

EXCHANGEABLE CATIONS, CATION EXCHANGE CAPACITY AND BASE SATURATION AND ITS RELATIONSHIP TO SOIL FERTILITY

E.M. 2894 (Rev.)

March 1968

OCTOBER, 1967

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Physically, soil is made up of sand, silt and clay (colloidal) particles. The sand particles are large enough that they can be seen with the unaided eye. Individual silt particles cannot be seen except with magnification. Clay (colloidal) particles can be seen only with the aid of a high powered microscope. Some colloidal particles can be seen only with the aid of an electron microscope. The colloidal particles are those soil particles that stay in suspension for days or even weeks when soil and water are mixed and then allowed to stand. The sand and silt particles settle out in a matter of minutes.

Some soils have very little clay and silt in them but a considerable amount of sand. These would be called sandy loam soils. Soils that contain a high proportion of clay to sand and silt are called clay loams. An intermediate type of soil would be a silt loam (high in silt, with a moderate amount of clay and a very small amount of sand). A number of descriptive terms such as sandy loams, clay loams, etc. are used to indicate in a general way, soil texture (the relative proportion of sand, silt, and clay). The texture of a soil determines, or at least will affect, many soil characteristics such as water holding capacity, rate of water intake, and "stickiness" as well as the amount of cations (nutrients such as potassium, calcium and magnesium) it can hold (cation holding capacity).

A sandy loam soil would have a high water intake rate, it wouldn't hold a great deal of water when saturated, it wouldn't be especially "sticky" when thoroughly wet, and it wouldn't be able to hold a large amount of cations. A clay loam soil on the other hand, would have a slow water intake rate, it would take considerably more water to saturate this soil than a sandy loam soil (has a higher water holding capacity), it would be very sticky when wet, and would have a high cation holding capacity.

The physical component of the soil that exerts the dominant influence of these physical characteristics is the clay (more correctly called colloidal particles). These colloidal particles are extremely small mineral particles which are crystalline in nature. Many occur in the soil as tiny plate-like particles, although some are angular or sub angular and even rectangular in shape.

COOPERATIVE EXTENSION SERVICE • COLLEGE OF AGRICULTURE • WASHINGTON STATE UNIVERSITY • PULLMAN

In cooperation with the United States Department of Agriculture

Issued in furtherance of the Acts of May 8 and June 30, 1914, by the Washington State University

Cooperative Extension Service, John P. Miller, Director

The clay (colloidal) particles play a major role in chemical reactions that take place in the soil, particularly those that are related to soil fertility.* The one property of colloids that is of major importance in this respect is the negative charge which they possess. The negative electrical charges occur for the most part, on the edge of the colloidal particles. In some cases some charges occur between layers of atoms within the crystal.

The plant food elements calcium, potassium, magnesium, iron, zinc, copper, and manganese (the chemical symbols are respectively: Ca, K, Mg, Fe, Zn, Cu and Mn) can and do occur in the soil in the ionic form (an ion is an atom with an electrical charge). These elements have a positive charge. The symbol used to show the ionic form is Ca^{++} , K^{+} , Mg^{++} , Fe^{++} , Zn^{++} , Cu^{++} and Mn^{++} . Since unlike electrical charges attract each other, these positively charged ions will be attracted to and held by the negatively charged colloidal clay minerals, somewhat like iron filings are attracted to and held by a magnet. The ions move to the clay since the ions are in solution in the soil water. These colloidal particles are many times larger than the plant nutrient ions so each colloidal particle may hold several ions. These ions are "available" to plant roots for absorption.

The various positively charged ions are each attracted to and held by the colloidal particles with different degrees of force. The force with which cations are held to the clay decreases in the following order: H^{+} , Ca^{++} , Mg^{++} , K^{+} , NH_4^{+} , Na^{+} . This means that if a water solution containing equal portions of calcium, magnesium, and potassium is allowed to filter through a soil, the ions would not be adsorbed in the same proportion as they occur in the solution. Note that the word adsorb is used when referring to the process of holding ions to colloidal particles. It is a phenomenon that occurs on surfaces. Absorbition refers to a process where something goes through a surface and to the interior portion of the absorbing object.

