Lime and calcium-magnesium silicate cause chemical attributes stratification in no-till fields

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ABSTRACT

The stratification of soil chemical properties under long-term no-till (NT) where different soil pH regimes are used and at different cropping-systems (CS) has yet to be studied. We aimed to evaluate the effect of the surface application of soil pH amendments on soil chemical attributes of stratified soil samples and their relationship with the subsequent yield of the soybean crop. The effect of the surface application of lime and calcium-magnesium silicate (CMS) on the chemical attributes of soil samples with increment depth (0–5, 5–10, 10–20, 20–40, and 40–60 cm) was evaluated. Also, their relationships with the subsequent soybean (*Glycine max*) yield on a tropical acidic soil under NT with four CS (SB: soybean—*Brachiaria brizantha*; SC: soybean—*Crotalaria spectabilis*; SF: soybean—fallow; and SW: soybean— *Triticum aestivum*) were compared. The NT operations caused the stratification of all soil chemical attributes studied regardless of the CS and soil pH amendment. Application of lime or CMS significantly decreased exchangeable aluminum (Al) and potential acidity (H+Al), and increased pH, calcium (Ca), magnesium (Mg), silicon (Si), the sum of base (SB), and base saturation (BS%) in the upper soil layers (up to 10 cm) for most CS studied. Soil acidity parameters from 0 to 5 cm were related to soybean yield, and the stratification of H+Al led to a difference of 2-ton ha^{-1} soil amendment needed (p < 0.001) when soil is sampled from 0 to 5 cm in comparison to the 0–20 cm sampling.

1. Introduction

Soil acidity limits crop growth and yield in many parts of the world. Especially in tropical regions, lime is commonly used to neutralize soil acidity although silicate-based products (e.g., calcium-magnesium silicates) may be a viable alternative to lime for correcting soil acidity (Deus et al., 2020). The composition of calcium magnesium silicates (CMS) varies depending on the type of steel making and furnace conditions, but usually contains CaO, MgO, and SiO$_2$ as the primary components (Yi et al., 2012), which have neutralizing capacity due to the silicate anion SiO$_3^{2-}$ reaction in the soil solution.

Associated with the common practice of applying soil pH

amendments, the adoption of the no-tillage system (NT) has also grown worldwide due to the benefits it can provide, such as minimizing soil loss through erosion, increasing soil organic matter, and enabling long-term crop productivity as well as decreased fossil fuel use (Pittelkow et al., 2015). In Brazil, more than 32 million hectares of farmland are cultivated under NT(Peixoto et al., 2019). With the adoption of the NT, soil pH amendments and fertilizers are applied on the surface without mechanical incorporation (Rheinheimer et al., 2018). Thus, stratification of the soil chemical attributes within the soil profile is likely to occur as a consequence of long-term organic matter accumulation in the topsoil and the surface application of soil amendments and fertilizers. Although the occurrence of such stratification has been widely recognized

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elsewhere in the literature, the standard soil sampling depth from cultivated fields including NT has been 0–15 or 0–20 cm, and the recommendations of fertilizer and lime rates are still based on such depth. There is still a lack of information regarding the need for fertilizer and/or lime rates when soil samples are taken from depths other than the standard depth. Since stratification always occurs under NT, it is likely that subsequent application of soil amendments would be reduced if the soil chemical attributes in the uppermost layer affect the yields of crops differently.

One of the main reasons for soil stratification is the low solubility of lime and its surface-dissolution reactions limiting the ability of surface-applied lime to correct acidity in the subsurface (Moreira et al., 2011; Leal et al., 2008). On the other hand, CMS is 6.8 times more soluble in water than the calcium-magnesium carbonate (Ca/MgCO$_3$) lime (Castro et al., 2016). Thus, the use of such amendment under NT can be an effective alternative for soil acidity correction, as it may promote greater mobility of SiO_3^{2-} in the soil profile, ensuring faster acidity neutralization in the subsurface compared to regular aglime (Deus et al., 2020).

