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Buffer capacity as a method to estimate the dose of liming in acid soils

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ABSTRACT

Objective: The study proposes using the dolomite buffer capacity ($BC_{Dolomite}$) as a method of estimating the lime requirement in soils that agronomically require a pH increase.

Design/methodology/approach: In six soil samples with different levels of response to the application of dolomite, the organic matter (OM), the content of sand, silt and clay, pH, K, Ca, Mg and the potential acidity (Al+H) were determined. Assuming an apparent density of 1000 kg/m^3 and a volume per hectare of 2000 m^3, the soils were placed in polyethylene containers and treated with dolomite in doses equivalent to 0, 750, 1500, 2250 and 3000 kg/ha, establishing the $BC_{Dolomite}$ as the inverse of the slope resulting from the relationship between the pH and the dose of dolomite.

Results: In soils with low response to the dolomite, the content of clay and OM was 280 and 26 g/kg, respectively, and in high response soils, the content of clay and OM was 240 and 47 g/kg, respectively. In all cases, a simple and direct linear relationship was observed (R^2>0.85; p<0.05) in the relationship between pH and dose of dolomite.

Limitations on study/implications: The results obtained under controlled conditions show that $BC_{Dolomite}$ constitutes a viable method to estimate the lime requirement.

Findings/conclusions: The $BC_{Dolomite}$ showed sensitivity to the complexity of the clay fraction and to the organic matter in the soil, for which the dolomite requirement is equal to the product of the desired pH increase and the $BC_{Dolomite}$.

Keywords: hydrogen, aluminum, dolomite, liming.

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INTRODUCTION

Some factors that cause acidification of soils are biological activity (plants and microorganisms), base washing (Ca, Mg, K) from the soil, decomposition of organic matter, and intensive production of crops (banana, oil palm, cacao, sugarcane), where the absorption of crops derives in an exhaustion of the soil bases and an increase in the saturation of aluminum and hydrogen (Agegnehu *et al.*, 2021; Goulding, 2016); and the degree of acidification, within a period of time, depends on the buffer capacity of the soil.

The buffer capacity is defined as the soil's resistance to change pH in the presence of the addition of an acid or a base, and the buffer capacity depends on the amount and type of clay (silica, non-silica, fixed load and variable charge particles) present in the soil and on the content and degree of stabilization of organic matter (Sanchez, 2019). For this reason, sandy soils present a greater resistance to acidification.

In acid soils, the efficiency of fertilization (available nutrient/applied nutrient) and the efficiency of nutrient absorption (absorbed nutrient/available nutrient) decrease (Baligar *et al.*, 2001), which is explained knowing that the soil pH has a relationship with the precipitation, solubilization, immobilization, mineralization, adsorption, and desorption of essential elements, bioavailability of toxic elements, and reduction of biomass of functional roots (Baligar *et al.*, 2001; Neina, 2019), conditions which together limit crop production.

To exceed the agronomic limitations associated to the acidity of soils, they are treated with products that contribute calcium, magnesium or both (Ca and Mg), capable of reducing the acidity and increasing the pH of soils to a specific degree, depending on the neutralization value of the product (type of product and purity), the relative efficiency (particle diameter of the product), and the buffer capacity of the soil (Chimdi *et al.*, 2012). However, although the technical foundations that determine the effectiveness of liming products are known, the classic methods to establish the dose of lime do not consider the level of pH that is intended to be increased in the soil, since they are mostly based on the concentration of exchangeable aluminum or the degree of saturation of bases (Teixeira *et al.*, 2020).

Defining the dose of the liming product to reach an agronomically adequate pH in the soil is determinant to ensure a correct physical, chemical and biological functioning of the soil, which favors the growth, development and production of crops. With this background, this study proposes the use of the buffer capacity of the soil with double calcium-magnesium carbonate ($BC_{Dolomite}$) as a fast method to estimate the liming dose and to correct the acidity of the soils.