Other positively charged ions occur in the soil too. Three of them are sodium, aluminum, and ammonium. All of the positively charged ions are classed as "cations".

There are also negatively charged ions in the soil - such as nitrate which is an important plant food, (chemical symbol NO_3). All negatively charged ions are called anions. They are not attracted to and held by the negatively charged colloidal particles. (Similar charges repel each other). This is why nitrates are so readily leached out of the soil. They simply move with the soil moisture, down through the soil and out the subsurface drainage ways if excess water is applied. Since it is the colloidal (clay) particles that attract and hold cations, it is obvious that the more clay (colloidal size particles) a soil has, the more cations it can hold. From the standpoint of maintaining a supply of the plant food elements (and those which are important in soil fertility management) cation holding capacity is important. For example, when potassium fertilizer is added to a soil, commonly muriate of potash ($-\text{KCl}-$), it goes into solution in the soil moisture. The potassium chloride ionizes into a potassium ion (K^{+}) and a chloride ion (Cl^{-}). The potassium is adsorbed and held by the colloidal particles-but not held so tightly that the plant can't get it. If it were not for this process of ionization and adsorbition potassium and other cations would leach away.

* Soil organic matter (humus) has properties that cause it to function in the same way as mineral colloids with respect to ability to hold and exchange cations. In fact "humus" can be a very important contribution to the soil's cation holding ability.

The chloride ion (Cl^-) being negatively charged and not attracted to and held by the clay, can be leached out of the soil.

A clay loam soil can hold a much larger amount of cations than can a sandy loam soil, simply because it has a higher content of clay - and consequently a larger number of negative charges for attracting positively charged cations.

Colloid With Cations

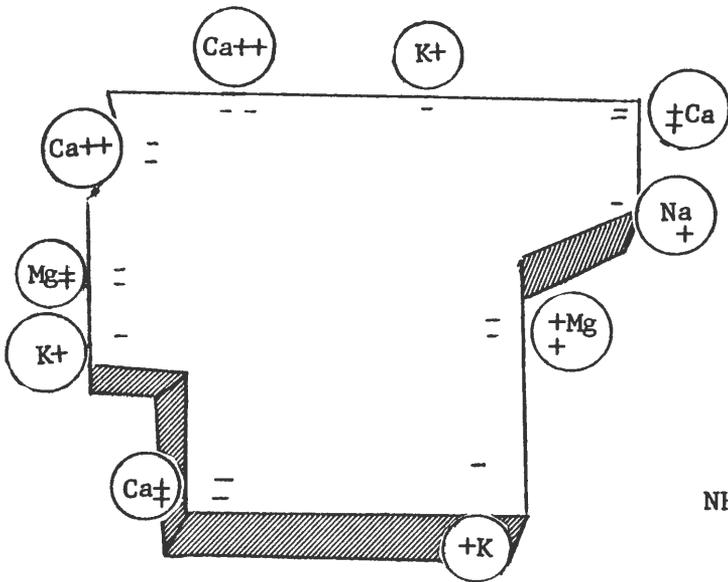


FIGURE I

A diagram of a colloidal particle saturated with the cations Ca^{++} , Mg^{++} and K^+ .

