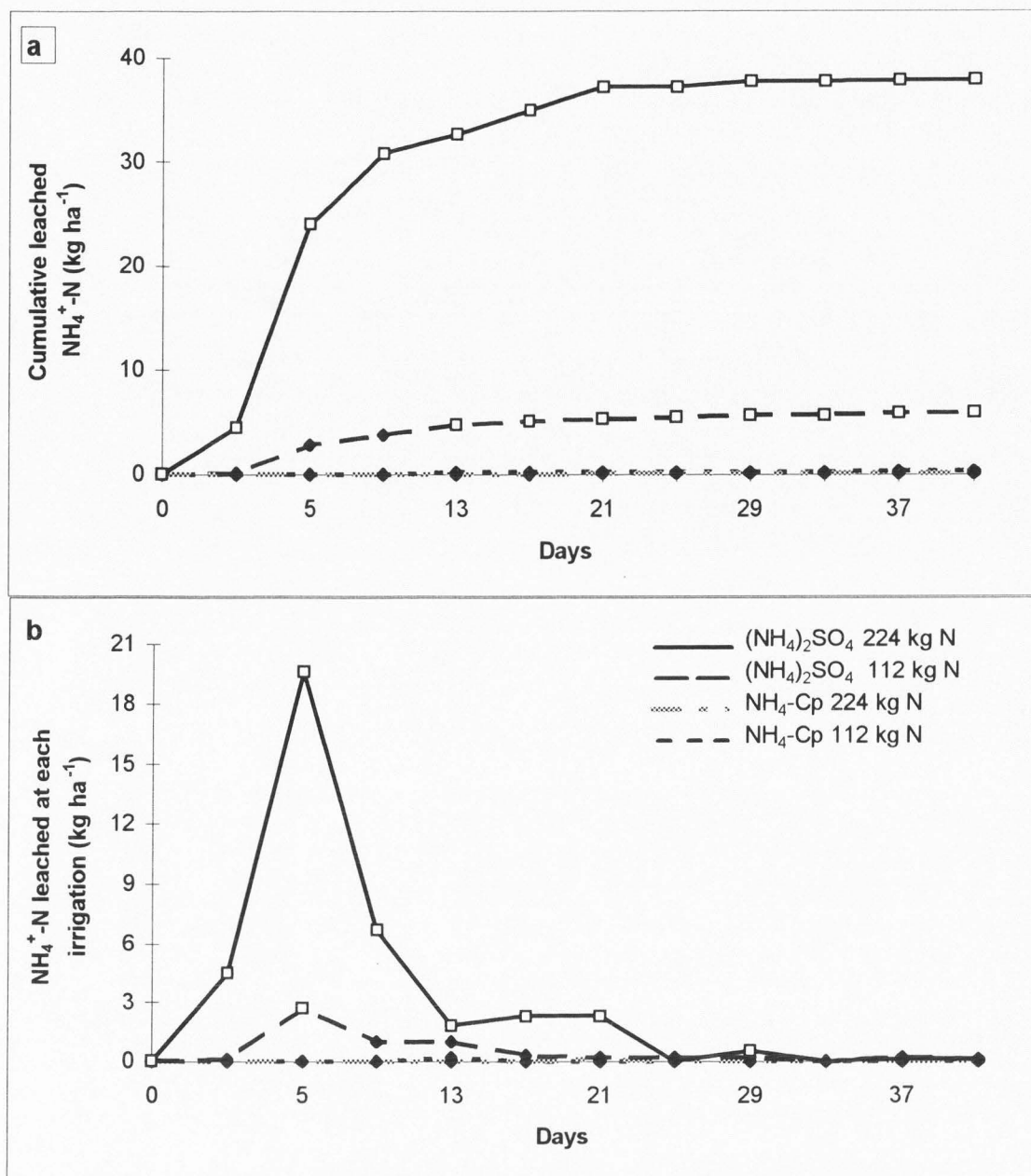


Fig. 15. Cumulative (a) and actual (b) kilograms of NH_4^+ -N that leached at each irrigation from the soil of experiment #2 amended with 112 and 224 kg N ha^{-1} . The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the NH_4^+ -Cp size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix K for ANOVA tables.

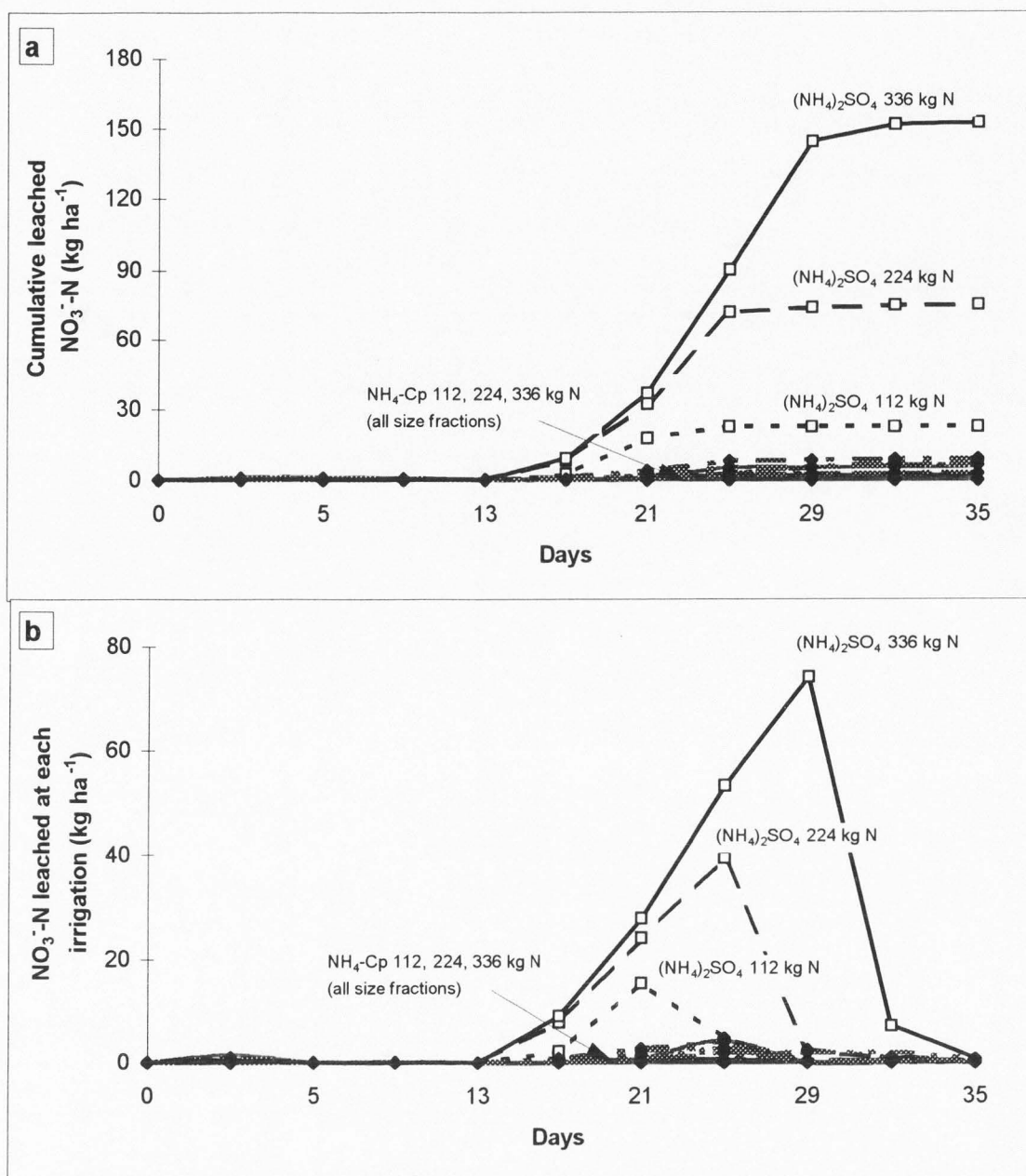


Fig.16. Cumulative (a) and actual (b) kilograms of $\text{NO}_3^- \text{N}$ that leached at each irrigation from the soil of experiment #1 amended with 112 and 224 kg N ha^{-1} . The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the NH_4^+ -Cp size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix L for ANOVA tables.

