ACID DEPOSITION - SOIL ACIDIFICATION.
LITERATURE REVIEW
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ABSTRACT

The current state of knowledge on the effects of acid precipitation on vegetation and soils is assessed. Research studies, mostly from North America and Scandinavia, dealing with the effects of acid rain on soil chemistry and soil biochemical processes are reviewed. The effects of acidic deposition in its three forms (dry deposition of gaseous materials, dry deposition as particulate and wet deposition) are currently less understood than the cause. A growing body of evidence suggests that acidic deposition is contributing to the acidification of certain freshwater lakes in the northeastern United States and eastern Canada. Several important conclusions from this review are presented.

RÉSUMÉ

On évalue l'état actuel des connaissances concernant les effets des précipitaitons acides sur la végétation et le sol. On examine des études effectuées pour la plupart en Amérique du Nord et en Scandinavie et portant sur les effets des précipitations acides sur la chimie du sol et les processus biochimiques qui ont lieu dans le sol. Les effets des retombées acides sous leurs trois formes (dépôt sec de matières gazeuses, dépôt sec de particules et dépôt humide) sont moins bien compris à l'heure actuelle que leur cause. Il y a de plus en plus de preuves que les retombées acides contribuent à l'acidification de certains lacs d'eau douce situés dans le nord-est des États-Unis et l'est du Canada. On présente un certain nombre de conclusions importantes de l'étude.

MANAGEMENT PERSPECTIVE

In recent years the atmosphere has become increasingly loaded
with anthropogenic sulfur and nitrogen gases which subsequently
undergo hydrolysis and oxidation to form sulfuric acid and nitric
acid, respectively. Both acids readily dissociate with the formation
of sulfate and nitrate anions, and the release of protons. As a
consequence, the pH of rainwater in pollution impacted areas may drop
considerably below the value of precipitation in equilibrium with
atmospheric carbon dioxide, thus adversely impacting the receiving
soils. A growing body of evidence suggests that acidic deposition is
contributing to the acidification of certain freshwater lakes in the
northeastern United States and eastern Canada. This report seeks to
present a synthesis of the present day knowledge about the problem of
soil acidification. This report is believed to be the first
open-literature review of the data.

RÉSUMÉ ADMINISTRATIF

Depuis quelques années, la teneur de l'atmosphère en soufre et en azote anthropogéniques s'accroît et ces gaz se transforment ensuite par hydrolyse et oxydation en acide sulfurique et acide nitrique respectivement. Ces deux acides se décomposent facilement pour donner des anions de sulfates et de nitrates et dégager des protons. Par conséquent, le pH de l'eau de pluie dans les régions touchées par la pollution peut tomber nettement plus bas que la valeur des précipitations en équilibre avec le gaz carbonique, ce qui est nuisible aux sols récepteurs. Il y a de plus en plus de preuves que les retombées acides contribuent à l'acidification de certains lacs d'eau douce situés dans le nord-est des États-Unis et l'est du Canada. Le présent rapport vise à présenter la synthèse des connaissances actuelles sur le problème de l'acidification des sols. Il semble être le premier à étudier les données dans tous les écrits publiés.

INTRODUCTION

The deposition inputs of acidic materials from the atmosphere, popularly referred to as 'acid rain', to terrestrial and aquatic ecosystems is a phenomenon which has recently received international attention. Over the past two decades this area of environmental concern has been the impetus for an exponential increase in activity on the scientific, and political fronts.

The essence of the acidic deposition issue is that materials emitted into the atmosphere as a result of anthropogenic activities, principally the combustion of fossil fuels, are transformed into acidic substances and then returned in a wet or dry form to lakes, croplands, forests, and other natural communities. Wet deposition not influenced by these anthropogenic contributions would have a theoretically "normal" pH of approximately 5.6, or slightly acid. Recent studies suggest "normal" precipitation pH actually falls within a range from slightly below 5.0 to greater than 6.0 in natural environments. Extensive monitoring efforts in recent years clearly have demonstrated average wet deposition pH values range between 4.0 and 4.5 in the eastern United States and Canada. Similar levels of wet deposition acidity have been illustrated at various locations throughout the world. Concern over the impact of these atmospheric inputs on natural ecosystems has fueled the tremendous interest in this environmental topic.

Acidic deposition, popularly referred to as 'acid rain', deals with the phenomenon of atmospheric materials which have a greater acid character than is expected in theoretically non-polluted environments. The majority of atmospheric acidity is due to S and N compounds which are emitted into the atmosphere due to modern anthropogenic activities. Most of these inputs are thought to be in the form of SO_2 and NO_x (NO and NO_x). These chemicals are then oxidized in the atmosphere by heterogeneous oxidation of dissolved gases in liquid aerosols and homogenous oxidation in the gas phase (Hileman, 1982). A large number of substances, however, are involved in atmospheric chemistry which are considered to be acidic or potentially acidifying materials such as: (a) sulfur compounds and radicals - sulfur dioxide (SO_2), sulfur trioxide (SO_3^{3-}), hydrogen sulfide (H_2S), dimethyl sulfide [$(CH_3)_2S$], dimethyl disulfide [$(CH_32S_2$], carbonyl sulfide (COS), carbon disulfide (CS_2), sulfate (SO_4^{2-}), sulfuric acid (H_2SO_4), methyl mercaptan (CH_3SH); (b) nitrogen compounds and radicals - nitric oxide (NO), dinitrogen oxide (N_2O), nitrogen dioxide (NO_2), nitrite (NO_2^-), nitrate (NO_3^-), nitric acid (HNO_3), ammonium (NH_4^+), ammonia (NH_3), and (c) chlorine compounds and radicals - chloride (Cl^-), hydrochloric acid (HCl).

Acidic deposition can be divided into wet and dry deposition. Wet deposition can be in the form of rain, snow, dew, fog, hail, rime or sleet, whereas dry deposition refers to gaseous or particulate atmospheric inputs. Theoretically, pure rainwater would have a pH of roughly 5.6 (2.5 μg/l H^+) as a result of a chemical equilibrium

between pure water and atmospheric CO_2, which currently averages 0.03 percent of the ambient atmosphere. Much of the precipitation falling on eastern North America is currently well below this theoretical pH as can be seen in Figure 1; the mean precipitation pH data for this region falls between 4.0 and 4.6.

Most of the acidity in acid precipitation is due to strong mineral acids (H_2SO_4 and HNO_3), which was shown by Lindberg et al. (1981) to account for 70 percent of the acidity in precipitation at the Walker Branch Watershed in eastern Tennessee. A large proportion of the mineral acid component of precipitation is due to S compounds, primarily as a result of SO_2 emissions. Glass et al. (1980) reported on New York and New England data which indicated 60 to 70 percent of the acid input was attributable to sulfuric acid, with only 30 to 40 percent associated with nitric acid.

The major sources of S are the burning of coal and petroleum products and ore smelting. Electric utilities currently contribute roughly two-thirds, and industry another one quarter of total anthropogenic SO_2 emissions. Industry has reduced these emission loads from 11 to 7 million tons in the last 20 years. Most of the NO_x emissions are associated with transportation (40 percent); however, the electric utilities and industry together supply an additional 55 percent of the total. The mix of S and N in precipitation does not appear to be static. In recent years the level of SO_2 emissions has declined; however, increases in NO_x emissions equal or greater in magnitude have occurred (Hileman, 1981). Of the total S in the atmosphere of the northeastern United States, 90

percent is thought to be contributed by anthropogenic sources. Similar data on NO_x is not available. However, it has been estimated that 56 percent of the NO_x emissions in 1972 were from within the northeastern region, and nitrate increases in precipitation are reasonably well correlated to anthropogenic N emissions (Evans et al., 1981).

Dry deposition deals with the removal of gases and particulates from the atmosphere by processes not associated with precipitation. It is now believed that the dry deposition component of the total atmospheric input of acidity may be equal to, or greater than, wet deposition input in many cases. Evidence suggests that the dry deposition contribution to total acidity increases relative to the wet deposition component as one moves closer to point sources of emissions.

The mechanisms of wet and dry deposition can be categorized into five general processes. For wet deposition, S and N are removed from the atmosphere as (a) rainout, or (b) washout. Rainout is considered the transfer of materials to cloud droplets before they make their descent as a raindrop, while washout is considered the process of transferring materials to the falling raindrop. Rainout usually involved cloud condensation nuclei as aerosols of $(NH_4)_2SO_4$, $(H_4)_3H(SO_4)_2$, H_2SO_4, gaseous SO_2 and NO_x compounds. Dry deposition of acidic materials from the atmosphere occurs as a result of (a) surface absorption of gases, (b) particle sedimentation, and (c) impaction of aerosols on vegetation, soil, water or snow.

NUTRIENT LEACHING LOSS

Basic Mechanism of Leaching

One of the initial concerns raised about acid rain was its reported effect on cation leaching. The basic process of nutrient leaching loss can best be understood by applying the principles of chemical equilibrium to the soil solution. Based on the necessity of maintaining electroneutrality, positive and negative charges in solution must always balance. The soil, however, is largely dominated by negative exchange sites associated with the surfaces of organic materials and clay minerals. Adsorption reactions thus restrict the mobility of cations. In order for nutrient leaching to occur the cations displaced from the exchange sites have to be accompanied by an equivalent amount of anions in solution. The rate of nutrient loss through leaching is therefore in essence determined by presence and mobility of the anion carriers (Cronan et al.; Johnson and Cole, 1977; McColl, 1972; McColl and Cole, 1968; Nye, 1981).

In temperate and tropical regions, the leaching process in undisturbed forest soils of pH values greater than 5, is dominated by the bicarbonate ion, which originates from intensive soil respiration(Johnson et al., 1977). In arctic and subalpine forest ecosystems, where soil activity is strongly inhibited by low temperatures, organic acids constitute the major leaching agents (Cronan et al.; Johnson et al., 1977; Ugolini et al., 1977). The

relative importance of the various anions in nutrient leaching for a number of major ecosystem types is indicated in Table 1.

Table 1. Anions Involved in Nutrient Leaching

Leaching Agent	Ecosystem
HCO_3	temperate
	tropical forests
NO_3	N-rich soils
	acid rain impacted soils
Organic acids	arctic
	alpine forests
SO_4	acid rain impacted soil
Cl	coastal soils

Effect of Acid Rain on Leaching

With acid precipitation, potential cation carriers are introduced to the soil system in addition to the proton load. Due to their inherent small size, hydrogen ions are usually strongly adsorbed to the exchange complex. Rate of leaching loss of the displaced cations is therefore largely controlled by the mobility of the added anions. Nitrate, for example, is highly mobile in most soils (Hingston et al.,

1967; Vitousek et al., 1970). Only immobilization through uptake by plants or microorganisms can effectively restrict this form of anion loss. This process is expected to occur in most of the forest soils in the Pacific Northwest known to be nitrogen deficient (Gressel et al., 1973). Biological uptake of nitrate will have little influence on the overall leaching process in soils with inherently high nitrogen content.

Nutrient losses can result when the anions from acidic deposition (SO_4^{2-} and NO_3^-) accelerate leaching losses of critical cationic nutrients (e.g. Ca^{2+}, Mg^{2+}, K^+) due to the chemical requirement for maintenance of electroneutrality in solution percolating through soils. Alterations in the microbiological soil community are suspected as a possible cause of decreased nutrient availability resulting from changes in the process of organic matter decomposition and carbon cycling. Due to increased atmospheric inputs and soil solution chemical alterations brought about by acidic deposition, some trace metals may reach soil levels which result in direct or indirect negative impacts on trees. These substances include Cd, Pb, Zn, Cu, Ni, V, Co, Mn, with the greatest concern being for the mobilization of Al in the soil.

