

SOIL ACIDIFICATION

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Summary

The main causes of soil acidification are ammoniacal forms of N in fertilizers and legumes which are oxidized to nitric and other acids, crop removal of basic cations, and acid rain. The reactions responsible for the acidification are presented together with those involved in the soil's response to the acid inputs. Accessions of acidity by soils from these sources contribute to soil degradation as a result of reactions which liberate toxic levels of Al^{3+} and Mn^{2+} , reduce the cation exchange capacity and promote the loss of basic cations (mainly Ca^{2+} and Mg^{2+}) by leaching. While such acidification can take a toll on crop yield and impair biological N fixation, the deleterious effects can readily be neutralized by the application of lime under agronomic conditions. In addition, the alternative strategy of incorporating organic matter is evaluated. However, in natural ecosystems such as forests and native grasslands, lime applications are usually not feasible and consequently accessions of acidity from acid rain can cause serious declines in the productivity of such systems for which no solution is at hand. Severe acidification in all systems can lead to the transfer of acidity to subsoils and surface

waters which would then also be negatively impacted. Once subsoils have been acidified, amelioration by lime incorporation is impractical and expensive. Alternative strategies such as the use of surface applied gypsum and the transfer of alkalinity from top- to subsoils are discussed.

1. Introduction

Soil acidification occurs naturally as the result of the leaching of soils with rainfall that is slightly acidic due to the presence of dissolved CO₂. However, this discussion will be limited to acidification due to anthropogenic sources. Soil acidification only really causes serious degradation when the pH falls below 5.5 at which point toxic levels of Al (and sometimes Mn) begin to be found. The outward manifestations of soil acidification are reduced biomass and sometimes the transfer of soluble Al to water bodies thus threatening aquatic life.

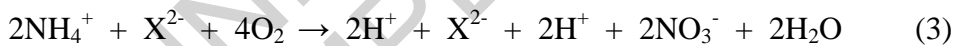
2. Sources of Acidity

2.1. Ammoniacal Fertilizers

Ammoniacal fertilizers, which are not in themselves acidic, do produce acid when the ammonium ion (NH₄⁺) is oxidized to nitrate (NO₃⁻) during nitrification which is favored in most soils. The amount of acidity formed depends on the type of fertilizer and on the fate of the NO₃⁻. Urea and anhydrous ammonia produce 1H⁺ per unit of ammoniacal N as follows:

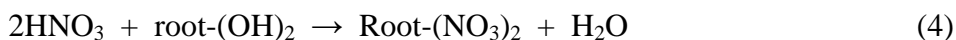


Ammonium salts produce 2H⁺ per unit of ammoniacal N as follows:

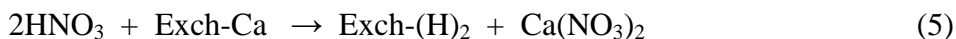


where X = SO₄²⁻, 2NO₃⁻, 2Cl⁻, 2H₂PO₄⁻, or HPO₄²⁻

These reactions reflect the maximum amount of acidity that can be produced during nitrification. The actual amount remaining in the soil depends on the fate of the NO₃⁻. If NO₃⁻ is taken up by the plant in the zone where it is formed, the acidity consumed is proportional to the amount of NO₃⁻ assimilated by the root as follows:

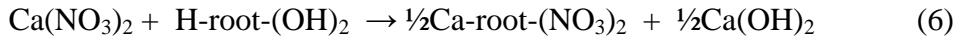


If NO₃⁻ is leached, the acidity remaining in the topsoil is proportional to the loss of basic cations in the form of Ca(NO₃)₂ as follows:

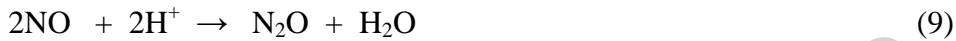
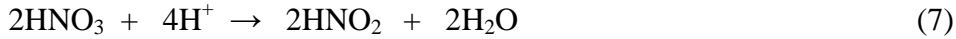


If Ca(NO₃)₂ is leached and roots are present in the subsoil, alkalinity may be produced

in the subsoil if roots take up more NO_3^- than Ca^{2+} which they usually do as follows:



If NO_3^- is denitrified, the amount of acidity consumed depends on the form in which the N is evolved to the atmosphere as illustrated below:



If all the NO_3^- is denitrified to N_2 , these reactions would consume 6H^+ per unit of N in the form of NO_3^- and thus denitrification has the potential to consume three times more acid than the maximum produced during nitrification.

