

# ACID SOILS OF THE TROPICS

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### INTRODUCTION

In all humid climates, acidification of soil is a natural process and one that has major ramifications for plant growth. As soils become more acid, particularly when the pH drops below 4.5, it becomes increasingly difficult to produce food crops. Aluminum becomes more soluble and toxic to plants, most plant nutrients become more limited in supply, and a few micronutrients become more soluble and toxic. These problems are particularly acute in humid tropical regions that have been highly weathered. According to Sanchez and Logan (1992), for example, one third of the tropics, or 1.7 billion hectares, is acid enough for soluble aluminum to be toxic for most crop plants. We will look at some of the causes of acidification and list some of the results that are expected from both the acidification process and the practice of liming for acid neutralization.

### WHAT CAUSES SOILS TO BECOME ACID?

The concept of acidity is one of the first chemical principles to be taught in elementary school science courses. Children are taught that pH 7.0 represents neutrality; pH values above this point represent increasingly alkaline conditions, and pH values below this point represent increasingly acid conditions. Both strongly alkaline and strongly acid conditions are generally detrimental to plant life. This is all true, but there are few chemical reactions in nature that occur at neutrality. There has been concern about acid rain, but almost all rain is acid. Pure rain containing no pollutants is essentially distilled water and distilled water in equilibrium with the atmosphere will have a pH of about 5.6 due to the dissolution of carbon dioxide in the water.



When pure water is in equilibrium with atmospheric carbon dioxide, the resulting hydrogen ion concentration will bring the pH to the 5.6 indicated. Plants will also produce carbon dioxide due to their respiration processes, and during active growing periods the roots can cause carbon dioxide in the soil to be many times that in the atmosphere. The result is an increase in the amount of carbon dioxide dissolved in soil water and thus higher acidity, or lower pH. Carbon dioxide is not the only source of hydrogen ions in the soil, however. In managed soils, fertilizer can become a major source of

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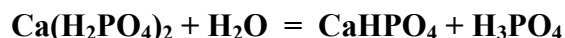
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hydrogen ions. Modern fertilizers commonly use ammonium as the nitrogen source, but oxidation of ammonium to nitrate is accompanied by release of hydrogen ions



In other words, two atoms of hydrogen are produced for every molecule of ammonium oxidized.

While it is less acidifying than ammonium, the monocalcium phosphate often used as one component of fertilizer can also be a factor. It will hydrolyze in water to form dicalcium phosphate and phosphoric acid

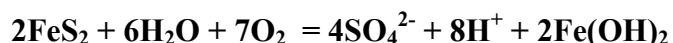


The phosphoric acid progressively dissociates as pH is raised from about 3.0 to above 7.0.



In general the third  $\text{H}^+$  is only lost at pH values above neutrality, so is not usually a factor. However, two  $\text{H}^+$  ions will readily be lost in the acid soil pH range, so are a factor. Because of the  $\text{H}_3\text{PO}_4$  dissolution, when phosphorus fertilizer is placed in a band, very low pH values can be attained in the band. This acidity will then gradually diffuse into the soil surrounding the band. According to Lindsay and Stephenson (1959), pH values as low as 1.5 can be found in a zone immediately around a fertilizer band.

All oxidation reactions in soil have hydrogen ions as a byproduct of the reaction, so are acidifying. One of the most effective inorganic acidification reaction is sulfur oxidation. In fact, sulfur is normally used if a soil has a pH higher than desired, and pH reduction is necessary. There are landscapes, such as mine spoil and mangrove reclamation areas, in which sulfur content is naturally high and therefore acidification is a serious problem. For example, if pyrite is present the reaction



readily occurs, producing 2 hydrogen ions for every sulfur ion oxidized. Up to 300 cmol ( $\text{H}^+$ )  $\text{kg}^{-1}$  (1 cmol is equal to 0.01 molecular weight.) of free  $\text{H}_2\text{SO}_4$  have been reported (Thomas and Hargrove, 1984), so unless a plentiful supply of a liming material is available, the soil pH can be driven to a very low value as has been reported for drained mangrove swamps in Africa. For perspective, 300 cmol ( $\text{H}^+$ )  $\text{kg}^{-1}$  is 10 to 30 times greater than the negative charge commonly measured in soils.

