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INFLUENCE OF NH_4-EXCHANGED CLINOPTILOLITE ON NUTRIENT CONCENTRATIONS IN SORGHUM-SUDANGRASS

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ABSTRACT

The ability of NH_4-exchanged clinoptilolite to influence the uptake of nutrients by sorghum-sudangrass was tested in greenhouse experiments in soil-phosphate rock (P-rock)-ammonium (NH_4)-zeolite systems in which soil pH decreased with increasing NH_4-clinoptilolite content (Weld and Red Feather soils, classified as Aridic Argiustoll and Lithic Cryoboralf, respectively) and in which the amount of NH_4-clinoptilolite had little influence on soil pH (Keith soil, a Typic Argiustoll). Clinoptilolite-P-rock ratios of 0 to as much as 7.5 were used, with P rates of 100 to as much as 400 mg P/kg soil. Top growth was harvested at 3- to 6-week intervals to obtain 5 or 6 cuttings. Nutrient uptake was studied by analysis of dried plant tissues, and the available nutrients remaining in the soil were determined using ammonium bicarbonate diethylenetriaminepentaacetic acid (AB-DTPA) extraction. The addition of NH_4-clinoptilolite increased yields by as much as 65% over control experiments and significantly increased the concentrations of nutrient elements in plant matter. For example, P was increased by as much as 100%, Cu by 100%, Mn by 450%, Ca by 50%, Mg by 30%, and Zn by 70%. Uptake of some nutrients may have been enhanced by an increase in their solubility due to a lowering of soil pH by as much as 2 units caused by nitrification of NH_4 ions with time. The concentrations of Cu and Mn in sudangrass, however, increased 23% and 12%, respectively, with increasing NH_4-clinoptilolite application rate independent from a pH effect for the Keith soil, suggesting that an ion-exchange mechanism may have enhanced availability. This concept is supported by an increase in AB-DTPA extractable soil elements (e.g., as much as 250% increase for Cu) with increasing clinoptilolite/P-rock ratio (0 to 6) for the Keith soil-P-rock-zeolite system used in plant growth experiments.

Similar extraction experiments using mixtures of NH_4-clinoptilolite and P-rock without soil at constant pH also demonstrated an increase in the availability of nutrients over that expected from simple mixtures (e.g., a two orders of magnitude increase in extractable Cu was noted over that predicted from a simple mixing of P-rock and zeolite), further emphasizing the importance of chemical reaction (i.e., ion-exchange) to nutrient release. The NH_4-clinoptilolite may have inhibited the uptake of K by plant tissues by as much as 50% in some experiments, suggesting that K-saturated clinoptilolite be used in K-poor soils.

INTRODUCTION

Zeolites are a class of non-swelling, porous, aluminous, tectosilicate minerals that have a large cation-exchange capacity (100 to 300 meq/100 g) and a large water-holding capacity (Mumpton, 1984). The most exploitable zeolites occur in enormous, near-surface deposits, many of which have formed from the alteration of volcanic ash in alkaline-saline lakes (Mumpton, 1977; Sheppard and Gude, 1982), although other types of natural occurrences are known (Ming and Mumpton, 1989). Their unusual cation-exchange properties and large abundance have led to suggestions that they be used as soil amendments in agriculture. For example, Mumpton (1984) discussed their potential use as slow-release N and K fertilizers; as carriers for insecticides, fungicides, and herbicides; and as traps for heavy-metal contaminants that might be found in soils amended with sewage sludge or in land reclaimed from mining operations.

Barbarick and Pirela (1984) indicated that zeolites may be used effectively in agricultural systems to prevent leaching losses of ammonium-type fertilizers, to reduce ammonia toxicity to plants, and to increase yields. Lewis *et al.* (1984) found that NH_4-exchanged clinoptilolite was effective as a slow-release N-fertilizer and that amendments of clinoptilolite could prevent injury by urea to radish plants. Barbarick *et al.* (1990) indicated that applications of NH_4-clinoptilolite and phosphate rock rendered P more available for uptake by sorghum-sudangrass than did applications containing phosphate rock alone. Ferguson *et al.* (1986) showed that clinoptilolite is an effective medium for the growth of turfgrass. Mineyev *et al.* (1990) found that zeolite could be amended to a contaminated soil to ameliorate Zn contamination of plants, and Leppert (1990) reported similar results for clinoptilolite on the uptake of Cs by sweet potatoes. Marcille-Kerslake (1991) found that, although the addition of K-clinoptilolite-rich rock to mixtures of non-calcareous soil and phosphate rock increased the amount of $NaHCO_3$-extractable P, yields of soybeans were decreased by the sequestration of Ca by the zeolite.

Because zeolites show such promise as agricultural amendments, more experiments are needed to learn about possible interactions between plants, soil, and zeolites. Soil-zeolite systems are very complex chemically, but several simple mechanisms can be postulated by which zeolites could influence nutrient uptake: (1) zeolites could decrease nutrient supply by sequestering nutrient cations such as K^+ or Ca^{2+} on exchange sites, thereby limiting uptake (Barbarick *et al.*, 1990; Marcille-Kerslake, 1991); (2) zeolites could increase nutrient cation supply by accepting onto their exchange sites cations that have been dissolved from sparingly soluble minerals, thereby rendering these cations more available for plant uptake (Bunzl, 1981; Eberl and Landa, 1985); (3) zeolites could increase nutrient anion supply by increasing dissolution of sparingly soluble minerals, for example, by lowering Ca^{2+} activity by cation exchange with the soil solution, thereby increasing dissolution of phosphate rock (Lai and Eberl, 1986; Chesworth *et al.*, 1988). The present investigation was undertaken to study how NH_4-exchanged clinoptilolite can influence plant uptake of a variety of chemical elements, including P, K, Cu, Mn, Zn, Mg, Ca, Fe, and Cd.

