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A proposal to clarify the use of Sum of Bases in the Brazilian Remineralizer Regulation and in Soil Science

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ABSTRACT: The term Sum of Bases has different meanings in Soil Science and the Remineralizer Regulations. This issue may cause misunderstandings in communication, particularly between the agricultural community and the mining community, becoming an obstacle to the advancement of the use of this soil amendment. In this scientific note we propose the use of subscript "R" (SB_R), standing for Rock, in English, and *Rocha*, in Brazilian Portuguese, and "S" (SB_S) standing for Soil in English and *Solo* in Brazilian Portuguese. In this way SB_R will refer to the Sum of Bases as defined in the Remineralizer Regulation (SB_R = %CaO + %MgO + %K_2O), and SB_S to the Sum of Bases as defined in Soil Science (SB_S = Ca ($mmol_c\ dm^{-3}$) + Mg ($mmol_c\ dm^{-3}$) + K ($mmol_c\ dm^{-3}$) + Na ($mmol_c\ dm^{-3}$)). This approach avoids confusion and facilitates the correct use of laboratory data. We provide a working example, a conversion table and a formula to estimate the potential increase in SB_S caused by SB_R.

Keywords: rock dust, remineralizer, petrochemistry, pedochemistry.

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INTRODUCTION

Farmers are aware of the use of carbonate and phosphate rocks as soil amendments since ancient times (Winiwarter and Blum, 2008). Silicate rocks have recently been incorporated into agricultural practices due to their wide availability, potential improvement of the soil-plant system and capability to accelerate atmospheric carbon capture through enhanced weathering.

Brazil has a great potential to use this technology because it is the world's fifth largest country in agricultural land area (FAO, 2021), the largest Silicate Carbon Sink (Zhang et al., 2021), and since 2013 has Federal Regulations for the production, registering and trade of rock dust (remineralizers) (Brasil, 2013). According to these regulations, silicate rock dust that successfully meets the IN5 requirements can be registered in the Agricultural Ministry (MAPA) as a remineralizer and be applied to agricultural soils (Brasil, 2016). One of the IN5 requirements is that the rock has to contain at least 9 % of Sum of Bases (Brasil, 2016).

The word Base was first used by chemists at the beginning of the 18th century to refer to any substance that reacts with acid resulting in a neutral salt (Jensen, 2006). In modern chemistry, a base is a substance that either releases a hydroxide anion when dissolved in water (Arrhenius concept) or accepts a proton (Bronsted-Lowry concept), or donates a pair of electrons in a reaction (Lewis concept). Although all chemical elements of columns I and II of Periodic Table could be listed as Bases, only Ca, Mg, K and Na are usually referred to as Bases and used in the concept of Sum of Bases, possibly because of their abundance in the geoecospheres and importance as life sustaining nutrients, both in geology as in soil science as well. However, in geology, the bases are measured as the total content in the rocks and expressed as oxides and their percentage in the rock mass (% CaO, % K2O, etc.). In soil science, the bases are considered in their cationic (Ca^{2+}, K^{+}) content in the soil exchange complex and expressed in $mmol_c$ dm^{-3} or in similar units.

The use of the terms Bases and Sum of Bases was recently challenged (Lambers and Barrow, 2020a,b, 2021). However, the issue addressed in the present paper concerns the potential misunderstanding caused by referring to two different concepts (and therefore to their different methods of measurement and formulae) by the same term (Sum of Bases, SB), and not challenging these terms themselves. In case the users of these terms agree to change them to a different one, "X", the use of the term as proposed here just must follow that change from SB_S and SB_R (see upfront) to X_S and X_R.

In a general sense, Sum of Bases is the sum of Ca, Mg, K and Na, although the IN5 Regulation does not consider the element Na in the Sum of Bases. Therefore, there are differences in units, methods and objectives for Sum of Bases depending on the context (Table 1).

As the use of remineralizers expands, a clear communication is needed among geologists, agronomists and stakeholders (farmers, miners, policy makers, gardeners, etc.), and these different approaches may cause confusion. Therefore, in this scientific note, we propose a differentiation between these two approaches, and present a numerical comparison between them to clarify their meaning and use.