Many forms of organic matter can also be acidifying, depending on the plant from which the organic matter is derived. Some plants contain significant quantities of organic acids. As their residues are decomposed the organic acids naturally affect the soil acidity. Other plants are acidifying simply because of the low concentrations of bases they contain. If the plant does not contain enough bases to satisfy microbial needs the decomposition of the plant debris will not only give off carbon dioxide, but will also remove base nutrients such as calcium and magnesium from the soil in the decomposition process.

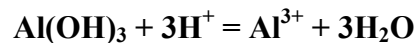
Even plant growth will contribute to acidification; a major nutrient uptake process is to exchange hydrogen ions at the root surface for needed base ions such as calcium, magnesium, and potassium.

Leguminous plants are particularly acidifying because the anion/cation uptake from the soil is more imbalanced toward cations than is uptake by non-leguminous plants. Since most nitrogen needs are satisfied by microbial nitrogen fixation within the plant structure little nitrate is taken from the soil. In non-leguminous plants nitrate uptake will partially balance base ion uptake so there is less hydrogen exchanged from the root to obtain these nutrients.

Acid rain contributes to acidification as well, but given all the other soil processes the contribution is minor in all but the most sensitive soils such as acid sands with very low cation exchange capacity. In general, tropical soils are high in sesquioxides<sup>1</sup> and already highly acid, so the small contribution from precipitation will have minimal effect. (Note: this is only true of soil, and many plants are quite sensitive to acid rain.)

### THE PH/ALUMINUM CONNECTION

At pH values greater than about 5.5, the ability of the soil to buffer<sup>2</sup> changes in pH is dependent on the amount of calcium available. By pH 5.5, however, the calcium content has usually been largely depleted. Therefore, below pH 5.5, other soil reactions must take over the buffer role. As it happens, aluminum hydrolysis reactions occur at the appropriate pH values, and the quantity of aluminum in most soils is sufficient for this ion to take over this role below pH 5.5. While there are several intermediary reactions, the overall buffer reaction is:



In other words, for every Aluminum ion three hydrogen ions can be “consumed”, thus pH will be only changed at a very slow rate in comparison to the acidification reactions. There is, however, a major problem with the process: the aluminum hydroxide is in a solid form, and when hydrogen ions are added it goes into the solution phase. Aluminum in the solid phase is a normal part of every soil and is benign or even beneficial, but in the solution it can become toxic to plants. Furthermore, the aluminum is now susceptible to movement to ground and surface water supplies, where in high enough concentrations it can be toxic to animals (including humans) using the supplies. In addition, the free aluminum now competes with positively charged nutrients on soil surfaces, causing them to be removed from the soil at an accelerated rate.

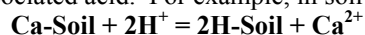
### EFFECTS OF THE ACIDIFICATION PROCESS

Soils typically carry a negative charge on particle surfaces, and these surfaces attract and hold positively charged base ions such as calcium, manganese, potassium, sodium, and others. With only minor exceptions, soil particles hold hydrogen ions more strongly than these other ions. This means that whenever one of the acidification reactions causes hydrogen ion concentration in the soil to increase, some of the hydrogen ions will then displace these base ions, which become susceptible to leaching out of the soil. Over time, well-drained humid region soils become quite acid and devoid of

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<sup>1</sup> Sesquioxides are technically the oxides of trivalent ions. As used in soil science the term refers to precipitated oxides and hydrous oxides of aluminum, iron, and manganese.