MATERIALS AND METHODS

Experimental materials included three soils, two phosphate rocks (P-rocks), and two clinoptilolites (Cp). The three soils were the Weld loam and Red Feather loamy sand (Aridic Argiustoll and Lithic Cryoboralf, respectively) and the Keith silty loam (Typic Argiustoll). The P-rocks were a North Carolina P-rock (NCPR) and the Idaho Mill Shale P-rock (IDPR). One clinoptilolite (WYCp) was from Rocky Mountain Energy Company's Fort LeClede deposit in the Washakie Basin in Wyoming (Weber *et al.*, 1984; Barbarick *et al.* 1988); it contains by X-ray diffraction analysis (XRD) quartz, sepiolite, and mica (biotite?) as trace impurities. The other clinoptilolite (SDCp) was from the Craven Creek area of the Pine Ridge Indian

Reservation in South Dakota (Desborough, 1989); it also contains (by XRD analysis) quartz, gypsum, anhydrite, calcite, illite, smectite, and feldspar as minor impurities. Selected properties of starting materials are listed in Tables 1 through 3.

Both clinoptilolite samples initially were exchanged with NH_4^+ by shaking approximately equal volumes of the finely ground clinoptilolites (<100 mesh) and 0.5 M NH_4Cl solution overnight and then washing them several times with distilled water to remove excess salt (supernatant was checked with $AgNO_3$ solution to insure all chlorides were removed). Sorghum-sudangrass [Sorghum bicolor (L.) Moench-S. sudanese (Piper) Stapf, 'NB280S'] was chosen for experimentation because it can be cropped several times.

Two experiments were conducted. The first experiment used NH_4-exchanged Wyoming clinoptilolite together with either Weld loam soil (Aridic Argiustoll) or Red Feather loamy sand (Lithic Cryoboralf) and North Carolina phosphate rock. Clinoptilolite/P-rock weight ratios of 0, 1.5, 3.0, 4.5, 6.0, and 7.5 were used in this study. Two rates of phosphate rock (170 and 340 mg P/kg) were used in factorial combination with each clinoptilolite/P-rock ratio, resulting in zeolite application rates of 0 to 52 Mg/ha. The complete data set, with further details on experimental design, are available in Barbarick *et al.* (1988, 1990).

The second experiment used NH_4-saturated South Dakota clinoptilolite, the Keith soil (Typic Argiustoll), and phosphate rock from Idaho (Mill Shale). Clinoptilolite/phosphate rock weight ratios of 0, 2, 4, and 6 were used at P-rates of 100, 200, 300, and 400 mg P/kg soil. Supplemental N in the form of solid urea (46-0-0) was added to provide at least 100 mg N/kg soil. Each clinoptilolite/P-rock mixture, ground to <100 mesh, was added to 2.5 kg of soil and mixed for about 1 min in an inverting mixer. The mixture was placed in 10-cm by 38-cm long PVC pipe having a plastic plate glued to the bottom to prevent drainage of soil solution. Urea was added to all pots after the first and second plant harvests to provide an overall total of 300 mg N/kg soil to all treatments. The complete data set, with further details on statistical methods and experimental design, are available in Barbarick *et al.* (1991).

Soils in both sets of experiments were air-dried and crushed to pass a 4-mm screen. Pots were arranged in randomized blocks (three replications for each treatment) and were placed under Na-vapor lamps to provide light 14 hr/d at a photon flux density of about 750 μmol/m^2/s. Six sorghum-sudangrass seeds were planted in each pot. The plants were thinned to leave the two largest in each pot after 21 d of growth. During the growing period, the pots were watered to field capacity by weight (0.31 g H_2O/g soil) at least once per week. The top growth (10 cm above soil surface) was harvested at 3- to 6-wk intervals to obtain 5 or 6 cuttings. The plants were rinsed in distilled water, dried at 70°C for 24 hr, and weighed to determine dry matter yield. Plant material was ground in a Wiley mill to pass a 20-mesh stainless steel screen. Each sample was digested with HNO_3 (Havlin and Soltanpour, 1980). The digest was analyzed on a Jarrel-Ash Model 975 Plasma Atomcorp Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for the chemical elements. The soil pH and ammonium bicarbonate diethylenetriaminepentaacetic acid (AB-DTPA)-extractable elements (Workman *et al.*, 1988) were determined after the final cutting.

Weighted-average element concentrations in the plant tissues were calculated as follows: the arithmetic average of elemental concentrations in the plant tissue for the three replicates for each treatment was multiplied by the arithmetic average yield for each treatment for each cutting and then summed

Table 1. Some initial properties of some of the experimental materials.

Property	IDPR	WYCp	SDCp	Keith soil	Weld soil	Red Feather
pH (paste)	6.9	8.7	7.7	6.5	5.5	5.3
EC (ds/m)	0.9	1.0	12.5	0.4	0.9	0.2
SAR	1.7	na	10.4	<1	na	na
$CaCO_3$ (g/kg)	16	nd	present	na	na	na
Total N (g/kg)	2	na	6	na	na	na
NH_4-N (mg/kg)	14	na	5520	na	na	na
NO_3-N (mg/kg)	4	na	11	14	20	11
Organics (g/kg)	na	na	na	na	13	26
CEC (meq/100 g)	nd	140	110	19	23.3	13.4

IDPR = Mill Shale phosphate rock from Idaho; WYCp = clinoptilolite from Wyoming; SDCp = clinoptilolite from South Dakota; na = not analyzed; nd = not detectable; CEC = cation-exchange capacity.

Table 2. AB-DTPA extractable elements (mg/kg) for experimental materials.

Element	IDPR	NCPR	WYCp	SDCp	Keith soil	Weld soil	R.F. soil
P	49	25	4	63	9	11	3
K	80	76	140	2712	887	493	72
Zn	55.0	18.4	3.3	3.0	1.0	1.0	1.5
Fe	89	24	21	15	11	3	77
Mn	6	1	12	12	3	4	17
Cu	5.5	0.7	3.4	5.0	1.5	1.2	0.7
Pb	1.0	<0.01	4.2	6.4	na	na	na
Cd	14.00	1.74	0.02	nd	na	na	na
Ni	5.70	1.74	0.15	0.10	na	na	na
Mo	0.30	1.26	0.01	nd	na	na	na
B	0.2	na	na	0.1	na	na	na
Cr	1.20	0.39	0.05	0.20	na	na	na
Sr	1.00	1.79	5.41	27.00	na	na	na
Ba	1.00	<0.01	34.20	23.00	na	na	na
Al	0.6	na	na	1.8	na	na	na
Ti	0.5	na	na	0.9	na	na	na

NCPR = North Carolina phosphate rock; R.F. soil = Red Feather soil; For other symbols, see Table 1.

over all cuttings to give the total uptake for a given element for a given P-rate. Total uptake was divided by total yield to find the weighted-average concentration of an element for a particular treatment at a particular P-rate. Generally, the regression equation for the arithmetic average of the mean concentrations over all P-rates is reported in the figures.