DEVELOPMENT

The concept refers to the sum of basic elements (Ca + Mg + K + Na) in a certain material, and in a certain chemical state. In Soil Science, the term Sum of Bases is used to express the exchangeable bases in $mmol_c$ dm^{-3} (Equation 1) and is used to calculate several soil indexes, such as Cation Exchange Capacity (CEC) (Equation 2), CEC at pH 7 (CEC_{pH7}) (Equation 3) and Base Saturation (V%) (Equation 4) (e.g., Santos et al., 2018, p. 318-319; Teixeira et al., 2017, p. 241).

Table 1. Comparison between the use of the term Sum of Bases in Remineralizer Regulation and in Soil Science

	Sum of Bases	
	Remineralizer	**Soil Science**
Units	• % mass (g $100g^{-1}$)	• $mmol_c\ dm^{-3}$ or $cmol_c\ dm^{-3}$ [(1,2)]
Methods (examples)	• X-ray fluorescence (XRF) - (e.g., Karathanasis and Hajek, 1996) • Dissolution in acids and measurement by ICP-OES or ICP-MS. - (e.g., Hossner, 1996; Soltanpour et al., 1996)	Extraction with: • dilute acid solution (ex: Mehlich-1); (e.g., Teixeira et al., 2017, p.224) • concentrated neutral salt (ex. KCl 1 mol L^{-1}) (e.g., van Raij et al., 2001, p.213) • exchange resin (e.g., van Raij et al., 2001, p.189) Determination with: • Titration (e.g., Teixeira et al., 2017, p.218) • Atomic Absorption Spectometry (AAS) (e.g., Wright and Stuczynski, 1996) • Atomic Emission Spectomery (AES)a (e.g., Wright and Stuczynski, 1996)
Calculation	• $\mathbf{SB_R}$ = **CaO** (%) + **MgO** (%) + $\mathbf{K_2O}$ (%) - Does not include Sodium (Na)	• $\mathbf{SB_S}$ = $\mathbf{Ca^{2+}}$ ($mmol_c\ dm^{-3}$) + $\mathbf{Mg^{2+}}$ ($mmol_c\ dm^{-3}$) + $\mathbf{K^+}$ ($mmol_c\ dm^{-3}$) + $\mathbf{Na^+}$ ($mmol_c\ dm^{-3}$) - Does include Sodium (Na)
Objectives	To measure the **total** content of basic cations in a sample	To measure the **exchangeable** content of basic cations in a sample

[(1)] The mol-charge is the amount of an ion that contains 1 mol of charge. The centimol-charge (1 $cmol_c$= 0.01 mol_c) and millimol-charge (1 $mmol_c$ = 0.001 mol_c) are used in soil science. [(2)] A cubic decimetre (dm^3) is in accord with the International System of Units and is equal to the volume of 1 liter.

$$\text{Sum of Bases } (mmol_c\ dm^{-3}) = Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} \quad \text{Eq. 1}$$

$$\text{CEC } (mmol_c\ dm^{-3}) = Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} + Al^{3+} \quad \text{Eq. 2}$$

$$CEC_{pH7}(mmol_c\ dm^{-3}) = Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} + H + Al^{3+} \quad \text{Eq. 3}$$

$$V(\%) = [(Ca^{2+} + Mg^{2+} + K^{+} + Na^{+})/CEC_{pH7}] * 100 \quad \text{Eq. 4}$$

The CEC, CEC_{pH7} and V% are important in several aspects of Soil Science, such as soil taxonomy and soil fertility. For example, the V% is used in some Brazilian States to estimate the amount of lime to neutralize soil acidity to a certain pH, and in soil taxonomy to define the euthrophic/distrophic character of a soil.