<sup>2</sup> A buffer reaction involves a salt and its associated acid. For example, in soil the reaction



is a buffer reaction: Ca-soil is the salt and H-soil is the associated acid. Since  $\text{H}^+$  tends to be more strongly held to soil particles than is  $\text{Ca}^{2+}$  the hydrogen will tend to displace calcium from the surface, and until most or all Calcium is displaced from the soil particles the reaction causes soil to be resistant to pH change.

base ions unless the bases are replaced by nature or by man. Eventually, as this process continues,  $H^+$  concentration on the surface becomes high enough that the mineral structures themselves are attacked, releasing  $Si^{4+}$ ,  $Fe^{3+}$ , and  $Al^{3+}$  as well as other ions that happen to be contained in the minerals. The released iron and aluminum ions tend to precipitate and polymerize as hydrous oxides (sesquioxides) which remain in the soil, whereas the silica ions leach to lower levels. Eventually the amorphous<sup>3</sup> hydrous oxides of aluminum and iron, along with Kaolinite<sup>4</sup>, become the dominant solids in the soil.

Since tropical soils tend to be highly weathered the nutrient holding capacity of the mineral fraction tends to be low. Most or all of the minerals which have a negative charge (eg. mica, smectite, vermiculite) have disappeared through the weathering process outlined above, leaving the very low charged Kaolinite as the dominate crystalline mineral in the soils. The non-crystalline amorphous materials, then, become the primary sources of negative charge. These materials are dominated by the sesquioxides formed as the weathering process proceeds. As previously noted, the aluminum oxides begin to dissolve at about pH 5.5. If the pH decreases to below 4.0, the aluminum oxides will be increasingly susceptible to dissolution and the free aluminum ions in the solution will be increased to levels toxic to many plants. The accompanying loss of negative charges also means there are less bonding sites for the nutrient cations. Furthermore, as the aluminum ion concentration in the solution is increased, this ion competes very successfully with other cations for the remaining negative sites. Thus, as the few remaining nutrient-containing minerals are weathered the base nutrients have a high probability of being leached from the soil rather than being held at negative sites. These are the primary reason many tropical soils are naturally low in fertility.

Another problematic acidification induced soil phenomenon is a tendency to fix phosphate. As aluminum and iron are released during the acidification/weathering process, they become more accessible on cation exchange sites, in solution, or simply on exposed surfaces. Both ions react readily with phosphate, forming a relatively insoluble precipitate, with the process being known as phosphate fixation. Tropical soils high in iron are particular problems in this regard, because their “appetite” for phosphate can sometimes become almost insatiable.

### **SOLUTION TO THE PROBLEM**

Addition of finely crushed oyster shells and similar materials to the soil is an ancient practice, and can be found in the writings of Cato, a Roman era writer. It was well known that adding such materials to the soil resulted in better crop yields. However, the reason for this observation was not discovered until the 1800’s, when Edward Ruffin, a Virginia farmer, correctly reasoned that such practice decreased the acidity of the soil. Crushed shells and coral sands are still an acceptable and inexpensive source of liming material, if available.

The common solution to acidity today is to add crushed limestone ( $CaCO_3$ ), if it is available, or the even more effective  $CaO$  or  $Ca(OH)_2$  may be used when economic considerations are favorable. These materials are more costly than limestone, but lower shipping costs can make them less costly on the basis of neutralization potential.

In subsistence farming, however, purchase of liming materials is often out of the question. Perhaps the oldest agricultural strategy in the humid tropics is that of shifting cultivation, often commonly known

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<sup>3</sup> Amorphous minerals are those having little or no crystallinity within their structure.

