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Soil Acidity and Liming

Intensive agriculture in the humid tropics has been primarily conducted on soils with a high level of native fertility. These soils generally have a reserve of weatherable minerals that provide calcium and magnesium and prevent formation of highly acid soils. On the other hand the soils that are not being used intensively often have a low soil pH and are very low in exchangeable bases, which limits crop production. The Campo Cerrado of Brazil and the Llanos of Colombia and Venezuela are examples. Attempts to lime the soils in the humid tropics close to neutrality according to the procedures used for soils in temperate regions have very often ended in failure. However, since 1950, ideas about soil acidity and liming have undergone marked changes. These new concepts about soil acidity should be very helpful in providing the basis for determining which soils in the humid tropics will respond to liming and how much lime is required for optimum crop growth.

CONCEPTS OF SOIL ACIDITY AND CATION EXCHANGE REACTIONS

Nature of Soil Acidity and Cation Exchange Reactions

For many years, it was assumed that soils with a low pH were primarily hydrogen saturated. However, in the early 1950's a great deal

of work by soil chemists showed that exchangeable aluminum was the predominant cation in acid mineral soils with a pH of 5 or lower (Coleman and Thomas, 1967). The acid nature of soils containing exchangeable aluminum is a result of the hydrolysis of aluminum in the soil solution and the production of hydrogen ions. Acid mineral soils were found to contain essentially no exchangeable hydrogen since hydrogen clays are very unstable and decompose to give aluminum ions and siliceous acid (Coleman and Craig, 1961). Thus, with acid mineral soils, we are dealing with exchangeable aluminum and not hydrogen. Above pH 5.6, most soils will have relatively small amounts of exchangeable aluminum.

Determinations are often made of the titratable acidity of soils by adding base to a soil. The amount of titratable acidity is generally much greater than the amount of exchangeable acidity. The titratable acidity includes not only exchangeable aluminum but also acidity that is not replaced with a neutral unbuffered salt. It consists of nonexchangeable hydrogen associated with carboxyl groups and hydrated oxides of iron and aluminum. This nonexchangeable acidity has no detrimental effect on plant growth, as does the exchangeable acidity (exchangeable aluminum).

Since the activity of aluminum is related to the pH of the soil, the method of extraction becomes very important. The conventional ammonium acetate procedure and other buffered solutions are unsatisfactory for measuring exchangeable aluminum. A neutral unbuffered salt solution such as potassium chloride or sodium chloride has been found to extract aluminum ions (Lin and Coleman, 1960). For all practical purposes, the pH of the soil in a neutral unbuffered salt solution will be close to that of the soil. Therefore, the amount of aluminum ions extracted will approximately equal the amount on the cation exchange sites. This is in contrast to the much higher amounts of aluminum extracted by acidified ammonium acetate solutions.

Relation between Exchangeable Aluminum and Aluminum in the Soil Solution

Exchangeable aluminum is held very tightly by soil colloids. Nye *et al.* (1961) found very little aluminum in the soil solution until exchangeable aluminum comprised 60 percent of the total exchangeable cations of clays. Likewise, Evans and Kamprath (1970) found that with surface soils an exchangeable aluminum saturation of 60 percent was required before a large amount of aluminum was present

in the soil solution. Soils of Guyana had less than 1 ppm of aluminum in the soil solution when the aluminum saturation was lower than 60 percent (Cate and Sukhai, 1964).

With an increase in the amount of salt in the system, there is an increase in the amount of aluminum in the soil solution (Fried and Peech, 1946). Thus, high rates of fertilization could result in an increase of aluminum in the soil solution.

Effective Cation Exchange Capacity and Base Saturation

Traditionally, the cation exchange capacity of a soil has been determined from the amount of the ammonium ion adsorbed by a soil equilibrated with ammonium acetate at pH 7. The cation exchange capacity determined from the use of buffered ammonium acetate would include not only sites occupied by exchangeable cations but also pH-dependent exchange sites associated with carboxyl groups and hydrated oxides of iron and aluminum. It has been amply demonstrated that the cation exchange capacity of soils with a substantial dependent charge increases as the pH increases. Thus, the cation exchange capacity of acid soils measured with ammonium acetate exceeds the sum of the exchangeable aluminum, calcium, magnesium, and potassium. Therefore, the base saturation of a soil calculated on the basis of the cation exchange capacity determined with ammonium acetate at pH 7 will always be less than 100 percent for soils with a pH less than 7 even though the soils do not contain any exchangeable aluminum.

