

DERIVATION OF DIFFERENTIAL BUFFER POWERS OF THE SOIL FOR CATIONS⁽¹⁾

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SUMMARY

Soil potassium (K) availability to plants is mainly a function of diffusion parameters, involving liquid and solid phases of the soil. General adoption of diffusion factors to determine K availability is dependent on a method that allows rapid analysis of these parameters, especially the buffer power. The objective of this paper is to derive mathematically buffer powers of the soil for K, Na, Ca, Mg, Mn, and Al. Gapon's exchange equation was assumed to describe the reactions of cations between solid and solution phases of the soil. Equilibration of the soil with strontium to determine the concentrations of the cations in the liquid phase is implied in the derivations. The soil was considered a closed system, with a constant cation exchange capacity. Monovalent and divalent cation activities in the soil solution were expressed as monovalent K activity equivalence and divalent Ca activity equivalence, respectively. Each buffer power equation developed includes all major soil cations. It is expected that these expressions may be useful in diffusion-controlled nutrient plant uptake models as well as in determining plant availability of soil cations. Buffer power equations of Ca and Mg might also be useful in modeling lime dissolution rates in the soil.

Index terms: potassium, sodium, calcium, magnesium, manganese, aluminum, derivation of exchange equations.

RESUMO: DERIVAÇÃO DO PODER TAMPÃO DIFERENCIAL DO SOLO PARA CÁTIONS

A disponibilidade de potássio (K) às plantas é, principalmente, função de parâmetros de difusão, envolvendo as fases líquida e sólida do solo. A adoção dos fatores de difusão para determinar a disponibilidade de K depende de um método que possibilite sua análise rápida, sobretudo do poder tampão. O objetivo deste trabalho foi derivar matematicamente o poder tampão do solo para K, Na, Ca, Mg, Mn e Al. Utilizou-se a equação de Gapon para descrever as reações de troca dos cátions entre as fases sólida e líquida do solo. Nas derivações, considerou-se ter sido o solo equilibrado com estrôncio (Sr) para determinar a concentração dos cátions na fase líquida. O solo foi considerado um sistema fechado, apresentando capacidade constante de troca de cátions. A atividade dos cátions monovalentes e divalentes foi expressa como equivalência monovalente em K e equivalência divalente em Ca respectivamente. Cada equação de poder tampão inclui todos os demais cátions considerados nas derivações. Espera-se que essas expressões possam ser úteis em modelos de absorção de nutrientes, cujo processo seja controlado por difusão, assim como na avaliação da disponibilidade de cátions às plantas. As equações do poder tampão de Ca e Mg podem, também, ser úteis na modelagem da taxa de dissolução de calcário no solo.

Termos de indexação: potássio, sódio, cálcio, magnésio, manganês, alumínio, derivação de equações de troca.

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INTRODUCTION

Significant advances have been obtained over the last 30 years on the understanding of nutrient flow from soil to roots since the papers of Bouldin (1961) and Barber (1962). However, most current K soil diagnosis methods (Haby et al., 1990) still are based on a single concentration of a certain chemical form (usually the exchangeable plus the solution amounts). Based on current knowledge about the process of transport of nutrients to plant roots, availability would be better expressed as a flux term instead of concentration. For nutrients like P and K this would imply expressing inflow (mol cm^{-1} of root) based on diffusion. The main limitation to implement this approach under practical conditions is the lack of methods to determine routinely the actual parameters that control diffusion. Since the buffer power is one of the most important factors in this process, the objective of this paper is to derive mathematically a differential buffer power of the soil for the major soil cations.

METHODS

The derivations are based on the assumption that the soil has been equilibrated with $\text{Sr}(\text{NO}_3)_2$ 0.002 mol L^{-1} (Wiethölter & Corey, 1994a). Exchange reactions between cations in the soil solution and on the solid phase were based on Gapon's exchange equation (Gapon, 1933).

Precipitation-dissolution reactions were assumed not to exist in any of the derivations presented.