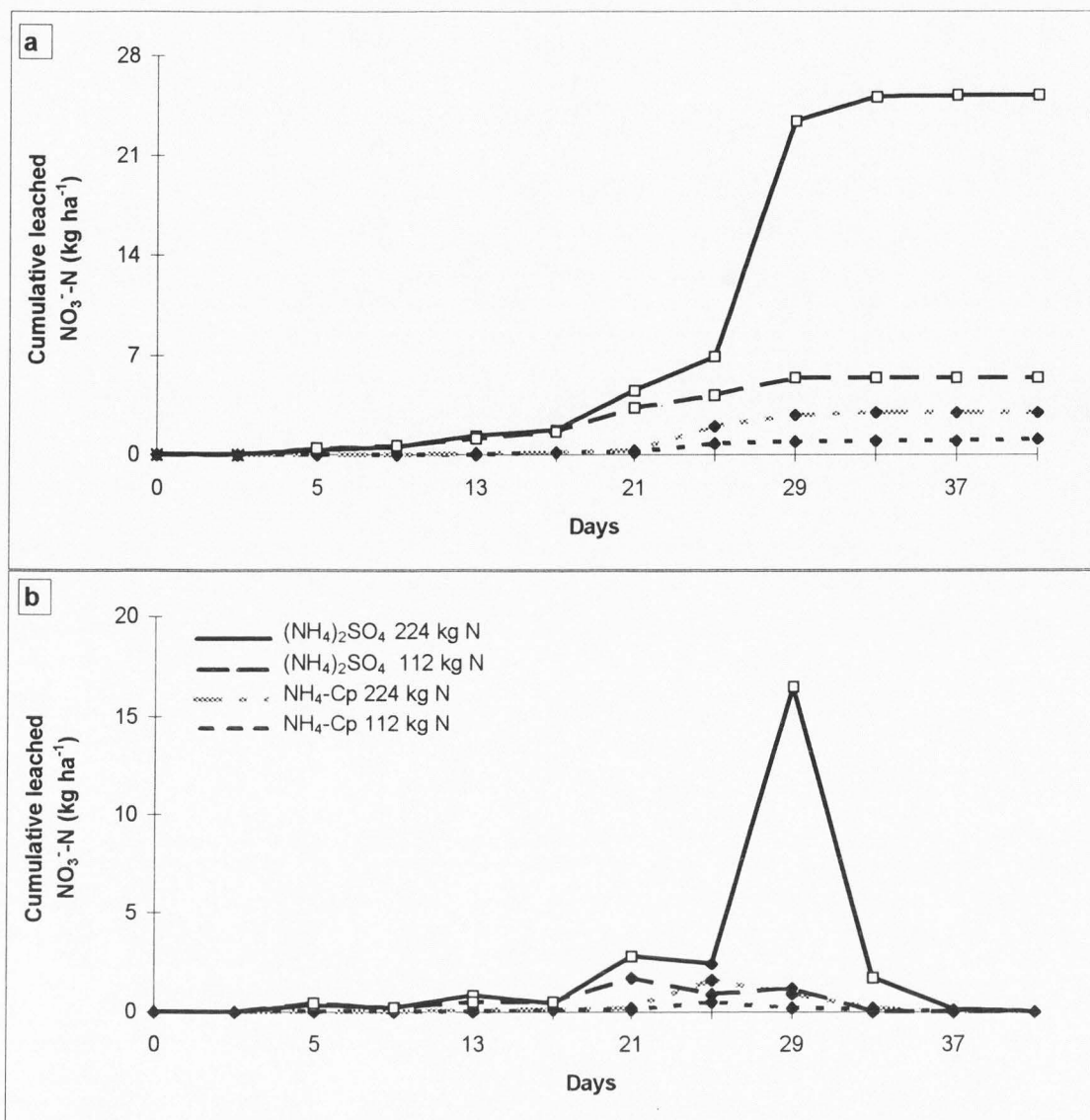


Fig. 17. Cumulative (a) and actual (b) kilograms of NO_3^- -N that leached at each irrigation from the soil of experiment #2 amended with 112 and 224 kg N ha^{-1} . The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the NH_4^+ -Cp size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix M for ANOVA tables.

have begun sooner due to high nitrifying bacteria populations. At 29 d, NO_3^- leaching decreased for all N amendments. This was probably due to N becoming limiting in the soil as corn N demands increased. Unlike the NH_4^+ leaching, the corn plant had a significant impact on reducing NO_3^- leaching. These results are based on the comparison of the corn #2 experiment and the soil leaching study (Chapter 2), which were performed with similar soil mass, temperature conditions, N rates, and amount of leached water (about 1 pore volume). The corn plant reduced NO_3^- -N leaching from the $(\text{NH}_4)_2\text{SO}_4$ fertilizer by 40 and 79 kg in the soils amended with 112 and 224 kg N ha^{-1} , respectively. In the soils amended with NH_4^+ -Cp, the corn plant reduced NO_3^- -N leaching by 10 to 20 kg N depending on the Cp size and N rate. This reduction of NO_3^- leaching indicates that good application timing of a N fertilizer will increase the N use-efficiency of the plant. On the other hand, poor application timing of a N fertilizer will decrease N use-efficiency for the plant, especially if the N fertilizer is similar to $(\text{NH}_4)_2\text{SO}_4$.

The $(\text{NH}_4)_2\text{SO}_4$ fertilizer leached significantly more of the total (NH_4^+ and NO_3^-) added N than the NH_4^+ -Cp size fractions. In experiment #1, 21, 46, and 73% of the added $(\text{NH}_4)_2\text{SO}_4$ -N leached from the soils containing 112, 224, and 336 kg N ha^{-1} , respectively (Fig. 18), and in experiment #2, 10% and 28% of the added $(\text{NH}_4)_2\text{SO}_4$ -N leached from the soils containing 112 and 224 kg N ha^{-1} , respectively (Fig. 19). In contrast, <4% and <2% of the added N leached from any of the NH_4^+ -Cp fertilizers in experiment #1 and experiment #2, respectively (Fig. 16 and 19). No significant differences in N leaching were found between NH_4^+ -Cp size fractions, indicating that all of the NH_4^+ -Cp size fractions are effective at reducing N leaching from the soil. It also suggests, in terms of economics, that extra sieving costs may be forgone because a combination of NH_4^+ -Cp size fractions could be used as a N fertilizer instead of a single size fraction. On the farm, the dramatic reduction of N leaching as a result of fertilizing with NH_4^+ -Cp would suggest that a farmer may save money because of reduced N needs while preventing water contamination. The validity of this suggestion, though, would need to be confirmed in field studies using an economic evaluation.

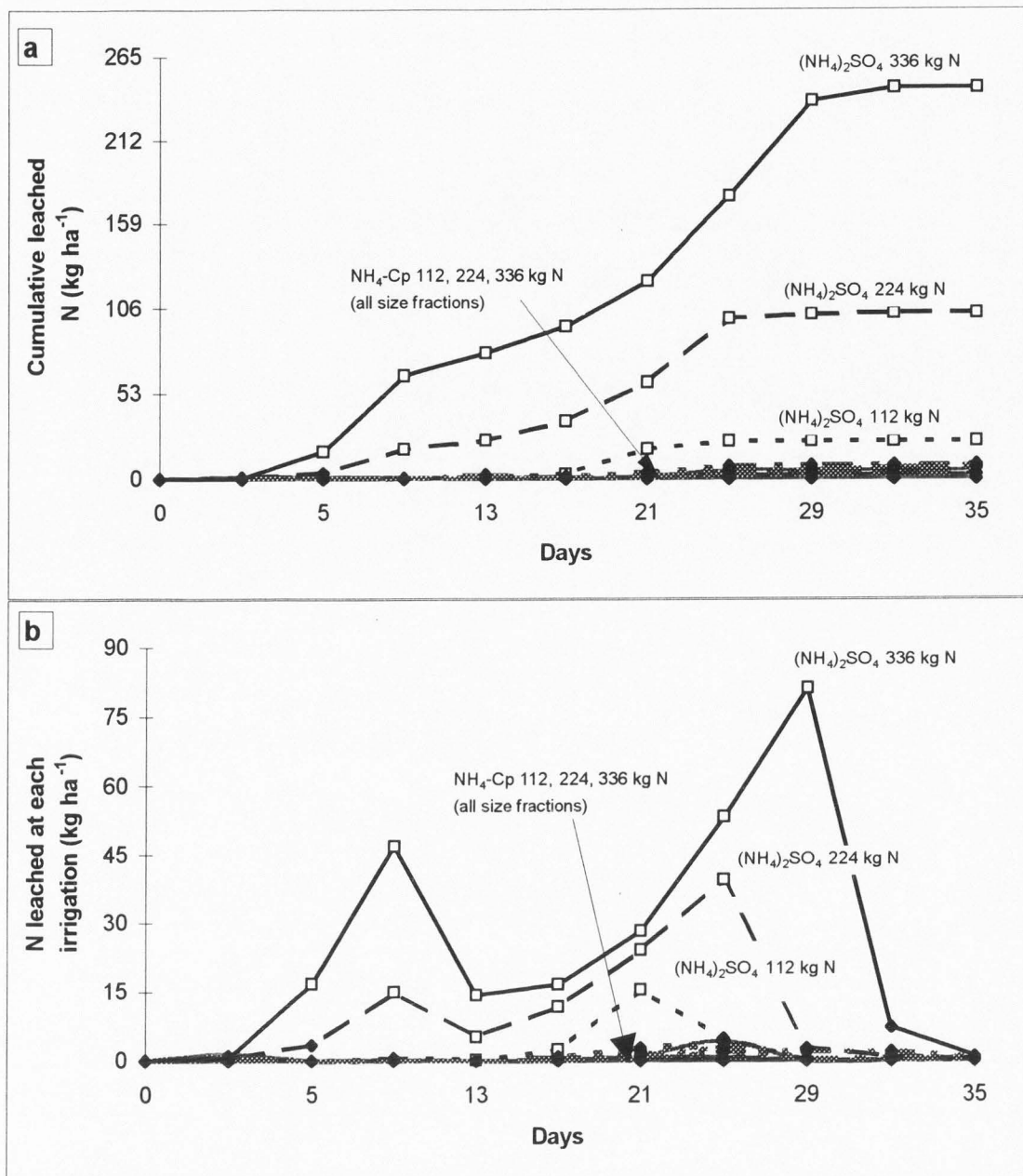


Fig. 18. Cumulative (a) and actual (b) kilograms of N ($\text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$) that leached at each irrigation from the soil of experiment #1 amended with 112, 224, and 336 kg N ha⁻¹. The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the $\text{NH}_4^+\text{-Cp}$ size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix N for ANOVA tables.

