Chapter VIII

Using Zeolites in Agriculture

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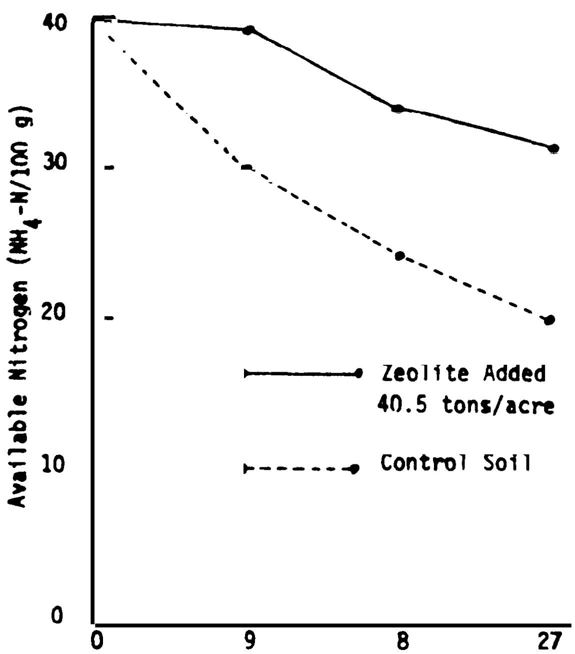
APPLICATIONS IN AGRONOMY

Fertilizer and Soil Amendments

Based on their high ion-exchange capacity and water retentivity, natural zeolites have been used extensively in Japan as amendments for sandy soils, and small tonnages have been exported to Taiwan for this purpose (52,31), The pronounced selectivity of clinoptilolite for large cations, such as ammonium and potassium, has also been exploited in the preparation of chemical fertilizers that improve the nutrient-retention ability of the soils by promoting a slower release of these elements for uptake by plants, In rice fields, where nitrogen efficiencies of less than 50 percent are not uncommon, Minato (52) reported a 63 percent improvement in the amount of available nitrogen in a highly permeable paddy soil 4 weeks after about 40 tons/acre zeolite had been added along with standard fertilizer (figure 7), Turner (84), on the other hand, noted little change in the vitrification of added ammonia when clinoptilolite was mixed with a Texas clay soil, although the overall ion-exchange capacity of the soil was increased. He attributed these conflicting results to the fact that the Japanese soils contained much less clay, thereby accounting for their inherent low ion-exchange capacity and fast-draining properties. The addition of zeolite, therefore, resulted in a marked improvement in the soil's ammonium retentivity. These conclusions support those of Hsu, et al. (31), who found an increase in the effect of zeolite additions to soil when the clay content of the soil decreased. Although additions of both montmorillonite and mordenite increase the cation-exchange capacity of upland soils, the greater stability of the zeolite to weathering allowed this increase to be retained for a much longer period of time than in the clay-enriched soils (22),

Figure 7.—Change of Soil Nitrogen of Paddy Soil With Time

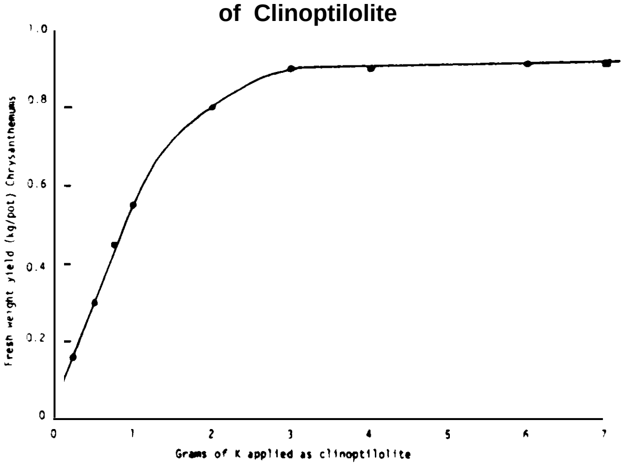


Vertical water seepage in soil = 1.35 cm/day (Yamagata Prefecture Board of Agriculture and Forestry, 1966; reported in Minato, 1968.)