In contrast, the sulfate anion can be removed through physical chemical processes typically associated with free Fe and Al oxides and, to a far lesser extent, through biological uptake (Hingston et al., 1967; Johnson and Cole, 1977, Mekaru and Vhara, 1972). In highly weathered soil enriched in Al and Fe sesquioxides, the mobility of sulfate may be strongly restricted as a result of anion adsorption

reactions. Younger soils as a result of a lower sesquioxide content, generally exhibit lower anion adsorption capacity, and are therefore more susceptible to nutrient losses triggered by atmospheric sulfate (Johnson, 1980). It would appear that soils high in organic matter block sulfate adsorption sites, increasing the potential for sulfate leaching (Johnson et al., 1979).

From the previous discussion, it can be deduced that the potential for nutrient leaching loss is enhanced by acid precipitation if:

(1) The acidifying anion of the acid rain is NO^{-3} rather than SO_4^{-2}.

(2) Biological immobilization of anions, especially NO_3^- remains low.

(3) Free Fe and Al oxides are relatively low, such as with young unweathered soils.

(4) Soil colloids are coated with organic substrates.

Finally, it should be pointed out that even though mobile anions may be introduced to the soil system, this does not necessarily imply that total nutrient leaching increases. If the mobile anions, entering a bicarbonate dominated soil solution, are entirely countered by an equivalent amount of hydrogen ions, then the total mobile anion pool is expected to remain unaltered in size. Indeed, for each proton entering the soil solution, one bicarbonate ion is converted into carbonic acid (Stumm and Morgan, 1982). The net effect of acid precipitation on leaching then merely amounts to a shift in anion composition, while the total nutrient removal remains unchanged (Cronan, 1980). If mobile anions are accompanied by other cation species besides hydrogen, then bicarbonate disappearance is only

partially able to compensate for anion addition and greater nutrient losses are to be expected. This would imply that the potential impact of the throughfall solution on nutrient leaching from the soil is greater than that of the ambient precipitation.

Leaching and Ion Exchange Processes

A major concern with respect to the long-term impacts of acidic deposition on forest productivity has centered on the possible nutrient depletion which could result from H_2SO_4 and HNO3-dominated soil solutions. In areas impacted by acidic deposition, the H^+ cation in precipitation, throughfall, and stemflow can replace essential cationic plant nutrients (e.g. Ca^{2+}, Mg^{2+}, K^+) upon interaction with soil colloids. The displaced cations can then be easily leached from the soil when associated with the charge balancing SO_4^{2-} and NO_3 anions, provided these anions are not retained in the soil through soil sorption or root uptake processes. Abrahamsen (1980) recently emphasized that the rate of weathering in nutrient-poor soils does not appear to compensate for the increased leaching losses.

Although the bicarbonate anion (HCO_3^-) is an important component in mildly acid to neutral, "natural" forest soil solutions, areas receiving S and N inputs via acidic deposition have soil solutions dominated by the strong mineral acids H_2SO_4 and HNO_3. The nature and behavior of organic acids appears also to play an important role in forest ecosystems with respect to acidic deposition impacts and acid neutralization.

Ulrich (1980) recently discussed some of the problems which appear to be occurring in the forests of central Europe. As a result of leaching losses from soil acidification, Mg deficiency symptoms have appeared in conifers as yellow coloured needles which are most evident in spring. He stated that boron (B) is also leached, and that while no evidence exists for deficiency symptoms, decreased wood tensile strength due to a lack of this element cannot be discounted. He also believes that the leaching of base cations from the rooting zone is complete in many Central European forest soils with Ca^{2+} saturation of the cation exchange capacity often less than 5 percent.

Mollitar and Raynal (1982) studied the potential effects of acid precipitation on a hardwood and coniferous stand in the Huntington Forest near Newcomb, New York. Solution chemistry was studied as bulk precipitation, throughfall, and soil solutions at the base of the O_2, A_2, and B_{23} horizons. The concentrations of NO_3^-, Ca^{2+}, Mg^{2+}, and Na^+ concentrations were significantly greater. Mean bulk precipitation pH was 4.2 (63 µg H^+/l) for the study. Conifer site throughfall, forest floor leachates, and A horizon leachates were significantly more acid than corresponding hardwood strata, yet solutions at the base of the B horizon in both stands did not differ significantly. It appeared that H^+ ion acidity was effectively neutralized in the soil while NO_3^- and K^+ ions were conserved. Sulfate and organic anion leaching were of equal importance in the hardwood site whereas organic anion leaching dominated the conifer site. The authors concluded that low concentrations of exchangeable cations in these soils suggest chronic

leaching losses of nutrient cations may adversely affect forest productivity.

Cronan (1980) subjected forest floor samples from a subalpine coniferous forest in the White Mountains of New Hampshire to three simulated throughfalls (pH 3.5, 4.0, and 5.7) and two temperature treatments (6° and 24°C) in a laboratory microcosm study. Results indicated that as treatment acidity increased, mass action ion exchange between H^+ ions and exchangeable cations in the forest floor caused increased leaching losses of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+. Higher temperatures also increased leaching losses of Ca^{2+}, K^+, NH_4^+, SO_4^{2-}, No_3^-, and organic anions due to increased microbiological decomposition of the organic substrate. The author pointed out the significant effects mineral soil retention and plant uptake may have on leaching losses under field conditions.

Johnson (1981) proposed an interesting conclusion with respect to the sensitivity of soils to groundwater acidification due to acid and sulfate inputs. Due primarily to the well known "salt effect" phenomenon described by soil chemists, it appears that those soil solutions that are already acid are most susceptible to further acidification, whereas the least acid solutions would be most resistant. Johnson explained that, since the exchange complex is dominated by H^+ and Al in acid soils, inputs of a mobile anion (i.e. SO_4^{2-}) from acid precipitation would require an equivalent increase in solution cation activity, thus elevating H^+ in soil solution or decreasing pH. In less acid solutions, H^+ constitutes a lower

proportion of the total cations and thus would contribute less to increased soil solution ionic strength or equilibrium.

One aspect of many forest soils which has been shown to be critical in understanding ion exchange relationships in these ecosystems is the tremendous contribution by organic materials to the cation exchange capacity (Kalisz and Stone, 1980). Highly organic forest floors, or humus materials, and mineral soil organic content are directly associated with soil cation exchange capacity. Cation exchange capacity originating from organic materials is considered pH-dependent, which means a decrease in soil pH would also reduce the cation exchange capacity resulting in a lower soil capacity to retain cationic nutrients. Kalisz and Stone (1980) demonstrated this phenomenon when they measured the cation exchange capacities of acid forest soil mor and mull samples from New York at field pH (pH 4 for mors and pH 4.9 to 5.4 for mulls) and at pH 7.0. Cation exchange capacities increased from 52 and 123 meq/100 g organic matter at field pH to 183 and 236 mg/100 g organic matter at pH 7 for the mor and mull samples, respectively.

Norton et al. (1980) discussed the implications of their research with regard to the effect acid precipitation is having on forested ecosystems in eastern North America and the Pacific Coast states. They concluded the increased acidity in precipitation, and associated heavy metal deposition has caused the accumulation of heavy metals (e.g. Pb), and the leaching of cations (e.g. Al^{3+}, Ca^{2+}, K^+, Mg^{2+}, and Mn^{2+}) in forest soils for these regions. Their conclusions were that

decreases in forest productivity will occur in the northeastern United States due to diminishing nutrient pools for these ecosystems.

A recent conference in Sweden on acidic deposition brought together experts from throughout the world on the ecological impacts of this environmental problem. In their conclusions, they stated that the exchange of H^+ in acid percolating waters will increase Ca^{2+}, Mg^{2+}, and K^+ leaching losses, and in soils below pH 5.0, increase the mobility of the potentially toxic Al, Mn, Cu, Cd, and Zn metals. These exchange processes with basic cations neutralize the water but acidify the soil. They felt soil acidification due to acidic deposition should be detectable over a 10 to 50 year period. Ulrich (1980) indicated a pH decrease over the last 20 years in Germany has been observed for the areas of Solling, Munster, and Berlin.

Theoretical calculations to examine the potential impact of acid precipitation on leaching and soil acidification may lead to significantly different results, depending upon the assumptions on which conclusions are based. In an earlier study of acidic deposition effects on soils, McFee et al. (1976) calculated that 100 years of pH 4.0 acid precipitation would cause a 0.8 pH unit decline and 20 percent decrease in base saturation for a typical midwestern forest soil. Strayer and Alexander (1981) recently used the same assumptions but made these calculations for the top 1.0 cm of soil depth and found only 5.2 years of pH 4.0 precipitation would be needed to produce the same results.
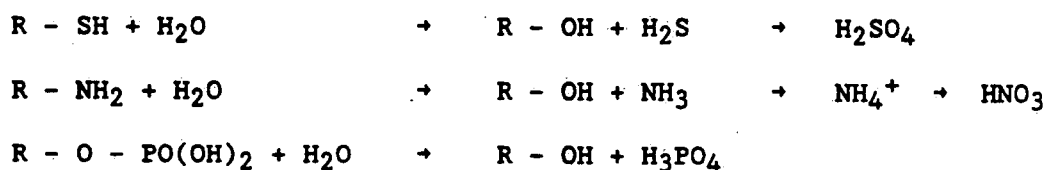
EFFECT OF ACID RAIN ON SOIL ACIDITY

Assessment of the overall effect of acidified precipitation on the soil system is possible only with full understanding of the processes which regulate chemical composition and acidity of the solution. Changes in ionic concentration are caused by the interaction between the various ecosystem components and the percolating water. Solution acidity expressed in terms of pH, more specifically reflects the relative importance of the hydrogen generating and hydrogen consuming processes at any given point along the vertical transect. Acid rain should simply be considered as another proton source, superimposed on a combination of proton sources and proton sinks which are characteristic for the unimpacted system. Its effect on soil acidity strongly depends on (a) initial pH of the soil; (b) buffering capacity of the soil. Only when preexisting hydrogen producing and consuming processes are fully quantified is it possible to predict the susceptibility of a particular site to acidification by atmospheric hydrogen input.

Natural Acidification Processes

(1) Organic Matter Decomposition - Microbial decomposition of organic matter, accumulated in the forest floor layer or incorporated in the mineral soil often has an acidifying effect on the surrounding environment. Nitrogen, sulfur are generally incorporated into biomass in a reduced form. Mineralization

followed by the oxidation of these elements leads to the formation of strong solutions (Reuss, 1977; Ulrich, 1980). Phosphorus differs from sulfur and nitrogen in that its conversion from the organic to the mineral form directly yields a strong acid, without a change in oxidation state.

$$R - SH + H_2O \quad\rightarrow\quad R - OH + H_2S \quad\rightarrow\quad H_2SO_4$$

$$R - NH_2 + H_2O \quad\rightarrow\quad R - OH + NH_3 \quad\rightarrow\quad NH_4^+ \rightarrow HNO_3$$

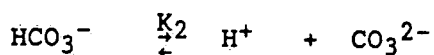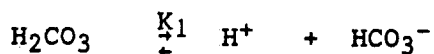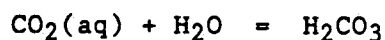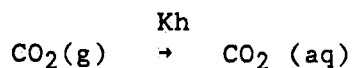$$R - O - PO(OH)_2 + H_2O \quad\rightarrow\quad R - OH + H_3PO_4$$

The acidifying effect on these mineralization reactions can be extremely strong.