Table 3. Total elemental content for some experimental materials.

Element	IDPR	NCPR	WYCp	SDCp
		(g/kg)		
Ca	212	352	203	9
Mg	2.0	3.0	3.9	6.0
Na	2.0	7.4	32.0	5.0
K	4.0	na	14.5	12.0
P	99	133	na	2
Al	1.2	2.1	61.9	3.6
Fe	1.1	4.9	11.5	1.4
Mn	nd	na	0.0	0.3
Ti	0.3	na	0.6	0.9
		(mg/kg)		
Cu	263	na	na	214
Zn	660	na	na	65
Ni	96	na	na	7
Mo	9.5	na	na	5.6
Cd	88	na	na	2
Cr	1340	na	na	7
Sr	742	na	na	430
B	47	na	na	nd
Ba	171	na	na	1320
Pb	40	na	na	48
V	705	na	na	18
As	25	na	na	2
Se	5.6	na	na	nd

Symbols as in Table 1.

RESULTS AND DISCUSSION

Yield

Yields of dry matter increased by about 65% with increasing clinoptilolite/P-rock ratio for the Weld soil (340 P-rate) and by about 7% for the Keith soil (average over all P-rates, Figure 1). A decrease in yield for the Red Feather soil had a significant quadratic effect for the 340 P-rate at large clinoptilolite/P-rock ratios (Figure 1), and may be attributed to a sequestering of K by clinoptilolite, as will be discussed below.

Soil pH

Uptake of nutrients by plants can be influenced strongly by soil pH. If a system has a small acid-buffering capacity, the presence of NH_4-saturated clinoptilolite can lower soil pH by nitrification of NH_4^+ ions released from clinoptilolite or by plant uptake of NH_4^+ in exchange for H^+. This effect is shown for the Weld and Red Feather soils in Figure 2, in which soil pH, measured after the sixth cutting, decreased by about two pH units with increasing clinoptilolite/phosphate rock ratio. In contrast, the pH of the Keith soil systems was insensitive to the clinoptilolite/phosphate rock ratio, probably because the clinoptilolite used in these systems (SDCp) contained calcite, which would buffer system pH.

Possible effects of clinoptilolite on nutrient uptake by sudangrass must be seen in both pH systems in order to separate pH effects from clinoptilolite effects. If the addition of clinoptilolite in these experiments had no measurable effect on the uptake of a nutrient, the results may mean either that the clinoptilolite was ineffective in aiding in the release of this nutrient to plants or that sufficient amounts of nutrient were available for plant uptake prior to addition of clinoptilolite.

Phosphorus

Analysis of sudangrass grown in the Weld and in the Red Feather soils indicated a correlation between P-concentration and the clinoptilolite/P-rock ratio (Figure 3). Barbarick *et al.* (1990) postulated that both lowered soil pH and the presence of clinoptilolite increased P-availability for these soils. Lai and Eberl (1986) and Barbarick *et al.* (1990) demonstrated that clinoptilolite saturated with monovalent cations was effective in releasing phosphate from phosphate rock by exchang-

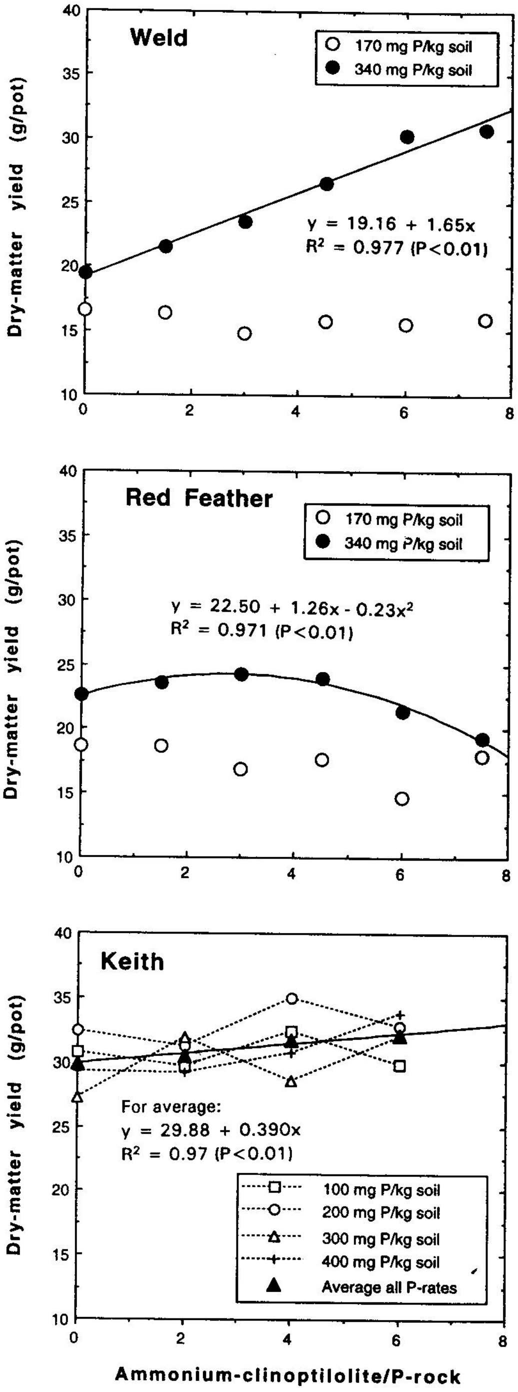

Figure 1. Relation between mean yields of dry matter and NH_4-clinoptilolite/phosphate rock ratio for the Weld and Red Feather soils (6 cuttings) for the Keith soil (5 cuttings).