Using clinoptilolite tuff as a soil conditioner, the Agricultural Improvement Section of the Yamagata Prefectural Government, Japan, reported significant increases in the yields of wheat (13 to 15 percent), eggplant (19 to 55 percent), apples (13 to 38 percent), and carrots (63 percent) when from 4 to 8 tons of zeolite was added per acre (83). Small, but significant improvements in the dry-weight yields of sorghum in greenhouse experiments using a sandy loam were noted when 0.5 to 3.0 tons of clinoptilolite per acre was added along with normal fertilizer (47). However, little improvement was found when raising corn under similar conditions. Hershey, et al. (29), showed that clinoptilolite added to a potting medium for chrysanthemums did not behave like a soluble K source, but was very similar to a slow-release fertilizer, The same fresh-weight yield was achieved with a one-time addition of clinoptilolite as with a daily irrigation of Hoagland's solution, containing 238 ppm K, for three months (total of 7 g potassium added), with no apparent detrimental effect on the plants (figure 8).

Experiments by Great Western Sugar Co. in Longmont, CO, using clinoptilolite as a soil amendment, resulted in a significant increase

Figure 8.—Yield of Chrysanthemums as a Function of Potassium Level Supplied by One-Time Additions of Clinoptilolite



Solid square represents total of 7 g of potassium supplied by daily irrigation with Hoaglan's solution containing 234 ppm K. Total time of experiment was 3 months. (From Hershey, et al., 1980.)

in total-matter production of sugar beets, although "high" levels of zeolite were required (1). The details of these experiments are considered proprietary and have not been released. The addition of ammonium-exchanged clinoptilolite in greenhouse experiments with radishes resulted in a 59- and 53-percent increase in root weight in medium and light clay soils, respectively (45). The nitrogen uptake by plant tops also increased with the zeolite treatment compared with an ammonium sulfate control (table 2). These authors also found that natural clinoptilolite added to soil in conjunction with urea reduced the growth suppression that normally occurs when urea is added alone (table 3). The presence of zeolites also resulted in less NO_3-N being leached from the soil (figure 9).

Both zeolite treatments apparently made considerably more ammonium available to the plants, especially when clay-poor soils were employed. The authors suggested that ammonium-exchanged clinoptilolite acted as a slow-release fertilizer, whereas, natural clinoptilolite acted as a trap for ammonium that was produced by the decomposing urea, and thereby prevented both ammonium and nitrate toxicity by disrupting the bacterial vitrification process. The ammonium selectivity of zeolites was exploited by Varro (85) in the formulation of a fertilizer consisting of a 1:1 mixture of sewage sludge and zeolite, wherein the zeolite apparently controls the release of nitrogen from the organic components of the sludge.

Coupled with its valuable ion-exchange properties which allow a controlled release of micronutrients, such as iron, zinc, copper, man-

Table 2.—Growth Response of Radishes to Ammonium-Exchange Clinoptilolite[a]

Parameter	130/0 clay soil[b]		6°/0 clay soil[c]	
	NH_4-Clinoptilolite	$(NH_4)_2SO_4$	NH_4-Clinoptilolite	$(NH_4)_2SO_4$
Leaf area (cm^2/plant)	243	187	187	150
Plant weight (dry weight) (g)	1.84	1.12	1.40	1.1
Root weight (g)	13.5	8.5	11.6	7.6
N uptake (mg N/plant top)	57.2	35.9	42.6	38.9

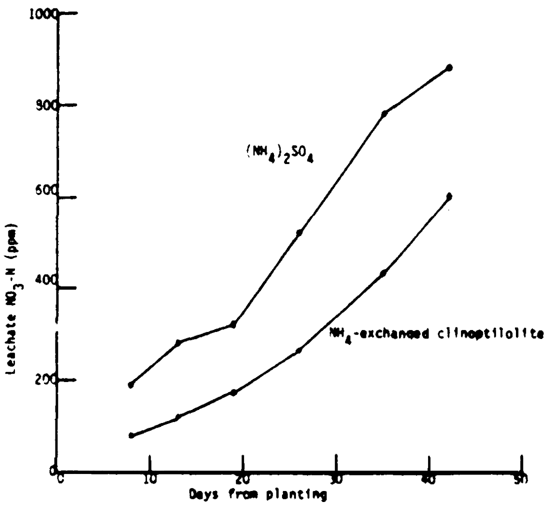
[a]Lewis, et al., 1980.
bPlants sampled 36 days after planting.
cLeached five times; plants sampled 34 days after planting.

