Journal of the Minnesota Academy of Science

Volume 47 | Number 2 Article 4

1981

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Acidification of Minnesota Soils by Nitrogen Fertilization and Acid Rain

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ABSTRACT — The effect of inputs of acidifying nitrogen fertilizer and acid rain on the pH of a typical Minnesota prairie agricultural soil was estimated. Experimental data from a long term continuous corn experiment at the Southwest Experiment Station near Lamberton were used to calculate the effects of nitrogen fertilizers. Acid rain effects were estimated using soil buffering data obtained in the experiment along with existing estimates of rainfall acidity. In a typical corn-soybean rotation, using 100 kg per ha of nitrogen additions to corn, a 0.25 unit pH drop is expected in about 38 years. The estimated acidity of the rainfall would cause the same pH drop in a minimum of 127 years.

Acidification of soils is a natural process in a climate such as that in Minnesota. Carbonic acid occurring naturally in rainfall plus organic acids produced by plants or microorganisms contribute to the weathering of soils and acidification (Jenny, 1941). Such acidification, however, is usually very slow and significant changes in soil pH may take centuries or longer. The introduction of industrial technology has resulted in increases in the rate of acidification of agricultural soil in Minnesota due to use of acid-forming nitrogen (N) fertilizers (ammonium sulfate, ammonium nitrate, ammonium phosphate, anhydrous ammonia and urea) plus the industrially produced acids in rainfall.

Ammonium in well-aerated soils is oxidized to nitrate by bacteria, producing two moles of H ion for every mole of N. The effects of this process in soils has been studied for more than 50 years (Pierre, 1928). In soils that are poorly buffered with respect to pH changes, the effects of heavy nitrogen fertilization can produce conditions of acidity that hinder agricultural production (Adams and Pearson, 1967). Addition of limestone is usually recommended to correct the problem.

The net effect of additions of acid-forming N fertilizers depends both on the buffer capacity of the soil and on the crop grown. The most extensive agricultural soils in Minnesota are highly-buffered prairie soils (Mollisols). On these soils, with the typical crops grown, acidification by N fertilization has not, as yet, resulted in the need for liming.

Acid rainfall may also contribute to the accelerated acidification of soils. In a 1980 paper Rauate suggested that acid rainfall may cause significant acidification of agricultural soils in Minnesota. No quantitative estimates of the effect were presented, however.

The objective of this paper is to present estimates of the relative effects of N fertilization and acid rain on acidification of agricultural soils in Minnesota using data from a long term N fertilization study and the existing data on rain acidity in Minnesota.

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Materials and Methods of Long-term Study

This study used a continuous corn experiment at the university's Southwest Experiment Station which at the time of sampling has been cropped for 19 consecutives seasons. The treatments, each replicated four times, were 0, 45, 90, and 180 kg N per ha per yr of urea or ammonium nitrate. An additional 16 kg per ha per yr was added with the starter fertilizer. The soil was predominantly a Nicollet clay loam (Aquic Hapludoll), a common agricultural soil of that region. Four 0-20 cm soil samples were taken in each plot. The pH of air dried sieved (2mm) soil was determined using 20g of soil and 20ml of distilled water (Peech, 1965). The quantity of the acidity on the cation exchange sites oG the soil (exchange acidity) was determined on a subset of 11 samples. The soil samples were equilibrated with a pH of 8.2 triethanolamine buffer containing 0.25M $BaCl_2$. After separation from the soil by filtration the solution was titrated to pH 4.5 (Peech, 1965). The quantity of exchangeable cations of strong bases (Ca^{2+}, Mg^{2+}, Na^+ and K^+) was determined on the same 11 samples by exchange with 1 M ammonium acetate and analysis by plasma emission spectroscopy.

Results Consistent with Earlier Study

The addition of urea and ammonium nitrate did result in significant decreases in pH (Table 1). There was no differenc between the acidifying effects of the two N sources. This is consistent with the findings of Pierre (1928). One half of the nitrogen in ammonium nitrate is already in the nitrate form. Since biological oxidation of one mole of NH_4 yields two moles of H ion, the net production of H ion from ammonium nitrate is one mole of H ion per mole of ammonium nitrate N. The hydrolysis of urea produces two NH_4 ions but the hydrolysis also produces one mole of CO_3. At the pH of the soils studied, most of the CO_3 combines with some of the H ions formed to produce H_2CO_3 (The pK_a for the first ionization of H_2CO_3 is 6.35). The net result is that for each mole of urea N added one mole of H ion is produced. The net reaction is:

$$4O_2 + (NH_2)_2CO_2 + 2H_2O \rightarrow H_2CO_3 + 2H^+ + 2NO_3$$

At soil solution pH values much greater than 6.0 the reaction is: $H_2CO_3 \rightarrow H^+ + HCO_3$. This results in a greater acidification per mole of N for urea compared with ammonium nitrate. Anhydrous ammonium, another commonly used fertilizer, also reacts in soil to yield one mole of acidity per mole of N according to the reaction:

$$2O_2 + NH_3 \rightarrow H^+ + NO_3 + H_2O$$

The 19 years of high N fertilization did not result in a decrease in pH sufficient to cause crop yield reduction. The Nicollet soil is well buffered with respect to pH decrease. One measure of the quantity of buffering is the quantity of exchangeable bases (Ca^{2+}, Mg^{2+}, K^+, Na^+). The soil samples in this study had exchangeable base contents of greater than 0.20 eq per g. This contrasts with the poorly buffered sandy soils of the forests of Northeastern Minnesota which can have exchangeable base contents of less than 0.02 eq per g. (unpublished data).