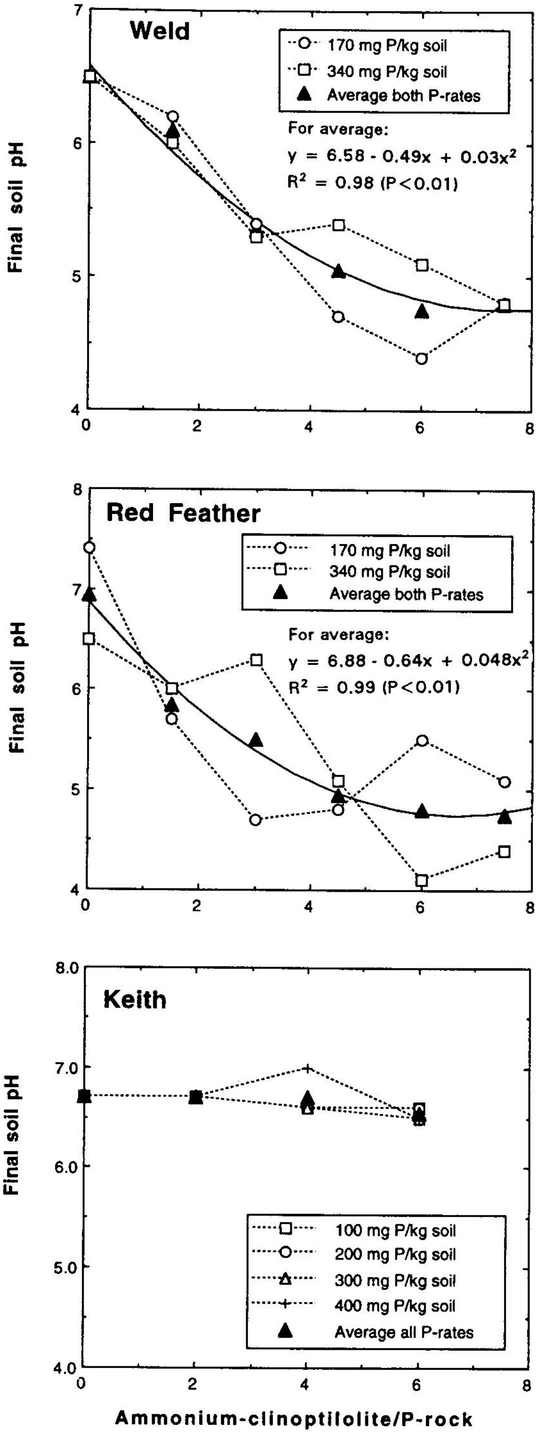

Figure 2. Change in soil pH with NH_4-clinoptilolite/phosphate rock ratio for three soils. Soil pH measurements were taken for the Weld and Red Feather soils after 6 cuttings, and for the Keith soil after 5 cuttings.

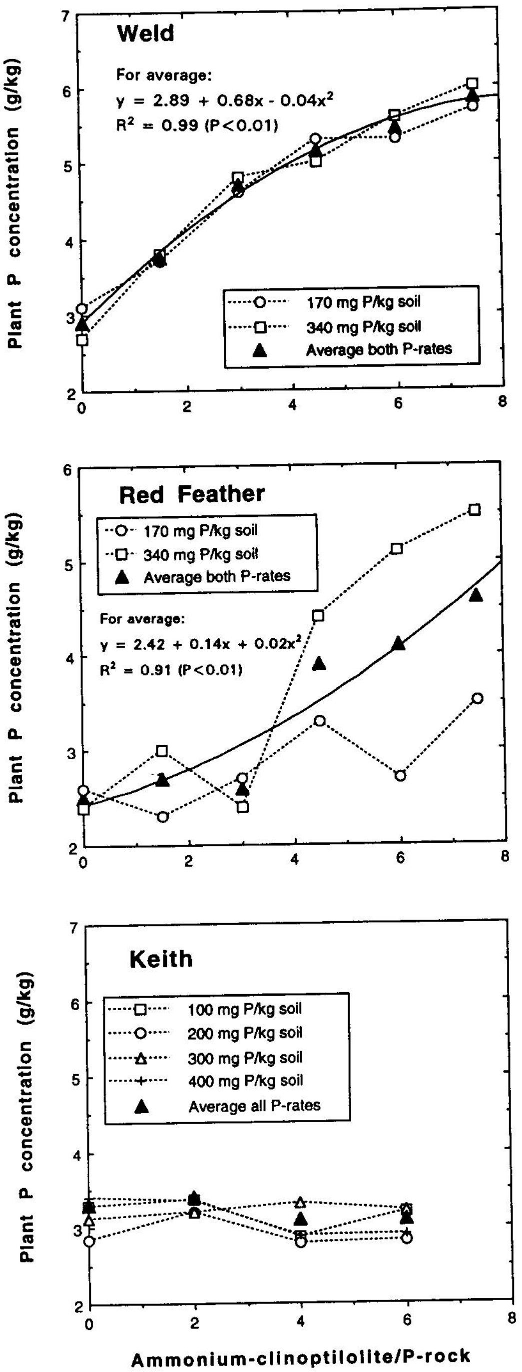

Figure 3. Relation between P concentration in plant matter and the NH_4-clinoptilolite/ phosphate rock ratio for the Weld and Red Feather soils (6 cuttings), and the Keith soil (5 cuttings).

