

CHEMICAL AND BIOLOGICAL RELATIONSHIPS RELEVANT TO THE  
EFFECT OF ACID RAINFALL ON THE SOIL-PLANT SYSTEM

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ABSTRACT

This paper deals with problems of measuring acidity in rainfall and the interpretation of these measurements in terms of effects on the soil-plant system.

Theoretical relationships of the carbon-dioxide-bicarbonate equilibria and its effect on rainfall acidity measurements are given. The relationship of a cation-anion balance model of acidity in rainfall to plant nutrient uptake processes is considered. It was concluded that average  $H^+$  concentration calculated from pH measurements is not a satisfactory method of determining  $H^+$  loading from rainfall unless the rain is consistently acid. Cation-anion balance or titration methods should be more reliable.

The flux of  $H^+$  ions in soil systems due to plant uptake processes and sulfur and nitrogen cycling is considered.  $H^+$  is produced by oxidation of reduced sulfur and nitrogen compounds mineralized during decomposition of organic matter. Plant uptake processes may result in production of either  $H^+$  or  $OH^-$  ions. Fluxes of  $H^+$  from these processes are much greater than rainfall  $H^+$  inputs, complicating measurement and interpretation of rainfall effects. The soil acidifying potential due to the oxidation of the  $NH_4^+$  in rainfall is examined, with the conclusion that acidity from this source is of a similar magnitude to direct  $H^+$  inputs common in rainfall.

I. INTRODUCTION

Recently evidence has been accumulated supporting the assumption that in some areas the acidity of rainfall has been increasing in recent years as a result of man's activity. This increase has been assumed to

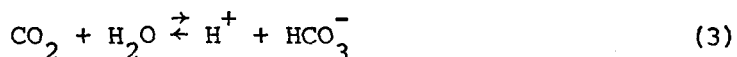
be largely due to increased atmospheric inputs of SO<sub>2</sub> from anthropogenic sources (Likens, 1972; Likens and Bormann, 1974). Various investigators have called attention to possible adverse effects of the acidity on terrestrial and aquatic ecosystems.

Several important aspects of this problem may not have received adequate attention in the scientific literature. It is not the purpose of this paper to support or to contest the validity of the hypothesized adverse ecological effects due to acid rainfall. Rather, the information and concepts presented here are intended to be useful in the formulation of testable hypotheses and to provide a firmer basis for future experiments designed to measure these ecological effects.

## II. CARBON DIOXIDE-BI-CARBONATE EQUILIBRIUM IN RAINFALL

Various investigators have recognized the importance of the carbon dioxide-bicarbonate system in determining the pH of otherwise neutral rainwater (Barret and Brodin, 1955; Pearson and Fisher, 1971; Likens and Bormann, 1974). Unfortunately many of the reporting practices and interpretations found in the literature suggest that this system is not adequately taken into account. Observed bicarbonate levels of rainfall are best understood by considering the equilibrium with atmospheric carbon dioxide. Perhaps a short explanation will be useful to workers concerned with rainwater chemistry and its ecological implications.

The generally accepted standard atmospheric CO<sub>2</sub> concentration is approximately 316 parts per million (ppm) or a partial pressure of  $3.16 \times 10^{-4}$  atmospheres. The reactions of CO<sub>2</sub> and water can be represented by (1) and (2) below and these are summed to obtain (3).



The logarithms to the base 10 of the equilibrium constants at 25°C for (1) and (2) are given by Sillen and Martell (1964) as -1.46 and -6.35 respectively. These are summed to obtain log K of -7.81 for (3), and the equilibrium expression is given by (4).

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]_g} = 10^{-7.81} \quad (4)$$

The  $[H^+]$  and  $[HCO_3^-]$  are the ion activities in moles per liter and are considered to be identical to concentration in this very dilute system. The  $[CO_2]_g$  refers to the partial pressure of  $CO_2$  in atmospheres.

If we restrict the system to atmospheric  $CO_2$ ,  $[CO_2]_g$  becomes  $3.16 \times 10^{-4}$  and (4) can be rearranged to (5).

$$[H^+] [HCO_3^-] = 10^{-11.31} \quad (5)$$

In a pure water system where no source of  $HCO_3^-$  is available other than from  $CO_2$ , and assuming the system to be sufficiently acid so that the direct hydrolysis of water will be insignificant in comparison to the  $[H^+]$  ion derived from the  $CO_2$  equilibrium process, the  $[H^+]$  concentration must equal  $[HCO_3^-]$ . Therefore, from (5) above we can write:

$$[H^+]^2 = 10^{-11.31}$$

$$[H^+] = 10^{-5.65}$$

Thus, we expect a pH of 5.65 (and  $pHCO_3$  of 5.65) for pure rainwater in equilibrium with atmospheric  $CO_2$  at  $25^\circ C$ . The concentration of  $H^+$  and  $HCO_3^-$  would be  $2.2 \times 10^{-6}$  moles per liter and with a rainfall of 1 meter annually, the "loading" would be  $2.2 \times 10^{-3}$  moles per square meter per year. Hydrogen ion loading values in this range are not meaningful as the concentrations within the soil system are controlled by the  $CO_2$  partial pressure in the soil. If rainfall or soil solution is more acid than pH 5.65 for reasons other than the effect of  $CO_2$ , the  $[H^+]$  term in Equation (5) increases and the  $[HCO_3^-]$  decreases. Bicarbonate concentrations decrease to insignificant levels between pH 5 and 4, and in more acid systems  $CO_2$  partial pressures become unimportant in controlling pH.

In basic or near neutral solutions in equilibrium with  $CO_2$ , the  $HCO_3^-$  ion is very important. From the dissociation of water at  $25^\circ C$  we obtain Equation (6).

$$[H^+] = \frac{10^{-14}}{[OH^-]} \quad (6)$$

Substituting (6) into (5) above we obtain (7).

$$\frac{[HCO_3^-]}{[H^+]} = 10^{2.69} \quad (7)$$

Equation (7) states that the concentration of  $HCO_3^-$  in equilibrium with atmospheric  $CO_2$  will be  $10^{2.69}$  or 490 times that of  $OH^-$ . This is a very important relationship and explains why we would not normally

expect to encounter a highly alkaline rain while acid rain is common. Alkaline earth cations entering the atmosphere as oxides, i.e., CaO, Na<sub>2</sub>O, MgO etc., on encountering water droplets would be hydrated to hydroxides. The hydroxides will be rapidly converted to bicarbonate, and at equilibrium 490 bicarbonate ions will be present for each hydroxyl. This provides an effective buffer and prevents highly alkaline conditions from occurring at the ionic concentrations found in rainfall.