According to a recent study of Gmach et al. (2020), crop residue maintenance under NT enhances soil C content even in the short-term, especially near the surface. Therefore, soil chemical properties within the soil profile may differently affected by cropping-systems. For example, cropping-systems including crops which are moderate to strong aluminum (Al) accumulators such as rice (*Oryza sativa*), corn (*Zea mays*), beans (*Phaseolus vulgaris*), and wheat (*Triticum aestivum*) (Delhaize et al., 1993; Brunner and Sperisen, 2013) likely present a depletion of exchangeable-Al in the upper layers (0–10 cm). Consequently, complexes formed within these plants presumably facilitate Al transport to lower depths and horizons (20 + cm). In contrast, cropping-systems involving forage crops such as palisade grass (*Brachiaria brizantha*) are well-known to exclude Al uptake (Arroyave et al., 2013). Thus, all these factors influence the soil chemical attributes differently and might lead to their stratification. In the particular cases mentioned above, and considering that Al is severely related to soil acidification (Antonangelo et al., 2022), recommendations of soil pH amendments and fertilizers would differ if stratified soil layers were sampled instead of only one fixed depth such as 0–20 cm.

In this context, crop rotation might be another reason for soil stratification under NT, and it is unlikely to be the main factor influencing soil chemical attributes within the soil profile unless it is accompanied by other soil management practices (Castro and Crusciol, 2013) such as those mentioned previously. To the best of our knowledge, there is no work relating to the stratification of soils under long-term NT where different soil pH regimes were used and at different cropping-systems. This study evaluated the effect of the surface application of soil pH amendments on soil chemical attributes of stratified soil samples (0–5, 5–10, 10–20, 20–40, and 40–60 cm) and their relationship with the subsequent yield of soybean crop on a tropical acidic soil under NT at four cropping-systems. Our hypotheses were (**i**) CMS could correct subsoil (>20 cm) acidity more effectively than lime in the long-term, even 24 months after the last application of soil amendments, regardless of the cropping-system, since the former is more water-soluble than the latter; (**ii**) soil chemical attributes used for liming and fertilizer recommendation are related to soybean yields when samples are taken from the stratified upper layer (0–5 cm) and lead to a different interpretation from samples collected from the commonly used 0–20 cm; (**iii**) since stratification occurs under NT, soil sampling depth different from the depth used for recommending lime and fertilizer can affect the amount of amendment or nutrient prescribed by a soil testing lab.

2. Material and methods

2.1. Area description, soil characterization, experimental design and treatments

The experimental area located in Botucatu, State of Sao Paulo, Brazil

(48° 23' W, 22° 51' S, 765 m a.s.l.) was cultivated under NT since 2002, with the present study commencing in 2006. Its full description can be found in Antonangelo et al. (2022). The soil is a clayey acidic Oxisol and its chemical and physical attributes at the start of the study are summarized in Table 1. The experimental design was a randomized block of split plots and four replications ($n = 4$), which is also fully described in Antonangelo et al. (2022). A treatment summary is presented in Table 2. The experimental plots consisted of four seasonal/rotational cropping-systems: SF: seasonal–fallow (no rotational crop); SB: seasonal–palisade grass (*Brachiaria brizantha*); SC: seasonal–showy rattlebox (*Crotalaria spectabilis*); and SW: seasonal–wheat (*Triticum aestivum*) (Table 2). The seasonal cash crops in 2006/07, 2007/08, 2008/09, 2009/10, 2010/11, 2011/12, 2012/13, and 2013/14 (mostly sown in November) were soybean (*Glycine max*), corn (*Zea mays*), rice (*Oryza sativa*), soybean, corn, bean (*Phaseolus vulgaris*), rice, and soybean, respectively (Table 2). Each plot was divided into subplots, comprising four replicates of three different soil pH amendments: control (no amendment), dolomitic lime, and calcium-magnesium silicate (CMS). They were applied once in October 2006 (3.8 Mg ha^{-1} lime, 4.1 Mg ha^{-1} CMS) and again in October 2011 (4.7 Mg ha^{-1} lime, 5.3 Mg ha^{-1} CMS) to achieve 70 % soil base saturation (BS). The characteristics of soil pH amendments used in 2006 and 2011 are shown in Table 2.