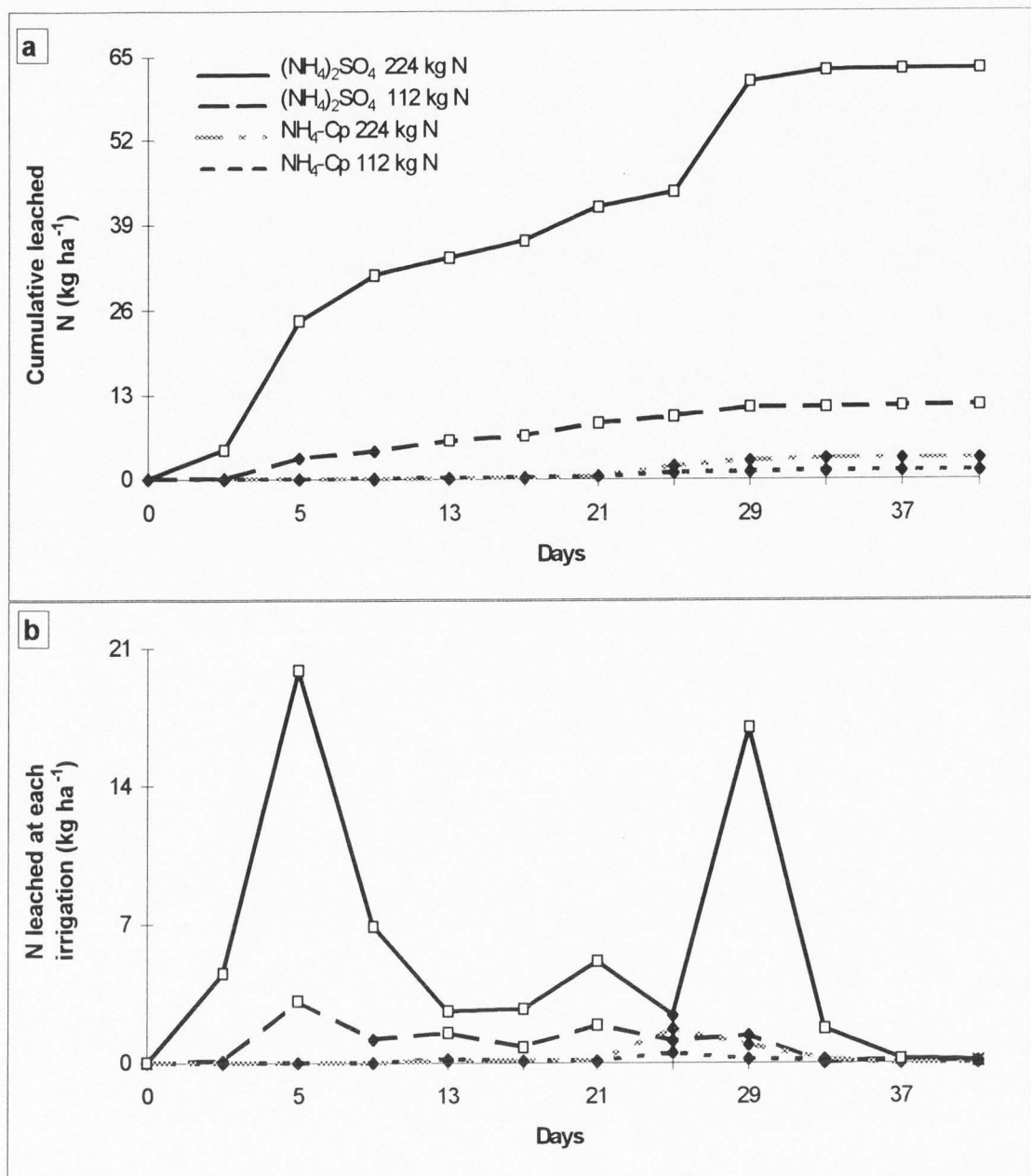


Fig. 19. Cumulative (a) and actual (b) kilograms of N ($\text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$) that leached at each irrigation from the soil of experiment #2 amended with 112 and 224 kg N ha⁻¹. The square symbols (\square) at each irrigation date are significant ($p < 0.05$) from the $\text{NH}_4^+\text{-Cp}$ size fractions within rates according to Tukey's test. Ammonium-Cp size fractions were not significantly different. Refer to Appendix O for ANOVA tables.

Corn Growth

Except for the 112 kg N ha⁻¹ of experiment #2, which suggested that the large NH₄⁺-Cp increased the RGR and NAR toward the end of the experiment, the RGR, LAR, and NAR of corn were not significantly different between the N sources in either of the experiments (see Appendixes P and Q for ANOVA tables and means of experiment #1 and experiment #2, respectively). At the end of the experiment #2, though, the 112 kg N ha⁻¹ RGR and NAR values of the small and medium NH₄⁺-Cp fertilized plants were significantly lower than the 224 kg N ha⁻¹ RGR and NAR values. In addition, the arrow-shaped yellowing of the lower leaves' midrib around 32 and 42 d for experiment #1 and the arrow-shaped yellowing of the lower leaves at 33 d and 40 d of experiment #1 and #2, respectively, suggested that the corn plants were becoming starved for N. Whole corn plant analysis confirmed this suspicion as N concentrations (Bennett, 1994) were low (1 to 1.5% N) for both experiments. The reason for the low N concentrations was the result of mistakenly using field N calculations for a greenhouse experiment. Although the N was applied at rates proportional to a hectare of soil in the field, the amount of total N that the plant needed for normal mature growth was neglected. In other words, the amount of N that a corn plant needs for normal growth is fixed. In the field, this N is placed around the rooting zone of the corn plant, which translates to a larger soil volume than what was used in these experiments. This soil volume difference between field and greenhouse situations was overlooked. According to Schrader et al. (1972), by 40 d, each plant should have taken up 300 to 400 mg N. However, only 111, 223, and 335 mg N were applied to each pot for the 112, 224, and 336 kg N ha⁻¹, respectively, in experiment #1, and in experiment #2, only 199 and 397 mg N were applied to each plant for the 112 and 224 kg N ha⁻¹, respectively. The deficiency of N in the pots affects the experiments in two ways. First, corn starts to exponentially take up N near 4 wk after emergence (Hanway, 1966; Mills and McElhannon, 1982). Because the corn had inadequate N to take up toward the end of the experiments, it is difficult to conclude whether NH₄⁺-Cp can meet a corn plant's N needs during this crucial time of plant growth, especially because, at the 224 and 336 kg N ha⁻¹, up to 39% of the added N was recovered from NH₄⁺-Cp fertilizers at the end of the experiments #1 and #2

(Table 4). Second, the leached N from the $(\text{NH}_4)_2\text{SO}_4$ fertilizer may be even more significant because only 15 to 20% of the corn plant's required N was applied (Hanway, 1966; Mills and McElhannon, 1982). In the field, this would suggest that vast amounts of N may be leached from the rooting zone of these plants early in the season.

Although these growth experiments indicate that NH_4^+ -Cp is a potential slow-release fertilizer in sandy soils, future field corn growth studies would help to better assess NH_4^+ -Cp as a N fertilizer.

N Budget

In experiment #1, 98, 93, and 100% of the added $(\text{NH}_4)_2\text{SO}_4$ -N was recovered from the 112, 224, and 336 kg N ha⁻¹, respectively (Table 4). This was unexpected for the 336 kg N ha⁻¹ because with an alkaline soil of pH 8.5, an irrigation water of pH 8.1, and soil with CaCO_3 , some N loss is expected due to NH_3 volatilization. In experiment #2, only 64 and 75% of the added $(\text{NH}_4)_2\text{SO}_4$ -N was recovered from the 112 and 224 kg N ha⁻¹, respectively. The added N that was recovered from the NH_4^+ -Cp fertilizers in both experiments averaged between 85 to 95% for all NH_4^+ -Cp sizes and rates (Table 4). The 5 to 15% of the unaccounted N is presumed to be the result of NH_3 volatilization and denitrification. The reason that more N was lost to these factors from the $(\text{NH}_4)_2\text{SO}_4$ fertilizer compared to the NH_4^+ -Cp fertilizers is due in part to the slow release of NH_4^+ from NH_4^+ -Cp, which allowed the plant to take up NH_4^+ before it was subject to volatilization or denitrification. Table 4 presents an itemized N budget for experiment #1 and #2.

In both experiments, the percent of added N recovered from the NH_4^+ -Cp increased as Cp sizes increased (Fig. 20). This indicates that the larger the NH_4^+ -Cp size the slower N is released. These results are similar to those reported in the quartz sand/soil leaching studies in Chapter 2. The large amount of N released from the NH_4^+ -Cp during these short experiments is noteworthy because Bartz and Jones (1983) suggested that NH_4^+ was available from NH_4^+ -Cp size fraction (<0.25 mm) for 242 d. However, in their leaching studies, Bartz and Jones used distilled water, which contains no cations to exchange with the NH_4^+ on the NH_4^+ -Cp. Like Bartz and Jones (1983), though, several researcher have used dH_2O and made conclusions about the release of NH_4^+ from NH_4^+ -Cp (MacKown

Table 4. Kilograms of N recovered from the soil and plant fractions of experiment #1 and experiment #2. Refer to Appendixes R and S for ANOVA tables of experiment #1 and experiment #2, respectively.

experiment	fertilizer [†]	rate	Cp N	leached N	soil N	root N [‡]	shoot N	total N	N use efficiency	
		kg N ha ⁻¹				kg N			%	
corn #1	small	112	2.0 b [§]	0.0 b	nd [¶]	20.9	83.8 a	106.7 a	95.2 [#]	
	medium	112	19.7 a	0.0 b	nd	17.5	69.9 a	107.1 a	94.7	
	large	112	15.8 a	0.7 b	nd	16.4	65.5 a	98.4 a	85.1	
	AS	112	na ^{††}	23.5 a	nd	17.1	68.4 a	109.0 a	76.3	
	small	224	19.3 b	2.5 b	nd	37.3	127.0 a	186.1 a	80.3	
	medium	224	40.2 ab	9.7 b	nd	30.9	105.0 b	185.8 a	73.9	
	large	224	67.6 a	6.4 b	nd	30.9	105.0 b	209.9 a	86.9	
	AS	224	na	103.3 a	nd	23.8	80.9 c	208.0 a	46.7	
	small	336	69.6 b	8.8 b	nd	56.8	159.0 a	294.2 b	81.0	
	medium	336	81.5 b	5.1 b	nd	48.2	135.0 a	269.8 b	72.0	
	large	336	117.0 a	3.1 b	nd	43.6	122.0 a	285.7 b	75.6	
	AS	336	na	245.0 a	nd	26.2	73.5 b	344.7 a	29.7	
	corn #2	small	112	20.2 a	1.5 b	0.2 a	20.3 a	61.1 a	103.2 a	88.8 a
		medium	112	20.7 a	1.2 b	0.0 a	21.5 a	56.3 ab	100.7 a	85.2 a
		large	112	25.3 a	1.2 b	0.0 a	14.8 a	51.9 ab	93.3 a	76.9 a
		AS	112	na	11.4 a	0.7 a	14.0 a	45.7 b	71.7 b	53.6 b
small		224	63.8 b	3.5 b	3.2 a	20.8 b	99.5 a	190.7 ab	76.6 a	
medium		224	80.2 ab	4.3 b	3.4 a	33.3 ab	90.3 ab	211.5 a	88.0 a	
large		224	88.3 a	1.7 b	3.1 a	39.3 a	84.6 ab	217.0 a	88.0 a	
AS		224	na	63.1 a	0.7 a	30.1 ab	74.0 b	167.9 b	46.6 b	

[†] Small, medium, and large represent NH₄⁺-Cp size fractions. AS is (NH₄)₂SO₄.

[‡] The root N from corn #1 was estimated from the results of the shoot/ root ratio of the corn #2 experiment in order to calculate a N use-efficiency.

[§] Different letters after each number within each column and each rate are significant according to Tukey's test (p<0.05).

[¶] nd=not determined, but assumed negligible due to leachate results at the end of the experiment.

[#] calculated from the modified N rate. p. 53.

^{††} na=not applicable.

