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J. E. Rechcigl *; D. L. Sparks *
* Department of Plant Science, University of Delaware, Newark, Delaware

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EFFECT OF ACID RAIN ON THE SOIL ENVIRONMENT: A REVIEW

KEY WORDS: acid rain, aluminum, soil acidity

J. E. Rechcigl and D. L. Sparks
Department of Plant Science
University of Delaware
Newark, Delaware, 19717-1303.

ABSTRACT

This paper reviews the literature on acid rain, with emphasis on soils and leaching of soil elements. Several questions still exist concerning the effects of atmospheric acid deposition on soils: 1) does acid rain enhance mobilization of harmful heavy metals in soils which could leach into the groundwater; 2) does acid rain accelerate the kinetics of weathering of primary minerals and of secondary clay minerals in soils which would release large quantities of Al, Fe, and Si into the groundwater making it unfit for human consumption; and 3) do the beneficial effects of acid deposition outweigh the negative effects or vice versa? Literature pertaining to these questions is addressed in this review.
INTRODUCTION

Acid rain is one of the most significant environmental problems facing the world today\(^2\). It is becoming a significant obstacle to agricultural production as well as an impediment to the development of our forest and water resources\(^3\). It could seriously hinder the prospects of using coal as an energy source.

According to the estimates of the U. S. Environmental Protection Agency (EPA), the U. S. annually discharges nearly \(5.0 \times 10^{16}\) kg of \(\text{SO}_2\) and \(\text{N}_2\text{O}\) into the atmosphere as a result of the combustion of large amounts of fossil fuels. These gases are converted into acids which return to earth as components in rain or snow. The resulting "acid rain" may produce serious ecological effects on the environment\(^3\).

The seriousness and the widespread nature of the problem can be shown by simply listing the components of the ecosystem which can be affected by acid rain. It affects soils, plants, and the spread of plant pathogens; alters lake and river biota; accelerates material corrosion and deterioration of buildings; and finally, it affects human health\(^4\).

While voluminous amounts of data have appeared on the effects of acid rain on plants and animals, few reports on acid effects on soils have appeared, yet there is increasing concern about the effect of acid rain on soils.

The Acid Rain Phenomenon

The first published reports on acid rain precipitation appeared in the mid-1950's\(^5\), and the
problem has been well documented for Scandinavia \(^4\) and eastern North America\(^6,7\). The phenomenon is apparently not limited to northern climates, as there have been reports of acid rain in the southern and western parts of the United States\(^8,9,10\).

In both Norway and Sweden, declines in rainfall pH of 0.02-0.05 units per year have been recorded over recent decades\(^11,12\). In the northwestern U. S., 4% of the mountain lakes had pHs below 5.0 in 1940, whereas in the 1970's 51% were less than 5.0 \(^13\), the average decline being 0.05 units per year\(^12\).

According to EPA, hundreds of lakes in North America and Scandinavia have become so acidic that they can no longer support fish life\(^3\). More than 90 lakes in the Adirondack mountains in New York State are fishless because acidic conditions have inhibited reproduction\(^3\). Other areas of the U. S., such as northern Minnesota may also be vulnerable\(^3\).

Data from New York State and New England indicate acid rain is 60-70% \(H_2SO_4\) and 30-40% \(HNO_3\) \(^14\). These strong acids are thought to stem primarily from gaseous man-made pollutants such as S and \(N_2O\).

Acid rain contains a variety of heavy metals, particularly in the vicinity of metal smelters\(^15\). In lake sediments in the northeastern U. S., Ag, Au, Cr, Ni, Pb, Sb, and V have been found in increased quantities\(^16,17\).

Acid rain also contains a number of plant nutrients such as Ca, K, S, N \(^18\) and possibly P \(^15\). These may be transferred from land to water. In addition, it can also carry a wide range of organic molecules, including alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters, and fatty acid
ethyl esters, as well as a variety of commonly used industrial chemicals such as polychlorinated biphenyls.