Soil samples were collected the month before sowing the final soybean crop (October 2013), cultivated after several years of cropping-systems establishment, and after two applications of soil pH amendments under long-term NT. The soil was sampled with a probe and separated into layers of 0–5, 5–10, 10–20, 20–40, and 40–60 cm (thus, 240 samples in total). Five subsamples were collected to make a composite sample from each plot; then samples were air-dried, lightly crushed, passed through a 2-mm sieve, and, stored in plastic bags away from light at room temperature until soil analysis.

2.2. Soil analysis

Soil chemical attributes were assessed following the methodologies proposed by Raij (2001). Soil pH was measured in a 0.01 mol L^{-1} CaCl$_2$ suspension (1:2.5 soil to solution volume ratio) and soil organic carbon (OC) determination followed the Walkley-Black method using potassium dichromate (K$_2$Cr$_2$O$_7$). Plant available phosphorus (P) and exchangeable basic cations calcium (Ca), magnesium (Mg), and potassium (K) were extracted using an ion-exchange resin. Phosphorus was

Table 1
Chemical and physical attributes of the Oxisol soil before the experiment (2006).

Attributes	Unit	—Soil layer (cm)—		
		0–5	5–10	10–20
Chemical[a]				
pH		4.7	4.4	4
OC	g dm^{-3}	13	11	10
P	mg dm^{-3}	8.7	7.9	2
K	mmol$_c$ dm^{-3}	2.1	1.1	0.6
Ca	mmol$_c$ dm^{-3}	21	11	10
Mg	mmol$_c$ dm^{-3}	9	6	4
Si	mg dm^{-3}	7.5	6.3	6.2
Al	mmol$_c$ dm^{-3}	4	6	5
(H+Al)	mmol$_c$ kg^{-1}	50.3	69.3	61.2
BS	%	27	25	24
		—Soil layer (cm)—		
		0–10	10–20	
Physical[b]				
Sand	g kg^{-1}	489	435	
Clay	g kg^{-1}	415	462	
Silt	g kg^{-1}	96	103	
Texture		Clay	Clay	

[a] Adapted from Antonangelo et al. (2021). OC = organic carbon. BS (base saturation) = SB / (SB + (H+Al)) × 100 %, where SB (sum of base concentrations) = Ca + Mg + K.
[b] Determined as Ashworth et al. (2001).

Table 2
Seasonal cash crops used during the experiment, soil amendments application time and properties, and cropping-systems used in the study.

Season	Seasonal cash crop		—Soil amendment—	
			Lime	CMS
2006/07	Soybean	(Glycine max)	X[a]	X[b]
2007/08	Corn	(Zea mays)	–	–
2008/09	Rice	(Oryza sativa)	–	–
2009/10	Soybean	–	–	–
2010/11	Corn	–	–	–
2011/12	Bean	(Phaseolus vulgaris)	X[a']	X[b']
2012/13	Rice	–	–	–
2013/14	Soybean[c]	–	–	–
	————Soil amendment properties (wt%)————			
	ECCE	CaO	MgO	SiO$_2$
a	90	35	12	–
a'	74	35	12	–
b	80	34	10	22
b'	66	32	9	22
c	—Cropping-systems used in the study before soybean sowing—			
SB	Seasonal cash crop / palisade grass (Brachiaria brizantha)			
SC	Seasonal cash crop / showy rattlebox (Crotalaria spectabilis)			
SF	Seasonal cash crop / fallow (no rotational crop)			
SW	Seasonal cash crop / wheat (Triticum aestivum)			