The forest floor material may on the other hand also act as a proton sink. Mineralization of organic salts, for instance, produces strong bases (Ulrich, 1980).

(2) <u>Respiration</u> - The breakdown of organic carbon compounds during root and microbial respiration produces large amounts of carbon dioxide, which primarily leaves this compartment through volatilization. A small portion dissolves into the percolating water according to Henry's law. Subsequent hydrolysis yields carbonic acid which dissociates into bicarbonate or further into carbonate, depending on the ambient pH (Stumm and Morgan, 1982).

$$(CH_2O)_n + O_2 + H_2O \quad \rightarrow \quad \text{organic acids}$$

$$\rightarrow \quad CO_2 + 2H_2O$$

$$CO_2(g) \xrightarrow{Kh} CO_2 \text{ (aq)}$$

$$CO_2(aq) + H_2O = H_2CO_3$$

$$H_2CO_3 \underset{\leftarrow}{\overset{K_1}{\rightarrow}} H^+ + HCO_3^-$$

$$HCO_3^- \underset{\leftarrow}{\overset{K_2}{\rightarrow}} H^+ + CO_3^{2-}$$

This will release one proton for each CO_2 molecule dissolved if bicarbonate is the end product, while two protons are released if the reaction proceeds as far as carbonate. Incomplete decomposition of the organic carbon in the forest canopy and litter layer does not yield carbon dioxide, but results in the formation of organic acids as end products. These acidifying substances were found to dominate the solution chemistry in arctic and alpine ecosystems (Cronan et al., Johnson et al. (1977), Ugolini (1977).

The soils' organic matter content and composition has long been recognized as a key factor in evaluating soil chemical and physical behavior. Agronomists have used this knowledge to manage agricultural soils for improved fertility and structure which is reflected in greater yields of marketable products. For forested ecosystems, the

various aspects of soil organic matter content, composition, and distribution is just beginning to be understood. It appears that the importance of this material, and the rate of carbon cycling, may be more significant in forest than most prior experiences have shown for agronomic crops. Much of the nutrient pool available for trees in many temperate climate forests is though to be associated with the forest floor and mineral soil organic matter content. A major concern with respect to acidic deposition impacts is that the rate of organic matter decomposition could be reduced, which would have the effect of tying up essential nutrients in the larger reserve of undecomposed organic materials. Some evidence exists indicating this may already be occurring in the northeastern United States (Bridge and Fairchild, 1981).

Hovland et al. (1980) examined the effects of dilute H_2SO_4 treatments (pH 2 and 3) and distilled water on the decomposition of spruce needles in a laboratory lysimeter experiment which was sampled after 16 and 32 weeks. The order of mobility for elements leached from tissues was K>Mg>Mn>Ca, with K loss showing the greatest sensitivity to leachate volume and Ca loss being most sensitive to leachate acidity. The evolution of CO_2 and changes in tissue dry matter, lignin, mannose, and xylose indicated treatment acidity promoted decomposition at first, but was followed by a period of reduced decomposition for the less easily degradable substances. Even the most acid treatments in this study reduced dry matter losses by less than 5 percent.

Locanzo and Morrison (1981) looked at hardwood sites near the Sudbury, Ontario metal ore smelter which were subjected to various levels of wet and dry deposition. Research on forests in this area was also discussed earlier in connection with the work done by Freedman and Hutchinson (1982). Locanzo and Morrison found total organic matter content, N concentrations, and cation exchange capacity of the surface organic horizons between sites impacted by varying levels of deposition did not differ significantly. In contrast to the surface organic horizon, total organic matter, N, and cation exchange capacity in the underlying mineral soils decreased significantly with increased levels of deposition damage to forests. The authors attributed these differences in mineral soil properties primarily to alterations in composition of the vegetative cover on the site.

Francis (1982) studied the effects of soil acidity on the microbial decomposition of organic matter and N transformations in an acid forest soil. Using amendments of oak leaves and pH adjustments, the author reported naturally acid and acidified forest soils had slow rates of nitrification and denitrification, and low bacterial populations. Overall, he concluded that acidification of forest soils by acid precipitation may lead to significant reductions in leaf litter decomposition and N recycling.

Much of the theoretical interpretation of acidic deposition impacts in German forests deals with what Ulrich has described as a spatial and temporal "discoupling" of the ion cycle. This is

associated with a shift in the soil state that results in a greater storage of N-poor organic matter in the forest floor with elevated Al concentrations in soil solution. These changes in decomposition conditions due to acidic deposition bring about the accumulation of C, N, P and Ca within the humus layer (Matzner and Ulrich, 1981).

Studies on forest soil organic horizons indicated that the microarthropod group of soil fauna may also be sensitive to acidic deposition-induced alterations. Hagvar and Abrahamsen's study (Hagvar and Abrahamsen, 1980) indicated species varied in their reaction to both acidification and liming. Overall, acidification decreased the rate of humus decomposition in these experiments.

Mineral Weathering

Considerable research has been done over the years to describe the causes and mechanisms which control pedogenetic processes under ambient conditions. Thermodynamic calculations have traditionally assumed precipitation pH to be roughly 5.6, and to be controlled by an equilibrium with atmospheric CO_2. The chemical properties of atmospheric deposition strongly influence the equilibrium conditions which control the direction and rate of mineral weathering for the landscape. In most northeast forest soils, the soil solution is dominated by SO_4^{2-} rather than a carbonate species (Bridge and

Fairchild, 1981).   This indicates that a very different equilibrium with mineral present will be established by soil solutions than what would be expected from theoretical calculations using "non-polluted" conditions.

Another aspect of acidic deposition impacts on mineral weathering deals with the rate of weathering for soil minerals or underlying bedrock.   Weathering of most minerals (quartz is an exception) leads to the consumption of H^+ ions and the release of bases (Seip, 1982). The greater the acidity, the greater the rate of mineral dissolution in soils and bedrock.

Bache (1982) recently discussed the critical factors controlling the rate of mineral decomposition, and thus the rate of acid neutralization by this mechanism.   The two general factors are (a) rock composition (or content of weatherable minerals) and (b) access of percolating waters to rock surfaces.   The key to the ability of rock weathering mechanisms to neutralize acid inputs depends on (a) the pattern of water flow, and (b) the residence time for solutions. He concluded that the capacity for rocks and minerals to neutralize acidity is infinite, but without adequate contact between minerals and solutions, these solutions may retain electrolytes and acquire further acidic components from the surface layers of the soil.

Johnson et al. (1981) published an excellent study of the interaction between acid rain, aluminum solubility, and chemical weathering in the Falls Brook watershed at the Hubbark Brook Experimental Forest in New Hamphshire.   Although the chemical weathering of primary aluminosilicates provides the ultimate sink for

H^+ and Al acidity, these authors described a two-step mechanism of acid neutralization which probably is active at Falls Brook and most acidic deposition-sensitive regions.

In the first step, incoming precipitation acidity, which is almost totally H^+ ion acidity, is initially neutralized by a "relatively soluble aluminum mineral, probably $Al(OH)_3$." The soil solution is enriched in Al acidity (and depleted in H^+ ion acidity) by the time it first appears as streamwater. The source of Al for water percolating through the soil appeared to be primarily from the humus and B2 soil horizons. The second step entails the neutralization of H^+ and Al acidity by the weathering of primary aluminosilicate minerals which releases bases (primarily Ca and Na) into solution. The critical factors which they pointed out as controlling the neutralization process were (a) water residence time in the soil zone, which is directly related to stream order, and (b) the rate of weathering of the primary aluminosilicate soil minerals. They also found that the proportion of the organically complexed Al increased steadily in the downstream direction.

Paces (1982) has examined the effect of man's activities on mineral weathering and runoff composition in central Europe. He found agricultural practices intensify the oxidation of pyrite and runoff acidity. Dissolved Al was considered the best indicator for the effects of acid rain on rock weathering. By comparing the results of river water analyses in 1892 and 1976, he determined 88 percent of the NO_3^-, 82 percent of SO_4^{2-}, 77 percent of Cl^- and 72 percent of Na^+ were currently of anthropogenic origin and not the result of natural

weathering.   His calculations also showed that environmental acidification in the Elbe River Basin has increased the rate of mineral weathering from 10 cm to 30 cm per 1000 years in catchments underlain by gneisses and granites.   It seemed that SO_4^{2-} and NO_3^- may originate from various sources but high Al always seems to indicate severe environmental acidification.

Heavy Metals and Micronutrients

Meaningful efforts by the scientific community to understand the effects of acidic deposition components on forests must include an evaluation of the intimately associated forest interactions with heavy metals.   The processes which produce atmospheric acids and acid precursors also contribute a variety of trace metals to the environment. Concern over the possible toxic consequences of elevated trace metal levels in the soil environment arise from (a) the deposition of these materials from the atmosphere, and (b) the increased mobility of trace elements in the soil environment resulting from greater levels of acidity.   It is a well known phenomenon to environmental chemists that most trace elements, a notable exception being the micronutrient molybdenum, become more soluble or active in soil solutions with decreasing pH. A closely related concern is for the acidic deposition-induced mobilization of potentially toxic metals which are then transported in groundwaters to lakes and streams with harmful consequences for aquatic systems. Some evidence appears to already exit, suggesting accelerated leaching of Mn and Zn due to

acidic deposition has occurred in areas from Vermont to the Gaspe Peninsula in Canada, while Pb, Cu, and zn are accumulating in this region's soils (Bridge and Fairchild, 1981).

Lindberg et al. (1981, 1982) have investigated the wet and dry deposition of various trace metals at the Walker Branch Watershed in eastern Tennessee. They found in one study that almost 100 percent of the Pb, 30 to 40 percent of the Cd and Zn, and 10 percent of the Mn flux to the forest floor during the growing season resulted from atmospheric deposition. The contributions of wet versus dry deposition were comparable for Pb, whereas wet precipitation dominated Cd and Zn inputs, with dry deposition playing the key role for Mn.

McColl (1981) measured Cu, Fe, Zn, and Mn concentrations in bulk precipitation, throughfall, stemflow, and in soil solutions at 10, 15, 25, and 30 cm depths for a Eucalyptus globulus forest in the Berkeley Hills of California. As a group, the elements Cu, Fe, and Zn behaved similarly, but Mn did not follow the same trends. Dry deposition by impaction on the forest dominated Mn and Zn inputs. Rain was the primary source of Cu and Fe inputs. All metals measured were negatively correlated with pH in the soil solution. Uptake of Mn by plants and its concentration in the various components measured far exceeded concentrations of the other elements in this study.

Percy (1982) described the heavy metal and S inputs to Sphagnum magellanicum Brid. within the Maritime Provinces of Canada. Measurable inputs of all elements measured were found which included Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, and Zn. Elements accumulated in the order $S > Fe > Mn > Zn > Pb > Cu > Ni > Cr > Co > Hg > Cd$ with significant

correlations for concentrations between the element pairs Fe-Co and Ni-Cr.

