ACID PRECIPITATION EFFECTS ON SOIL pH AND BASE SATURATION OF EXCHANGE SITES[1]

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ABSTRACT

The typical values and probable ranges of acid-precipitation are evaluated in terms of their theoretical effects on pH and cation exchange equilibrium of soils characteristic of the humid temperature region. The extent of probable change in soil pH and the time required to cause such a change are calculated for a range of common soils. Hydrogen ion input by acid precipitation is compared to cation inputs from nutrient cycling and other sources. For example it can be calculated that 100 years of acid precipitation (10,000 cm at pH 4.0) could be expected to shift the percentage base saturation in the top 20 cm of a typical midwestern forest soil (cation exchange capacity of 20 meq/100 g) downward 20%, thus lowering the pH of the A1 horizon by approximately 0.6 units, if there are no countering inputs of basic materials.

INTRODUCTION

As our understanding of air pollutants expands it becomes increasingly evident that the forms and effects of these substances as they pass through terrestrial systems may be of equal or greater importance than their final sink. To date most research has been directed toward the effects of air pollutants on plant growth and development (Tamm and Aronsson 1972) while the effects of air pollutants on the soil has received little attention (Bohn 1972). Acid precipitation, a by-product of air pollution, is a phenomenon receiving increased attention in the literature. We believe that the influence of acid precipitation on soil pH and cation exchange equilibria may prove to be the most significant effect of all. It is likely to be quite permanent and have far reaching

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influences both on the vegetation growing upon it and the waters draining from it. This paper will use extant data to determine the theoretical effects of acid precipitation on pH and cation exchange equilibria of soils. The magnitude of H^+ ion input by acid precipitation will be compared to cation inputs from nutrient cycling and other sources, and the probable change in soil pH and the time required to cause such a change will be calculated.

DISCUSSION

Likens and Bormann (1974) have noted that water in the atmosphere is generally in equilibrium with prevailing CO_2 pressures and will produce a pH of about 5.7; while Nihlgard (1970) reports a slightly lower value (5.2) for incident precipitation in southern Sweden. Soviet scientists have recorded values ranging from 5.1 to 6.1 (Mina 1965). However, pH values as low as 2.1 have been observed in north central New Hampshire (Likens et al. 1972). Fisher et al. (1968) reports that weekly samples of precipitation collected over a two year period at the Hubbard Brook Experimental Forest were frequently less than 4.0. Mean annual values of 3.9, 3.9, and 4.0 have been reported for three locations in up state New York (Likens 1974). According to data presented by Fisher et al. (1968), Likens et al. (1972) and Likens (1974), H^+ accounts for 44 to 69 percent of the cations in precipitation, while the anions are $SO_4^=$, 59 to 62 percent; NO_3^-, 21 to 23 percent; and Cl^-, 14 to 20 percent.

Acid precipitation entering the soil has three possible fates: (1) it may be neutralized by free bases such as $CaCO_3$ or $NaCO_3$, (2) the acid water may pass through into the ground water or drainage water in soils that are already quite acid and/or have low cation exchange capacity, e.g., sands with low organic matter contents, and the most common situation, (3) acidic ions enter into exchange reactions with cations already present on the soil cation exchange complex.

The ability of soils to store cations and to resist rapid changes in pH is due to their negatively charged particles which behave like cation exchangers (Fig. 1). It is the interaction of H^+ from acid precipitation with this cation exchange capacity (C.E.C.) that determines the effect of the added acidity on soil properties. Cation exchange capacity in soils is almost exclusively a property of decayed organic matter and silicate clays (Table 1) and is usually quantified in milliequivalents per 100 g of soil (meq/100 g).

The composition of the cations attracted to the humus and clay particles determines the soil pH and availability of many plant nutrients. A high C.E.C. results in a high nutrient storage capacity and a resistance to pH shifts. If most of the cations are basic in nature such as Ca^{++}, Mg^{++}, K^+ and Na^+, we say the soil has a high "percent base

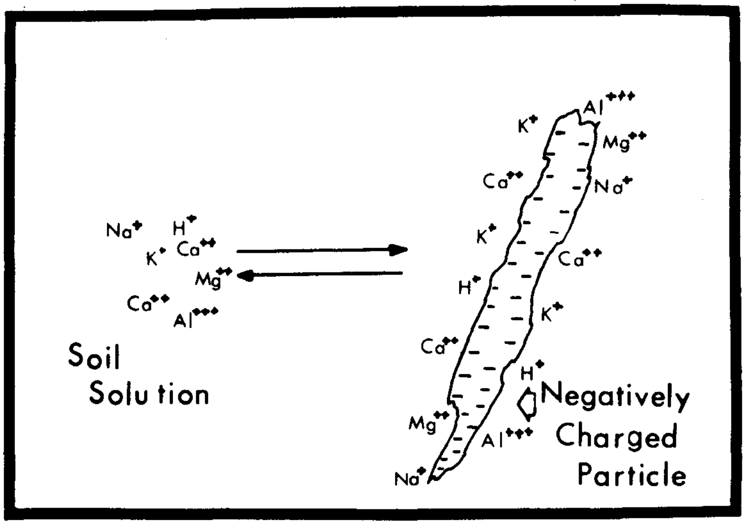

Figure 1. Equilibrium between cations in solution and those absorbed on soil colloids.