In petrology, the term ‘basic’ dates back over 100 years (Eyles and Simpson, 1921) and has long been used in textbooks to describe those igneous rocks rich in calcium and magnesium, to distinguish them from the ‘acidic’ igneous rocks that are rich in silica and (paradoxically) the alkalis K and Na. The concept of ‘basicity’ in igneous rocks and metallurgical slags is in accordance with the Lewis theory of acids and bases (Duffy, 1993). In recent petrology texts, the terms ‘felsic’ replaces ‘acidic’, and ‘mafic’ replaces ‘basic’ for the description and classification of rocks (e.g., Klein and Philpotts, 2017). However, the use of the terms ‘acidic’, ‘intermediate’, ‘basic’ and ’ultrabasic’ are still used as adjectives convenient for the description of igneous rocks.

Given the use of chemical analyses of igneous and metamorphic rocks in their recent regulation as remineralizers (Brasil, 2016), the use of the term Bases continues and extends their use as a descriptor of a rock. In remineralization the term Sum of Bases is used to express the percentage (%, g 100 g^{-1}) of CaO, MgO and K_2O in the rock composition (Na_2O is not considered).

In remineralizer Regulations, the IN 5 (Brasil, 2016), chapter 1, section 1 (definitions), paragraph VI, defines the Sum of Bases as: *"soma de bases: garantia dos remineralizadores constituída pela soma dos teores de CaO+MgO+K_2O ou pela soma dos teores de CaO+K_2O ou pela soma dos teores de MgO+K_2O;"*. Freely translated as: *"sum of bases: the remineralizer guarantees the sum of the content of CaO+MgO+K_2O or the sum of the content of CaO+K_2O or the sum of content of MgO+K_2O"*.

In the present scientific note, we will assume the Sum of Bases in remineralizers as stated in the IN 5 (Brasil, 2016) as shown in equation 5:

$$\text{Sum of Bases (\%)} = \%CaO + \%MgO + \%K_2O \quad \text{Eq. 5}$$

The Sum of Bases in this context should be at least 9 % in the rock dust candidate to be registered as remineralizer by the Brazilian Ministry of Agriculture, MAPA. As can be seen, the term Sum of Bases has different meanings, methods of measurement, units, and interpretations depending on its use in Soil Science or Remineralizer Regulation (Table 1).

Total chemical analysis of a material, as done for remineralizer samples, can also be performed in soil samples, resulting in the total amount of an element in the soil composition. Total chemical analysis results are the total amount of chemical elements in the sample, in all states (e.g., covalently bonded, exchangeable, in reduced or oxidized state, etc.)

Exchangeable cations are a small fraction of the total amount of chemical elements (compare Line 2 and 4 in Table 2). The term refers to the amount of cations adsorbed onto the electrically charged surfaces of soil particles, and can vary depending on the method used to measure them (for example, KCl 1 mol L^{-1} method or the exchange resin method; Table 1). They are assumed to be in equilibrium with the soil solution and therefore, bioavailable (that is, able to be transferred across the cell membrane). The amount of exchangeable bases usually is slightly different depending on the method used to measure them.

Therefore, we propose a slight addition to these terms to avoid confusion and miscommunication when using the term Sum of Bases.

Table 2. Example of results and calculations to compare SB_R and SB_S.

Line		Total											SB_R
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	SUM	
		%											
1	Rock	52.10	11.90	14.45	6.94	3.45	3.06	1.59	3.27	0.75	1.02	97.51	11.98
2	Soil(1)	81.40	6.87	3.32	0.11	0.07	<0.01	0.04	1.45	0.1	6.46	99.86	0.22
					Exchangeable								SB_S
					Ca^{2+}	Mg^{2+}	Na^+	K^+					
		$mmol_c\ dm^{-3}$											
3	Soil				22.0	17.0	0.0	5.7					44.70
					Exchangeable								SB_S(3)
					Ca^{2+}	Mg^{2+}	Na^+	K^+					
		% mass(2)											
4	Soil				0.044	0.021	0.00	0.022					0.087

(1) Azevedo. A. C. unpublished data. Soil layer of 0.00-0.05 . (2) Considering soil density D = 1 Mg m^{-3}. (3) For comparison purposes. The SB_S in the cell is expressed in % mass.