Locanzo and Morrison (1981) examined wet and dry deposition to hardwood sites downwind of the Sudbury smelter complex in Ontario, Canada. The more highly impacted sites (3 km downwind of the Coniston smelter) showed decreased Ca, Mg, Mn, and Zn in tissue which was a reflection of decreased soil levels. On the other hand Cu, Al, Co, and especially Ni were at critically high concentrations in soil. The authors pointed out that such complex interactions as Ni-induced Zn deficiency must also be addressed in the interpretation of these types of data.

As part of their work on tree establishment for the polluted soils near Sudbury, Locanzo and Morrison (1982) treated white pine and white spruce seedlings with Ni and Cu solutions in growth chambers. After a 20-week period, substantial growth reductions occurred when Ni and/or Cu concentrations equalled or exceeded 10 ppm in nutrient solutions. Foliage Ni and Cu concentrations increased in relation to their concentration in solution. Foliar concentrations of Fe decreased in relation to Ni and Cu supply; Zn decreased in relation to Ni supply only.

Tyler (1981) quantified the amount of Na, K, Mg, Ca, Al, Fe, Mn, Ni, Cr, V, Cu, Zn, Cd, and Pb leached from the Podzolic A-horizon of a spruce forest soil in southern Sweden over a 2.5 year period. He found conditions which favored the leaching of organic matter, Fe and Al (i.e. relatively high temperature and precipitation periods) were associated with considerable losses of Pb, Cr, Ni, and V from the A

horizon. Metals which occurred largely in the exchangeable fraction (e.g. Mg, Ca, Zn, Cd) were more susceptible to minor fluctuations or atmospheric deposition of acidic materials would reduce the retention time for this second group of elements.

Tyler (1982) later discussed the influences of the metal polluting industry on forest soils in Sweden. He pointed out that acidic deposition combined with metal deposition seemed to increase the toxicity of metals in forest soils influenced by the higher metal inputs. However, he concluded that it is not yet possible to determine whether acidic deposition causes adverse effects on decomposition, mineralization, or toxic metal availability at background concentrations in soils. Due to its accumulation in the food chain and mobility in soils, Cd appears to pose the greatest heavy metal toxicity problem in Sweden today.

Nitrogen Chemistry

The chemistry of N plays an important part in the interactions between acidic deposition and forest soils. Nitrogen is a major cause, along with S, of the acidity in precipitation due to the formation of HNO_3 in the atmosphere. Upon interaction with the terrestrial ecosystem, N is readily taken up by vegetation and incorporated into organic compounds. This is especially true in forested ecosystems where N is usually a limiting nutrient and therefore readily taken up by the tree roots. Johnson et al. (1982) recently compared N and S cycles in forests and stated both elements

are accumulating in forests at the Walker Branch Watershed, and are involved in protein synthesis. These two elements differed, however, in that N supplies were limiting, whereas S was in excess of vegetation demands. They summarized the behaviour of these elements as (a) N cycling being dominated by biological processes whereas (b) S cycling is dominated by geochemical processes.

Total N content is usually reflected by total organic matter content in forest soils. Decreased rates of organic matter decomposition due to acidic deposition would imply an immobilization of critical nutrients, particularly N, in the undecomposed organic material. On the other hand, environmental conditions favoring the decomposition and mineralization of soil organic materials would increase the production of HNO_3 and organic acids in soils. Ulrich (1981) referred to this relationship when he recently described acidic deposition-induced ion decoupling processes for German forest soils. In discussing the internal H^+ ion transformation in soils, he stated, "Due to the quantitative importance of nitrogen in this transformation, we can state in simplified form that, as a general rule, nitric acid occurs with mineralization, while nitric acid is absorbed with ion absorption."

Nilssen et al. (1982) pointed out that N is generally the nutrient taken up in greatest amounts by plants. Since N may enter the roots as NH_4^+ or NO_3^-, this element plays a critical role in determining the cation/anion balance of soil and plant solutions. They stated that in temperate and boreal forests, N is primarily taken up as NH_4^+, with little nitrification occurring. Uptake of N by tree

roots as NH_4^+ should be mainly associated with a net release of H^+. Complete mineralization of organic matter would counteract this acidity. Temporal differences in these two processes, however, could lead to periods of increased acidity prior to complete mineralization.

Galloway and Dillon (1982) discussed the role of N in the acidic deposition issue. They pointed out that the major forms of N in wet deposition are NH_4^+ and NO_3^-, with dry NO_x deposition considered to be rapidly oxidized to HNO_3 in the soil environment. They summarized the fate of NH_4^+ in terrestrial ecosystems as (a) oxidation to NO_3^-, with the subsequent production of two equivalents of acidity, (b) uptake by roots producing one equivalent of acidity for each equivalent of NH_4^+ taken up, or (c) discharge from soil solutions into lakes. They showed data indicating most NH_4^+ deposited is retained in the watershed, therefore having an acidifying effect by the first two processes listed.

These authors summarized NO_3^- retention mechanisms in the watershed as (a) assimilatory reduction or uptake producing a maximum of one equivalent of alkalinity for each equivalent of NO_3^- taken up, (b) dissimilatory reduction as denitrification or ammonification which produces a maximum of two equivalents of alkalinity for each equivalent of NO_3 reduced, and (c) discharge from soil solutions to lakes or streams. They pointed out that the amount of acid consumed in the first two processes is greater than the NO_3 retained; therefore the alkalinity produced only partly counters the associated strong acids. To fully understand these processes, the cations and anions associated with NH_4^+ and NO_3^- in deposition and soil solutions must be known.

Several efforts have been made to apply modeling techniques to N cycles in terrestrial ecosystems. Aber et al. (1982) reported on work utilizing the JABOWA and FORTNIT simulation models to describe the effects of acid precipitation on soil nitrogen and forest productivity. They pointed out that, to date, acid precipitation has not been shown to change forest production. Five factors suggested as delaying or counteracting a growth response are (a) acid precipitation may not significantly acidify soils compared to natural processes, (b) pH may not affect N mineralization, (c) decreased N mineralization may offset N inputs, (d) short-term N depletion may be compensated for by translocation of N in tissue, and (e) the vegetation may be tolerant of N depletion. Their results from computer simulation models suggested that since N is a limiting nutrient, acid precipitation impacts on pH-sensitive N availability processes may potentially alter forest growth.

Ågren (1982) used modeling techniques to evaluate C and N cycles in Scots pine and Norway spruce. Of prime concern in this research was the evaluation of acidic deposition N additions to soils versus decreased N mineralization rates. His results showed site quality to be critical to impact evaluation. For example, poorer forest sites were considered most susceptible to decreased mineralization but had the greatest capacity to absorb incoming N before reaching saturation, possibly taking several hundred years to reach saturation at low deposition rates.

Temporal variations in climate are also important to N effects on soil acidification. During dry periods, much of the N and S deposited remains in soils and vegetation. With adequate aeration, these substances are oxidized and cause runoff during the following rainy period to be extremely acid (Johnson et al., 1982). Likewise, fluctuations between periods of warm, dry years and cool, moist years can induce acidification incidents due to mineralization surges associated with warmer temperatures (Ulrich, 1982).
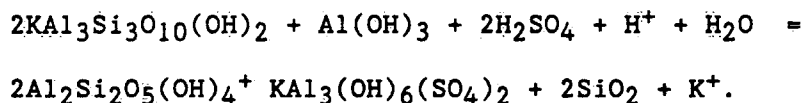
Sulfur Chemistry

Anthropogenic S emissions and the effects of elevated atmospheric S has become a key focal point for ecological research on the acidic deposition issue. Although N contributes significantly to acidic deposition, S deposition impacts and S cycling have received a greater emphasis in acidic deposition studies to date. Much of the impetus for this concern is due to (a) anthropogenic sources accounting for the majority, roughly 90 percent in the northeastern United States (Evans et al., 1981), of the S in the atmosphere, (b) the rare occurrence of S deficiencies in forest ecosystems, (c) the marked ability of some forest soils to accumulate S, and (d) the significant impact of soil solution SO_4^{2-} on cation mobility. Mollitor and Berg (1980) felt that current SO_4^{2-} inputs to Adirondack forests pose a real threat to the nutrient status of those ecosystems. Their work showed SO_4^{2-} to be extremely mobile in soil solutions and directly related to the leaching losses of basic cations from soil profiles.

The potential benefits of excess S are not clear. Some evidence exists to suggest the close relationship between S and N in plant protein synthesis may cause atmospheric S inputs to benefit N fertilized forest sites. This could arise where rapid soil S utilization due to N fertilizer additions resulted in S deficiencies for some soils. Moderate S inputs due to acidic deposition could benefit these N-amended woodlands (Johnson et al., 1982; Turner et al., 1980). Excess SO_4^{2-} may also aid in change balances with regard to plant uptake of cationic nutrients (e.g. NH_4^+). The uptake of SO_4^{2-} by tree roots could reduce the root release of protons into the soil solution (Evans et al., 1981; Turner et al., 1980).

Wolt and Lietzke (1982) examined soils of the Copper Basin area in southeastern Tennessee to evaluate the effects of various levels of acid-sulfate input. Using sites at low, medium, and high intensities of S input downwind from the original smelter operations, they found greater S deposition resulted in decreased soil pH, increased exchangeable acidity, and greater effective cation exchange capacity. Anthropogenic S inputs were not related to changes in exchangeable bases or base saturation.

These workers found some mineralogical evidence indicating greater S inputs resulted in the destruction of gibbsite and the weathering of K-mica to kaolinite. They also proposed that secondary sulfate mineral formation could increase the acid buffering capacity of these soils by the dissolution of hydroxy-Al and the formation of an Al-hydroxy-sulfate compound. Ulrich et al. (1980) discussed a similar mechanism. Wolt and Lietzke (1982) postulated that the

reaction could result in alunite formation by the thermodynamically feasible reaction,

$$2KAl_3Si_3O_{10}(OH)_2 + Al(OH)_3 + 2H_2SO_4 + H^+ + H_2O =$$

$$2Al_2Si_2O_5(OH)_4^+ KAl_3(OH)_6(SO_4)_2 + 2SiO_2 + K^+.$$

Recent publications by Johnson and coworkers (1982) have highlighted the important distinction which exists between the processes of soil acidification and cation leaching in soils. Although both processes may occur simultaneously as a result of acidic phenomena. Soils may adsorb both H^+ and SO_4^{2-} which would increase permanent cation exchange capacity, and therefore decrease pH, base saturation, and pH-dependent cation exchange capacity, yet have no effect on net cationic nutrient losses. Similarly, soil organic matter humification increases the soil exchange capacity but does not contribute to cation content. Thus it is feasible that soil acidification could occur without increases losses of bases by leaching.

On the other hand, acidic deposition may increase base cation release due to an acid-induced accelerated rate of mineral weathering. This source of cations could effectively offset any declines in base saturation or pH. The result would be accelerated cationic leaching without a simultaneous acidification of the soil.

Dillon et al. (1982) measured the input and output of elements for 11 lakes and 35 watersheds in Sudbury and Muskoka-Haliburton, Ontario in Canada. Their results and observations suggest SO_4^{2-}

precursors and strong acid inputs measured by bulk precipitation samplers (i.e. by collection in continuously open containers) underestimated total inputs. They concluded deposition of SO_2 was the most likely explanation for the discrepancies in element balances.