Based on these kinds of considerations, Coleman *et al.* (1959) suggested that the sum of the exchangeable calcium, magnesium, potassium, and the acidity extracted with a neutral unbuffered salt solution be called the effective cation exchange capacity. The effective cation exchange capacity can be considered the exchange sites that are participating in exchange reactions at the particular soil pH. On this basis most mineral soils would be 100 percent base-saturated at pH 6. As judged by plant growth, this is a much more realistic manner of expressing base saturation.

Causes of Acid Soil Infertility

Poor growth of plants on acid soils is in many instances related to the toxic effect of aluminum and manganese. This is discussed in detail by Adams and Pearson (1967). Also, calcium and other nutrients may

be seriously deficient on the highly leached acid soils. Under acid conditions, molybdenum tends to be held quite tightly by soil clays and hydrated oxides of iron and aluminum, and thus its availability to plants may be inadequate. Magnesium deficiencies have been observed on sandy soils where the pH is 5 or less and the exchangeable aluminum saturation is relatively high (Kamprath, 1967).

Crop Tolerance to Aluminum and Manganese

Crops vary in their tolerance to aluminum and manganese. Hewitt (1948) has classified a number of plants on the basis of their tolerance to aluminum and manganese. Tomato, lucerne, carrot, celery, barley, and sugar beet were particularly susceptible to aluminum toxicity. Swede, kale, lucerne, and tomato were the crops most affected by excess manganese content.

Cotton and barley were very sensitive to aluminum toxicity; soybeans were not as sensitive; and corn was relatively tolerant (Foy and Brown, 1964). Varieties of a particular plant species may vary widely in their tolerance to aluminum. Wheat varieties developed in the eastern United States where the soils are acid were more tolerant to aluminum than those developed in the Great Plains and western states where the soils are neutral to alkaline. Wheat varieties from Brazil had the highest tolerance to aluminum (Foy *et al.*, 1965).

The acidity problems of surface soils can be eliminated by liming. However, at present it is not feasible to lime acid subsoils. Where subsoil acidity is a problem, selection of aluminum-tolerant varieties is very important so that roots will grow into the subsoils and utilize moisture and nutrients present there. Where the amount and distribution of rainfall are adequate, liming the surface soil may be sufficient.

Response to Liming Based on Neutralization of Exchangeable Aluminum

Coleman *et al.* (1958) suggested that lime recommendations should logically be based on the amount of exchangeable aluminum in the soil. Kamprath (1970) found that lime rates based on milliequivalents of exchangeable aluminum times 1.5 resulted in neutralizing 85 to 90 percent of the exchangeable aluminum in soils containing 2 to 7 percent of organic matter. As the pH is increased from 5.5 to 6.0, some of the hydrogen ions associated with organic matter and hy-

drated oxides ionize and react with lime. For this reason a factor of 1.5 is used.

Results of field and greenhouse studies indicated that the aluminum saturation at the pH of the soil in the field should be less than 45 percent for maximum growth of corn, 20 percent for maximum growth of soybeans, and 10 percent for maximum growth of cotton (Kamprath, 1970). Growth of sugarcane was severely depressed on a soil with an exchangeable aluminum saturation of 70 percent. Addition of lime to reduce the aluminum saturation to 30 percent resulted in a fourfold increase in growth (Abruna and Vicente-Chandler, 1967).

Root Development

Considerable research has been done on the effects of calcium and aluminum on the root development of the cotton plant (Adams and Lund, 1966; Adams *et al.*, 1967; Adams and Pearson, 1970; Howard and Adams, 1965; Lance and Pearson, 1969; Rios and Pearson, 1964). Cotton roots do not penetrate a calcium-deficient soil; roots are restricted when the calcium concentration in the soil solution is less than 0.5 meq/liter. Roots will grow at pH 4.6 in the presence of adequate calcium. The root restriction in acid soils may be attributed to aluminum toxicity rather than to calcium deficiency; restriction is observed when the concentration of the aluminum ion in the soil solution is greater than 0.002 meq/liter. Aluminum depresses the uptake of calcium by the roots and reduces the permeability of the plasmalemma. When the concentration of aluminum in the roots exceeded 0.2 percent, yield was reduced. There appeared to be a close interaction between aluminum toxicity and calcium deficiency.