The dolomitic lime (Lime) and calcium-magnesium silicate (CMS) were applied (X) once in Oct 2006 (3.8 Mg ha-1 lime, 4.1 Mg ha-1 CMS) and again in Oct 2011 (4.7 Mg ha−1 lime, 5.3 Mg ha−1 CMS) in an effort to achieve 70 % soil base saturation (BS). BS = SB / (SB + (H+Al)) × 100 %, where SB (sum of base concentrations) = Ca + Mg + K and (H+Al) is exchangeable acidity. ECCE: effective CaCO3 equivalence. "-": not applicable.

determined colorimetrically using a spectrophotometer, and Ca, Mg, and K by atomic absorption spectrometry (AAS). The Exchangeable aluminum (Al^{3+}) was extracted using 1 mol L^{-1} KCl in a 1:10 soil to solution ratio as the following. The mixture was shaken for 30 min and, after equilibrium, the extract was filtered by a quantitative filter paper. A fraction of the extract (25 ml) was titrated with 0.025 mol L^{-1} sodium hydroxide (NaOH) in the presence of phenol red as an indicator to determine the Al^{3+}, which was calculated based on the volume of NaOH used in the blank and each sample. The potential acidity (H+Al) was measured immediately after measuring soil pH by adding 5 ml of SMP buffer solution (pH = 7.0) to the suspensions. The samples were mechanically shaken for 15 min and sat for another 1 h. The SMP index has a high correlation with the value of potential acidity, and its determination is made indirectly, through a standard curve that correlates both values (pH$_{SMP}$ and $H^+ + Al^{3+}$ obtained directly with a calcium acetate solution). Thereafter, effective cation exchange capacity (CEC) and base saturation (BS) were calculated as described in Antonangelo et al. (2022).

The sulfur (S) determination was based on the extraction of sulfate (SO_4^{2-}) from soil samples using a 0.01 mol L^{-1} Ca(H$_2$PO$_4$)$_2$ solution and quantification by turbidimetry caused by the presence of BaSO$_4$, formed by the reaction of SO_4^{2-} with BaCl$_2$0.2 H$_2$O. The plant available micronutrients iron (Fe), copper (Cu), manganese (Mn), zinc (Zn), and boron (B) were extracted with DTPA and determined by an inductively coupled plasma optical emission spectroscopy (ICP-OES). Available silicon (Si) analysis followed the methodology proposed by Korndörfer et al. (2004), in which soil samples were extracted using a 0.01 mol L^{-1} CaCl$_2$ solution and quantified colorimetrically using a spectrophotometer.

2.3. Soybean yield

The soybean cultivar used was the 'BMX Potência RR' and was harvested in March/April 2014 at phenological stage R8 (full maturity) using a Nurserymaster plot combine (Wintersteiger) from the useable area of each subplot. Grain yields (kg ha^{-1}) were calculated based on the area harvested and adjusted to 130 g kg^{-1} moisture content.

2.4. Data analysis

An effect test was conducted for the full factorial arrangement [*amendments* (A) × *cropping-system* (CS) × *soil layer* (SL)] to verify the significance of isolated and interacted factors (Table 3). This was used to further break down results into relevant factors to be analyzed according to their agronomic importance.

The isolated factor of SL was significant for all soil chemical attributes thus highlighting the remarkable stratification of an Oxisol under long-term NT (Table 3), as illustrated with the distribution of soil OC using the whole dataset of measurements (Fig. 1). However, according to the greatest significance level and agronomic importance of soil management practices, cropping-system treatments were compared for P, K, and S whereas soil amendments were compared for all the remaining variables, where the significant influence of the interaction [*amendments* (A) × *cropping-system* (CS)] was greater (Table 3). Thus, most of the soil chemical attributes were analyzed using one-way ANOVA and a Tukey post-hoc test with α = 0.05 to compare treatments including pH amendments for each cropping-system within the soil profile.