**Sensitivity of Soils to Acid Rain**

Acid rain may bring about variable effects on soil, depending on the type and properties of the soil involved. The sensitivity of soil to acid rain is determined by four key parameters: 1) the total buffering capacity or the cation exchange capacity (CEC) provided primarily by clay and soil organic matter contents; 2) the base saturation of that exchange capacity, which can be estimated by the pH of the soil; 3) the management system imposed on the soil, whether it is cultivated and fertilized or renewed by flooding or other additions; and, 4) the presence or absence of carbonates in the soil profile.

A change in soil pH is most closely linked to its CEC. If the soil has a low CEC (<12 cmol (+)/kg), then the acid precipitation is likely to reduce the soil and the groundwater pH quickly. However, a soil with a high CEC (>12 cmol (+)/kg) is strongly buffered against changes in pH or leachate composition. The original pH of the soil also has a great bearing on the sensitivity of the soil to acid precipitation. According to McFee, acid soils with a pH near that of acid rain will not change in pH rapidly in response to acid inputs. Also, soils with a low CEC have a low reserve of plant nutrients (such as Ca, Mg, or K) and slight losses may be significant to their productivity.

McFee categorized soil areas into three major classes based on their sensitivity to acidity:
1) **Nonsensitive Areas (NS)** include a) all soils that are calcareous (i.e., contain free carbonates) in the surface layer (within 0.25m); b) all soils that are subject to frequent flooding (it is assumed that the renewal effects of fresh deposition would negate acid precipitation effects); and, c) all soils with an average CEC greater than 15.4 cmol (+)/kg in the top 0.25m.

2) **Slightly Sensitive Areas (SS)** include areas not in class 1a or 1b that have average CEC in the range of 15.4 to 6.2 cmol(+)/kg in the top 0.25m.

3) **Sensitive Areas (S)** include those areas not in class 1a or 1b that have average CEC less than 6.2 cmol(+)/kg in the top 0.25m.

Using the above criteria, McFee constructed maps of soil sensitive regions for the eastern U. S., including New York, North Carolina, West Virginia, Pennsylvania and Indiana\(^{23}\).

In similar fashion, Klopatek et al.\(^{26}\) prepared computer maps of soil pH, CEC, base saturation, and base content for the eastern U. S., using county-level data. By overlaying these maps with computer maps of the H ion loading, maps of acid-sensitive and insensitive soils were made. Of 1572 counties in the eastern U. S., 117 were classified as being acid-sensitive.

**Sensitivity of Soil Orders of the U. S. Soil Classification System To Acid Rain (after Petersen\(^{27}\))**
Petersen\textsuperscript{27} has classified the major soil orders as to their sensitivity to acid rain. This classification is given below.

**Mollisols** - are soils containing a high percentage of humus. They have not been subject to much leaching and often contain CaCO\textsubscript{3}. Their base saturation percentage and buffer capacity are usually fairly high, and thus they are not likely to be sensitive to acid precipitation.

**Oxisols** - are red soils usually containing a considerable percentage of clay which contains a large amount of Fe and Al oxides and kaolinite, and they have a low CEC. The humus content is also very low and the soil itself is highly weathered and leached. Therefore, they have a low pH and low buffering capacity. This soil is sensitive to acid precipitation.

**Vertisols** - are black heavy clay soils having a high degree of base saturation. The clay consists mainly of smectite which has a high CEC. Thus, these soils most likely would not be affected by acid rain.

**Histosols** - consist predominantly of organic matter and have a high buffering capacity. These soils are already very acid and any additional acidity would not change the pH very much.

**Alfisols and Ultisols** - have a high clay content, and the Alfisols have a high base saturation percentage. Alfisols are not likely to be very sensitive to acidity, whereas Ultisols, with their low base saturation percentage, may be susceptible to acidity.