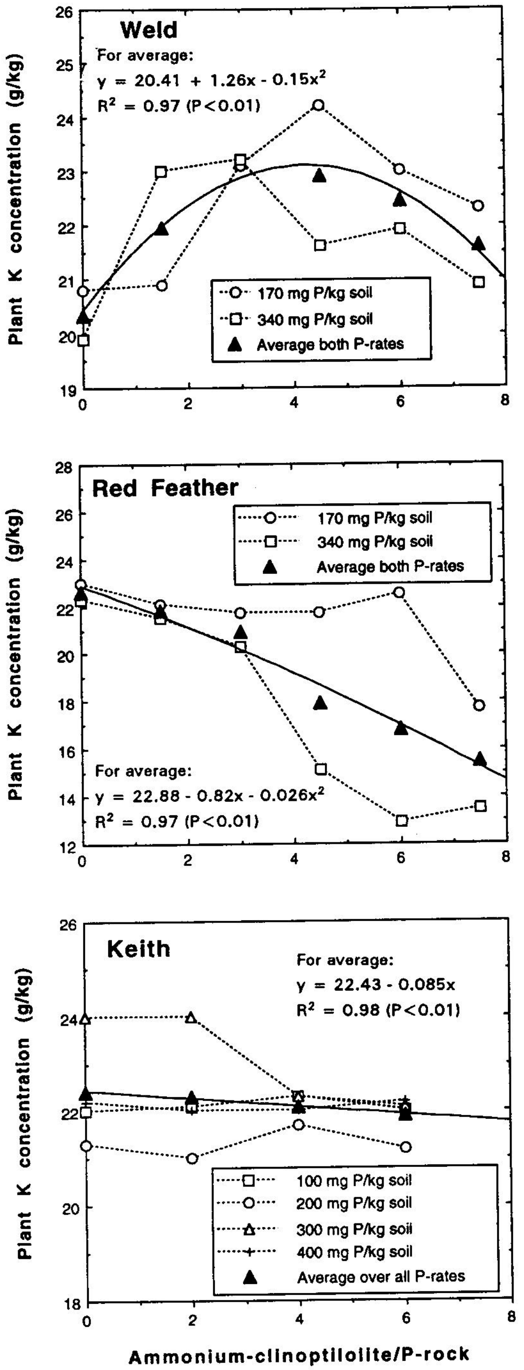

Figure 4. Relation between K concentration in plant material and the NH_4-clinoptilolite/ phosphate rock ratio for the Weld and Red Feather soils (6 cuttings) and for the Keith soil (5 cuttings).

ing Ca^{2+} into zeolite exchange sites. No such correlation was seen for experiments using the Keith soil. Lack of P-response for the Keith soil system may be related to the presence of calcite, anhydrite, and gypsum in the NH_4-clinoptilolite (SDCp) used in the Keith soil experiments. Because these Ca-minerals are more soluble than apatite in P-rock, Ca^{2+} for exchange in the zeolite came mostly from their dissolution, thereby releasing predominately carbonate and sulfate rather than phosphate to the soil solution (Lai and Eberl, 1986).

Potassium

As Barbarick *et al.* (1990) reported, results for sudangrass grown in the K-deficient Red Feather soil indicated a significant negative correlation between K-concentration in the plant material and the clinoptilolite/phosphate rock ratio, whereas results for the Weld soil, a soil not deficient in K, indicated a significant decrease in plant K concentrations at NH_4-clinoptilolite/P-rock ratios greater than 4.0 (Figure 4). Results for the Keith soil also indicated a small but significant decrease in K-concentration with increasing clinoptilolite/phosphate rock ratio (Figure 4), even though the soil is high in available K (Table 2). Marcille-Kerslake (1991) found a similar relation between K uptake and clinoptilolite/phosphate rock ratio for soybeans grown on an acid soil. These patterns in K-uptake may be due to the strong preference of clinoptilolite for K^+. This preference is strong enough that NH_4-saturated clinoptilolite is able to deprive plants of K, particularly in K-deficient soils, and thereby lead to a decrease in yields (Barbarick *et al.*, 1990). When K-saturated (rather than NH_4-saturated) clinoptilolite was used in similar experiments, the clinoptilolite/phosphate rock ratio either had no effect on plant K-concentrations or showed a positive correlation (unpublished data). The latter experiment indicates that, whereas NH_4-saturated clinoptilolite may inhibit K-uptake by sudangrass, K-saturated clinoptilolite may serve as a K-source.

Copper and manganese

Increasing clinoptilolite/P-rock ratios significantly increased Cu concentrations in sorghum-sudangrass for the Weld and Keith soils (Figure 5). Copper concentrations correlated negatively (plots not shown) to the final soil pH for the Weld ($R^2 = 0.94$) and Red Feather soils ($R^2 = 0.87$), but no correlation was found between Cu concentration and final soil pH for the Keith soil. A pattern similar to that for Cu was found for plant Mn concentrations (Figure 6) for all three soils. The Mn concentrations correlated negatively to final soil pH (plots not shown) for the Weld ($R^2 = 0.96$) and Red Feather ($R^2 = 0.92$) soils, but no correlation was found between Mn concentration and final soil pH for the Keith soil. Therefore, for the Weld and Red Feather soils, both the decrease in soil pH and the direct action of the clinoptilolite could have increased plant Cu and Mn concentrations. For the Keith soil, however, pH did not influence plant Cu and Mn, indicating that the changes observed were the direct result of the clinoptilolite addition, possibly through an ion-exchange mechanism.

Zinc, magnesium, calcium, iron, and cadmium

The concentrations of Zn, Mg, and Ca tended to increase in the plant material with increasing clinoptilolite/phosphate rock ratio for the Weld or Red Feather soils (Figure 7), but showed no regular tendency for the Keith soil (Barbarick *et al.*, 1991). Therefore, their increase in concentration may have resulted from a lowering of soil pH for the former two soils (Figure 2), rather than from some specific effect that can be attributed to the action of the clinoptilolite. Plant Fe