A convenient form of Equation (5) above is shown in (8).

$$[\text{HCO}_3^-] = 10^{\text{pH}-11.31} \quad (8)$$

Equation (8) shows clearly that, for a system in equilibrium with atmospheric CO<sub>2</sub> at any given pH, the HCO<sub>3</sub><sup>-</sup> concentration is fixed or, conversely, for any HCO<sub>3</sub><sup>-</sup> concentration the pH is fixed. If data are reported that do not fit this relationship the system may not have been in equilibrium with a CO<sub>2</sub> partial pressure of 3.16 x 10<sup>-4</sup> atmospheres. The graphical presentation in Figure 1 over the range usually encountered in rainfall samples shows clearly that alkaline rainfall could only occur in the presence of very high bicarbonate levels. In most cases the HCO<sub>3</sub><sup>-</sup> ion may be regarded as the alkaline component of rainfall rather than the OH<sup>-</sup> ion. When rainfall containing HCO<sub>3</sub><sup>-</sup> enters an acid soil, the bicarbonate acts as a base, each HCO<sub>3</sub><sup>-</sup> reacting with 1 H<sup>+</sup> ion to form CO<sub>2</sub> and H<sub>2</sub>O as shown by the reverse of equation (3).

The above discussion ignores the carbonate ion. This need not concern us here, because the mole fraction of dissolved carbon in the CO<sub>3</sub><sup>2-</sup> forms is negligible at the pH values considered. As pH increases, CO<sub>3</sub><sup>2-</sup> increases. If pH values above about 8.5 were encountered, this ion would become significant.

Changes in CO<sub>2</sub> partial pressure during sample collection and storage could significantly affect pH and bicarbonate measurements on many rainwater samples. For illustration, I have plotted in Figure 2 the HCO<sub>3</sub><sup>-</sup> and pH values for a series of rainwater samples reported by Egner and Eriksson (1955a, 1955b). The reported pH values are generally about 0.5 unit lower than would be consistent with a CO<sub>2</sub> concentration of 300 ppm but are generally much more consistent with 1000 ppm CO<sub>2</sub>. The 1000 ppm level could easily exist in confined collection vessels or storage containers, but there is no way to be certain that this is the cause of the discrepancy. Granat (1972) has reported a similar and consistent effect in a large number of samples. He suggests that it is due to the presence of undissolved materials that yield the major ions commonly found in rainfall upon dissolution, but he does not suggest any compounds with the necessary properties.

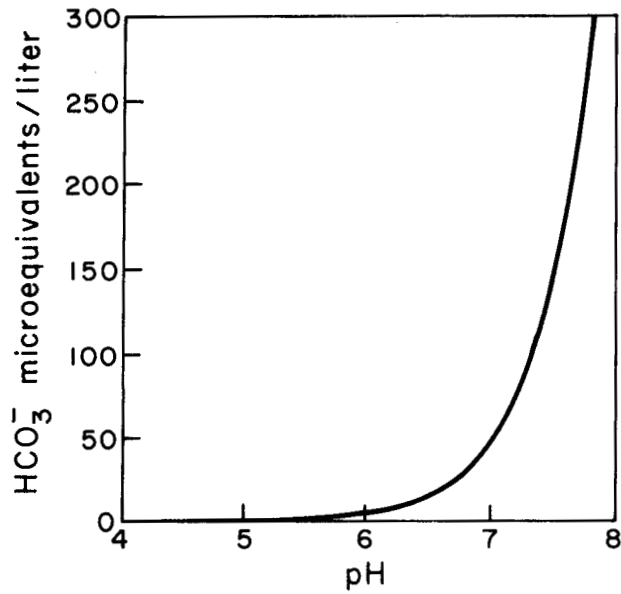


Figure 1. The relationship between pH and HCO<sub>3</sub><sup>-</sup> activity in equilibrium with atmospheric CO<sub>2</sub>, (316 ppm).

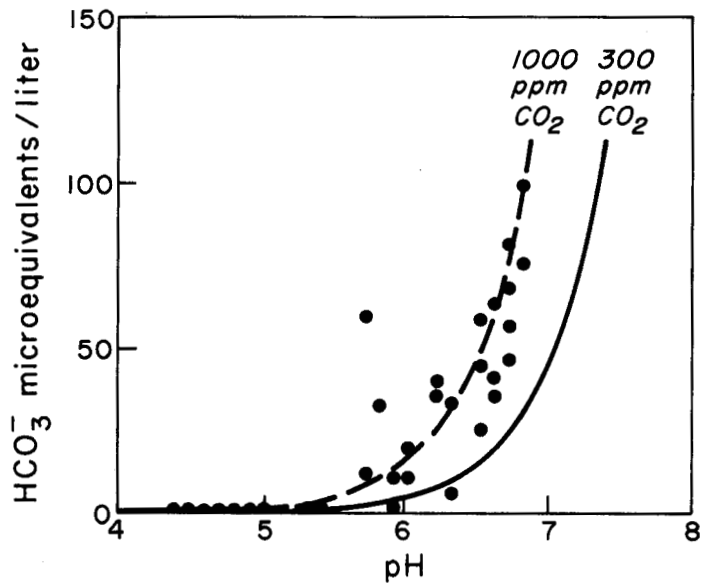


Figure 2. Plot of the pH and HCO<sub>3</sub><sup>-</sup> levels reported by Egner and Eriksson (1955b, data set D501.).

In practice few errors will result from pH measurements at unknown CO<sub>2</sub> concentrations if the rainfall is consistently acid. However, if non-acidic events are interspersed with acid events, the errors could be substantial. The diagram shown in Figure 3 should prove useful in

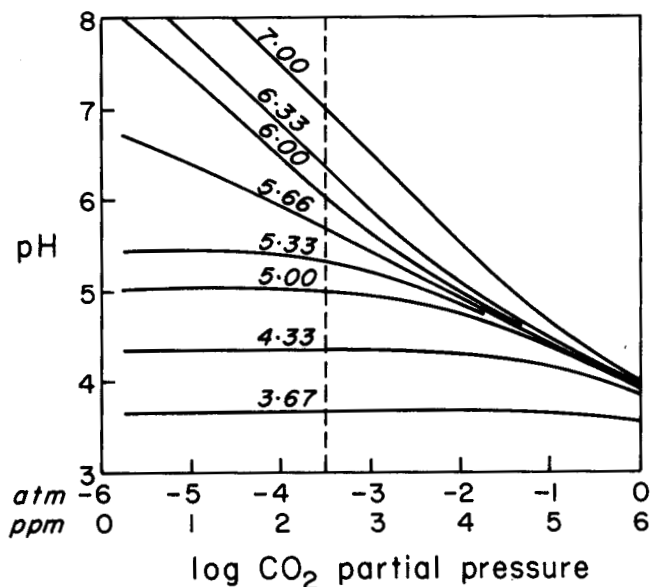


Figure 3. Diagram showing the effects of varying CO<sub>2</sub> partial pressure on pH. Dotted line indicates 316 ppm CO<sub>2</sub> and numbers refer to pH at 316 ppm CO<sub>2</sub>.

