THESIS

CLINOPTILOLITE, AS A N, K, AND Zn SOURCE FOR PLANTS

Submitted by

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY MICHAEL D. LEWIS ENTITLED CLINOPTILOLITE, AS A N, K, AND Zn SOURCE FOR PLANTS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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ABSTRACT OF THESIS

CLINOPTILOLITE, AS A N, K, AND Zn SOURCE FOR PLANTS

Clinoptilolite was tested for its capacity to enhance availability of N, K, and Zn in the production of vegetable and flower species.

Ammonium charged zeolite and mixtures of zeolite plus ammonium sulfate or urea were evaluated in a greenhouse experiment involving a medium (13% clay) textured alkaline soil with no drainage provided and a light (6% clay) textured soil which was leached 6 times during the course of the experiment. Controls were ammonium sulfate and urea. Banding provided the most effective method of application of zeolite compared to incorporation when radish, Raphanus sativus cv. Improved Scarlet Globe, was used as a test species.

Banded ammonium charged zeolite increased radish growth in both medium and light textured soils. A decrease in NO_3-N loss occurred in the leached light soil. A physical mixture of uncharged zeolite and ammonium sulfate provided no increase in radish growth or reduction in leachate nitrate. Banding zeolite, in conjunction with urea, reduced growth suppression which occurred when only urea was added.

Growth response of tomato Lycopersicon esculentum cv. Spring Giant, were evaluated under field conditions, using banded treatments of ammonium charged zeolite, ammonium charged zeolite plus ammonium sulfate and uncharged zeolite plus ammonium sulfate. No differences in plant growth occurred among zeolite and control treatments due to unavoidable additions of nitrate nitrogen in the irrigation water.

Two greenhouse experiments were used to evaluate the influence of zeolite on vegetables, cut flowers and potted plant crops in two different media. Radish, *Raphanus sativus* cv. Improved Scarlet Globe responded positively to charged and naturally potassic zeolites, equaling growth obtained by the fertilizer injection method. Lettuce, *Lactuca sativa* cv. Grand Rapids Forcing (H-54); beans, *Phaseolus vulgaris* cv. Cherokee; chrysanthemums, *Chrysanthemum morifolium* cv. Bonnie Jean and snapdragon, *Antirrhinum majus* cv. Missouri growth was not positively affected by predesigned zeolite levels. Pot crops of poinsettia, *Euphorbia pulcherrima* cv. Dark Red Annette Hegg and Easter lily, *Lilium longiflorum* cv. Ace also were not responsive.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

Appendix Tables		Page

LIST OF FIGURES

LIST OF TREATMENT CODES

CZ-21 and CZ-NH_4 -- clinoptilolite, charged with NH_4^+ using $(NH_4)_2SO_4$

UZ-21 and NUZ -- uncharged clinoptilolite granulated with $(NH_4)_2SO_4$

UZ-45 -- uncharged clinoptilolite granulated with $CO(NH_2)_2$

21 -- $(NH_4)_2SO_4$

45 -- $CO(NH_2)_2$

STD-Z -- uncharged clinoptilolite

NN, NK and NZn -- No N, K or Zn was added

B -- banded

I -- Incorporated

C.V. -- coefficient of variation

CZ-21 + 21 -- clinoptilolite, charged with NH_4 using $(NH_4)_2SO_4$ physically mixed with $(NH_4)_2\ SO_4$

Injected -- N, K, and Zn applied through the irrigation system

UZ + injected -- uncharged clinoptilolite incorporated into medium together with N, K, and Zn applied through the irrigation system

CZ-K -- naturally potassic clinoptilolite

CZ-Zn -- clinoptilolite charged with Zn^{++} using $ZnSO_4$

INTRODUCTION

Zeolites are a group of minerals that are receiving greater attention in the agronomic and horticultural world due to their abundance, availability, and their physical and chemical uniqueness. Zeolite has been used in Japanese agriculture for hundreds of years as a soil amendment, yet very little scientific data has been published with regard to its usefulness as a nutrient source. Clinoptilolite, a naturally occurring zeolite, noted for its ion selectivity and affinity for NH_4^+, has in the past quarter-century, received the greatest attention.

Crop production is becoming increasingly difficult with increasing fertilizer cost. Crop demand for nutrients, especially N, K and some cases Zn, varies with the species and stage of growth. Frequent surface irrigations in the arid West and high rainfall areas of the East result in severe leaching of plant nutrients, primarily N; thus, establishing a priority in agricultural research to develop new nutrient sources and/or new ways to increase fertilizer efficiency.

Nitrogen is often the most limiting nutrient in crop production. This important nutrient undergoes a biological transformation in soil from NH_4^+, essentially an immobile form, to NO_3^-, a mobile form. The effectiveness of a nitrogen application can be increased by maintaining that element in the root zone in the NH_4^+ form by suppressing or delaying nitrification.

This study investigates the feasibility of using zeolite, clinoptilolite, to control the availability of NH_4, K, and Zn in soils and "artificial" media using primarily plant growth as an indicator in both field and greenhouse environments.

Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement by the author of this thesis is implied.

LITERATURE REVIEW

History and Characteristics of Zeolites

Early history reveals zeolites were used as building stones as long ago as 600 B.C. (75), although the first reported discovery of zeolites was in 1756 by Baron Axel Frederick Cronstedt, a Swedish mineralogist (77), who gave zeolite its name. An 1891 report documented the occurrence of phillipsite zeolite in deep sea sediments (79). Prior to the early 1950's, most zeolite occurrences were in fracture and vesicle fillings in igneous rocks, particularly basaltic rocks; occasional non-igneous occurrences were also reported (75). In the 1960's, three-fourths of more than 350 reports described zeolites as being found in sedimentary rocks (96,50). Modern technology and a more thorough understanding of how zeolites form (37) assisted in bringing about this rather sudden change. Since their "rediscovery" in the 1950's, more than a thousand occurrences of zeolite minerals have been reported from sedimentary rocks of volcanic origin in more than forty countries (75). By 1971, Breck (25) recognized 34 naturally occurring species of which analcime, chabazite, phillipsite, erionite, mordenite and clinoptilolite were the most common sedimentary zeolites.

Zeolites, among the most common authigenic (secondary) silicate minerals, form directly from silicic glass by a solution-precipitation mechanism (96). Hay (49) in 1966, correlated zeolite mineralogy with composition of host, water chemistry, age, and burial depth for the purpose of establishing the conditions under which zeolite-bearing mineral assemblages form and react in sedimentary rocks. Zeolite impurities of quartz, feldspars, phyllosilicates and volcanic glass may be found in minute to major quantities (24).

A review of the literature reveals various zeolite structure classification schemes (71,85,99). The literature also provides a very modern classification scheme based on framework topology as well as an excellent discussion of the unique chemical and physical properties of various zeolites (13,24,45,100).

Zeolite is a crystalline hydrated aluminosilicate of the alkali and alkaline earth cations, having infinite three-dimensional structures which classified it as a tektosilicate (77). Their ability to gain and lose water reversibly and to exchange cations without major structure change are unique characteristics.

One natural zeolite group, Clinoptilolite (klino-tee-lo-lite), has, in the past quarter-century, received the greatest attention. Clinoptilolite was first discovered in a basaltic rock from Wyoming (87). It was named "amygldales" and later given its present name by Schaller in 1932 (91). Occurrence of clinoptilolite was first documented as an alternation product of vitric tuffs of marine origin.

One of the earliest reports on clinoptilolite in sedimentary rock, was published in Japan (82). Sheppard (96) and Barrer (12) agreed that clinoptilolite is abundant in the United States in rocks of the cenozonic age and is a product of low-temperature reactions between sediment and saline lake waters. Early problems arose in classifying zeolites but a redefining of clinoptilolite established it separate from heulandite (74). The design of clinoptilolite framework is the reason for its unique physical and chemical properties.

Clinoptilolite has both eight-membered and ten-membered oxygen ring structures (31), with dimensional openings (windows) of 3.0 x 4.4 Å and 3.5 x 7.9 Å (108) respectively. Unlike feldspars, which are also tektosilicates, the zeolite framework contains large cavities (the exchange site in which cation and water are bound) and two or three-dimensional channels (restrictions between exchange sites) (13,26,49). A two-dimensional system has main channels which are linked by a network of smaller channels, where a three-dimensional system is composed of two types of channels which are equidimensional or non-equidimensional (24). The exact channel arrangement has not been satisfactorily determined. The electrostatically charged structure comes from replacement of quadrivalent silicon by trivalent aluminum, balanced by mono and divalant cations (77). The reasons for ion selectivity of the windows and/or the channels include: (a) nature of cation species with respect to hydrated radius and charge; (b) solution temperature; (c) concentration and distribution of cation, anion species, and (d) structural characteristics of the particular zeolite (68). A thorough discussion of the ion-sieve properties (59) and detailed descriptions on the adsorption properties of zeolites are available (27,77). Ames (8) showed that the structural water of clinoptilolite is not firmly bound to the zeolite framework. Thus, ammonium does not attract as much water via hydration and therefore, is free to move through the lattice and closely approach the exchange sites. Barrer et al. (14) described a steric effect in the exchange process of adsorbed cation and organic ions. Due to the selectivity effect of clinoptilolite, the cation exchange capacity (CEC) varies from approximately 160 to 200 meq per 100 g (107) to a high of 230 meq per 100 g (77). Barrer et al. (14) found that the exchange capacity corresponded to 98% of the total possible capacity. Thus, practically all of the exchange sites in clinoptilolite are accessible by alkali and alkaline earth metal ions.

Ames (7) identified the selectivity or lyotropic series for the Cs^+ exchange of clinoptilolite from the Hector, California deposit as Cs > Fe > Al > Mg > Li. In a later study on Na-based clinoptilolite, part of the series was later confirmed, Cs > NH_4 >> Na, by Howery and Thomas (57). Vaughan (108) states, "Clinoptilolite works best when the cation to be removed is present (in solution) in low concentrations." Also, appreciable quantities of Ca^{++} and Mg^{++} have detrimental effects on the NH_4^+ exchange capacity of this zeolite. One of the most unique properties of clinoptilolite is its affinity and selectivity for NH_4^+ which was investigated by Ames (10) and Mercer et al. (72).

The ion exchange and diffusion rates of clinoptilolite were studied by Ames (9), who demonstrated how the diffusion coefficient decreased with increasing cation balance and clinoptilolite particle size. His findings were based on the sum of interspace and intracrystalline diffusion of which intracrystalline was the controlling phase of the diffusion.

Zeolite as a Fertilizer Carrier and/or Slow Release Fertilizer

Due to the affinity of clinoptilolite for NH_4^+, numerous industrial and agricultural uses have arisen. A review of its uses includes lightweight aggregates, filler in the paper industry, ion exchange processes, animal husbandry and aquacultural applications, soil amendments and fertilizers (75,76,106).

Very little research has been reported on the use of zeolites as a slow-release type fertilizer or fertilizer carrier, especially clinoptilolite. Nitrogenous fertilizers, $(NH_4)_2SO_4$, NH_4Cl, NH_4NO_3 and urea, were treated with zeolite or bentonite to prevent hygroscopicity or loss by leaching when applied to soil (53). Sasaharu (90) utilized domestic animal wastes and zeolites as a fertilizer. Synthetic zeolites have been patented as a formulation in which zeolite is mixed with NPK fertilizer (92). Mumpton (76) stated, "In Japan, the ion-exchange selectivity of clinoptilolite has been exploited in the preparation of chemical fertilizers which tend to improve the nitrogen retention of soils by prompting a slow-release of ammonium ions." No literature was cited to support this statement.

Zeolite has also been used as a pesticide carrier. Organophosphate, granulated with zeolite, was used to prevent the development of stem blast in rice paddies (112).

A comprehensive study on the use of erionite and two clinoptilolites, as potential soil amendments and N fertilizer carriers for two soils, was reported by MacKown (68). He showed that the chemical and physical properties of the experimental soils were affected very little by the zeolite at rates of 10 g zeolite/kg soil ($\sim$ 10 tons/acre), although a significant increase in CEC of both soils was noted with increasing additions of the 0.85 to 0.3 mm sized zeolites. By leaching a saturated column containing mixtures of a silty clay loam textured soil, and erionite and clinoptilolite at rates of 0 to 50 g zeolite/kg of soil, MacKown (68) showed a significantly greater retention of applied NH_4^+-N with increasing zeolite rates. The author (68) suggested that retention of NH_4^+ was influenced by the CEC of the soil and would probably be favored by restricting the depth of zeolite incorporation at a given rate of application. This seems to indicate that a band application of zeolite might be very effective. In another experiment using a loamy sand and a silty clay loam amended with natural and NH_4-preadsorbed zeolites (charged zeolites), MacKown (68) indicated that by changing the particle size from 0.85-0.30 mm to 2.0-1.0 mm size range, the NH_4^+ preadsorbed zeolites reduced nitrification. A greenhouse experiment with ryegrass grown in nonfree drainage containers was used to evaluate the availability and utilization of NH_4^+-N and benefits of zeolite amended soils on plant growth. The results showed no positive effects due to zeolite additions on plant growth or N utilization. A second greenhouse experiment using Sudan-grass grown in silty clay loam soil, amended with natural erionite and NH_4^+ preadsorbed erionite, resulted in greater yields and utilization of applied N especially in the preadsorbed form. Although the leachate data were inconclusive and indicated no significant treatment differences.

In areas of heavy rainfall, where nutrient loss due to leaching is a constant problem and in areas with soils of high fixing capacity, slow-release fertilizers may be a partial answer for increasing production. The concept of nitrogen immobilization was first reported in 1948 by Goring and Clark (44) and later supported by Legg and Allison (63).

The ultimate goal of a slow-release source, either fertilizer or zeolite, is to release nutrients at a rate equal to, or slightly greater than the demands of a growing plant, yet resist loss due to various soil and environmental phenomena.

Parr (84) listed a number of problems that occur with most common nitrogen and other fertilizers which can decrease the efficiency to approximately 50% under many agriculture situations.

The concept of controlled release fertilizer is to take a common fertilizer, such as urea or ammonium nitrate, and coat it with an inert, water-resistant coating or membrane-like plastic, resin, wax, paraffin, asphaltic compounds or elemental sulphur.

Oertli and Lunt (81) showed that the release of N from coated granules of ammonium nitrate could be regulated by varying the thickness of the coating; K was released at a slower rate compared to the N. They also concluded that the soil pH, biologically tolerable salt concentration in soil solution and soil moisture conditions within normal plant growth ranges had very little effect on release rates. Oertli and Lunt (81) further stated that the temperature was directly related to release rates and was the biggest rate controlling factor. Dahnke (36) using polyethylene membranes effectively controlled the rate of release of the fertilizer constituents, NPK. In 1952, Goring (42,43) reported a classic example of the inhibitor approach in which N-serve acts as a repressor or inhibitor of the genus Nitrosomonas bacteria, which is the ammonium oxidizer in the nitrification sequence.

Other types of coating have been reported. Army (11) listed a slow-release concept utilizing three different membrane-type coatings.

In later studies, the slow-release trend shifted toward resinous membranes (51) and coating granular fertilizers, especially K^+ (61). Lunt and Kwate (66) used K-frit successfully to supply K^+ for prolonged periods to chrysanthemums, poinsettias, hydrangeas, cyclamen and cotton grown in pots. Using a capsuled 24-5-10 fertilizer, Dahnke (36) reported an insignificant difference in yield but a more uniform growth of Kentucky bluegrass. Cochrane and Matkin (33) designed an experiment to evaluate the efficiency of slow-release fertilizers. It was concluded that the organic and synthetic fertilizers were not highly efficient in providing a slow-release of potassium. Hershey et al. (52) evaluated clinoptilolite as a controlled-release K source by leaching in growth studies of Chrysanthemum morifolium Ramat. The authors (52) determined that clinoptilolite from the amount of K^+ released, did not behave like a soluble K^+ fertilizer but similar to a slow-release fertilizer.