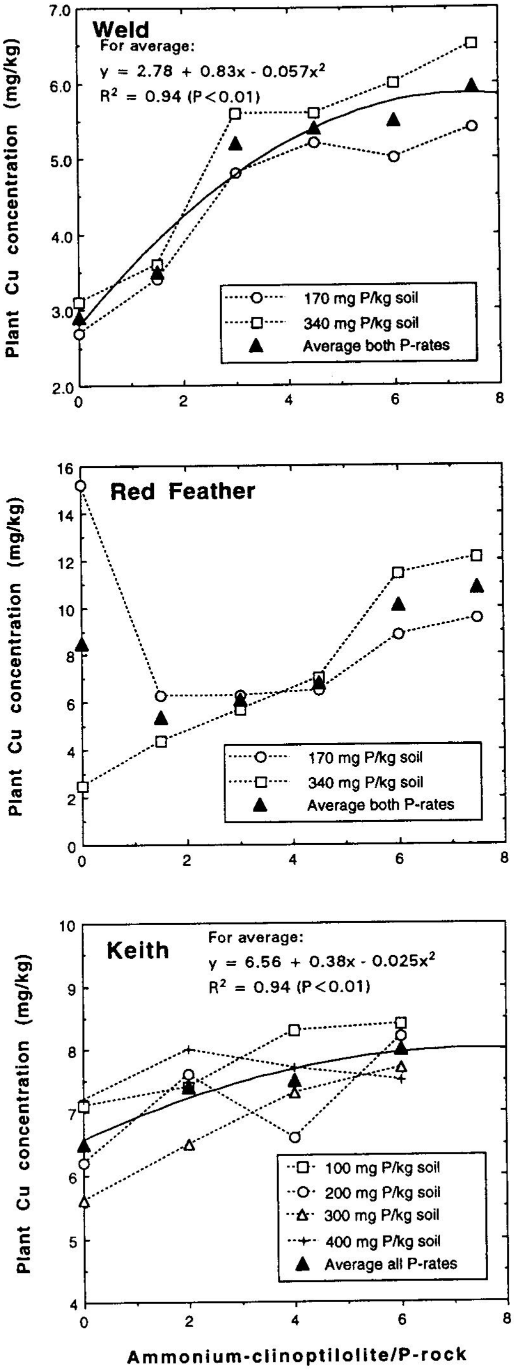

Figure 5. Relation between Cu concentration in plant material and the NH_4-clinoptilolite/phosphate rock ratio for the Weld and Red Feather soils (6 cuttings) and the Keith soil (5 cuttings).

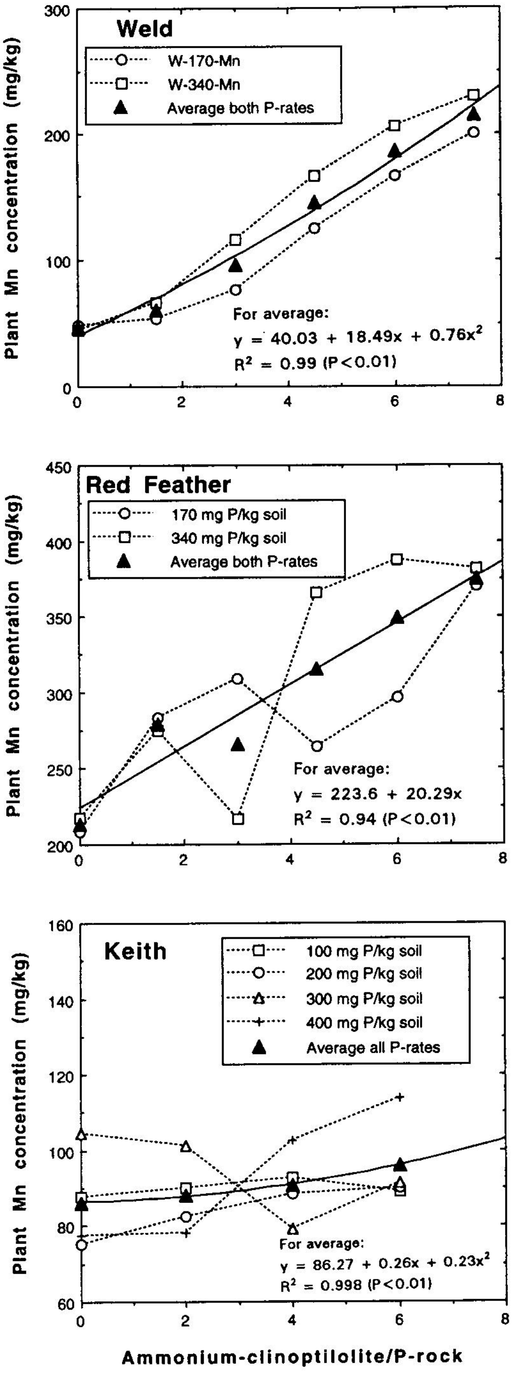

Figure 6. Relation between Mn concentration in plant material and the NH_4-clinoptilolite/phosphate rock ratio for the Weld and Red Feather soils (6 cuttings) and the Keith soil (5 cuttings).

concentrations were not significantly affected by clinoptilolite/P-rock ratio (Barbarick *et al.*, 1991). Cadmium concentrations (maximum concentration = 3.6 mg/kg, but generally <2.0 mg/kg) were measured only for experiments with Keith soil; no correlation between Cd concentrations and clinoptilolite/phosphate rock ratios was noted (Barbarick *et al.*, 1991).

AB-DTPA extractable elements

If NH_4-clinoptilolite took up elements by cation exchange from sparingly soluble minerals in the soil system during growth experiments (thereby making cations more available for absorption by sudangrass), a relation should exist between AB-DTPA extractable elements and the amount of clinoptilolite in the system. Such tendencies were found for all elements measured at constant pH in the Keith soil (P, K, Cd, Mn, Zn, Fe, and Cu; Barbarick *et al.*, 1991). The highest correlations were found for K, Cu, Mn, and P (Figure 8). The strong correlation between extractable K and clinoptilolite/P-rock ratio (Figure 8A) was to be expected if the clinoptilolite did indeed exchange K from the soil solution, as was discussed above. Copper had a greater AB-DTPA extractability after the last cutting than was predicted from Table 2 from a simple mixture of soil, clinoptilolite, and Mill Shale P-rock (Figure 8B); thus a chemical reaction, such as dissolution by ion-exchange, probably occurred to make this element more available. Like Cu, Mn also was more available after the final cutting than was predicted from Table 2 from a simple mixture, even if no clinoptilolite was present (NH_4-clinoptilolite/P-rock = 0, Figure 8C). Evidently, Mn was mobilized during the experiment, perhaps by Eh changes related to wetting and drying of the soil. Potassium and P (Figures 8A and 8D, respectively) were less available than was predicted from Table 3 from a simple mixture, probably because growing plants absorbed these elements faster than they were released by the soil system.

