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Base saturation is an inadequate term for Soil Science

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ABSTRACT: Bases are chemical species that donate electrons, accept protons, or release hydroxyls (OH⁻) in aqueous solution. In Soil Science, “base saturation”, “exchangeable bases” or “basic cations” has been widely used to distinguish Ca²⁺, Mg²⁺, Na⁺, and K⁺ from H⁺ and Al³⁺ cations. This terminology is confusing since none of these cations are truly a base in chemistry sense. However, in the absence of the proposition of a correct term, the term “base saturation” remains in use nowadays, causing confusion among students, professionals, and even among professors and researchers in Soil Science, as it leads to the erroneous interpretation that the soil acidity can be corrected by adding these cations to the soil. Here, we present the historical background of this nomenclature and a theoretical foundation that justifies the abolition of the use of these terms in Soil Science. We consider that the most correct is to call it “Ca-Mg-K-Na saturation”, which, despite being long, would refer directly and without any misinterpretation of the terminology. In Soil Fertility, the “base saturation” is often calculated only as a function of the sum of Ca, Mg, and K, since the Na content is negligible in most tropical and subtropical soils. Thus, one could use the term “Ca-Mg-K saturation”. Likewise, it is also suggested to abolish the use of the term “sum of bases” and use the term “sum of Ca-Mg-K” or “sum of Ca-Mg-K-Na” instead when necessary.

Keywords: basic cations, soil acidity, exchangeable cations.

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INTRODUCTION

Most of South America's tropical and subtropical agriculture developed in naturally acidic soils, with high aluminum (Al^{3+}) and low levels of exchangeable nutrients such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), as a result of the intense soil weathering (Rabel et al., 2018). An increase in soil pH through the addition of bases is necessary to cultivate these soils with crops sensitive to high acidity and with the presence of phytotoxic Al^{3+} (Bellinaso et al., 2021), which are chemical species that donate electrons, accept protons, or release hydroxyls (OH^-) in aqueous solution (Atkins et al., 2017). The bases most used in Brazil are called agricultural limestones, obtained from grinding sedimentary or metamorphic carbonate rocks. Other products can be used to correct soil acidity, such as quicklime, hydrated lime, and calcined limestone. In addition, there are also other materials with alkaline reactions used on a smaller scale in agriculture, such as by-products or industrial residues (e.g., cellulose industry or metallurgy) and some silicate rock powders.

These products capable of correcting soil acidity are composed by chemical bases such as carbonates (CO_3^{2-}), bicarbonates (HCO_3^-), hydroxides (OH^-), and oxides (O^{2-}), and their accompanying cations, such as Ca^{2+} , Mg^{2+} , and, in some cases, silicon (Si^{4+}). Examples of this are calcium carbonate (CaCO_3), magnesium carbonate (MgCO_3), calcium and magnesium carbonate [$\text{CaMg}(\text{CO}_3)_2$], calcium oxide (CaO), magnesium oxide (MgO), calcium hydroxide [$\text{Ca}(\text{OH})_2$], magnesium hydroxide [$\text{Mg}(\text{OH})_2$], calcium silicate (CaSiO_3), and magnesium silicate (MgSiO_3). After solubilization and dissociation of CaCO_3 , which is one of the most used bases to correct soil acidity, OH^- is generated, with the anion HCO_3^- as an intermediate anion (Equations 1, 2 and 3). The hydroxyl reacts with the acidity of the soil solution (active acidity), increasing the pH. More specifically, there is a diffusion of H^+ ions from the soil solution to the Diffusion Boundary Layer of the limestone particle. After that, the neutralization occurs through the destruction of the mineral and the release of carbon dioxide gas (CO_2). This promotes the dissociation of hydrogen ions (H^+) (or more precisely, the hydronium ion - H_3O^+) and the Al^{3+} ion adsorbed to soil functional groups (potential acidity), buffering the consumption of protons from the solution until a new chemical equilibrium is reached. The same reaction occurs when we add carbonates combined with other accompanying cations, such as MgCO_3 or $\text{CaMg}(\text{CO}_3)_2$, in which the production of bases is the same but differs in molecular mass (e.g., $\text{CaCO}_3 = 100$ g, $\text{MgCO}_3 = 84.3$ g) and cations released (i.e., Ca^{2+} and Mg^{2+}).



During this process, functional groups on the surfaces of colloidal soil particles (clay minerals, oxides, and organic matter), which are either blocked by Al^{3+} (or its hydrolyzed forms: $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$), or not yet dissociated (H^+), will form surface complexes with the cations accompanying the liming materials. Thus, when these substances are added, at the same time that the pH of the soil increases, there is also an increase in the amount of cations adsorbed to the soil (e.g., Ca^{2+} and Mg^{2+}), including those previously present in the soil solution, reaching a new equilibrium between the activity of ions in the soil solution and the ions forming surface complexes.