MATERIALS AND METHODS

Soil samples and physicochemical characterization

In the locality of Quevedo (Province of Los Ríos – Ecuador), having as criterion for soil sample selection the historical effect of liming on pH (low, medium and high response), six soil samples were collected classified within the Inceptisol order with a source of Andean influence (SIGTIERRAS, Sistema Nacional de Información y Gestión de Tierras Rurales e Infraestructura Tecnológica), 2017). The samples were identified as Soil A, Soil B, Soil C, Soil D, Soil E and Soil F. The samples Soil A and B are of low response, the samples Soil C, D and E of medium response, and the sample Soil F of high response. According to the classification system of ecosystems in Ecuador (Ministry of the Environment, MAE (*Ministerio del Ambiente del Ecuador*), 2013), the locality of Quevedo is found in a seasonal evergreen forest ecosystem characterized by a mean annual temperature of 25.5 °C and an annual precipitation of 1650 mm.

The soil samples were subject to a physical and chemical characterization, following procedures accepted by Ecuador's Society of Soil Science and described by Rodríguez and

Rodríguez (2015). In each soil sample organic matter was determined with the Walkley Black method; the sand, loam and clay content with the hydrometer method; the pH in water $\left(pH_{H_2O}\right)$ with the potentiometric method using a weight:volume ratio of 1:2.5; the exchangeable K, Ca and Mg, with the Olsen – Modified method; the potential acidity (Al+H) with the KCl 1N method and titration with NaOH 0,01N. Likewise, through a particle-size analysis and titration, the dolomite used in this study was determined to have a relative efficiency and neutralization value of 100 and 87%, respectively.

Buffer capacity

Based on the determination methods of the buffer capacity and the estimation of lime requirements described by Follett and Follett (1983), 10 polyethylene containers with screw tops were prepared for each soil sample, placing in each container 50 g of soil (dried at room temperature and sieved at 2 mm) and treated by duplicate with dolomite in doses equivalent to 0, 750, 1500, 2250 and 3000 kg/ha, assuming a volume per hectare of 2000 m^3 and an apparent density of 1000 kg/m^3. Then, the pH_{H_2O} was determined after incubation for 24 hours, at constant temperature (40 °C) and moisture (40% p/p). The $BC_{Dolomite}$ was determined by the inverse of the resulting slope when evaluating the variation of pH in function of the dose of dolomite added to the soil (Ng *et al.*, 2022).

Data analysis

The physical and chemical characterization of the soil samples is summarized presenting the arithmetic average and the standard deviation (Tables 1 and 2). The content of organic matter, loam, sand and clay, was determined immediately after the initial preparation of the soil samples (drying and sieving) (Table 1), while the pH_{H_2O}, content of K, Ca and Mg, and potential acidity (Al+H) were determined in the soil samples with and without dolomite treatment in doses equivalent to 1500 kg/ha (Table 2), and the statistical differences were established through a t-test for paired samples.

After the incubation period of the soil samples, the buffer capacity was evaluated through a regression analysis (Figure 1), relating the pH of each soil sample in function of the dose of dolomite (0, 750, 1500, 2250 and 3000 kg/ha). The following regression equation was obtained: , where: pH of the soil exposed to a specific dose of dolomite, slope associated to the dose of dolomite, intercept. In the model, the coefficient of determination (R^2) and the statistical significance (p-value) were determined.

RESULTS AND DISCUSSION

The results evidence that a slight change in pH (low response) of the soils facing the addition of dolomite cannot always be explained by a high content of clay, since the soil with a high response (Soil F) has a clay content (240 g/kg) similar to soils of low response (Soil A, Soil B) (average clay 280 g/kg), while the soils of medium response (Soil C, Soil D, Soil E) have an average content of clay (180 g/kg) lower than the soil with a high response (Soil F) (240 g/kg). The soils that have a medium response of pH change in the presence of the addition of dolomite, specifically soils C and D, have a low content of clay but a high content of organic matter (both soils with more than 6% of organic matter) (Table 1).