this regard. It is developed by utilizing the principle that the net alkalinity  $b$  is independent of CO<sub>2</sub> partial pressure, and in systems where the CO<sub>3</sub><sup>-</sup> ion is negligible, is defined by (9).

$$b = [\text{OH}^-] + [\text{HCO}_3^-] - [\text{H}^+] \quad (9)$$

Rearranging (9):

$$[\text{HCO}_3^-] = b - [\text{OH}^-] + [\text{H}^+]$$

Substituting for [HCO<sub>3</sub><sup>-</sup>] in (4) above, replacing [OH<sup>-</sup>] by 10<sup>-14</sup>/[H<sup>+</sup>], and rearranging we obtain (10).

$$[\text{H}^+]^2 + [\text{H}^+]b - 10^{-7.81} [\text{CO}_2] - 10^{-14} = 0 \quad (10)$$

For any combination of pH and CO<sub>2</sub> partial pressure, [OH<sup>-</sup>] and [HCO<sub>3</sub><sup>-</sup>] may be calculated by means of (4) and (6) and  $b$  calculated from (9). To construct figure 3 arbitrary pH values were selected and the values

of  $b$  determined for 316 ppm  $\text{CO}_2$ . The lines were then generated by calculating  $[\text{H}^+]$  as a function of  $[\text{CO}_2]$  using (10).

No significant effects due to  $\text{CO}_2$  partial pressure variations would be expected where the lines on Figure 3 are horizontal. In general the  $\text{CO}_2$  pressures of interest are in the range of 300 to 1000 ppm, but higher values may occur. From the graph we see that with samples below pH 4.33 no effects occur within the range of interest, but at pH 5.0  $\text{CO}_2$  pressures above 1000 ppm would depress measured pH. With samples above pH 5.00 the error due to variations in  $\text{CO}_2$  becomes unacceptable.

Several methods might be employed to minimize possible errors. First, I suggest that reported pH values should be those taken only after equilibration with known  $\text{CO}_2$  partial pressures. This would assure uniformity between samples and provide a uniform basis for comparing data from different investigations. This equilibration is particularly important with samples above pH 5.0. Secondly,  $\text{H}^+$  ion loadings per unit area should not be calculated by simply determining total  $\text{H}^+$  from pH and volume measurements. The long-term effects on soil systems are more likely to be related to the net  $\text{H}^+$  loading over time. This would be the difference between  $\text{H}^+$  and titratable alkalinity or, in practical terms,  $\text{H}^+$  minus  $\text{HCO}_3^-$ . The  $\text{HCO}_3^-$  represents the alkaline component of the rainfall so in order to estimate net  $\text{H}^+$  loading from pH measurement, any  $\text{HCO}_3^-$  must be subtracted from the total  $\text{H}^+$  found. This method has been used by Granat (1972). If all major cations and anions are determined, a method of calculating net acidification using anion-cation balances as discussed in the next section should be considered.

### III. CATION-ANION BALANCE IN RELATION TO ACID RAINFALL

An important property of solution systems, whether soil solution or rainfall, is that electrical neutrality is maintained. The chemist analyzing precipitation or stream water utilizes this property when he checks his results to ascertain whether the cations found equal the anions. If the difference exceeds normal analytical uncertainty, either an analytical error has been made or some important constituent has not been determined.

This property may be utilized effectively in determining the acidity of rainfall in the absence of pH measurements, provided the major cations and anions have been accurately determined. The major anions other than  $\text{HCO}_3^-$  involved in the system are  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . Major cations commonly encountered are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$ . If the anions exceed the cations, electrical neutrality of the system

is maintained by  $H^+$  ions and the system is acid. This is the situation we would expect when acidification occurs due to  $H_2SO_4$  and  $HNO_3$  formed from  $SO_x$  and  $NO_x$  gases in the atmosphere. Excluding  $HCO_3^-$  and  $H^+$ , the excess of anions over cations on an equivalent basis may be used to estimate net acidity as shown by (11).

$$e = 2 [SO_4^{2-}] + [NO_3^-] + [Cl^-] - 2 [Ca^{2+}] - 2 [Mg^{2+}] - [K^+] - [NH_4^+] \quad (11)$$

where:  $e$  = excess acid in moles per liter ( $-e$  = alkalinity).

For certain ecosystem effects this measurement may be more appropriate than direct  $H^+$  measurements. For instance, the long-term effects of soil acidification are probably more appropriately considered in terms of a deficit of basic cations than in terms of  $H^+$  ions directly. If the excess anions in acid rainfall are mobile, they will be leached from the soil in association with bases from the exchange complex, resulting in base depletion and acidification. Some soils, particularly those that are acid and highly weathered, exhibit significant anion exchange properties. In these soils anion mobility is reduced, and an excess of acid anions over basic cations may not result in base depletion. This condition is discussed more fully in relation to the sulfur system in Section IV.

If the basic cations in rainfall exceed the anions, the deficit would be made up by  $OH^-$  ions in solution if no  $CO_2$  was present. In the atmosphere, the  $OH^-$  ions are rapidly converted to  $HCO_3^-$  as explained above. At any rate, the excess of basic cations over anions (excluding  $HCO_3^-$ ) should be an appropriate measure of the ability of the rainwater to increase the base status of the lithosphere or hydrosphere.

In practice rainfall acidity measurements derived from anion minus cation calculation should correspond very closely to values obtained by subtracting  $HCO_3^-$  from  $H^+$  derived from pH measurements. Rainwater at pH 5.0 contains 10 micromoles  $H^+$  per liter and 100 micromoles per liter at pH 4.0. Cation levels are generally of the same order of magnitude, so measurements that give acceptable accuracy of the cations and anions in this range should also combine to give acceptable estimates of net acidity or alkalinity. Occasionally rainwaters may be encountered with ionic concentrations of the order of several thousand micro-equivalents per liter. Cation-anion balance may not give acceptable values for acidity of the initial rainfall in these cases as the total ion content is much higher than the  $H^+$  concentration and relatively small analytical errors would drastically affect the estimated acidity. Unfortunately, when higher concentrations are present, direct pH measurements may also be a poor indicator of the effect of the water on the acid base relationships of the soil due to the increased probability of incomplete ionization of acids or bases.



