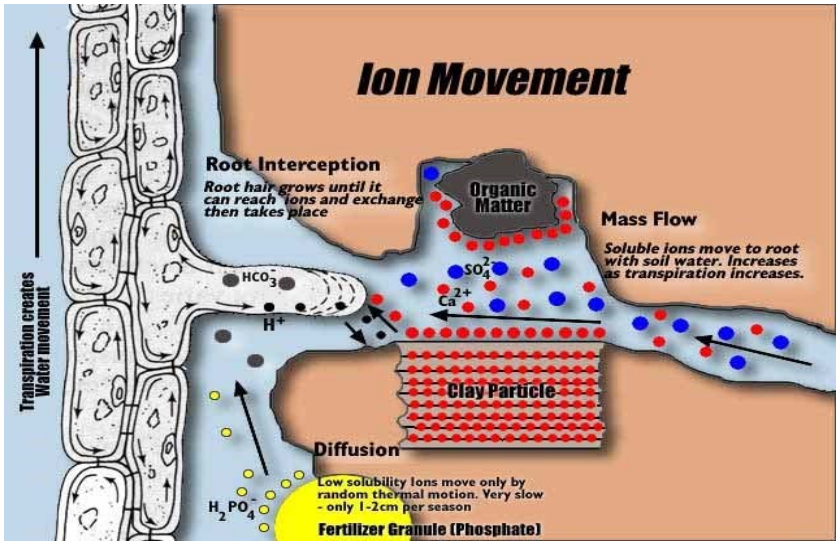
A Comprehensive Examination of Cation Exchange Capacity (CEC)

Concepts, Terms, Definitions, and Effects on Recommendations

Cation exchange capacity can be a confusing term in soil testing, in no small part because it can be defined or estimated in different ways. **In the simplest terms, cation exchange capacity is the total negative charge of soil particles.** This negative charge is concentrated on the smallest particles of mineral material (clays) and finely broken down organic matter (humus), since these small particles have a high surface area relative to their size. The surfaces of clay particles carry a permanent negative (-) electrical charge. The surface charge of organic particles can vary, as will be explained later.



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Almost all nutrient uptake by plants is through the soil water. Nutrients dissolved in the soil water have either a plus (+) charge and are called **cations** or a negative (-) charge and are called a**nions**. Essential nutrients with a plus charge (cations) include calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^{+1}), and ammonium (NH_4^{+1}), among others. Other non-nutrient ions also carry a plus charge, including sodium (Na^{+1}), aluminum (Al^{+3}), and hydrogen (H^{+1}). Essential nutrients with a negative charge (anions) include nitrate (NO_3^{-1}), phosphate (PO_4^{-3}), and sulfate (SO_4^{-2}). Anions are held in the soil by other means and will not be covered in this article. Calcium, magnesium, potassium, and sodium are dominant in higher pH soils. These are often referred to as **base cations**. Aluminum, iron (Fe^{+2}), and manganese (Mn^{+2}) are dominant in lower pH soils.

Because opposite charges attract, cations are attracted to and held by the negative surface charges of the soil particles. Cations on particle surfaces are always in equilibrium with those dissolved in soil water and may be *exchanged* between a surface and soil water. For example, as the soil water level of potassium (K) is depleted by plant uptake, it is replenished by release of K held on a negative charged sites, in exchange for some other cation in the soil water. This phenomenon is why negative surface sites are referred to as **exchange sites**. The total *active*

negative surface charge in the soil is called **Cation Exchange Capacity**. It is a gauge of the ability of the soil to hold and supply nutrient cations and carry them through one or more growing seasons. CEC is also sometimes referred to as the soil's **nutrient holding capacity**, even though this doesn't apply to *all* nutrients. Because this a measurement of particle surface charge, the units are in terms of quantity of charge per weight of dry soil: milliequivalents per 100 grams (meq/100g) or centimoles charge per kilogram (cmolc/kg). The 2 units are numerically identical.

Since most surface charge in soil resides on clay or humus particles, CEC is higher in soils with greater clay content and higher in soils with more organic matter content. Clay content of soil does not change significantly over time. So one of the easiest ways to increase CEC or nutrient holding capacity is by adding more organic matter.