Consequently it is very difficult to predict the extent of acidification which will result from a given fertilizer application. In some cases such as surface application of urea, ammonia (NH_3) may be volatilized from the soil surface and thus this quantity of N would not enter the nitrification reaction. However in most cases, application of ammoniacal fertilizers will result in the net acidification of soils and some examples of the actual extent of acidification caused by various ammoniacal fertilizers under field conditions are illustrated in Table 1. These data are in complete accord with the predictions made in Reactions (1)-(3) with $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ being the most and NH_2CONH_2 , NH_4NO_3 and NH_3 being the least acidifying per unit of ammoniacal N. Continued use of ammoniacal fertilizers causes the penetration of acidity to deeper layers as shown in the case of Soil 1 (Table 1).

| N source | Soil 1 | | | Soil 2 | | Soil 3 | | Soil 4 | |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | N kg/ha | pH ^a | pH ^b | N kg/ha | pH | N kg/ha | pH | N Kg/ha | pH |
| Control | 0 | 5.7 | 5.7 | 0 | 5.2 | 0 | 5.8 | 0 | 6.3 |
| $(\text{NH}_4)_2\text{SO}_4$ | 1636 | 4.0 | 4.6 | 1210 | 4.4 | 1560 | 5.00 | 336 | 4.3 |
| NH_4NO_3 | 1636 | 4.7 | 5.2 | 1210 | 5.0 | 1560 | 5.6 | 336 | 4.8 |
| NH_2CONH_2 | 1636 | 4.8 | 5.2 | 1210 | 5.0 | 1560 | 5.7 | 336 | 4.8 |
| $(\text{NH}_4)_2\text{HPO}_4$ | nd ^c | nd ^c | nd ^c | 1210 | 4.6 | 1560 | 5.2 | nd ^c | nd ^c |
| NH_3 | 981 | 5.1 | 5.1 | nd ^c | nd ^c | nd ^c | nd ^c | nd ^c | nd ^c |

^a 0-0.25 m depth

^b 0.25-0.40 m depth

^c nd = no data

Table 1. Effect of various cumulative rates of ammoniacal fertilizers on soil pH

2.2. Legumes

In a perfectly cycling system with no gains or losses of N by leaching and crop removal, no acidity is produced. However, in legume based production systems (both pure and mixed stands), acidity produced is equivalent to the excess of inorganic cations over anions taken up by the plants. In addition, product export and NO₃⁻ leaching contribute to the total H⁺ produced in the system. It is possible to predict the acidity produced in such systems using the following equation:

$$R_sH^+ + L_NH^+ = [(\Delta SN + XN)(\Sigma C_s - \Sigma A_s)/N_c] + \Sigma NO_{3L}^- \quad (11)$$

where R_sH⁺ = permanent acidity in the sward (mol H⁺/ha)

L_NH⁺ = acidity generated by NO₃⁻ leaching (mol H⁺/ha)

ΔSN = increase in soil, plant or animal N (kg/ha)

XN = quantity of N exported from the system (kg/ha)

ΣC_s = mean annual accumulated Ca²⁺+Mg²⁺+K⁺+Na⁺ in the sward (mol_c/kg)

ΣA_s = mean annual accumulated SO₄²⁻+H₂PO₄⁻+Cl⁻ in the sward (mol_c/kg)

N_c = N concentration in the sward (kg N/kg)

ΣNO_{3L}⁻ = cumulative amount of NO₃⁻ leached (mol_c/ha).

The results of such predictions, which are remarkably good, are presented in Table 2.

| Farm | Fixed N | ΔSN | XN | ΣNO _{3L} ⁻ | R _s H ⁺ | L _N H ⁺ | Total H ⁺ | CaCO ₃ requirement (kg/ha/yr) | |
|---------------|----------------------|-----|-----|--------------------------------|-------------------------------|-------------------------------|----------------------|--|-------|
| | (kg/ha/yr) | | | | (kmol/ha/yr) | | | Pred. | Meas. |
| Waikat(?)o | 267(94) ^b | 8 | 112 | 110 | 3.51 | 7.85 | 11.36 | 550 | 420 |
| Canterbury(?) | 180(95) | 20 | 30 | 100 | 1.46 | 7.14 | 8.60 | 430 | 420 |

See text for definition of symbols

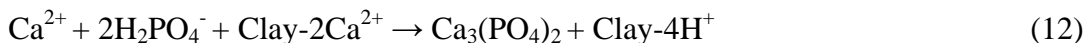
Values in brackets are the percentage contribution of fixed N in the system with the remainder from rainfall.

Source: Bolan N.S., Hedley M.J. and White R.E. (1991). Processes of soil acidification during nitrogen cycling with emphasis on legume based pastures. *Plant Soil Interactions at Low pH*, (ed. Wright R.J. et al.) 169-179. Boca Raton, FL: CRC Press.

Table 2. Quantities of protons on two New Zealand farms on which most of the N requirements were contributed by legumes and the predicted and measured lime requirements

2.3. Other Fertilizers

When phosphatic fertilizers such as superphosphate are applied to soil, less soluble compounds precipitate or the phosphate is adsorbed resulting in the production of acidity:



Because only small amounts of P relative to N are added to soils, this source contributes relatively little to the overall acidification of a soil.