In order to examine the validity of this relationship, a data set was selected from the literature and  $H^+$  ion loading calculated by the anion minus cation method. The observed vs. predicted values were then compared by linear regression. For the data of Pearson and Fisher (1971), the relationship obtained using all 37 points was:  $Y = 9.24 + .758 X$  with a correlation coefficient ( $r$ ) = .826; where  $Y$  is the observed  $H^+$  minus  $HCO_3^-$  in millimoles per square meter per year and  $X$  is the anions minus cations in milliequivalents per square meter. It was also noted that a good deal of the scatter resulted from a few coastal points where high  $Na^+$  and  $Cl^-$  levels appeared to be erratic. When the coastal points were excluded the least squares regression equation for the remaining 30 observations was;  $Y = 5.71 + 0.90 X$  with a correlation coefficient ( $r$ ) of 0.900. This relationship is shown in Figure 4. A similar comparison was made using data given by Egner

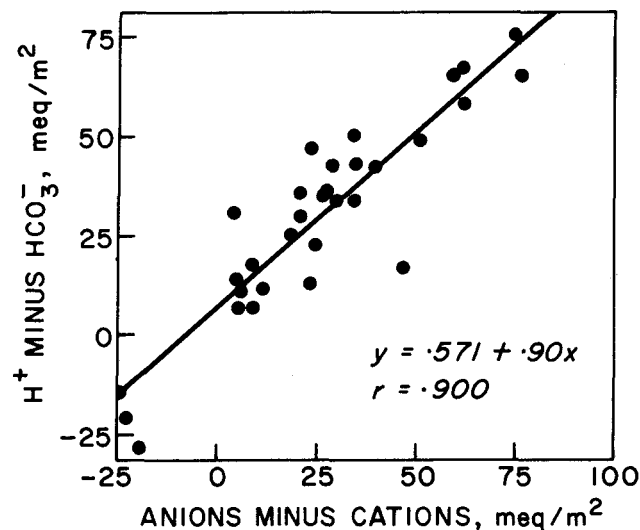


Figure 4. Relationships between net acidity as calculated by anions (excluding  $HCO_3^-$ ) minus basic cations, and observed  $H^+$  minus  $HCO_3^-$  for data set reported by Pearson and Fisher (1971). Coastal stations were not included.

and Eriksson (1955b). In this case the least squares regression equation was  $Y = 0.12 + 0.571 X$  with a correlation coefficient ( $r$ ) of 0.750; where  $Y$  is observed  $H^+$  minus  $HCO_3^-$  and  $X$  is calculated from anions minus cations. One location extremely high in  $Na^+$  and  $Cl^-$  was excluded. This case is interesting because most of the values are negative, i.e. the samples were effectively basic. The bulk of the

scatter appears to arise from the negative values. Whether this reflects analytical errors or is due to other causes is not known. It is entirely possible that the anion minus cation values more accurately reflect the net  $H^+$  loading of the system than the  $H^+$  minus  $HCO_3^-$  values.

Granat (1972) has proposed a model for calculating acidity of rainfall from the concentration of the individual ions as follows:

$$a = 2 ([SO_4^{2-}] - \frac{27.6}{457} [Na^+] + [NO_3^-] - [NH_4^+])$$

$$b = \frac{1}{2} ([K^+] - \frac{9.7}{457} [Na^+]) + ([Mg^{2+}] - \frac{55.6}{457} [Na^+])$$

$$+ ([Ca^{2+}] - \frac{10.0}{457} [Na^+])$$

$$e = a - 2b$$

Where: a = amount of available acid  
 b = amount of base expressed as moles of carbonate  
 e = excess acid in moles per liter (-e = alkalinity)

This model assumes that all sodium in rainfall is of marine origin. The fraction of the  $SO_4^{2-}$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  assumed to be of marine origin is equal to the concentration of sodium times the ratio of the respective ion in sea water to the concentration of sodium in sea water. The model is apparently intended to represent the net acidity or alkalinity of rainfall assuming it to be an aqueous solution or suspension formed from sea salts, sulfuric acid, nitric acid and ammonia. Implicit in the model is the assumption that the ratio of  $Cl^-$  to  $Na^+$  is the same in rainfall as in sea water. Granat shows that the model is reasonably accurate in predicting the net acidity or alkalinity of rainfall.

It may not be readily apparent to the casual reader, but this model is actually a form of the strong acid anion minus basic cation method of calculating acidity shown in equation (11). The models are identical if the molar ratio of  $Cl^-$  to  $Na^+$  in the rainfall is 1.19, the ratio found in sea water. Deviations of acidity or alkalinity calculated by Granat's model from measured values should be equal to the difference between measured  $Cl^-$  concentration and an estimated  $Cl^-$  concentration determined by multiplying the  $Na^+$  concentration by 1.19.

The concept of cation-anion balance and electrical neutrality of the system is also useful in considering acid-base relationships of plant uptake of ions. In order to maintain electrical neutrality in the system, the plant must either take up equal amounts of cations and anions on an equivalent basis or, if the amounts are unequal, it must release to the solution an amount of ions equal to the difference and of the same charge as the excess. A reasonable conceptual model of

this effect is that the plant gives off  $H^+$  ions equal to the excess of cations over anions taken up, and indeed this seems to be the case (Fried and Broeshart, 1967 p. 97). The converse of this is that an excess of uptake of anions over cations is balanced by a release of  $OH^-$  ions which appear in the media as  $HCO_3^-$  due to the presence of  $CO_2$ .

Most plants take up more anions than cations, but this may be reversed if the bulk of the nitrogen uptake occurs as  $NH_4^+$  rather than  $NO_3^-$ . Variations of a magnitude sufficient to cause major differences in the acidity relationships of the media may occur. Healthy plants usually contain substantially lower quantities of the usual anions, i.e.  $NO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and  $H_2PO_4^-$ , than of the basic cations. This results from the reduction of  $SO_4^{2-}$  and  $NO_3^-$  to reduced forms of S and N which are utilized in the protein structure. The excess of basic cations are electrically balanced by organic anions formed in the plant. During the breakdown of the dead plant material, these basic salts of organic acids may be hydrolyzed. The bases are removed and leached as bicarbonates and the remaining litter is acidic due to the presence of these organic acids. If the pH lowers to the point that bicarbonates can no longer exist, this mechanism of leaching is no longer operative. Bases then can only leach in conjunction with the above anions or by chelation with certain organic complexes.