**Inceptisols** - with a high clay content, they are rather insensitive to acid rain, whereas the sandy Inceptisols are rather susceptible to acidity.
Entisols - have a high degree of variation, and thus a generalization as to their sensitivity cannot be made.

Soil Acidification Process

While acid rain may be a major source of soil acidity, it is not the only source. Acidification of soils is a natural process occurring continuously. There are several natural sources of soil acidity. One such source is $H_2CO_3$. Water in equilibrium with the 0.03% $CO_2$ in the atmosphere may have a pH of 5.6. When this water comes into contact with soil, the equilibrium with $CO_2$ no longer exists. This is because topsoils may have a higher concentration of $CO_2$ due to the respiration of soil flora and fauna. The $CO_2$ concentration between air and soil will occasionally vary as much as 0.01% by lowering the pH from 5.6 to 4.9. A pH of 5 is thus quite common in subsurface soils where $H_2CO_3$ is the only source of acidity.

Another source of soil acidity is nitrification. Plant residues and humus break down naturally in soils by heterotrophic microflora, producing $NH_4$ ions. Nitric acid is then formed when autotrophic bacteria oxidize $NH_4$ to $NO_3$. The reaction is as follows:

$$NH_4^+ + O_2 + H_2O \rightarrow 2H_3O^+ + NO_3^-$$

According to Bache, the theoretical amount of acid rain produced by the nitrification of 100 kg N/ha added
as NH₄ salt is 13 kg. This would be equivalent to 286 kg Ca, requiring 714 kg of CaCO₃ for neutralization.

Still another source of acidity could be organic acids formed from the decomposition of plant residues by microbes. These acids are particularly important in the formation of the podzolic soils²²,³⁰.

Finally, the oxidation of pyrite by exposure to the air may cause Fe₂(SO₄)₃ and H₂SO₄ to be formed which may produce acid SO₄²⁻.

Acidification of soils may cause the loss of the cations Ca, Mg, K, and Na. These losses are dependent on the soil type, pH and the amount of percolating water²² ³¹. A decrease in soil pH may also cause a reduction in CEC because the charges on the weak acid exchange sites are pH dependent and the acids become undissociated at a low pH. Thus, CEC is reduced as pH decreases²²,²³,³¹.

Degradation of primary and secondary soil minerals may result following large inputs of mineral acids into acid soils²². Where soil is extremely acidified, the organic matter in the soil may be changed due to sulfonation of carboxylated benzene rings of "humic acids"³². These altered molecules will have strengthened capacities to bind metals and will prevent leaching into groundwater. This area has not yet been extensively investigated.

One of the extreme effects of acidification is the process of podzolization. Podzol soils are found in cool, humid regions of North America, Europe and Asia. They are usually confined to sandy parent materials when there is enough rainfall to result in severe leaching. Podzol soils must have an acid reaction and usually have a low content of plant nutrients as well
as a low content of Al, Fe, and organic matter in the surface. This is the result of leaching. The Al, Fe, and organic matter are immobilized in the lower profile of the soil. The solubility of Al(OH)$_3$ is high enough to account for a significant equilibrium concentration of dissolved Al at pH 3.0-3.5. This range of pH is often found in the surface horizon of Podzols.

The capacity of soils to adsorb and retain anions increases with a decreasing pH and with the concentration of Fe- and Al-oxides and hydroxides. The polyvalent anions, such as PO$_4^{3-}$ and SO$_4^{2-}$, are bound by the hydrated Fe- and Al-oxides and hydroxides. This anion effect increases with the ratio of Al$_2$O$_3$ + Fe$_2$O$_3$ to SiO$_2$ in the soil.$^{30}$

**Effects of Acid Rain on Soil Exchange Properties**

Anion adsorption is a very important feature of soils in terms of regulating the leaching rates of anions other than bicarbonate. Bicarbonate leaching is regulated by soil CO$_2$ pressure and solution pH.