Table 3.—Growth Response of Radishes to Natural Clinoptilolite Plus Urea[a]

Parameter	13% clay soil[b]		6°/0 clay soil[c]	
	Zeolite + Urea	Urea	Zeolite + Urea	Urea
Leaf area (cm^2/plant)	210	187	208	116
Plant weight (dry weight) (g)	1.59	1.23	1.38	0.71
Root weight (g)	13.8		12.4	6.3
N uptake (mg N/plant top)	45.5	38.6	44.4	18.9

[a]Lewis, et al., 1980.
bPlants sampled 36 days after planting.
cLeached five times; plants sampled 34 days after planting.

Figure 9.—Cumulative Leachate NO_3-N for Banded NH_4-Exchanged Clinoptilolite and Banded Ammonium Sulfate (Lewis, et al., 1980)



ganese, and cobalt, the ability of clinoptilolite to absorb excess moisture makes it an attractive addition to chemical fertilizers to prevent caking and hardening during storage and to animal feedstuffs to inhibit the development of mold (82). Spiridonova, et a]. (78), found that 0.5 percent clinoptilolite added to ammonium nitrate fertilizer decreased caking by 68 percent.

pesticides, Fungicides, Herbicides

Similar to their synthetic counterparts, the high adsorption capacities in the dehydrated state and the high ion-exchange capacities of many natural zeolites make them effective carriers of herbicides, fungicides, and pesticides. Clinoptilolite can be an excellent substrate for benzyl phosphorothioate to control stem blasting in rice (88). Using natural zeolites as a base, Hayashizaki and Tsuneji (26) found that clinoptilolite is more than twice as effective as a carrier of the herbicide benthiocarb in eliminating weeds in paddy fields as other commercial products. Torii (82) reported that more than 100 tons of zeolite were used in Japan in 1973 as carriers in agriculture. A Russian patent was issued to Aleshin, et a], (2), for grouting compound containing 3 to 5 percent clinoptilolite to control herbicide percolation from irrigation canals to ground waters.

Heavy Metal Traps

Not only do the ion-exchange properties of certain zeolites allow them to be used as carriers of nutrient elements in fertilizers, they can be exploited to trap undesirable metals and prevent their uptake into the food chain. Pulverized zeolites effectively reduced the transfer of fertilizer-added heavy metals, such as copper, cadmium, lead, and zinc, from soils to plants (18). The selectivity of clinoptilolite for such heavy metals has been noted by several workers (e. g., 74,19,1 1,76).

In view of the attempts being made by sanitary and agricultural engineers to add municipal and industrial sewage sludge to farm and forest soils, natural zeolites may play a major role in this area also. The nutrient content of such sludges is desirable, but the heavy metals present may accumulate to the point where they become toxic to plant life or to the animals or human beings that may eventual] y eat these plants. Cohen (12) reported median values of 31 ppm cadmium, 1,230 ppm copper, 830 ppm lead, and 2,780 ppm zinc for sludges produced in typical U.S. treatment plants. Zeolite additives to extract heavy metals may be a key to the safe use of sludge as fertilizer and help extend the life of sludge-disposal sites or of land subjected to the spray-irrigation processes now being developed for the disposal of chlorinated sewage. Similarly, Nishita and Haug (64) showed that the addition of clinoptilolite to soils contaminated with radioactive strontium (Sr^{90}) resulted in a marked decrease in the uptake of strontium by plants, an observation having enormous import in potential treatment of radioactive fallout that contaminates soils in several pacific atolls where nuclear testing has been carried out,