Pearson correlations were performed to assess the relationship between soil chemical attributes and yield response of soybean to every stratified soil sampling. Based on the results, a simple linear regression analysis was further conducted to test the relationship between lime needs, according to the base saturation (BS%), of soil samples collected from 0 to 5 cm and those collected from the common arable layer (0–20 cm), calculated by the average of 0–5, 5–10, and 10–20 cm. All statistical analyses were performed with SAS ver9.4 and graphs were plotted using excel and Origin 2019.

3. Results and discussion

3.1. The effect of amendments on organic carbon, phosphorus, potassium, and sulfate-S

Organic carbon (OC) contents decreased sharply with increased soil depth regardless of the cropping-system and soil amendments for soil acidity (Fig. 1). These findings show that crop residue maintenance enhances soil OC content over time, especially near the surface. According to Kalbitz et al. (2000), the main reason behind the greater amount of OC content occurring primarily in the upper horizon is due to its strong adsorption onto Al- and Fe-oxide minerals of the solid fraction and complexation with the same metals in the aqueous solution, thus affecting its redistribution within the soil profile (Sparling et al., 2016). The OC content ranged from 1 % to 2 % with the greater values being observed at the uppermost soil layer (Fig. 1). Those values are above the expected OC contents for conventionally tilled acidic soils denoting the importance of NT adoption to increase carbon stock.

Phosphorus (P) content was not influenced by the amendments used (Table 3); however, it was affected by the cropping-systems only in the upper layer 0–5 cm (Fig. 2). Overall, the SF and SC cropping-systems resulted in greater available P in the topsoil (Fig. 2). For the SF, such higher P accumulation in the soil surface is most likely justified by the fact that no crop is cultivated between seasonal crops thus a lesser P uptake is expected. In the case of SC, even if an increased P uptake is likely to occur in comparison to the SF, its return to the soil via nutrient cycling of plant residues under NT is faster than other cropping-systems such as SB and SW. This is because a legume crop, presenting a lower C: N ratio, is cultivated in the SC cropping-system, thus its residue decomposition is supposed to be faster (Thomas and Asakawa, 1993). Furthermore, mineralization of root-derived organic P could contribute to enhanced P uptake for wheat (Wu et al., 2021), and palisade grass (*B. brizantha*) is capable of using chemically adsorbed P on Fe- and Al-oxides (Merlin et al., 2015), which enhances its P uptake and justifies its excellent adaptation to infertile acid soils (soil pH < 5.5). These facts might be associated with a greater P uptake in the SW and SB

Table 3
Analysis of variance for the effect of cropping-systems, the addition of soil amendments, and five soil layers on soil chemical attributes and soybean yield.

Effect (Pr>F)	pH	OC	P	K	Mg	Ca	S	Si	Al	H+Al	SB	CEC	BS	Cu	Fe	Mn	Zn	B	Yield
CS	0.05	0.22	*	*	*	**	***	**	**	*	**	0.69	*	0.08	***	*	***	0.07	***
A	***	0.67	0.19	0.29	***	***	0.84	***	***	***	***	0.51	***	0.06	***	0.13	0.15	0.78	***
CS×A	**	0.13	0.55	0.75	***	***	0.07	**	***	**	***	**	***	*	**	*	*	0.13	***
SL	***	***	***		***	***	***	***	***	***	***	***	***	***	***	***	***	***	NA
CS×SL	0.75	0.2	0.53	0.23	0.99	0.88	0.87	0.07	0.97	0.34	0.92	0.17	0.94	0.74	0.07	0.65	0.07	0.98	NA
A×SL	***	0.25	0.47	0.99	***	***	0.93	*	***	***	***	0.25	***	0.99	***	0.59	0.84	0.44	NA
CS×A×SL	0.21	0.85	0.62	0.99	0.91	0.19	0.96	0.09	0.99	0.88	0.39	0.15	0.97	0.86	0.14	0.99	0.55	0.90	NA