In general, the order of affinities of major anions to soil is: PO$_4^{3-}$ > SO$_4^{2-}$ > Cl$^-$ = NO$_3^-$. The first two anions can be adsorbed non-specifically or specifically, while the latter two can only be adsorbed non-specifically. Specific adsorption is the penetration of the anion into the coordination sphere of metal oxides, and nonspecific adsorption refers to anion retention in the diffuse double layer next to oxide surfaces.

The anion adsorption capacity of a soil is related to the content of positively charged sesquioxides in the soil.$^{33,34,35}$. Highly weathered, Al- and Fe-rich
soils have higher adsorption capacities than younger Al- and Fe-poor soils. The addition of specifically adsorbed anions to a soil will result in the mobilization of non-specifically adsorbed anions. Phosphate is the most strongly adsorbed anion and will displace specifically adsorbed SO₄ as well as non-specifically adsorbed anions, such as Cl and NO₃. Nitrate and Cl are considered indifferent anions, since they do not specifically adsorb and can be completely desorbed by eliminating the positive charge on sesquioxide surfaces.

This problem was investigated by Wiklander using the following soils:

1. Cambisols, cultivated, loamy clay, (Fe, Al)₂O₃/SiO₂,
2. Humo-orthic podzol, A₂ (bleached) and B₂ (rusty) horizons, and (Fe, Al)₂O₃/SiO₂ medium, and
3. Latosol from Kenya, lateritic clay, (Fe, Al)₂O₃/SiO₂ high.

Sodium, K, Mg, and Ca combined with Cl, NO₃, SO₄, H₂PO₄, or HPO₄ were added to the above soils. The salts were added to solutions in amounts used in fertilization or higher levels. After equilibrium was established, the solution was separated with centrifugation or membrane filtration and analyzed. Without exception, the adsorption of N, K, Mg, and Ca varied with the type of salt anion and increased in the following order:

\[\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{H}_2\text{PO}_4^- < \text{HPO}_4^{2-}\]

The solubility of the added salts was highest for Cl and NO₃, somewhat less for SO₄, and least for H₂PO₄.
Wiklander\textsuperscript{24} thus showed that anions and soil type directly affect the adsorption of cations on the soil.

The results were similar for single salts with Na and NH\textsubscript{4} as for combined salts with Ca, Mg, K and Na. The lateritic soil, the B horizon from the podsol and cultivated cambisol soils behaved similarly, with the anion effect varying quantitatively with soil type.

Removal of hydrated oxides in the Latosol before the salt addition strongly reduced the differences in retention of Ca, Mg, K, Na between the H\textsubscript{2}PO\textsubscript{4}, SO\textsubscript{4} and NO\textsubscript{3} systems caused by decreased adsorption of H\textsubscript{2}PO\textsubscript{4} and SO\textsubscript{4}. It was found that the capacity of a soil to bind cations in exchangeable form depends not only on the soil properties but also on the anion of the salt used for saturation.

The increased retention and reduced leaching of salt cations by adsorbed polyvalent anions are processes of great significance in soil formation, geochemical circulation of nutrients, fertilization in agronomic and horticultural systems and also in pollution of soils and waters.

The mobility of SO\textsubscript{4} in soils is an important consideration in studying the possible effects of acid rain on nutrient mobilization from the soil. According to experiments conducted by Johnson and Cole\textsuperscript{37}, it cannot be assumed that inputs of H\textsubscript{2}SO\textsubscript{4} will result in equivalent outputs of cation-SO\textsubscript{4} solutions from the soil. To test this, Johnson and Cole\textsuperscript{37} added H\textsubscript{2}SO\textsubscript{4} to a gravelly Everett soil. Results showed that significant increases in leaching occurred in the A horizons, but no increase was noted in the B horizons. Through soil analysis, it was found that all applied SO\textsubscript{4} was retained in the soil profile.
In another study, Johnson et al.\textsuperscript{38} compared atmospheric \( \text{H}_2\text{SO}_4 \) inputs and leaching in a tropical and temperate forest soil. In both cases, H was mostly removed in the forest canopy. The tropical forest appeared to be accumulating \( \text{SO}_4 \), whereas the temperate forest was near steady state with respect to S. In both soils, the lower horizon adsorbed more \( \text{SO}_4 \) than did the upper horizon. The tropical soil had a high capacity permanently to retain \( \text{SO}_4 \) which was probably related to its high sesquioxide content, rendering it very resistant to leaching by atmospheric \( \text{H}_2\text{SO}_4 \) inputs.