PROPOSITION

The Sum of Bases as used in the context of the Remineralizer Regulation should be followed by the subscript "R", standing for "Rocha" in Portuguese and "Rock" in English, becoming SB_R; and the "Sum of Bases" as used in Soil Science should be followed by the subscript "S", standing for "Solo" in Portuguese and "Soil" in English, becoming SB_S.

By adopting this rule, these terms would be used according to Equation 6 and Equation 7:

$$SB_R\,(\%) = CaO\,(\%) + MgO\,(\%) + K_2O\,(\%) \qquad \text{Eq. 6}$$

$$SB_S\,(mmol_c\,dm^{-3}) = Ca^{2+}\,(mmol_c\,dm^{-3}) + Mg^{2+}\,(mmol_c\,dm^{-3}) + K^{+}\,(mmol_c\,dm^{-3}) + Na^{+}\,(mmol_c\,dm^{-3}) \qquad \text{Eq. 7}$$

EXAMPLE

As an example, total chemical analysis was measured in both a rock (Table 2, line 1) and in a soil sample (Table 2, line 2). The SB_R was calculated from these results using equation 6 for the rock results (Table 2, line 1) and for demonstration purposes, for soil results (Table 2, line 2). The exchangeable cations were measured in the same soil sample (Table 2, line 3) and SB_S was calculated as equation 7 (Table 2, line3). To compare the order of magnitude of SB_R and the SB_S, the SB_S was expressed as % mass in table 2, line 4.

In addition, the SB_R value in table 2, line 1 can be converted to $mmol_c$ $tonne^{-1}$ rock using the conversion factors given in table 3. This simply expresses % mass values for the oxides as millimole-charge ($mmol_c$) per megagram (Mg) or per tonne for the cation within the oxide.

To avoid confusion between megagram, Mg, and the symbol of the chemical element magnesium, Mg, we will use the equivalent non-S.I. unit, tonne, since 1 tonne = 1 megagram = 10^6 grams.

By converting the values, the SB_R of the rock is 4.53 10^6 $mmol_c$ $tonne^{-1}$ rock (2.48 10^6 $mmol_c$ $tonne^{-1}$ for Ca^{2+}, 1.71 10^6 $mmol_c$ $tonne^{-1}$ for Mg^{2+} and 3.37 10^5 $mmol_c$ $tonne^{-1}$ for K^+). If the Na^+ is considered, so SB_R becomes comparable to SB_S, the value is 5.52 10^6 $mmol_c$ $tonne^{-1}$ (9.88 10^5 $mmol_c$ $tonne^{-1}$ for Na^+), or 5.52 10^3 $mmol_c$ kg^{-1} rock. Therefore, in this example, the total content of bases (in $mmol_c$) in 1 kg of rock is about

Table 3. Factors F to convert major rock elements from % oxide (m/m, rock) to elemental $mmol_c$ $tonne^{-1}$ rock

Oxides	F[(1)]
%	
SiO_2	6.66 10^5
Al_2O_3	5.88 10^5
Fe_2O_3 (FeIII)	3.76 10^5
FeO (FeII)	2.78 10^5
CaO	3.57 10^5
MgO	4.96 10^5
Na_2O	3.23 10^5
K_2O	2.12 10^5
TiO_2	5.01 10^5
MnO	2.82 10^5

[(1)] Atomic mass taken from the IUPAC period table (Prohasca et al., 2022).

three orders of magnitude (10^3) greater than the content of exchangeable bases (also in $mmol_c$) in 1 kg of soil (assuming soil density 1 tonne m^{-3}).