CS: Cropping-system (SB, SC, SF, and SW). A: Amendment (Control, Lime, and CMS). SL: Soil layer (0–5, 5–10, 10–20, 20–40, and 40–60 cm).
OC: Organic carbon. SB: Sum of base. CEC: Cation exchange capacity. BS: Base saturation.
Non-significant when p > 0.05. NA: not applicable.
BS (base saturation) = (SB / CEC) × 100 %, where CEC = SB + (H+Al), and SB (sum of base concentrations) = Ca + Mg + K.
*** : $p < 0.001$;
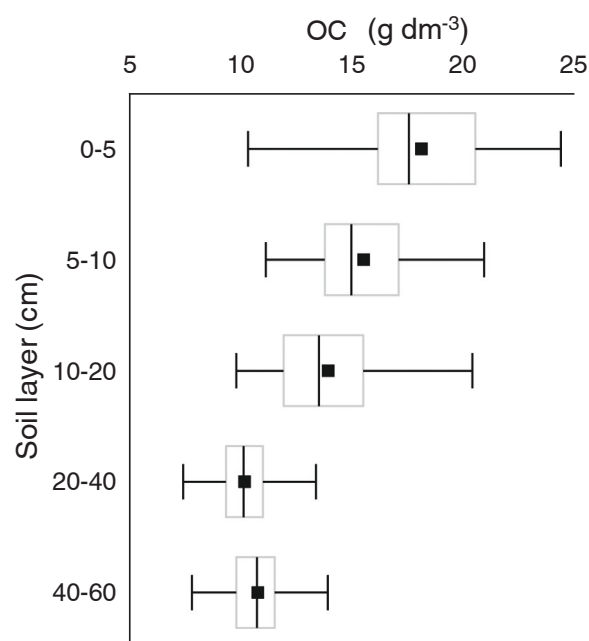** : $p < 0.01$;
* : $p < 0.05$;

Fig. 1. Boxplots of soil organic carbon (OC) for different soil layers (each with $n = 48$ comprising both cropping-systems and soil amendments). Data are normally distributed following the Shapiro-Wilk test. Boxes span the 25th to 75th data percentile, whiskers represent $1.5 \times$ the interquartile range, horizontal lines denote the median, and points denote the mean.

cropping-systems, respectively, thus a lower available content in the 0–5 cm in comparison to SC and SF is well justified. Finally, in a general context, P is an immobile nutrient in the soil particularly in the acidic lands in the tropics, which severely reduces its movement down the profile thus the sampling depth can also affect P recommendation for NT since P is less mobile than others and its available contents are greater from 0 to 10 cm (Table 3 and Fig. 2).

Phosphorus ranged from 20 to 40 mg dm^{-3} in the topsoil depending on the cropping-system (Fig. 2). Although those values are above the minimum required for the optimum yield of soybean (Raij, 2001), the highest value of around 40 mg P dm^{-3} observed from 0 to 5 cm was attributed to the SF, probably because other CS, presenting other crops between seasonal cash crops, were responsive to the available P thus presented a greater P uptake, as previously mentioned.

Potassium (K) did not show any relevant results as observed with P, except that differences among cropping-systems were found only for soil samples collected from 10 to 20 cm (Fig. 2). In this case, greater K available contents were led by the SB cropping-system and a reason behind this observation might be associated with the deeper root system featured by this grass (Galdos et al., 2020) thus some root exudates might contribute to the increased available K in that last stratified sample of the soil arable layer. Although no significant differences were found among cropping-systems for the 0–5 cm layer, the range of 1.5–2.5 mmol$_c$ K dm^{-3} presented in that layer is within the range of the minimum required for optimum soybean production.