Many researchers have noted higher soil \( \text{SO}_4 \) to be found in subsoil horizons than in surface horizons \textsuperscript{36,39-42}. Hesse\textsuperscript{39} suggested that there was a \( \text{SO}_4 \) cycle operating somewhat independently of the biological S cycle in an East African forest. He suggests that the \( \text{SO}_4 \) leached from foliage or from input in precipitation can leach past the organic soil horizons and adsorb to sesquioxide surfaces in lower horizons. It may be that surface organic matter blocks \( \text{SO}_4 \) adsorption sites to some extent. This would explain why more \( \text{SO}_4 \) is found in the subsoil than in surface horizons of many soils.

The relationship between \( \text{SO}_4 \) adsorption and soil sesquioxide content has been demonstrated by several other investigators\textsuperscript{38,42,45}. Soils that adsorb \( \text{SO}_4 \) tend to maintain an equilibrium between \( \text{SO}_4 \) in solution and that sorbed into soil surface as shown below.

\[
\text{SO}_4^{2-} \text{ (solution)} \rightleftharpoons \text{SO}_4^{2-} \text{ (sorbed)}
\]

The Freudlich and Langmuir adsorption isotherms have been used to describe this equilibrium\textsuperscript{38,41,46}. 
Johnson and Henderson\textsuperscript{17} undertook a laboratory study to determine whether S accumulates by SO\textsubscript{4} adsorption in a mixed deciduous forest soil. Sesquioxide rich subsurface soils which had a large reservoir of NaH\textsubscript{2}PO\textsubscript{4} solution were found to have adsorbed SO\textsubscript{4}-S at a level of 2700 kg/ha but would not permanently adsorb more. The surface soils had no detectable adsorbed SO\textsubscript{4} but had a substantial reserve of H\textsubscript{2}O-soluble-SO\textsubscript{4}-S (110 kg/ha). This high proportion of H\textsubscript{2}O soluble solution SO\textsubscript{4} appeared to have played an important role in determining SO\textsubscript{4} concentrations in headwater streams. It was also found that these surface soils were capable of adsorbing more SO\textsubscript{4} in forms not extractable with water or PO\textsubscript{4} solution.

Tyler\textsuperscript{48} studied the leachability of some metal ions (Mn, Zn, Cd, Ni, V, Cr, Pb) in two purely organic spruce soils: one control soil and one similar soil heavily polluted with Cu and Zn from a brass foundry in southern Sweden. Artificial rain water acidified to pH 4.2, 3.2 and 2.8 was used in the experiments. The leachability of heavy metals through the action of precipitation was found to vary greatly between the different elements. The leaching rate of Ni in the control soil (similar to that of Mn) was considerably high. In the polluted soil, only V and Zn were released more rapidly with the pH 4.2 acid rain. At pH 4.2 the 10\% residence time estimated from Tyler's experimental data varied from 3-yr (Mn) to 70 to 90-yr (Pb) in the control soil and from 2-yr (V) to 200-yr (Pb) in the polluted soil. Residence time for most elements in this study (except V and Cr) decreased with pH of the precipitation\textsuperscript{16}. 
Reuss\textsuperscript{46} came up with a simulation model that provides a quantitative system using established relationships from soil chemistry to predict the most likely effect of rainfall acidity on the leaching of cations from noncalcareous soils. The model utilizes: the relationships between lime potential (pH-$\frac{1}{2}$p Ca) and base saturation described by Clark and Hill\textsuperscript{49} and by Turner and Clark\textsuperscript{50}; the equilibrium between CO$_2$ partial pressure and H and HCO$_3$ in solutions; the apparent solubility product of Al(OH)$_3$; the equilibrium of cations and anions in solution; the Langmuir isotherm description of SO$_4$ adsorption; and mass balance considerations to predict the distribution of ions between the solution and sorbed or exchangeable phases. The ionic composition of leachates in response to rainfall composition can thus be computed. The model predicts almost exact chemical equivalence between basic cations removed in the leachate and strong acid anions entering the system in the rainfall if pH-$\frac{1}{2}$p Ca is above 3.0, at which point the base saturation will generally not exceed 20%.