<sup>4</sup> A clay mineral, Kaolinite is a relatively stable and practically inert product of chemical weathering in tropical regions.

as “slash and burn” farming. The forest is usually cut and burned, although other clearing systems are used (Norman, 1979) and about three years of crops can be harvested before the regrowing forest canopy begins to close over the area. A primary nutrient pool in humid tropic ecosystems is the above ground vegetation. Thus, by burning, nutrients are released for use by the food crops planted in the ash. A decrease of acidity will be noted as a result of burning; base ions such as  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  will cause the ash to be alkaline, therefore capable of neutralizing some of the soil acidity. The area is planted to a combination of annuals, biennials, and perennials, the latter being plants capable of growing in the understory of maturing trees. This is a sustainable cultural practice *providing* the average fallow time is sufficient for the primary plant community to be reestablished - often no less than about 20 years. If the area is cropped more frequently the soil will become increasingly infertile and acid, since subclimax vegetation will not be as effective in restoring soil organic matter, fertility status, and physical state (Norman, 1979). The fallow time is required for the climax vegetation to accumulate the required nutrients and for associated soil chemical and physical conditions to be established.

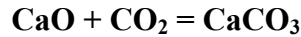
Bones are also good sources of calcium and can be used as liming materials on limited areas. Usually the bones are boiled to remove all meat and soften the bones, which can then be readily crushed for addition to the soil. The supply of bones is usually not sufficient for large-scale use, though.

In a few limited localities other materials such as slag or fly ash from industries may be available. These are usually much lower in neutralization capability, but they can sometimes be obtained very inexpensively which makes their use attractive. Care must be exercised in using such materials, though, because they often contain heavy metals, such as cadmium, copper, chromium, nickel, lead, mercury, or zinc. Many soils can accept a small amount of these metals, and trace amounts of a few are even required by plants and animals. If the ions are allowed to accumulate in the soil, however, they can become toxic to plants. Wood ashes will increase the soil pH, but adding wood ashes from off site as a means of pH adjustment is not recommended. Wood normally has a high potassium to calcium ratio, so use of wood ash can throw these nutrients out of balance. While the ash from wood growing on a site is safe enough, it is better to use the wood ash from off-site sparingly as a potassium fertilizer, rather than as a liming material.

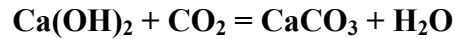
If the soil pH is not too low, it may be possible to build soil fertility without addition of liming material. In Central America, for example, the Velvet Bean has been used as an intercrop and a green manure crop. Legumes are normally considered to be acidifying plants because their uptake of cation and anion nutrients are unbalanced due to fixation of nitrogen within the plant structure. The excess cation uptake is effected by exchange of hydrogen ions for soil cations at the root surface. It appears that this acidifying action may not occur when Velvet Bean is used. Buckles et al. (1998), for example, have indicated that soil pH was maintained, and possibly slightly increased under a continuous velvet bean-maize rotation. This could be associated with the large amounts of dry matter produced by the bean and the base nutrients contained therein. Velvet bean does not, however, do well in very acid soils with pH at or below 4.5, so if pH of the soil approaches this level some type of liming management will be needed.

### WHAT HAPPENS WHEN A SOIL IS LIMED?

As noted by McLean (1971), a number of events occur when lime is added to an acid soil, most of them occurring simultaneously. Regardless of the form calcium is added to the soil, in the presence of atmospheric carbon dioxide it will be converted to calcium carbonate in the soil. For example,



or



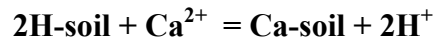
In an acid soil, the calcium carbonate then dissociates:



and, 1) the hydrogen ions in the soil are neutralized



2) the base saturation<sup>5</sup> increases as calcium (and magnesium, if present) replaces the hydrogen ions on the soil surface



the hydrogen ions being neutralized as above, resulting in a pH increase and a shift in the ratios of basic cations adsorbed and in solution. Both results usually make the soil more favorable to plant growth.

3) aluminum ions on the surface are also displaced into the solution with both these ions and the aluminum ions already in solution being transformed back into the solid state sesquioxides



thus decreasing the aluminum concentration below that which might be toxic to plants. As the amount of solid aluminum sesquioxide increases, 4) there will be an accompanying increase in soil cation exchange capacity, so additional cationic plant nutrients can be held in the soil. Conversely, 5) pH dependent anion exchange capacity decreases, forcing anions such as sulfate into solution where they are more available for plant uptake or leaching out of the soil.