All derivations imply a closed system with a defined total cation exchange capacity, excluding H^+ . The inclusion of H^+ would probably increase the validity of the buffer powers if a closed system of electrical neutrality were considered, as indicated by Bouldin (1989).

The derivations include the following steps: 1) substitution of the cation exchange capacity equation (Eq. [1]) and definition of the ratio between exchangeable K and K activity in the soil solution (Eqs. [2] to [11]); 2) definition of the differential equation (Eqs. [12] and [13]); 3) differentiation of the former equation and calculation of the K buffer power (Eqs. [14] to [20]); 4) similar procedures are then repeated and equations to express the buffer power of the soil for Na, Ca, Mg, Mn, and Al are derived.

DERIVATIONS

Potassium buffer power

The cation exchange capacity {CEC} of a soil is usually expressed with the following equation:

$$\{\text{CEC}\} = \{\text{MX}\} + \{\text{D}_{1/2}\text{X}\} + \{\text{Al}_{1/3}\text{X}\}, \quad [1]$$

in which { } represents $\text{cmol}_c \text{ kg}^{-1}$, X^{-1} refers to one equivalent of anionic charge, M is the summation of the monovalent cations (Na and K), and D is the summation of the divalent cations (Sr, Ca, Mg, and Mn). Strontium (Sr) is here included because it is assumed that the soil has been equilibrated with $0.002 \text{ mol L}^{-1} \text{ Sr}(\text{NO}_3)_2$. In principle, Sr could simply be omitted from this derivation and the final result would not be affected, as long as any other method would be used to determine the concentrations in the liquid and solid phases of the soil.

Exchangeable amounts

Using Eqs. [19] and [25] of Wiethölter & Corey (1994a),

$$k_{\text{D}_{1/2}}^{\text{M}} = \frac{[\text{MX}] (\text{D}^{2+})_{\text{Ca}}^{1/2}}{[\text{D}_{1/2}\text{X}] (\text{M}^+)_{\text{K}}} \quad [2]$$

and

$$k_{\text{Al}}^{\text{M}} = \frac{[\text{MX}] (\text{Al}^{3+})^{1/3}}{[\text{Al}_{1/3}\text{X}] (\text{M}^+)_{\text{K}}}, \quad [3]$$

Eq. [1] then becomes

$$\{\text{CEC}\} = [\text{MX}] + \frac{[\text{MX}] (\text{D}^{2+})_{\text{Ca}}^{1/2}}{k_{\text{D}_{1/2}}^{\text{M}} (\text{M}^+)_{\text{K}}} + \frac{[\text{MX}] (\text{Al}^{3+})^{1/3}}{k_{\text{Al}}^{\text{M}} (\text{M}^+)_{\text{K}}}, \quad [4]$$

in which () refers to activity in solution (mmol L^{-1}), and $k_{\text{D}_{1/2}}^{\text{M}}$ and k_{Al}^{M} are Gapon's selectivity coefficients (Gapon, 1933). $(\text{M}^+)_{\text{K}}$ and $(\text{D}^{2+})_{\text{Ca}}$ are, respectively, the monovalent K activity equivalence and the divalent Ca activity equivalence, as proposed by Eqs. [16] and [13] of Wiethölter & Corey (1994a), and are expressed by the following equations:

$$(\text{M}^+) = (\text{K}^+) + k_{\text{K}}^{\text{Na}} (\text{Na}^+) \quad [5]$$

$$(\text{D}^{2+})_{\text{Ca}} = (\text{Ca}^{2+}) + k_{\text{Ca}}^{\text{Sr}} (\text{Sr}^{2+}) + k_{\text{Ca}}^{\text{Mg}} (\text{Mg}^{2+}) + k_{\text{Ca}}^{\text{Mn}} (\text{Mn}^{2+}). \quad [6]$$

The values of k_{K}^{Na} , $k_{\text{Ca}}^{\text{Sr}}$, $k_{\text{Ca}}^{\text{Mg}}$, and $k_{\text{Ca}}^{\text{Mn}}$ are also Gapon's selectivity coefficients, obtained in the same type of expression as presented for Eqs. [2] and [3].