Sulfate-S (SO$_4$-S) did not exhibit any significant difference among cropping-systems although it was visually higher for the SF mainly at deeper soil layers (Fig. 4). The influence of SF is confirmed in Table 3 for the 'CS' effect, which considers both soil pH amendments and soil layers as random factors. As previously mentioned for P, a reason behind this might the greater accumulation of available S in the soil profile as a consequence of lower S uptake in the SF in comparison to other cropping-systems. Also, as expected, the SO$_4^{2-}$-S increased as soil depth increased regardless of the cropping-systems probably due to leaching. Such behavior was opposite to the pattern of P distribution in the soil profile given the strong mobility of sulfate, especially in well-drained
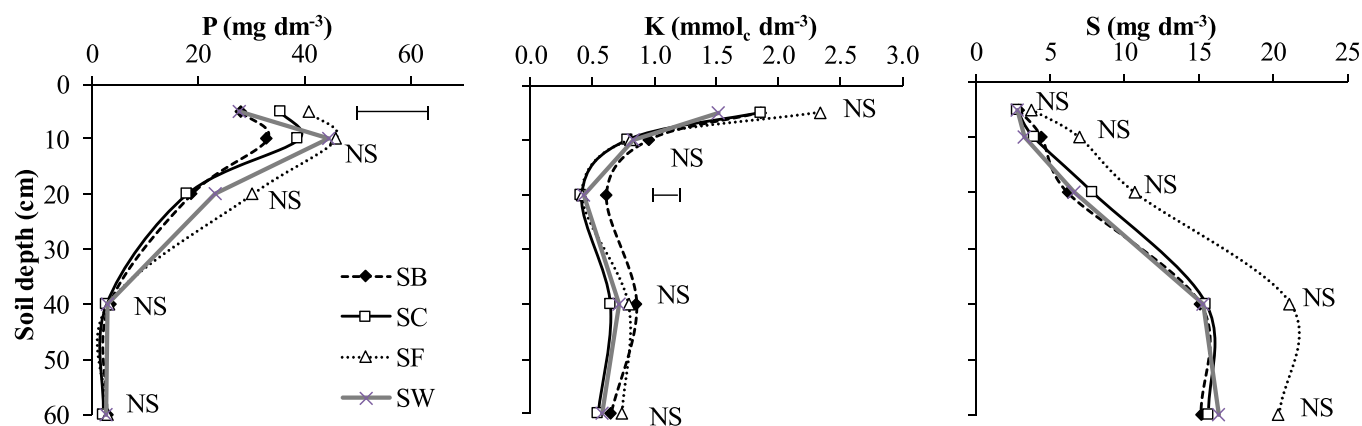
Fig. 2. Exchangeable-phosphorus (P), K, and S within the soil profile as a function of 4 cropping-system — SB: seasonal/palisade grass (*Brachiaria brizantha*), SC: seasonal/showy rattlebox (*Crotalaria spectabilis*), SF: seasonal/fallow (no rotational crop), and SW: seasonal/wheat (*Triticum aestivum*). Points are the average of replicates ($n = 4$) comprising all soil amendments ($n = 3$) — Control, Dolomitic lime (Lime), and Calcium-magnesium silicate (CMS) ($n = 4 \times 3 = 12$). Horizontal bars indicate the Least Significant Difference (LSD) at $p \leq 0.05$. NS: not significant. Please note the different scales in the *x-axis* of graphs.

soils from upland reliefs (Schoenau and Malhi, 2015), where tropical Oxisols are mostly present.

For those essential macronutrients (P, K, and S), a strong stratification was observed along with the soil profile (Table 3 and Fig. 2) with P and K showing greater contents in the upper layers while S increased with soil depth. It remains to be known whether the higher P and K contents in the 0–5 cm soil layer would strongly affect the yield of the subsequent soybean crop. If so, the recommended P and K rates for optimum (or desired) yield would be lower than if the soil was sampled from 0 to 20 cm. Thus, studies focusing on the soil depth from which the root system/architecture is more active and more efficient as far as nutrient uptake is concerned are highly encouraged to be carried out shortly.