In two experiments, Holden and Brown (55) showed that zinc glass in small applications increased yields as compared to five crystalline zinc sulfates and that zinc ammonium phosphates supplied adequate zinc in the powder form compared to the granulated form. Sharpee et al. (95) conducted a study on the uptake of zinc, copper, and iron by four successive crops of corn (Zea mays L.) from applications of trace elements-sulfur fusion to plain field sand in pots. The results showed that the various zinc treatments gave increased total yields and that the concentrations of tissue zinc were inversely related to granule size of the ZnO-S and $ZnCO_3$-S fusions. This supported earlier reports that slowly soluble zinc carriers must be at least as fine as 200 mesh for satisfactory performance (32). Hoeft and Welsh (54) demonstrated the effectiveness of granular Zn frit-CSP mixtures. The chelating compounds provided another source of Zn to fulfill plant requirements. Zn EDTA increased the Zn content of the crop, twice as much as zinc sulfate in the neutral soil, and up to six times as much in the calcareous soil. Boekle and Lindsay (20) reported that banded chelates may be more effective than inorganic Zn sources because of their greater mobility in the root zone.

Zeolite Effect on Plant Nutrient Availability

Nitrogen

The growth of agricultural plants is limited more often by a deficiency of nitrogen than any other nutrient. Nitrogen present in soils, the bulk in organic form, is negligible compared to the total nitrogen of the earth (19). The principal source of nitrogen used by plants that do not fix nitrogen by symbiosis with microorganisms is in the mineral form of nitrogen. This mineral form constitutes the chemically combined nitrogen which is the sum of the exchangeable ammonium and the ammonium, nitrite, and nitrate in the soil solution. It should be noted that many of the chemical and biological transformations of nitrogen in the environment are not clearly understood.

The soil is an environment governed by various interactions between phases. Thus, a comparison of zeolite and clay effects on these phases and nitrification is warranted. The importance of the relationship between the soil adsorbed phase of plant nutrients and their availability to the plant by means of ion exchange has been emphasized (21,69,105). The role of surface areas on nitrification is conflicting and inconclusive. Enhancement of microbe respiration, thus population, by addition of clay minerals was observed by Stotzky (101) and Stotzky et al. (103). Discrepancies about the site of nitrification exist (1,2,62,63). It was not until 1955 (41) that researchers using active cultures of nitrifying bacteria concluded that the NH_4^+ availability to nitrifying bacteria was directly related to the solution phase NH_4^+ or to the NH_4^+ released by the cation exchange process. This is contradictory to previous reports (1,2,62,63).

Kai and Harada (58) investigating the effects of nitrification rates by adding clay minerals to culture solutions, concluded that the addition of montmorillonite and halloysite to a culture solution led to the stimulation of nitrification in various degrees, thus depending on the type and amount of clay minerals added and upon the concentration of NH_4-N applied. They also found significant positive correlations between nitrifying activity and calcium saturation degree of clay minerals. Some support to these results was given in an earlier report (56) that calcium acts as a catalysis in nitrogen fixation by Azotobacter, stimulating population increases. Stotzky and Rem (103), supported with unpublished work by Macura and Stotzky (102), reported that nitrification was enhanced, not by kaolinite, but by montmorillonite. They concluded that the pH sensitive nitrifier activities may have been enhanced by a pH buffering mechanism of the montmorillonite clay (103).

Nitrification researchers have reported on other factors that influenced the nitrifying process. High concentrations of total salts, > 2000 ppm, and a concentration of NH_4^+-N > 200 ppm in solutions, was directly related to the depression of the ammonification process (48).

Conflicting evidence has been reported on the effects of zeolite on nitrification. Sims and Little (97) used a tertiary activated sludge pilot plant aeration tank with recirculated sludge to evaluate effects of additions of clinoptilolite on nitrification (97). They provided very weak evidence that clinoptilolite increased nitrification efficiency in the activated sludge process, and that zeolite provided an ideal surface for attachment of nitrifying bacteria. Semmens and Goodrich (93) undertook a study to determine whether nitrifying bacteria could "regenerate" clinoptilolite and to what extent. Regenerate was defined as the removal of ammonium. They found that the rate of nitrification during regeneration was always observed to be much slower than the rate of nitrification of the free NH_4^+ in the solution. This seems to support early reports on NH_4^+ exchange association with nitrification in clays (41). Semmens et al. (94) developed an equation to show that the amount of NH_4^+ displaced from zeolite is influenced both by the amount of absorbed NH_4^+ on the zeolite and the salt concentration in solution. They also concluded that the rate of nitrification was dependent upon the solution concentration of NH_4^+. Surface area enhancement of nitrification was considered negligible, thus, observed differences in nitrification rates were attributed to difference in the rates of ion exchange between the two different zeolite particle sizes. Therefore, by decreasing the particle size of clinoptilolite and increasing the salt concentration in the solution, the rate of ion exchange would increase. A study conducted by the Environmental Protection Agency (EPA) revealed a simplified technique for quickly approximating the absorption capacity for clinoptilolite and varying concentrations of competing cations (107).

An earlier EPA report by Koon and Kaufman (59) showed the pH range to be 4 to 8 for optimum conditions for ammonium exchange of zeolite, which decreased rapidly outside this range. Also, the ammonium exchange capacity was observed to decrease sharply with increasing competing cation concentrations. This is in agreement with Semmens et al. (94).

MacKown (68) reported on a clay fixation study by Faurie, and Faurie et al., which confirmed that a reduction in nitrification by clay additions to a calcareous coarse-textured soil, employing a perfusion technique, was due to initial adsorption and fixation of NH_4^+ by the clay fraction. Their conclusion was similar to that of Allison et al. (5), which also stated that ammonium fixation is shown to be a factor of importance in agriculture, especially where NH_4^+ fertilizers are added to the soil of nonkaolinitic soils. Allison et al. (5) showed, by using a leaching method in a glass extraction tube with NH_4Cl and wetting and drying methods, that illite and vermiculite containing soils are able to fix ammonium, especially under wet conditions. The pH was of little importance. The authors (5) also demonstrated using fine-textured, nonkaolinitic soils, that nitrification could be increased 20 to 100% by first preventing fixations before addition of the ammonium. Welch and Scott (110) later demonstrated how added K^+ interfered with nitrification of adsorbed NH_4^+ because it blocked the release of the NH_4^+. Certain colloids exhibit unusually high preferences for specific cations. This affinity may be due to the relative hydration energies of various ions and of individual cation exchange sites on different minerals (21), as may be the case with the zeolite cavity. The conclusion of limited availability of fixed NH_4^+ to plants, has been reported by previous researchers (4,5,6).

Denitrification losses are in the order of 10–30% of nitrogen lost within a year (28). The term denitrification refers to the biological reduction of nitrate and nitrite to volatile gases, usually nitrous oxide and/or molecular nitrogen. Broadbent and Clark (28) described enzyme denitrification as a biological process where the anaerobic bacteria under aerobic conditions oxidize carbohydrates such as glucose to CO_2 and water. In the absence of oxygen the anerobic bacteria with nitrate present are capable of nitrate respiration which is expressed as:

$$C_6H_{12}O_6 + 4\ NO_3^- \rightarrow 6\ CO_2 + 6\ H_2O + 2\ N_2$$

Cooper and Smith (34) reported the distribution of various nitrogen species as a function of time in soils, within a closed atmosphere condition and in an anaerobic system using gas chromatography. The sequence was: $NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$. Broadbent and Clark's (28) review of the literature showed that poor soil aeration and the presence of nitrate and organic matter were requirements for denitrification. They (28) also listed factors that affect denitrification; partial pressure of oxygen, organic matter, pH, moisture content, nitrate concentration and redox potential. A complete discussion of each factor is presented. They also stated that enzymatic denitrification can occur following use of ammoniacal fertilizers, provided there are suitable conditions for nitrification; nitrate formed by nitrification processes and fertilizer nitrate are equally susceptible.

Clinoptilolite, with the NH_4^+ adsorbed internally could act as a depressant against NH_4^+ fixation by the soil clay faction and denitrification in anaerobic conditions, and microbial immobilization.

The movement of nitrogen in and on soils is receiving greater attention from our society today due to the pollution aspect. The two forms of nitrogen in the soil that are utilized by the plant are NH_4^+ and NO_3^-, with the latter form being the most readily lost in leaching. Reports listed the factors or characteristics of the leaching process that supplies the root zone with an adequate distribution of ions (40,88,111). The amount of percolating water and the soil porosity were reported to determine the magnitude of leaching (104). Fuller (40) reviewed the influence of environmental factors peculiar to arid and semiarid calcarceous soils on the reactions and movement of nitrogen fertilizers. The relative leaching series (111) of some common ions are as follows:

$$Na \gg K;\ Mg > Ca;\ Cl \geq NO_3 > SO_4 \gg H_2PO_4$$

The exchangeable basic cations in soils consist mainly of Ca, Mg, K and Na; the other cation nutrients usually occur only in very small amounts (19,105).

Nitrate nitrogen, in pH ranges of waste water, moves quite freely in soil columns (88). Bates and Tisdale (15) using laboratory techniques predicted NO_3^- movement when certain factors were known. Preul and Schroepfer (88) reported that NH_4^+ flow through a soil bed, under well aerated conditions, was determined by total nitrification. The authors (88) concluded that the CEC plays an important role in N movement in the soil, due to the physical adsorption of NH_4^+, and that the NH_4^+ adsorption may be influenced by other ions. They summarized that the adsorption and biological action are the main factors which control movement of nitrogen through soils. This report gave support to earlier reports (22,80) that movement of ammonium by leaching in coarse textured, calcareous soils may be significant and influenced mainly by the soil CEC.

As early as 1935, various N-source fertilizers were categorized by Parker (83) based on the retention of the N-source by the soil: sodium nitrate, readily leached; urea, ammonium sulfate and insoluble organics, leached with difficulty.

Using a small percolation-type lysimeter with Norfolk sand treated with several nitrogenous materials, Benson and Barnette (16) summarized that all nitrogen applied as nitrate was leached and one-third of the ammonium nitrogen applied as ammonium sulfate or ammonium nitrate was leached. They also conducted a second series of cultures using four soil types which were treated with sodium nitrate, ammonium sulfate, urea, castor bean pomace and no fertilizer treatment. The results substantiated the earlier findings and further showed urea was not found in any of the leachates.

Potassium

Potassium is absorbed by plants in larger amounts than any other mineral element with the exception of nitrogen and is present in relatively large quantities in most soils. However, only a fraction, water-soluble plus exchangeable, of the total potassium in most soils is available to plants (19). Terry and McCants (104) reported that in certain

North Carolina soils, the order of leaching of ions was Mg > NO_3 > K = NH_4. Lunt and Kwate (66) stated, "The depletion of potassium from bench soils, either by plant absorption or leaching, can be very rapid." A complete review of the factors influencing movement of K^+ in soils is provided by Munson and Nelson (78). In general, the greater the percentage clay, the higher the exchange capacity and moisture holding capacity which interact to retard K^+ movement. The authors (78) noted that the leachability of added K^+ was markedly reduced as pH approached neutrality. Lunt et al. (67) reported decreasing K^+ levels in fine-textured and higher losses in coarse-textured soils, in raised benches. The range was 1.7 to 0.7 meq per 100 g in a period of 4 months. Working with nursery soils, Krause (60) showed a need for an adjustment of rate and frequency of K^+ fertilization according to pH and base saturation. This lends support to an early report (86) that demonstrated physiologically acid nitrogen sources greatly increased the downward movement of potassium. Pearson (86) after conducting various experiments and reviewing the literature stated, "It is obvious that efficient use of potassium fertilizer demands that it be applied frequently in relatively small amounts and the source of nitrogen used and the calcium status of the soil affect the rate of leaching of potassium."

Zinc

Zinc deficiency in the semiarid Great Plains area is a serious problem. Chesnin (32) reported that zinc deficiencies are not necessarily confined to this area. The deficiency may occur on soils of both acid and alkaline conditions. The acid soil may contain low total zinc whereas the alkaline soil may be considered low in available Zn although very high in total zinc content. Zinc is relatively immobile in most soils (17,20,105). The normal level ranges between 10-300 ppm total zinc, although reported accumulation rates of up to 358 and 13,960 kg Zn/ha for Nebraska field corn on acid and alkaline soils, respectively, without the appearance of toxicity (32). Berger (17) describes instances in New York where leached Zn concentrations of 23,000 to 67,000 ppm accumulated in peat and muck soils. Very little has been published on the toxicity of Zn to plants. The predominant zinc species in solutions below pH 7.7 is Zn^{2+}, although $ZnOH^{+}$ is more prevalent above this pH. Lindsay (64) provided an estimation of the equilibrium constant for the reaction:

$$\text{Soil-Zn} + 2H^{+} \rightleftharpoons Zn^{+2} \quad \log K° = 5.8$$

He also showed using graphs and equations that the solubilities of various zinc minerals decrease 100-fold for each unit increase in pH. Tisdale and Nelson (105) reported on a study carried out in Illinois that suggested zinc retention by soils has the following relation to other cations:

$$H > Zn > Ca > Mg > K.$$

The problems that cause or are related to zinc deficiency in various soils are: zinc fixation with inorganic and organic forms, leaching losses, positional unavailability, temperature and phosphorous-induced zinc deficiency. Detailed reports on these problems are available for review (20,23,32,73,105).

Zeolite Influence on Ammonia and Nitrite Toxicity

Autotrophic ammonium-oxidizing organisms are sensitive to combinations of high concentrations of ammonium and high pH values developed in soil by ammonium containing-producing fertilizers.

Smith (98) investigated the mineralization and nitrification of alfalfa particles when added to soil mixtures. The author stated that the nitrification rate decreased with decreasing CEC of the soil. Smith (98) concluded that the decreasing CEC, and the resulting increase in soil solution pH, produced a NH_3 concentration that is toxic to *Nitrobacter*.

The U.S. Environmental Protection Agency reported that NH_4 fertilizer, when added to various soils, increased the pH (107). Fuller (40) noted that the nitrifying rates and availability to plants of N-fertilizer sources vary in calcareous soils. It has also been reported that banding an organic N-source, like urea, in a calcareous coarse textured soil, may drive the pH to levels $\geq$ 9.0 (20,35). Urea hydrolysis produces a N source for the nitrifiers of NH_4^+ and NH_3 (48). As the pH increases, the equilibrium in equation [1] shifts to the left increasing the NH_3 concentration.

$$NH_3^\circ + H^+ \rightleftharpoons NH_4^+ \quad \log K^\circ \; 9.28 \quad [1]$$

$$NH_3(g) \rightleftharpoons NH_3^\circ \quad \log K^\circ \; 1.76 \quad [2]$$

From Lindsay's (64) equations [1,2], it can be calculated that at pH of 9.28 NH_4^+ and NH_3° are equal in concentration. Therefore, adding certain NH_4^+ fertilizers in calcareous soils, increases the concentration of ammonia. The proportion of the total NH_3 that is ionized depends on the pH (40) and the dissociation constant for that molecule (98,109). Hence, with increasing pH, NH_3 may be lost through volatization to atmosphere (40) and/or may accumulate in the soil to a level toxic to seedlings (19,105) and the nitrite oxidizer, Nitrobactor agilis (3,94). Court et al. (35) reported that volatization of NH_3 from the soil, initial pH of 7.4, during the first week could be detected by smell. Excellent discussions on nitrification and its associated equations are available (19,48,105).

MacKown (68) suggested that NH_4^+ preadsorbed erionite and to a limited extent, natural erionite reduced toxic effects of high concentrations of NH_3, although no justifications were given.

Koon and Kaufman (59) demonstrated that regeneration or removal of NH_3 from clinoptilolite using sodium salts, calcium being second, proved to be the most effective, at pH 12.5. It was hypothesized that the unionized ammonia formed at the high pH was able to diffuse through the zeolite pores more readily than the ammonium ion.

Fuller (40) reported that nitrite will accumulate at almost any pH level above neutral, depending upon the concentration of NH_4^+ as it interacts with the pH levels. Chapman and Liebig (30) attributed nitrite accumulation to the inhibition of Nitrobacter by ammonia under neutral or alkaline conditions. They concluded that heavy applications of ammonium or ammonium-forming fertilizer are likely to lead to high levels of nitrite. It was pointed out that levels of 10 ppm of NO_2-N at 20% soil moisture in the root zone might inflict plant damage (18).

Court et al. (35) provided an excellent review on nitrite toxicity arising from use of urea. Grogan and Zinc (46) discussed how toxicity of nitrite and ammonia nitrogen may possibly be dependent upon the absorption and utilization or detoxification within the plant.

