LONG-TERM EFFECTS OF NITROGEN FERTILIZERS ON SOIL ACIDITY

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Abstract

Agroecosystems are domesticated ecosystems intermediate between natural ecosystems and fabricated ecosystems, and occupy nearly one-third of the land areas of the earth. Chemical perturbations as a result of human activity are particularly likely in agroecosystems because of the intensity of that activity, which include nutrient inputs intended to supplement native nutrient pools and to support greater biomass production and removal. At a long-term fertility trial at Arlington, WI, significant increases in exchangeable acidity were accompanied by decreases in cation exchange capacity (CEC), base saturation, and exchangeable Ca^{2+} and Mg^{2+} with application of ammoniacal N fertilizer. Similar trends have been noticed in other long-term fertility experiments.

Introduction

Agricultural activities have become the dominant ecological force over nearly one-third of the land areas of the earth. Agroecosystems differ from natural systems in the auxiliary energy sources to enhance productivity, leading to high fluxes of inputs and outputs, and in the external, goal-oriented control rather than internal control via subsystem feedback. Key to the modern agroecosystem is nutrient inputs intended to supplement native nutrient pools and to support greater biomass production and removal.

Almost none of the fertilizer materials in common usage are acidic, with the exception of sulfuric and phosphoric acids, which are a very small part of total fertilizer consumption in the U.S. (Meister, 1995). Many nutrient inputs, however, are themselves acid-forming, a fact recognized by the pioneering work of the soil scientist W.H. Pierre in 1933 and codified in the Association of Official Analytical Chemists (AOAC) Method 936.01 for determining the acid-forming or non-acid forming quality of fertilizers. [Of interest, W.H. Pierre was an alumnus of the Soils Department of the University of Wisconsin and had a long and distinguished career in the Department of Agronomy at Iowa State University.]

The most important acid-forming reaction for fertilizers is microbial oxidation of ammoniacal fertilizers, which may themselves be strong bases, by the following reactions:

1) $NH_3 + 2O_2 = H^+ + NO_3^- + H_2O$ (nitrification of ammonia)
2) $NH_4NO_3 + 2O_2 = 2H^+ + 2NO_3^- + H_2O$ (nitrification of ammoniacal nitrate)
3) $CO(NH_2)_2 + 4O_2 = 2H^+ + 2NO_3^- + H_2O + CO_2$ (hydrolysis of urea and nitrification of products)

The materials above are the most common synthetic N inputs to agroecosystems, either as single or mixed NPK fertilizers, and will oxidize to the equivalent of nitric acid under the well-drained, aerobic conditions of most dryland agricultural soils.

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Interestingly, the assimilation of nitrate-N and sulfate-S to their organic forms (N_{org} and S_{org}, respectively), both consume protons, i.e., generate alkalinity, by the reactions:

4) $R{\cdot}OH + NO_3^{-} + H^{+} = R{\cdot}NH_2 + 2O_2$
5) $R{\cdot}OH + SO_4^{2-} + 2\,H^{+} = R{\cdot}SH + 2O_2 + H_2O$

Although uptake and assimilation of nitrate and sulfate cause release of alkalinity from the root, some of the alkalinity generated is retained in the shoot as organic anions. Uptake and assimilation of nitrate by biota, both plants and microorganisms, is, from a redox and proton production point of view, opposite in direction and is the reverse of the process of nitrification, although separated temporally and spatially. The net reaction of ammoniacal N addition, nitrification, and subsequent nitrate uptake and assimilation by biota is acid/base neutral:

6) $[NH_4NO_3, 2NH_3, CO(NH_2)_2] + 2R{\cdot}OH = 2R{\cdot}NH_2 + H_2O\ (+2O_2)\ (+CO_2)$

From this perspective, soil acidification due to nitrification of N inputs is not directly caused by N inputs themselves but rather: i) N inputs greater than those assimilated by biota and stored either in biota or soil organic matter, and ii) incomplete return to soil of the alkalinity of organic anions.