The third factor determining CEC (and often the most confusing), is soil pH. CEC increases as soil acidity is neutralized with a lime application and pH increases. The 2 cations that are responsible for most of the active acidity in our soils are hydrogen (H^{+1}) and aluminum (Al^{+3}). Soil acidity, by definition, is the concentration of H^+ in the soil water. However, in most of our soils Al is the predominant acid-forming ion, as it is in most geologically young soils. Aluminum forms acidity (H^+) by splitting H_2O water molecules into H^+ and OH^- ions. Al forms very strong bonds with the OH^- ions, creating $Al(OH)_3$ and is neutralized. The 3 H^+ ions remaining create acidity. This process is called **aluminum hydrolysis**. Because of the +3 charge on Al bound to exchange sites, it can effectively block some of those sites for active exchange. By raising pH, Al is removed from some of these sites, which are opened up for occupation by nutrient cations. This is one way active CEC increases with pH.

The second, and more significant way, CEC increases with pH is by the creation of additional exchange sites on organic matter particles. As pH increases, H^+ ions are released from organic molecules. This creates many new (-) charge cation exchange sites where H^+ was tightly bound at lower pH. The higher the pH, the more new exchange sites are created. This variable charge on organic matter is called **pH-dependent Cation Exchange Capacity**.

So to summarize, CEC is higher in soils with greater clay content, higher organic matter, and higher soil pH. CEC is lower in sandier soils, soils low in organic matter, or soils with low pH.

Buffering Capacity

A high CEC soil holds a large pool of available nutrients, relative to crop plant requirements, so each nutrient will be depleted by plant uptake more slowly over time. This is an example of the concept of **buffering capacity**. Higher CEC soils are said to have a greater buffering capacity. Nutrients are depleted more slowly, but more nutrients are needed to replenish the supply once they are depleted. Lower CEC soils are more poorly buffered. They are depleted more rapidly, but require less nutrient input to be replenished.

Buffering also applies to soil acidity. A higher CEC soil requires more lime to neutralize a low pH, because of the relatively large amount of acidity. Those same soils will maintain ideal pH range longer and need lime less often than soils with low CEC.

Exchange Site Selectivity

Different soils hold and supply essential nutrient cations with varying degrees of efficiency. Not all exchange sites are equal in how well they hold K, Ca, Mg and other cations. The relative makeup of clay-based vs organic-based exchange sites is called the **exchange complex**. Organic-based sites have a high affinity for divalent cations, like Ca^{+2} and Mg^{+2}, and a relatively low affinity for monovalent cations, like K^{+1} and NH_4^{+1}(Evangelou and Blevins, 1985). Clay-based exchange sites have a higher affinity for K. Sandy soils, with little clay content, tend to hold less K on exchange sites and release more to the soil water. This makes K more susceptible to depletion and is part of the reason why it is so difficult to build up K levels in sandy soils. Soils with higher clay content hold more K on exchange sites and release it more gradually over time. This is another part of the definition of **buffering capacity** in soils. Sandy soils, with a higher proportion of organic-based exchange sites, are well-buffered with respect to Ca and Mg and poorly buffered with respect to K, compared to soils with higher clay content.

Measuring or Estimating CEC

Cation exchange capacity can be directly measured in the lab by "direct displacement". The soil is flooded with a single exchangeable cation (usually ammonium NH_4^+) at a specific pH (usually pH 7), forcing a mass exchange of all cations and saturating all exchange sites (active at the pH of the solution) with NH_4^+ ions. The NH_4^+ is removed by a second "displacing" cation in an extracting solution, where it can be measured. Because of the labor and time involved, this is an expensive procedure and not practical for large numbers of samples.

Most soil testing labs, including Maine, <u>estimate</u> active CEC by calculation. Nutrient extraction methods are measuring most or all exchangeable cations. Adding together Ca, K, Mg, and acidity according to their amount of (+) charge (milliequivalents), provides a good estimate of CEC. This is called s**ummation CEC**. In practice, non-nutrient cations like sodium are often ignored in the summation, since they are present at very low levels in most soils.