MATERIALS AND METHODS

Plant Responses to Zeolite-N Governed by Soil Texture and Leaching

Two experiments were conducted in the Plant Science Greenhouse, Colorado State University, Fort Collins, Colorado (105° 4' W. Long. and 40° 35' N. Lat., Elev. 1550 m). Each experiment involved a different soil, created by combinations of clay loam obtained from W. D. Holley Plant Environmental Research Center at CSU and sand purchased from Sterling Sand and Gravel Co., Fort Collins. Both the clay loam soil and sand were steam pasteurized at 83°C for 24 hours, air-dried, passed through a 6.35 mm screen, then mixed in a 57 liter portable cement mixer in proportions to form the media referred to as "medium" and "light" textured soils (Tables 1 and 2). Nutrients were available in adequate quantities, except nitrogen (Table 1).

Charged and uncharged natural zeolites, California clinoptilolite deposits, were donated by J. J. Lawson, Resource Industries International Ltd., Denver, Colorado 80222. The samples as supplied, Tables 3 and 7, had been crushed and sieved to retain those particles that passed through .044 mm screen. The cation exchange capacity (CEC) of the clinoptilolite was 1.93 meq/g (Appendix Explanation 1). The experiments consisted of 2, 12 x 12 Latin Squares, one for each soil and the treatments were as follows:

1. Ammonium charged zeolite, CZ-21, incorporated, 2.99% N which 2.86% was exchangeable N and 0.13% was associated N.

2. Uncharged zeolite mixed with ammonium sulfate and granulated, UZ-21, incorporated, 2.76% N.
3. Uncharged zeolite mixed with urea and granulated, UZ-45, incorporated, 2.34% N.
4. Ammonium sulfate, 21, incorporated, 21.2% N.
5. Urea, 45, incorporated, 46.65% N.
6. Ammonium charged zeolite, CZ-21, banded, 2.99% N which 2.86% was exchangeable N and 0.13% was associated N.
7. Uncharged zeolite mixed with ammonium sulfate and granulated, UZ-45, banded, 2.76% N.
8. Uncharged zeolite mixed with urea and granulated, UZ-45, banded, 2.34% N.
9. Ammonium sulfate, 21, banded, 21.2% N.
10. Urea, 45, banded, 2.99% N.
11. Uncharged zeolite, STD-Z.
12. No nitrogen added, NN.

Treatments were added to both soils to provide levels of supplemental N of 300 and 400 mg/2 kg of dry soil in the medium and light soil, respectively. Each treatment was mixed in bulk with each of the two soils in a cement mixer for 3 minutes.

Medium soil containers were lined with 25 x 36 x 0.010 cm polyethylene bags to eliminate possible contamination. Light soil containers, in which a leaching study was conducted, were coated with an asphalt based paint and center-punched in the bottom with a 2.5 cm diameter hole for drainage.

All containers (2.4 liter, number 10 cans) were equalized with regard to weight and soil surface height (2 cm from the top) by means of lead shot (contained) and perlite prior to the addition of the soil. Screens separated perlite and soil and covered the drainage hole in the light soil containers. Each container held 2 kg of air dried soil.

Twenty-one Captan® treated seeds of radish, Raphanus sativus, cv. Improved Scarlet Globe, were planted on a 2.54 cm grid, 0.6 cm deep in each container, on April 26, 1979.

Watering was accomplished with untreated tap water, using a weighing technique. Both soils were maintained within their respective field capacity ranges; medium soil at 12-20% and light soil at 16-28%, by weight. The field capacity was predetermined by saturating 2 kg of each soil, allowing it to drain for 48 hours, then determining the moisture content.

The greenhouse was heated to 15-17°C day and night. Cooling began when air temperatures reached 25°C. A slight aphid infestation was controlled by use of Pirimor.®

Emergence counts were taken for a period of 145 hours after planting. Coefficient of velocity of emergence (Appendix Explanation 2) and median time until 50% emergence (F. D. Moore, III, personal communications) were used to determine the possible influence of treatments on germination.

Harvests occurred on the 11, 15, 20, 25, 33 and 36 and 11, 15, 20, 25, 29 and 34 days from planting, in the medium and light soil, respectively. Controlled harvesting acted as a thinning process, allowing two plants to remain for the fifth and sixth harvest, thus avoiding plant competition. Plants were harvested, washed to remove soil, blotted dry and placed in plastic bags. Roots and leaves were separated at the hypocotyl and leaf area was measured with a Lambda #LZ-3100 photoelectric meter leaf area meter (resolution to 0.1 mm^2).

Root diameter, fresh root weight and commercial grade roots ($\geq$ 16 mm diameter) were recorded only on the fifth and sixth harvests. Harvested tops and roots were dried in a forced-draft oven at 70°C for 48 hours, and dry weight were taken. Dried plant tops were ground with a Wiley Mill through a 40-mesh stainless steel screen, then combined to form three samples per treatment (Reps 1-4, 5-8, 9-12) and analyzed at the CSU Soil Testing Laboratory for total N.

A leaching study was conducted in the light soil. Six leachings were carried out at 8, 13, 19, 35 and 41 days after planting. Three hundred ml of tap water were added to each container; the leachate, approximately 75 to 125 ml, was collected and analyzed for NO_3-N using the specific ion electrode method (70).

After final harvest, soil samples were taken and combined to form four samples per treatment (Reps 1-3, 4-6, 7-9, 10-12). Subsequent analysis for NH_4-N and NO_3-N was completed by the Soil Testing Laboratory at CSU. Unpaired t-test, paired t-test or analysis of variance with mean separation using Tukey's H.S.D. was used in evaluating data. Mean separation was at the 5% level of probability in all cases.

Effects of Zeolite-N Combinations on Field Tomatoes

The Horticultural Research Farm, 6.5 km West and 3.2 km North of Fort Collins, Colorado, was the site for this experiment. Previous crop was potatoes. The soil chemical and physical characteristics are presented in Tables 4 and 5, respectively.

Zeolite used in this experiment was the same as in the Plant Science greenhouse experiment, however, the N charge level was slightly higher. The field nutrition treatments consisted of:

1. Ammonium charged zeolite, CZ-21, 4.64% N, which contained 2.66% exchangeable N and 1.98% associated N.
2. Ammonium sulfate, 21, 21.2% N.
3. Ammonium charged zeolite plus ammonium sulfate, CZ-21+21, physical mix 50/50 by weight, 12.8% N.
4. Uncharged zeolite plus ammonium sulfate, NUZ, in bead form from the manufacturer, 4.07% N, which contained 1.80% exchangeable N and 2.28% associated N.

All treatments were applied at the rate of 56 kg/ha, sidebanded (10 x 10 cm) on one side at transplanting. Adequate nutrients were available for optimum plant growth except NO_3-N and P. Phosphorus was broadcast at a rate of 36 kg P/ha (84 kg P_2O_5/ha) and incorporated prior to treatment application and planting.

An 'All American Selection,' <u>Lycopersicon</u> <u>esculentum</u> cv. Spring Giant, a 65 day maturing determinate hybrid was seeded, 2 Captan® treated seeds per cell in flats of peat-vermiculite on April 17, 1979. Seedlings were thinned to one plant per cell on May 8. Watering was with untreated tap water until seedling emergence, thereafter with nutrient solution (47) until transplanting.

Plants were acclimated for 5 days, selected for vigor and uniformity, then transplanted to the field on June 13.

Treatments were applied preplant to the field. Transplants were planted on 102 cm row centers with a 61 cm intrarow spacing. Border rows were planted along perimeter and one in center of plot. A randomized complete block, with 10 replications each of which consisted of 10 plants, provided a total of 500 plants employed, for a population density of 2631 plants per hectare. Only the center four plants per treatment per replication were harvested for data. Planting depth was to bottom leaves of transplants.

Irrigation frequency was determined by tensiometers placed at 15 cm and 31 cm depth across the center of field plot. Fifty centibars was the soil matric potential when furrow irrigation began. The field was cultivated, hand-weeded as needed and plants sprayed twice, once each with Malathion® and Sevin.® Visual observations of treatment differences were noted and pictures taken throughout the experiment.

Ripe fruit were harvested, weighed and counted on a weekly basis from August 27, 1979 to October 2, 1979, a total of six harvests. Green fruit were also included in the last harvest. On October 10, tops of the two middle plants of the four plant treatment were cut at ground level, placed in paper bags, dried in forced-draft ovens at 70°C for 48 hours and weighed.

The data were subjected to analysis of variance and Tukey's H.S.D. mean separation at the 5% level of probability.

Effects of Zeolite on Growth of Bench Crops and Potted Plants

Bench Crops

The determination of zeolite influence on radish, lettuce, snapbean, chrysanthemum and snapdragon in a standard bench medium was conducted at the Department of Horticulture Bay Farm Facility.

Greenhouses were heated to 12-14°C day and night in the "cool" house and 15-17°C day and night in the "warm" house. Cooling in both houses began when air temperatures reached 23°C.

Raised benches in the fiberglass covered greenhouses were disinfected with Amphyl® prior to adding the growing medium. They were sectioned off with 6 mil polyethylene dividers so that each treatment held approximately 57 liters of medium.

The growing medium (2:1:1) consisted of 2 parts top soil, 1 part #6 horticulture grade perlite and 1 part Canadian sphagnum peat moss, by volume (Table 6).

The bench medium for each plant species was mixed in bulk with each treatment in a 170 liter paddle mixer for 5 minutes.

All zeolite used in this experiment was of the clinoptilolite group. The NH_4^+ charged material was the same as that used in the Plant Science greenhouse experiment. The bulk composition of the naturally potassic zeolite is presented in Table 7. The bench nutrient treatments were as follows:

NH_4 Experiment

1. Injected -- Ammonium sulfate (20-0-0) was injected at the rate of 75 ppm N per watering, total N injected per bench varied due to the number of waterings required.

2. No nitrogen (NN) -- No form of nitrogen was added to the irrigation water or the growing medium.

3. Uncharged zeolite (UZ + injected) -- Untreated natural zeolite was incorporated in the same proportions as the charged zeolite. Nitrogen was injected at the same rate as the control.

4. Ammonium charged zeolite (CZ-NH_4^+) -- Has been NH_4^+ exchanged or charged. It contains 2.99% total N, of which 2.86% is exchanged and 0.13% is associated.

   Note: The zeolite was incorporated into the medium to maintain a base level of 75 mg/kg (75 ppm) N, which was 0.25% of the total medium weight. No form NH_4^+ was added through the irrigation system.

<u>K Experiment</u>

1. Injected -- Potassium chloride (0-0-62) was injected at the rate of 52.25 ppm K^+ (75 ppm K_2O) per watering. Total K_2O injected per bench varied due to number of waterings required.

2. No potassium (NK) -- No form of potassium was added through the irrigation system or to the growing medium.

3. Uncharged zeolite (UZ + injected) -- Untreated natural zeolite was incorporated in the same amounts as the charged zeolite. Potassium was injected at the same rate as the control.

4. Potassium zeolite (CZ-K) -- Naturally potassic zeolite, contained 2.7% exchangeable K^+.

Note: The zeolite was incorporated into the medium to raise the base fertility level to 62.26 ppm K^+ (75 ppm K_2O), which was 0.23% of the total medium weight. No K^+ was added through the irrigation system.

Zn Experiment

1. Injected -- Zinc sulfate was injected at the rate of 0.5 ppm Zn per watering. Total Zn injected per bench varied due to the number of waterings required.
2. No zinc (NZn) -- No form of zinc was added through the irrigation system or to the growing medium.
3. Uncharged zeolite (UZ + injected) -- Untreated natural zeolite was incorporated in the same amounts as the charged zeolite. Zinc was injected at the same rate as the control.
4. Zinc charged zeolite (CZ-Zn) -- The zinc charged zeolite has been zinc exchanged and contains 2.1% Zn, all of which should be exchangeable.

   Note: The zeolite was incorporated into the medium to maintain a base level of 0.5 ppm Zn, which was 0.0024% of the total medium weight. No zinc was added through the irrigation system.

Standard nutrients (47) less the treatment element were injected with a Commander®, 1 to 128, proportioning pump, through a Chapin® twin wall drip irrigation system.

Experimental plants included radish and lettuce in the cool house and snapbean, chrysanthemum and snapdragon in the warm house. The plant spacing was determined by commercial recommendations (K. L. Goldsberry, personal communication).

Radish, Raphanus sativus cv. Improved Scarlet Globe, Captan® treated, was planted on April 19 at a 1 x 5 cm spacing. Each treatment had a population of 100 plants and was replicated three times. Outer rows of all treatments were considered border rows.

Ten randomly chosen plants were harvested, washed to remove soil, blotted dry and placed in plastic bags on May 23. Harvested roots and leaves were separated at the hypocotyl and leaf areas measured with a Lambda #LI-3100 photoelectric meter (resolution to 0.1 mm^2). Root diameter and fresh weight were taken. Leaves and roots were dried in a forced-draft oven at 70°C for 48 hours and dry weight were taken.

Lettuce, Lactuca sativa cv. Grand Rapids Forcing (H-54), (31 days maturing), was sown in plastic flats of peat-vermiculite on April 23, and transplanted in the plots on May 14, 1979, at a density of 32 plants/m^2. The treatments were replicated three times and 6 of the 9 plants per treatment were used for data. Border rows consisted of outer perimeter plants and outside rows of each treatment.

All treatments were harvested at ground level on June 20, 1979, and fresh weight taken.

Snapbean, Phaseolus vulgaris cv. Cherokee, was sown on May 12; a 5 x 10 cm plant spacing was utilized. A total of 16 seeds per treatment was planted and replicated 3 times. Perimeter plants were used as border rows. On June 23, 14 plants from each replication were harvested and fresh weight taken.

Rooted cuttings of chrysanthemums, Chrysanthemum morifolium cv. Bonnie Jean, were planted April 7. The 10 week, intermediate, white daisy variety was spaced 10 x 15 cm. A total of 21 plants per treatment was planted and replicated 3 times. End rows and perimeter plants were used as border rows. Pirimor® was used to control slight aphid infestation.

Seven plants in each replication were sampled for fresh weight, plant height and commercial grade (N. F. Gaone and K. L. Goldsberry, personal communication).

Snapdragon, Antirrhinum majus cv. Missouri was sown on March 7 and transplanted on April 17. Stems were harvested (June 19) and the same parameters measured as used on the chrysanthemums.

Following harvest, soil samples were taken of all treatments with the exception of the radish bench, only the NH_4^+ section was sampled. Analysis was completed by CSU Soil Testing Laboratory for routine analysis, NH_4-N and total nitrogen.

The experimental design was a randomized complete block, using the sectioned benches for three charged zeolite treatments and a control, replicated three times. Data were subjected to analysis of variance and the L.S.D. mean separation at the 5% level of probability.

Potted Plants

Rooted poinsettia cuttings, Euphorbia pulcherrima cv. Dark Red Annette Hegg were transplanted into 14 cm plastic Azalea pots on September 21. The growing medium consisted of equal parts Fort Collins clay loam, horticulture grade perlite #6, and Canadian sphagnum peat moss (Table 8) plus the treatment. Medium involving all treatments was mixed in 170 liter paddle mixer for 5 minutes. Zeolite was slowly added in dry form as each medium treatment was mixed.

Plants were grown on raised benches in a fiberglass covered greenhouse, heated to an air temperature of 15–17°C day and night. Thermostats were set to cool at 23°C.

The clinoptilolite, NH_4^+ charged and naturally potassic zeolite (Tables 3 and 7) were the same as those used in the bench plant experiment. The poinsettia nutrition treatments were as follows:

NH_4 Experiment

1. 0 ppm -- No nitrogen added (NN).
2. 125 ppm -- Ammonium charged zeolite (CZ-NH_4) contained 2.66% associated N and 1.98% exchanged N for a total of 4.64% N.
3. 250 ppm -- CZ-NH_4.
4. 500 ppm -- CZ-NH_4.
5. 250 ppm -- Ammonium sulfate (20-0-0) was added with each watering. No zeolite was added to medium.

K Experiment

1. 0 ppm -- No potassium added (NK).
2. 75 ppm -- Potassium zeolite (CZ-K). Naturally potassic zeolite contained 2.7% exchangeable K^+ (3.24% K_2O).
3. 150 ppm -- CZ-K.
4. 300 ppm -- CZ-K.
5. 150 ppm -- Potassium chloride (0-0-62) was added with each watering. No zeolite was added to medium.