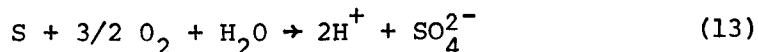
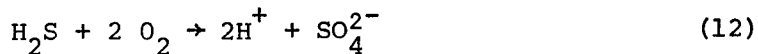
The acid base relationship of this soil-plant system is complex. It does not seem justified to regard this in terms of a simple input-output system of  $H^+$  ions; the cation-anion balance and acidity relationships of the whole soil-plant system must be considered. Apparently one critical research need, in terms of evaluating ecological effects of acid rainfall, is to synthesize present knowledge of the acidity and cation-anion relationships into an overall model from which testable hypotheses can be developed. Some important aspects of this system are considered in more detail in the following sections.

#### IV. ACIDITY RELATIONSHIPS OF THE SULFUR CYCLE

Possible effects of sulfur inputs from anthropogenic sources on soil-plant systems are an important aspect of the acid rainfall problem. As it would seem desirable to consider possible effects from the standpoint of the total sulfur cycle, a brief description of the acidity relationships of this cycle appears appropriate.

While sulfur may be present in a variety of forms in plant tissue and residues, it is mostly in reduced ( $S^{2-}$ ) form. The bulk of the sulfur is found in the amino acid units of the various proteins. Microorganisms that break down plant residue and soil organic matter may utilize the reduced sulfur in the organic material or, in some

cases, may utilize sulfate sulfur from the surrounding media. At any rate, the organic sulfur compounds are transformed to reduced or incompletely oxidized forms such as sulfides, elemental S, thio-sulfates etc., (Starkey, 1966). These reduced or incompletely oxidized compounds are then oxidized to sulfate by aerobic chemautotrophs. The oxidation of the reduced sulfur from the soil organic matter to the sulfate form will inevitably be accompanied by the release of two  $H^+$  ions for each sulfur atom oxidized. This general reaction may be represented by equations (12) and (13) for sulfide and elemental sulfur:



In Figure 5, the oxidation of organic sulfur to  $SO_4^{2-}$  is shown as releasing 2  $H^+$  ions.  $H_2S$  may also act as an acid, but the dissociation constants are such ( $pK_1 = 7.24$ ,  $pK_2 = 14.92$ ) that it would be largely non-ionized in acid soil systems.

If we assume the  $SO_4^{2-}$  released is rapidly taken up by plants, the acid formed by the oxidation will be balanced by the release of 2  $OH^-$  (or  $HCO_3^-$ ) ions from the plant in the uptake process (Figure 5). The net change in  $H^+$  ions for the overall process in the soil is zero (2  $H^+$  and 2  $OH^-$  ions formed), and no change in acidity results. The consideration of the  $OH^-$  ions released by the plant as a result of uptake of anions is an essential point. However, it cannot be validly considered in isolation, but must be considered as a part of the total cation-anion balance of nutrient uptake and plant processes.

Plants apparently take up sulfur almost entirely as the sulfate ion but, as noted previously, the preponderance of sulfur in the plant is in the reduced form. Sulfate is reduced to the  $S^{2-}$  form within the plant prior to its incorporation into the structure of the plant in the sulfur containing amino acids. This reduction results in the removal of 2  $H^+$  (Figure 5) ions according to a reaction that may be considered the reverse of (12) above. The consumption of 2  $H^+$  ions at this point balances the loss of 2  $OH^-$  ions, (which may be considered as equivalent to formation of 2  $H^+$  ions) during the uptake of sulfur.

The total  $H^+$  ion production and consumption of the sulfur cycle (Figure 5) is balanced and no net change in acidity should result. While the cycle represents a drastic simplification of the sulfur oxidation-reduction processes in the system, the acidity relationships should be basically valid.

The anaerobic reduction of sulfate to sulfide (Figure 5) requires low oxygen levels and a fixed carbon energy source, as it is carried out by heterotrophic anaerobic organisms. High concentrations of sulfide compounds may accumulate in flooded soils where sulfate is

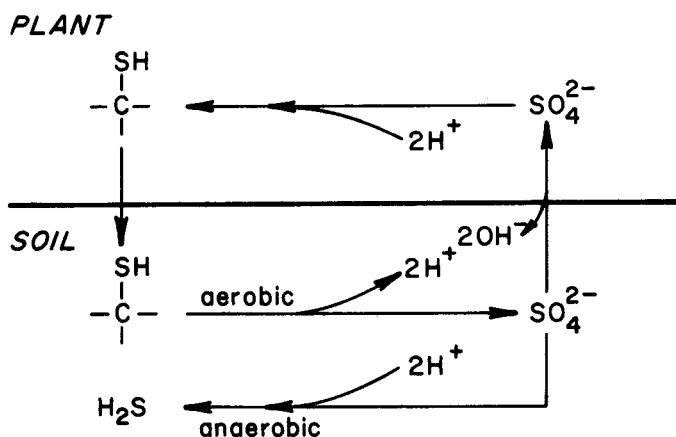


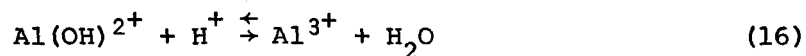
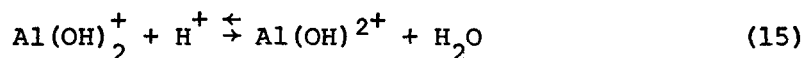
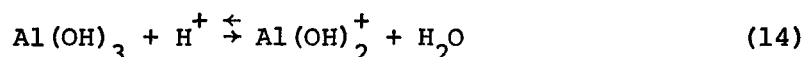
Figure 5. Simplified sulfur cycle showing acid formed or consumed by the various processes.

continually replenished, such as river deltas. This process tends to produce neutral or basic soils as  $\text{H}^+$  ions are consumed. Drainage of these soils results in rapid acidification due to  $\text{H}^+$  produced during the oxidation of  $\text{S}^{2-}$  to  $\text{SO}_4^{2-}$ .

While the sulfur cycle is inherently balanced as far as acid production and consumption are concerned, it does provide some potential for leaching of bases and subsequent development of soil acidity. This arises because lags may occur between oxidation to sulfate and uptake of the sulfate ion. If sulfate ions accumulate, there is a concomitant increase in  $\text{H}^+$  formed in the oxidation of reduced sulfur to sulfate. The  $\text{H}^+$  ions replace basic cations on the clay and organic matter complexes, and these bases may be leached from the soil in association with the  $\text{SO}_4^{2-}$  anion. The quantification of any acceleration of this loss of cations that may be due to acid rainfall is a critical aspect of the assessment of possible ecological effects that may result.

In neutral or acid soils sulfate ions may remain in the soil solution or become adsorbed on soil particles. Various conceptual models have been proposed but for our purposes it is most useful to consider this adsorption to be an anion exchange phenomenon. Soil particles are generally negatively charged but some positive charges exist as the result of the amphoteric nature of soil organic matter

and broken bonds on the edges of the clay lattices. As soils become acid, the aluminosilicates tend to decompose as represented by equations (14-16).



