How Soil Properties Affects Nutrient Adsorption

Natural and Human Effects of Soil pH

Soil pH is conceivably the single most important characteristic of soil chemistry. The pH of soil, sometimes referred to as "soil reaction", is a measure of the acidity or alkalinity of the soil.

First, let's define what pH is. pH is translated as "potential hydrogen". It is the way we calculate the amount of hydrogen ions (H^+) and hydroxyl ions (OH^-). A pH of 7 is defined as neutral. This means that there are equal amounts of the H^+ and OH^- ions.

Although the pH scale ranges from 1.0-14.0 the pH of soil normally falls between 4.0 - 9.0. Therefore an extremely acidic soil will range in the 4.0 - 4.75 and an extremely alkaline soil from 8.5 - 9.0. A neutral soil will range between 6.6 - 7.3.

The parent material of soils affect soil pH. Soils that originate from granite are typically acidic. Limestone based soils are usually alkaline. However, soil pH can amend over time. Rainfall and irrigation typically control the pH of most soils.

Percolation of a soil depends on the soil particle size and on the chemical structure of the soil material. Soils become acidic or sour, by the oxidation of the organic matter and by selective leaching of salts (alkali and alkaline earth metals) by the passing ground water.

In regions that have profuse amounts of precipitation, the water leaches basic ions such as calcium, magnesium, and potassium and replaces them with acidic ions such as hydrogen and aluminum.

Other natural processes that increase soil acidity include root growth and decay of organic matter by soil microorganisms. Whereas the decay of organic matter gradually will increase acidity, adding sources of organic matter with high pH values (such as some manures and composts) can raise soil pH.

Human activities that increase soil acidity include fertilization with ammonium containing fertilizers and production of industrial by-products such as sulfur dioxide and nitric acid, which ultimately enter the soil via rainfall.

Adding anhydrous ammonia as the primary source for nitrogen may significantly increase soil alkalinity if moisture and Ca and/or Mg is present in the soil. These two cations, more so for Mg with the higher electronegativity, causes a polarization of water thereby increasing the protonation of ammonia.

The chemical reaction is: $H_2O + NH_3 \rightarrow NH_4^+ + OH^-$.

As illustrated with the reaction, ammonia, which is extremely soluble in water forms ammonium (NH_4^+) a weak acid and hydroxyl (OH^-) a strong base. This may substantially increase the pH of the soil water. The consequences of the rapid increase in hydroxyl ions is the oxidation of the soil organic matter. The newly synthesized ammonium ions in the soil solution are available for cation exchange reactions in the soil.

In areas particularly in low rainfall regions, high sodic (high sodium content) and/or saline soils are more prevalent. Why? Because there is less rainfall to leach the alkali and alkaline earth metals deep into the soil.

If the soil water containing hydroxyl ions leaches or evaporates, the hydroxyl ions remain in the soil therefore are components of basic alkaline salts. Therefore due to the high concentrations of these materials, the soil becomes alkaline.

As the pH increases so does the formation of deposits such as calcium carbonate and magnesium carbonate. Irrigating with water high in bicarbonates gradually increases soil pH and can lead to alkaline conditions.

In most cases, changes in soil pH, whether natural processes or human activities cause them, occur slowly. This is due to the tremendous buffering capacity (resistance to change in pH) of most mineral soils. An exception to this is high-sand-content soils, where buffering tends to be low, as we'll discuss below.

Cation Exchange Capacity and Availability of Nutrients

The *cation exchange capacity* (CEC) of the soil is determined by the amount of clay and/or humus that is present. Sandy soils with very little organic matter (OM) have a low CEC, but heavy clay soils with high levels of OM have a much greater capacity to hold cations.

The disadvantages of a low CEC include the limited availability of nutrients to the plant and the soil's inefficient ability to retain nutrients. Plants will expend energy searching the soil for mineral nutrients. Soluble mineral salts (e.g. potassium sulfate) applied in large doses to soil with a low CEC cannot be held efficiently because the cation warehouse is too small.

The CEC of a soil is a value given on a soil analysis report to indicate its capacity to hold cation nutrients. CEC is not something that is easily adjusted, however. It is a value that indicates a condition, or possibly a restriction that must be considered when working with that particular soil. The two main types of colloidal particles in the soil are clay and humus and neither is practical to apply in large quantities.

Soil particles and organic matter have negative charges on their surfaces. Mineral cations can absorb to the negative surface charges or the inorganic and organic soil particles. Once adsorbed, these minerals are not easily lost when the soil is leached by water and they also provide a nutrient reserve available to plant roots. These minerals can then be replaced or exchanged by other cations.