Treatment levels of NH_4^+ and K^+ were based on recommendations presented in the Poinsettia Handbook (39). The K and NH_4 experimental pots were placed on separate lath-covered benches.

Nutrient solutions were injected with drip irrigation pot watering equipment. All treatments received phosphate at rates of 21.5 ppm P (50 ppm P_2O_5). The K experiment was supplied with NH_4^+ at 250 ppm while the NH_4 experiment received K^+ at 150 ppm (180 ppm K_2O) to maintain balanced fertility, except for the element in question.

All pots were drenched with three separate applications of Banrot® throughout the growing season, at rates of 0.6 g per liter of water.

A randomized complete block design with three replications was used for each experiment. Each treatment consisted of nine plants per replication (45 pots per block). Perimeter plants on each bench were considered border plants and not included in the data. No border was placed between replications. The total population per experiment was 141 plants for a density of approximately 10 pots/m^2.

No statistical data was taken on vegetative growth. Visual observations were noted and pictures taken for comparison.

Post NH_4 and K experimental soil samples were taken and analyzed by CSU Soil Testing Laboratory for K^+ and total N.

Precooled Easter lily bulbs, Lilium longiflorum cv. Ace were planted in 15 cm standard plastic pots using a 1:1:1 v/v growing medium plus treatments, on December 21, at the W. D. Holley Plant Environmental Research Center (P.E.R.C.) on campus of CSU. The growing medium and clinoptilolite were the same as those used in the poinsettia experiment (Tables 3, 7 and 8).

Lilies were grown on raised benches in fiberglass covered greenhouse, heated to an air temperature of 15-16°C during the day and night and cooled to 22-23°C. Plants were forced for a period of

5 weeks starting February 29, by covering both experiments with 4 mil clear polyethylene and adding supplemental heat to raise the night temperature to a minimum of 21°C. The greenhouse effect created by the poly cover on sunny days raised the temperature to 30-32°C. Cooling of the plastic canopy occurred at 32°C by opening the ends of the cover to allow air circulation. The lily nutrition treatments were as follows:

NH_4 Experiment

1. 0 ppm -- No nitrogen added (NN).
2. 125 ppm -- Ammonium charged zeolite (CZ-NH_4) contained 2.66% associated N and 1.98% exchanged N for a total of 4.64% N.
3. 250 ppm -- CZ-NH_4.
4. 500 ppm -- CZ-NH_4.
5. 250 ppm -- Ammonium sulfate (20-0-0) was injected with each watering. No zeolite was added to medium.

K Experiment

1. 0 ppm -- No potassium added (NK).
2. 75 ppm -- Potassium zeolite (CZ-K), naturally potassic zeolite contained 2.7% exchangeable K^+ (3.24% K_2O).
3. 150 ppm -- CZ-K.
4. 300 ppm -- CZ-K.
5. 150 ppm -- Potassium chloride (0-0-62) was injected with each watering. No zeolite was added to medium.

Treatment levels of NH_4^+ and K^+ were based on the same recommendation for the poinsettias (39). The bulbs were potted and K and

NH_4 experiments placed on separate benches. Plants were watered with nutrient solution every watering.

All treatments received phosphate at rates of 21.5 ppm P (50 ppm P_2O_5). The K experiment was supplied with NH_4^+ at 250 ppm while the NH_4 experiment received K^+ at 150 ppm (180 ppm K_2O) to maintain a balance fertility, except for the element in question.

Pots were drenched with three separate applications of Banrot® throughout the growing season, at rates of 0.6 g per liter of water.

A randomized complete block design was utilized with 4 replications, which consisted of 6 plants per replication, 30 pots per block. Perimeter plants were considered border rows. Total population per experiment was 120 plants for a density of approximately 25 plants per m^2.

Stem heights were taken from ground level and number of primary buds were counted. Data were subjected to analysis of variance and L.S.D. mean separation at the 5% level of probability. Visual observations were noted throughout the growing season.

Table 1. Initial chemical characteristic of the soils used in the Plant Science greenhouse experiments.

Analysis	Medium soil (13% clay)	Light soil (6% clay)
pH[z]	8.1	8.6
Total soluble salts (mmhos/cm)[y]	3.8	2.7
Organic matter (%)[x]	2.6	1.1
P (ppm)[w]	68.0	26.0
K (ppm)[v]	428.0	122.0
Zn (ppm)[v]	4.2	2.2
Fe (ppm)[v]	20.8	10.4
Cu (ppm)[v]	1.5	0.5
Mn (ppm)[v]	52.4	13.3
NO_3-N (ppm)[u]	41.0	22.0
NH_4-N (ppm)[t]	33.0	11.0
Total nitrogen (%)[s]	0.152	0.044

[z]Paste method.

[y]Filtered extract from saturated soil paste was measured for conductivity.

[x]Sulfuric acid/potassium dichromate oxidation with colorimetric determinations.

[w]Ammonium bicarbonate/DTPA bicarbonate and colorimetric determination.

[v]Ammonium bicarbonate/DTPA extraction and inductively coupled plasma spectrometry.

[u]Chromotropic acid (CTA) colorimetric determination.

[t]Potassium citrate (KCT) extraction and ammonium ion selective electrode.

[s]Kjeldahl distillation method.

Table 2. Initial physical characteristics of the soils used in Plant Science greenhouse experiments.

Texture^{z}	Medium soil	Light soil
Sand %	76	88
Silt %	11	6
Clay %^{y}	13	6
Classification	Sandy loam	Sand

^{z}Hydrometer method.

^{y}The clay fraction of both soils is approximately 35% illite and vermiculite (W. T. Franklin, Department of Agronomy, Colorado State University, Fort Collins, Colorado, personal communication).

Table 3. Bulk composition of natural zeolite, clinoptilolite. Supplier's sample, ZBS-14.

Oxides	Amount[z] % by weight
SiO_4	65.4
Al_2O_3	10.4
CaO	1.75
MgO	0.65
TiO_2	0.1
Na_2O	3.25
K_2O	1.81
Fe_2O_3	1.26
MnO	0.03
SrO	0.44
BaO	0.15

[z]The sample was 80% ± 5% clinoptilolite with a trace of mordenite. Percentage does not include water. Contaminants are quartz, feldspar, and clay (J. J. Lawson, personal communications).

Table 4. Initial chemical characteristics of the clay soil from the field experiment.

Analysis	Clay soil
pH[z]	8.0
Total soluble salts (mmhos/cm)[y]	2.9
Organic matter (%)[x]	2.4
P (ppm)[w]	7.7
K (ppm)[v]	429
Zn (ppm)[v]	2.3
Fe (ppm)[v]	13.2
Cu (ppm)[v]	5.8
Mn (ppm)[v]	3.8
NO_3-N (ppm)[u]	15
NH_4-N (ppm)[t]	23
Total nitrogen (%)[s]	0.152

[z]Paste method.

[y]Filtered extract saturated soil paste was measured for conductivity.

[x]Sulfuric acid/potassium dichromate oxidation with colorimetric determinations.

[w]Ammonium bicarbonate/DTPA bicarbonate and colorimetric determination.

[v]Ammonium bicarbonate/DTPA extraction and inductively coupled plasma spectrometry.

[u]Chromotropic acid (CTA) colorimetric determination.

[t]Potassium citrate (KCT) extraction and ammonium ion selective electrode.

[s]Kjeldahl distillation method.

Table 5. Initial physical characteristics of the soil from the field experiment.

Texture[z]	%
Sand	26
Silt	31
Clay	43
Classification	Clay

[z]Texture-hydrometer method.

Table 6. Initial chemical characteristics of the 2:1:1 medium used in greenhouse bench crop experiment.

Analysis	Medium (2:1:1)
pH[z]	7.1
Total soluble salts (mmhos/cm)[y]	1.0
Organic matter (%)[x]	4.9
P (ppm)[w]	4
K (ppm)[v]	114
Zn (ppm)[v]	1.2
Fe (ppm)[v]	1.2
Cu (ppm)[v]	56.0
Mn (ppm)[v]	7.5
NO_3-N (ppm)[u]	23

[z]Paste method.

[y]Filtered extract from saturated soil paste was measured for conductivity.

[x]Sulfuric acid/potassium dicromate oxidation with colorimetric determination.

[w]Ammonium bicarbonate/DTPA extraction and colorimetric determination.

[v]Ammonium bicarbonate/DTPA extraction and inductively coupled plasma spectrometry.

[u]Chromotropic acid (CTA) colorimetric determination.

Table 7. Bulk composition of naturally potassic zeolite, clinoptilolite. Supplier's sample, ZBS-6.

Oxides	Amount[z] % by weight
SiO_2	64.6
Al_2O_3	10.4
CaO	1.54
MgO	0.44
TiO_2	0.3
Na_2O	0.5
K_2O	4.35
Fe_2O_3	1.17
MnO	0.02

[z]The sample was 80% ± 5% clinoptilolite with a trace of mordenite. Percentage does not include water. Contaminants are quartz, feldspar, and clay (J. J. Lawson, personal communications).

Table 8. Initial chemical characteristics of the 1:1:1 medium used in the greenhouse potted plant experiment.

Analysis	Medium (1:1:1)
pH[z]	7.0
Total soluble salts (mmhos/cm)[y]	2.1
Organic matter (%)[x]	6.1
P (ppm)[w]	123
K (ppm)[v]	717
Zn (ppm)[v]	5.2
Fe (ppm)[v]	45.3
Cu (ppm)[v]	15.8
Mn (ppm)[v]	2.6
NO_3-N (ppm)[u]	72
Total nitrogen (%)[t]	0.192

[z]Paste method.

[y]Filtered extract from saturated soil paste was measured for conductivity.

[x]Sulfuric acid/potassium dichromate oxidation with colorimetric determination.

[w]Ammonium bicarbonate/DTPA extraction and colorimetric determination.

[v]Ammonium bicarbonate/DTPA extraction and inductively coupled plasma spectrometry.

[u]Chromotropic acid (CTA) colorimetric determination.

[t]Kjeldahl distillation method.

RESULTS

Plant Responses to Zeolite-N Governed by Soil Texture and Leaching

Seedling Emergence Rate

There was no significant difference among radish seed emergence rates with regard to the treatments in either of the two soils (Appendix Table 22).

Banding vs. Incorporation

In most cases radishes responded positively to all treatments containing nitrogen; however, no significant difference was noted between the STD-Z and NN (Appendix Tables 22-28).

In some cases seedling injury and death resulted from applying urea without zeolite in the medium and light soils. Generally this treatment reduced growth and resulted in a large coefficient of variation (C.V.), Appendix Tables 23 through 28.

Banding resulted in a greater growth response to zeolite-nitrogen treatments than did incorporation. Significant increases in root fresh weight due to banding of CZ-21, UZ-21 and UZ-45 in the light and medium soils, with the exception of the UZ-21 treatment in the medium soil, are shown in Figures 1, 2 and 3, respectively. The fresh root weight increases, due to banding of zeolite-nitrogen treatments, ranged from 4.7 to 33.3% in the medium soil and 11.5 to 58.8% in the light soil. Additional results of band (B) and incorporation (I) treatments are in Appendix Tables 22-36.

Since the band method of application proved superior to incorporation, the following results are based on banding, only.

Ammonium Charged Zeolite vs. Ammonium Sulfate in Medium Soil

A positive response due to CZ-21 occurred in all growth parameters (Appendix Tables 23, 25 and 27). Leaf area, dry weight and root fresh weight were increased 25, 63 and 59%, respectively, compared to the 21, control (Table 9).

The number of commercial grade radishes was positively affected by the zeolite-N treatments in the medium and light soil (Appendix Table 29).

One way analysis of variance with replications was used to analyze all N-uptake data due to combining of replications. CZ-21 demonstrated the only significant increase in N-uptake of the zeolite-N treatments in the medium soil (Table 9).

Higher levels of NH_4-N were available for plants and soil nitrifiers when CZ-21 was used (Table 10).

Ammonium Charged Zeolite vs. Ammonium Sulfate in Light Soil

Plant responses to CZ-21 were generally positive (Appendix Tables 24, 26 and 28), considering the soil was leached 6 times. However, the magnitude of the difference between the CZ-21 and 21 was not as great as that found in the medium soil. Leaf area and root weight exhibited significant increases of 25 and 53%, respectively (Table 11). No other parameters were of significance.

N-uptake, based on a sampling 34 days from planting, did not show a significant increase due to the presence of CZ-21 (Table 11).

High significant residual soil NH_4-N and NO_3-N levels were responsible for the 290% increase in available N when contrasted with 21 (Table 12).

There was no significant difference in the leachate NO_3-N content in the zeolite-N and the controls (Appendix Table 36) with one exception; there was a definite reduction in leachate NO_3-N due to the addition of CZ-21 (Fig. 4).

Uncharged Zeolite Plus Ammonium Sulfate vs. Ammonium Sulfate in Medium Soil

UZ-21 plant response and N-uptake were not significant when compared to 21 (Table 9).

A significant level of residual soil NH_4-N was maintained by the UZ-21 although NO_3-N and available N levels were not significantly higher than the 21, control (Table 10).

Uncharged Zeolite Plus Ammonium Sulfate vs. Ammonium Sulfate in Light Soil

Generally, a positive increase in the growth response of the UZ-21 treatment was noted. Leaf area and fresh root weight showed an increase of 32 and 59%, respectively, because of the UZ-21 addition when compared to the 21, control (Table 11).

The UZ-21 treatment maintained high residual soil levels of NH_4-N and available N when contrasted with 21 (Table 12). The UZ-21 soil NO_3-N level was higher than the 21 but the difference was not significant.

No statistical difference in leachate NO_3-N was determined between UZ-21 and 21 treatments.

<u>Uncharged Zeolite Plus Urea vs. Urea in Medium Soil</u>

The UZ-45 treatment demonstrated no significant responses in the four plant growth parameters when compared with the 45, control (Table 9).

Higher levels of NH_4-N and NO_3-N, in the UZ-45 treatment, increased the available N by 22% compared to the 45, control (Table 10).

<u>Uncharged Zeolite Plus Urea vs. Urea in Light Soil</u>

The effect of applying zeolite with urea contributed to positive responses in all four plant growth parameters as compared to the application of urea, alone (Table 11). Leaf area, dry weight and root fresh weight were increased 79, 94 and 97%, respectively. N-uptake demonstrated the largest increase of 135% due to the UZ-45.

The residual soil NH_4-N was maintained at a significantly higher level due to the UZ-45 treatment compared to the 45 treatment (Table 12). The available N levels due to UZ-45 additions, although not significant, were slightly higher than those in the 45 treatments.

No statistical leachate NO_3-N difference was exhibited between the UZ-45 and 45 treatments.

Effects of Zeolite-N Combinations on Field Tomatoes

Fruit numbers and weight are present in Tables 13 and 14, respectively. No significant differences were noted among treatments at the 5% level of probability.

Although there were no significant differences between measured parameters, treatment NUZ provided the largest increase in cumulative tomato weight (g) per plant (Fig. 5) and the cumulative number of tomatoes per plant (Fig. 6) of ripe fruit produced.

Effects of Zeolite on the Growth of Bench Crops and Potted Plants

Bench Crops

RADISH: No significant differences were observed among most radish N, K and Zn treatments, but a definite growth response was noted between the treated and untreated (Table 15).

The growth response due to the addition of zeolite, although not significant, was in most parameters slightly less than that noted for the fertilizer injected treatment; the UZ plus fertilizer injected treatment showed the highest increase.

A slight yellowing occurred in the radish leaves of the CZ-NH_4 treatment at harvest time (approximately 35 days after planting).

LETTUCE: The uncharged zeolite plus injected fertilizer and the injected fertilizer treatments attributed a significant increase in lettuce fresh weight with no response from the CZ-treatments when contrasted with the untreated in the NH_4, K and Zn experiments (Table 16).

BEAN: Bean plants were used only to evaluate growth responses of Zn^{++} charged zeolite. The UZ plus injected fertilizer treatment demonstrated a significant increase in whole plant top fresh weight when compared to the nontreated (Table 17). Although no significant difference was found between the zeolite and the nontreated, an increase in the fresh weight was noted.

CHRYSANTHEMUMS: The presence of zeolite combined with injected fertilizer increased the salable quality of cut chrysanthemums (Table 18). In the NH_4 experiment, the CZ-NH_4 treated plants showed less response in the above-ground fresh weight, but were approximately equal in height when compared to the injected fertilizer treatment. A slight yellowing of older leaves at harvest time was noted.