In Soil Science, the use of the term cation exchange capacity (CEC) is conventional for the purpose of comparing the amount of charges or functional groups among soils and as a result of anthropic action. However, this term does not represent the maximum amount of cations a soil can adsorb, nor its desorption. Although extremely limited as

an indicator of the reactivity of cations, it can still be used to express in a simplified way the behavior of some cations of agro-environmental interest (Rheinheimer et al., 2022). Thus, the proportion of CEC occupied by cations such as Ca^{2+} , Mg^{2+} , K^+ , and Na^+ is erroneously called “base saturation” in several books and scientific articles. Similarly, the term “sum of bases” is also often misused to express the sum of the contents of the same cations. This term is related to the classification of chemical elements in the periodic table, in which sodium (Na) and K are classified as alkali metals, and Ca and Mg are classified as alkaline earth metals (Atkins et al., 2017). The term alkaline was used because these metals, in their ground state (Na^0 , K^0 , Ca^0 , and Mg^0), react with water forming alkaline substances (such as hydroxides) spontaneously, without the need to supply energy for the reaction occurs. However, in soil, fertilizers, correctives, and plants, these elements do not occur in their ground states, in which they can react with water to form a base. They are always found in their ionic form, as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . However, although incorrect by any modern definition of this term, it has been used in the literature of Soil Chemistry since the first experiments dealing with ion exchange in soils were carried out. In 1850, J. Thomas Way discovered that soils can exchange Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , and used the term “*base exchange*” to describe this process (Sparks, 2006). Although this terminology is confusing, since none of these cations are truly a base in the chemistry sense according to what we discuss here, soil scientists still use the term “*exchangeable bases*” or “*basic cations*” to distinguish Ca^{2+} , Mg^{2+} , Na^+ , and K^+ from H^+ and Al^{3+} cations.

Similarly to “*exchangeable bases*” or “*basic cations*”, the term “*base saturation*” also persists in Soil Science as an index of soil acidity. From numerous investigations on soils and clays, it is well known the role of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ when soil becomes acidic due to recurrent leaching. Since the early leaching experiments in a soil column with an ammonium sulfate solution were carried out, it is known that such a process led to the appearance of Ca sulfate in the leachate (Thomson, 1850). As a result of the soil leaching, a hydrogen-aluminum system is formed (Seatz and Peterson, 1984). Therefore, an environment with greater leaching potential (e.g., increasing rainfall) will be more acidifying. One of the effects of this process is the transport of soluble anions (such as nitrate, chloride, and carbonic acid) coupled with Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , to maintain the electrical neutrality of the soil solution. Then, as the pH decreases due to the rainfall acidity, these anions and cations leach, decreasing the “*base saturation*”. In this way, soil acidity has been characterized by the percent saturation of exchangeable Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , on soil CEC at pH 7.0.

Moreover, soil pH can also be affected by plant uptake of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . When plants absorb these cations, electrical neutrality of cell roots is maintained through the uptake of an anion or extrusion of H^+ and/or organic acids. However, when cation exceeds anions’ uptakes, excess of H^+ is released in the rhizosphere (Marschner, 2012). Then, an imbalance in cation/anion uptake alters the soil pH. In this way, as “*basic cations*” decreases in soil solution due to plant uptake, the rhizosphere pH decreases. This effect is very common in the soil since most plants take up more cations than anions (Havlin et al., 2014).

On the other hand, the addition of these cations (e.g., Ca^{2+} and K^+) in the soil in the form of neutral salts actually promotes a decrease in pH. The difference between the pH measured in distilled water and the pH measured in saline solution (e.g., CaCl_2 0.01 mol L^{-1} , or KCl 1.0 mol L^{-1}) has been used for several decades to characterize soils with variable charges in soil genesis and classification studies (Botelho et al., 2014). This occurs because, when CaCl_2 solution is added to the soil, for example, Ca^{2+} and Cl^- ions in high concentration will interact with the surface charges of soil particles. If the soil presents a predominance of negative surface charges, the Ca^{2+} present in the soil solution between the “action zone” of the soil particles replaces part of the H^+ or Al^{3+} adsorbed on the soil functional groups, displacing them to the soil solution in

greater amounts than the OH⁻ displaced by Cl⁻ and, therefore, lowering the pH of the soil solution. The same phenomenon occurs when we measure the pH in a KCl solution.