Table 1. Content of organic matter (OM), sand, lime and clay, and textural class of six soils belonging to the Inceptisol order from the locality of Quevedo, Los Ríos – Ecuador. SD=standard deviation.

Soil sample	OM	Sand	Silt	Clay	Soil texture
	g kg^{-1}				
Soil A	30	300	420	280	Clay loam
Soil B	22	360	360	280	Clay loam
Soil C	61	520	320	160	Loam
Soil D	66	540	320	140	Sandy loam
Soil E	17	460	300	240	Loam
Soil F	47	460	300	240	Loam
Mean	41	440	337	223	
SD	21	93	46	60	

The magnitude of pH change varies in the different soils facing the same dose of liming, evidencing that the soils differ in their resistance to change pH depending on the content of organic matter, type and amount of clay (Uthida and Hue, 2000); thus, in soil samples with similar pH in water (≈4,30) and $CaCl_2$ (≈3,75), differences of 11% were observed in the clay content (Sanaullah and Shamsuddin, 2010), and when evaluating the effect of the dose of dolomite in an Ultisol and an Inceptisol, an increase in the pH of 0.14 and 0.20 units/ton, respectively, was observed (Lukman and Yudha, 2020).

The solid reactive fraction (particles with colloidal characteristics) of the soils can be of permanent charge (vermiculite, illite, montmorillonite) or of variable charge (caolinite, allophane, ferrihydrite), reason why the clays can transfer H^+ to the medium from deprotonation, depending on whether the medium is acid or alkaline (Jeon and Nam, 2019). Therefore, the soils exhibit a variable resistance to changing pH, which explains why the soils with dominion of clays with permanent charge have a high response in the presence of the lime addition, contrary to what happens in soils with dominion of clays with variable charge.

The addition of 1500 kg/ha of dolomite caused a significant increase of pH of 0.43 tenths, with the pH of soil changing on average from 5.89 to 6.23, while no significant changes were observed at the level of exchangeable Ca and Mg of the soil since dolomite is a correction that contributes exchangeable Ca and Mg, the same that a change at the level of potential acidity (Al+H) was not observed; however, the ECEC increased significantly by 1.05 mEq/100g, with ECEC going on average from 9.66 to 10.71 mEq/100g (Table 2).

In acidic soils, predominant in tropical regions (high precipitation and temperature) and intense agricultural activity, exhaustion of the bases in the soil (K, Ca, Mg) and high saturation of Al^+ and H^+ (>50 %) are frequently observed (Jakovljević *et al.*, 2005; León-Moreno *et al.*, 2019), which is why liming is recurrent. Ca^{2+} or Mg^{2+} (from liming) concentrate in the soil and generate a mass effect that displaces the linked Al^+ (saturation of Al^+) to the clays (Amberger, 2006; Cunha *et al.*, 2018), which suggests a higher probability of hydrolysis of Al^{3+} and a higher resistance of the soil to increasing the pH, because the hydrolysis of Al^+ generates H^+ ions.

Table 2. Values of pH, exchange bases (K, Ca, Mg), potential acidity (Al+H), and effective cation exchange capacity (ECEC) of six soils, with and without dolomite treatment (calcium-magnesium carbonate), belonging to the Inceptisol order from the locality of Quevedo, Los Ríos – Ecuador. SD=standard deviation.