No differences between treatments were noted in the three growth parameters in the K experiment. The Zn experiment had a significant response between treatments; the zeolite treatments produced the greatest increases in plant height compared to the nontreated. Number of salable quality flowers in the Zn experiment was higher due to the zeolite treatments.

SNAPDRAGON: Plant responses to the addition of charged and uncharged zeolite at the concentrations used in this experiment were not significantly effective (Table 19). Although the zeolite treated plants produced less fresh weight, the number of salable quality flowers was 333% greater than the untreated in the NH_4 experiment.

Potted Plants

POINSETTIAS: No statistical data were taken on the poinsettias. The results were determined through visual observations and photographs for the NH_4 and K experiments.

The poinsettias showed a response to the NH_4^+ treatment levels (Fig. 7). The 250 ppm N injected fertilizer treatment, with no added zeolite, had the best growth characteristics including excellent color, good bract (upper modified colored leaves) development, height and compactness. There was a positive response to the NH_4^+ charged zeolite treatments of 500, 250 and 125 ppm N compared to 0 ppm N treatment but very limited and directly related to the treatment concentration.

No visual poinsettia response between the four concentrations of natural potassic zeolites and injected fertilizer treatments was observed (Fig. 8).

EASTER LILY: Significant increases in plant heights due to treatments were obtained in the NH_4 experiment (Table 20). The injected N-fertilizer treatment exhibited the largest response in plant height in comparison to the 0 ppm N treatment although there was no significant difference in plant height between 250 and 500 ppm NH_4 charged zeolite and the fertilizer injected treatment.

There was no significant difference among treatments in plant height and number of open buds, within the K experiment (Table 21).

Table 9. Growth response of radish to banded applications of zeolite-N in medium soil.[z] Plant Science greenhouse experiment.

Growth parameter	CZ-21	UZ-21	21 (control)	UZ-45	45 (control)
Leaf area (cm^2/plant)	243*	188	167	210	187
Dry weight (g/whole plant)	1.84*	1.20	1.12	1.59	1.23
Root weight (g f.w./plant)	13.5*	10.0	8.5	13.8	9.2
N-uptake (mg N/plant top)	57.2*	34.0	35.9	45.5	38.6

[z]Sampled plants 36 days after planting.

*Differed significantly from respective control at the 5% level of probability using an unpaired t-test.

Table 10. Residual soil N after zeolite-N applications to medium soil.[z] Plant Science greenhouse experiment.

N-form (ppm)	CZ-21	UZ-21	21 (control)	UZ-45	45 (control)
NH_4-N	18.3*	16.8*	10.0	14.5*	8.0
NO_3-N	66.5	79.5	72.3	74.5*	65.2
NH_4-N + NO_3-N (available N)	83.0	96.2	82.3	89.0*	73.2

[z]Soil was sampled 43 days from planting.

*Differed significantly from respective control at the 5% level of probability using an unpaired t-test.

Table 11. Growth response of radish to banded applications of zeolite-N in light soil.[z] Plant Science greenhouse experiment.

Growth parameter	CZ-21	UZ-21	21 (control)	UZ-45	45 (control)
Leaf area (cm^2/plant)	187*	198*	150	208*	116
Dry weight (g/whole plant)	1.40	1.26	1.10	1.38*	0.71
Root weight (g f.w./plant)	11.6*	12.1*	7.6	12.4*	6.3
N-uptake (mg N/plant top)	42.6	32.6	38.9	44.4*	18.9

[z]Leached 5 times; plants sampled 34 days after planting.

*Differed significantly from respective control at the 5% level of probability using an unpaired t-test.

Table 12. Residual soil N after zeolite-N applications to light soil.[z] Plant Science greenhouse experiment.

N-form (ppm)	CZ-21	UZ-21	21 (control)	UZ-45	45 (control)
NH_4-N	82.8*	36.8*	4.2	13.0*	5.5
NO_3-N	48.8*	37.8	29.8	31.2	36.2
NH_4-N + NO_3-N (available N)	132.3*	74.5*	34.0	44.2	41.8

[z]Leached 6 times; sampled 43 days from planting.

*Differed significantly from respective control at the 5% level of probability using an unpaired t-test.

Table 13. Total number of ripe, green and ripe plus green tomato fruit per plant based on 6 harvests. Analysis of variance on each parameter indicated no significant difference at the 5% level of probability.

Treatments	Ripe	Green	Ripe + Green
1. NH_4 charged zeolite (CZ-21)	51.6	20.7	72.3
2. $(NH_4)_2SO_4$ (21)	48.9	23.8	72.7
3. $(NH_4)_2SO_4$ + NH_4 charged zeolite (50/50)	52.0	18.8	70.8
4. $(NH_4)_2SO_4$ + uncharged zeolite (NUZ)	55.4	21.0	76.4
Zeolite - no zeolite*	0.5	0.5	1.0

*The response to the control was subtracted from the average response to the zeolite treatments. The differences for each of the 3 parameters were not significant at the 5% level of probability.

Table 14. Weight of ripe, green and ripe plus green tomato fruit per plant based on 6 harvests. Analysis of variance on each parameter indicated no significant difference at the 5% level of probability.

Treatments	Ripe (g)	Green (g)	Ripe + Green (g)
1. NH_4 charged zeolite (CZ-21)	6355	1395	7750
2. $(NH_4)_2SO_4$ (21)	6368	1685	8053
3. $(NH_4)_2SO_4$ + NH_4 charged zeolite (50/50)	6505	1346	7851
4. $(NH_4)_2SO_4$ + uncharged zeolite (NUZ)	6923	1449	8372
Zeolite - no zeolite*	266	-288	-62

*The response to the control was subtracted from the average response to the 3 zeolite treatments. The differences for each of the 3 parameters were not significant at the 5% level of probability.

Table 15. Influence of zeolite and injected fertilizer treatments on the growth of radish, i.e., 4 parameters. Greenhouse bench crop experiment.

	Leaf area (cm^2/plant)	Dry weight (g/plant)	Root fresh weight (g/root)	Commercial grade roots (no. $\geq$ 16 mm)
NH_4 Experiment				
1. Injected	15.4	0.65	7.2	7.0
2. NN	2.2	0.15	1.0	0.0
3. UZ + injected	15.7	0.65	7.0	7.0
4. CZ-NH_4	11.5	0.59	6.8	6.7
L.S.D., 5%	4.5	0.24	3.2	3.3
K Experiment				
1. Injected	15.5	0.67	8.0	7.0
2. NK	12.8	0.55	4.5	4.3
3. UZ + injected	17.2	0.72	8.3	8.3
4. CZ-K	15.3	0.73	8.2	8.3
L.S.D., 5%	3.5	0.17	3.2	3.4
Zn Experiment				
1. Injected	15.1	0.61	6.3	6.0
2. NZn	10.2	0.53	5.4	4.0
3. UZ-injected	16.9	0.73	8.7	8.0
4. CZ-Zn	12.8	0.70	8.4	7.3
L.S.D., 5%	2.3	0.12	3.0	3.0

Table 16. Influence of zeolite and injected fertilizer treatments on lettuce fresh weight. Greenhouse bench crop experiment.

	Fresh weight (g)
NH_4 Experiment	
1. Injected	205.7
2. NN	21.4
3. UZ + injected	226.2
4. CZ-NH_4	29.4
L.S.D., 5%	57.9
K Experiment	
1. Injected	231.9
2. NK	136.7
3. UZ + injected	208.7
4. CZ-K	123.7
L.S.D., 5%	49.4
Zn Experiment	
1. Injected	196.2
2. NZn	185.3
3. UZ + injected	158.1
4. CZ-Zn	110.5
L.S.D., 5%	76.2

Table 17. Influence of zeolite and injected fertilizer treatments on bean fresh weight. Greenhouse bench crop experiment.

	Fresh weight (g)
Zn Experiment	
1. Injected	107.7
2. NZn	83.3
3. UZ + injected	122.0
4. CZ-Zn	99.8
L.S.D., 5%	25.6

Table 18. Influence of zeolite and injected fertilizer treatments on the growth of chrysanthemum, i.e., 3 parameters. Greenhouse bench crop experiment.

	Fresh weight (g)	Height (cm)	Salable quality (no.)
NH_4 Experiment			
1. Injected	60.1	46.2	0
2. NN-N	7.7	26.4	0
3. CZ + injected	54.1	49.7	1.3
4. CZ-NH_4	30.0	45.7	0
L.S.D., 5%	24.4	6.6	0.6
K Experiment			
1. Injected	69.2	48.7	1.3
2. NN-K	60.7	49.5	0.7
3. UZ + injected	70.4	51.5	1.3
4. CZ-K	62.1	51.7	0.7
L.S.D., 5%	12.2	2.7	2.7
Zn Experiment			
1. Injected	86.1	51.5	1.7
2. NN-Zn	55.8	46.2	0.3
3. UZ + injected	74.7	54.3	2.7
4. CZ-Zn	69.4	52.5	2.3
L.S.D., 5%	17.8	4.0	1.3

Table 19. Influence of zeolite and injected fertilizer treatments on the growth of snapdragon, i.e., 2 parameters. Greenhouse bench crop experiment.

	Fresh weight (g)	Salable quality (no.)
NH_4 Experiment		
1. Injected	71.5	0.3
2. NN-N	5.1	0
3. UZ + injected	64.2	1.0
4. $CZ-NH_4$	27.3	1.0
L.S.D., 5%	26.9	1.3
K Experiment		
1. Injected	76.2	2.0
2. NN-K	71.4	2.7
3. UZ + injected	54.5	1.7
4. CZ-K	40.8	1.0
L.S.D., 5%	23.2	1.2

Table 20. Influence of zeolite-N concentrations and injected fertilizer treatments on Easter lily heights. Greenhouse potted plant experiment.

	Plant height (cm)
NH_4 Experiment	
1. 0 ppm N (NN)	25.6
2. 125 ppm N (CZ-NH_4)	24.8
3. 250 ppm N (CZ-NH_4)	27.2
4. 500 ppm N (CZ-NH_4)	27.2
5. 250 ppm injected-N	28.2
L.S.D., 5%	2.3
K Experiment	
1. 0 ppm K^+ (NK)	29.5
2. 75 ppm K^+ (CZ-K)	28.7
3. 150 ppm K^+ (CZ-K)	30.0
4. 300 ppm K^+ (CZ-K)	28.4
5. 150 ppm injected-K^+	33.1
L.S.D., 5%	4.1

Table 21. Influence of zeolite-N concentrations and injected fertilizer treatments on Easter lily buds. Greenhouse potted plant experiment.

	Plant buds (no.)
NH_4 Experiment	
1. 0 ppm N (NN)	4.1
2. 125 ppm N (CZ-NH_4)	4.2
3. 250 ppm N (CZ-NH_4)	4.6
4. 500 ppm N (CZ-NH_4)	4.1
5. 250 ppm injected-N	4.3
L.S.D., 5%	0.7
K Experiment	
1. 0 ppm K^+ (NK)	4.2
2. 75 ppm K^+ (CZ-K)	5.0
3. 150 ppm K^+ (CZ-K)	4.4
4. 300 ppm K^+ (CZ-K)	4.1
5. 150 ppm injected-K^+	4.6
L.S.D., 5%	0.8

Fig. 1. Banding versus incorporation of ammonium charged zeolite. Plant Science greenhouse 5th and 6th (final) harvests were combined. Application methods differed significantly at the 5% level of probability in the light soil only.

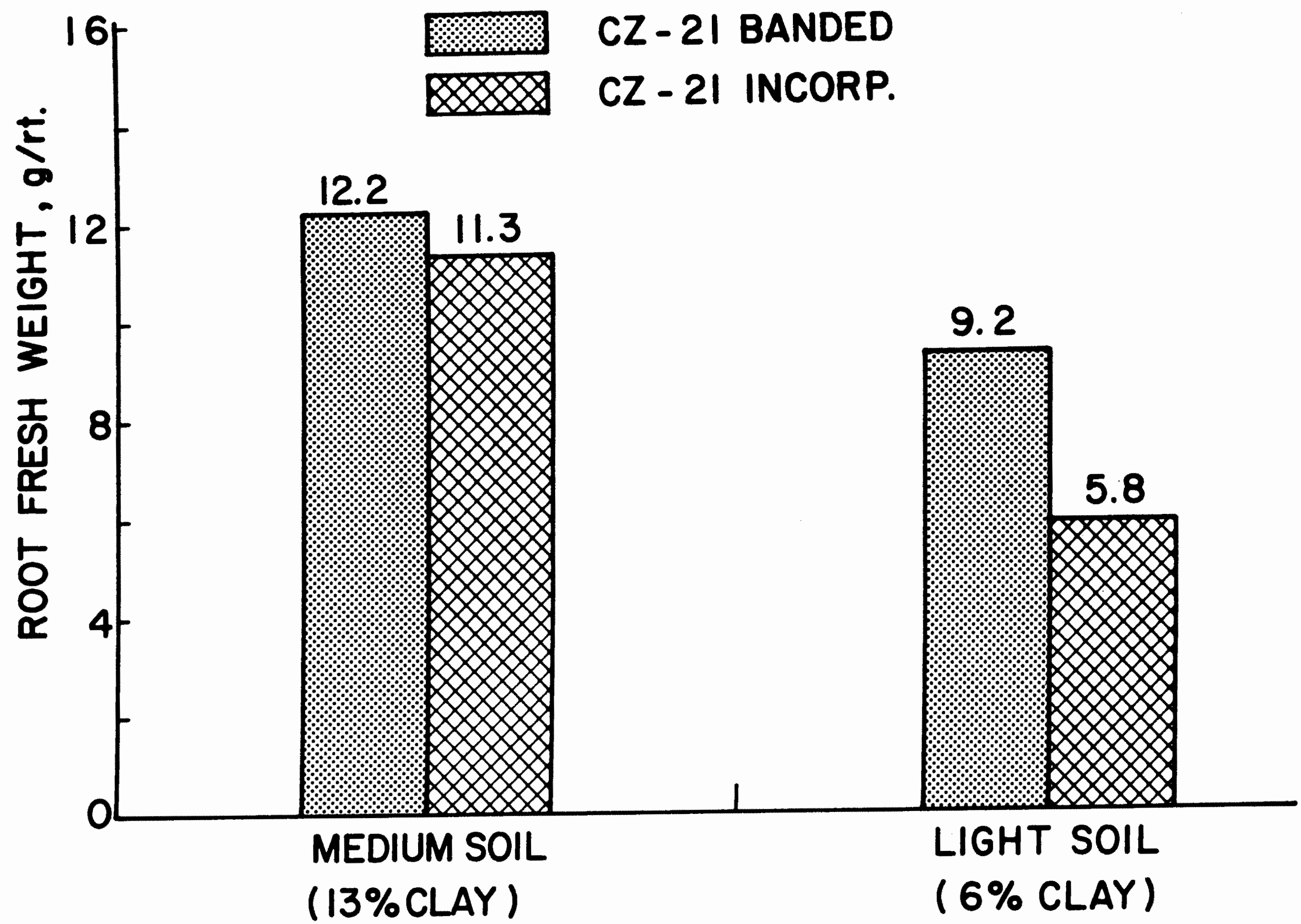
CZ - 21 BANDED
CZ - 21 INCORP.
ROOT FRESH WEIGHT, g/rt.
16
12
8
4
0
12.2
11.3
9.2
5.8
MEDIUM SOIL
(13% CLAY)
LIGHT SOIL
(6% CLAY)

Fig. 2. Banding versus incorporation of uncharged zeolite plus ammonium sulfate. Plant Science greenhouse, 5th and 6th (final) harvests were combined. Application methods differed significantly at the 5% level of probability in the light soil only.