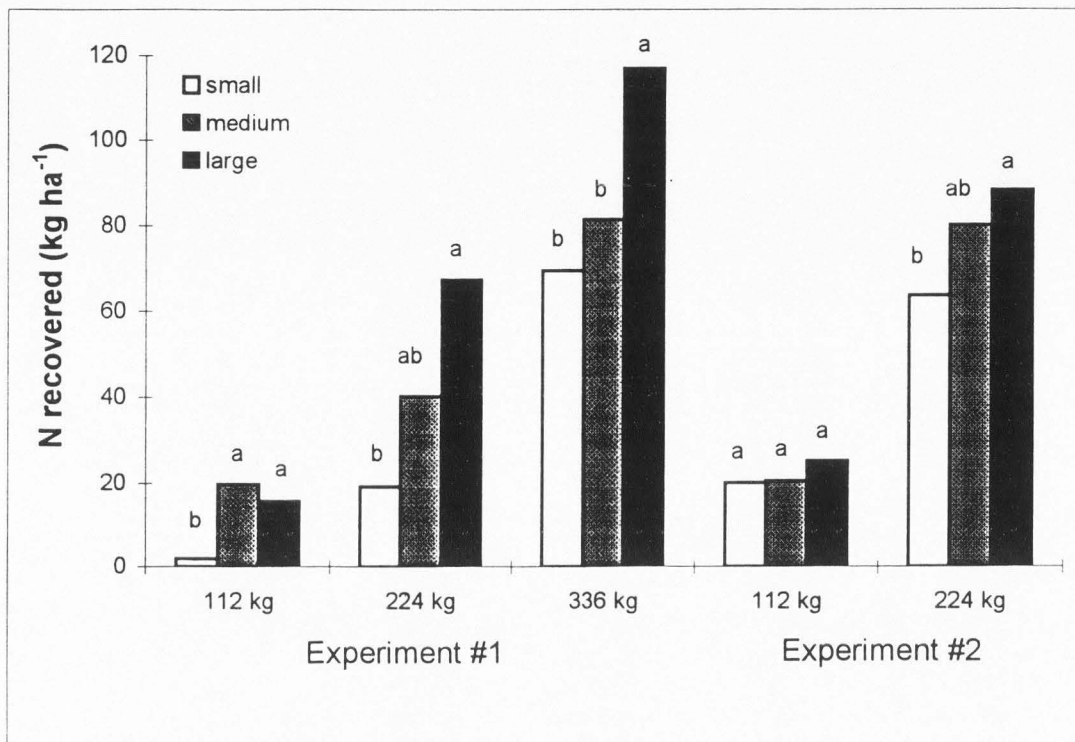


Fig. 20. Kilograms of N recovered from the small, medium, and large NH_4^+ -Cp size fractions which were extracted from experiments #1 and #2. Different letters within each experiment and each rate are significant ($p < 0.05$) according to Tukey's test. Refer to Appendixes R and S for the ANOVA tables of experiments #1 and #2.

and Tucker, 1985; Barbarick et al., 1990) without any discussion on the potential influence that a field irrigation water may have on NH_4^+ release from NH_4^+ -Cp. Other researchers never reported the composition of the watering solution (Lewis et al., 1983; Ferguson et al., 1986; Huang and Petrovic, 1994). However, some researchers have observed and mentioned the influence of solution cations on NH_4^+ release from NH_4^+ -Cp. Hershey et al. (1980) observed that a modified Hoagland's solution (without K^+) caused K^+ release from a K^+ -rich Cp, due to cation exchange reactions presumably from the cations in the modified Hoagland's solution. Perrin (Chapter 2) leached field irrigation water through quartz sand and a sandy soil amended with three size fractions of NH_4^+ -Cp. Over a 40-d leaching period, up to 90% of the NH_4^+ was released from the NH_4^+ -Cp due to cation exchange, presumably with the cations in the field irrigation water and to some extent the soluble cations in the soil. The lack of discussion on the potential effects of water salinity, composition, and neglecting to report water characteristics in many experiments is a serious oversight if researchers are trying to apply this technology to the "real" world of agriculture and horticulture. Ammonium-Cp's effectiveness as a N fertilizer will most likely depend on the type and quantity of cations in the irrigation water, i.e., high cation concentrations in the irrigation water will probably release ample NH_4^+ from NH_4^+ -Cp via cation exchange reactions, but low cation concentrations in the irrigation water may not release enough NH_4^+ to sustain plant growth. Further leaching studies that compare the effect of different qualities of irrigation water on NH_4^+ release from NH_4^+ -Cp are needed to confirm this hypothesis.

The 2 M KCl extraction analysis of NH_4^+ -Cp recovered from the soils had a noteworthy observation. Although most of the N was recovered as NH_4^+ , 3 to 10% of the N recovered was NO_3^- -N. This would support the suggestion that nitrification is occurring on the surface of the NH_4^+ -Cp (see Chapter 2).

More N was assimilated in the corn shoots of the plants fertilized with NH_4^+ -Cp than the plants fertilized with $(\text{NH}_4)\text{SO}_4$ (Table 4). This was true for all rates in both experiments. Nitrogen recovered from the root N was similar between N amendments. Because of high variability of root N

values, no trends, like in the results of the shoot N, were found in the N recovered from the roots. The increase of N use-efficiency due to fertilization with NH_4^+ -Cp fertilizers increased from 10 to 50% as the N rate increased. The modified N use-efficiency calculation explained in Material and Methods (this chapter) was used for these calculations.

As NH_4^+ -Cp size fraction became smaller, significantly more N was assimilated in the corn plant. This indicates that the smallest NH_4^+ -Cp size fraction had the most available N for the corn plant. This correlates with the observation that the least amount of N recovered from NH_4^+ -Cp was in the smallest NH_4^+ -Cp size fraction.

Although it is impossible from these experiments to estimate yields from sweet corn fertilized with NH_4^+ -Cp, using NH_4^+ -Cp appears beneficial for corn in this soil because a combination of N (NH_4^+ and NO_3^-) is available to the plant. Other greenhouse (Schrader et al., 1972; Mills and McElhannon, 1982; Alexander et al., 1991; Anderson et al., 1991; Barber et al., 1994) and field studies (Below and Gentry, 1987; Barber et al., 1992; Below and Gentry, 1992), in which corn has been grown, have observed that a combination of NH_4^+ and NO_3^- enhances corn growth more than a dominant supply of NO_3^- or NH_4^+ . The combination of NH_4^+ and NO_3^- provided by NH_4^+ -Cp will be affected by the activity of nitrifying bacteria, which are sensitive to soil pH. This soil's pH was optimum for nitrifying bacteria activity (pH 8.5). At low pH's (about 5), however, nitrification may be limited (Tisdale et al., 1993). This could increase the $\text{NH}_4^+/\text{NO}_3^-$ ratio.

CONCLUSIONS

Ammonium-Cp is a slow-release fertilizer that decreases N leaching in sandy soils compared to $(\text{NH}_4)\text{SO}_4$. No significant differences in RGR, NAR, or LAR due to N fertilizers were found in this experiment, although the corn grown in soils amended with NH_4^+ -Cp assimilated significantly more N than the corn grown in the soils amended with $(\text{NH}_4)\text{SO}_4$. Ammonium-Cp's effectiveness in field application needs further study because the short growing period and the small soil volumes used in these experiments may not be applicable to field studies.

Ammonium-Cp size fractions did not significantly influence N leaching from this soil. However, NH_4^+ -Cp size fractions significantly correlated with N uptake and the amount of N released from the NH_4^+ -Cp size fractions: The smaller the NH_4^+ -Cp size fraction, the more N was released and the more N the corn assimilated.

Although not tested here, water quality, i.e., the concentration of cations in solution, appears to be a factor controlling release of NH_4^+ from NH_4^+ -Cp. This may influence NH_4^+ -Cp's effectiveness in regions with irrigation water with low or high concentrations of cations. Further leaching studies are needed to confirm this hypothesis.

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CHAPTER 4

CONCLUSIONS

Sandy soils require high irrigation rates to sustain plant growth. As a result, N fertilizers are commonly leached from the rooting zone of crops, decreasing N use-efficiency and increasing the chance for water contamination. I hypothesized that NH_4^+ -Cp, prepared from the deposit in Cache Valley, Utah, applied as a slow-release fertilizer would increase N use-efficiency and reduce N leaching while sustaining normal plant growth.

To test this hypothesis, two leaching studies without plants and two leaching studies with plants were conducted. In all experiments, the soils amended with NH_4^+ -Cp leached less N ($p < 0.0001$) than did soils amended with a traditional ammonium fertilizer, $(\text{NH}_4)_2\text{SO}_4$. This difference in N leaching was even greater as the rate of $(\text{NH}_4)_2\text{SO}_4$ fertilizer increased. This increased N leaching due to increased N rates is noteworthy because a common farm practice is to apply extra N on soils in order to offset poor plant growth due to N losses via leaching or volatilization. From these studies, NH_4^+ -Cp would be an excellent alternative fertilizer for farmers in environments that are conducive to N losses, especially if the N losses are due to leaching and potential for water contamination is high. Whether NH_4^+ -Cp reduces N losses due to volatilization or denitrification is uncertain and will require further research.

The timing of the N released from the NH_4^+ -Cp fertilizers was more uniform in the soil than the $(\text{NH}_4)_2\text{SO}_4$ fertilizer. In general, the leached N from the soils amended with NH_4^+ -Cp was fairly constant throughout the experiment. On the other hand, the $(\text{NH}_4)_2\text{SO}_4$ fertilizer leached N at two distinct periods, at the beginning of the experiment when NH_4^+ leached and towards the end of the experiment when NO_3^- leached. This suggests that plants fertilized with NH_4^+ -Cp may have a higher N use-efficiency because the N is released in quantities that match the quantities of N the plant can incorporate. This was the case in the leaching studies with plants. Although no significant differences were found in corn growth between the corn fertilized with NH_4^+ -Cp or $(\text{NH}_4)_2\text{SO}_4$, the corn assimilated significantly more N from the NH_4^+ -Cp fertilizers than the $(\text{NH}_4)_2\text{SO}_4$ fertilizer. This

resulted in higher N use-efficiency values for the NH_4^+ -Cp fertilizers than the $(\text{NH}_4)_2\text{SO}_4$ fertilizer. This may translate to dollars saved by the farmer because the farmer does not have to apply extra N fertilizer to sustain normal plant growth (although this savings is dependent on unit N cost and application costs). From these studies, NH_4^+ -Cp would be a good alternative fertilizer for plants that generally have a low N use-efficiency, such as onions, horticulture crops, and turf planted in golf greens. Field studies are needed to confirm this hypothesis, especially because the plant growth experiments were short, 35 and 42 d.

The NH_4^+ -Cp sizes affected NH_4^+ release from NH_4^+ -Cp. Although this was suspected from the leaching data in the experiments, analysis of the NH_4^+ -Cp after the experiments showed that as the NH_4^+ -Cp size decreased, the amount of NH_4^+ released increased. The results from these experiments also implied that fertilizer placement (banding or broadcasting), water salinity, and irrigation scheduling may affect the NH_4^+ release from NH_4^+ -Cp, suggesting that N release from NH_4^+ -Cp may be manipulated. However, the influences of these factors are hypotheses. Further research is needed to assess their influence on NH_4^+ release from NH_4^+ -Cp.