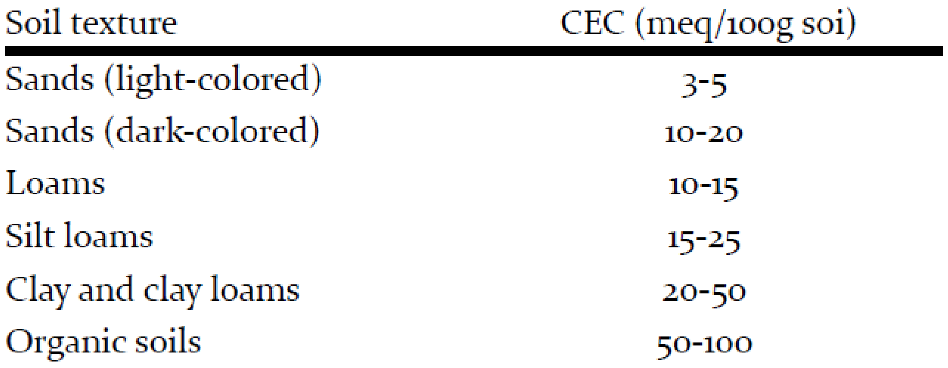
Two factors determine the relative proportions of the different cations adsorbed by clays.

First, cations are not held equally tight by the soil colloids. When the cations are present in equivalent amounts, the order of strength of adsorption is Al3+ >H^+ > Ca2+ >

Mg2+ > K+ > NH4$^+$ > Na+.
Second, the relative concentration of the cations in soil solution helps determine the degree of adsorption. Very acidic soils will have high concentrations of H^+ and Al3+. In neutral to moderately alkaline soils, Ca2+ and Mg2+ dominate. Poorly drained arid soils may adsorb Na^+ in very high quantities.

CEC is highly dependent upon soil texture and organic matter content. In general, the more clay and organic matter in the soil, the higher the CEC. Clay content is important because these small particles have a high ratio of surface area to volume. Different types of clays also vary in CEC. Smectites have the highest CEC (80-100 millequivalents 100 g-1), followed by illites (15-40 meq 100 g-1) and kaolinites (3-15 meq 100 g-1).

Examples of CEC values for different soil textures are as follows:



Soil texture	CEC (meq/100g soi)
Sands (light-colored)	3-5
Sands (dark-colored)	10-20
Loams	10-15
Silt loams	15-25
Clay and clay loams	20-50
Organic soils	50-100

Base Saturation

The proportion of CEC satisfied by basic cations (Ca, Mg, K, and Na) is termed percentage base saturation (BS%). This property is inversely related to soil acidity. As the BS% increases, the pH increases. The availability of nutrient cations such as Ca, Mg, and K to plants increases with increasing BS%.

Base saturation is usually close to 100% in arid region soils. Base saturation below 100% indicates that part of the CEC is occupied by hydrogen and/or aluminum ions. Base saturation above 100% indicates that soluble salts or lime may be present, or that there is a procedural problem with the analysis.

The Two Types of Cation Exchange Capacity

Two adsorbed ions are primarily responsible for soil acidity - hydrogen and aluminum. They differ in their relationship to the source and nature of the charge to which each of these ions is attracted. Two types of negative charges exist on soil colloids (a) permanent, and (b) pH dependent.

The first type involves a consistent permanent negative charge within the soil that is associated primarily with silicate clays and its electrostatic forces. The charge sites are located mostly on internal surfaces. Cations are exchangeable at all pH levels at the permanent charge sites.

The second type of negative charge varies in relation to soil pH. The charge is low in acidic soils and increases as pH rises. This charge is thought to have many sources. There are SiOH (Silicon Hydroxide) and AlOH (Aluminum Hydroxide) groups along the edges and external surfaces of silicate clay. In addition, there are carboxyl (COOH) and phenol (phenyl-OH) functional groups located on the humus colloids.

All of these groups each contain covalent bonded hydrogen which is not dissociated at low pH values. As the pH increases, hydrogen dissociates, leaving an available negative exchange site. Thus the hydrogen is replaced by metallic cations, which in turn become exchangeable.

Effect of a low pH on Cation Exchange Capacity

Nutrient availability varies according to the soil pH. The best pH for overall nutrient availability is around 6.5, which is one reason why this is an optimal pH for most plants.

In acid soils, complex aluminum and iron hydroxy ions are tightly adsorbed on clays. These ions block some of the negative charge sites of the colloid, reducing its cation exchange capacity. As the pH is raised, the complex ions are removed, forming insoluble $Al(OH)_2$ and $Fe(OH)_2$ and releasing the exchange sites.

In strong acid conditions aluminum becomes soluble and is present in the form of aluminum or aluminum hydroxy cations. The absorbed aluminum is in equilibrium with aluminum ions in the soil solution. Aluminum ions contribute to soil acidity through their tendency to hydrolyze. The hydrogen ions released give a very low pH value in the soil solution and are a major source of hydrogen in most very acid soils.

Adsorbed hydrogen is a second source of hydrogen ions in very acid soils. Hydrogen ions, which may be held by covalent bonds with some iron and aluminum, are so tightly adsorbed that it contributes little to the soil solution.