Table 1. Cation Exchange Capacities of Soil Components

	C.E.C. meq/100 g
Organic Matter (Humus)	200*
Silicate Clays	
vermiculite	150
montmorillonite	100
kaolinite	10
illite	30
Hydrous Oxide Clays	4
Silts and Sands	negligible

*Variation is commonly 40% of these mean values.

saturation". Since the large ratio of exchangeable ions to those in the surrounding solutions is on the order of 1000:1, the compostion of the soil solution, including pH, is controlled by the degree of base saturation on the exchange sites. The relationship shown in Figure 2

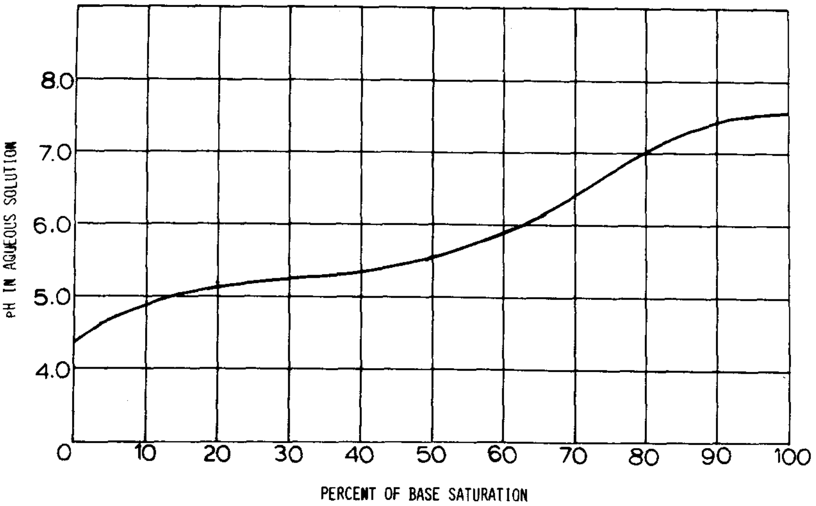

Figure 2. Typical relationship of soil pH to the percent base saturation of the soil cation exchange sites (Lathwell and Peech 1964).

was developed by Lathwell and Peech (1964) for some soils in the northeastern United States. Similar relationships are available in most regions. In general as base saturation goes down so does pH, but not in a linear fashion.

Utilizing existing information about the soil one should be able to determine the magnitude of pH shift that is likely over a given number of years of acid precipitation at a known pH. The following is an example of how one might proceed utilizing a simple set of assumptions. We chose a 1000 square cm area for convenience in unit size and the fact that 1 cm of precipitation then equals 1 liter.

$$1 \text{ cm of precipitation} = 1 \text{ L}/1000 \text{ cm}^2$$

If we examine 20 cm of soil depth we could expect 26,000 g in the reference area if the soil bulk density is 1.3 g/cc, a common value for surface soils.

$$1000 \text{ cm}^2 \times 20 \text{ cm} \times 1.3 \text{ g/cm}^3 = 26{,}000 \text{ g soil}$$

With a C.E.C. of 20 meq/100 g (common in Alfisols and Mollisols, high in Spodozol regions) there would be 5.2 equivalents (eq) of exchange capacity under 1000 square cm to a depth of 20 cm.

$$26{,}000 \text{ g soil} \times 20 \text{ meq}/100 \text{ g soil} = 5.2 \text{ eq}$$

Consider the acid input and its affect on this soil system. On our reference area, 100 cm of pH 4.0 rain (one year's precipitation) would provide .01 eq H^+ to react with the exchange sites (5.2 eq) under the 1000 cm^2 reference area 20 cm deep.

$$100 \text{ cm precipitation} = 100 \text{ L } H_2O/1000 \text{ cm}^2$$

$$\text{pH } 4.0 = .0001 \text{ eq } H^+/L$$

$$.0001 \text{ eq } H^+/L \times 100 \text{ L} = .01 \text{ eq } H^+$$

That is assuming that pH is a fair measure of total acidity which is true only if it is a strong acid, completely dissociated. With a precipitation PH of 4.0 we could get 1 eq. H^+/1000 eq cm in 100 years; at pH 3.7, 50 years would be required; and at pH 3.0, 10 years would be required. Under these conditions, how long would it take to get a measurable pH shift and how great would it be? If all the H^+ input (1 equivalent in this example) exchanges for basic cations in the top 20 cm of soil we can calculate the shift in percent base saturation. In this example total exchange capacity equals 5.2 eq., one equivalent of acid exchanging with one equivalent of base would produce a 19% base saturation decrease. Using Figure 2 we see that such a shift would result in a pH drop to 5.2 if the initial pH were 6.0. Results differ somewhat depending on the starting pH. If the soil is lower in C.E.C., the shift in base saturation would be proportionately greater and the pH shift somewhat greater depending on the initial pH and percent base saturation.