Because of the low %N of NH_4^+ -Cp (around 2 to 2.5%), benefits of NH_4^+ -Cp will probably be realized to the greatest degree in coarse-textured soils found in gardens, lawns, golf courses, nurseries, and low-acreages where high-value crops such as onions are grown. On farms with livestock, though, Cp may offer a more unique benefit than fertilization. Work done by Bernal et al. (1993) and MacQueen (1996) suggests that Cp may be used to adsorb ammonium and other nutrients from animal waste. This would reduce potential water-quality problems inherent with livestock waste, produce a fertilizer for the field, and help clean and improve the living conditions of the livestock.

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APPENDICES

APPENDIX A

Comparison of Kjeldahl Digestion and 2 M KCl Extraction on Nitrogen Recovery

Kjeldahl digestion and 2M KCl extraction methods were analyzed for N recovery efficiencies from NH_4^+ -Cp by analyzing Cp which was loaded with known amounts of NH_4^+ . This analysis was done by soaking Cp in 100ml of 1M $(\text{NH}_4)_2\text{SO}_4$ for 7 d and then rinsing the Cp with 4L of dH_2O . The rinsing solution was analyzed on Lachat (QuickChem Method 10-107-06-1-A) for NH_4^+ . The Cp was air-dried and the mass was adjusted for gravimetric water content. The dried Cp samples were analyzed for ammonium by Kjeldahl digestion or by shaking the NH_4^+ -Cp for 1h in 2M KCl and then analyzing the solution for NH_4^+ on the Lachat (QuickChem Method 12-107-06-1-B). The ammonium recovery efficiency for the Kjeldahl digestion was calculated by adding the NH_4^+ recovered from the rinsing solution to the NH_4^+ recovered from the Kjeldahl digestion. The ammonium recovery efficiency for the 2M KCl extraction was calculated by adding the NH_4^+ recovered from the rinsing solution to the NH_4^+ recovered from the 2M KCl extraction.

For comparison, the medium (0.25 to 2mm) NH_4^+ -Cp prepared for the experiment was analyzed for N via 2M KCl extraction, Kjeldahl digestion, and high temperature combustion (Leco).

Results

The calculated N on the Cp was 1.5% by weight. The Kjeldahl digestion and 1-h 2 M KCl extraction recovered 95 and 99%, respectively, of the known NH_4^+ exchanged on the Cp. This suggests that either procedure is probably acceptable for measuring the NH_4^+ when a portion of the Cp's exchange sites are filled by NH_4^+ .

Analyzing the saturated NH_4^+ -Cp via 2M KCl extraction, Kjeldahl digestion, and the Leco resulted in 1.81, 2.20, and 2.12% N, respectively. This indicates that a 1-h 2 M KCl extraction is probably insufficient at recovering NH_4^+ from saturated NH_4^+ -Cp, and that the Kjeldahl and Leco procedures are better indicators of the %N on the saturated NH_4^+ -Cp.

APPENDIX B

ANOVAs for NH_4^+ -N that Leached from Quartz Sand

ANOVA (average of all dates) of cumulative NH_4^+ -N that leached from the quartz sand (for Figures 1a, 2a, and 3a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	14.4	264142	0.0001	0.999	4.28
N-source	3	62.4	138858	0.0001		
rate*N-source	6	17.4	106545	0.0001		
error a	24	0.5	767			
date	10	3.7	13735	0.0001		
error b	20	0.0	26			
N-source*date	30	0.9	1068	0.0001		
rate*date	20	0.4	658	0.0001		
rate*N-source*date	60	0.2	110	0.0001		
error c	220	0.1	15			

ANOVA (average of all dates) of NH_4^+ -N that leached from the quartz sand at each irrigation (for Figures 1b, 2b, and 3b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	1.6	2892	0.0001	0.987	48.4
N-source	3	4.5	5551	0.0001		
rate*N-source	6	1.3	781	0.0001		
error a	24	0.1	9			
date	10	19.6	7211	0.0001		
error b	20	0.2	33			
N-source*date	30	49.2	6031	0.0001		
rate*date	20	6.1	1118	0.0001		
rate*N-source*date	60	17.5	1069	0.0001		
error c	220	1.3	22			

APPENDIX C

ANOVAs for NO_3^- -N that Leached from Quartz Sand

ANOVA (average of all dates) of cumulative NO_3^- -N that leached from the quartz sand (for Figures 4a, 5a, and 6a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	2.5	980.5	0.014	0.927	53.8
N-source	3	13.8	3572.0	0.0001		
rate*N-source	6	1.1	136.3	0.71		
error a	24	5.9	191.7			
date	10	45.2	3514.0	0.0001		
error b	20	0.9	34.9			
N-source*date	30	17.0	441.0	0.0001		
rate*date	20	4.2	161.8	0.0001		
rate*N-source*date	60	2.2	28.5	0.284		
error c	220	7.2	25.6			

ANOVA (average of all dates) of NO_3^- -N that leached from the quartz sand at each irrigation (for Figures 4b, 5b, and 6b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	3.7	101.0	0.0043	0.849	81.6
N-source	3	14.3	262.3	0.0001		
rate*N-source	6	1.8	16.3	0.382		
error a	24	6.4	14.6			
date	10	29.7	163.4	0.0001		
error b	20	1.5	4.1			
N-source*date	30	14.6	26.7	0.0001		
rate*date	20	6.6	18.1	0.0001		
rate*N-source*date	60	6.3	5.8	0.0152		
error c	220	15.1	3.8			

APPENDIX D

ANOVAs for Total N that Leached from Quartz Sand

ANOVA (average of all dates) of cumulative N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the quartz sand (for Figures 7a, 8a, and 9a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	16.3	297116	0.0001	0.998	5.8
N-source	3	55.8	678331	0.0001		
rate*N-source	6	16.6	100756	0.0001		
error a	24	0.7	994			
date	10	7.5	27375	0.0001		
error b	20	0.0	73			
N-source*date	30	1.9	2294	0.0001		
rate*date	20	0.7	1256	0.0001		
rate*N-source*date	60	0.3	195	0.0001		
error c	220	0.2	36			

ANOVA (average of all dates) of N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the quartz sand at each irrigation (for Figures 7b, 8b, and 9b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	2.2	4064.0	0.0001	0.984	41.7
N-source	3	3.2	3918.0	0.0001		
rate*N-source	6	1.1	646.2	0.0001		
error a	24	0.1	22.8			
date	10	16.7	6134.4	0.0001		
error b	20	0.2	37.7			
N-source*date	30	51.4	6296.7	0.0001		
rate*date	20	5.8	1060.2	0.0001		
rate*N-source*date	60	17.8	1093.0	0.0001		
error c	220	1.5	25.7			

APPENDIX E

ANOVAs for N Budgets for Quartz Sand and Soil

Quartz Sand N Budget

ANOVA for kilograms of N recovered from NH_4^+ -Cp amended to the quartz sand (for Figure 10).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	26.1	9731	0.0001	0.97	22.9
N-source	3	57.1	14205	0.0001		
rate*N-source	6	13.8	1719	0.0001		
error	24	3.0	92			

ANOVA for kilograms of added N recovered from the quartz sand leaching experiment (for Table 3).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	73.0	96000	0.0001	0.971	10.1
N-source	3	16.2	14183	0.0001		
rate*N-source	6	7.9	3454	0.0001		
error	24	2.9	315			

Soil N Budget

ANOVA for kilograms of N recovered from NH_4^+ -Cp amended to the soil (for Figure 10).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	15.3	11445	0.0001	0.964	20.8
N-source	3	13.3	3315	0.0001		
rate*N-source	3	4.3	1061	0.0001		
error	15	1.2	61			

ANOVA for kilogram of N recovered from the soil (for Table 3).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	13.3	4	0.096	0.414	38.2
N-source	3	19.1	2	0.253		
rate*N-source	3	9.1	1	0.556		
error	14	58.6	1			

ANOVA for kilograms of added N recovered from the soil leaching experiment (for Table 3).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	33.4	24899	0.0001	0.892	21.5
N-source	3	6.6	1653	0.004		
rate*N-source	3	1.1	278	0.372		
error	15	5.0	248			

APPENDIX F

ANOVAs for NH_4^+ -N that Leached from SoilANOVA (average of all dates) of cumulative NH_4^+ -N that leached from the soil (for Figure 11a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	8.5	3865	0.0475	0.983	53.5
N-source	3	29.9	4532	0.0092		
rate*N-source	3	24.9	3779	0.018		
error a	16	29.5	838			
date	10	0.9	43	0.0001		
error b	20	0.2	5			
N-source*date	30	2.2	33	0.0001		
rate*date	10	0.6	27	0.0001		
rate*N-source*date	30	1.7	25	0.0001		
error c	140	1.7	5			

ANOVA (average of all dates) of NH_4^+ -N that leached from the soil at each irrigation (for Figure 11b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	2.1	50	0.022	0.57	510
N-source	3	7.9	62	0.002		
rate*N-source	3	6.2	49	0.0053		
error a	16	5.4	8			
date	10	3.6	9	0.41		
error b	20	6.6	8			
N-source*date	30	11.3	9	0.218		
rate*date	10	3.4	8	0.355		
rate*N-source*date	30	10.4	8	0.317		
error c	140	43.0	7			

APPENDIX G

ANOVAs for NO_3^- -N that Leached from SoilANOVA (average of all dates) of cumulative NO_3^- -N that leached from the soil (for Figure 12a).

Source	df	% SS	MS	Pr > F	R ²	C.V
rate	1	2.1	1935.0	0.006	0.954	63.8
N-source	3	17.7	5377.7	0.0001		
rate*N-source	3	3.1	944.3	0.0142		
error a	16	3.5	196.4			
date	10	36.0	3275.1	0.0001		
error b	20	0.5	21.9			
N-source*date	30	23.8	723.3	0.0001		
rate*date	10	3.8	344.2	0.0001		
rate*N-source*date	30	4.9	150.1	0.0001		
error c	140	4.6	29.9			

ANOVA (average of all dates) of NO_3^- -N that leached from the soil at each irrigation (for Figure 12b).

Source	df	% SS	MS	Pr > F	R ²	C.V
rate	1	2.9	234.0	0.002	0.897	82.1
N-source	3	16.1	434.0	0.0001		
rate*N-source	3	3.4	91.7	0.008		
error a	16	3.2	16.2			
date	10	36.1	291.3	0.0001		
error b	20	0.7	2.7			
N-source*date	30	19.0	51.1	0.0001		
rate*date	10	3.5	28.2	0.0001		
rate*N-source*date	30	4.9	13.3	0.0009		
error c	140	10.3	5.9			

APPENDIX H

ANOVAs for Total N that Leached from Soil

ANOVA (average of all dates) of cumulative N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the soil (for Figure 13a).

