INTERNATIONAL PLANT NUTRITION INSTITUTE

Cation Exchange: A Review

n almost all agricultural soils the surface charge is negative, meaning that they will retain positively charged ions (cations). The negatively charged soil will hold enough positively charged ions to balance the negative charge—called the cation exchange capacity (CEC). A soil with a larger negative charge can retain more positively charged ions and has a greater CEC.

Where does CEC comes from?

The cation exchange capacity is primarily determined by four soil properties:

- **Clay content (soil texture).** Since clays are usually the site of most of the cation exchange, the presence of more clay will result in a higher CEC than the same soil with less clay.
- The type of clay (mineralogy). The chemical conditions that were present when the clay was crystallizing determine the amount of negative charge locked in crystals (called isomorphic substitution). This negative charge is a part of the clay and does not readily change.



Figure 1. Up to 90% of the negative charge of humus is due to organic carboxylic and phenolic functional groups.



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- Soil organic matter. There is no permanent charge locked in organic matter, but its CEC depends on the surrounding chemical conditions. As the soil pH increases, the hydrogen cations are stripped from the organic matter (OM) and leave a negative charge that will retain a soil cation. As the pH increases, the CEC of organic matter increases; called pH-dependent charge. (Figure 1).
- **Soil pH.** The CEC provided by organic matter is entirely determined by the soil pH. As the soil becomes more acidic, organic matter loses its ability to retain cations. (**Figure 2**).

Clay also has a pH-dependent charge. For some clays such as kaolinite, 50% or more the CEC can be pH dependent, while for other clays, such as montmorillonite or vermiculite, less than 10% of the CEC is affected by soil pH.

The CEC of a soil is measured in how many positively charged ions (centimoles of charge, cmol_c) will be held in a kilogram of soil. For example, if a soil contains 20 cmol_c/kg soil, it can retain 20 cmol of H⁺ and exchange it with 20 cmol of another single-charged cation such as K⁺ or Na⁺. This same soil can retain half as many atoms (10 cmol) of a doublecharged cation such as Ca²⁺ or Mg²⁺ (20 cmol of charge). This soil can only retain 20 cmol of charged cations, regardless of what single or combination of cations might be present.

The kind and amount of clay minerals and OM influence the CEC of a soil. Most soils have a CEC between 5 and 40 cmol_c/kg , however, some can be as low as 2 cmol_c/kg or as high as 100 cmol_c/kg (**Table 1**).

Table 1.	Range of cation	exchang	e ca	pacity	in typi	cal agricul-
	tural soils.					

	Soil Textural Class	CEC (cmol _c /kg)
CEC is higher in soils	Sands (light color)	2 - 4
with:mostly 2:1 clays	Sands (dark color)	8 - 16
 high clay content 	Loams	10 - 15
 high organic matter content 	Silt Loams	15 - 25
content	Clay & Clay Loams	20 - 50
	Organic Soils	50 - 100

Abbreviations and notes: K = potassium; Ca = calcium; Mg = magnesium; Na = sodium; H = hydrogen; Al = aluminum; Cu = copper; Fe = iron; Mn = manganese; Ni = nickel; Zn = zinc; NH_4 = ammonium



Figure 2. Some of the H⁺ ions are neutralized as the pH rises, increasing the negative charge of these organic molecules.

To understand how cation exchange works, it is helpful to understand the internal and external surfaces of clay particles. The internal layers consist of two planes of atoms on both sides of the interlayer space at the base of each tetrahedral sheet. The external surfaces are simply the outside edges of the clay. Both the internal and external surfaces generally have a negative charge and retain cations. The total surface area of different clays has a large impact on the CEC (**Figure 3**).

Of the cations held on exchange sites, only a small percentage will be dissolved in the soil water at any given time and be immediately available for plant uptake. The remaining cations held on exchange sites provide a valuable reservoir of nutrients that will be slowly released into soil solution as nutrients are acquired by plants or are leached from the soil with rainfall or excess irrigation.

Measuring the CEC of a soil is a good indicator of the nutrient holding and buffer capacity of the soil, but is not by itself sufficient for managing soil nutrients. However, knowing both the amount and chemical composition of the cations is very useful for managing soil nutrients.

Base saturation is used to describe the proportion of so-called basic cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) that are held



Electron micrographs of two clay minerals showing the difference in surface area among clay types. **Source:** Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University.



Figure 3. Cations are retained by negatively charged sites in internal sites and on the clay edges. Vermiculite clay can retain K in the interlayer with especially strong affinity (K fixation).

on the cation exchange sites. In acid soils, H^+ and Al^{3+} become more prevalent. Other micronutrient cations (such as Mn^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Co^{2+}) are also found on cation exchange sites, but they only account for a very small percent of the total exchangeable cations.

Is there an ideal ratio of these cations?