Other acid/base reactions involving the N cycle are denitrification, which consumes protons, and ammonia volatilization, which generates one proton for each cation reacting. It should be noted that reactions causing soil acidification and alkalinization, other than nitrification and assimilation of N, are known (Van Breeman et al., 1983). The most significant of these are redox changes, most notably with metals such as Fe and Mn. However, these processes will generally be of small magnitude in well-drained, well-aerated soils compared to redox reactions of N added as fertilizers. In fact, the acid/base cycle of soils is intimately linked to the various components of the nitrogen cycle.

Effect of N fertilizer on pH and exchangeable acidity

A long-term experiment was laid out in 1962 by Dr. Lloyd A. Peterson at the Arlington Agricultural Research Station, located in south central Wisconsin, as a 4x4x4 NPK fertility trial. After 30 years of fertilizer additions, soil samples were analyzed and reported by Barak et al. (1997). Application of ammonium nitrate and urea N fertilizers at the long-term fertility trial at Arlington, Wisconsin, had caused soil acidification. Mean treatment values of pH ranged from 5.6 to 4.8 when measured in water and from 5.5 to 4.1 when measured in 1 M KCl for 0 to 150 lb N/acre annually treatments, respectively. Exchangeable acidity was strongly dependent upon the rate of N fertilization applied during the course of the 30-yr fertility trials but in a nonlinear manner. As much as 11% of the potential acidity added as ammoniacal N fertilizers remained in the top 20-cm as exchangeable acidity.

Changes in CEC

The increase in exchangeable acidity associated with N fertilization was accompanied by a decline in exchangeable base cations. The decline was most significant in exchangeable Ca^{2+}, which was 31% less in the 150 lb N/acre treatment than in the zero N control, and 36% less exchangeable Mg^{2+}. Statistically higher NH_4^+ was found in the 150 lb N/acre treatments, probably due to inhibition of nitrification in the more acidified plots, were noted (Liu et al., 1997).

Although exchangeable acidity increased most in those treatments in which exchangeable base cations were most depleted, the losses of exchangeable bases were not entirely offset by the addition of exchangeable acidity. The cation exchange capacity (CEC) of the long-term fertility plots, determined here as the sum of exchangeable base cations and exchangeable acidity and sometimes termed effective cation exchange capacity (ECEC), showed a strong negative correlation to the rate of N fertilizer.

The annual rate of CEC reduction in the Arlington experiments would below practical detection in a single-year field study, but can be detected only in long-term experiments. Indeed, several other long-term fertility plots have similar findings. For example, Blevins et al. (1977) found that a Kentucky silt loam (Paleudalf) planted to no-till and conventional tillage corn lost as much as 4.3 $cmol_c\ kg^{-1}$ exchangeable bases, and gained 1.0 $cmol_c\ kg^{-1}$ exchangeable acidity (and 0.7 $cmol_c\ kg^{-1}$ Mn) in the 0 to 5 cm soil depth, upon fertilization with 336 $kg\ N\ ha^{-1}\ yr^{-1}$ as NH_4NO_3 for 5 yr. The effective CEC was therefore reduced from 8.9 to 6.13 $cmol_c\ kg^{-1}$. At a fertilizer application rate of 168 $kg\ N\ ha^{-1}\ yr^{-1}$, CEC was reduced to 7.1 $cmol_c\ kg^{-1}$ over 5 yr. This is a 31% and 20% reduction in CEC, respectively, over 5 years, similar to the results obtained in this study.

In other work, Schwab et al. (1989) reported that for a Kansas silt loam (Pachic Argiustoll) in bromegrass with up to 224 $kg\ N\ ha^{-1}\ yr^{-1}$ for 40 yr, CEC measured by neutral salt ($CaCl_2$) decreased from 19.1 to 12.8 $cmol_c\ kg^{-1}$, compared to 0 N treatments. This is a 33% reduction in CEC over 40 years. The results of Bouman et al. (1995) show that a loamy Saskatchewan soil fertilized with up to 180 $kg\ N\ ha^{-1}\ yr^{-1}$ as urea for 9 yr lost 1.8 $cmol_c\ kg^{-1}$ exchangeable cations (bases and acids) in the 0 to 15 cm soil depth, compared to a 0 N control. The increase in exchangeable acidity and decline in cation exchange capacity due to application of acid-forming N fertilizers observed at Arlington, WI fits into the context of long-term fertility studies in the United States that demonstrate the same phenomena and similar rates of change.