Kelley and Johnson (1982) treated loblolly pine seedlings with N and S additions in a greenhouse pot experiment using a Typic Hapludult soil from Tennessee. They found that mixing and warming the study soil greatly increased availability by stimulating S mineralization. It was stated that intensive site preparation in the field has much the same effect on soil and may have analogous consequences on S availability.

Lee et al. (1982) used open-top field chambers to treat agricultural soils with various levels of SO_2 to examine the effects of this form of atmospheric S inputs on soil acidification and exchangeable Al content. Ambient conditions were 0.002 ppm SO_2 in the atmosphere with a soil pH of 5.63 and trace amounts of exchangeable Al. Increased SO_2 treatment levels induced simultaneous increases in exchangeable soil Al. Soil pH decreased significantly only after exposure to the 0.24 ppm treatment. The concentration of SO_2 in treatments revealed a significant, linear, and positive correlation with soil SO_4^{2+} levels.

Johnson and Henderson (1979) conducted a laboratory study to examine the hypothesis that SO_4^{2-} accumulating in forest ecosystems established on highly weathered soils was due to soil SO_4^{2-} adsorption. Although high levels of adsorbed SO_4^{2-} were detected, further SO_4^{2-} adsorption could not be induced.

Subsequent research on the same soil series was conducted by Johnson et al. (1981) utilizing (a) soil samples beneath and adjacent to an old house, (b) lysimeter studies, and (c) SO_4^{2-} salt applications. They concluded from these investigations that SO_4^{2-} had accumulated, was accumulating, and would continue to accumulate in the Fullerton series soil on Walker Branch Watershed. Critical unresolved questions identified in their conclusions were: (a) Why did laboratory and field results differ? (b) How long can those soils continue to accumulate SO_4? and (c) If atmospheric S inputs were reduced, would the adsorbed insoluble pool of SO_4^{2-} become soluble?

Johnson et al. (1982) recently synthesized the results from much of the work done on S cycling in the Walker Branch Watershed hardwood forest. These studies indicate that the soil compartment has the largest pool of total S, with available forms far in excess of tree S requirements. Total S input was estimated as 25 to 30 kg S ha^{-1} yr^{-1} with roughly 50 percent attributable to dry deposition. Of the total S input to the forest floor (38.6 kg ha^{-1} yr^{-1}), 73 percent was in solution and 80 percent was soluble SO_4^{2-}. The entire ecosystem was accumulating 15 to 17 kg S ha^{-1} yr^{-1} with only about 2 kg ha^{-1} yr^{-1} attributable to the vegetation component. Most of the annual S accumulation (and 90 percent) was due to mineral soil adsorption in Fe and Al oxide-rich B horizons. They concluded that the S cycle in this forested ecosystem was dominated by geochemical processes.

Singh et al. (1980) treated forest soils of southern Norway with simulated acid rain to examine SO_4^{2-} mobility. It was found that

SO_4^{2-} mobility was determined by the soil sesquioxide content, and specifically the Al content for the soils studied. The authors suggested S accumulation in soils may, by specific adsorption of SO_4^{2-}, increase cation exchange capacity and promote the retention of cations.

Although much of the concern has been for inorganic SO_4^{2-} in soil chemical investigations regarding S, David et al. (1982) found that organically bound S averaged 92 percent of the total S pool in a Beckett soil from the Huntington Forest in the Adirondack Mountains of New York. In this study they measured total S, carbon-bonded S, ester-SO_4^{2-}, and inorganic SO_4^{2-} in the O1, O2, A2, B21h, B22hir, B3, and C1x horizons for soils supporting both hardwood and conifer forests. The highest SO_4^{2-} levels were found in B22hir and B23 horizons, with the softwood site having greater SO_4^{2-} than was detected from the hardwood site. Carbon-bonded S was the dominant organic form of S, averaging 74 percent of total soil S. Both organic and carbon-bonded S decreased with depth in the profile. Ester SO_4^{2-} averaged 18 percent of total S and showed no significant change with depth. The authors stressed the importance of considering organic S in future research with particular concern for S transformations in forest soils.

Mitchell et al. (1981) pointed out that deposition, soil sorption capacity, leaching, oxidation-reduction potential (Eh), pH and decomposition are processes affecting S fluxes and transformations between organic and inorganic forms of terrestrial and aquatic

ecosystems. They suggested that monitoring S fluxes and transforma-
tions may provide and index to the acidification process in these
ecosystems.

David et al. (1982) pointed out that organically combined S
constituted an average of 93 percent of the total S in Adirondack
forest soils. The authors stressed the importance of recognizing
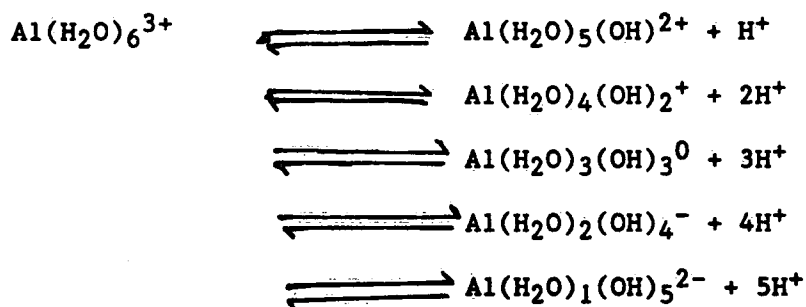other S fractions in soils besides SO_4^{2-} with regard to ecological
studies.

Aluminum Chemistry

The role of Al in the chemistry of soils has been the subject of
extensive research during the last century. Most of this work was
done by plant and soil scientists in an attempt to understand and
improve fertilization and liming practices on agricultural croplands
(Pearson, 1967). More recently, efforts to evaluate nutrient cycles
in forested ecosystems, and specifically the relationship between soil
chemistry and tree nutrition, have revealed the significance of Al in
forest soil solutions. Due in part to the climate, type of vegetative
cover, and limited management practices on forested landscapes, soils
supporting these plant communities are commonly acid. It is well
known that the predominance of Al in soil chemical phenomena increases
with increased soil acidity. Research designed to evaluate the
impacts of acidic deposition on forested ecosystems has begun to
reveal the important role played by Al in observed and potential
ecological phenomena. Increased Al activity can be an indirect

consequence of acidic deposition-induced environmental changes. However, elevated Al levels in soils, soil solutions, and freshwater environments can have direct, toxic consequences for the biological community (e.g. tree roots, soil microorganisms, and aquatic biota).

The form and activity of Al in aqueous solutions is extremely sensitive to pH variations. The Al ion in solution is surrounded by six water molecules which undergo a series of stepwise hydrolysis reactions as a function of pH. Lindsay (1979) showed the reaction series to be:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+$$

$$\rightleftharpoons Al(H_2O)_4(OH)_2^+ + 2H^+$$

$$\rightleftharpoons Al(H_2O)_3(OH)_3^0 + 3H^+$$

$$\rightleftharpoons Al(H_2O)_2(OH)_4^- + 4H^+$$

$$\rightleftharpoons Al(H_2O)_1(OH)_5^{2-} + 5H^+$$

This series represents a simple $Al-H_2O$ system but points out a mechanism by which Al can buffer soil solutions to changes in pH. Increased H^+ inputs may not result in a pH decline but rather an increase in the ionic change of Al, often coinciding with an increased mobility for this element.

Buffering of H^+ inputs from acidic deposition may also involve the formation of a new Al compound containing S due to the greater concentrations of S in acidic deposition-impacted soils. Wolt and Lietzke (1982) suggested the formation of alunite, $KAl_3(OH)_6(SO_4)_2$, by the reaction described earlier in the Sulfur Chemistry Section.

Ulrich et al. (1980) considered the reaction, $AlOOH + 2H^+ + SO_4^{2-}$ $AlOHSO_4 + H_2O + H_2O$, to be responsible for soil buffering along with the production of Al ions.

The rate of reaction between soil Al and acid inputs is dependent on the fraction of Al with which these atmospheric inputs react. Table 2 illustrates the various soil Al fractions and their reaction rates with H_2SO_4 as presented by Cronan (1980). For solutions percolating through soils with limited residence time in the soil, the first three Al fractions play the primary role in Al release.

Table 2. Soil aluminum fractions which may release inorganic aluminum to the soil solution in forested ecosystems exposed to acid precipitation

Aluminum Fraction *	Reaction Rate with H_2SO_4
Exchangeable aluminum	Rapid
Amorphous aluminum hydroxide	Moderately rapid
Organic-aluminum complexes	Moderately rapid
$Al_x(OH)_y$ interlayers in expansible clay minerals (e.g. vermiculite)	Relatively slower
Aluminum in clay lattices	Relatively slower
Undecomposed aluminum silicates	Relatively slower

*The fractions are ranked according to their hypothesized ability to release dissolved aluminum to a H_2SO_4-dominated soil solution.

In studies where simulated acid rain treatments were applied to soil microcosms, Cronan (1980) found increased treatment acidity resulted in greater Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ leaching but Al losses did not increase. He postulated that lack of increased Al reflected a kinetic lag which occurred in the mobilization of this element.

McFee and Cronan (1981) and Cronan (1980) discussed evidence suggesting an alteration of Al chemistry has occurred in podzolized forest soils leached by atmospheric H_2SO_4 inputs. For most soils subjected to podzolization, a soil weathering process, Al and other metals undergo solution and organometallic complexation in the surface horizons. These materials leach downward with one result being the transport and accumulation of Al into the B2 soil horizon due to changes in the soil chemical environment with depth in the profile. This mechanism effectively removes Al from solution such that very little is detected in groundwater supplies. By contrast, it appears that acidic deposition-impacted, podzolic soils show a continuous increase in dissolved Al concentration as water percolates through the profile, which is ultimately reflected as elevated results could be (a) a small but significant decrease in soil solution pH throughout the profile which increases Al mobility, or (b) whereas organic acid acidity is removed from solution by other mechanisms, mineral acid neutralization may be primarily controlled by H^+-ion exchange and weathering reactions which are not kinetically or thermodynamically favored in acid soils leached with solutions of pH 4 or 4.5.

McFee and Cronan (1981) also pointed out an important distinction between "acidic deposition" and "soil acidification". The first term describes the atmospheric input of acids, acid precursors, and associated substances to the earth's surface. The second term describes a process which is always occurring in soils of humid regions, regardless of the level of acidic substances in the atmosphere.

Soil acidification is a naturally occurring process in the vast majority of forest soils. The sum total acidifying effect of natural pedogenetic processes in humid climates probably far exceeds the effects of acidic deposition alone. What needs to be determined is whether "acidic deposition" contributes a significant increment toward increasing natural "soil acidification" processes.

The recent research on Al chemistry discussed above provides some insight into the previously discussed two-step process of 'acid rain' neutralization in a Hubbard Brook watershed proposed by Johnson et al. (1981). In this process, H^+-ion acidity is neutralized by soil aluminum which is the dominant mechanism in the upper reaches of the stream. Streamwater acidity and inorganic monomeric Al decreased, while organically complexed Al increased steadily in a downstream direction. They pointed out that earlier studies at Hubbard Brook showed the humus layer and B2 soil horizons to be the primary source of Al for acid waters percolating through the soil.