Rearranging Eq. [4] yields

$$\frac{[\text{MX}]}{(\text{M}^+)_{\text{K}}} = \frac{\{\text{CEC}\}}{(\text{M}^+)_{\text{K}} + a}, \quad [7]$$

where,

$$a = \frac{(\text{D}^{2+})_{\text{Ca}}^{1/2}}{k_{\text{D}_{1/2}}^{\text{M}}} + \frac{(\text{Al}^{3+})^{1/3}}{k_{\text{Al}}^{\text{M}}}. \quad [8]$$

It can also be stated that

$$\{\text{MX}\} = \{\text{KX}\} + \{\text{NaX}\} \quad [9]$$

and

$$k_K^{Na} = \frac{[NaX](K^+)}{[KX](Na^+)} \quad [10]$$

Substituting Eqs. [9] and [10] into Eq. [7], the distribution coefficient of K becomes

$$\frac{[KX]}{(K^+)} = \frac{[CEC] - [KX]}{k_K^{Na}(Na^+) + a} \quad [11]$$

Letting $Y = \{KX\}$, $X = (K^+)$, $C_1 = \{CEC\}$ and $C_2 =$ denominator of the right hand side of Eq. [11],

$$C_2 Y = C_1 X - X Y \quad [12]$$

Since Y can not be solved explicitly in terms of X , to differentiate Eq. [12] it is necessary to use the method of implicit differentiation. Thus,

$$\frac{dY}{dX} = \frac{C_1 - Y}{X + C_2} \quad [13]$$

It should be noted in Eqs. [12] and [13] that both C_1 and C_2 are assumed constants in the soil while $\{KX\}$ and (K^+) are changing. This should be a reasonable assumption considering that the derivative of Y with respect to X implies an infinitesimal change in both Y and X . As a consequence, C_1 and C_2 may be assumed constants.

The slope of $\{KX\}$ vs. (K^+) is known as the tangential buffer capacity (BC), expressing the capacity of the solid phase to buffer the activity of K in the soil solution. Substituting the values for X , Y , and C_2 in Eq. [13], BC becomes

$$BC = \frac{d[KX]}{d(K^+)} = \frac{[CEC] - [KX]}{(K^+) + k_K^{Na}(Na^+) + \frac{(D^{2+})_{Ca}^{1/2}}{k_{D_{Ca}}^M} + \frac{(Al^{3+})^{1/3}}{k_{Al}^M}} \quad [14]$$

Multiplying and dividing the right hand side of Eq. [14] by $k_{D_{Ca}}^M$ and, from Eqs. [2] and [3],

$$\frac{k_{D_{Ca}}^M}{k_{Al}^M} = k_{D_{Ca}}^{Al} \quad [15]$$

Eq. [14] becomes

$$BC = \frac{k_{D_{Ca}}^M [CEC] - [KX]}{k_{D_{Ca}}^M (K^+) + k_{D_{Ca}}^M (Na^+) + (D^{2+})_{Ca}^{1/2} + k_{D_{Ca}}^{Al} (Al^{3+})^{1/3}} \quad [16]$$

The buffer power (b) of the soil for K is generally expressed as the change of the labile pool concentration (C) with respect to the concentration in the soil solution (C_{ii}). It has been demonstrated by Van Rees et al. (1990) that the use of BC instead of b in uptake models might result in erroneous estimations of diffusion. Therefore, letting

$$b = \frac{dC}{dC_{ii}} \quad [17]$$

where

$$C = \{KX\} + 0.25(K^+)/\gamma^+ \quad [18]$$

and

$$C_{ii} = (K^+)/\gamma^+ \quad [19]$$

being γ^+ the monovalent activity coefficient, which can be calculated with Eq. [4] of Wiethölter & Corey (1994a) and the equation proposed by Davies (1962, p.41), expressed in a general form with Eq. [38] of Wiethölter & Corey (1994b). The differential buffer power of K then becomes

$$b_K = 10\rho \left\{ \frac{k_{D_{Ca}}^M [CEC] - [KX]}{[k_{D_{Ca}}^M (K^+) + k_{D_{Ca}}^{Na} k_K^{Na} (Na^+) + (D^{2+})_{Ca}^{1/2} + k_{D_{Ca}}^{Al} (Al^{3+})^{1/3}]/\gamma^+} + 0.25 \right\} \quad [20]$$