According to this model most reserve acidity in soils does not consist of  $\text{H}^+$  ions adsorbed on negatively charged soil colloids but exists in the form of monomeric  $\text{Al}^{3+}$  and positively charged hydroxy aluminum complexes and polymers. These positive charges neutralize negatively charged colloids or adsorbed anions such as  $\text{SO}_4^{2-}$ . As soils become more acid their cation exchange capacity decreases due to neutralization of negative charges by this mechanism. The increase in positive charges with acidification increases the capacity of soils to adsorb anions such as sulfate (Harward, Chao, and Fang, 1962; Harward and Reisenaur, 1966). Apparently as acidity increases due to anthropogenic sulfur inputs, the ability of the soil to hold the sulfate ion through the adsorption mechanism would also increase.

If reduced sulfur such as elemental  $\text{S}^0$  is added to an aerobic soil system, we can expect oxidation to  $\text{SO}_4^{2-}$  by soil organisms releasing  $2\text{H}^+$  ions. When rainfall containing  $\text{H}_2\text{SO}_4$  enters the system, the  $\text{H}^+$  ions are supplied directly. If the rainfall contains a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_3$  (Brosset, 1973), the pH of the rainfall would not be as low as for a similar concentration of  $\text{H}_2\text{SO}_4$  alone, due to the lower dissociation of  $\text{H}_2\text{SO}_3$  but the  $\text{H}_2\text{SO}_3$  would undoubtedly be oxidized to  $\text{H}_2\text{SO}_4$  when temperature and moisture conditions are favorable. Thus, the net effect on the acidity of the soil system would be the same of  $\text{H}_2\text{SO}_3$  as for  $\text{H}_2\text{SO}_4$ .

Recent data of Nyborg et. al., (1973) indicate that direct soil absorption of  $\text{SO}_2$  may be substantial. This would also result in  $\text{H}_2\text{SO}_3$  formation in the soil.

From the above we see that the net increase in acidity per mole of sulfur added is identical for  $\text{S}^0$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_3$ , or  $\text{H}_2\text{SO}_4$ . However, if the  $\text{SO}_4^{2-}$  is rapidly absorbed by the plant systems, the resultant release of  $\text{OH}^-$  ions (Figure 5) would tend to balance the extra acidity.

Sulfur loads calculated from the data of Pearson and Fisher (1971) for the northeastern U. S., tend to be in the range of 8 to 15  $\text{kg ha}^{-1} \text{yr}^{-1}$ . Jonsson and Sundberg (1970) give a value of 9  $\text{kg ha}^{-1} \text{yr}^{-1}$  for the Swedish forests. Values of this magnitude could probably be absorbed by most agricultural ecosystems as they are in the same general range as harvest removals of sulfur. In forest ecosystems a

a long-term build up of sulfur in soils, plants, and litter might be expected. If loading is greater than the capacity of the ecosystem to utilize or store sulfur, leaching losses will probably occur, bases will be lost in conjunction with the  $\text{SO}_4^{2-}$ , and the soil will become more acid.

The above discussion refers specifically to inputs of sulfur that are not balanced by basic cations. If rainfall inputs of sulfate are accompanied by similar amounts of basic cations, i.e.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{K}^+$ , little change in soil acidity would be expected. Over long periods of time, however, if the distribution of these input ions is different than the distribution of ions in the soil solution and in equilibrium with exchangeable cations in the soil, a shift in the cation equilibria could occur.

The capacity to utilize additional sulfur is often closely related to the nitrogen cycle. Nitrogen sulfur ratios of most plant proteins will be in the range of 12:1 to 16:1, while ratios in soil organic matter tend to be of the order of 8:1 or 10:1 (Stewart and Whitfield, 1965). When nitrogen being taken up by plants is largely derived from soil organic matter, the growth limiting nutrient is more likely to be nitrogen than sulfur. The sulfur mineralized will usually be sufficient for utilization of the nitrogen mineralized. However, if nitrogen comes from an outside source such as fixation of atmospheric nitrogen or nonsulfur containing fertilizers, the probability of sulfur deficiency is substantially increased. Sulfur responses in agriculture are generally found on legume crops such as alfalfa and clover or on crops where heavy nitrogen fertilizer applications are made using fertilizer materials that do not contain sulfur. In forest ecosystems where nitrogen fixation is rapid such as in alder stands, there is a definite possibility that anthropogenic sulfur inputs would result in accelerated growth. In such systems the removal of sulfur as a growth limiting factor would probably increase productivity. It is even possible that sulfuric acid in rainfall would not result in increased soil acidity due to the balancing effect of the  $\text{OH}^-$  ions given off by the plant in the uptake of  $\text{SO}_4^{2-}$ .

Mature timber stands or other systems in which nitrogen is supplied largely from internal cycling are less likely to be sulfur limited. If the capacity of these ecosystems to utilize sulfur inputs is exceeded, the probability of deleterious effects from sulfuric acid in rainfall would be increased.

Finally, the effect of sulfur inputs on base rich soils should be considered. Such soils are generally found in arid areas, but occasionally occur under humid or subhumid conditions. These soils are virtually 100% base saturated, i.e., all cation exchange positions are occupied by bases, and they generally contain free alkaline earth carbonates. The acid-base relationships of the sulfur cycle here are identical to those discussed above except for the effect of excess

acid. Free carbonates result in a large buffering capacity. Acid rainfall high in sulfate ion would dissolve calcium carbonate, and sulfates would tend to accumulate and precipitate out as gypsum.

Gypsum cannot ordinarily be considered toxic as many productive soils naturally contain gypsum crystals, but changes in plant communities might occur on soils that did not normally contain gypsum. Also many calcareous grassland soils have an acidic layer a few centimeters thick near the surface. Acid rainfall or  $\text{SO}_2$  sorption would be expected to intensify this layer. The possible ecological effects of these changes are unknown.

## V. ACID-BASE RELATIONSHIPS OF THE NITROGEN CYCLE

In light of the recent interest in the effect of anthropogenic sulfur inputs on the acid-base relationship in soil-plant systems, it is appropriate to call attention to the role of the nitrogen system in this regard. From an overall ecosystem point of view, the nitrogen cycle can be expected to release or consume much greater quantities of  $\text{H}^+$  ions than would be involved in the sulfur cycle. Also the contribution of nitrogen compounds to the potential of rainwater to acidify soil systems may be much greater than generally recognized. Plant uptake of nitrogen occurs in both the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  forms. Factors that determine the relative uptake in each of these forms include the nature of the plant and the presence or absence of conditions favorable to the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  in the soil system.