Soil sample	pH	K	Ca	Mg	Al+H	ECEC
		mEq 100g^{-1}				
	Dolomite dose=0 kg ha^{-1}					
Soil A	6,62	0,21	9,40	2,64	0,21	12,46
Soil B	6,30	0,19	8,44	1,99	0,25	10,87
Soil C	5,95	0,44	7,41	1,05	0,26	9,16
Soil D	5,35	0,48	6,00	0,96	0,38	7,82
Soil E	5,92	0,21	7,01	1,73	0,37	9,32
Soil F	5,20	0,84	6,32	0,92	0,26	8,34
Mean	5,89	0,40	7,43	1,55	0,29	9,66
SD	0,54	0,25	1,29	0,69	0,07	1,72
	Dolomite dose=1500 kg ha^{-1}					
Soil A	6,81	0,22	11,67	2,77	0,20	14,86
Soil B	6,59	0,18	8,45	2,05	0,27	10,95
Soil C	6,27	0,43	7,85	1,27	0,29	9,84
Soil D	5,51	0,49	6,11	0,99	0,42	8,01
Soil E	6,38	0,32	7,20	3,38	0,32	11,22
Soil F	5,83	0,88	6,97	1,23	0,28	9,36
Mean	6,23	0,42	8,04	1,95	0,30	10,71
SD	0,48	0,25	1,95	0,96	0,07	2,34
t-test (p-value)	0,0052	0,2361	0,1365	0,1755	0,5646	0,0408

Organic soils, or mineral soils with high contents of organic matter, exhibit a high resistance to changing pH, because in an acidic medium the carboxyl groups of the organic matter of the soil would adsorb H^+, and in an alkaline medium they would transfer H^+, aspects that agree with the findings by Chi *et al.* (2017), when they reported an increase in the buffer capacity of pH of an Ultisol by adding biochar derived from plant residues to the soil. Thus, taking into account the complexity of the interaction between organic matter and chemical elements, it is possible to explain that organic soils generally have a low response to liming compared to mineral soils, which are rich in clays with permanent charge.

Dolomite $\left[CaMg\left(CO_3\right)_2\right]$ or calcite $\left(CaCO_3\right)$, when entering into contact with the soil moisture, have the capacity of increasing the soil's pH when Ca^{2+}, Mg^{2+} are liberated, and OH^- is produced; thus, Ca^{2+}, Mg^{2+} are exchanged with Al^{3+}, H^+ is linked electrostatically with the solid fraction of the soil, while OH^- ions react with Al^{3+} and with H^+ to form $Al(OH)_3$ and H_2O, respectively. This explains why in barley fields (*Hordeum vulgare* L.) of the central high plateau of Ethiopia, a linear increase of the pH (5.20 to 5.90) is observed at increasing doses (0 to 220 g/m^2) of calcium carbonate, and the Al^{3+} decreases exponentially (1.35 to 0.15 mEq/100g) (Desalegn *et al.*, 2017). In addition, the studies reveal that there is not a stoichiometric relationship between the liming dose and the increase of pH observed.

The Ca^{2+} and Mg^{2+} ions contained in the dolomite increase the exchangeable calcium and magnesium in the soil, although the magnitude of increase of exchangeable calcium or magnesium depends on the quality (neutralization value and relative efficiency) and liming dose (Sanchez, 2019), because as a whole they control the ionic force generated in the soil solution and therefore the capacity of Ca^{2+} and Mg^{2+} of garnering the exchange sites when Al^{3+} and H^{+} are displaced. Thus, in a 10-year study carried out with a Typic Palexerult soil, an increase of exchangeable calcium and magnesium was observed after the incorporation of 10900 kg/ha of dolomite in the first 20 cm of soil and, therefore, an increase of the effective cation exchange capacity (ECEC) and a reduction of the exchangeable aluminum (Al^{3+}) (Olego *et al.*, 2021).

When evaluating the pH variations of the soil against the dose of dolomite, a positive (direct) correlation was observed in every case, which adjusts to a simple linear model (R^2>0.85; $p<0.05$). In addition, the lower response of the soil to liming was seen to correspond with a lower value of the slope of the linear model, and a higher response of the soil corresponds to the higher value of the slope. It was found that in the soils with low (Figures 1a and 1b) and high (Figure 1f) response, the slope was 0.00015 and 0.00049, respectively.