2.4. Fossil Fuel Emissions

When fossil fuels, which contain N and S are combusted, oxidation results in the formation of nitric oxide (NO), nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) which in the presence of light and moisture are converted to HNO₃ and H₂SO₄ and when they fall to earth constitute acid rain. In industrialized areas, acid rain can contribute between 1 and 6 kmol H⁺/ha/yr. By comparison with agricultural inputs of acidity (fertilizers and legumes), the worst cases of acid rain would contribute only 7 to 25% as much acidity to soils. However, major problems arise when such rain falls on natural ecosystems such as forests and natural grasslands where there is little chance of neutralizing the acid inputs. In such cases, the rate of degradation is crucially dependent on the amount of acid rain and the buffer capacity of the soil. Measurements of the effects of acid rain on soil acidity have been contradictory with some workers finding no declines in soil pH over extended periods whereas others have found substantial declines in pH. Part of the problem associated with these contradictory observations seems to stem from the lack of suitable control plots. In Scandinavia, the results of long-term studies of soil acidification over 20 to 50 years showed that the magnitude of the decline in pH decreases with decreasing initial soil pH. At initial pH values > 5 and < 3.5, the declines in pH were of the order of 1 to 1.5 and about 0.3 pH units, respectively. In Germany, many forest profiles have reached the Al or even Fe buffering zones as a result of atmospheric acid inputs. Nevertheless, there is general agreement that acid inputs result in the loss of basic cations and solubilization of toxic elements such as Al³⁺ and Mn²⁺, which in addition to impairing tree growth, reduce biological activity and nutrient cycling. Any acidification of arable soils due to acid precipitation is easily corrected by applications of limestone.

2.5. Removal of Basic Cations in Harvests and Crop Residues

When plant components (grain, fruit, residues, etc) are removed from a given field, they carry with them substantial quantities of basic cations such as Ca²⁺, Mg²⁺ and K⁺. These removals represent a loss of alkalinity from the system which is the same as a gain in acidity. Estimates of the magnitude of the acidification caused by crop nutrient removal are presented in Table 3. These data are for the complete removal of the crop. If only a portion is removed, the amounts would be correspondingly less.

| Crop | Basic cations in contained in crop (kmol/ha) | | | Total cations (kmol/ha) | CaCO ₃ Equivalent (t/ha) | Yield (t/ha) |
|--------------|--|-------|------|-------------------------|-------------------------------------|--------------|
| | K | Ca | Mg | | | |
| Alfalfa | 5.36 | 8.96 | 2.33 | 16.65 | 0.33 | 12 |
| Corn | 4.65 | 3.24 | 4.67 | 12.56 | 0.25 | 9.4 |
| Sorghum | 5.24 | 24.92 | 3.36 | 33.52 | 0.67 | 9 |
| Potato | 7.39 | 2.8 | 1.4 | 11.59 | 0.23 | 27 |
| Bermudagrass | 4.29 | 1.84 | 2.05 | 8.19 | 0.16 | 14 |
| Wheat | 2.62 | 0.89 | 1.68 | 5.19 | 0.10 | 4 |

| | | | | | | |
|---------|------|------|------|-------|------|---|
| Tobacco | 4.52 | 5.88 | 2.24 | 12.64 | 0.25 | 3 |
|---------|------|------|------|-------|------|---|

Table 3. Estimates of basic cation removal in crops and equivalents in terms of pure calcium carbonate

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Biographical Sketch

Dr. Sumner is Regent's Professor of Environmental Soil Science in the Department of Crop and Soil Sciences at the University of Georgia. He received a B.Sc. Agric. Degree (1954) in Chemistry and Soil Science and an M.Sc. Agric. (*Cum laude*) (1957) degree in Soil Physics from the University of Natal, South Africa, and a D.Phil. Degree (1961) in Soil Chemistry from the University of Oxford, UK. The University of Natal awarded him an honorary Doctor of Science degree in recognition of his career contributions to Soil Science. He is a fellow of both the American Society of Agronomy and the Soil Science Society of America. He holds the Agronomic Research Award and the Werner L. Nelson Award for Diagnosis of Yield Limiting Factors from the American Society of America. He was awarded a Doctor of Science Degree (*Honoris causa*) by the University of Natal, South Africa for his contributions to soil science. He is the holder of many other awards and distinctions including the Sir Frederick McMasters Visiting Fellowship (Australia) and the DW Brooks Faculty Award for Excellence in Research and International Agriculture (University of Georgia). He has presented addresses at more than 100 universities and research institutions on his research findings. He has served as Associate Editor for the *Soil Science Society of America Journal* and is a member of Editorial Boards of many other journals. His published works cover a wide range of topics including subsoil acidity, the agricultural uses of gypsum, the beneficial use of anthropogenic wastes and transport of nutrients in soils. A widely respected author, Dr. Sumner's works include *Soil Acidity* (Springer-Verlag, 1991), *Soil Crusting: Chemical and Physical Processes* (Lewis Publishers, 1992) and *Sodic Soils: Distribution, Properties, Management and Environmental Consequences* (Oxford University Press, 1998). He has authored or co-authored over 220 refereed journal papers and has contributed chapters to over 30 books.