Soils with a significant capacity to adsorb SO$_4$ tend to dampen the effect of H$_2$SO$_4$ induced leaching of basic cations. The leaching of bases will respond more slowly to acid inputs than on non-SO$_4$ adsorbing soils, but will reach a similar equilibrium rate of leaching as the SO$_4$ adsorption capacity reaches equilibrium with the rainfall SO$_4$.

Atmospheric inputs of H$_2$SO$_4$ and HNO$_3$ to noncalcareous higher elevation watersheds in the Adirondack regions lead to comparatively higher concentrations of dissolved Al in the surface horizon and in the groundwater. This appears to result from
increased soil Al leaching. Aluminum leaching is enhanced in well drained acid soils where there are significant inputs of organic acids from litter decay and canopy leaching. In the presence of organic ligands, the solubility of Al can be greatly enhanced by the formation of soluble organic-Al complexes. Aluminum and Fe are transported from upper to lower soil horizons by means of such soluble organometallic complexes. Such increased Al concentrations can lead to fish mortality. There may be indirect effects on P availability through increased inorganic precipitation of AlPO₄. Accelerated Al leaching may also have implications for soil forming processes, the health of plant communities, and alterations in the clay mineralogy of the soil. On the positive side, Al has been found to neutralize strong acids from acid precipitation.

Wiklander has demonstrated that neutral salts in the precipitation reduce the acidification of soils by acid precipitation. The magnitude of the salt effect depends on the relative bonding energy of H₃O and of Ca, Mg, Na, K, NH₄ in the soil as well as concentrations of H₃O and the above cations in the precipitation.

The salt effect may be considerable in very acid soils. It decreases with rising pH to become very small or negligible in neutral soils, chiefly due to the increasing bonding energy of H₃O in this direction. The adverse effect of acid precipitation, therefore, is likely to be less in very acid soils such as podzols than in slightly acid and neutral soils with low buffering capacity against pH change.
Effect of Acid Rain on Soil Microorganisms

In the past, enormous literature accumulated in soil microbiology on various changes which are brought about by the acidification of soils, associated with the use of fertilizers. Similar stresses induced by acid precipitation have renewed interest in this area. The subject has been recently reviewed by Alexander.53

The studies in microbiological processes are usually performed in a laboratory setting which makes it difficult to directly extrapolate the findings to the field.

There are six major microbial groups residing in the soil ecosystem, i.e., bacteria, actinomycetes, fungi, algae, protozoa and viruses. The various species have been found in widely dissimilar soils, and only a few possess a distinct biogeographical characteristic.

Microorganisms are involved in at least four key processes affecting the soil and plant productivity. First, they are essential for plant growth by affecting certain essential nutrients which would otherwise be unavailable. A case in point is N, P and S, which are normally found in combination with organic materials, a form of which is unavailable to higher plants. Microorganisms convert the organic forms to the inorganic state which is a vital step in maintaining plant growth.

Microorganisms also play a key role in affecting the characteristic soil structure. This is, in part, due to the formation of humus and, in part, to the binding of soil particles as aggregates.