With fairly well buffered soils, those with a moderate amount of clay or humus, the movement of pH is going to be slow in terms of experimental time, but fast geologically, This indicates that in many experiments measuring changes in soil pH due to acid precipitation is not a reasonable research goal. Further, in the preceeding example certain simplifying assumptions were made: (1) cation input is H^+ only, (2) exchange of H^+ for basic cations is complete, and (3) there are no counteracting forces. These assumptions might lead to the conclusion that complete removal of basic cations to a depth of 20 cm is likely in 520 years if the precipitation has a pH of 4.0, since this would result in an input of 5.2 equivalents of H^+ per 1000 cm^2. This is not likely, however, since the above assumptions do not hold.

There are many countering forces that will reduce the final affect of acid precipitation. Four such countering forces are neutralization by basic substances in the polluting medium itself, nutrient recycling, mineral soil decomposition and exchangeable cations present on negatively charged soil particles. Cation input of H^+ only is not the case as was assumed in the example calculation. Many acidic anthropogenic substances are neutralized by basic substances of similar origin. As shown in Table 2, there is a significant input of the cations Na^+, K^+, Ca^{++}, and Mg^{++} in precipitation. The precipitation input at Indianapolis given by Carroll (1962) has a concentration of .26 ppm Na, .12 ppm K, .69 ppm Ca, and .27 ppm NH_4. Converted to equivalents there are a total of .06 meq of basic cations per liter compared to .1 meq

Table 2. Basic Cations in Precipitation From Several Locales in the United States

	Inputs kg/ha/yr			
	Ca	Mg	Na	K
Indianapolis, IN (Carroll 1962)	6.9	-	2.6	1.2
Walker Br, TN (Henderson et al. 1975)	14.2	2.2	4.0	3.4
Coweeta, NC (Henderson et al. 1975)	5.0	1.1	4.4	2.3
Hubbard Br, NH (Fisher et al. 1968)	2.7	0.6	1.6	0.7
H. J. Andrews, OR (Henderson et al. 1975)	5.0	1.0	1.8	0.2

H^+/liter in pH 4.0 rain. Therefore we could not expect the exchange of H^+ for other cations on the exchange sites to proceed as rapidly or completely as it would if H^+ were the only cation, since other ions will also be competing for exchange sites and thus decrease the effectiveness of the added H^+. The basic cations in precipitation are directly offsetting and have the same effect as the agricultural practice of liming to restore base saturation to a high level.

Likewise, basic substances leached from living plant tissue react with acidic substances to neutralize their acidity. For example, Tamm (1951) and Madgwick and Ovington (1959) report ten-fold increases in calcium content of precipitation collected beneath the forest canopy while Voigt (1960) reports a five-fold increase. Likens et al. (1967) reports average inputs of calcium magnesium, potassium and sodium to the soil of 3.0, 0.7, 2.5, and 1.0 kg/ha respectively. These examples serve to illustrate that significant quantities of basic materials are available to react with acidic materials prior to entering the soil.

A second source of neutralizing substances is the annual litter fall. Gosz et al. (1972) estimated annual litter fall at Hubbard Brook to be 5700 kg/ha. Calcium, potassium, manganese, magnesium, and sodium inputs from the same study were 40.7, 18.3, 10.3, 5.9, and 0.10 kg/ha respectively. In a similar study on a pine forest annual litter fall was 1657 kg/ha with 10.6 kg/ha of calcium, 8.2 kg/ha of potassium, 6.1 kg/ha of magnesium, 1.9 kg/ha of manganese, and 0.5 kg/ha of sodium, (Scott 1955).

Total weight of litter on the forest floor in the northeast as determined by Scott (1955) ranges from 6000 to 133,000 kg/ha with most forests having between 25,000 and 35,000 kg/ha. McFee and Stone (1965) reported a mean forest floor weight of 243,000 kg/ha under undisturbed forests in the Adirondack Mountains of New York containing 101 kg/ha of potassium, and 185 kg/ha of calcium. Obviously, litter fall will be effected by stand age and site quality but the values presented give some indication of the total amount of material deposited as well as the input of basic elements, which may slow the soil acidification process. Forest vegetation recycles a significant amount of basic cations (Table 3) which act as countering forces in the soil acidification process.

