Soil Reaction

Refers to the degree of soil acidity or alkalinity. Soil reaction is important because it affects nutrient availability, microbial activity and plant growth.

It is measured in units of pH, which is approximately defined as

$pH = -\log [H^+]$

Most plant species perform best in pH range 5.5 to 6.5 or 7.0 but some prefer extremes. For example azaleas and blueberries grow best under more acidic conditions. In contrast alfalfa does best under somewhat alkaline conditions.

Sources of H^+ and OH^-

Strongly acid soils $pH < 5$

Adsorbed H^+ and Al^{3+} dominate of the CEC. Equilibrium with these cations in solution accounts for low solution pH.

Moderately acidic soils 5 pH < 6.5

In this pH range, there is a lower fraction of adsorbed acidic species and higher percentage base saturation. Adsorbed and solution Al is more highly hydrolyzed. Exchangeable H^+ and $Al(OH)_x^{(3-x)+}$ are responsible for the moderate soil acidity.

Neutral to alkaline soils pH 6.5

The CEC is dominated by basic cations. Remaining H^+ and $Al(OH)_x^{(3-x)+}$ is associated with pH-dependent exchange sites may be considered bound. Exchange equilibria very strongly favor adsorption of these species at these type sites so their concentration in solution is low. In the relative absence of acidic cations, pH may rise above 7.

Carbonate and bicarbonate salts are present at alkaline pHs. Hydrolysis of these anions generates OH^-. For example,

$CaCO_3 \; W \; Ca^{2+} + CO_3^{2-}$
$CO_3^{2-} + 2H_2O \; W \; H_2CO_3 + 2OH^-$

Classification of Soil Acidity

Active
Exchangeable
Residual
Total

Active acidity refers to H^+ in solution. Exchangeable refers to adsorbed H^+ and $Al(OH)_x^{(3-x)+}$ that is subject to displacement by addition of an excess of extracting cation such as K^+. Residual is adsorbed H^+ and $Al(OH)_x^{(3-x)+}$ that is unextractable by unbuffered salts. Total acidity includes active, exchangeable and residual acidity.

Buffering

Refers to the tendency of soils to resist a change is pH upon addition of acid or base.

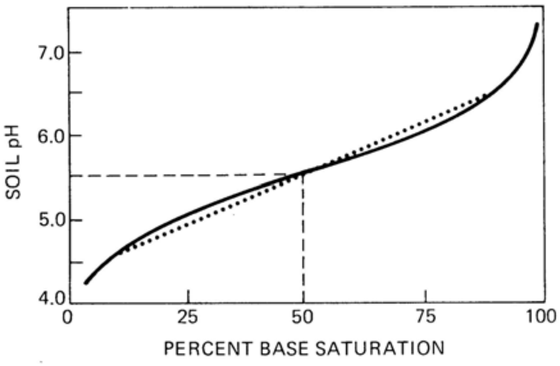
Addition of acid leads to increased adsorption of H^+ or consumption of H^+ by reaction with $Al(OH)_3$ to form soluble Al-hydroxy ions, $Al(OH)_x^{(3-x)+}$. At high soil pH, carbonates or bicarbonates will react with added acid,

$CO_3^{2-} + 2H^+ \; W \; H_2CO_3$

$H_2CO_3 \; W \; H_2O + CO_2$

On the other hand, addition of OH^- leads to its consumption by reaction with H^+ or $Al(OH)_x^{(3-x)+}$.

Magnitude of buffering is quantified in the buffer curve for a soil which relates solution pH to percentage base saturation. Buffer curves for a soil differ depending on the types and amounts of different colloids in the soil.



Example buffer curve showing increase in pH with increase in percentage base saturation.

Since percentage base saturation depends on CEC as well as adsorbed basic cations, the larger the CEC the greater is the amount of acid or base required to affect a change in soil pH.

Changes in Soil pH

Soils tend to become acidic as they weather and become leached of basic cations. How a soil is managed also affects its pH.

Natural acidification

Carbonic acid, organic acids and H^+ released during the oxidation of reduced N and S in organic matter exchange for basic cations on soil colloids. Basic cations are subject to leaching loss under humid conditions. Consequently, the percentage base saturation decreases and pH is lowered.

Acidifying fertilizers

Microbial oxidation of reduced N is a source of H^+

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

Disposal of organic wastes

Results in a greater rate of acidification due to organic and mineral acids produced by microbial oxidation. Acidification be averted if lime is added to organic material.