Table 1

Effect of ammonium nitrate and urea on soil pH after 19 years of continuous corn at the Southwest Experiment Station near Lamberton, Minnesota.

Nitrogen $kg\ ha^{-1}\ yr^{-1}$	pH
0	6.26
45	6.20
90	6.05
180	5.75
Significance (0.05)	0.39

The decrease in pH shown in Table 1 is too small to account for all of the acidity produced by the nitrogen fertilizers. The pH of an ion-exchange medium like soil is a function of the relative saturation of the exchanger with acidity. For soils with the same cation exchange capacities, the relationship between acidity in the soil and the pH can be seen by plotting exchange acidity vs. pH as in Figure 1. Since the exchange acidity is linearly correlated with pH (Figure 1) it is a straight forward procedure to calculate the H ion absorbed in the surface 0-20 cm of the soil. Nineteen years of 180 kgN per ha per yr. resulted in a decrease in pH of 0.5 units (Table 1) which is correlated with the absorption of 2,400 eq per ha per yr. of H ion. The acidity produced from the quantity of fertilizer added is 25,700 eq per ha per yr. Thus, soil acidification accounts for only 9 percent of the theoretical H ions produced. This is a much lesser effect than that observed by Jolly and Pierre (1977) in Iowa. At two different sites soil acidification accounted for 20 percent and 50 percent of the H ion produced by nitrogen fertilizers.

The remainder of the acidity from fertilizer cannot be accounted for by leaching from the surface soil. In a soil with a high cation exchange capacity, ammonium ions are retained in the surface soil until oxidized to nitrate and the resultant acidity is rapidly absorbed. Jolly and Pierre (1977) showed that most of the acidity that resulted from N fertilization reacts in the 0-15 cm depth with no acidification found below 30 cm. Three reasons were given by Jolly and Pierre (1977) for the less than theoretical recovery of H ions as soil acidity: (1) ammonium that is nitrified, then denitrified produces no net H ions, (2) for every mole of nitrate ions taken up by corn plants then removed in the grain, there is a neutralization of 0.95 moles of acidity by hydroxyl or bicarbonate released from the roots, (3) the incorporation of soil ammonium N in soil organic matter results in no net H ion production. An additional factor may be the slow neutralization of some of the acidity by reaction with primary minerals.

Crops vary in their mode of uptake of nitrogen such that the measured net acidification by N fertilization for corn may not apply to other crops. Unlike corn, which takes up most of its nitrate by exchange with bicarbonate from the roots, crops like buckwheat take up nitrate along with a charge balancing metallic cation (Pierre, et al. 1970). Buckwheat also releases significant quantities of acidity from the roots such that the acidification generated after N fertilization may be greater than that due to ammonium oxidation (Pierre, et al. 1970). Oats are quite similar to corn in their uptake of nitrogen (Pierre, et al. 1970).

Corn is not commonly grown continuously on one field, and 180 kg per ha per yr. is greater than the quantity of N used by most farmers. A very common rotation is corn with soybeans. In such a rotation corn may be planted on the average of one out of two years with a typical N fertilization of 100 kg per ha per yr. Soybeans are not generally fertilized with nitrogen. Assuming that the effect of N fertilizer is the same, per kilogram of N, regardless of the quantity applied, it can be estimated that corn-soybean rotation produces average acidification of the soil of about 670 eq per ha per yr. Then, 100 kg per ha applied on the average of every other year should, according to the data in Table 1, result in about unit 0.25 pH unit decrease after 38 years. Thus, on the prairie soils of Minnesota the acidification of soils due to N application in a normal farming operation will only be an important factor in soil pH reduction after many decades. In soils with lower buffering capacities acidification will be more rapid, but since soil pH is routinely monitored by all soil testing laboratories, most farmers will know when to expect problems with excess soil acidity. Agricultural limestone is readily available and is a fairly inexpensive input.