While plants may contain many types of nitrogen compounds, the major portion of the nitrogen is found in the structural proteins. This nitrogen is in the  $\text{N}^{3-}$  oxidation state, the same as is found in  $\text{NH}_3$ ,  $\text{NH}_4^+$  and soil organic nitrogen. When plants take up nitrogen in the  $\text{NH}_4^+$  form, no change in oxidation state in the system is required. Starting with the soil organic component in Figure 6, we consider the release of N to be a simple deamination of  $-\text{CNH}_2$  to  $\text{NH}_3$  with no change in acid-base status required. This  $\text{NH}_3$  will require 1  $\text{H}^+$  ion to ionize as  $\text{NH}_4^+$ .

The uptake of  $\text{NH}_4^+$  by a plant results in the release or exchange of an  $\text{H}^+$  ion so the net change in acidity for the soil system is zero. The acid-base relationships in the plant are relatively simple when nitrogen is taken up in the  $\text{NH}_4^+$  form. One  $\text{H}^+$  is released in the conversion to  $\text{NH}_3$  or  $\text{C-NH}_2$ . This balances the  $\text{H}^+$  ion released in the uptake process so the net change is again zero. The acid-base relationship of the cycle appears to balance as one would intuitively expect.



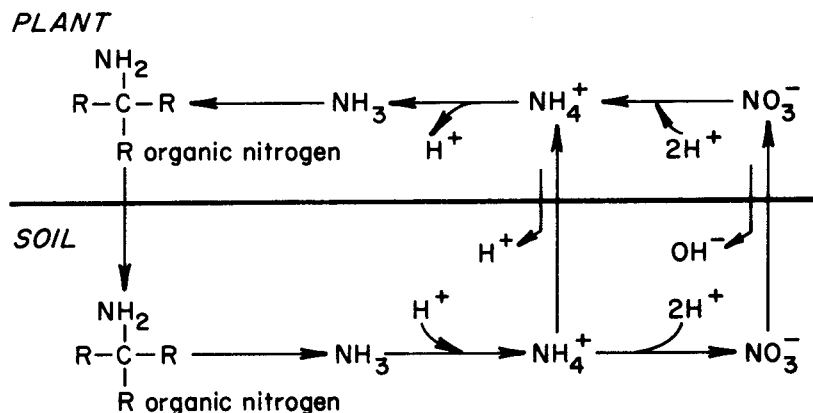
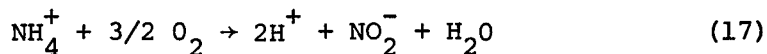


Figure 6. Simplified nitrogen cycle showing acid formed or consumed by the various processes.

The system becomes more complex when we consider the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and the subsequent uptake of the nitrate ion. The oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  and subsequently  $\text{NO}_3^-$ , releases a total of  $2\text{H}^+$  ions, as shown below:



These transformations are carried out in the soil largely by chemautotrophs, step (a) by organisms of the genus *Nitrosammonas* and (b) by *Nitrobacter*. The subsequent uptake of  $\text{NO}_3^-$  releases  $1 \text{OH}^-$ , which balances one half the acidity released in the oxidation. The other half is balanced by the  $\text{H}^+$  utilized in the protonation of  $\text{NH}_3$ . Again, we find the net change in the soil is zero and the system balances, provided the cycle is completed by plant uptake.

The plant transformations may be regarded as the reverse of those found in the soil. Two  $\text{H}^+$  ions are consumed in the reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  by the nitrate reductase enzyme system. One of these is balanced by the loss of an  $\text{H}^+$  to form  $\text{NH}_3$  prior to the amination. The other is balanced by the release of the  $\text{OH}^-$  that occurred during the uptake of  $\text{NO}_3^-$ , as an  $\text{OH}^-$  lost by the plant is equivalent to the formation of an  $\text{H}^+$ .

Even though the overall system can be considered balanced, the nitrogen cycle offers potential mechanisms for losses of bases and acidification of the soil system. When mineralization occurs followed by the oxidation of  $\text{NH}_4^+$  to nitrate, the  $\text{H}^+$  ions formed will replace a basic cation on the cation exchange complex. This basic cation is then subject to leaching in conjunction with the  $\text{NO}_3^-$  ion. If conditions

allow any build-up of  $\text{NO}_3^-$ , the potential for leaching exists when water passes through the profile. Most natural ecosystems tend to maintain low nitrate levels as the nitrates formed are rapidly taken up by the plants.

Some interesting questions arise when one considers the potential acidity relationships of mineral nitrogen inputs in precipitation. Any anion taken up by a plant will cause the release of an  $\text{OH}^-$  ion, so nitrate could be considered as resulting in a basic reaction. The highly mobile nitrate ion is rapidly absorbed by the plant, and Pearson and Fisher (1971) note that stream loads of mineral N are less than precipitation inputs. Even though this possible basic effect may be valid, one must be cautious in the interpretation of this effect in isolation from the rest of the cation-anion system.

Perhaps the most interesting aspect of the nitrogen cycle in relation to rainfall acidity involves the ammonium ion. If the  $\text{NH}_4^+$  falling in precipitation is oxidized in the soil to the nitrate form, 2 moles of  $\text{H}^+$  will be formed for each mole of  $\text{NH}_4^+$  oxidized. The data of Pearson and Fisher (1971) show that this effect may be substantial. Table 1 shows values of the mean ionic concentration and loading for Mays Point, New York in 1966, calculated from their data. The  $\text{NH}_4^+$

Table 1. Average ionic loading and composition for rainwater collected at Mays Point, New York in 1966 (Pearson and Fisher, 1971).

<u>Cations</u>	<u>Milligram Equivalents* meter<sup>-2</sup>. year<sup>-1</sup></u>	<u>Microgram Equivalents* liter<sup>-1</sup></u>
$\text{Ca}^{2+}$	35.7	45.9
$\text{Mg}^{2+}$	11.7	15.0
$\text{Na}^+$	8.1	10.4
$\text{K}^+$	3.1	4.0
$\text{NH}_4^+$	15.1	19.4
$\text{H}^+$	34.9	44.8
<u>Anions</u>		
$\text{SO}_4^{2-}$	87.9	113.0
$\text{Cl}^-$	10.5	13.5
$\text{NO}_3^-$	2.7	3.5

\*Data as shown by Pearson and Fisher was in units of tons per square mile per day. Precipitation totaled 78 centimeters.

value of 15.1 milliequivalents of  $\text{NH}_4^+$  per square meter at this location also happens to be the mean value for all locations and years that they report. They report an  $\text{H}^+$  loading of 34.9 milliequivalents per year which would correspond to a mean value of 44.8 microequivalents per liter with a total precipitation of 78 centimeters. This mean  $\text{H}^+$  concentration results in an "average pH" of 4.35. If 2 moles of  $\text{H}^+$  are released in the oxidation of each mole of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  the oxidation of 15.1 milliequivalents of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  will result in the release of 30.2 milliequivalents of  $\text{H}^+$  per square meter, an amount very similar to the 34.9 milliequivalents reported as the direct input from  $\text{H}^+$  loading.

