



What's Inside:

What Causes Soil to Become Acid?

Soil pH and Aluminum

Effects of Acidification

Solution to the Problem

What Happens When Soil is Limed

Dangers of Over-Liming the Soil



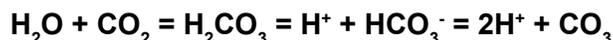
Humid, tropical conditions where soil acidity is likely to occur.

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Acidification of soil is a natural process with major ramifications on plant growth. As soils become more acid, particularly when the pH drops below 4.5, it becomes increasingly difficult to produce food crops. As soil pH declines, the supply of most plant nutrients decreases while aluminum and a few micronutrients become more soluble and toxic to plants. 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 expected results of both acidification and the practice of liming for acid neutralization.

What causes soil 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, and that values above this point represent alkaline conditions while those below 7.0 represent 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 is essentially distilled water, and the pH of distilled water in equilibrium with the atmosphere is about 5.6 due to the reaction of carbon dioxide (CO₂) with the water.



When pure water is in equilibrium with atmospheric carbon dioxide, the resulting hydrogen (H⁺) ion concentration brings the pH to the 5.6 indicated. Plants 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 hydrogen ions. Modern fertilizers commonly use ammonium (NH₄⁺) as the nitrogen source, but the eventual conversion of ammonium to nitrate (NO₃⁻) is accompanied by release of hydrogen ions.



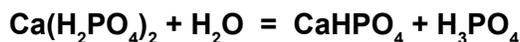
In other words, two hydrogen ions are produced for every ammonium ion converted to nitrate.

A popular nitrogen fertilizer is urea which, in soil with pH less than 6.3, is decomposed as follows:

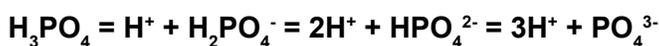


In other words, two hydrogen ions are consumed for each urea molecule decomposed. This tends to increase pH in the surrounding soil, but the ammonium ion is then converted to nitrate as indicated above, with four hydrogen ions being released by the two ammonium ions. Thus, while there may be a short term increase in pH when urea is applied, the overall reaction is still acidifying. (If the soil pH is greater than 6.3 the reaction is similar, and the short term pH increase can cause loss of the ammonium through by volatilization.)

While it is less acidifying than ammonium, the monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$] often used as one component of fertilizer can also be a factor. It will react with water to form dicalcium phosphate (CaHPO_4) and phosphoric acid (H_3PO_4).

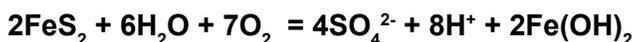


The phosphoric acid progressively releases hydrogen ions to the soil as pH is raised from about 3.0 to above 7.0.



In general the third hydrogen is only lost at pH values above neutrality, so is not usually a factor. However, two hydrogen ions will readily be lost in the acid soil pH range, so are a factor. Phosphorous fertilizer is typically placed in a narrow zone or band parallel to a row of plants. Because of the tendency for H_3PO_4 to give up some of its hydrogen ions, very low pH values can occur 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 similar reactions in soil have hydrogen ions as a byproduct of the reaction, so are acidifying. One of the most significant inorganic acidification reactions 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 (H^+) kg^{-1} (1 cmol is equal to 0.01 molecular weight.) of free H_2SO_4 have been reported (Thomas and Hargrove, 1984). For perspective, 300 cmol (H^+) kg^{-1} is 10 to 30 times greater than the negative charge commonly measured in soils. Soil particles of most soils, therefore, do not possess sufficient negative charge to attract all of the hydrogen ions to their surfaces. The remaining unbound hydrogen ions in the soil solution reduce soil pH. 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.

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.

Even plant growth will contribute to acidification; a major nutrient uptake process is to exchange hydrogen ions at the root surface for needed base cations (positively charged ions) such as calcium, magnesium, and potassium. Leguminous plants are particularly acidifying because they take up more cations, in comparison to anions (negatively charged ions), than non-leguminous plants. Legumes take up little nitrate from the soil because most of their nitrogen needs are satisfied by microbial nitrogen fixation within the plant structure. In non-leguminous plants, nitrate uptake partially balances base cation (e.g. Ca_2^+ , Mg_2^+ , K^+) uptake, so less hydrogen is 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 sesquioxides¹ 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.)