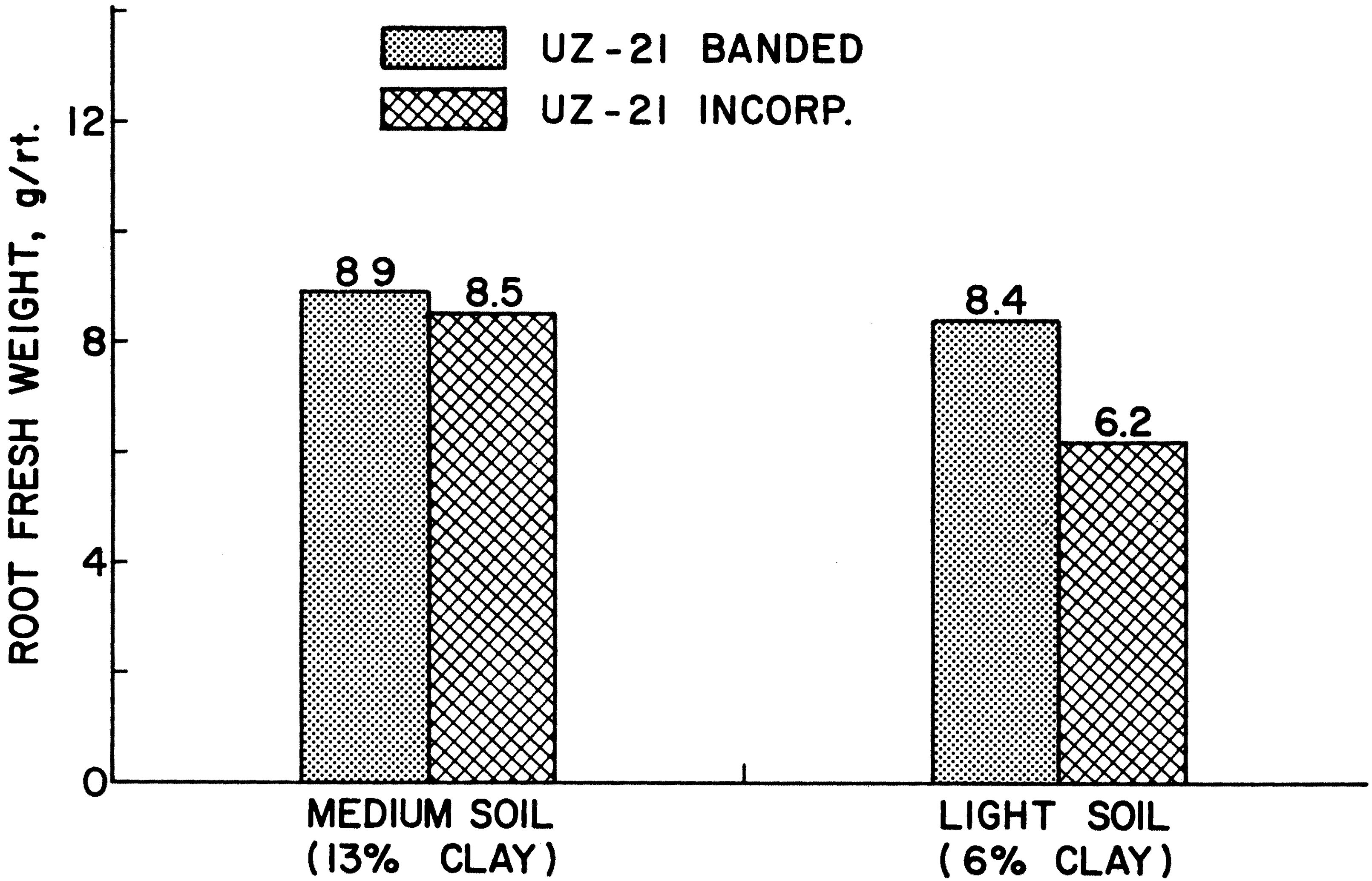
UZ-21 BANDED
UZ-21 INCORP.
ROOT FRESH WEIGHT, g/rt.
12
8
4
0
8 9
8.5
8.4
6.2
MEDIUM SOIL
(13% CLAY)
LIGHT SOIL
(6% CLAY)

Fig. 3. Banding versus incorporation of uncharged zeolite plus urea. Plant Science greenhouse, 5th and 6th (final) harvests were combined. Application methods differed significantly at the 5% level of probability in both soils.

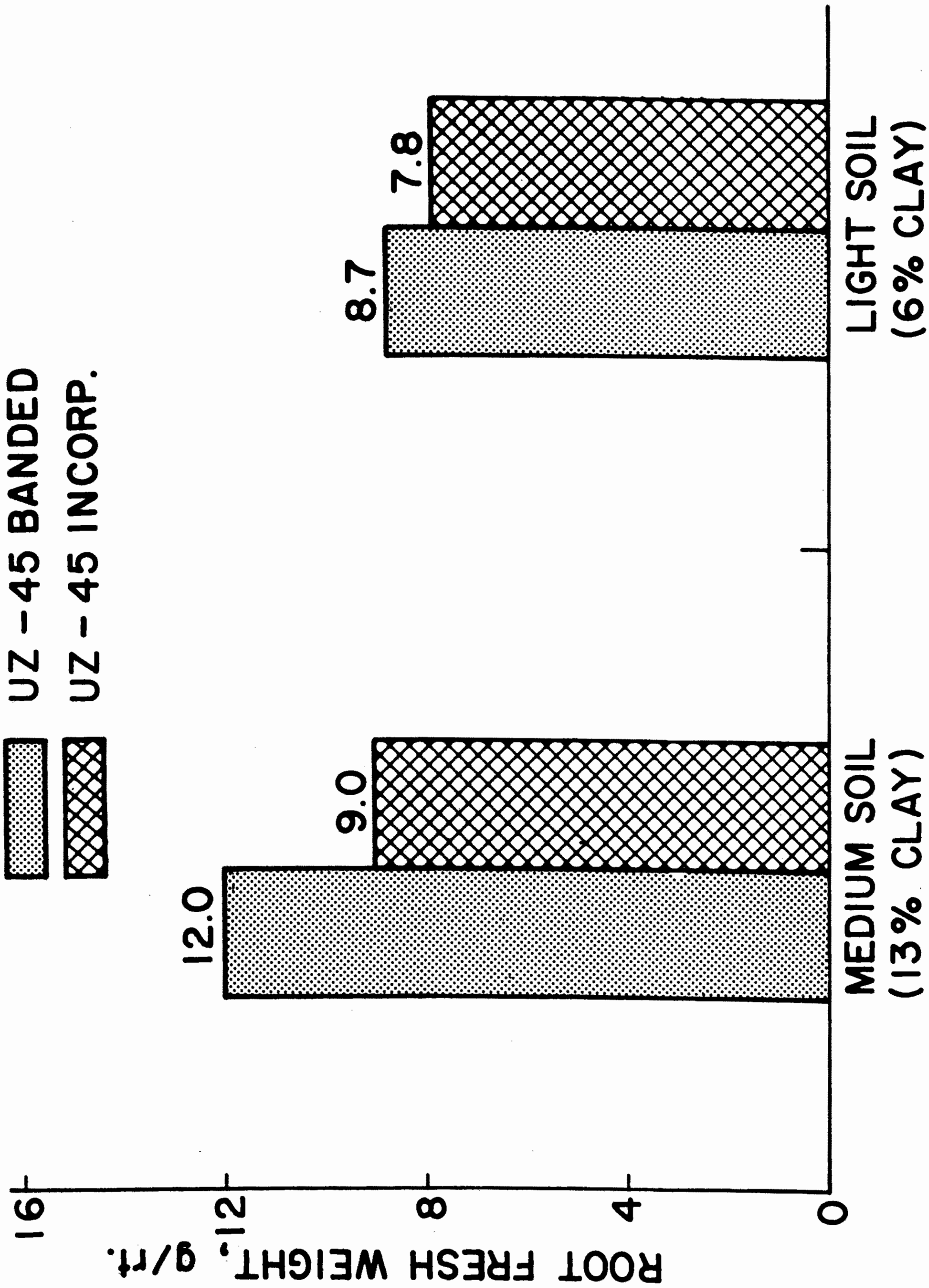
UZ - 45 BANDED
UZ - 45 INCORP.
ROOT FRESH WEIGHT, g/rt.
0
4
8
12
16
12.0
9.0
8.7
7.8
MEDIUM SOIL
(13% CLAY)
LIGHT SOIL
(6% CLAY)

Fig. 4. Cumulative leachate NO_3-N comparing banded ammonium charged zeolite and banded ammonium sulfate. Treatments differed significantly at the 5% level of probability. Plant Science greenhouse experiment.

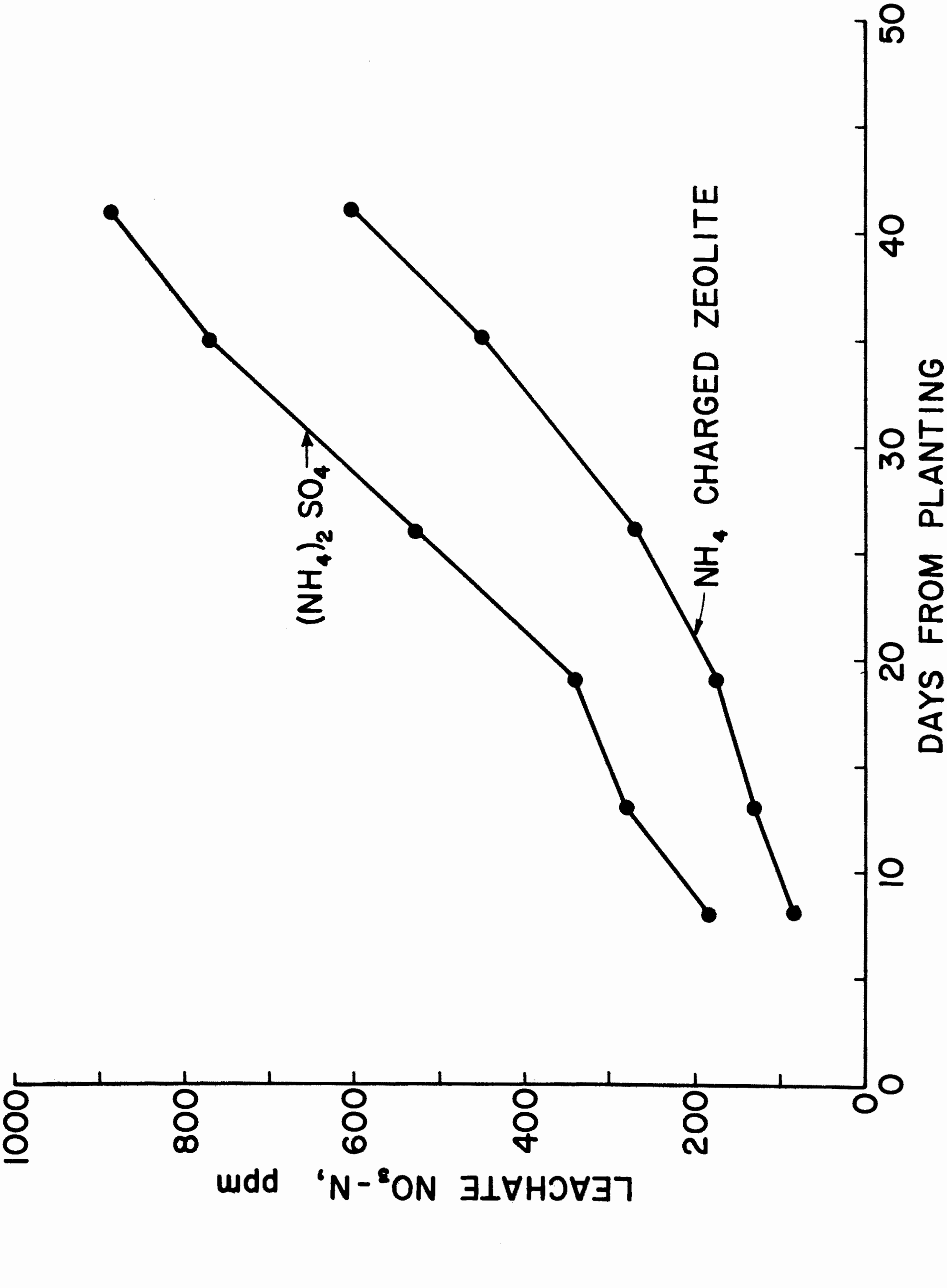
LEACHATE NO_3-N, ppm
1000
800
600
400
200
0
0
10
20
30
40
50
DAYS FROM PLANTING
$(NH_4)_2SO_4$
NH_4 CHARGED ZEOLITE

Fig. 5. Cumulative ripe tomato fruit weight comparing three banded zeolite treatments and banded ammonium sulfate. There was no significant difference among treatments at the 5% level of probability. Field experiment.

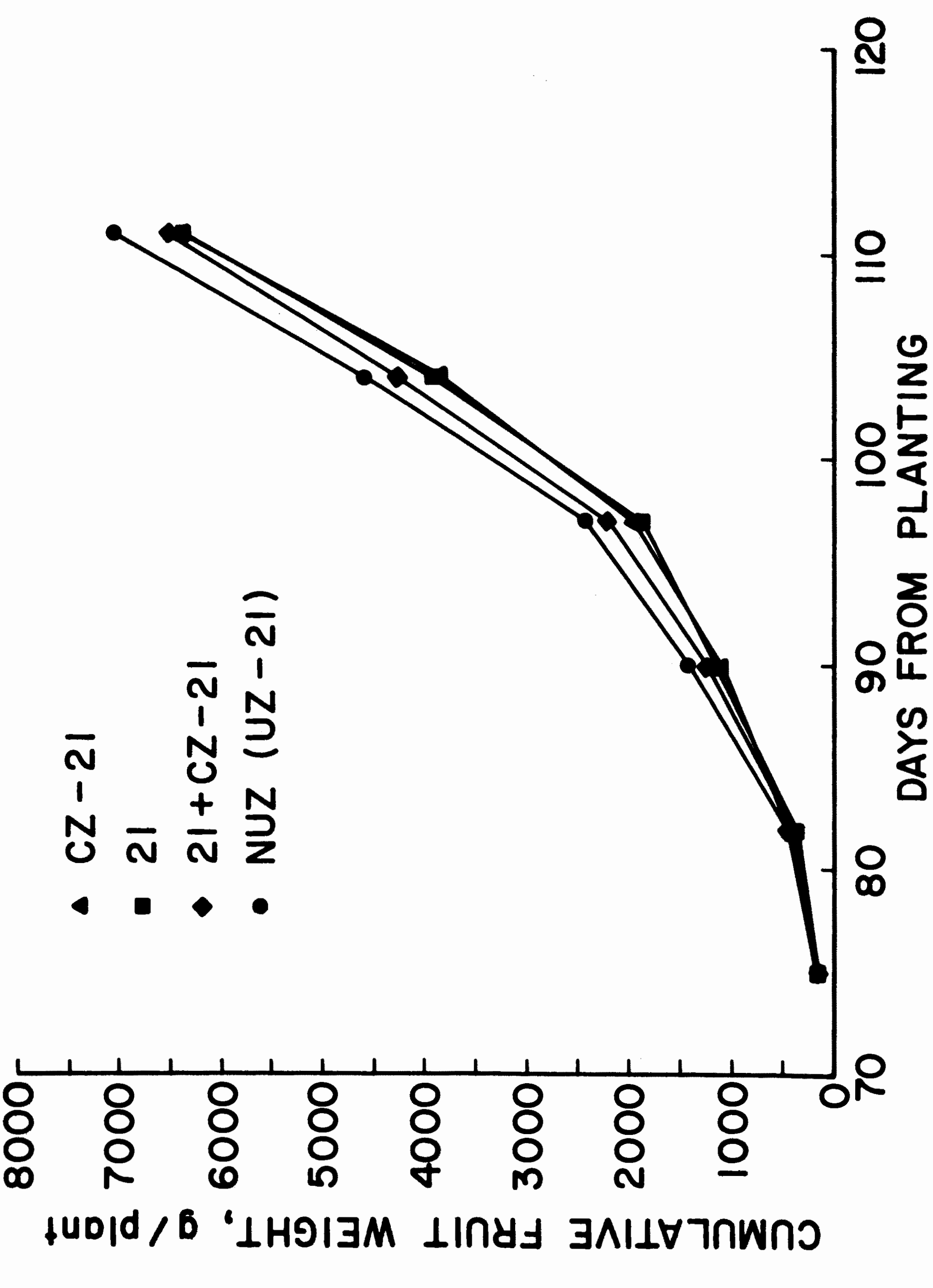
CZ-21
21
21+CZ-21
NUZ (UZ-21)
CUMULATIVE FRUIT WEIGHT, g/plant
0
1000
2000
3000
4000
5000
6000
7000
8000
DAYS FROM PLANTING
70
80
90
100
110
120

Fig. 6. Cumulative number of ripe tomato fruit comparing three banded zeolite treatments and banded ammonium sulfate. There was no significant difference among treatments at the 5% level of probability. Field experiment.