Peanut roots behaved differently from cotton roots. The former penetrated acid subsoil layers that cotton roots would not penetrate. This was explained by assuming that peanut roots absorb lower-valence ions to the exclusion of the higher-valence aluminum ions. Consequently, they are tolerant to relatively high aluminum ion concentrations in the soil solution. These experiments on cotton and peanut root development were done on Ultisols.

Ragland and Coleman (1959) observed that growth of sorghum and corn roots in unlimed subsoils was inversely related to the amount of exchangeable aluminum present. Addition of potassium chloride to unlimed soils increased the concentration of aluminum in the soil solution to the point of drastic root reduction. This interference with root growth was corrected by liming.

Experiments on root development of the leguminous plant *Leucaena glauca* in Hawaii (Plucknett, 1961; Plucknett *et al.*, 1963) strongly indicated that phosphorus deficiencies in the subsoil restricted root proliferation. Phosphorus had to be applied to the subsoil to stimulate root growth. Root development in the subsoil was more highly related to the phosphorus supply than to aluminum toxicity. Lime in the subsoil decreased active aluminum but did not stimulate root growth. Phosphorus, on the other hand, did not decrease the amount of active aluminum present but did stimulate root development.

There has been no evidence of aluminum toxicity to root development of sugarcane in acid soils in Hawaii, even at pH values below 5.0. Adequate available calcium was the determining factor. In Hawaii, calcium is added as a nutrient, rather than to change the acidity. Aluminum toxicity in sugarcane soils in Guyana did not occur unless the exchangeable aluminum saturation was more than 60 percent.

Effect of Liming on Availability of Fertilizer Phosphorus in Ultisols and Oxisols

Woodruff and Kamprath (1965) found that liming increased the efficiency of fertilizer phosphorus on acid soils that had an appreciable amount of exchangeable aluminum. The optimum level of liming for improved solubility of fertilizer phosphorus in Hawaiian soils was between pH 5 and 6 (Fox *et al.*, 1962). The increase in phosphorus solubility was related to neutralization of exchangeable aluminum.

When the pH of acid aluminous soils was adjusted to 7, phosphorus uptake was drastically decreased (Fox *et al.*, 1964). As pH 7 is approached, these soils have a very high buffer capacity so that high rates of lime are required. Since calcium is readily replaced from pH-dependent sites, excess calcium at the root surfaces may have precipitated phosphorus.

CHEMICAL CHARACTERIZATION AND MEASUREMENTS OF SOIL ACIDITY

Characterization

Analysis of some soils from the Llanos of Colombia indicates that these highly weathered, acid mineral soils are predominately satu-

TABLE 1 pH, Exchangeable Cations, and Percentage of Aluminum Saturation for 26 Soils of the Llanos Orientales, Colombia[a]

Comparison	pH	Exchangeable Calcium plus Magnesium (meq/100 g)	Exchangeable Aluminum (meq/100 g)	Aluminum Saturation (%)
Average	–	1.54	3.05	68
Range	4.15-5.12	0.05-9.09	0.6-5.80	29-86

[a] Data from Vargas (1964).

rated with exchangeable aluminum and that they have a low content of exchangeable bases (Table 1). The effective cation exchange capacity of these soils is quite low, compared with Mollisols of the temperate region.

Chemical data of representative soils from Brazil show that when the pH is less than 5, aluminum is the predominant exchangeable cation (Table 2). Above pH 5, the exchangeable aluminum saturation was low.

Samples of acid soils from the state of São Paulo, Brazil, were low in exchangeable calcium and magnesium and had an appreciable content of exchangeable aluminum (Table 3). These soils from the Campo Cerrado had a very low effective cation exchange capacity, generally in the range of 2 to 5 meq/100 g of soil.

Representative soils from Malaysia also had a high exchangeable aluminum saturation and a low effective cation exchange capacity (Table 4).

TABLE 2 pH, Exchangeable Cations, and Percentage of Aluminum Saturation for Representative Soils of Brazil[a]

Soils (Number)	pH	Exchangeable Calcium plus Magnesium (meq/100 g)	Exchangeable Aluminum (meq/100 g)	Aluminum Saturation (%)
14	5.0	1.2	1.9	58
18	5.0-5.5	5.9	0.6	16
11	5.5-6.0	6.5	0.1	2

[a] Data from Anastacio (1968).