There is no single ideal ratio of these cations in *all* soils. This theory of an "ideal cation proportion" was first introduced in the 1930s and 1940s. The proposed ratios were 65% Ca, 10% Mg, 5% K, and 20% H. The concept, frequently referred to as the "base cation saturation ratio" (BCSR), has been repeatedly examined for over 60 years in greenhouse, field, and laboratory research, and has consistently reported to be unfounded. Plants grown with these specific cation ratios would not have any cation nutrition problems, but there is no evidence that they will grow better or have superior cation nutrition than plants fertilized according to traditional soil testing recommendations.

While an adequate cation supply is essential for plants, there is no one ratio that must be forced in all situations (as evidenced by the productive agriculture that occurs under very diverse global soil conditions) as long as certain minimum requirements are met. Trying to achieve a single "ideal" ratio under all circumstances is unnecessary for plant growth and frequently very expensive to reach and maintain. Consider the problem posed in calcareous soils where soil Ca levels are high, but Mg and K levels are more than sufficient as well. With the BSCR approach, additional Mg and K are generally recommended to counterbalance the abundant Ca, but no crop responses are observed.

The BCSR concept has been applied in hydroponic production, but even there the *concentrations* of the cations are also important, not just their ratio. Additionally, nutrient requirements change as the plant develops and different crops have different nutrient ratios in their vegetative and reproductive parts. Soils are commonly sampled in the 0 to 6 inch depth, while roots extend far below this depth so where should the BCSR be measured? The notion of maintaining some H⁺ on the exchange sites was popular in the 1940s, especially in the acid soils where this concept was developed. We now understand that measurement of exchangeable H⁺ is largely a result of lab procedures and that it does not occur on most soil exchange sites, particularly in common Western soils! The BCSR system may be most useful for identifying extreme cation ratios that need special attention and correction.

Measuring Cation Exchange Capacity

Direct measurement of CEC in the laboratory is relatively expensive, so many soil testing labs estimate the total CEC instead. These estimates are made by measuring and summing the extractable basic cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) and estimating H⁺ and Al³⁺ from soil and buffer pH measurements. These estimates are generally adequate for making management decisions. If gypsum has recently been applied or an acidic extractant is used for a high pH soil that contains limestone, then erroneous measurement of exchangeable Ca²⁺ will result.

Another common technique for estimating CEC involves first saturating all the exchange sites with NH_4^+ and then replacing the NH_4^+ with Ca^{2+} . The amount of displaced NH_4^+ is then measured, and the CEC calculated. The CEC is also estimated by some laboratories based on the soil texture, which provides a reasonable estimate as long the clay content and mineralogy are known. The results from analysis of exchangeable cations are sometimes converted to units of "pounds of nutrients per acre". This is done by accounting for the charge on the cation, the atomic weight, and using an average of 2 million pounds in the soil surface of an acre to a depth of 6 2/3inches (**Table 2**). This information gives an estimate of the pounds of available cations, but still needs to be calibrated to crop response before it is meaningful. It reflects the quantity of exchangeable cations, not the total quantity present in the soil.

Cation exchange in soils is a familiar concept that we too often overlook. It is a fundamental soil property that allows us to manage cations in a way that promotes healthy crop growth and sustainable use of plant nutrients.

Table 2.Exchangeable cations can be converted to pounds per
acre as an estimate of the total quantity of potentially
available nutrients in the surface soil.

cmol _c /kg	(Equivalent weight x 20) = pounds/A*
Са	x 400
Mg	x 243
К	x 782

^{*}Based on assumption of 2 million pounds of soil in the 0 to 6 2/3 inch depth in one acre)

Example: 5 cmol_c K⁺/kg would convert to 3,910 lb/A of exchangeable K⁺. This does not mean that the soil contains only 3,910 lbs of K⁺, but provides an indication of potentially exchangeable nutrient. The specific number does not give a recommendation for nutrient management until it has been calibrated with crop response.

Nutrient Source Specifics

is a series of brief, condensed, one-page fact sheets highlighting common commercial fertilizers and nutrient sources in modern agriculture. They are available as PDF files at this URL: >www.ipni.net/ specifics<

- 1. Urea
- 2. Polyphosphate
- 3. Potassium Chloride
- 4. Compound Fertilizer
- 5. Potassium Sulfate
- 6. Potassium Magnesium Sulfate: Langbeinite
- 7. Urea-Ammonium Nitrate
- 8. Thiosulfate
- 9. Monoammonium Phosphate
- 10. Ammonia
- 11. Potassium Nitrate
- 12. Ammonium Sulfate
- 13. Sulfur
- 14. Triple Superphosphate
- 15. Nitrophosphate
- 16. Gypsum
- 17. Diammonium Phosphate
- 18, Calcium Carbonate (Limestone)
- 19. Phosphate Rock
- 20. Coated Fertilizer
- 21. Single Superphosphate
- 22. Ammonium Nitrate