Table 3. Basic Cations Returned to the Soil Surface as a Part of the Annual Litter Deposition Under Forests

	kg/ha/yr			
	Ca	Mg	Na	K
Walker Br, TN (Henderson et al. 1975)	46	8.0	-	19
Coweeta, NC (Henderson et al. 1975)	44	-	-	18
Hubbard Br, NH (Gosz et al. 1972)	40	5.9	-	-
H. J. Andrews, OR (Henderson et al. 1975)	67	-	-	8

The transport of basic cations from deep in the soil back to the surface will have a moderating effect depending on the type of vegetation and the acidity of its decay products. The quantity of basic ions in this litter is frequently as much as .02 equivalents per 1000 cm^2 per year which is more than the acid input expected from 100 cm of pH 4.0 precipitation. However, these are not new bases, but rather ones recycled from the soil below. Still the effect would be to slow down cation loss and the rate of acidification.

Another countering force is the release of basic cations by weathering or decay of the soil minerals themselves. This is difficult to measure and will vary tremendously depending on the nature of soil parent material. The values in Table 4 are estimates based on balance

Table 4. Estimates of Cations Released by Soil Weathering

	kg/ha/yr			
	Ca	Mg	Na	K
Walker Br, TN (Henderson et al. 1975)	58.0	47.0	-	-
Coweeta, NC (Henderson et al. 1975)	0.8	1.8	4.3	2.0
Hubbard Br, NH (Bormann and Likens 1970)	8.0	1.8	4.6	0.1

sheet approaches but give us an idea of the magnitude of this countering effect. In old, highly weathered soils developed from rocks low in calcium and magnesium this would not be important whereas in some soils, especially shallow soils over calcareous materials, it would be an effective countering force.

As pointed out by Norton[2], the aluminum in the soil, which is very important in acid reactions, becomes very soluble and the aluminum oxides behave as bases at low pH giving up OH^-. Further the accelerated decay of silicates in the soil may cause an increase in the release of bases or it may lead to the destruction of clays and the loss of some of the exchange capacity.

The exchange or replacement of basic cations by H^+ should be predicted by laws of mass action such as the Donnan equilibrium where the ratio of two monovalent ions in the soil solution should be the same as the ratio of adsorbed ions on the organic matter and clay.

$$\frac{(H^+)_{ad}}{(M^+)_{ad}} = \frac{(H^+)_s}{(M^+)_s}$$

In the case of monovalent-divalent systems the divalent cation is held more tightly and the relationship given by Gapon (1933) approximates the situation.

$$\frac{(H^+)_{ad}}{(M^{++})_{ad}} = \frac{(H^+)_s}{\sqrt{(M^{++})}_s}$$

These relationships do not hold very well when H^+ is one of the ions involved since it is held very tightly on clays and often enters into the clay lattice displacing a structural ion such as aluminum. These relationships along with the mixed input of cations point out that all acid ions do not replace basic ions and therefore the acidification of the soil is slower than our initial estimate.

The quantity of exchangeable basic cations that tend to buffer the soil against acidification is quite large in many soils. Cline and Lathwell (1963) found in the top 70 cm of a clayey soil exchangeable calcium averaged 7.7 meq/100 gm, magnesium 9.0 meq/100 gm, potassium 0.4 meq/100 gm, and sodium 0.2 meq/100 gm. In the same study a silty profile was found to contain 21.7 meq/100 gm calcium, 4.1 meq/100 gm magnesium, 0.3 meq/100 gm potassium, and 0.1 meq/100 gm sodium. Follett and Trierweiler (1973) report the average calcium, potassium, magnesium, and manganese levels for soils used for the production of field crops in Marion County, Ohio to average 5318, 262, 930 and 32 kg/ha respectively. Calcium, potassium, magnesium, and manganese levels at 3057, 250, 520, and 104 kg/ha respectively are generally lower in unglaciated Washington County, Ohio. These two examples illustrate

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[2] See paper this volume.

that a considerable amount of exchangeable basic material does exist in the mineral soil and as such is available to offset incoming acidity.

There are some other limits on the speed and extent of acidification. For example, as the pH of the precipitation approaches the soil pH, the affects are lessened because the equilibrium of solution ions to exchangeable ions is not affected.

SUMMARY

Acidification of soils is a complicated, many faceted process that is important in plant nutrition, but even with its many complications it would be useful in planning research to calculate the theoretical effects using the techniques above to determine the probable changes in soil pH and base saturation. This will be an important aid in research planning by directing our efforts toward finding parameters that will change measurably during the experimental period. When planning research on acid precipitation effects consideration should be given to those parameters which can be quantified in studies of only a few years duration. Our discussion points out the resistance of most soil systems to pH change, the small likelihood of rapid soil degradation due to acid precipitation, and the difficulty of evaluating this and associated changes in the normal experimental time frame.

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