TABLE 3 pH, Exchangeable Cations, and Percentage of Aluminum Saturation for Various Classifications of Soil in São Paulo, Brazil[a]

Classification	pH	Exchangeable Calcium Plus Magnesium (meq/100 g)	Exchangeable Aluminum (meq/100g)	Aluminum Saturation (%)
Red Yellow Latosol (Ultisol)	4.3	0.3	1.7	83
	4.0	0.2	1.2	82
	5.5	4.2	0.1	2
	4.6	0.2	1.9	89
	4.3	1.2	3.2	72
	4.5	1.3	0.8	36
Red Latosol (Oxisol)	4.2	0.2	1.0	67
	4.2	0.1	0.7	82
	4.1	0.2	1.9	88
Red Yellow Podzolic (Ultisol)	4.8	1.8	2.3	54
	4.5	6.0	3.5	35
	3.7	0.3	3.8	90
	5.4	0.9	0.1	10

[a] Data from Pratt and Alvahydo (1966).

The available evidence indicates that many acid soils of the humid tropics have a high percentage of exchangeable aluminum saturation when the pH is less than 5, are very low in calcium and magnesium, and have a low effective cation exchange capacity. The nature of soil acidity in many humid tropical soils, therefore, is similar to that of

TABLE 4 pH, Exchangeable Aluminum, Total Exchangeable Cations, and Percentage of Aluminum Saturation for Some Malaysian Soils[a]

Soil Series	pH (Calcium Chloride)	Exchangeable Aluminum (meq/100 g)	Total Exchangeable Cations (meq/100 g)	Aluminum Saturation (%)
Rengam	4.0	1.92	2.93	66
Serdang	3.8	5.08	5.89	86
Selangor	3.6	12.40	15.96	78
Kuantan	4.3	0.90	2.63	34
Segamat	4.3	0.70	2.05	34
Batu Anam	3.8	3.10	4.75	65
Chemor	4.2	1.33	2.25	59
Ulu Tiram	4.2	1.60	2.51	64

[a] Data from Mohinder Singh and Talibudeen (1969).

the highly weathered, acid mineral soils of the southeastern United States.

Measurements of Soil Acidity

Meaningful measurements of soil acidity can be obtained by extracting soils with a neutral unbuffered salt solution such as potassium chloride, sodium chloride, or barium chloride. This will extract the aluminum ion, the predominant exchangeable cation in acid mineral soils at pH 5 and below. Inferences can then be made as to whether soil acidity *per se* is likely to be a growth-limiting problem.

The effective cation exchange capacity—sum of exchangeable aluminum, calcium, magnesium, and potassium—gives a meaningful characterization of the exchange properties of humid tropical soils. Use of the effective cation exchange capacity to calculate the base saturation of soils provides a more realistic basis for evaluating the fertility status of soils.

Characterization of the Cation Composition of the Soil Solution

Since plants absorb cations from the soil solution, the composition of the soil solution is important in determining the cation content of plants. The concentration of cations in the soil solution depends upon the percentage of saturation of the cation exchanger by the cation and the nature of the cation exchanger. Montmorillonite, kaolinite, sesquioxide-coated clays, allophane, and organic matter are important cation exchangers. As these cation exchangers bind cations with different affinities, it is necessary to determine not only the cation saturation of the exchanger but also the cation composition of the soil solution. This will give a better understanding of the availability of cations and differences between soils in their response to the addition of fertilizer cations, such as magnesium and potassium.

Calcium, magnesium, and potassium are generally held more strongly by montmorillonite clays than by kaolinite, organic matter, allophane, and sesquioxide-coated clays. Generally, when the exchange sites are pH dependent, the basic cations are not held as tightly as when the exchange sites have a permanent charge.

Measurement of Exchangeable Manganese and Water-Soluble Manganese

Since manganese has been identified as being the cause of poor growth in certain acid soils, exchangeable manganese and water-

soluble manganese should be measured. Problems of manganese toxicity in acid soils are most likely to occur on soils formed from rocks having a high content of ferromagnesium minerals.