Stottlemeyer (1981) reported a rapid neutralization of acid precipitation (weighted mean pH ranged 3.87 to 4.88) in the upper reaches of a watershed in northern Michigan. Very little Al was

detected in these streamwaters with pH values averaging 6.0 to 7.0; however, one acid rain event caused the pH to drop to 5.5, which also showed a sharply increased Al level in streamwater.

With regard to forest productivity, the concern for elevated levels of soil solution Al centre around the toxic effects of this element on soil microorganisms are evident in decreased rates of organic matter decomposition, while trees may show foliar damage and mortality. Matzner and Ulrich (1981) pointed out the importance of the Ca/Al molar ratio in soil solutions. They also reported that soil solution Al concentrations in the Solling forestlands have increased over the last decade. Concentrations of Al in soil solutions from beech stands roughly have doubled (from 1 to 2 mg/l to 2 to 5 mg/l) while beneath spruce there has been nearly a tenfold increase (from 1-2 mg/l to 15-18 mg/l). Ulrich (1982) stated that below pH 4.2 in soil solutions, even Al-tolerant tree species may show toxicity symptoms. The degree of toxicity below this pH depends on the Ca/Al molar ratio and the presence of dissolved organic material available to chelate Al ions. When the Ca/Al molar ratio is below 1.0, Al toxicity is thought to become a problem. Complete growth inhibition occurs below Ca/Al molar ratios of 0.15 in soil solution.

Ulrich (1982) stated that Al ions in the soil solution may damage the endodermis in tree roots, the result being the loss of control over the ionic composition of the solution entering the plant's xylary vessels. Plants cannot separate damaged from undamaged roots, nor can they originate new roots from the undamaged parts under these conditions. He listed the possible consequences of this condition as

(a) secondary diseases originating from pathogen spore transport into the xylem, (b) damage by root decomposing fungi increasing the windthrow hazard, (c) nutrient deficiencies due to lack of control over ionic composition of transpiration stream, (d) decreased production of secondary plant substances which inhibit insect and fungi attack, and (e) reduced buffering ability to acid inputs by leaf and bark surfaces. Increased susceptibility to drought stress also results from damage to root systems.
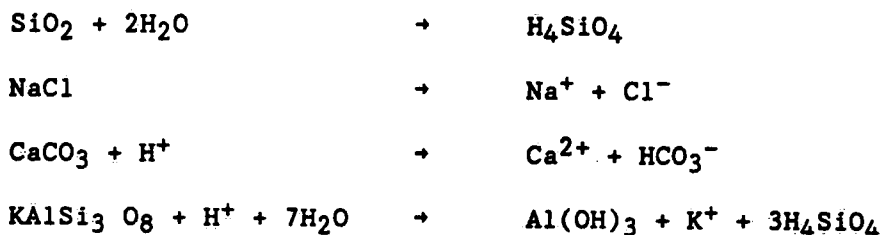
Soil Buffer Mechanisms

Each of the following mechanisms may be involved in the buffering of the soil and solution against excess acidity associated with acid precipitation. The term "excess" indicates the difference in proton load between the solution under consideration and precipitation in equilibrium with atmospheric CO_2. It should be emphasized that the processes mentioned are not mutually exclusive. On the contrary, various mechanisms may contribute simultaneously to the overall buffer capacity of a particular soil system.

(1) <u>Weathering Reactions</u> - Weathering of rock minerals can be represented by various reaction equations, depending on the mineralogical and chemical composition of the parent material. In most cases, however, weathering will consume hydrogen ions and can thus act as a sink for excess acidity entering the system (Norton, 1980; Ulrich, 1980). Exceptions should be made for those reactions
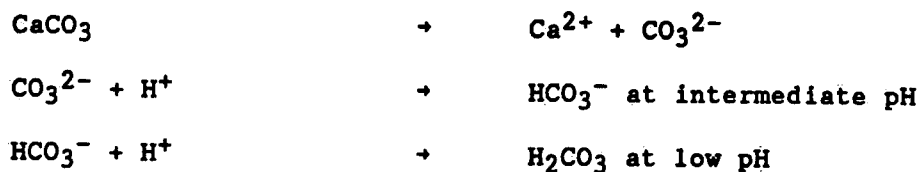
during which neither cations nor anions are released, or whereby the chemical equation does not include H^+ or OH^- ions (Norton, 1976).

A few examples of each type of weathering reaction are given below:

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4$$

$$NaCl \rightarrow Na^+ + Cl^-$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

$$KAlSi_3 O_8 + H^+ + 7H_2O \rightarrow Al(OH)_3 + K^+ + 3H_4SiO_4$$

Except in the case of calcareous soils, weathering generally proceeds at a slow rate. It is therefore primarily of importance as a buffer against slow acidification, while playing a rather limited role in countering sudden heavy proton loads in solution.

However, in soils underlain by calcareous rocks (e.g. calcite and dolomite), dissolution of carbonate minerals constitutes an important pH buffer mechanism. The proton consuming reactions can be represented as following:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \text{ at intermediate pH}$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \text{ at low pH}$$

The carbonate ion released during dissolution of calcite (or dolomite) is stable only at a solution pH higher than 10 (Stumm and Morgan, 1982). As most soils, and more particularly forest soils, have a pH

far below this value, carbonate is rapidly converted into a more stable form. Depending on the ambient solution pH, either bicarbonate or carbonic acid is formed. Each calcite molecule entering into solution thus has the capacity to neutralize one or two protons depending on the inherent system acidity.

(2) <u>Bicarbonate Buffering</u> - Soil buffer capacity is also related to the activity of bicarbonate in solution. Apart from carbonate weathering, inorganic carbon in soil water may originate from microbial and root respiration in the soil. The protons released during the dissolution and hydrolysis of the carbon dioxide formed, contribute to the natural acidity of forest soil solutions. Excess protons entering the solution, however, disrupt chemical equilibrium and force the reaction in the direction of carbonic acid formation. The acid neutralizing capacity of the soil solution is a function of its bicarbonate concentration and the inherent system pH (Stumm and Morgan, 1982). As one will recall from an earlier discussion on soil respiration, the amount of dissolved bicarbonate varies with the CO_2 partial pressure in the soil and the ambient pH. It can at any time be expressed in terms of these system characteristics, the dissolution constant, and the first dissociation constant.

$$\text{Acid neutralizing capacity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

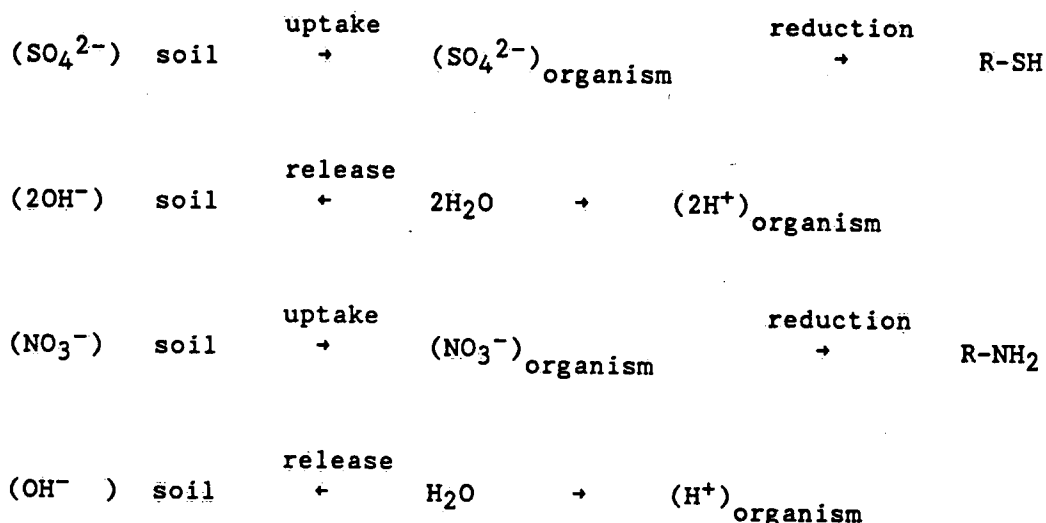$$HCO_3^- = \frac{(Kh)\ (pCO_2)\ (K_1)}{(H^+)}$$

(3)   Nitrogen and Sulfur Reduction - Soil pH buffering is also achieved through uptake or reduction of the sulfate and nitrate anions following their entry into the soil. It is proposed by Kilham (1982) as the mechanism responsible for the alkalinization of acid rain impacted lakes. He argued that the alkalinization reactions which occur as a result of biological uptake or reduction of the added nitrate and sulfate, are sufficient to completely neutralize the hydrogen load of acid rain. Hemond (1980) made parallel observations studying bog ecosystems. The reasoning is simply based on the application of the First Law of Thermodynamics and the Principle of Electroneutrality. The Principle of Electroneutrality requires that a charge balance be maintained between plants and their environment. As was mentioned earlier, the uptake of anions by plants or microorganisms results in the release of an equivalent amount of hydroxide (Nye, 1981).

The reactions can also be viewed by examining differences between initial and final chemical state of the system (application of the First Law of Thermodynamics). Both nitrate and sulfate represent the maximum oxidation state of nitrogen and sulfur, respectively. Any chemical or biological transformation, irrespective of the pathway followed, is one of reduction and hydrogen consumption.

A basic distinction can be made between assimilatory and dissimilatory reduction. The first term refers to the uptake and transformation processes by either plants or microorganisms for the purpose of biomass buildup. Both sulfur and nitrogen are incorporated

in the living tissue in reduced form. A charge balance following uptake and reduction will be maintained by consumption of the appropriate amounts of hydrogen ions (Reuss, 1977).

$$(SO_4^{2-}) \text{ soil} \xrightarrow{\text{uptake}} (SO_4^{2-})_{organism} \xrightarrow{\text{reduction}} R-SH$$

$$(2OH^-) \text{ soil} \xleftarrow{\text{release}} 2H_2O \rightarrow (2H^+)_{organism}$$

$$(NO_3^-) \text{ soil} \xrightarrow{\text{uptake}} (NO_3^-)_{organism} \xrightarrow{\text{reduction}} R-NH_2$$

$$(OH^-) \text{ soil} \xleftarrow{\text{release}} H_2O \rightarrow (H^+)_{organism}$$

The term dissimilatory reduction is used when little free oxygen is present in the soil, and anaerobic bacteria utilize sulfate or nitrate as electron acceptors. Once again, the overall process yields one hydroxide ion for the consumption each anionic equivalent, which causes the soil pH to rise.

$$4NO_3^- + 5(CH_2O) \rightarrow 2N_2 + 3H_2O + 5CO_2 + 4OH^-$$

$$SO_4^{2-} + 2(CH_2O) \rightarrow H_2S + 2CO_2 + 2OH^-$$

Biological uptake of added nitrate or sulfate is not an unlikely contributor to the overall buffer capacity in a wide variety of forest
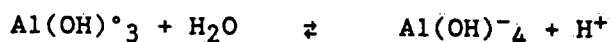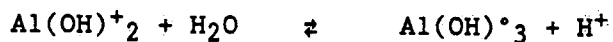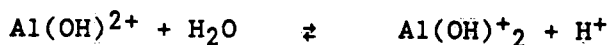
ecosystems. Nitrogen is indeed considered to be a growth limiting factor in a lot of forests throughout the world while sulfur deficiency has been reported in forests of the northwestern United States and eastern Australia (Abrahamson, 1980; Johnson, 1981). In these areas, immediate uptake by the vegetation of all nitrate and/or sulfate entering the soil with rainwater could thus easily counter the acidifying effect of the associated protons in solution.