Data for the AB-DTPA extractability of the Weld and Red Feather soils are not presented because of the complicating effect of changing soil pH (Figure 2). A simple mixture of North Carolina phosphate rock and NH_4-clinoptilolite (WYCp), without soil and without a pH change, however, showed how clinoptilolite can affect AB-DTPA extractability (Figure 9). In this figure, the concentration of extractable elements is plotted as a function of the fraction of clinoptilolite in the mixture [clinoptilolite/(clinoptilolite + phosphate rock)]. A ratio of zero means the solid in the system contained no clinoptilolite and was only P-rock; a ratio of 1.0 indicates only clinoptilolite in the system; intermediate values indicate that the systems contained a mixture of clinoptilolite and P-rock. Reactions between clinoptilolite and P-rock released Cu in greater amounts than predicted from Table 2 for a simple mechanical mixture of the clinoptilolite and P-rock end members (Figure 9A). Enhanced release was also exhibited for K, Cd, and Pb (Barbarick *et al.*, 1991). The release of Mn was near the theoretical line expected from a mixture (Figure 9B); therefore little reaction involving this element took place between the clinoptilolite and phosphate rock. The enhanced availability of Mn to plants in a similar system containing soil (Figure 6) may have resulted from reaction between the clinoptilolite and the soil. Other elements for which availability was predicted approximately from simple mixtures of the North Carolina phosphate rock and the clinoptilolite, or that showed a slight decrease in availability, were Ni, Cr, and Mo (Barbarick *et al.*, 1991). Interestingly, the solubility of Ba decreased markedly with increasing P-rock (Figure 9C). This pattern may have been related to the formation of an insoluble Ba phosphate by a reaction between Ba from the clinoptilolite and phosphate from the mineral

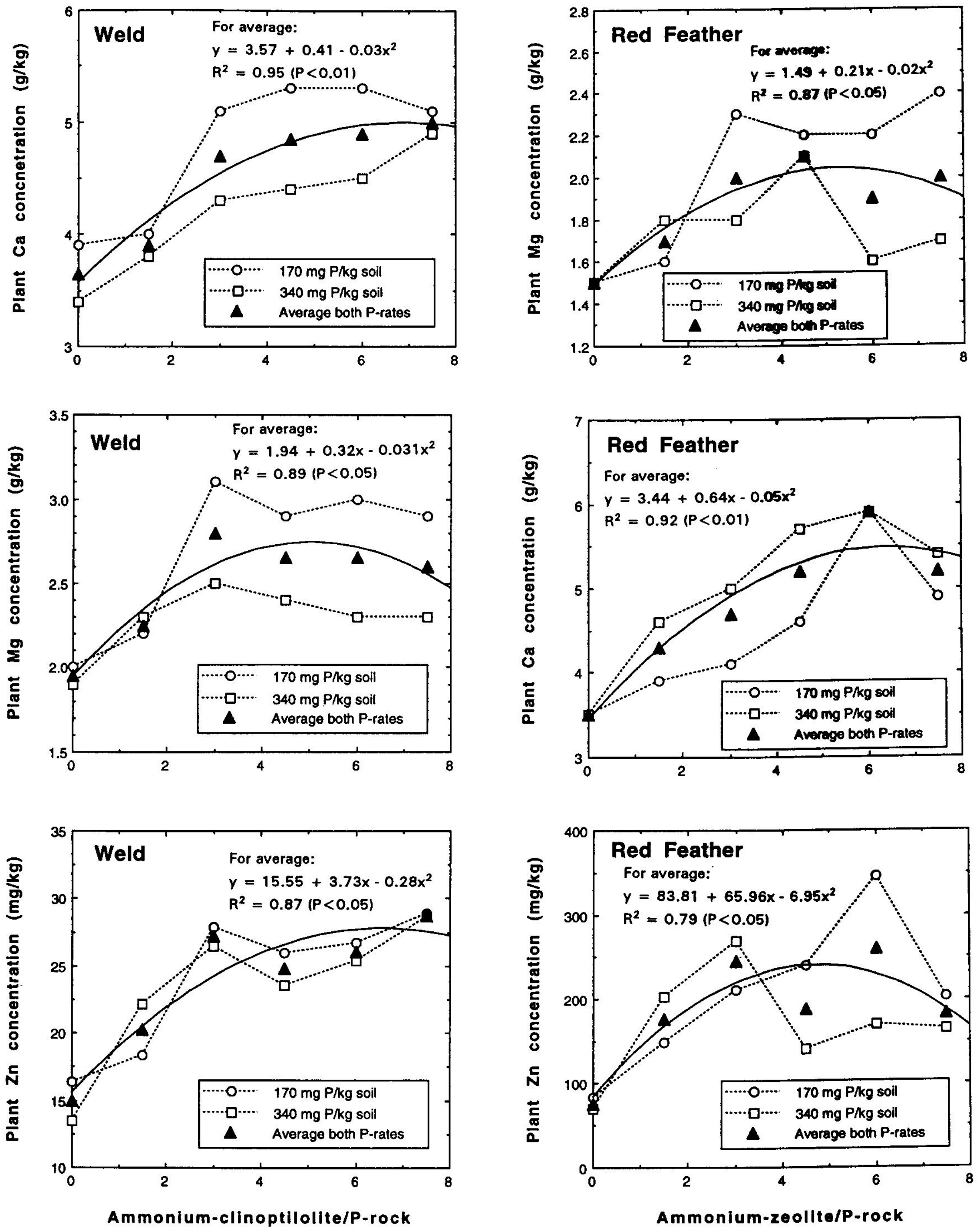

Figure 7. Relation between concentrations of Zn, Mg, and Ca in plant material, and the clinoptilolite/phosphate rock ratio for the Weld and Red Feather soils (6 cuttings).