The constant 0.25 in Eq. [20] converts mmol K^+ L^{-1} solution to $cmol_c kg^{-1}$ (10 g of soil and 25 mL of 0.002 mol L^{-1} $Sr(NO_3)_2$ are used in the Sr equilibration procedure), 10ρ is the conversion factor from $(cmol_c kg^{-1})/(mmol L^{-1})$ to $(mmol cm^{-3} soil)/(mmol cm^{-3} solution)$ and ρ is the bulk density of the soil, in units of $g soil cm^{-3} soil$. Therefore, the units of b_K are $(mmol cm^{-3} soil)/(mmol cm^{-3} solution)$.

According to Eq. [20], the buffer power of K is directly proportional to the selectivity coefficient between monovalent and divalent cations ($k_{D_{Ca}}^M$) and the cation exchange sites not occupied with K, $\{CEC\} - \{KX\}$; it is also inversely proportional to the concentration (activities divided by γ^+) of all major soil cations.

Sodium buffer power

Solving Eq. [10] for $\{KX\}$ and substituting it and Eqs. [5] and [9] into Eq. [4] and taking the derivative of $\{NaX\}$ with respect to $[Na^+]$, in a similar approach as used for Eq. [11], the buffer power of the soil for Na becomes:

$$b_{Na} = 10\rho \left\{ \frac{k_K^{Na} k_{D_{Ca}}^M [CEC] - [NaX]}{[k_{D_{Ca}}^M (K^+) + k_K^{Na} k_{D_{Ca}}^M (Na^+) + (D^{2+})_{Ca}^{1/2} + k_{D_{Ca}}^{Al} (Al^{3+})^{1/3}]/\gamma^+} + 0.25 \right\} \quad [21]$$

Calcium buffer power

Solving Eq. [2] for $\{MX\}$ and Eq. [3] for $\{Al_3X\}$; changing the units of the exchangeable amounts of Sr, Ca, Mg, and Mn of Eqs. [2], [7] and [8] in Wiethölter & Corey (1994a) from $cmol kg^{-1}$ to $cmol_c kg^{-1}$; using Eq. [6] and substituting into Eq. [1]; and, taking the derivative of $\{D_{1/2}X\} + 0.5[Ca^{2+}]$ with respect to $[Ca^{2+}]$, the differential buffer power of Ca is obtained,

$$b_{Ca} = 5\rho \left\{ \frac{[CEC] - [Ca_{1/2}X]}{(D^{2+})_{Ca}^{1/2} \left[k_{D_{Ca}}^M (M^+) + (D^{2+})_{Ca}^{1/2} + k_{D_{Ca}}^{Al} (Al^{3+})^{1/3} \right] / \gamma^{2+}} + 0.5 \right\}, \quad [22]$$

where γ^{2+} represents the divalent activity coefficient and can be obtained from the same equation used to calculate γ^+ . The units of b_{Ca} are (mmol cm⁻³ soil)/(mmol cm⁻³ solution).

Magnesium buffer power

Using a similar approach as in Eq. [6], the divalent Mg activity equivalence is

$$(D^{2+})_{Mg} = (Mg^{2+}) + k_{Mg}^{Sr} (Sr^{2+}) + k_{Mg}^{Ca} (Ca^{2+}) + k_{Mg}^{Mn} (Mn^{2+}), \quad [23]$$

where, upon transformations, k_{Mg}^{Ca} and k_{Mg}^{Mn} can be obtained from Eqs. [14] and [15] of Wiethölter & Corey (1994a).