Because of the pH-dependent nature of CEC, the acidity factor used or assumed in the summation can vary considerably from lab to lab. This leads to discrepancies between labs when comparing CEC values. Many labs estimate CEC at pH 7.0, by adding the amount of acidity to be neutralized to reach pH 7.0. Some labs use no acidity factor at all and are estimating CEC at <u>current</u> soil pH. In Maine, we are able to estimate acidity at several different target pH levels. These acidity factors are in turn used to calculate the lime application to reach each target pH. The target pH assumption used to calculate CEC is explicitly stated on each of our reports. Unfortunately this is not a common practice among most labs.

When estimating CEC at <u>current</u> soil pH, exchangeable acidity should be factored in at lower soil pH levels. Low pH soils have an abundance of aluminum, some of which is readily or easily exchangeable. This **readily exchangeable acidity** diminishes to near zero as soil pH approaches 5.8 – 6.0 range. However at lower soil pH levels, readily exchangeable acidity can occupy a

large portion of active exchange sites. CEC at current soil pH is also known as **effective cation exchange capacity (ECEC).**

A common bias in the summation estimate of CEC occurs in situations of high pH, near or above 7, when unreacted lime (calcium/magnesium carbonate) is present. Since almost all commercial and University labs use an acidified extracting solution (Morgan, modified Morgan, Mehlich III), some of the Ca (and Mg) extracted may be from dissolved carbonates and not from exchange sites. This leads to a significant, sometimes major, overestimation of CEC. Labs compensate for this in different ways. Some just place an upper limit on CEC, corresponding to the upper limit of unlimed soils they typical run. Alternatively, CEC can be roughly estimated with soil pH and organic matter content (2 of the 3 factors determining CEC). This is the system used at Maine, where the summation CEC is adjusted if it exceed 130 % of the alternative estimate based on pH and organic matter.

Another less common bias in summation CEC is in cases of extremely high fertility, where nutrient content exceeds nutrient holding capacity. If a significant portion of the cations exist as "free salts" (not held on exchange sites) in the soil water, the summation will overestimate active CEC. This occurs most commonly in high tunnel production, especially in cases of very high water soluble salt content. Soil fertility management in these cases can often be achieved by monitoring and managing cation levels only in the soil water.

Saturation Percentage

Once CEC has been measured or estimated, it can then be used to determine the proportion of this negative surface charge occupied by each of the nutrient cations and soil acidity. The amount of charge (milliequivalents) of each cation used in the summation calculation is divided by the total and presented as a **percent saturation** of the CEC. Most soils in the pH 6 – 7 range have the majority of the exchange capacity occupied by calcium and magnesium. Soils with a low pH may have a large proportion of the exchange capacity occupied by acidity (aluminum or hydrogen). In some cases where sodium is present in a significant amount, it may be factored into the summation estimate of CEC and also presented as percent saturation. The sum of Ca, Mg, K, (and Na) saturations is often referred to as **base saturation**. The relative amount of soil acidity used in the summation is often labeled as % H, even though most acidity is derived from exchangeable Al as noted above.

Cation Saturation vs Total Available Quantity

For the base cations, current soil test levels can be presented in two different ways: as a quantity (parts per million or pounds per acre) or as percent saturation of the CEC. Many labs report Ca, K, and Mg both ways. However, interpretation (Low-Medium-Optimum) is based either by one system or the other, but not both. Commercial labs typically interpret the quantity, as do many University labs. Maine interprets by percent saturation for most, but not all crops. Ideal cation percentages were first proposed in the 1940's by Bear and Toth (1948), studying alfalfa response on New Jersey soils. They suggested ideal saturation levels of 65 % for Ca, 10 % for Mg, and 5 % for K. Several researchers seized on this concept and started promoting strict ratios between cations (**nutrient balance**) as an ideal fertility management strategy. It was promoted very

extensively by Albrecht during his long career and extensive writings (summarized in The Albrecht papers, 1975). The cation saturation ratio system is still often referred to as the "Albrecht system" (Schonbeck, 2000).