Another example of the possible significance of the effect of acidification due to oxidation of  $\text{NH}_4^+$  can be seen from data shown by Likens (1972) and Likens and Bormann (1974). Likens (1972) calls attention to an apparent shift from  $\text{NH}_4^+$  to  $\text{NO}_3^-$  as the dominant form of inorganic nitrogen in New York since about 1945. Likens and Bormann (1974) note increasing acidity of rainfall over the same period as evidenced by pH values of about 4.0 at present. No direct pH measurements are available for the early samples, but they are inferred to be higher due to the recorded presence of bicarbonates and from their reaction to methyl orange indicator. The data are presented in graphical form, but apparently a value of 0.9 milligrams  $\text{NH}_4^+$  per liter is representative of the bulk of the observations prior to 1945, with a few values above 3.0. The release of 2  $\text{H}^+$  ions per mole on oxidation of 0.9 milligrams  $\text{NH}_4^+$  per liter would release 0.106 milligrams  $\text{H}^+$  per liter.

Data from six collection stations in this area in 1970-71 (Likens 1972) averaged 0.48 milligrams  $\text{NH}_4^+$  per liter or 0.053 milligrams  $\text{H}^+$  per liter on oxidation. The direct  $\text{H}^+$  input for these samples was 0.105 milligrams per liter or an "average" pH of 3.99. These data clearly illustrate the importance of the  $\text{NH}_4^+$  component to the capacity of rainfall to acidify soils. It should also be recognized that if the high  $\text{NH}_4^+$  contents of the pre-1945 samples are indeed representative of rainfall from that era, the potential to acidify soils would have been substantial even though the rainfall was apparently not acid.

When ammonium is taken up directly by the plant, acidification still occurs due to the  $\text{H}^+$  given off by the plant in the uptake process. The magnitude of this effect is often underestimated. In the past many experiments showing poor growth in solution and pot cultures when ammonium was used as a nitrogen source were interpreted as a toxic effect of  $\text{NH}_4^+$  ion when in fact the toxicity was caused by acidity developed in the medium. Carnation producers had long considered  $\text{NH}_4^+$  as an unsuitable source of nitrogen, but it has been shown that they do well when  $\text{NH}_4^+$  is used if  $\text{CaCO}_3$  is added to prevent acidification (Schekel, 1971).

Ammonium inputs, whether oxidized to nitrate or not, can thus be shown to have an acidifying effect. While it is probably extreme to consider the total potential acidification as representing two moles  $H^+$  per mole of  $NH_4^+$ , the effect should be recognized in our evaluation of the effect of rainfall acidity.

If ammonium inputs are important, it may be well to consider their source and distribution. In past years, many measurements of nitrogen inputs in rainfall were made for the purpose of evaluating their agricultural significance. Results vary widely, and it is impossible to accurately evaluate whether the variation is due to contamination and analytical inaccuracies or actual variation in amounts. It has been noted that the results quite consistently show a 2:1 ratio of ammonium to nitrate N (Stevenson, 1965), but the results of Pearson and Fisher (1971) show widely varying ratios both between locations and between years at a single location.

Atmospheric ammonia levels vary widely. Sources of ammonia often widely quoted include industrial, atmospheric fixation (electrical and photochemical), and volatilization from land surfaces. Recently Luebs, Davis, and Laag (1973) have shown much higher atmospheric concentrations of  $NH_3$  in a dairy area in California than in a control area. They also claimed  $NH_4^+$  inputs in the precipitation in the dairy area to be three times that of the control area. Hutchinson and Viets (1969) have reported high ammonia absorption by traps near feedlot operations. Thus, the possible effects of high concentrations of livestock must be considered as well.

Atmospheric  $NH_3$  reacting with sulfuric acid aerosols would form ammonium sulfate and bisulfate salts. The resultant solution would be much less acidic than aerosols not neutralized by  $NH_3$ , yet the system would retain the capacity to acidify soils as shown by the mechanisms discussed above. Therefore, the neutralization of acid aerosols by atmospheric  $NH_3$  may not reduce the capacity of the rainfall to acidify soils.

In conclusion, it probably is not possible at the present time to predict quantitatively the effect of nitrate and ammonium on the capacity of acid rainfall to acidify the soil system. On theoretical grounds we could expect substantial effects, and evaluation of this contribution should be included among the goals of future research on the acid rainfall problem.

## VI. SUMMARY

A number of chemical and biological considerations relevant to understanding the effects of rainfall acidity on soil-plant systems have been discussed. The following points are particularly important and should be thoroughly understood by researchers engaged in acid rainfall investigations.

A. Due to the effect of atmospheric  $\text{CO}_2$  the basic component of rainfall exists largely as  $\text{HCO}_3^-$ . If samples are above pH 5.0, pH measurements are subject to serious errors due to fluctuations in  $\text{CO}_2$  partial pressure.

B. The potential of rainfall to acidify soil or waters is characterized by its containing more acid anions than basic cations. This excess of anions can be an appropriate measure of the capacity of the rainfall to contribute to the acidity of soil systems.

C. The acidity of a plant growth medium is affected by the relative uptake of cations and anions by the plants growing in the medium. The overall effect of acid rainfall is not only the effect of  $\text{H}^+$  ions added to the system but may also reflect the relative plant uptake of the various ions added to the system.

D. In the natural sulfur cycle  $\text{H}^+$  ions are continually being formed and consumed by various biological processes. An important aspect of the acid rainfall question involves the effect of additional sulfur loading on these processes.

E. Soil nitrogen transformations normally involve a substantial production and consumption of  $\text{H}^+$  ions. This flux of  $\text{H}^+$  ions is much larger than that involved in sulfur transformations or the input from acid rainfall. Measurement of the effects of  $\text{H}^+$  inputs from outside the system may be complicated by this larger flux due to normal nitrogen transformations.

F. The oxidation of ammonium to nitrate by aerobic chemautotrophic bacteria results in the production of acid. Oxidation of the ammonium contained in rainfall may result in an  $\text{H}^+$  in acid rain. The consideration of this process substantially complicates the interpretation of rainfall induced  $\text{H}^+$  loading.

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