Drainage of certain coastal wetlands that contain high levels of reduced S

Oxidation of S or S^- in the drained material produces H_2SO_4. Very low pH may develop.

Acid deposition

Combustion of fuels that contain N and S releases partially oxidized S and N. Further oxidation and hydration in the atmosphere leads to sulfuric and nitric acids. The H_2SO_4 and HNO_3 represent an additional acidification burden on soil and accelerate the natural leaching acidification process. Acid deposition is considered a more severe problem for forest soils that may already be acid, have a low buffer capacity and for which, unlike agricultural soils, liming is not feasible.

Irrigation water quality

Accumulation of a high concentration of Na^+ will tend to elevate soil pH to high values. Other ill effects include dispersion of soil colloids, resulting in poor hydraulic conductivity, and salinization.

pH Measurement

Indicator dyes have been used for a long time. These change color depending upon whether the undissociated or dissociated form is present. The glass pH electrode is comparatively new. A potential develops across the glass membrane when immersed in a solution of H^+ activity different from the internal solution. This potential difference is calibrated to solution pH.

Controlling Soil pH

Depending upon plants to be grown (or other objective), it may be desired to raise or lower soil pH. To lower soil pH, S is typically added. It is oxidized to sulfuric acid

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

More commonly, however, one wants to raise soil pH and lime is used. Carbonates, oxides and hydroxides of Ca and Mg are *agricultural limes.* Of these, ground limestone is the most commonly used.

$CaCO_3$	Calcite
$CaMg(CO_3)_2$	Dolomite

Called *calcitic* if Ca mostly present or *dolomitic* if there is a mix of Ca and Mg.

CaO	Burned lime (quicklime)
$Ca(OH)_2$	Hydrated lime

When lime is added to an acid soil bicarbonate is formed

$$CaO + 2H_2CO_3 \rightarrow Ca(HCO_3)_2 + H_2O$$

$$Ca(OH)_2 + 2H_2CO_3 \rightarrow Ca(HCO_3)_2 + 2H_2O$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

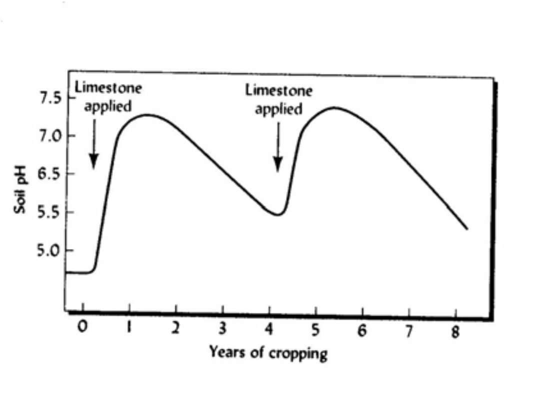
Bicarbonate reacts with H^+

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

Reduction of solution H^+ drives the desorption of adsorbed H^+ and acidic hydrolysis of $Al(OH)_x^{(3-x)+}$ to $Al(OH)_3$.

Even though one may have raised soil pH by addition of lime, acidification of soil continues due to leaching of newly added basic cations, organic matter decomposition and so forth. More lime is eventually needed.



Liming isn't a one time proposition.

Lime Requirement

Depends on: 1) target pH change, 2) buffer capacity of soil, 3) type and purity of lime material and 4) fineness of lime

Oxides and hydroxides react more quickly than limestones, however, these are more expensive. Laws on the sale of agricultural limes require that the composition of the material be stated in a guarantee. And since the finer the limestone, the faster it will react, there is also a fineness guarantee. In general, if at least 50 % of the particles pass a 60 mesh screen (0.25 mm), the limestone will reduce soil acidity adequately fast.

Subsoil Acidity

Due to the low solubility of limestone, it is most effective if incorporated. This poses no problem for correcting topsoil acidity, but deep incorporation of lime to reduce subsoil acidity is difficult and expensive. An alternative is gypsum, $CaSO_4 \cdot 2H_2O$, which is much more soluble. It is not a lime material and raises soil pH indirectly. The Ca^{2+} exchanges for some adsorbed Al^{3+}, making the Al^{3+} subject to leaching. The SO_4^{2-} may precipitate Al^{3+}. Also, SO_4^{2-} tends to be specifically adsorbed on soil colloids, displacing OH^- in the process.