Care must be taken to interpret this conversion. It does not mean that the application of 1 tonne of rock will add thousands of $mmol_c$ kg^{-1} of bases in soil because:

1. The dilution of 1 tonne of remineralizer in 1 hectare (ha) of soil has to be accounted for and is of the order of magnitude of 10^3. The dilution factor considering the layer of 0.00-0.10 m is 1:1000 per ha, and 1:2000 to a depth of 0.20 m, if the soil density is 1 tonne m^{-3}. If the more realistic soil density of 1.3 tonne m^{-3} is taken, the dilution is 1:1300 and 1:2600, for 0.00-0.10 and 0.00-0.20 m layers, respectively. This 10^3 order of magnitude of dilution brings the base content in the rock to the same order of magnitude as the exchangeable bases in soil (units to tens of $mmol_c$ kg^{-1} soil, usually).

2. This amount is not instantly bioavailable, since:

   a. rock dissolution is not instantaneous;

   b. silicate rock dissolution is rarely complete;

   c. silicate rocks dissolve incongruently (meaning some elements are solubilized faster than others); and

   d. as rock dissolves, not all basic cations go to the exchange surfaces in the soil, but also are lost by leaching and absorbed by plants, for example.

Equation 8 accounts for the dilutions and conversions discussed above and includes Na since it is accounted for in SB_S. Taking the example in table 2, the use of 1 tonne of rock in the conditions above would result in the **potential maximum** increase of 2.12 $mmol_c$ kg^{-1} soil.

Equation 8 estimates the Input i of basic cations in soil as a result of the application of 1 tonne of rock in 1 hectare of soil. To obtain the value for greater doses, multiply the result by the number of tonnes applied.

$$i\ (mmol_c\ kg^{-1}\ soil) = (\ (3.57\ (\%CaO_R)) + (4.96\ (\%MgO_R)) + (2.12\ (\%K_2O_R)) + (3.23\ (\%Na_2O_R)))/(100\ d\ D) \quad \text{Eq. 8}$$

in which: $\%CaO_R$, $\%MgO_R$, $\%K_2O_R$ and $\%Na_2O_R$ are the total content (%) of CaO, MgO, K_2O and Na_2O in the rock; d is the depth of mixing of the rock material into the soil (m); and D is the soil density (tonne m^{-3}). The 1/100 factor is the ratio of 10^5, which is the order of magnitude of $mmol_c$ per tonne of rock (Table 3), and 10^7, which is the order of magnitude of tonnes of soil per hectare (10^4 m^2) times the conversion of tonnes to kg of soil (1 tonne = 10^3 Kg). Therefore $10^5/10^7 = 1/100$

For example, the input i from the application of 1 tonne of rock with the composition as in line 1 of table 2, mixed to a depth of 0.20 m in a soil with bulk density of 1.3 tonne m^{-3} is:

$$i\ (mmol_c\ kg^{-1}\ soil) = (\ (3.57\ (6.94)) + (4.96\ (3.45)) + (2.12\ (1.59)) + (3.23\ (3.06))/(100\ (0.2)(1.3))$$

$$i\ (mmol_c\ kg^{-1}\ soil) = 55.14\ /\ 26.0$$

i = **2.12** $mmol_c$ kg^{-1} soil

If 5 tonnes of rock is applied, the i value is:

i = (2.12) (5) = 10.60 $mmol_c$ kg^{-1} soil

Again, the i value estimates the content of bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) added into the soil by the rock but it is not the actual increase to be expected in SB_S.

It is useful, though, to demonstrate how SB_R and SB_S are contrasting quantities and to check analytical issues. For example, if the increase in SB_S due to the sole application of remineralizer is greater than the i value, it is not realistic and sources of errors along the process of SB_S measurement should be verified.

CONCLUSION

We recommended the use of subscript "R" for rock and "S" for soil when referring to the Sum of Bases (SB_R and SB_S, respectively). This procedure improves the communication of results of chemical analyses of rocks and soils, in the context of using remineralizers in soils. The need to discriminate between the two (SB_R and SB_S) becomes clear when SB_R is converted to the similar units as SB_S for comparison purposes. In addition, SB_R does not account for Na as SB_S does. We provided a working example of SB_S and SB_R calculation, as well as a conversion table and a general formula to estimate the potential increase in SB_S caused by SB_R. This approach avoids confusion and facilitates correct use of laboratory data.

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