(4) Cation Exchange Reactions - Mobility of cations through the soil profile is often limited by adsorption to the cation exchange complex. It results from the electrostatical forces exerted by the negative charges associated with clay minerals and soil organic matter. Part of the negative charge is permanent and originates from isomorphic substitution within the silicate structure. The other part of the charge is pH-dependent and changes with the dissociation of organic compounds and silicates (Coleman, 1967). The relative abundance of a particular cation on the exchange complex is controlled by the ionic strength and species composition of the solution and the selectivity constant. The latter term is a reflection of the differential attraction of the exchange sites towards different cations. Indeed, depending on individual charge and size, particular cations are held more tightly. They have the ability to displace less strongly attracted cations and take their place on the exchange sites (Bache, 1980). Such exchange reactions give rise to another important

pH buffering mechanism in the soil. Incoming protons, by their inherent small size are strongly adsorbed and easily displace other cations from the exchange sites. Their cation displacing efficiency, and the importance of the cation exchange buffer reactions, are influenced by the acidity and the total base content of the soil.

Soil with high CEC and with a large portion of the exchange sites occupied by exchangeable bases are strongly buffered against changes in pH (Klopalek et al., 1980; McFee, 1980; McFee et al., 1977). As total base content declines, cation displacement becomes less likely and susceptibility of the site to acidification increases, provided of course that the system pH is higher than the pH of the incoming solution. Soils whose acidity approaches that of the rainfall are considered insensitive to further acidification. However, due to their low base status, these soils are not expected to buffer the pH of the percolating water (Johnson, 1981).

(5)   Aluminum Buffering - Aluminum compounds may also play an important role in buffering the soil pH against external acidification. No consensus has thus far been reached among soil chemists regarding the exact nature of the aluminum species. Aluminum may be present as exchangeable monomeric Al or in the form of hydrous oxide polymers (Bohn, 1976; Coleman and Thomas, 1967). In spite of this diversity in Al compounds, acidity control mechanisms can basically be represented by the following simplified hydrolysis reactions:

$$Al^{3+} + H_2O \rightleftarrows Al(OH)^{2+} + H^+$$

$$Al(OH)^{2+} + H_2O \rightleftarrows Al(OH)^+_2 + H^+$$

$$Al(OH)^+_2 + H_2O \rightleftarrows Al(OH)^{\circ}_3 + H^+$$

$$Al(OH)^{\circ}_3 + H_2O \rightleftarrows Al(OH)^-_4 + H^+$$

The relative abundance of a particular hydrolyzed form is a function of the system acidity (Bohm, 1979):

Dominance range

pH	<4.7	4.7-6.5	6.5-8	>8
Species	Al^{3+}	$Al(OH)_2^+$	$Al(OH)_3^{\circ}$	$Al(OH)_4^-$

Excess protons entering the soil generally drive the equilibrium reactions to the left, and decrease in solution pH is avoided. Similarly, increased hydrolysis will buffer the solution against sudden alkalinization of the system.

SOIL SENSITIVITY TO ACIDIC DEPOSITION

An information need which has emerged as being of imminent practical importance in addressing the acidic deposition issue is the evaluation of ecosystem sensitivity to atmospheric inputs. Much of the work done in this area has examined the sensitivity of either (a) plants, (b) soils, (c) bedrock, or (d) aquatic ecosystems. With regard to forest productivity, sensitivity to acidic deposition can be approached either as direct impacts on vegetation or impacts on forest productivity due to soil-mediated interactions. Current knowledge on forest effects has shown soil-mediated interactions to be a key component to sensitivity assessment for acidic deposition. The reader is referred to the 1978 NATO conference proceedings (Hutchinson, and Havas, 1980) for a collection of papers by highly respected soil scientists involved in this area of acidic deposition research.

The conference of an international group of experts on the soil acidification issue which was convened in Sweden to assess the current state of knowledge on acidic deposition, in their final report (Ecological effects of acid deposition, 1982), cited sandy, well drained soils of pH 5 to pH 6 as being most susceptible to acidification. They defined acidification as a loss of neutralizing capacity by the soil. In regard to forest ecosystems, they believed the greatest risk was for forests on thin, silty or sandy acidic soils overlying non-calcareous bedrock.

Wiklander (1980) defined soil acidification as a decrease in pH and base saturation due to internal and external H^+ ion sources.

Bache (1980) felt that highly unsaturated, acidic soils were most susceptible to further acidification but occurred in areas where this would not result. He stated, however, that slightly acid, poorly buffered, shallow sandy soils may show a striking loss in productivity, particularly for forested areas, with relatively little acidification.

In some cases, the assessment of ecosystem sensitivity to acidic deposition may be highly correlated to bedrock properties. Shilts (1981) has prepared an assessment of the sensitivity of Canadian bedrock types to acid precipitation. Hendry et al. (1980) looked at the sensitivity of bedrock types in the eastern United States. In their classification scheme for the United States, sensitivity was evaluated based on the percent of highly alkaline rock types underlying the area.

With regard to tree growth, geologic ratings for acidic deposition sensitivity may often be inadequate. Tree roots permeate the upper zone of the regolith and are more directly affected by the physical and chemical properties of forest soils. For soils developing from glacial, alluvial, lacustrine, marine, or aeolian parent materials, bedrock geology information may provide little indication as to the properties of the overlying soil material. Even within the soil, the genesis of distinct horizon sequences can offer complex problems for the classification of these materials, particularly with regard to acidic deposition sensitivity.

McFee (1980) developed a set of criteria to rank soil sensitivity to the effects of acid precipitation. His scheme is based on the

cation exchange capacity of soils, flooding occurrence, and the presence or absence of carbonates in the top 25 cm of soil. Soil sensitivity was evaluated with respect to "... any change brought about by acid precipitation that would be important in the local ecosystem." Three sensitivity groups were designated.

(1) Non-sensitive areas: Soils which are calcareous, subject to frequent flooding, or have an average cation exchange capacity of greater than 15.4 meq/100 g in the top 25 cm.

(2) Slightly sensitive areas: Soils with a cation exchange capacity between 15.4 to 6.2 meq/100 g in the top 25 cm.

(3) Sensitive areas: Soils with a cation exchange capacity less than 6.2 meq/100 g in the top 25 cm.

This model is one of the most frequently cited efforts to date which delineates soils information in U.S.A. with respect to acidic deposition. A primary advantage of this type of classification is the availability of the necessary soils information. The major disadvantages are (a) it is too general for detailed site-specific analyses, and (b) as McFee himself admits, the use of cation exchange capacity alone without base saturation may not be adequate to appraise soil sensitivity. McFee and Cronan (1981) also pointed out this system fails to consider soil sulfate adsorption capacity, the presence of easily weatherable minerals, or differences between low cation exchange capacity soils.

Glass et al. (1982) discussed the sensitivity of crops, soils, forests, rock formations, and surface waters to acid precipitation,

using New York State as an example in their analysis. They utilized McFee's (1980) classification system to rate the soils of New York to acidic deposition sensitivity and found sensitive areas to be concentrated in the Adirondack region, east of the Hudson River, and on Long Island. In addition to the properties suggested by McFee (1980) and McFee and Cronan (1981), they also added the need for information on soil physical characteristics and climate in the analysis.

Gibson and Lindhurst (1982) suggested that research shows soils likely to undergo significant changes in basic cation composition due to acid inputs were: (a) not renewed by flooding or other processes, (b) free of carbonates to a considerable depth, (c) low in cation exchange capacity but have pH values between 5.5 to 6.0 or higher, and (d) not high in sulfate adsorption capacity.

Because most humid climate soils would have lower pH values than 5.5 to 6.0, they believed short-term effects to forest productivity by nutrient losses were unlikely. However, the effects of elevated soil solution Al in acidic soils were considered to be the most likely problem for impacted forest ecosystems.

Regardless of the intent of a classification for forest soil sensitivity, the chemical interaction between incoming precipitation and the soil matrix depends on the initial composition of these components. Ulrich (1980) has described a series of soil buffering ranges which were delineated by soil pH. This classification can be summarized as:

(1) <u>pH 6.5 to 8.3 - Carbonate Buffering Range</u>: soil buffering of incoming H^+ primarily due to the dissolution of $CaCO_3$,

(2) <u>pH 5.0 to 6.5 - Silicate Neutralization Range</u>: soil buffering of incoming H^+ due to the dissolution of silicate minerals,

(3) <u>pH 4.2 to 5.0 - Cation Exchange Neutralization Range</u>: soil buffering of incoming H^+ due to the displacement of bases (e.g. Ca^{2+}, Mg^{2+}) by H^+ (and sometimes by dissolved Al ions due to the H^+ input) from the soil exchange complex,

(4) <u>pH 3.0 to 4.2 - Aluminum Buffering Range</u>: soil buffering of incoming H^+ due to the release of Al^{3+} primarily from soil polymeric hydroxy Al compounds, and

(5) <u>pH below 3.0 - Iron Buffering Range</u>: soil buffering of incoming H^+ due to the formation of Fe ions by release from Fe-oxides.

The dominant soil neutralization mechanism will remain in a steady state as long as the rate of H^+ deposition equals the rate of neutralization. Once the H^+ deposition rate exceeds the rate of neutralization, the dominant mechanism of soil buffering will shift to the next lower pH range.

Klopatek <u>et al</u>. (1980) developed a sensitivity rating to acidic deposition for soils in the eastern United States based on pH, cation exchange capacity, and base saturation. Base content was calculated as the product of cation exchange capacity and base saturation which provided an index to the base reserves in the soil. Soils of low cation exchange capacity and pH values greater than 5.0 were considered most susceptible to further acidification. Soils already

acid were considered critical with respect to the impact on associated freshwater systems due to acidic deposition. This model is similar yet somewhat more comprehensive than McFee's. However, it differs with respect to the mechanics of the computations and therefore direct comparison between the systems is difficult.

A great deal of work has been done in Canada to assess soil sensitivity to acidic deposition. Wang and Coote (1981) and Coote et al. (1981) classified soil sensitivity to acidic deposition for agricultural land in eastern Canada. Their emphasis was on developing a system simple enough to use in the field. Utilizing the relationships between soil base saturation with soil pH, and soil texture with cation exchange capacity, they arrived at three sensitivity classes.

(1) Nonsensitive: All calcareous soils

                                 Clayey with pH below 5.0

                                 Loamy with pH below 5.5

(2) Moderately Sensitive: Sandy with pH below 5.5

                                 Clayey with pH 4.5 to 5.0

                                 Loamy with pH 5.0 to 5.5

(3) Sensitive: Clayey with pH below 4.5

                                 Loamy with pH below 5.0

                                 Sandy with pH below 5.5

This rating is for the upper 15 cm of unlimed soil

Cowell et al. (1981) developed an ecological rating system to evaluate the effects of acid rain on the terrestrial environment of eastern North America. Their classification system recognized

different factors which need to be considered when determining the effects of acidic deposition on forest soils with respect to (a) forest productivity versus (b) soil-mediated aquatic impacts. Table 3 by Cowell et al. illustrates the factors considered important by these authors in evaluating forest soil sensitivity to acidic deposition, specifically in relation to forest productivity. They considered low pH soils (i.e. less than pH 4.5) were most sensitive in this regard since any further loss of cations would be significant to forest growth. Rubec (1981) published information on the characteristics of acidic deposition-impacted areas in Canada with computer summaries of the data as part of the Canadian effort to classify the sensitivity of natural ecosystems.