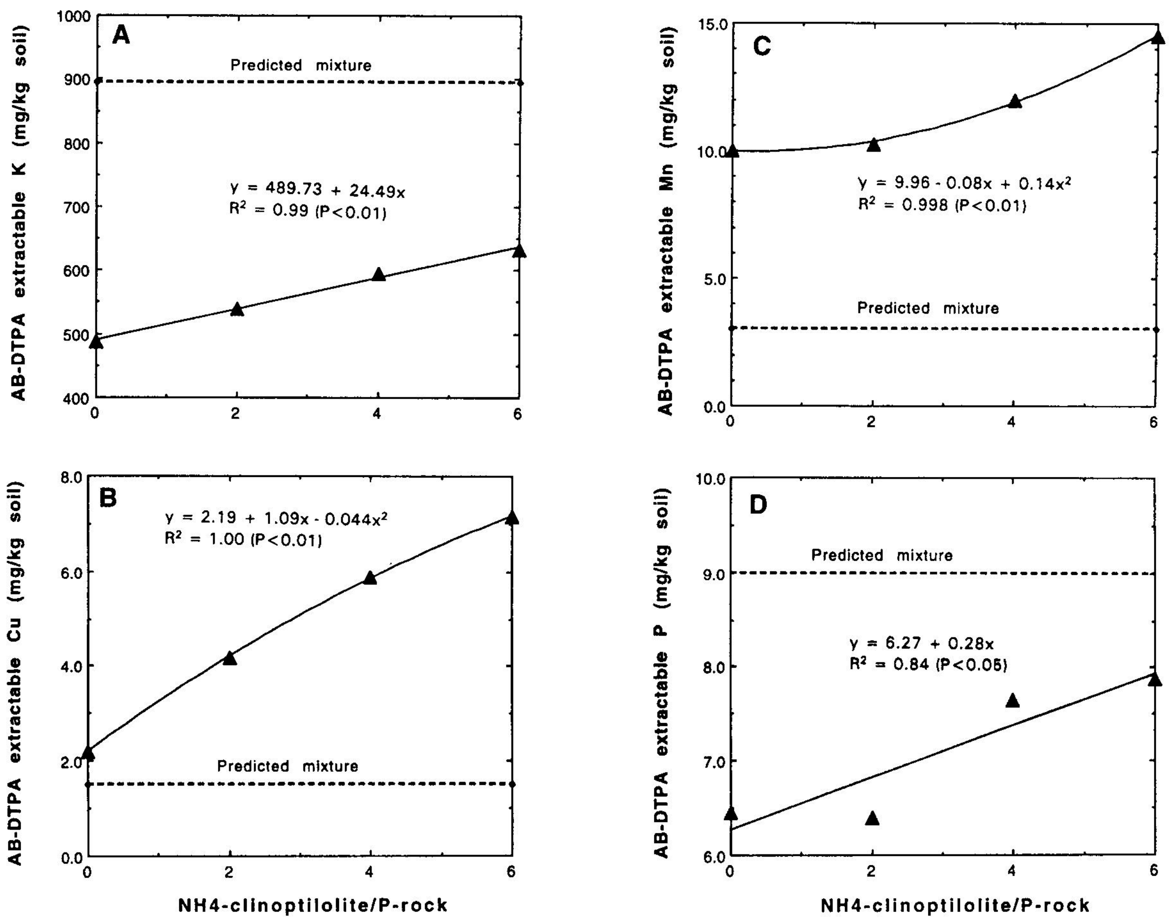

Figure 8. Relation between AB-DTPA-extractable K (A), Cu (B), Mn (C), and P (D) and the NH_4-clinoptilolite/phosphate rock ratio for the Keith soil after 5 cuttings. Dotted line is amount of extractable elements expected from simple mixtures of soil, zeolite and phosphate rock (see Table 2).

apatite in the P-rock, thereby indicating another type of reaction that can occur in these chemically complex systems. The availability of Sr was variable with increasing clinoptilolite content (Barbarick *et al.*, 1991).

SUMMARY AND CONCLUSIONS

The present plant-growth and chemical-extraction experiments show that NH_4-clinoptilolite can mobilize some nutrients and trace elements (particularly Cu and Mn), thereby rendering them more available for uptake by plants. At least two mechanisms appear to be involved in this mobilization: (1) a lowering of soil pH caused by nitrification of NH_4^+ ions from the clinoptilolite; and (2) enhanced availability of nutrients in exchange sites, from which they were made available by dissolution by ion-exchange from sparingly soluble minerals. The experiments further indicate that NH_4-clinoptilolite can enhance yields and, also, that it may limit yields by depriving plants of K, thereby suggesting that K-saturated clinoptilolite should be used in soils that are K-deficient. In general, the experiments support the use of NH_4-clinoptilolites in agriculture as effective soil amendments.

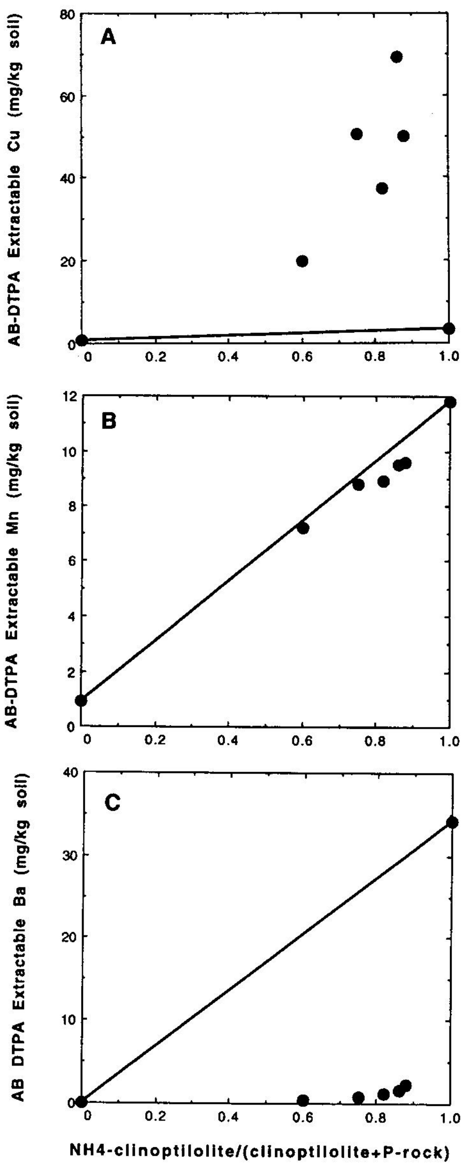

Figure 9. Relation between AB-DTPA extractable Cu (A), Mn (B), and Ba (C) and NH_4-clinoptilolite/(clinoptilolite + phosphate rock) ratio for extractions using North Carolina phosphate rock and NH_4-clinoptilolite (WYCp), without soil. Solid line indicates concentration of extractable elements expected for mixture of end-member zeolite (ratio = 0) and end-member phosphate rock (ratio = 1).

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