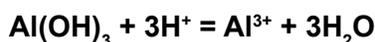
Causes of soil acidity discussed above are summarized in Table 1:

Table 1. Processes contributing to increased levels of hydrogen (H⁺) ions in soil solution, thereby resulting in increasingly acidic conditions.

Source of hydrogen ions	Reaction
Carbon dioxide	$H_2O + CO_2 = H_2CO_3 = H^+ + HCO_3^- = 2H^+ + CO_3^{2-}$
Ammonium	$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$
Phosphate fertilizer	$Ca(H_2PO_4)_2 + H_2O = CaHPO_4 + H_3PO_4$ $H_3PO_4 = H^+ + H_2PO_4^- = 2H^+ + HPO_4^{2-} = 3H^+ + PO_4^{3-}$
Pyrite (iron/sulfur)	$2FeS_2 + 6H_2O + 7O_2 = 4SO_4^{2-} + 8H^+ + 2Fe(OH)_2$
Organic matter	Decomposition processes
Nutrient uptake by plant roots	Release of H ⁺ in exchange for nutrient cations
Acid rain	Reaction in atmosphere of water with pollutants

The pH/Aluminum connection

At pH values greater than about 5.5, the ability of the soil to buffer² 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, the quantity of aluminum in most soils is sufficient for this ion to take over this role below pH 5.5. In what are called “hydrolysis” reactions, aluminum compounds [e.g. Al(OH)₃]—at the appropriate pH values—react with hydrogen ions to release aluminum. 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 changes 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 replaces plant nutrient ions such as calcium, magnesium, and potassium on negatively charged soil surfaces, moving them into the soil solution. In the short term it can make these ions more available to plants, but in the long term it makes them more susceptible to removal from the soil by leaching.

Effects of the acidification process

Soils typically carry a negative charge on particle surfaces, and these surfaces attract and hold positively charged base cations 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 base ions unless the bases are replaced by nature or by man. Eventually, as this process continues, hydrogen (H⁺) concentration on the surface becomes high enough that the mineral structures themselves are attacked, releasing silica (Si₄⁺), iron (Fe₃⁺), and aluminum (Al₃⁺) as well as other ions contained in the minerals. Whereas the silica ions leach to lower levels, the released iron and aluminum ions tend to come out of soil solution and form hydrous oxides (sesquioxides) which remain in the soil. Eventually insoluble amorphous hydrous oxides of aluminum and iron, along with Kaolinite, become the dominant solids in the soil.

Since tropical soils tend to be highly weathered, the nutrient holding capacity of minerals in these soils tend to be low. Most or all of the minerals with significant negative charge have disappeared through the weathering process outlined above, leaving 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 free aluminum ions in the soil solution will be increased to levels toxic to many plants. The accompanying loss of negative charges also means there are fewer 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. Weathering, therefore, is the primary reason many tropical soils are naturally low in fertility.

Another problematic effect of soil acidification is the tendency for phosphorous to be rendered unavailable for plant uptake. 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 relatively insoluble compounds through a process known as phosphate fixation. Phosphate fixation is especially problematic in tropical soils high in iron 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 practices decreased the acidity of the soil. Crushed shells and coral sands, if available, are still an acceptable and inexpensive source of liming material.

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, the purchase of liming materials is often out of the question (due to cost or availability). Perhaps the oldest agricultural strategy in the humid tropics is that of shifting cultivation, often commonly known as “slash and burn” farming. The forest is usually cut and burned, although other clearing systems are used (Norman, 1979), with crops grown and harvested for about three years 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 cations such as potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) will cause the ash to be alkaline and , 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 (initially established after clearing) will not be as effective in restoring soil organic matter, fertility, and structure (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 them. They 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.

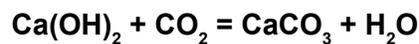
If the soil pH is not too low, it may be possible to build soil fertility without addition of liming material. In Central America, for example, Velvet Bean has been used as an intercrop and a green manure crop. As discussed earlier, legumes are normally considered to be acidifying plants because their uptake of cation and anion nutrients is unbalanced due to fixation of nitrogen within the plant structure. The excess cation uptake occurs as is affected by exchange of hydrogen ions are exchanged 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 due to 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 in which calcium is added to the soil, in the presence of atmospheric carbon dioxide it will be converted to calcium carbonate (CaCO_3). For example,



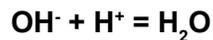
or



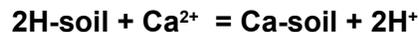
In an acid soil, the calcium carbonate then dissociates:



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



(2) the base saturation 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 (onto soil particles) and in solution. Both results usually make the soil more favorable to plant growth. (3) aluminum ions held by negative sites on soil particle surfaces are displaced into soil solution and, along with aluminum ions already in solution, are transformed back into the solid state sesquioxides [e.g., Al(OH)_3],



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 the soil's capacity to hold and exchange cationic plant nutrients. Conversely, (5) the soil's pH-dependent capacity to hold and exchange anions 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 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 and nitrogen mineralization from plant 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. High infiltration rates and consequent rapid leaching of bases from many tropical soils is due to their highly stable structure resulting from the tendency of iron and aluminum oxides to bind soil particles together into what are called aggregates. Overliming can cause a destabilization of this structure which, in turn, causes soil aggregates to break apart resulting in reduced permeability and lack of adequate drainage. With the addition- from lime- of calcium and magnesium to a soil, the number of small aggregates increases at the expense of larger ones. Presumably this is a case of sesquioxide (Fe and Al)-stabilized aggregates being broken up by 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. Observed favorable crop responses to liming appear 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 the breakup of soil aggregates 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 requirements 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.

Application Hints

1. Select fertilizers that contribute little or no acidity. Choose nitrate over ammonium sources of nitrogen. Ammonium sulfate, for instance, is very acidifying while calcium nitrate is non-acidifying. Diammonium phosphate and triple super phosphate are less acidifying than mono ammonium phosphate. Velvet bean is less acidifying than other leguminous sources of organic matter.
2. Apply organic and inorganic fertilizers wisely to keep nitrates within the crop rooting zone, keeping in mind that plant uptake of nitrate anions reduces root exchange of hydrogen ions for base cations. Avoid applying too much fertilizer, split applications of fertilizer instead of applying all at once, and/or use slow-release fertilizers.
3. Minimize loss of base cations to leaching or runoff. Plant cover crops during the off season. On sloped lands, establish barriers along contours to prevent runoff.
4. Incorporate non-leguminous plants into the farming system. Grasses planted between leguminous trees along contour lines of sloped land help slow erosion.
5. Supply calcium - in any of its multiple forms - to acidified soil. Monitor responses of soil pH and/or plants to these materials to avoid raising the pH too high.
6. Plant crops that are tolerant to acidity and/or aluminum. A publication entitled "[Nitrogen Fixing Tree Start-up Guide](#)" has a listing of acid-tolerant tree species (Elevitch and Wilkonson 1999). In general, any plant that grows well in the humid tropics is reasonably tolerant of acidity.

Bibliography

- Buckles, Daniel, Bernard Triomphe, and Gustave Sain. 1998. Cover Crops in Hillside Agriculture, Farmer Innovation with Mucuna. International Development Research Centre, Ottawa, Canada. 230 pp.
- Elevitch, C. and K. Wilkonson. 1999. Nitrogen Fixing Tree Start-Up Guide. Agroforester. P.O. Box 428 Holualoa, HI 96725. <http://www.agroforester.com>
- Lindsay, W.L. and H.F. Stephenson. 1959. Nature of the reactions of monocalcium phosphate monohydrate in soils: I. The solution that reacts with the soil. Soil Sci. Soc. Am. Proc. 23:12-18.
- McLean, E.O. 1971. Potentially beneficial effects from liming: chemical and physical. Soil Crop Sci. Soc. Fla. Proc. 31:189-196.
- Norman, M.J.T. 1979. Annual cropping system in the tropics: An introduction. University Presses of Florida. Gainesville, FL
- Sanchez, Pedro A. and Terry J. Logan. 1992. Myths and science about the chemistry and fertility of soils in the tropics. In R. Lal and P. A. Sanchez. Myths and science of soils of the tropics. Soil Science Society of America special Publication no. 29.
- Soares, Wilson, V. Edson Lobato, Enrique Gonzalez, and George C. Naderman, Jr. 1975. Liming soils of the Bazilian Cerrado. In Elemer Bornemisza and Alfredo Alvarado (Eds) Soil Management in Tropical America. Proceedings of a Seminar at CIAT, Cali, Columbia, Feb 10-14, 1974. Soil Sci. Dept., NC State Univ., Raleigh, NC.
- Thomas, Grant W. and William L. Hargrove. 1984. The chemistry of soil acidity. Soil Acidity and Liming. Agronomy Monograph # 12 (2nd Ed.). American Society of Agronomy, Madison, WI. pp 3-56.