The microfiora also perform a crucial role by preventing the excessive accumulation of organic matter
with the likely build-up of high concentrations of toxic chemicals.

Finally, microflora are involved in the maintenance of environmental quality, particularly as it affects the soil ecosystem. Modernized society has introduced into soil a variety of toxic substances, be they synthetic chemicals or natural waste materials. The degradations of these materials is entirely dependent on microbial action.

It should be borne in mind that most microbial transformations in soil may involve more than one population. The elimination of any one population therefore does not necessarily have to be detrimental, since unaffected populations(s) may continue to carry out the chemical reactions in question. An example of this is the conversion of organic N to inorganic forms.

However, there are a few processes which are known to be carried out only by a single microbial species. In a situation like that, elimination of the particular population would be detrimental. This is especially true about the nitrification process which converts NH₄ to NO₃, and the nodulation of legumes for which the bacteria are quite specific, depending on the leguminous host.

As it turns out, of the various microflora, autotrophic nitrifying bacteria are particularly sensitive to acidity. Their activity falls rapidly with decreasing pH and is undetectable below pH 4.5. Limited nitrification that is observed in acid soils may be the result of the action of heterotrophic organisms.

Soil acidification can also be expected to cause a general reduction in population of bacteria and
actinomycetes and an increase in the abundance of fungi. The increase in fungi has been attributed to decreased competition from other heterotrophic organisms at low pH\textsuperscript{54}.

Acidity is generally linked with decreased rates of humus decomposition, while liming will promote conversion of the humic compounds to CO\textsubscript{2}. However, in some instances, depending on the soil and the nature of the organic materials, rapid degradation can be observed even at moderate or extreme acidities, such as pH 1.8\textsuperscript{55}.

Increasing acidity can also profoundly decrease biological N fixation rates. The nodulation, which is the essential prelude to the development of the N-fixing system involving legumes and Rhizobium, is especially sensitive to acid conditions. In the case of clover, nodulation is frequently absent at pH 5.2 or below\textsuperscript{56}. The reduced numbers of root-nodule bacteria were also reported below pH 5.0\textsuperscript{57}. No information exists at present on the effect of acidity on N fixation in the roots of non-leguminous plants. In the case of free-living N fixers, a majority seem to be sensitive to low pH, although a few may be quite resistant\textsuperscript{58}.

Conversion of soil organic N to NH\textsubscript{4}, in contrast with nitrification, apparently does not show a marked pH sensitivity\textsuperscript{54}. In fact, the acid soils may show elevated NH\textsubscript{4} levels in contrast to non-acid soils in which NO\textsubscript{3} is the dominant form of N.

Denitrification, which converts NO\textsubscript{3} to N\textsubscript{2} and N\textsubscript{2}O, is also adversely affected by low pH. The number of bacteria which carry out this reaction was shown to be inversely correlated with acidity\textsuperscript{59}. 
The decomposition of organic matter is an important part of nutrient cycling in natural ecosystems. Many nutrients taken up by plants are returned to the soil through litter fall.

The effect of artificial rain on the organic matter decomposition process and on the organisms involved, has been studied by Abrahamsen et al., using the ecosystem approach. Fungi from decomposing litter were isolated and their growth measured at different H ion concentrations. Soil animals were extracted from soil samples taken from laboratory and field experiments, with applications of simulated acid rain and lime.

In coniferous forests located on acid podzolic soils, the abundance of many soil invertebrate animals were found to increase under the more acidic conditions induced by the simulated acid rain, whereas a few animals were observed present when soil acidity was reduced by liming. The increased population of certain species of soil animals may have been due to an increase in availability of fungus food reserves available to animals due to the more acid-tolerant fungal species outcompeting more acid-sensitive bacteria for available food.