The fate of the missing cation exchange capacity in these studies is not known based on any direct evidence for these soils. Many soils have mixed constant and variable charge components and CEC is pH-dependent, either due to a high content of free oxides of Fe, Al, and Si (typical of more weathered soils) or humic substances in the soil organic matter, which contain weakly acidic and very weakly acidic groups. A rough calculation of the expected amount of organic charge reduction can be made using values from the often-cited study of 60 Wisconsin soils by Helling et al. (1964) which apportioned pH-dependent CEC by statistical correlation into clay and organic matter fractions. For an average difference of 0.86 pH units in water between 0 and highest N treatments at the

Arlington, WI site, containing 1.6% C and 12% clay, the expected charge reduction is 0.71 $\mathrm{cmol_c\ kg^{-1}}$ attributable to 1.6% C and 0.64 $\mathrm{cmol_c\ kg^{-1}}$ attributable to 17% clay content. The total predicted pH-dependence of CEC is therefore 1.35 $\mathrm{cmol_c\ kg^{-1}}$, which is less than half of the observed drop in CEC between these N treatments.

Other possible explanations for CEC reductions due to prolong soil acidification include both mineral weathering, including weathering of the clay minerals themselves, and formation of nonexchangeable hydroxy-Al complexes in the interlayer region of the clays. Acid dissolution studies conducted under laboratory conditions have shown that the rate of dissolution of montmorillonite clay minerals is correlated to the degree of substitution in the clay lattice (Shainberg et al., 1974). Work by Laird et al. (1991a) has shown that the smectitic mineral in the fine clay fraction from a Minnesota soil (similar in parent material, climate, and vegetation to that at Arlington, WI) is a high-charge, Fe-rich montmorillonite with octahedral substitution in the soil clay exceeding that of the reference clays analyzed by Shainberg et al. (1974). This suggests that the soil clays at the Arlington site and elsewhere in the loess-derived soils of the Upper Midwest may be particularly prone to dissolution upon soil acidification. On the other hand, although all permanent negative charge in the phyllosilicate clays must be balanced with cations, not all of the cationic charge is necessary exchangeable. Formation of polynuclear hydroxy-Al interlayers in the 2:1 expansible clay minerals, either smectite or vermiculite, is associated with reduction in cation exchange capacity because the polynuclear hydroxy-Al material forms nonexchangeable "atolls" or "pillars" in the interlayer (Barnhisel and Bertsch, 1989). The process of formation of hydroxy-Al interlayers is a recognized form of soil weathering, often termed "chloritization" because of its tendency to form aluminous chlorite as an end product.

The extent of reversibility of the charge reduction associated with soil acidity at this site is unknown. Of the three explanations for CEC reduction, clay mineral dissolution and chloritization are almost certainly not reversible processes within a soil environment, and certainly not reversible with aglime amendment. If the cation exchange capacity reduction is due to variable charge considerations, then the reduction may be reversible by pH amelioration and base supply with agliming, although hysteresis cannot be ruled out. Without studying the mechanism of charge reduction in this soil and the extent of the reversibility of the phenomenon, the extent to which soils have been permanently altered by common agronomic fertilization practices will be unresolved.

Comparison of acid inputs due to fertilizer with acid deposition (“acid rain”)

At the Arlington, Wisconsin site, precipitation-weighted mean atmospheric deposition includes 2.61 kg $\mathrm{NH_4}$-N and 0.19 kg $\mathrm{H^+}$ (pH 4.63) $\mathrm{ha^{-1}\ yr^{-1}}$ (NADP, 1993), indicating an acid input of ~0.5 kmol $\mathrm{ha^{-1}\ yr^{-1}}$. Compared to agricultural inputs of 12 kmol $\mathrm{ha^{-1}\ yr^{-1}}$ in this study and cash-grain agriculture in this region, the rate of acidification due to fertilizer is underway at a rate that is ~25 times faster than the rate induced by acid rain. In such a case, the 30-year records established by long-term fertility plots might represent the effects of 750 years of soil weathering by acid rain and perhaps thousands of years by pristine rain on fertile soils of the Upper Midwest region.