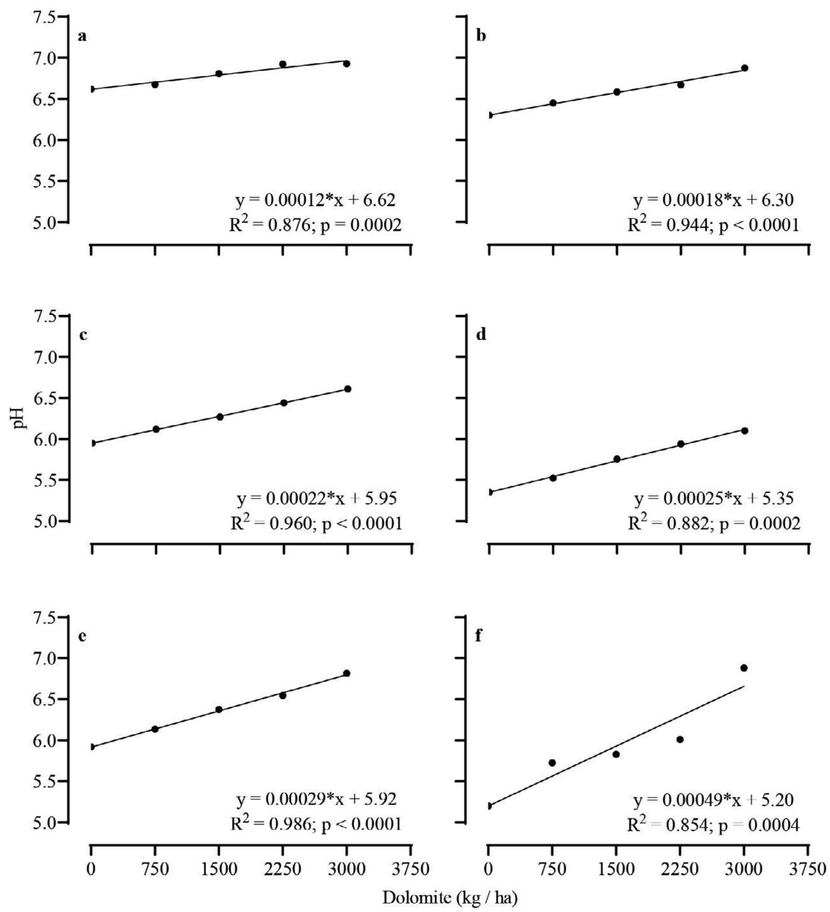

Figure 1. Values of pH in soils of low (a, b), medium (c, d, e) and high (f) response in the presence of the dose of double calcium-magnesium carbonate (Dolomite), in soils belonging to the Inceptisol order from the locality of Quevedo, Los Ríos – Ecuador. The full circles (•) represent the average of two data (n=2).

The resistance of the soils to change pH has been associated dominantly with the content and type of secondary minerals (silicate, non-silicate, crystalline and amorphous) and to the organic matter in different degrees of stabilization, which make up the active solid fraction of the soils and which differs between the different types of soils (Sanchez, 2019). The variability inherent to the active solid fraction of the soil confers to each soil a specific resistance in face of the increase or reduction of the pH; thus, in soils where the same increase of pH is sought, different doses of the same liming material are required, as evidenced in this study where Soil A had a $BC_{Dolomite}$ of 1/0.00012, while in the Soil F the $BC_{Dolomite}$ was 1/0.00049 (Figure 1).

CONCLUSIONS

The buffer capacity of the soil in the presence of the addition of dolomite ($BC_{Dolomite}$), constitutes a viable method to estimate the liming requirement of the soils, since the $BC_{Dolomite}$ changes in the different soils within the limits evaluated in this study. This evidences that it is a method which is acceptably sensitive to the complexity of the clay fraction and the organic matter of the soil. Stemming from the fact that $BC_{Dolomite}$ is the inverse of the resulting slope when evaluating the pH_{H_2O} in function of the dose of dolomite, it is suggested that the requirement of dolomite ($R_{Dolomite}$) is equal to the product of the desired increase in pH (ΔpH) and the $BC_{Dolomite}$ $\left(R_{Dolomite} = \Delta pH \times CT_{Dolomite}\right)$.

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