Decomposition studies showed that the initial decomposition of plant remains was only slightly influenced by acidification. However, decomposition of raw humus material was pH dependent, and decreased with increased acidity. It should be noted that the effects observed were produced with much higher concentrations of H ions than normally found in precipitation, and as a consequence, cannot be applied directly to the acid rain problem. Long-term studies with more realistic
inputs of H are necessary to assess acid rain effects under natural conditions.

A case study of forest litter decomposition near the Ni smelter at Sudbury, Ontario was recently reported. A series of field plots of various distance from the smelter were used to examine potential effects of heavy metal and SO\textsubscript{4} burdens. Decreasing inputs and accumulations of Cu, Ni, Fe and S were shown in organic soil horizons and vegetation along a 60 km SSE transect away from the smelter. There was, however, no effect on the pH of the precipitation or on the distance of the soil litter horizons from the smelter. Rates of litter-fall were determined to be unchanged as a function of distance from the smelter, but the litter standing crop was increased close to the source, implying an effect on litter decomposition. Lower rates of decomposition of leaves in litter bags occurred at contaminated sites, together with low rates of soil metabolic activity. These included soil CO\textsubscript{2} flux and acid phosphatase activity. Lower populations of soil microfungi and microarthropods also occurred. In a laboratory experiment involving the addition of Cu and/or Ni to a litter homogenate, a depression of litter mineralization and CO\textsubscript{2} flux was shown to occur at metal concentrations similar to those observed at contaminated sites in the field. Whereas the observed vegetation toxicity near the smelter was likely primarily an effect of SO\textsubscript{2} and of heavy metals in soils, and the effects on litter decomposition were primarily due to heavy metals, specifically Cu and Ni. Overall, the negative effects attributable to acid precipitation near the smelter appeared to be small,
relative to the effects of $\text{SO}_2$ and heavy metal residue in soils.

As was mentioned above, several nutrients in the soil are bound in organic form and thus unavailable to the plants. In the case of P, 15-85% is organic. An inhibition in the mineralization process would have serious repercussions on the plant productivity. According to Halstead et al.\textsuperscript{62}, there may be in fact a decrease in the microbial conversion of organic to inorganic forms of P in more acid environments; however, the data are too limited to make definite conclusions. There is also some evidence for slower conversion of organic S compounds in humus to products that can be assimilated by plants under comparable conditions\textsuperscript{63}.

**SUMMARY**

Acid rain is a phenomenon of modern times. The first published reports on acid rain appeared in the mid-1950's. Since that time it has become widespread - occurring in all parts of the United States. While its effects on aquatic systems are fairly well documented, its effects on soils are still not fully understood.

In this review we have discussed the sensitivity of soils to acid rain. Acid rain may bring about variable effects on soils, depending on the type and properties of the soil involved. These parameters include: the total buffering capacity or the total cation exchange capacity, the base saturation of the exchange complex, the management system imposed on the soil, viz., whether it is cultivated, fertilized, or renewed by flooding or other additions, and the
presence or absence of carbonates in the soil profile. Other topics discussed in our review include the soil acidification process, the effects of acid rain on soil exchange properties, and the effects of acid rain on soil microorganisms.

Several questions still exist concerning the effects of atmospheric acid deposition on the chemistry of soils:

1) does acid rain enhance mobilization of harmful heavy metals in soils which would leach into the groundwater;

2) does acid rain accelerate the kinetics of weathering of primary (feldspar, mica) minerals and of secondary clay minerals (kaolins, smectites, and vermiculites) in soils which would release large quantities of Al, Fe, and Si into the groundwater making it unfit for human consumption; and

3) do the beneficial effects of acid deposition outweigh the negative effects, or vice versa?

These questions must be answered through basic research since the stability of soils is an important, and often unappreciated attribute of ecosystem continuity.

REFERENCES

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2. Former Graduate Research Assistant and Associate Professor of Soil Chemistry, respectively. The address of the senior author is Dept. of Agronomy, VPI and SU, Blacksburg, VA 24061.


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