Colloid Saturated With Ammonium ions

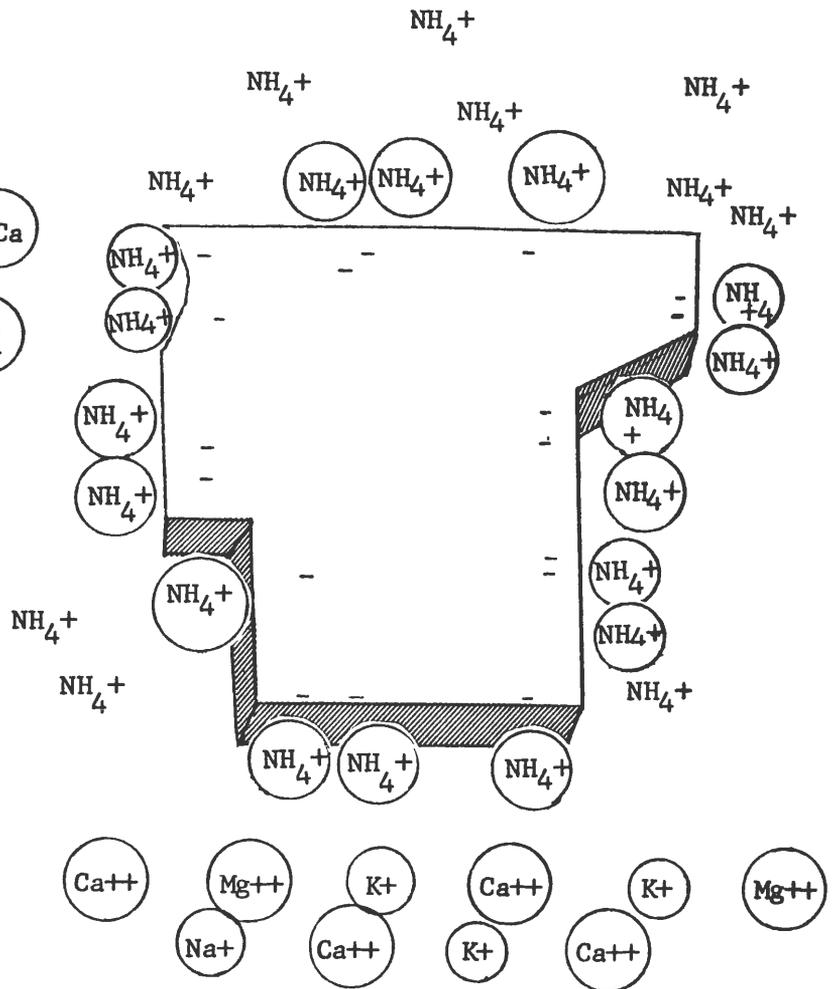


FIGURE II

Replacement of cation on colloidal particle with a solution containing ammonium ion.

CATION EXCHANGE

The cations held by the soil colloids can be replaced by other cations. For example, if a moderately concentrated solution containing ammonium cations NH_4^+ , is added to a soil and allowed to percolate through, there will be a replacement of the other cations by the ammonium ions. This process of replacing (or exchanging) the cations in the soil by another is the process used in the laboratory to replace the cations held by the soil so they can be determined. These cations can be exchanged, hence the term exchangeable cations. The total amount - or quantity of cations that a soil can hold - is called its cation exchange capacity. This is determined by saturating the soil with a cation such as ammonium, washing out the excess, replacing all the adsorbed ammonium, then determining the amount of ammonium held by 100 grams of soil.

Quite commonly the capacity to hold cations is called base exchange capacity. This is not the correct term to use. It came into use because the cations present in largest quantities and most often studied in relation to soil fertility are the bases potassium, calcium, and magnesium. These are called bases since the oxides of these elements when added to water, will form a strongly basic solution (pH above 7.0 - usually pH 8.0 - 11.0). Sodium is also in this category - but it is not a plant nutrient. Except for sodic (alkali) soils it is generally present in the soil in only small quantities. It is not correct to speak of base exchange capacity since cations other than the bases can be - and usually are, held by the soil.