The strict cation ratio system has not proven to be valid in several studies (Graham, 1959; Liebhart, 1981; McLean, et al, 1983), which found that yield and quality are equally good through a range of cation ratios. For those systems that still interpret by cation saturation, a range of saturation levels is considered as Optimum (for example 3-5 % K, 10-20% Mg, 60-80 % Ca). Saturation percentages substantially outside the optimum ranges can be problematic. Nutrient cations are, after all, mutual competitors for retention on exchange sites and for uptake into plants. A huge excess of one cation, above the optimum range, can have a "displacement effect" on one or more others – forcing them into the soil water where they can be lost to leaching out of the root zone. For example, an overapplicaton of calcitic lime or lime-stabilized biosolids will over-saturate exchange sites with Ca, displacing K and Mg. This is sometimes characterized as an "induced deficiency". The general concept of balance between cations is valid, even if strict ratios are not necessary.

One problem with the percent saturation system is that it doesn't scale properly for soils with very high or very low CEC levels. This is primarily an issue with potassium. For example, a sandy/low organic matter soil with a CEC of 3 meq/100 gm has a very limited nutrient hold capacity. An "ideal" % K of 5% saturation would correspond to less than 120 pounds per acre of available K. This would not be sufficient to cover the K requirement of a high demand crop like potato or tomato, which easily need twice that much or more available K for the growing season. A saturation-based interpretation and recommendation system should also monitor and ensure a minimum quantity of availability and compensate for it in the recommended additions to low CEC soils.

At the other extreme, a loamy soil with high organic matter with a CEC of 18 meq/100 gm would require over 700 pounds per acre of available K to reach 5 % saturation. In a low K status soil, this would require cost-prohibitive fertilizer inputs to achieve this "ideal" K level. So a saturation-based interpretation and recommendation system requires limitations on maximum amounts recommended for any one cropping year, especially for high CEC soils. Maine K recommendations compensate for both minimum lb/A available K levels and limits maximum K application rates at any one time.

Sufficiency vs Buildup and Maintenance

There are two general philosophies used when making recommendations for K. The Sufficiency Level system recommends enough nutrient to achieve the minimum soil test level (the "critical soil test level") that statistically correlates to economic maximum yield (Olson, et.al., 1982). Economic maximum yield takes into account the cost of inputs to achieve that yield. The sufficiency level system minimizes input costs, while maximizing yield in an average year. It runs the risk of running short in an exceptional growing season. It does not seek to build soil test levels, though studies have shown that it does tend to build levels in years of poor growing conditions and lower yield. Fertilizer input costs are spread over several years in this system.

The Buildup and Maintenance system is designed to rapidly build soil test levels to the top of the Optimum range (either pounds per acre of K or percent saturation of K) plus compensate for anticipated crop removal. This system results in more up-front costs for inputs, but ensures enough nutrient availability for exceptional growing seasons. Since crop removal is factored in, a soil should theoretically still be at optimum test level after the next crop is grown and harvested. Ongoing input costs should be minimal and limited to crop removal quantities.

Many soil testing recommendation systems are referred to as "Modified Sufficiency Level", building soil test levels slightly higher than the statistical minimum "critical level". This is to hedge against higher than expected nutrient demand in exceptional growing seasons and to slowly build soil test levels over time. This marginally increases up-front input costs, though not as much as a full buildup and maintenance system. Maine uses both Buildup and Maintenance and Sufficiency Level recommendation systems, depending on the crop. For example, commercial potatoes receive K_2O recommendations based on both systems, presented side by side.

Summary and Implications

Cation Exchange Capacity is affected by many factors, but can be consistently measured or estimated using standardized methods. The assumptions used in calculations and measurement conditions should be clearly defined if they are to be understood by the end user. Laboratory transparency on soil test reports can go a long way toward understanding the assumptions used in presenting the test data. Assumptions used in calculating CEC and saturation percentages are not well documented in many cases. Lab certification programs do generally require a listing of the basic test methodology used, but not a listing of recommendation assumptions and philosophies.

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