Rainfall is also a source of added acidity to soils, whether or not the rain contains anthropogenic inputs. Distilled water in equilibrium with atmospheric CO_2 has a pH of 5.6 and contains 10 micromoles per liter H_2CO_3 plus 2.5 micromoles per liter of free H ions and an equal concentration HCO_3. The effect on soils of rain containing CO_2 depends on the pH of the aqueous phase in the soil (soil solution). As stated before, the pK_a of reaction 2 is 6.35. If the soil solution pH = 6.35 (soil solution pH values are a few tenths less than the laboratory pH values reported in Table 1) then 7 microequivalents per liter of H ions would be added to the soil by rainfall. At greater soil pH values more acidity would be absorbed with the maximum being 25 microequivalents per liter for soils of pH = 7.5 or greater. At lower soil pH values less acidity would be absorbed by the soil. For soils with pH less than 5, carbon dioxide in rain has almost no acidifying effect. The mean annual rainfall at the Southwest Experiment Station averages 61 mm per year (Baker et al. 1967). The estimated contribution of CO_2 to the acidification of a soil with a soil solution pH = 6.35 is only 43 eq per ha per yr.

Rainfall in Minnesota does contain acidity in addition to CO_2. Measurements of rainfall in the vicinity of a coal-fired power plant in Sherburne County suggest that the rain

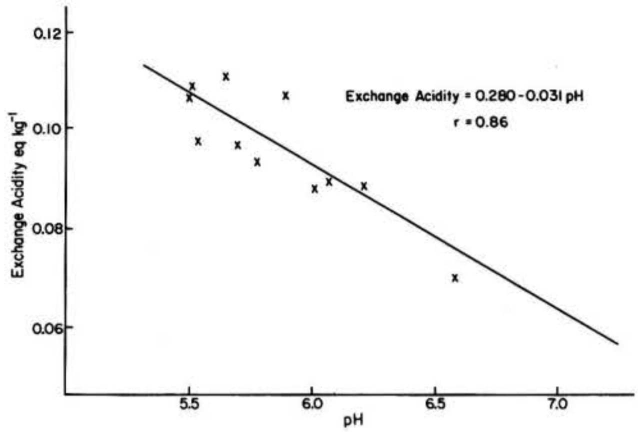

Figure 1.— The variation of pH with exchange acidity for a soil under continuous corn at the Southwest Experiment Station of the University of Minnesota. Variation in pH is caused by nitrogen fertilizer additions.

in central Minnesota has an average pH of 5.24 and contains an average of 13.5 microequivalents per liter of strong acid, as reported in a thesis by D.W. Gardner in 1980. The pH measurements of the rainfall at the southwest station suggest that the acidity of the rainfall there is similar to that in Sherburne County (Sagar, Krupa). Thus, the strong acid input can be estimated to be about 80 eq per ha per year. Rain at Lamberton likely also contains an equal quantity of non-volatile weak acid (personal communication). Adding the strong and weak acid components to the carbon dioxide component gives a total acidity that would have an impact on a soil with a soil solution pH of 6.35 of 200 eq per ha per yr. Assuming that neutralization by dissolution of primary minerals is not an important factor, the time for a 0.25 unit pH decrease would then be 127 years. It is likely, however, that mineral dissolution does contribute to slow neutralization of acidity inputs and that the pH decreases at a slower rate. Dust inputs that originate from the high pH soils in the Dakotas may also be a factor in maintaining soil pH.

Lower rainfall pH values have been measured at the Marcell experimental forest in Northeastern Minnesota (E.S. Verry, personal communication). The average pH of the rain and snow from July 1978 to July, 1979 was 4.3., which corresponds to a strong acid concentration of 50 microequivalents per liter. With this acidity the rainfall at the Southwest Experiment Station would contribute a quantity of acidity that is about 45 percent of the effective input by N fertilization. In an extreme case it might be assumed that with increased use of coal and decreased environmental controls, the acidity of the rainfall could approach that of the rainfall in the northeastern part of the United States. Recent measurements of the rainfall pH in the White Mountains of New Hampshire indicate that the average pH of the rains in that area is 4.08 (Cronan and Schofield, 1979) and that the rain contains 83 microequivalents per liter of acidity. Such low pH rains would contribute about 75 percent of the effective acidity from average N fertilization. Again, these estimates are likely high because of the neutralization of acidity by soil minerals.

Assessment of Acid Effect in State Soils

Ammonium-based nitrogen fertilizers make small but significant contributions to acidification in the highly-buffered prairie soils in Minnesota. The impact of acidity in rainfall is very much less than that of nitrogen fertilizers. Even assuming a much greater acid concentration in the rainfall than is currently found, nitrogen fertilization will continue to be a more important factor than acid rain on acidification of agricultural soils. The acidification of agricultural lands by N fertilization (or acid rains) is not of great economic consequence because lime is readily available. Direct damage of crops by acid rains that results in damage to leaves, inhibition of seed set, etc, may be of more importance..

Soil acidification is a greater potential problem in forests where liming is not practical. The potential for damaging effects is greatest in the northeastern portion of the state where the soils tend to be shallow and poorly buffered. More research is needed to determine the chemistry of rainfall in this region and the buffering characteristics of the soils.

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