In moderately acid soils aluminum and hydrogen compounds also account for soil solution hydrogen ions. These soils have somewhat higher percentage base saturations and pH values. The aluminum cannot exist as Al^{3+} ions but are converted to aluminum hydroxy ions by reactions such as:

$Al^{3+} + OH^{-} \rightarrow Al(OH)^{++}$ and $Al(OH)^{++} + OH^{-} \rightarrow Al(OH)_2^{+}$

In moderately acid soils, with the rise in pH, some hydrogen ions which were strongly held through covalent bonds by organic matter and clay are now subject to release in association with the pH dependent sites.

Soils that are neutral to alkaline in reaction are no longer dominated by either hydrogen or aluminum ions. The permanent charge exchange sites are now occupied mostly by exchangeable bases, both the hydrogen and the aluminum hydroxy ions having been largely replaced.

Soil pH affects the availability of all nutrients one way or another. Therefore, maintaining pH close to the ideal level - 6.0 to 7.3 for most plants - is important.

How Acidic Soil is Modified

When pH levels are very acidic the soil becomes overloaded with hydrogen cations. At this point plants are not able to effectively get enough nutrition. Low soil pH such as 5.6 or below can be improved by adding ground limestone to the soil.
The amount of limestone required depends on the pH, temperature, and the amount of soil organic matter.

The chemical reaction is: lime ($CaCo_3$) + hydrogen (H^{+}) → calcium (Ca^{++}) + carbonic acid (H_2CO_3). Then the carbonic acid breaks down into water and carbon dioxide as follows: carbonic acid (H_2CO_3) → water (H_2O) + carbon dioxide (CO_2).

In summary then, $CaCO_3$ works by reacting with the free H^{+} ions in the soil and transforming it into water and carbon dioxide. This opens up the exchange sites in the soil thereby increasing the storage capacity of nutrients in the soil.

The Ideal Solution

We recommend that an application of SoilTech on acidic soils precede the lime application. Why? Because SoilTech will help perform some of the initial reactions including removal of the hydrogen and the hydroxy ions. The negatively charged sites on SoilTech will attract these ions and help to open up the exchange sites in clay soil. After a 30 day period, a lime application should follow.

On moderately acidic soils, we have found that SoilTech alone can help remediate the pH of soil. For soils that are very acidic, we recommend two applications of

SoilTech followed by an application of lime. Early spring or late fall is the best time of the year to do this.

Lime Requirements

The amount of lime required is a direct relation to the soil pH. To increase the pH from 4.5 to 5.5 on a 5,000 sq. ft. area would require 10 - 50# bags of limestone. The amount of clay in the soil will also affect the amount required. The higher the clay percentage, the more lime that will be required to open up the exchange sites in the soil.

The reaction rate for limestone increases when the soil moisture and temperature is high and whether the limestone is granular or crushed. Due to the fact that limestone is calcium carbonate, the solubility is very low. By purchasing crushed limestone, you will achieve better results. Be sure to periodically monitor the pH of the soil with a pH meter.

Relationship Between CEC and Fertilization Practices

Recommended liming and fertilization practices will vary for soils with widely differing cation exchange capacities. Soils having a high CEC and high buffer capacity change pH much more slowly under normal management than low-CEC soils. Therefore, high-CEC soils generally do not need to be limed as frequently as low-CEC soils; but when they do become acidic and require liming, higher lime rates are needed to reach optimum pH.

CEC can also influence when and how often nitrogen and potassium fertilizers can be applied. On low-CEC soils some leaching of cations can occur. Fall applications of ammonium N and potassium on these soils could result in some leaching below the root zone, particularly in the case of sandy soils with low-CEC subsoils. Thus, spring fertilizer application may mean improved production efficiency. Also, multi-year potash applications are not recommended on low-CEC soils.

Higher-CEC soils (greater than 10 meg/100g), on the other hand, experience little cation leaching, thus making fall application of N and K a realistic alternative. Applying potassium for two crops can also be done effectively on these soils. Thus, other factors such as drainage will have a greater effect on the fertility management practices used on high- CEC soils.

Buffering Capacity

Cations on the soil's exchange sites serve as a source of resupply for those in soil water which were removed by plant roots or lost through leaching. The higher the CEC, the more cations which can be supplied. This is called the soil's buffer capacity.

Buffering capacity is the ability of soil to resist changes in pH. Soils with a high buffering capacity require a great deal of amendment to alter pH. This is good if the soil already has a desirable pH, but it can be a problem if the soil needs pH modification. Normally, soils high in clay or organic matter (those that have high CECs) have high buffering capacities.

Calcareous soils often have high buffering capacities because lime effectively neutralizes acid - a great deal of acidification may be necessary to eliminate the lime before you can realize a significant drop in pH. Conversely, in lime-free soils, acid treatment can drop pH significantly. Soils also can resist upward changes in pH, depending on their composition.

Because buffering capacity determines how much amendment it will take to change pH, this is an important characteristic. Soil labs determine buffering capacity and adjust their recommendations according to the buffer pH.