Evidence of CEC reduction due to N inputs, and its potential for reversibility, might be more widespread if repeated measurements of CEC of agricultural fields were made routinely or well-documented soil samples were more commonly archived. Instead, CEC is rarely measured in evaluation of soil fertility, let alone measured repeatedly on the same field or plot. Instead, evidence for CEC reduction comes only from long-term fertility studies, as noted in the studies above, and then only by side-by-side comparison with controls receiving no fertilizer N input rather than comparison with archived soil samples.

Not only CEC may be altered due to acidification caused by nitrogen fertilizers. Both nitrification of ammonium and mineralization of organic matter may be affected, as well as generation of phytotoxic levels of Mn. Changes in CEC may affect the nutrient retention properties of soils, increasing the level of fertility management required for productivity. Even though changes in CEC have been detected, weathering of other soil components less easily quantified, such as minerals in the silt fraction, may be occurring at an accelerated rate due to acidity.

Conclusion

Total nitrogen consumption by American agriculture has more than quadrupled since the 1960s, when the long term plots at Arlington were established. Average nitrogen recovery in crops in the U.S. is estimated at 49 to 51%, indicating a large potential for residual soil acidity. AOAC Method 936.01 for determining the acid-forming nature of fertilizers–which recommends 1.8 lb $CaCO_3$ per lb of N supplied an anhydrous ammonia, urea, or ammonium nitrate–has been designated as “obsolete” by the AOAC due to apparent lack of usage, not because of inaccuracy, and has not been republished in recent compendia of AOAC Methods except by reference to earlier printings. At the same time, total application of acid from acid-forming fertilizers to noncalcareous cropland in the U.S. and acid deposition substantially exceeds the total amount of agricultural limestone equivalent required to neutralize that acidity.

References:

Barak P, B.O. Jobe, A.R. Krueger, L.A. Peterson, D.A. Laird. 1997. Effects of long-term soil acidification due to nitrogen inputs in Wisconsin. Plant and Soil 197:61-69.

Barnhisel R I and Bertsch P M 1989 Chlorites and hydroxy-interlayered vermiculite and smectites. *In* Minerals in Soil Environments. 2nd Ed. J B Dixon and S B Weed. pp. 729-788. Soil Sci. Soc. Am., Madison, WI.

Blevins R L, Thomas G W and Cornelius P L 1977 Influence of no-tillage and nitrogen fertilization on certain soil properties after 5 years of continuous corn. Agron. J. 69, 383-386.

Bouman O T, Curtin D, Campbell C A, Biederbeck V O and Ukrainetz H 1995 Soil acidification from long-term use of anhydrous ammonia and urea. Soil Sci. Soc. Am. J. 59, 1488-1494.

Laird D A, Barak P, Nater E A and Dowdy R H 1991a Chemistry of smectitic and illitic phases in interlayered soil smectite. Soil Sci. Soc. Am. J. 55, 1499-1504.

Liu Y, Laird D A and Barak P 1997 Dynamics of fixed and exchangeable NH_4 and K in soils under long-term fertility management. Soil Sci. Soc. Am. J. 61, 310-314.

Meister R T (Ed.) 1995 Farm chemicals handbook ‘95. Vol. 81. Meister Publ. Co., Willowby, OH.

National Atmospheric Deposition Program 1993 NADP/NTN Annual Data Summary. Precipitation Chemistry in the United States. 1992. National Resource Ecology Laboratory, Colorado State Univ., Fort Collins, CO. 480 pp.

Schwab A P, Ransom M D and Owensby C E 1989 Exchange properties of an argiustoll: effects of long-term ammonium nitrate fertilization. Soil Sci. Soc. Am. J. 53, 1412-1417.

Shainberg I, Low P F and Kafkafi U 1974 Electrochemistry of sodium-montmorillonite suspensions: I. Chemical stability of montmorillonite. Soil Sci. Soc. Am. Proc. 38, 751-756.

Van Breemen N, Mulder J and Driscoll C T 1983 Acidification and alkalinization of soils. Plant and Soil 75, 283-308.