Source	df	% SS	MS	Pr > F	R ²	C.V
rate	1	5.8	11271.0	0.0013	0.972	48.6
N-source	3	30.3	19779.0	0.0001		
rate*N-source	3	12.9	8454.7	0.0003		
error a	16	6.0	739.0			
date	10	19.8	3884.4	0.0001		
error b	20	0.4	43.3			
N-source*date	30	15.3	997.9	0.0001		
rate*date	10	2.6	504.5	0.0001		
rate*N-source*date	30	4.0	261.7	0.0001		
error c	140	2.8	39.5			

ANOVA (average of all dates) of N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the soil at each irrigation (for Figure 13b).

Source	df	% SS	MS	Pr > F	R ²	C.V
rate	1	4.8	501.0	0.0001	0.817	105.6
N-source	3	23.7	822.3	0.0001		
rate*N-source	3	7.8	271.3	0.0001		
error a	16	2.7	17.4			
date	10	23.9	248.4	0.0001		
error b	20	2.2	11.7			
N-source*date	30	11.4	39.5	0.0001		
rate*date	10	1.9	19.5	0.172		
rate*N-source*date	30	3.4	11.6	0.683		
error c	140	18.3	13.6			

APPENDIX I

Means of N ($\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and Total N) that Leached from Soil in Small Containers

Cumulative kilograms of $\text{NH}_4^+\text{-N}$ that leached from the small containers which held soil amended with 112 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0 a [†]	0 a	0 a	0 a	0.1 a	0.5 a	0.8 a	0.8 a	0.8 a	0.8 a	0.8 a
medium	0 a	0 a	0 a	0 a	0 a	0.1 a	0.1 a	0.1 a	0.1 a	0.1 a	0.1 a
large	0 a	0 a	0 a	0 a	0 a	0.2 a	0.2 a	0.2 a	0.2 a	0.2 a	0.2 a
(NH_4) ₂ SO ₄	0.1 a	1.6 a	3 a	4.3 a	5.5 a	7.6 a	7.6 a	7.6 a	7.6 a	7.6 a	7.6 a

Cumulative kilograms of $\text{NO}_3^-\text{-N}$ that leached from the small containers which held soil amended with 112 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0.1 a	1.8 a	3 a	5.2 a	11.8 a	16.6 a	21.4 a	30.8 a	34.4 a	37 a
medium	0 a	0 a	2.1 a	4.4 a	8.2 a	21.4 a	30.9 a	44.6 a	55.6 a	57.8 a	58.5 a
large	0 a	0 a	1 a	2 a	5.5 a	17.1 a	25.5 a	34.3 a	39.8 a	42 a	46.2 a
(NH_4) ₂ SO ₄	0.1 a	0.1 a	1.8 a	3.1 a	5.5 a	11.4 a	17 a	17 a	17.7 a	18.5 a	19.1 a

Cumulative kilograms of N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the small containers which held soil amended with 112 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0.1 a	1.8 a	3 a	5.3 a	12.3 a	17.4 a	22.2 a	31.6 a	35.2 a	37.8 a
medium	0 a	0 a	2.1 a	4.4 a	8.2 a	21.5 a	31 a	44.7 a	55.7 a	57.9 a	58.6 a
large	0 a	0 a	1 a	2 a	5.5 a	17.3 a	25.7 a	34.5 a	40 a	42.2 a	46.4 a
(NH_4) ₂ SO ₄	0.2 a	1.7 a	4.8 a	7.4 a	11 a	19 a	24.6 a	24.6 a	25.3 a	26.1 a	26.7 a

$\text{NH}_4^+\text{-N}$ that leached at each irrigation from the small containers which held soil amended with 112 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0 a	0 a	0 a	0 a	0.1 a	0.4 a	0.3 a	0 a	0 a	0 a	0 a
medium	0 a	0 a	0 a	0 a	0 a	0.1 a	0 a	0 a	0 a	0 a	0 a
large	0 a	0 a	0 a	0 a	0 a	0.2 a	0 a	0 a	0 a	0 a	0 a
(NH_4) ₂ SO ₄	0.1 a	1.5 a	1.4 a	1.3 a	1.2 a	2.1 a	0 a	0 a	0 a	0 a	0 a

$\text{NO}_3^-\text{-N}$ that leached at each irrigation from the small containers which held soil amended with 112 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0 a	1.7 a	1.2 a	2.2 a	6.6 a	4.8 a	4.8 ab	9.4 a	3.6 a	2.6 a
medium	0 a	0 a	2.1 a	2.3 a	3.8 a	13.2 a	9.5 a	13.7 a	11 a	2.2 a	0.7 a
large	0 a	0 a	1 a	1 a	3.5 a	11.6 a	8.4 a	8.8 ab	5.5 a	2.2 a	4.2 a
(NH_4) ₂ SO ₄	0.1 a	0 a	1.7 a	1.3 a	2.4 a	5.9 a	5.6 a	0 b	0.7 a	0.8 a	0.6 a

† Different letters after numbers within columns are significant according to Tukey's test ($p < 0.05$).

Total added N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached at each irrigation from the small containers which held soil amended with 112 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a [†]	0 a	1.7 a	1.2 a	2.3 a	7 a	5.1 a	4.8 ab	9.4 a	3.6 a	2.6 a
medium	0 a	0 a	2.1 a	2.3 a	3.8 a	13.3 a	9.5 a	13.7 a	11 a	2.2 a	0.7 a
large	0 a	0 a	1 a	1 a	3.5 a	11.8 a	8.4 a	8.8 ab	5.5 a	2.2 a	4.2 a
(NH_4) ₂ SO ₄	0.2 a	1.5 a	3.1 a	2.6 a	3.6 a	8 a	5.6 a	0 b	0.7 a	0.8 a	0.6 a

Cumulative kilograms of NH_4^+ -N that leached from the small containers which held soil amended with 224 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0 a	0 a	0 a	0 a	0 b	0.4 b	0.4 b	0.4 b	0.4 b	0.4 b	0.4 b
medium	0 a	0 a	0 a	0.2 a	0.2 b	0.7 b	0.9 b	0.9 b	0.9 b	0.9 b	0.9 b
large	0 a	0 a	0 a	0 a	0 b	0 b	0 b	0 b	0 b	0 b	0 b
(NH_4) ₂ SO ₄	1.3 a	11.7 a	16.9 a	23.4 a	29.2 a	40.8 a	42.9 a	43.4 a	43.4 a	43.4 a	43.4 a

Cumulative kilograms of NO_3^- -N that leached from the small containers which held soil amended with 224 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.2 a	0.2 a	1.7 a	3.2 ab	6.1 a	18.6 a	30.4 a	50.6 a	71.9 a	81.6 a	95.4 a
medium	0.1 a	0.2 a	1.8 a	3.1 ab	5.6 a	18.1 a	28.9 a	43.2 a	53.9 a	58.7 a	66.8 a
large	0 a	0 a	0.4 a	2.9 b	6.5 a	20.5 a	33 a	47.5 a	76.1 a	84.4 a	98 a
(NH_4) ₂ SO ₄	0.1 a	0.2 a	1.8 a	4.3 a	9.6 a	24.7 a	44.6 a	47.6 a	48.2 a	48.2 a	48.2 a

Cumulative kilograms of N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the small containers which held soil amended with 224 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.2 a	0.2 a	1.7 a	3.2 b	6.1 b	19 b	30.8 b	51 a	72.3 a	82 a	95.8 a
medium	0.1 a	0.2 a	1.8 a	3.3 b	5.8 b	18.8 b	29.8 b	44.1 a	54.8 a	59.6 a	67.7 a
large	0 a	0 a	0.4 a	2.9 b	6.5 b	20.5 b	33 b	47.5 a	76.1 a	84.4 a	98 a
(NH_4) ₂ SO ₄	1.4 a	11.9 a	18.7 a	27.7 a	38.8 a	65.5 a	87.5 a	91 a	91.6 a	91.6 a	91.6 a

NH_4^+ -N that leached at each irrigation from the small containers which held soil amended with 224 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0 a	0 a	0 b	0 b	0 b	0.4 b	0 b	0 a	0 a	0 a	0 a
medium	0 a	0 a	0 b	0.2 b	0 b	0.5 b	0.2 b	0 a	0 a	0 a	0 a
large	0 a	0 a	0 b	0 b	0 b	0 b	0 b	0 a	0 a	0 a	0 a
(NH_4) ₂ SO ₄	1.3 a	10.4 a	5.2 a	6.5 a	5.8 a	11.6 a	2.1 a	0.5 a	0 a	0 a	0 a

† Different letters after numbers within columns are significant according to Tukey's test ($p < 0.05$).

NO₃⁻-N that leached at each irrigation from the small containers which held soil amended with 224 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.2 a [†]	0 a	1.5 ab	1.5 a	2.9 a	12.5 a	11.8 a	20.2 a	21.3 a	9.7 a	13.8 a
medium	0.1 a	0.1 a	1.6 a	1.3 a	2.5 a	12.5 a	10.8 a	14.3 a	10.7 a	4.8 a	8.1 a
large	0 a	0 a	0.4 b	2.5 a	3.6 a	14 a	12.5 a	14.5 a	28.6 a	8.3 a	13.6 a
(NH ₄) ₂ SO ₄	0.1 a	0.1 a	1.6 a	2.5 a	5.3 a	15.1 a	19.9 a	3 a	0.6 a	0 a	0 a

Total added N (NH₄⁺ + NO₃⁻) that leached at each irrigation from the small containers which held soil amended with 224 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.2 a	0 a	1.5 b	1.5 b	2.9 b	12.9 a	11.8 a	20.2 a	21.3 a	9.7 a	13.8 a
medium	0.1 a	0.1 a	1.6 b	1.5 b	2.5 b	13 a	11 a	14.3 a	10.7 a	4.8 a	8.1 a
large	0 a	0 a	0.4 b	2.5 b	3.6 b	14 a	12.5 a	14.5 a	28.6 a	8.3 a	13.6 a
(NH ₄) ₂ SO ₄	1.4 a	10.5 a	6.8 a	9 a	11.1 a	26.7 a	22 a	3.5 a	0.6 a	0 a	0 a

Cumulative kilograms of NH₄⁺-N that leached from the small containers which held soil amended with 336 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0 b	0 b	0 b	0 b	0.1 b	0.6 b	0.6 b	0.6 b	0.6 b	0.6 b	0.6 b
medium	0 b	0 b	0 b	0 b	0 b	0.7 b	0.7 b	0.7 b	0.7 b	0.7 b	0.7 b
large	0 b	0 b	0 b	0 b	0 b	0.1 b	0.1 b	0.1 b	0.1 b	0.1 b	0.1 b
(NH ₄) ₂ SO ₄	0.8 a	21.9 a	33.9 a	46.1 a	53.3 a	70 a	74 a	74.1 a	74.1 a	74.1 a	74.1 a

Cumulative kilograms of NO₃⁻-N that leached from the small containers which held soil amended with 336 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0.1 a	1.1 a	2.7 a	6 a	18 a	32.8 a	50.4 a	78.2 a	93.3 a	110 a
medium	0.1 a	0.1 a	4.4 a	6.3 a	9.3 a	30 a	56.2 a	95.4 a	124.6 a	140.8 a	159.3 a
large	0.2 a	0.2 a	2.2 a	3.9 a	7.3 a	25.1 a	38.5 a	59.1 a	65 a	72.9 a	87 a
(NH ₄) ₂ SO ₄	0.2 a	0.2 a	2.7 a	5 a	11.1 a	42 a	80.7 a	88.8 a	92.1 a	96.3 a	99.2 a

Cumulative kilograms of N (NH₄⁺ + NO₃⁻) that leached from the small containers which held soil amended with 336 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0.1 b	1.1 b	2.7 b	6.1 b	18.6 b	33.4 b	51 b	78.8 a	93.9 a	110.6 a
medium	0.1 a	0.1 b	4.4 b	6.3 b	9.3 b	30.7 b	56.9 b	96.1 ab	125.3 a	141.5 a	160 a
large	0.2 a	0.2 b	2.2 b	3.9 b	7.3 b	25.2 b	38.6 b	59.2 b	65.1 a	73 a	87.1 a
(NH ₄) ₂ SO ₄	0.9 a	22.1 a	36.6 a	51.1 a	64.4 a	112 a	154.7 a	162.9 a	166.2 a	170.4 a	173.3 a

† Different letters after numbers within columns are significant according to Tukey's test (p<0.05).