In humid regions, (regions of high rainfall) the cations other than the bases may constitute a large part of the cations held by the soil colloids. For example, the soils of Western Washington have formed under moderate to heavy rainfall. The exchange complex in these soils may have a relatively small proportion of its electrical charges satisfied by the bases potassium (K^+), calcium (Ca^{++}), and magnesium (Mg^{++}). The cation hydrogen (H^+) - the one that gives soil its acid reaction - may be held in moderate amounts. Also under acid conditions moderately large amounts of aluminum (Al^{+++}), manganese (Mn^{++}), and iron (Fe^{++}) may be held by the colloids. Soil that provides the best growing conditions for most crops should have little or no aluminum and hydrogen and only small quantities of manganese, and iron on the exchange complex. It should have a relatively high proportion of the three bases - calcium, potassium and magnesium. (Iron and manganese are essential plant nutrients, but in excessive amounts, especially manganese, they can be toxic. Aluminum is not essential and in even relatively small quantities can be toxic to plants.) For a crop like alfalfa, the cation holding capacity should be saturated with the bases Ca, Mg and K to the extent of about 65 percent or more.* A ratio of Ca:Mg:K commonly found in fertile soils is 10:2:1. There is no one proportion or ratio of these cations that is ideal. The ratio is important but another important factor is that each cation be present above a certain minimum level. The optimum ratio and amount is also different for different crops. When 65 percent base saturation is reached, there is little likelihood of toxic amounts of manganese or aluminum being present. Some crops can be grown satisfactorily at a considerably lower level of base saturation. White clover, for instance, does well at 35 percent base saturation. Cereal crops and grasses do well at considerably lower levels than this.

* Base saturation values will vary some from method to method. Reference here is to the method used at the WSU Soil Testing Laboratory.

Base saturation, as indicated above, refers to the proportion of the exchange complex which is occupied by the bases sodium (Na+), potassium (K+), calcium (Ca++), and magnesium (Mg++). It is preferable that sodium be less than 5% of the cation exchange capacity. Soils in high rainfall areas - e.g. Western Washington - generally contain only insignificant amounts of sodium. Sodium is not essential for plant growth. In regions of low rainfall - e.g. the Columbia Basin - sodium may be present in relatively large amounts. If present to the extent of more than 15 percent of the exchange capacity, "alkali soil" (more correctly called "sodic soils") conditions begin to appear. In normal soils, calcium is the cation that is usually present in the largest quantities. This is one of the reasons why lime is added to soils with low base saturation because calcium is needed in large amounts (lime is calcium carbonate) and lime is one of the least costly bases to add. Lime also neutralizes the hydrogen ion - the one that makes soil acid.

Since the cations are attracted to and held by the soil colloids, they will not readily leach away. This is important from the standpoint of conserving nutrients and for maintaining a ready reserve of nutrients for plants.

TERMS AND SYMBOLS USED TO EXPRESS AMOUNTS OF CATIONS

Exchangeable cations are not reported in terms of pounds per acre. Milliequivalents per 100 grams of soil is the basis used for expressing quantities. One milliequivalent of any one element is chemically equal to one milliequivalent of any other in terms of its capacity to satisfy the electrical charges on the soil. It is not true, for instance, that one pound of calcium can neutralize as many electrical charges as one pound of magnesium or sodium - but 20 milligrams of calcium, 39 of potassium, 12 of magnesium can each neutralize the same number of negative charges on the soil colloids. Each of these quantities is referred to as a "milliequivalent". From the soil scientist's standpoint, this means of expressing the amounts of cations has much more meaning as it shows at a glance the chemical proportion of each cation (element) to the other. Expressing the cations in terms of pounds per acre does not show directly the chemical proportion of these cations.

To help understand what milliequivalents per 100 grams of soil means in terms of pounds per acre, (assuming 2,000,000 lbs. of soil per acre inches of depth) the following table will serve as a guide.

<u>Milliequivalent</u> <u>(Meq) of each</u>	=	<u>lbs./A</u> <u>6 inches of soil</u>	<u>equivalent to:</u>
Na+		460	1170 lbs. of (sodium chloride)
K+		780	1490 lbs. of (muriate of potash)
Ca++		400	1000 lbs. CaCO ₃ (lime)
Mg++		240	2460 lbs. Mg SO ₄ · 7H ₂ O (Epsom salts)