Through a process similar to that outlined for b_{Ca} , the differential buffer power of Mg can be derived:

$$b_{Mg} = 5\rho \left\{ \frac{[CEC] - [Mg_{1/2}X]}{(D^{2+})_{Mg}^{1/2} \left[k_{D_{Mg}}^M (M^+) + (D^{2+})_{Mg}^{1/2} + k_{D_{Mg}}^{Al} (Al^{3+})^{1/3} \right] / \gamma^{2+}} + 0.5 \right\}, \quad [24]$$

Since lime dissolution rate in the soil is a function of Ca and Mg diffusion away from the lime particle, Eqs. [22] and [24] might be useful in modeling this process.

Manganese buffer power

Based on the similarity between Eqs. [6] and [23] for Ca and Mg, the divalent Mn activity equivalence can be defined by the following equation:

$$(D^{2+})_{Mn} = (Mn^{2+}) + k_{Mn}^{Sr} (Sr^{2+}) + k_{Mn}^{Ca} (Ca^{2+}) + k_{Mn}^{Mg} (Mg^{2+}). \quad [25]$$

Following the same reasoning used for Ca and Mg, the differential buffer power of the soil for Mn becomes:

$$b_{Mn} = 5\rho \left\{ \frac{[CEC] - [Mn_{1/2}X]}{(D^{2+})_{Mn}^{1/2} \left[k_{D_{Mn}}^M (M^+) + (D^{2+})_{Mn}^{1/2} + k_{D_{Mn}}^{Al} (Al^{3+})^{1/3} \right] / \gamma^{2+}} + 0.5 \right\}, \quad [26]$$

Aluminum buffer power

Solving Eq. [25] for {MX} and taking the reciprocal of Eq. [26], both of Wiethölter & Corey (1994a),

and then substituting into Eq. [1], it can be demonstrated that the differential buffer power of the soil for Al is given by

$$b_{Al} = 3.33\rho \left\{ \frac{[CEC] - [Al_{1/2}X]}{(Al^{3+})^{2/3} \left[k_{Al}^M (M^+) + k_{Al}^D (D^{2+})_{Ca}^{1/2} + (Al^{3+})^{1/3} \right] / \gamma^{3+}} + 0.75 \right\}, \quad [27]$$

where γ^{3+} is the trivalent activity coefficient and is calculated from the same equation used to estimate γ^+ .

It should be considered that b_{Al} is meaningless for soils with a pH above 5.6, since the activity of Al in the soil solution is then controlled by the solubility product of Al(OH)₃. Under such circumstances, precipitation-dissolution reactions are involved, which are not predicted by the Gapon type of exchange equation.

DISCUSSION

In studies of K uptake modeling and especially in the quantity/intensity (Q/I) approach (Beckett, 1964), it has been assumed that the slope of {KX} vs. (K⁺) is linear, which is valid over a narrow range of concentrations of K. However, for soils that are either very high or very low in K content, the relationship is not linear (Beckett, 1971). Therefore, the inclusion of both {KX} and (K⁺) itself in the buffer power equation presents probably some advantage, since this accounts for the appropriate slope at any point along the isotherm curve. However, this is true only if the relationship between K on the solid phase and in the soil solution can be described by a Gapon approach (when all sites have the same binding energy and only electrostatic exchange occurs). In addition, the inclusion in Eq. [20] of all major cations that compete with K for exchange sites, makes, in principle, the buffer power of K applicable for a wide variety of soils.

Buffer powers of Na, Ca, Mg, Mn, and Al probably have much less meaning than the buffer power of K in terms of plant nutrient availability. However, the equations derived do express the importance of one cation on the buffer power of another cation. In addition, buffer powers of Ca and Mg might be applicable in studies of lime dissolution rates.

CONCLUSIONS

Using the Sr equilibration procedure to estimate concentrations of the major cations in the soil solution and assuming solely electrostatic exchange reactions between liquid and solid phases, differential buffer powers of K, Na, Ca, Mg, Mn, and Al were derived mathematically. The buffer power equation for each element includes all cations used in the derivations.

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