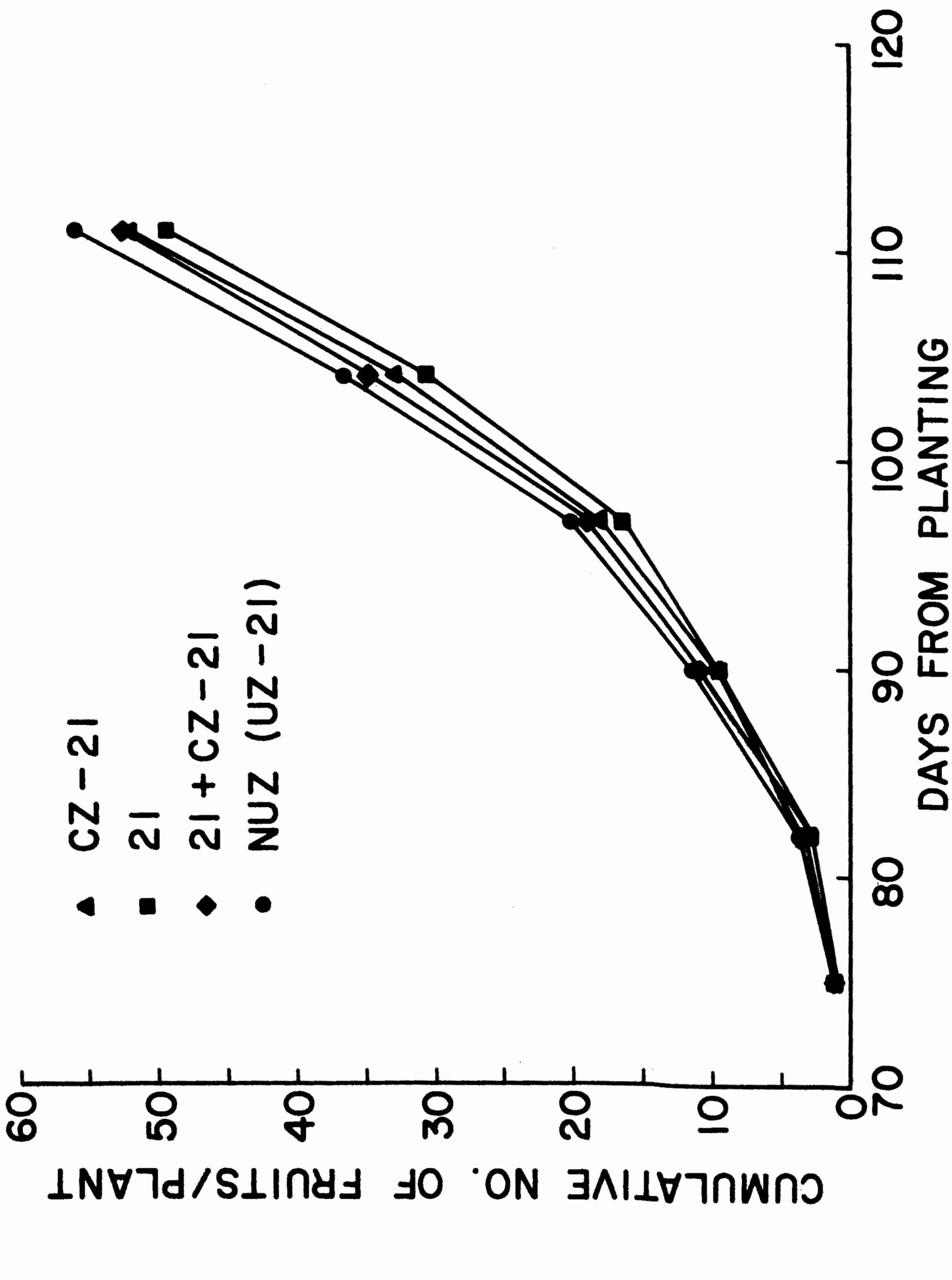
CZ - 21
21
21 + CZ - 21
NUZ (UZ - 21)
CUMULATIVE NO. OF FRUITS/PLANT
0
10
20
30
40
50
60
70
80
90
100
110
120
DAYS FROM PLANTING

Fig. 7. Growth response of poinsettia to zeolite treatments in the NH_4 experiment. Greenhouse potted plant experiment.

Fig. 8. Growth response of poinsettia to zeolite treatments in the K experiment. Greenhouse potted plant experiment.


Rep 2
Rep 1
NH4
T-1
NH4
T-2


Rep 2
Rep 1

DISCUSSION

Plant Responses to Zeolite-N Governed by Soil Texture and Leaching

An unpublished report (F. D. Moore et al.) indicated that incorporation of ammonium charged zeolite hastened seedling emergence in a soil with a conductivity of 3.6 mmhos/cm. No beneficial effect of zeolite on seedling emergence was evident in his study, however.

One of the objectives of this study was to determine the most effective method of applying clinoptilolite-nitrogen combinations. Banding clinoptilolite treatments increased growth and N-uptake, while maintaining higher levels of available soil N compared with incorporation of these treatments in both medium and light soils. Therefore, a banding experiment was developed for use in a field tomato experiment.

The mode of action of charged clinoptilolite in soil depends on many factors; the concentration of the preadsorbed ion on the zeolite and in the soil solution as well as the solution cation concentration, soil pH, leaching pressure, and other factors (26,77,101,108). Initially, banded zeolite should be less influenced by such factors, than when incorporated, due to limited contact between the band and the soil. Zeolite bands should eventually become active in the exchange process after a period of time.

The radish growth response was highly influenced by the banding of ammonium charged zeolite in the medium soil. The clay fraction of the two soils was approximately 35%, by weight, illite and vermiculite, which are known for their ability to render NH_4^+ unavailable. Reduced fixation of NH_4^+ may have been partially responsible for the growth responses in the medium soil which contained more than twice the amount of illite and vermiculite than did the light soil. A reduction in possible denitrification N loss, due to lack of drainage, by ammonium charged zeolite is not to be ruled out. The addition of ammonium charged zeolite may have provided a fairly uniform flow of NH_4^+ for the soil nitrifiers and plants via the exchange process, thus increasing plant response. It has been shown that combinations of available NH_4^+ and NO_3^- contributes to greater plant yields than N supplied as NH_4^+ or NO_3^- (53). Riggert (89), a nitrification suppression researcher stated: "It appears that with a portion of the N supplied and maintained as NH_4^+, plant growth and development may be accelerated."

The high levels of soil NH_4-N maintained by the ammonium charged zeolite when compared with the ammonium sulfate control, indicated that more NH_4-N was available for both the plant and soil nitrifiers in the medium soil.

Plant responses to ammonium charged zeolite in the light soil were in general positive; however, the magnitude of the differences between the ammonium charged zeolite and ammonium sulfate was not as great as that found in the medium soil.

Even though the light soil was leached 6 times, the ammonium charged zeolite treatment seemed to provide adequate nitrogen as indicated by radish leaf area and fresh root weight. Other indications of how ammonium charged zeolite withstood the severe leaching pressure, were the 290% higher available nitrogen level and the definite reduction in leachate NO_3-N when contrasted with ammonium sulfate. Mackown (68) reported similar results on the retention of residual NH_4-N in soil containing ammonium charged zeolite. It should be noted that the residual soil NH_4-N concentration was lower in the medium soil, compared to the leach stressed light soil; however, initial soil nitrogen level plus the nitrogen treatment additions brought the preplant nitrogen base to approximately equal levels in both soils. It is hypothesized that the suppressed availability of the adsorbed NH_4^+ ion within the ammonium charged zeolite, to the soil solution and soil nitrifying bacteria, was the main reason for the decrease in NO_3-N loss in the leached soil. The rate at which zeolite-ammonium is made available to the soil-root system is probably due to two factors, cation exchange and _Nitrosomonas_ sieving.

If the charged zeolite is placed in an arid or semiarid soil, K^+ would probably play a role in the ammonium exchange because of its position in the lyotropic series of clinoptilolite (10). Although the affinity of clinoptilolite is less for Na^+, Ca^{++}, and Mg^{++}, these cations are present in arid and semiarid soils in large quantities and therefore could also exchange for zeolite-ammonium by mass action (21). It is also hypothesized that the NH_4^+ on the outer exchange sites is immediately available for oxidation. However, only after exchange from the central cavity sites, exiting the channel, is the adsorbed NH_4^+ available to the nitrifiers, due to the sieving of the 8000 Å nitrifying organism by the 3.0-4.4 and 3.5-7.9 Å channel window openings.

Zeolite may provide an optimum environment for microbial activity. An increase in microorganism population around zeolite particles has been observed (J. J. Lawson, personal communication).

Plant growth responses to uncharged zeolite plus ammonium sulfate, were generally significant in the light soil only. In both the medium and light soils, a significant soil NH_4-N level was demonstrated by the uncharged zeolite plus ammonium sulfate compared to the ammonium sulfate control. It is conjectured that the uncharged zeolite may have the potential to "self-charged," i.e., adsorb ammonium ions internally by the association with ammonium sulfate, in the soil band. No positive evidence was unveiled in this experiment, however.

Uncharged zeolite plus urea showed no statistical difference in plant response compared with the addition of urea alone, in the medium soil. The residual medium soil N levels were higher in the uncharged zeolite plus urea treatment when contrasted with the urea treatment. When urea is applied to coarse textured alkaline soils, especially as a band, increases in pH and therefore, NH_3 concentration, occur (19). Some clay soils will buffer the pH of such a reaction thus possibly reducing the detrimental effects of urea (102). Theoretically, the medium soil (13%) clay should have approximately twice the pH buffering capacity as the light (6%) soil. Thus, the potential for demonstrating the ability of the zeolite to absorb ammonia was not as great as in the more alkaline light textured soil which also received one-third more zeolite and urea.

The benefit of adding zeolite in conjunction with high amounts of urea, as in the light textured soil, was well illustrated by the significant increases in the four plant growth parameters (leaf area, dry weight, root fresh weight, and N-uptake). The protection provided by the zeolite is probably due to the ability of the zeolite to absorb ammonia (59) thereby depressing ammonia toxicity as well as nitrite toxicity by preventing disruption of the nitrification process (98).

It should be noted that the N content of the zeolite N treatment was low and the added zeolite comprised 0.5% by weight of the medium soil, 0.86% by weight of the light soil. The application rates were of heavy fertilizer quantities and should not influence soil structure as do zeolites used as soil conditioners or amendments (68).

Effects of Zeolite-N Combinations on Field Tomatoes

The lack of response to zeolite used, not as a soil amendment but as a slow-release N source or N fertilizer facilitator in this phase of research, may have been due to availability of residual soil nitrogen. Soil analysis revealed that the organic matter content was 2.4% with an unknown N mineralization rate. Soil available N was 85 kg of N per hectare, and approximately 108 kg of nitrate N per hectare may have been unavoidably applied in the irrigation water, as determined from water analysis (Appendix Table 37). Therefore, a base level of 193 kg of N/ha plus a small amount from mineralized organic matter, would normally not stress tomato plants, which require approximately 168 kg of N per hectare as a minimum (38,65). However, the N requirement must have been high since the yield of ripe fruit was estimated at 50 metric tons.

Although no beneficial effects of zeolite were apparent, no detrimental effects were noted.

Effects of Zeolite on the Growth of Bench Crops and Potted Plants

Bench Crops

Plants treated with zeolite demonstrated a growth response equal to or less than those in injected fertilizer treatments. Of the plants evaluated, the radish showed the best response, especially to the NH_4^+ charged zeolite treatment. Apparently, the 75 ppm N application through NH_4^+ charged zeolite can supply adequate nitrogen to short-lived crops under the conditions of this experiment.

However, the yellowing symptom, exhibited by the ammonium charged zeolite treated plants at harvest, 35 days after planting, was probably due to the low base level at which the zeolite was incorporated. Therefore, due to the apparent N depletion, a base level of 100 ppm N should be considered in the future for radish production in clay loam modified soils. The NH_4^+ fertilizer injected treatments produced larger radish leaf area, compared to the NH_4^+ charged zeolite, yet all three treatments produced approximately the same root fresh weight. The zeolite treatment seemed to provide a more effective growth response by producing less top and more root.

The uncharged zeolite plus injected fertilizer treatment produced slightly greater root fresh weight than the ammonium charged zeolite treatment. It is possible that a "self-charging" phenomenon of the uncharged zeolite occurred due to the high rates of injected NH_4^+, which helped to maintain a greater level of NH_4^+ for the plants and soil nitrifiers between waterings.

The lettuce displayed a much greater requirement for nitrogen than radishes, but a smaller requirement for K^+ and Zn^{++}. Also, it seemed that the lettuce required NH_4-N or NO_3-N faster than the ammonium charged zeolite could exchange it. The growth response of the lettuce to the zeolite treatments was in contrast to the results of other plants tested. Thus, due to the inconclusive results, another greenhouse lettuce experiment is warranted. It is also suggested that a range of 75 to 300 ppm N, supplied by the ammonium charged zeolite, be incorporated into the experiment to determine required levels for maximizing lettuce yields.

The bean variety used to evaluate growth responses of zinc charged zeolites may not have been as Zn^{++} sensitive as other varieties. The beans did not significantly respond to the Zn^{++} treatment with the exception of the uncharged zeolite plus injected fertilizer treatment. The significant response of the uncharged zeolite plus injected fertilizer treatment seemed to demonstrate how fertilizer efficiency could be increased. Future experiments should include Zn-deficient seed, grown in Zn-deficient soil, especially for field experiments.

Although the presence of zeolite increased the yield of cut chrysanthemums, a slight yellowing was noted in the NH_4 experiment during harvest. Again, an exhausted zeolite-N supply was probably a factor. Levels of 100 to 500 ppm nitrogen should be used as a range in the next chrysanthemum growth study.

The K experiment showed no significant plant fresh weight difference response between chrysanthemum treatments. The results were not in agreement with an earlier reported potted chrysanthemum research (52). The naturally potassic and the zinc charged zeolite treatments showed no increases in plant height, suggesting that K^+ and Zn^{++} were being made available to the plant by the medium.

Snapdragon responses to the zeolite treatments were inconclusive. The ammonium charged zeolite treatment, in both the NH_4 and K experiments, produced smaller plant fresh weight than the injected fertilizer treatments. The snapdragons were elongated at transplanting time and may have influenced the response. Inadequate NH_4^+ and K^+ levels may have again been partially responsible for the poor zeolite treatment response.

Potted Plants

The responses of the poinsettia and the Easter lily were basically identical. The N-fertilizer injection treatment produced the highest quality plants in NH_4 experiment; there were no growth differences between treatments in the K experiment. The response of the two plant species to higher ammonium charged zeolite treatment levels seemed to indicate that zeolite cannot exchange NH_4^+ at a rate high enough or the base level was not adequate to provide enough N for optimum plant growth, at least under the conditions of this experiment. The presence of Fort Collins clay loam in the medium, plus the decomposition of the peat moss may have supplied sufficient amounts of K^+ to maintain adequate growth in the K experiments.

Observations made at initial "watering in" of Easter lily bulbs, revealed a slight off-white colored suspension in the leachate. An experiment was designed to evaluate zeolite movement in two different media, with and without zeolite of two different mesh. The results indicated that zeolite was not leached out of the soils.

The soluble salts level in the bench medium was 1.0 mmhos/cm, whereas the potting medium was 2.1 mmhos/cm. Both levels would allow slower exchange rates of zeolite adsorbed NH_4^+, thus varying the availability of N for the plant and microorganisms. Vaughan (108) stated, "Clinoptilolite works best when the cation to be exchanged is present in low concentrations." Also, "appreciable quantities of Ca^{++} and Mg^{++} have detrimental effects on the NH_4^+-exchange capacity of this zeolite."

SUMMARY AND CONCLUSIONS

Among methods of application for zeolite-N, the band application proved to be the most effective resulting in increased radish root fresh weight, ranging from 5 to 33% in the medium soil and 11 to 59% in the light soil, when compared to the incorporation method.