NH₄⁺-N that leached at each irrigation from the small containers which held soil amended with 336 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0 b†	0 b	0 b	0 b	0.1 b	0.5 b	0 b	0 a	0 a	0 a	0 a
medium	0 b	0 b	0 b	0 b	0 b	0.7 b	0 b	0 a	0 a	0 a	0 a
large	0 b	0 b	0 b	0 b	0 b	0.1 b	0 b	0 a	0 a	0 a	0 a
(NH ₄) ₂ SO ₄	0.8 a	21.1 a	12 a	12.2 a	7.2 a	16.7 a	4 a	0.1 a	0 a	0 a	0 a

NO₃⁻-N that leached at each irrigation from the small containers which held soil amended with 336 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0 a	1 a	1.6 a	3.3 a	12 a	14.8 a	17.6 ab	27.8 a	15.1 a	16.7 a
medium	0.1 a	0 a	4.3 a	1.9 a	3 a	20.7 a	26.2 a	39.2 a	29.2 a	16.2 a	18.5 a
large	0.2 a	0 a	2 a	1.7 a	3.4 a	17.8 a	13.4 a	20.6 ab	5.9 a	7.9 a	14.1 a
(NH ₄) ₂ SO ₄	0.2 a	0 a	2.5 a	2.3 a	6.1 a	30.9 a	38.7 a	8.1 b	3.3 a	4.2 a	2.9 a

Total added N (NH₄⁺ + NO₃⁻) that leached at each irrigation from the small containers which held soil amended with 336 kg N ha⁻¹.

Days	1	4	7	10	13	16	19	22	29	36	43
small	0.1 a	0 b	1 b	1.6 b	3.4 b	12.5 b	14.8 a	17.6 ab	27.8 a	15.1 a	16.7 a
medium	0.1 a	0 b	4.3 b	1.9 b	3 b	21.4 ab	26.2 a	39.2 a	29.2 a	16.2 a	18.5 a
large	0.2 a	0 b	2 b	1.7 b	3.4 b	17.9 b	13.4 a	20.6 ab	5.9 a	7.9 a	14.1 a
(NH ₄) ₂ SO ₄	0.9 a	21.1 a	14.5 a	14.5 a	13.3 a	47.6 a	42.7 a	8.2 b	3.3 a	4.2 a	2.9 a

Kilograms of N recovered from NH₄⁺-Cp which was amended to the small containers containing soil.

rate	112 kg N	224 kg N	336 kg N
small	12.8 bc	13.4 b	15.3 b
medium	24.8 ab	21.2 ab	27.1 b
large	35.3 a	29.1 a	47.2 a

Total kilograms of the added N recovered from the small containers containing soil.

rate	112 kg N	224 kg N	336 kg N
small	50.6 a	109.2 a	126 a
medium	83.4 a	88.9 a	187.2 a
large	81.7 a	127 a	134.3 a
(NH ₄) ₂ SO ₄	26.8 a	91.5 a	173.4 a

† Different letters after numbers within columns are significant according to Tukey's test (p<0.05).

APPENDIX J

ANOVAs for NH_4^+ -N that Leached from Soil in Experiment #1

ANOVA (average of all dates) of cumulative NH_4^+ -N that leached from the soil in experiment #1 (for Figure 14a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	10.2	14089	0.0001	0.992	32.3
N-source	3	34.2	138858	0.0001		
rate*N-source	6	30.7	14089	0.0001		
error a	60	3.1	144			
date	9	2.8	860	0.0001		
error b	36	0.0	3			
N-source*date	27	8.4	860	0.0001		
rate*date	18	2.4	370	0.0001		
rate*N-source*date	54	7.3	370	0.0001		
error c	396	0.8	5			

ANOVA (average of all dates) of NH_4^+ -N that leached from the soil in experiment #1 at each irrigation (for Figure 14b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	3.5	334	0.0001	0.927	167
N-source	3	12.1	770	0.0001		
rate*N-source	6	10.5	334	0.0001		
error a	60	1.1	3			
date	9	8.6	182	0.0001		
error b	36	0.6	3			
N-source*date	27	25.8	182	0.0001		
rate*date	18	7.6	81	0.0001		
rate*N-source*date	54	22.8	81	0.0001		
error c	396	7.3	4			

APPENDIX K

ANOVAs for NH_4^+ -N that Leached from Soil in Experiment #2

ANOVA (average of all dates) of cumulative NH_4^+ -N that leached from the soil in experiment #2
(for Figure 15a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	6.8	4252	0.0001	0.994	25.7
N-source	3	44.2	138858	0.0001		
rate*N-source	3	28.0	5818	0.0001		
error a	39	11.8	189			
date	10	1.4	84	0.0001		
error b	50	0.3	4			
N-source*date	30	3.9	82	0.0001		
rate*date	10	0.7	41	0.0001		
rate*N-source*date	30	2.3	48	0.0001		
error c	340	0.6	1			

ANOVA (average of all dates) of NH_4^+ -N that leached from the soil in experiment #2 at each irrigation
(for Figure 15b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	1.3	34	0.0001	0.868	251
N-source	3	10.0	87	0.0001		
rate*N-source	3	5.5	48	0.0001		
error a	39	1.2	1			
date	10	9.2	24	0.0001		
error b	50	4.0	2			
N-source*date	30	29.4	26	0.0001		
rate*date	10	6.0	16	0.0001		
rate*N-source*date	30	20.1	18	0.0001		
error c	340	13.2	1			

APPENDIX L

ANOVAs for NO_3^- -N that Leached from Soil in Experiment #1

ANOVA (average of all dates) of cumulative NO_3^- -N that leached from the soil in experiment #1
(for Figure 16a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	2.7	5212.0	0.0002	0.974	63.5
N-source	3	19.3	25242.0	0.0001		
rate*N-source	6	6.5	4240.5	0.0001		
error a	60	7.9	518.8			
date	9	13.0	5669.1	0.0001		
error b	36	0.2	16.7			
N-source*date	27	28.9	4208.9	0.0001		
rate*date	18	5.6	1220.4	0.0001		
rate*N-source*date	54	13.5	979.2	0.0001		
error c	396	2.6	25.4			

ANOVA (average of all dates) of NO_3^- -N that leached from the soil in experiment #1 at each irrigation
(for Figure 16b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	2.0	564.5	0.0001	0.885	148
N-source	3	14.9	2742.0	0.0001		
rate*N-source	6	5.2	474.7	0.0001		
error a	60	1.8	16.4			
date	9	13.7	839.8	0.0001		
error b	36	1.1	17.4			
N-source*date	27	28.3	577.6	0.0001		
rate*date	18	5.8	178.7	0.0001		
rate*N-source*date	54	15.6	159.6	0.0001		
error c	396	11.5	16.0			

APPENDIX M

ANOVAs for NO_3^- -N that Leached from Soil in Experiment #2

ANOVA (average of all dates) of cumulative NO_3^- -N that leached from the soil in experiment #2
(for Figure 17a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	4.6	617.0	0.0001	0.942	69.9
N-source	3	21.1	951.7	0.0001		
rate*N-source	3	7.5	336.0	0.0001		
error a	39	4.9	17.0			
date	10	17.0	230.3	0.0001		
error b	50	0.9	2.4			
N-source*date	30	18.8	84.9	0.0001		
rate*date	10	7.6	102.3	0.0001		
rate*N-source*date	30	11.8	53.2	0.0001		
error c	340	5.8	2.3			

ANOVA (average of all dates) of NO_3^- -N that leached from the soil in experiment #2 at each irrigation
(for Figure 17b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	2.0	35.0	0.0001	0.872	180.3
N-source	3	7.1	41.0	0.0001		
rate*N-source	3	3.5	20.3	0.0001		
error a	39	2.0	0.9			
date	10	13.6	23.7	0.0001		
error b	50	2.0	0.7			
N-source*date	30	23.7	13.8	0.0001		
rate*date	10	10.2	17.8	0.0001		
rate*N-source*date	30	23.1	13.4	0.0001		
error c	340	12.8	0.7			

APPENDIX N

ANOVAs for Total N that Leached from Soil in Experiment #1

ANOVA (average of all dates) of cumulative N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the soil in experiment #1 (for Figure 18a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	6.5	35726	0.0001	0.99	34.6
N-source	3	30.8	112865	0.0001		
rate*N-source	6	18.3	33529	0.0001		
error a	60	5.8	1059			
date	9	7.3	8871	0.0001		
error b	36	0.1	24			
N-source*date	27	17.5	7131	0.0001		
rate*date	18	3.6	2197	0.0001		
rate*N-source*date	54	9.3	1890	0.0001		
error c	396	1.0	27			

ANOVA (average of all dates) of N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the soil in experiment #1 at each irrigation (for Figure 18b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	4.8	1720.0	0.0001	0.894	115
N-source	3	26.8	6389.3	0.0001		
rate*N-source	6	13.2	1571.7	0.0001		
error a	60	1.8	21.1			
date	9	8.1	645.1	0.0001		
error b	36	1.0	20.4			
N-source*date	27	17.3	459.7	0.0001		
rate*date	18	4.4	173.6	0.0001		
rate*N-source*date	54	12.1	160.0	0.0001		
error c	396	10.6	19.2			

APPENDIX O

ANOVAs for Total N that Leached from Soil in Experiment #2

ANOVA (average of all dates) of cumulative N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the soil in experiment #2 (for Figure 19a).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	7.3	8326	0.0001	0.99	29.6
N-source	3	43.6	16635	0.0001		
rate*N-source	3	24.4	9316	0.0001		
error a	39	6.3	184			
date	10	4.3	489	0.0001		
error b	50	0.3	7			
N-source*date	30	7.2	274	0.0001		
rate*date	10	2.3	267	0.0001		
rate*N-source*date	30	3.9	150	0.0001		
error c	340	1.0	3			

ANOVA (average of all dates) of N ($\text{NH}_4^+ + \text{NO}_3^-$) that leached from the soil in experiment #2 at each irrigation (for Figure 19b).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	3.1	139.0	0.0001	0.866	156
N-source	3	16.6	247.0	0.0001		
rate*N-source	3	8.8	131.3	0.0001		
error a	39	1.1	1.3			
date	10	8.4	37.5	0.0001		
error b	50	3.0	2.7			
N-source*date	30	22.8	33.9	0.0001		
rate*date	10	5.8	25.8	0.0001		
rate*N-source*date	30	17.0	25.3	0.0001		
error c	340	13.4	1.8			

APPENDIX P

ANOVAs and Means for RGR, LAR, and NAR of Experiment #1

ANOVA (average of all dates) for corn RGR of experiment #1.