Johnson (1981) discussed the theoretical impact of increased acidic deposition on groundwaters and soil solutions for selected Alaskan sites. He concluded these solutions already acid were most susceptible to further acidification, the reason being H^+ constitutes a much higher proportion of the total cations in the more acid solutions and will therefore be more likely to accompany the SO_4^{2-} anion in solution. Johnson (1980) also discussed the importance of soil SO_4^{2-} adsorption capacity and sesquioxide content in assessing H_2SO_4 impacts on cation leaching processes.

Johnson et al. (1982) discussed the differences between forest soil sensitivity to cation leaching by H_2SO_4 and HNO_3 inputs. According to the anion mobility concept, the major factor influencing the base cation leaching loss in soils is the mobility of the associated anion in soil solution. These authors suggested sites

sensitive to leaching by H_2SO_4 are low in Fe and Al oxides and clay, but high in pH and organic matter content. These properties lead to less adsorption of SO_4^{2-} by the soil, resulting in greater cation leaching losses. Johnson and Todd (1982) recently discussed methods and applications for soil SO_4^{2-} adsorption analysis. As for sites sensitive to HNO_3 leaching losses, soils with adequate available N for tree growth would cause very little of the atmospheric N to be taken up, resulting in HNO_3 leaching losses being greater from N-abundant forest sites (Johnson et al., 1982).

Troedsson and Nilsson (1980) applied forest soil sensitivity information to the evaluation of areas suitable for the siting of coal-fired power plants in Sweden. They considered the sensitivity of soils for increased acidification to be a function of (a) the use of the land in question (e.g. deciduous versus coniferous forest soils, (b) the texture of the soil, (c) the thickness of the soil layer, (d) hydrological conditions, (e) mineralogical properties, including soil type, and (f) chemical properties.

SUMMARY AND CONCLUSIONS

Acidified rainwater is characterized by a substantial anion load in addition to an elevated hydrogen activity when compared to a solution in equilibrium with atmospheric carbon dioxide. The potential effect of acid rain on soil systems, for that reason, consists of two separate components: increased leaching loss and soil acidification.

(1) Indirect impacts of acidic deposition on forest productivity would likely occur through alterations in forest soils. The most important factors which may affect tree growth appear to be (a) added nutrients (e.g. N and S), (b) accelerated leaching of base cationic nutrients (e.g. Ca, Mg, K), (c) changes in organic decomposition and nitrification processes, and (d) mobilization of toxic elements (e.g. Al).

(2) The acidic deposition phenomenon has been associated with greater levels of heavy metals (e.g. Pb, Zn, Cu, V, Cr, Ni) in soils and soil solutions due to (a) greater atmospheric inputs of these substances, and (b) acid-induced alterations in the mobility of these metals.

(3) Atmospheric contributions of N are largely retained in the forest ecosystem through biological utilization. The availability of N is intimately associated with the rate of organic matter decomposition, and the form of N utilized (i.e. NH_4^+ or NO_3^-) plays a critical role in soil acidification processes.

(4) Atmospheric contributions of S to forest soils (a) may be adsorbed by soil sesquioxides, (b) may leach from the soil with an associated cation, (c) could be taken up by tree roots and incorporated into vegetative tissues, (d) may form a solid soil phase with Al, (e) has an important role in determining soil cation exchange capacity, and (f) can become part of a total soil S pool dominated by organic S forms.

(5) Evidence has shown that acidic deposition may increase the level
     of mobile Al in soils with detrimental impacts on terrestrial and
     aquatic ecosystems. In regard to forest species, elevated soil
     solution Al can damage tree roots and alter their physiological
     functioning.

(6) The mobility and toxicity of Al in soil solutions is a strong
     function of soil solution pH and the level of organic materials
     in solution. The level of Ca and the Ca/Al ratio in soil
     solutions also plays an important part in Al toxicity to
     biological processes. The source of Al from podzolic forest
     soils appears to be dominated by Al from humus and B2 horizons.

(7) Soil sensitivity to acidic deposition must be clearly defined
     with regard to the impacts considered (e.g. forest productivity,
     soil acidification, cation leaching, aquatic effects) in order to
     (a) determine the critical parameters to measure, and (b)
     correctly interpret the soil's sensitivity.

(8) The various schemes currently available to assess soil
     sensitivity to acidic deposition primarily utilize the following
     parameters: (a) soil pH, (b) cation exchange capacity, (c) base
     saturation, (d) soil texture, (e) soil depth, and (f) soil
     organic matter content. The ability to adsorb SO_4^{2-} is also seen
     as a critical parameter.

The magnitude of nutrient loss induced by acid rain is largely
determined by the concentration and mobility of the anions dissolved
in rainwater. Nitrate is usually very mobile in the soil, whereas the
mobility of sulfate may be restricted by adsorption to Fe and Al

sesquioxides in the soil. Both anions, however, are in some instances removed from the soil solution by plant uptake, before they can trigger additional cation loss.

Buffering of the soil system against acidification from the incoming proton load may result from one or more of the following hydrogen neutralizing reactions: (a) weathering, (b) bicarbonate buffering, (c) N and S reduction, (d) cation exchange, (e) aluminum buffering. None of the buffer mechanisms are mutually exclusive. On the other hand, not all buffer reactions need to be activated simultaneously in order for a given soil to be resistant to acidification. The effect of one buffer mechanism may create favorable conditions for another neutralization reaction, thus increasing the resistance against a change in system pH even more.

Due to these multiple processes by which buffering can take place, soils can be considered highly resilient with respect to acid rain. Thus they should play an important role in diminishing the impact of pollution on the streamwater system.

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Table 3. Acid rain effect on soil sensitivity.

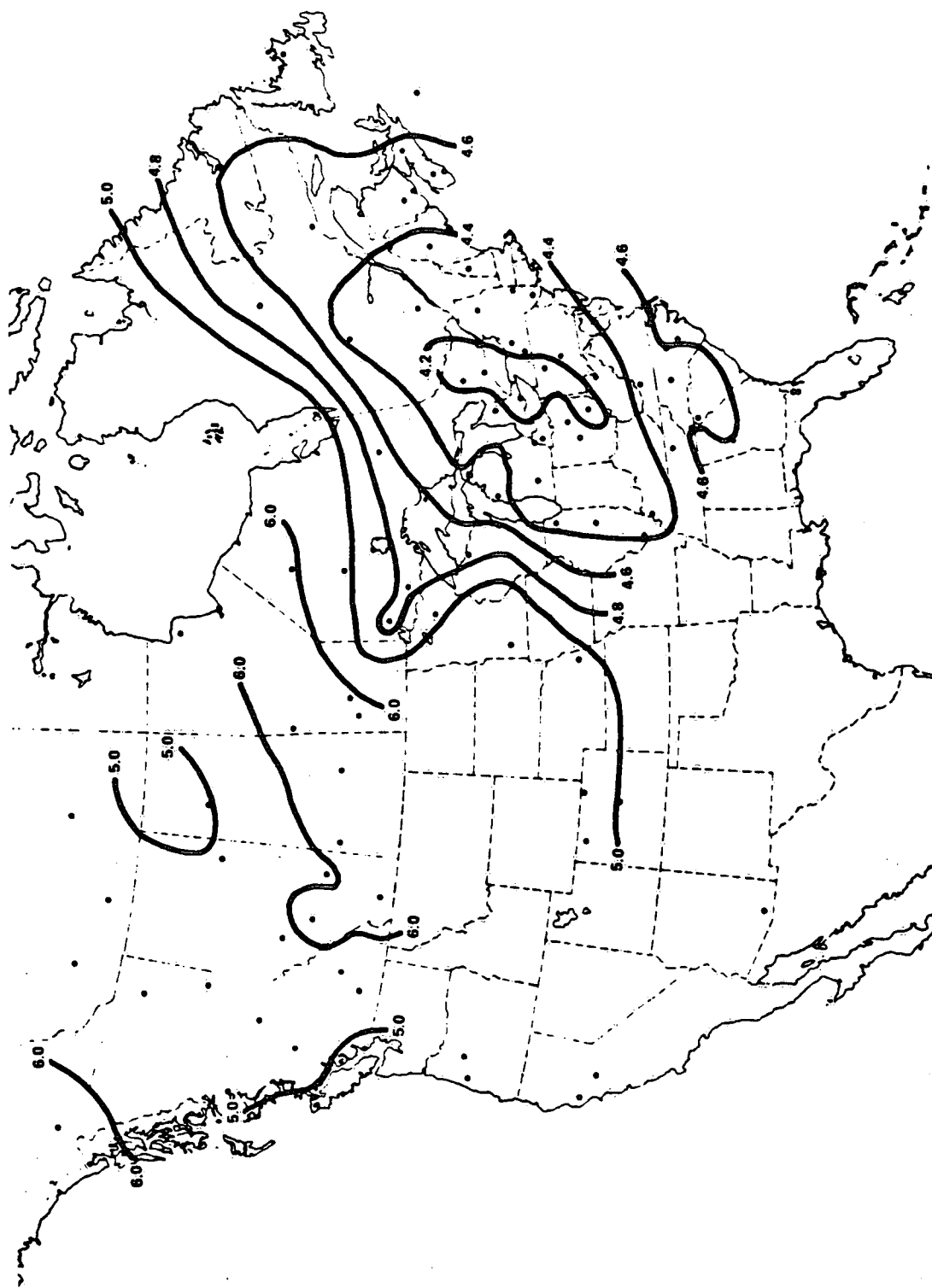| Terrestrial Factors	Sensitivity		
	Low	Moderate	High
Soil Chemistry			
i) Exchangeable Basis Surrogate: Combinations of pH in water (or % Base Saturation) and one of	>15 meq/100 g	6 to 15 meq/100 g	<6 meq/100 g
	clayey, >pH 5.0 loamy, >pH 5.5	clayey, pH 4.5 to 5.0 loamy, pH 5.0 to 5.5 sandy, >pH 5.5	clayey, <pH 4.5 loamy, <pH 5.0 sandy, <pH 5.5
(a) Family Particle Size	all calcareous soils		
or (b) Texture	clay, silty clay, sandy clay (>35% clay)	silty clay loam, clay loam, sandy clay loam, silt loam (10 to 35% clay)	silt, sandy loam, loamy sand, sand (<10% clay)
or (c) Cation Exchange Capacity	>25 meq/100 g	10 to 25 meq/100 g	<10 meq/100 gr
ii) SO_4^{2-} Adsorption Capacity as determined by:	low organic matter AND high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$		high organic matter AND low Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$
Soil Depth*	>25 cm	>25 cm	<25 cm*
*If soil depth is less than 25 cm, Underlying Material is incroporated			
Underlying Material i) Parent Material	carbonate bearing	non-carbonate bearing	non-carbonate bearing
ii) Bedrock Material	limestone, dolomite and metamorphic equivalents, calcarous clastic rocks, carbonate rocks interbedded with non-carbonate rocks	volcanic rocks, shales, greywackes, sandstones, ultramafic rocks, gabbro, mudstone, meta-equivalents.	granite, granite gneiss, orthoquartzite, syenite

From Cowell et al. (1981)

Figure 1. Mean annual pH of precipitation in the United States and Canada, 1979-1980.