There are a number of associated changes in soil as the above reactions proceed. 6) The increase in soil pH affects the solubility of most plant nutrients, making most more available to the plant, but making a few less available. 7) toxic concentrations of aluminum, manganese, and possibly other substances are neutralized (or otherwise inactivated). 8) Nitrogen usually becomes more available as a result of more favorable conditions for both nitrogen fixation<sup>6</sup> and nitrogen mineralization<sup>7</sup> from plant

<sup>5</sup> Base saturation is an expression of ratio of bases (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) to H<sup>+</sup> and Al<sup>3+</sup> in the soil.

<sup>6</sup> Microbial alteration of N<sub>2</sub> in the atmosphere to ammonium, NH<sub>4</sub><sup>+</sup>.

<sup>7</sup> Alteration of organic N in plant residue to plant-available inorganic NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, a byproduct of microbial decomposition of plant residues.

residues. Finally, 9) acid weathering of primary and secondary minerals is curtailed, with possible decrease in nutrients available to the plant.

In addition, liming a soil can affect its physical and microbial properties. Soil permeability may be either increased or decreased, depending on the nature of the soil to which lime is added. In general, increasing calcium content and pH of the soil will stimulate microbial growth, affecting nitrogen availability, as noted, as well as certain other nutrients. Conversely, the increased microbial growth may result in more rapid loss of soil organic matter, which is usually viewed negatively.

### **DANGERS OF OVERLIMING**

In temperate region soils there tends to be little danger from adding too much lime, but this is not true of tropical soils. In fact, liming of most tropical soils is better viewed as calcium fertilization than pH adjustment, and the target pH should probably not exceed about 6.0, with optimum being more in the range of 5.0 to 5.5. In this pH range the aluminum and manganese concentrations in the soil solution are substantially decreased and these ions are no longer toxic to plants. Continued increase in pH, however, can cause molybdenum to become toxic. In addition, plants can become deficient in nutrients such as copper, zinc, boron, and manganese. This is both a result of these nutrients being less soluble at higher pH levels and decreased acid weathering of the few nutrient containing minerals still in the soil.

Perhaps one of the most important problems of overliming tropical soils is physical, rather than chemical. As noted, soil permeability can be affected by liming. The structure in many tropical soils is stabilized by iron and aluminum oxides binding particles together and the structure has reached a high level of stability, accounting for the high infiltration rates and consequent rapid leaching of bases from these soils. Overliming can cause a destabilization of this structure and dispersal of soil particles, resulting in reduced permeability and lack of adequate drainage. Calcium and magnesium have a dispersing action that increases the number of small aggregates at the expense of larger ones. Presumably this is a case of sesquioxide (Fe and Al)-stabilized aggregates being dispersed by  $\text{Ca}^{2+}$ . Since sesquioxide stabilized soils are typically found in the humid tropics, the reduced permeability, due to aggregate destabilization, can result in wet soils and complete change in the ecosystem.

### **SUMMARY**

So far as plants are concerned, two important results of the soil acidification process are the solubilization of aluminum and the loss of cation nutrients from the soil. Aluminum toxicity at low pH levels seems to be the major limiting factor in growth of plants in acid highly weathered tropical soils, and observed favorable crop response from liming appears to be primarily due to aluminum deactivation (McLean, 1971; Soares et al, 1975). Tropical soils, therefore, usually require only enough liming material to raise the pH to about 5.5. This pH level will deactivate the aluminum and provide enough calcium to meet crop needs. Raising the soil pH higher can result in deficiencies of some micronutrients and detrimental physical effects such as aggregate dispersal with accompanying loss of soil permeability. It must be remembered, however, that different plants have different resistance to aluminum toxicity and different nutrient and pH requirement for optimal growth. In addition, soils differ in their nutrient content and potentially toxic ions that will be in solution at any given pH range. Where there is a question as to the best pH adjustment methods in any given location small scale trials of different rates and materials are advisable.

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