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	4.8	498	0.206	0.731	13.8
N-source	3	1.3	138858	0.826		
rate*N-source	6	2.3	81	0.943		
error a	23	32.4	294			
date	1	2.0	428	0.174		
error b	2	1.0	100			
N-source*date	3	7.7	539	0.178		
rate*date	2	17.8	1860	0.008		
rate*N-source*date	5	3.9	161	0.74		
error c	19	26.9	296			

ANOVA (average of all dates) for corn LAR of experiment #1.

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	1.6	24	0.035	0.969	10.4
N-source	3	1.5	15	0.081		
rate*N-source	6	3.4	17	0.031		
error a	23	4.6	6			
date	1	83.2	2521	0.0013		
error b	2	0.2	3			
N-source*date	3	0.1	1	0.846		
rate*date	2	1.9	30	0.0095		
rate*N-source*date	5	0.2	1	0.921		
error c	19	3.1	5			

ANOVA for corn NAR of experiment #1.

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	55.5	39.8	0.0001	0.636	18.4
N-source	3	2.3	1.1	0.7		
rate*N-source	6	5.9	1.4	0.71		
error	23	36.4	2.3			

Corn RGR for experiment #1

rate	112 kg N	112 kg N	224 kg N	224 kg N	336 kg N	336 kg N
day	23	35	23	35	23	35
small	133 a [†]	125 a	135 a	123 a	128 a	110 a
medium	110 a	149 a	md [‡]	121 a	128 a	118 a
large	123 a	129 a	127 a	125 a	140 a	107 a
(NH ₄) ₂ SO ₄	121 a	137 a	124 a	121 a	126 a	98.1 a

Corn LAR for experiment #1

rate	112 kg N	112 kg N	224 kg N	224 kg N	336 kg N	336 kg N
day	23	35	23	35	23	35
small	26.5 a	13.2 a	26.4 a	14.1 a	27.4 a	16.9 a
medium	29.6 a	13.9 a	md	15.4 a	27.8 a	16.6 a
large	28 a	14.1 a	27.7 a	14.9 a	27 a	16.5 a
(NH ₄) ₂ SO ₄	28.7 a	13.1 a	29.9 a	16.2 a	28.4 a	19.5 a

Corn NAR for experiment #1

rate	112 kg N	224 kg N	336 kg N
day	35	35	35
small	9.5 a	8.7 a	6.6 a
medium	10.8 a	8.1 a	7.1 a
large	9.3 a	8.4 a	6.5 a
(NH ₄) ₂ SO ₄	10.5 a	7.7 a	5.2 a

[†] Different letters within each column and each rate are significantly different according to Tukey's test (p<0.05).

[‡] md=missing data.

APPENDIX Q

ANOVAs and Means for RGR, LAR, and NAR of Experiment #2

ANOVA (average of all dates) for corn RGR of experiment #2.

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	0.1	1810.0	0.0001	0.965	12.8
N-source	3	0.0	126.3	0.0014		
rate*N-source	3	0.0	8.0	0.755		
error a	39	0.0	20.2			
date	5	95.0	580286.6	0.0001		
error b	25	0.3	382.5			
N-source*date	15	0.2	402.3	0.835		
rate*date	5	0.2	1248.8	0.081		
rate*N-source*date	15	0.7	1524.5	0.003		
error c	170	3.5	625.0			

ANOVA (average of all dates) for corn LAR of experiment #2.

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	0.4	1	0.12	0.917	3.2
N-source	3	0.5	138858	0.42		
rate*N-source	3	0.6	0	0.29		
error a	39	6.3	0			
date	5	78.3	30	0.0001		
error b	25	1.4	0			
N-source*date	15	1.4	0	0.028		
rate*date	5	0.1	0	0.884		
rate*N-source*date	15	2.8	0	0.0001		
error c	170	8.3	0			

ANOVA (average of all dates) for corn NAR of experiment #2.

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	0.3	83	0.0027	0.939	20
N-source	3	0.1	6	0.568		
rate*N-source	3	0.0	3	0.785		
error a	39	1.0	8			
date	4	90.2	7267	0.0001		
error b	20	0.6	10			
N-source*date	12	0.4	10	0.764		
rate*date	4	0.3	26	0.13		
rate*N-source*date	12	1.2	32	0.014		
error c	136	6.0	14			

Corn RGR for experiment #2, 112 kg ha⁻¹.

Days	7	14	21	28	35	42
small	263	358 ab [†]	243 a	176 ab	75.5 a	53.7 ab
medium	263	384 a	238 a	165 b	62.2 a	51.3 ab
large	263	303 b	259 a	191 a	75.8 a	58.8 a
(NH ₄) ₂ SO ₄	263	348 ab	250 a	180 ab	74.8 a	40.2 b

Corn RGR for experiment #2, 224 kg ha⁻¹.

small	263	332 a	259 a	184 a	89.5 a	71.8 a
medium	263	326 a	260 a	190 a	85.3 a	69.3 a
large	263	351 a	251 a	178 a	80.8 a	61.2 a
(NH ₄) ₂ SO ₄	263	333 a	253 a	181 a	83.2 a	67.4 a

Corn LAR for experiment #2, 112 kg ha⁻¹.

Days	7	14	21	28	35	42
small	8.4	8.9 a	10.1 a	10.7 a	10.1 ab	9.5 a
medium	8.4	9.2 a	10.2 a	10.7 a	10.3 a	9.5 a
large	8.4	9.1 a	10.2 a	10.6 a	10.1 ab	9.4 a
(NH ₄) ₂ SO ₄	8.4	9 a	10.2 a	10.4 a	9.8 b	9.4 a

Corn LAR for experiment #2, 224 kg ha⁻¹.

small	8.4	9 a	10.2 a	9.8 a	9.2 a	9.4 a
medium	8.4	8.7 a	9 a	10.6 a	10.1 a	9.5 a
large	8.4	8.9 a	10 a	10.5 a	10.1 a	9.5 a
(NH ₄) ₂ SO ₄	8.4	9 a	10.1 a	10.8 a	10.3 a	9 a

Corn NAR for experiment #2, 112 kg ha⁻¹.

Days	14	21	28	35	42
small	39 ab	23.7 a	16.5 ab	8.1 a	5.7 ab
medium	40.5 a	23.1 a	15.4 b	6.5 a	5.4 ab
large	32.9 b	25.1 a	18 a	8.1 a	6.3 a
(NH ₄) ₂ SO ₄	37.5 ab	24.3 a	17.6 ab	8.3 a	4.3 b

Corn NAR for experiment #2, 224 kg ha⁻¹.

small	35.9 a	25.2 a	18.5 a	10 a	7.7 a
medium	36.8 a	25.7 a	18 a	9.1 a	7.3 a
large	38.3 a	24.9 a	17 a	8.6 a	6.5 a
(NH ₄) ₂ SO ₄	36.4 a	24.6 a	16.7 a	8.7 a	6.66 a

† Different letters within each column and each rate are significantly different according to Tukey's test ($p < 0.05$).

APPENDIX R

ANOVAs for N Budget of Experiment #1

ANOVA for kilograms of N recovered from NH_4^+ -Cp amended to experiment #1 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	36.8	9950	0.0001	0.923	36.7
N-source	3	41.2	7428	0.0001		
rate*N-source	6	14.3	1288	0.0002		
error	23	7.7	180			

ANOVA for kilograms of N recovered from the corn shoots (leaves and stalk) from experiment #1 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	44.2	7296	0.0001	0.908	11.4
N-source	3	33.2	3660	0.0001		
rate*N-source	6	13.5	742	0.001		
error	23	9.2	132			

ANOVA for kilograms of added N recovered from experiment #1 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	2	88.0	102832	0.0001	0.958	9.97
N-source	3	3.4	2634	0.0029		
rate*N-source	6	4.5	1751	0.0057		
error	23	4.2	422			

APPENDIX S

ANOVAs for N Budget of Experiment #2

ANOVA for kilograms of N recovered from NH_4^+ -Cp amended to experiment #2 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	42.8	22562	0.0001	0.953	20.9
N-source	3	39.3	6910	0.0001		
rate*N-source	3	13.2	2321	0.0001		
error	39	4.7	64			

ANOVA for kilograms of N recovered from the soil in experiment #2 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	8.8	69	0.0536	0.12	295
N-source	3	0.8	2	0.948		
rate*N-source	3	2.7	7	0.753		
error	39	87.6	18			

ANOVA for kilograms of N recovered from the corn shoots (leaves and stalk) from experiment #2 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	70.0	13496	0.0001	0.837	12.7
N-source	3	13.0	832	0.0001		
rate*N-source	3	0.8	50	0.608		
error	39	16.3	80			

ANOVA for kilograms of N recovered from the corn roots from experiment #2 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	30.6	2075	0.0001	0.504	38.5
N-source	3	6.5	147	0.181		
rate*N-source	3	13.2	298	0.025		
error	39	49.6	86			

ANOVA for kilograms of added N recovered from experiment #2 (for Table 4).

Source	df	% SS	MS	Pr >F	R ²	C.V
rate	1	87.0	131543	0.0001	0.948	9.8
N-source	3	6.3	3179	0.0001		
rate*N-source	3	1.5	761	0.018		
error	39	5.2	202			