Ammonium charged clinoptilolite appeared to act as a type of slow-release fertilizer, increasing growth of radishes in both a medium and light textured soil and decreasing NO_3-N loss due to leaching in the light soil. Clinoptilolite, when physically combined with ammonium sulfate, had only minimal effects; yet, when combined with urea, there were positive plant growth responses and retention of soil nitrogen in the ammonium form. Clinoptilolite apparently acted as a type of "protectant" against the injurious effect of urea when the two were combined and added to an alkaline soil.

The lack of response to the zeolite treatments in the field tomato experiment was attributed to excessive nitrogen particularly that from the irrigation water. Further field experiments need to be conducted using low N irrigation water in field soils across the United States in order to determine their impact on the mode of action of clinoptilolite.

The ammonium charged and the naturally potassic clinoptilolite were very effective in increasing yield of short-lived greenhouse bench radishes, probably because they acted as a type of slow-release fertilizer. Zinc charged zeolite proved to be an effective zinc source by also increasing the yield of radishes. The nutrient level of

75 ppm N, supplied by the clinoptilolite, was not adequate for optimum growth of lettuce, bean, chrysanthemum and snapdragon. The potted plants failed to attain desired yield with additions of 500 ppm nitrogen from the ammonium charged clinoptilolite and 250 ppm K from the naturally potassic clinoptilolite. Therefore, it is suggested for future research, that ammonium charged clinoptilolite be added at a minimum base level of 100 ppm N for bench crops and 500 ppm N for potted plants. Naturally potassic clinoptilolite should also be added at a minimum base level of 100 ppm K. Increasing levels of zeolite-N and potassic zeolite should be added to determine the concentration required for maximum growth of greenhouse crops grown in artificial media.

Ammonium charged clinoptilolite should be a beneficial product when used in high rainfall areas, in irrigated areas and/or in modified greenhouse soils, where leaching is known to be a problem. The use of ammonium charged clinoptilolite might overcome problems of nitrogen loss due to nitrogen fixation by clay and organic matter and possibly denitrification which is related to poor drainage.

The plant protection provided by clinoptilolite when combined with urea could prove advantageous by preventing plant injury when urea is used in alkaline soils with low cation exchange capacity. The absorption of ammonia by the clinoptilolite, could be the main reason for this reduction in plant injury. More detailed study in this area is warranted.

Zeolite as a fertilizer facilitator or "specialty" fertilizer could be used in certain horticultural industries. The injection of fertilizer is very effectively used in the production of greenhouse crops, however, the addition of clinoptilolite to the media may increase the efficiency of the injected fertilizer.

Clinoptilolite charged with Zn^{++} or Fe^{++} micronutrients could be beneficial as a source of micronutrients frequently deficient in soils of arid or semiarid regions.

The evaluation of the usefulness of zeolite-nutrient combinations for the production of plants and plant products of economic importance, has just begun. With the expanding agronomic and horticultural world, new and more effective nutrient sources are in great demand. The results of my research suggest that clinoptilolite can act in a beneficial way, however, its economic value has yet to be determined.

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APPENDIX

Appendix Explanation 1: Cation Exchange Capacity (CEC-T)

The CEC-T procedure consists of the following:

1. Place approximately 50 mg of finely ground zeolite samples in 10 ml centrifuge tubes. Weigh to ±0.0002 g.

2. Add 10 ml of 2 N NaCl to each tube and let stand overnight at 25±2°C. Centrifuge and discard the supernatant liquors.

3. Add 5 ml of 2 M NaCl to each tube, mix thoroughly and let stand for about 4 hours at 25°C. Centrifuge and discard the supernatant liquors.

4. Repeat Step 3.

5. Add 10 ml of distilled water to each tube and mix thoroughly. Centrifuge and discard the supernatant liquors.

6. Repeat Step 5 three times.

7. Place tubes in a drying oven at 110°C overnight. Weigh each tube when sample is dry to 0.0002 g.

8. Add 10.0 ml of 0.1 M $(NH_4)_2SO_4$ to each tube and mix with contents at 25°C several times over a period of about 4 hours.

9. Centrifuge and add 0.1 ml of each supernatant solution to 9.9 ml of a solution of 1000 ppm La and mix each thoroughly.

10. Prepare standards from 0.1 ml of 0.01 M Na_2SO_4 and 0.1 ml of 0.001 M Na_2SO_4, each added to 9.9 ml of 1000 ppm La.

11. The Na concentrations of the sample solutions from Step 9 are determined by AA using the standards described and a blank solution prepared by adding 0.1 ml of 1 M $(NH_4)_2SO_4$ to 9.9 ml of 1000 ppm La.

12. The CEC-T of the zeolite samples is calculated from the Na concentration of the final solutions and weight of the samples obtained by the difference in weights of each empty tube and the weights of each tube containing the sample following the overnight drying described in Step 7.

13. The calculation is as follows:

$$\text{CEC-T (meq/g)} = [Na^+] \text{ in final solution} \times 0.01 \times 1000 \text{ (meq/mole)} \times \frac{1}{\text{sample wt. (g)}}$$

This procedure was designed for zeolite CEC determination (S. W. Boese., Dept. of Geology, Univ. of Wyo., personal communications).

Appendix Explanation 2: Formula for coefficient of velocity of emergence

$$\text{Coefficient of velocity} = 100 \times \frac{A_1 + A_2 + . . . + A_x}{A_1T_1 + A_2T_2 + . . . + A_xT_x}$$

where: A_* = percentage of seedlings

T_* = number of days after planting corresponding to A

* = the first day any seedlings were observed, was taken as day "1".

Kotowski, Felix. 1926. Temperature relations to germination of vegetable seed. Proc. Amer. Soc. Hort. Sci. 23:176-184.

Table 22. Influence of zeolite on speed of radish germination, i.e., 2 parameters. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Coefficient of velocity, %								
Medium soil	I	19.5	19.3	19.4	19.0	19.2	19.5	19.4
	B	19.2	19.4	19.5	19.4	19.5	-	-
Light soil	I	19.9	19.6	19.8	19.2	19.9	19.9	19.9
	B	19.8	19.8	19.7	19.7	20.0	-	-
P_{50}, days								
Medium soil	I	3.6	3.7	3.9	3.9	3.8	3.5	3.5
	B	3.4	4.0	3.6	3.6	3.5	-	-
Light soil	I	3.3	3.5	3.3	3.9	3.4	3.5	3.3
	B	3.3	3.3	3.5	3.6	3.2	-	-

Table 23. Mean[z] radish leaf area of final harvest comparing the effect of zeolite and N-fertilizer in medium soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Leaf area (cm^2)	I	226.5	212.5	182.7	137.5	77.3	135.4	144.4
	% C.V.[y]	20	26	30	37	94	14	17
	B	243.4	188.3	210.6	167.1	162.2	-	-
	% C.V.	15	30	38	34	56	-	-

Analysis of Variance

Source	df	MS	F value
Rows	11	6424.3	2.4*
Column	11	5763.3	2.1*
Treatment	11	26085.8	9.6**
Error	110	2726.0	

[z]H.S.D., 5% = 71.1

[y]Overall coefficient of variation = 8.6

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 24. Mean[z] radish leaf area of final harvest comparing the effect of zeolite and N-fertilizer in light soil. Plant Science greenhouse experiment.

	Treatments						
	CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Leaf area (cm^2) I	182.8	156.5	185.6	165.8	103.4	56.0	51.2
% C.V.[y]	25	16	36	31	63	27	27
B	187.4	198.5	208.5	149.7	116.0	-	-
% C.V.	28	26	43	20	60	-	-

Analysis of Variance

Source	df	MS	F value
Rows	11	4147.5	1.6
Columns	11	3988.3	1.5
Treatments	11	3518.0	13.4**
Error	110	2622.5	

[z]H.S.D., 5% = 74.2

[y]Overall coefficient of variation = 10.8

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 25. Mean[z] radish dry weight of final harvest comparing the effect of zeolite and N-fertilizer in medium soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Dry weight (g)	I	1.681	1.343	1.192	0.757	0.455	1.304	1.486
	% C.V.[y]	24	33	42	46	110	19	34
	B	1.836	1.195	1.585	1.125	1.233	-	-
	% C.V.	20	47	42	44	65	-	-

Analysis of Variance

Source	df	MS	F value
Rows	11	0.457	2.04*
Columns	11	0.494	2.21*
Treatments	11	1.544	6.90**
Error	110	0.224	

[z]H.S.D., 5% = 0.645

[y]Overall coefficient of variation = 10.7

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 26. Mean[z] radish dry weight of final harvest comparing the effect of zeolite and N-fertilizer in light soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Dry weight (g)	I	1.088	0.997	1.138	1.082	0.604	0.476	0.483
	% C.V.[y]	35	25	34	38	73	23	32
	B	1.402	1.264	1.384	1.098	0.708	-	-
	% C.V.	36	44	27	38	66	-	-

Analysis of Variance

Source	df	MS	F value
Rows	11	0.0969	0.65
Columns	11	0.1437	0.96
Treatments	11	1.3086	8.75**
Error	110	0.149	

[z]H.S.D., 5% = 0.528

[y]Overall coefficient of variation = 11.4

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 27. Mean[z] root fresh weight of final harvest comparing the effect of zeolite and N-fertilizer in medium soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Root weight (g)	I	12.11	8.26	10.25	4.32	2.43	12.56	15.00
	% C.V.[y]	50	43	46	66	154	27	33
	B	13.51	9.96	13.84	8.54	9.16	-	-
	% C.V.	33	56	43	71	74	-	-

Analysis of Variance

Source	df	MS	F value
Rows	11	31.4	1.43
Columns	11	47.0	2.14*
Treatments	11	173.1	7.88**
Error	110	22.0	

[z]H.S.D., 5% = 6.40

[y]Overall coefficient of variation = 13.54

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 28. Mean[z] root fresh weight of final harvest comparing the effect of zeolite and N-fertilizer in light soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Root weight (g)	I	8.18	8.96	11.23	6.64	4.46	4.43	3.74
	% C.V.[y]	57	32	38	51	108	34	39
	B	11.60	12.10	12.38	7.62	6.27	-	-
	% C.V.	26	34	35	53	82	-	-

Analysis of Variance

Source	df	MS	F value
Rows	11	5.5	0.37
Columns	11	22.2	1.50
Treatments	11	118.4	8.03**
Error	110	14.7	

[z]H.S.D., 5% = 5.24

[y]Overall coefficient of variation = 13.63

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 29. Mean number of commercial grade radishes (dia. $\geq$ 16 mm) of the 5th and 6th (final) harvests in two soils. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Medium soil	I	10	10	8.5	6	1.5	11.5	11.5
	B	9	9	10	4	8	-	-
Light soil	I	4.5	6	7	4	3	1.5	1.5
	B	9	8.5	7	5.5	3.5	-	-

Table 30. Mean[z] N-uptake [% total N (Appendix Table 30) times mg of dry leaf tissue (Appendix Table 31)] of the final harvest comparing the effect of zeolite and N-fertilizer in medium soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
N-uptake (mg)	I	63.87	49.97	32.83	24.80	15.40	17.60	16.87
	B	57.23	33.97	45.47	35.87	38.40	-	-

Analysis of Variance

Source	df	MS	F value
Treatments	2	14.86	0.15
Replications	11	759.55	7.43**
Error	22	101.78	

[z]H.S.D., 5% = 29.41

*,**Indicates significance at the 5% and 1% level of probability, respectively.

Table 31. Mean[z] N-uptake [% total N (Appendix Table 30) times mg of dry leaf tissue (Appendix Table 31)] of the final harvest comparing the effect of zeolite and N-fertilizer in light soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
N-uptake (mg)	I	42.70	29.67	32.07	43.67	20.30	6.00	7.77
	B	42.63	32.60	44.43	38.93	18.93	-	-

Analysis of Variance

Source	df	MS	F value
Treatments	2	18.73	0.28
Replications	11	563.82	8.3**
Error	22	67.47	

[z]H.S.D., 5% = 23.95

*,** Indicates significance at the 5% and 1% level of probability, respectively.

Table 32. Total N (%) per radish plant of leaf tissue of final harvest in two soils. Plant Science greenhouse experiment.

Rep			Treatments CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Medium soil	1	I	5.9	6.0	5.8	5.5	6.3	3.9	3.6
		B	6.0	6.0	6.0	6.4	6.2	-	-
	2	I	5.8	6.3	5.8	5.1	4.9	3.6	3.6
		B	6.0	6.3	6.3	6.6	6.3	-	-
	3	I	6.0	6.2	6.0	5.5	6.2	4.0	4.0
		B	6.0	6.2	6.2	6.2	6.4	-	-
Light soil	1	I	6.3	6.3	6.3	6.4	5.9	3.5	3.2
		B	6.2	6.5	6.4	6.5	6.2	-	-
	2	I	6.4	6.3	5.9	6.5	6.2	4.6	3.1
		B	6.1	6.4	6.1	6.4	6.2	-	-
	3	I	6.3	6.2	6.0	6.1	6.4	3.2	3.3
		B	6.0	6.1	6.5	6.2	6.6	-	-

Table 33. Dry weight per radish plant of leaf tissue of final harvest in two soils. Plant Science greenhouse experiment.

Rep			Treatments						
			CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
Medium soil	1	I	1100	897	457	421	134	458	397
		B	920	713	920	560	791	–	–
	2	I	892	843	619	440	408	435	494
		B	898	284	843	611	817	–	–
	3	I	1261	690	604	534	284	489	471
		B	1051	658	453	510	244	–	–
Light soil	1	I	613	584	564	508	468	142	157
		B	727	387	602	708	316	–	–
	2	I	615	323	756	791	332	170	449
		B	556	482	884	551	360	–	–
	3	I	792	516	264	713	202	163	132
		B	805	682	629	569	227	–	–

Table 34. Mean residual soil N after final harvest[z] in medium soil. Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
NO_3-N (ppm)	I	66.2	69.2	61.7	70.0	83.5	11.2	13.7
	B	66.5	79.5	74.5	72.2	65.2	-	-
NH_4-N (ppm)	I	12.0	14.2	13.7	12.5	13.0	7.2	6.5
	B	18.2	16.7	14.5	10.0	8.0	-	-
Available-N (ppm)	I	78.2	83.5	75.5	82.5	96.5	18.2	20.2
	B	83.0	96.2	89.0	82.2	73.2	-	-

[z]Soils were sampled 43 days from planting.

Table 35. Mean residual soil N after final harvest[z] in light soil.[y] Plant Science greenhouse experiment.

		Treatments						
		CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
NO_3-N (ppm)	I	38.5	36.7	24.7	24.2	34.0	3.1	4.5
	B	48.7	37.7	31.2	29.7	36.2	-	-
NH_4-N (ppm)	I	12.2	8.0	7.0	5.2	7.0	5.5	5.0
	B	82.7	36.7	13.0	4.2	5.5	-	-
Available-N (ppm)	I	50.7	44.2	31.7	29.5	41.0	8.6	9.5
	B	132.2	74.5	44.2	34.0	41.7	-	-

[z]Soils were sampled 43 days from planting.

[y]Leached 6 times.

Table 36. Influence of zeolite on leachate NO_3-N (ppm). Plant Science greenhouse experiment.

Days from planting		Treatments CZ-21	UZ-21	UZ-45	21	45	STD-Z	NN
8	I	90	111	78	101	61	71	74
	B	84	144	144	174	94	-	-
13	I	47	49	36	58	40	32	34
	B	47	70	68	96	55	-	-
19	I	45	42	32	38	30	15	16
	B	43	57	45	59	37	-	-
26	I	136	138	123	103	74	4	4
	B	93	138	73	186	89	-	-
35	I	224	258	190	205	168	4	4
	B	178	228	120	240	220	-	-
41	I	138	143	99	101	92	4	4
	B	151	146	110	115	150	-	-

Table 37. Chemical characteristics of the Horticulture farm water.

pH[z]	7.6
Conductivity (micromhos/cm, EC x 10^{-6})	3000.0
	ppm
Cation[y]	
Calcium	424
Magnesium	146
Sodium	166
Potassium	12
Anions	
Carbonate[w]	0
Bicarbonate[v]	292
Chloride[u]	38
Sulfate[t]	1411
Nitrate[s]	52
SAR	1.8
Salinity hazard	High
Sodium hazard	Low

[z]Paste method.

[y]Inductively coupled plasma spectrometry.

[x]Titration determination.

[v]Titration with standard acid determinations.

[u]Ion selective electrode determination.

[t]Barium sulfate turbidimetric determinations.

[s]Chromotropic acid (CTA) colorimetric determinations.