LIME STUDIES ON SOILS OF THE HUMID TROPICS

Rate and Frequency of Liming

The rate of liming should be based on the amount of lime required to neutralize the exchangeable aluminum. Sufficient rates should be tested to obtain a range of exchangeable aluminum saturation. This will provide information on the amount of exchangeable aluminum that needs to be neutralized in order to obtain maximum growth. Measurements also should be made of the calcium and magnesium content of the plant. One of the objectives of lime studies should be the development of a soil test for determining the amount of lime to add. Since the predominant cation of very acid soils is exchangeable aluminum, it seems logical that a soil test for determining lime rates should be based on a measurement of exchangeable aluminum.

One question that will have to be answered is how frequently to apply lime to soils of the humid tropics. Rainfall, evapotranspiration, occurrence and intensity of a dry season, cation exchange characteristics of the soil, water adsorption and movement characteristics of the soil—all will influence how fast calcium and magnesium are leached from soils. Mahilum *et al.* (1970) reported that considerable amounts of calcium were leached from a Hydrol Humic Latosol (Inceptisol). One interesting aspect of their work was that once the exchangeable aluminum was displaced, it did not readily reoccupy exchange sites even when calcium was removed by leaching.

Frequency of liming will depend upon how quickly calcium and other basic cations are removed by leaching and how soon exchangeable aluminum reappears on the exchange sites. Long-term field studies are needed to answer these questions.

Sources of Lime

Since many highly weathered acid soils are low in magnesium, studies are needed to determine the need for magnesium. Use of both calcitic and dolomitic sources of lime would be desirable. Another approach would be to determine the level of exchangeable magne-

sium required for optimum crop production. Where magnesium-containing limestones are not available, the use of soluble magnesium fertilizer materials should be evaluated.

Tolerance of Crops to Soil Acidity

As has been pointed out, crops vary considerably in their tolerance to soil acidity. In addition, varieties within a species may differ in this respect. Where new varieties are to be introduced in an area, information should be obtained on their tolerance to soil acidity.

Tolerance to soil acidity as it relates to growth of roots into acid subsoils can be very important in utilization by the plant of water and nutrients from the subsoil.

LIME-FERTILIZER INTERACTIONS

Phosphorus Availability as Influenced by Liming

Availability of fertilizer phosphorus has been increased by liming when the soils contained appreciable amounts of exchangeable aluminum. The addition of high rates of lime markedly reduced phosphorus availability in certain acid soils but not in others (Fox *et al.*, 1964). These authors suggested that the decreased availability was due to the greatly increased availability of calcium, which resulted in precipitation of phosphorus. This could very likely happen where calcium is not held tightly by the soil complex and where the concentration of phosphorus in the soil solution is relatively low because of fixation of phosphorus in sparingly soluble forms.

On the other hand, in some instances large amounts of phosphorus appear to be fixed, but the phosphorus is easily desorbed and a high concentration of phosphorus is maintained in the soil solution. Under these conditions, a high concentration of calcium might not be as detrimental as it is where the concentration of phosphorus in the soil solution is much lower.

Studies are needed to determine the nature of these lime-phosphorus interactions and to characterize the soil properties associated with different kinds of reactions. With sufficient information, it should be possible to identify soils where high calcium levels will have a detrimental effect on phosphorus availability.

Effect of Lime on the Availability of Micronutrients

Molybdenum

One beneficial effect of lime on certain soils is an increased availability of soil molybdenum, which is of particular importance in the growth of legumes. Most studies indicate that a pH of around 6.5 is required in order to get maximum availability of soil molybdenum. However, at pH 6.5, availability of some of the other micronutrients may be markedly reduced. Thus, it becomes important in liming studies to evaluate the interaction between lime and availability of soil molybdenum. Where humid tropical soils are low in molybdenum, treating seed with molybdenum is more feasible than liming the soil to pH 6.5.

Other Micronutrients

Availability of zinc, copper, manganese, and boron is often drasticall reduced when highly weathered soils are limed much above pH 6. Liming studies with humid tropical soil should take into account any possible effect on the availability of these micronutrients.

NEED FOR CHARACTERIZATION AND CLASSIFICATION OF HUMID TROPICAL SOILS

Interpretation of the results of liming studies requires a knowledge of ion exchange reactions in soils and the nature and properties of cation exchangers in soils. One of the objectives of liming studies is to be able to extrapolate the findings to soils with similar chemical properties. This requires detailed soil chemistry studies and use of the chemical data in classifying and grouping of soils.

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