Therefore, contrary to what the term “base” suggests (i.e., decrease in acidity), an opposite effect can occur in soils with a predominance of a negative surface charge. Therefore, there are no plausible justifications for continuing to use the term “base saturation” to characterize the percentage of the sum of Ca²⁺, Mg²⁺, K⁺, and Na⁺ desorbable by a soft extractor (generally KCl 1.0 mol L⁻¹ or NH₄Cl 1.0 mol L⁻¹), in relation to the estimated negative charges of the soil (CEC). This fallacy stems from the days when the bases CaO and MgO were thought to be interchanged, not the ions Ca²⁺ and Mg²⁺. This was based on what was known about chemistry more than 200 years ago by the doctrine of Berzelius (1814), which later served as the basis for the work of Carl Sprengel and Justus von Liebig on the chemical nature of the nutrients necessary for the growth of plants (Lambers and Barrow, 2020a; Lambers and Barrow, 2021). It makes no sense that we continue to perpetuate this in the 21st century.

However, in the absence of the proposition of a correct term, the term “base saturation” remains in use today, causing confusion among students, professionals, and even among professors and researchers in Soil Science, as it leads to the erroneous interpretation that the soil acidity can be corrected by adding these cations to the soil. Unfortunately, it is common to hear people mention that “Ca from limestone neutralizes the acidity”, creating almost a “Ca worship”, preached by many in soil fertility management in recent decades. This is not true, and it is a scientific absurdity since the neutralization of acidity depends exclusively on the reaction of the anion accompanying these cations present in the substance added to the soil. When we add to the soil carbonates (CaCO₃, MgCO₃), hydroxides [Ca(OH)₂, Mg(OH)₂, KOH], and oxides (CaO, MgO), acidity neutralization and pH increase will occur due to the reaction of the anions present in these materials. As a consequence, there will also be the addition of cations, which accompany and counterbalance the neutralizing anions. These cations, which are commonly Ca²⁺ and Mg²⁺, will then be adsorbed to the soil particles, increasing the so-called “base saturation”. However, it is important to emphasize that the increase in “base saturation” is therefore a consequence of acidity neutralization and not the cause of it.

On the other hand, when the same cations mentioned above are added via neutral salts, which are commonly used in agriculture to supply nutrients to plants, the products of their dissociations do not consume protons and, therefore, do not generate hydroxyls. Examples of this are the reactions of agricultural gypsum (CaSO₄), magnesium sulfate (MgSO₄), and potassium chloride (KCl) in the soil (Equations 4, 5 and 6). If K⁺ was a base, it would be expected that the simple addition of KCl to the soil over the years would correct the soil acidity, without the need to add an acidity corrector. It is important to emphasize that, although there are reports on the effect of the addition of these salts at high rates on the soil pH, these effects are small and of little practical relevance. For example, in the case of agricultural gypsum, depending on the rate used, the conditions of the environment, and the minerals present in the soil, it is possible to slightly increase the soil pH (up to 0.4 units) due to the replacement of the OH⁻ bound to the soil particle charges by SO₄²⁻ (Jerk, 2021). By contrast, it is also possible to slightly decrease the soil pH (up to 0.6 units) due to the replacement of H⁺ and Al³⁺ bound to soil particle charges by Ca²⁺ (Eckert et al., 2022).



By contrast, the term “Al saturation” does not have the same problems as the term “base saturation”, since the proportion of a certain cation (Al^{3+}) is being indicated over a total of charges estimated by the CEC of the soil. If it was really necessary to identify the saturation by “bases” or “acids”, the use of the term “acid saturation” instead of “Al saturation” to indicate the proportion of Al^{3+} in the effective CEC would make much more sense than calling “base saturation” the proportion of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$ in the soil CEC at pH 7.0. This is because Al^{3+} (or more precisely $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$) is a cation that causes an acid reaction when hydrolyses their solvation water molecules, generating 3 mols of H^+ , which is the acidity itself, for each mol of Al^{3+} present in the soil solution (Equation 7), thus, this cation is both the cause and the consequence of soil acidity.



An alternative to the term “base saturation” could be the use of “cation saturation”, as proposed by Lambers and Barrow (2020b). However, this term can lead to an inadequate interpretation since, by definition, it can also encompass cations such as Al^{3+} , which is not a nutrient, and should not be included in the currently called “base saturation”. Another possibility would be to use the term “alkali metal saturation”, since Ca, Mg, K, and Na are alkali metals and alkaline earth metals. However, the term “alkaline” would again refer to an erroneous idea of some alkaline reaction of these cations in the soil.

Thus, we consider that the most correct is to call it “Ca-Mg-K-Na saturation”, which, despite being long, would refer directly and without any misinterpretation of the terminology. In Soil Fertility, the “base saturation” is often calculated only as a function of the sum of Ca, Mg, and K, since the Na content is negligible in most tropical and subtropical soils. Thus, one could use the term “Ca-Mg-K saturation”. Likewise, it is also suggested to abolish the use of the term “sum of bases” and use the term “sum of Ca-Mg-K” or “sum of Ca-Mg-K-Na”, when necessary.

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