3.2. The effect of amendments on soil pH and calcium, magnesium, and silicon availability

Soil pH had a similar pattern within the soil profile when amended with lime or CMS (Fig. 3). For all cropping-systems, soil acidity neutralization only significantly impacted soil amendment applications for the uppermost soil layer (0–5 cm) from which soil stratification along with the profile was observed, whereas the average soil pH for the control plots was stable at 4.1 ± 0.4 throughout all five soil layers and four cropping-systems (Fig. 3). Exclusively for SB cropping-system, soil amendments corrected pH down to 10 cm depth; however, no differences were found between lime and CMS, as also observed for all other cropping-systems. One possible reason for SB cropping-system showing soil pH increase down to 10 cm due to the application of soil amendments might be attributed to the fact that *B. brizantha* (and other perennial grasses cultivated over the years) have established a deep root system which enhanced amendment downward movement (Bodner et al., 2015).

It was expected that CMS would be more efficient in neutralizing acidity down the profile due to its higher solubility compared with lime. However, many studies carried out under NT have shown that the efficiency of the surface application of soil amendments on correcting subsurface depends on the application rates, soil texture, rainfall, and time since application (Oliveira and Pavan, 1996; Soratto and Crusciol, 2008; Castro and Crusciol, 2013). Thus, our results have fallen in agreement with the findings of Castro and Crusciol (2013) who observed no differences between CMS-based products and lime in stratified soil layers from a soil presenting very similar characteristics as ours. In both studies, soils containing a high clay content (Table 1 in case of the current study) present a greater reserve acidity which requires increased rates of amendments to neutralize soil pH. High application rates reduce

lime solubility mainly when it is applied on the surface of NT systems without incorporation. Also, the greater organic matter in the topsoil under NT is able to hold more water from rainfall thus affecting its vertical drainage. This will reduce the lime movement down the soil profile.

Calcium (Ca) and magnesium (Mg) exhibited a similar pattern of stratification as that observed for soil pH (Fig. 3), which makes sense since the soil amendments applied on the soil surface have Ca and Mg in their composition (Table 2).

Available silicon (Si) in the control plots, in contrast to pH, and exchangeable-Ca and -Mg, exhibited greater variation among different soil layers and cropping-systems (average $Si = 5.1 \pm 1.1$ mg kg^{-1}; Fig. 3). This might rely on the fact that silica (or monosilicic acid) exists in charge-neutral H_4SiO_4 and thus its mobility in soils is increased in comparison to charged elements or functional groups. Similar behavior was observed for soils receiving the surface application of amendments; however, the average values were overall genuinely higher (5.5 ± 1 and 5.2 ± 1.2 mg kg^{-1} respectively for CMS and lime) than the control with most expressive results observed in the uppermost soil layer (Fig. 3). Although significant differences were not found for the SB and SW, the surface application of lime or CMS caused divergent changes in Si in upper soil layers (up to 10 cm) for the other cropping-systems SC and SF (Fig. 3).

Under cropping-systems using monocots (SB and SW) instead of legumes (SC), the crops may have taken up a greater amount of soil available Si, which is typical for most grasses (Pereira et al., 2007). Furthermore, the Si uptake by monocots is proportional to the concentration of silicic acid (H_4SiO_4) in soil solution, and the combination of NT with silicate application may increase the response of Si accumulating plants. The subsequent return of Si to the soil by organic matter decomposition is slow since silicate application induces the reaction of H_4SiO_4 with diphenols and esters, lignin precursors in the plant, which result in highly stable and low soluble silicon complexes, called polyphenolic compounds (Fernandez et al., 2009). As a consequence, the cell walls become even more resistant to degradation by microorganisms. However, the overall accumulation of Si on the soil surface for the SC cropping-system, as observed in our study, is probably due to the Si following its cycle through the plant on the way back to the soil in the long-term in addition to the application of a silicon-based CMS; and Si is prone to undergo more accumulation in the surface of the SF cropping-system since no crops are cultivated between seasonal crops.

3.3. The effect of amendments on soil acidity parameters

Exchangeable aluminum (Al), like pH and exchangeable-Ca, -Mg,
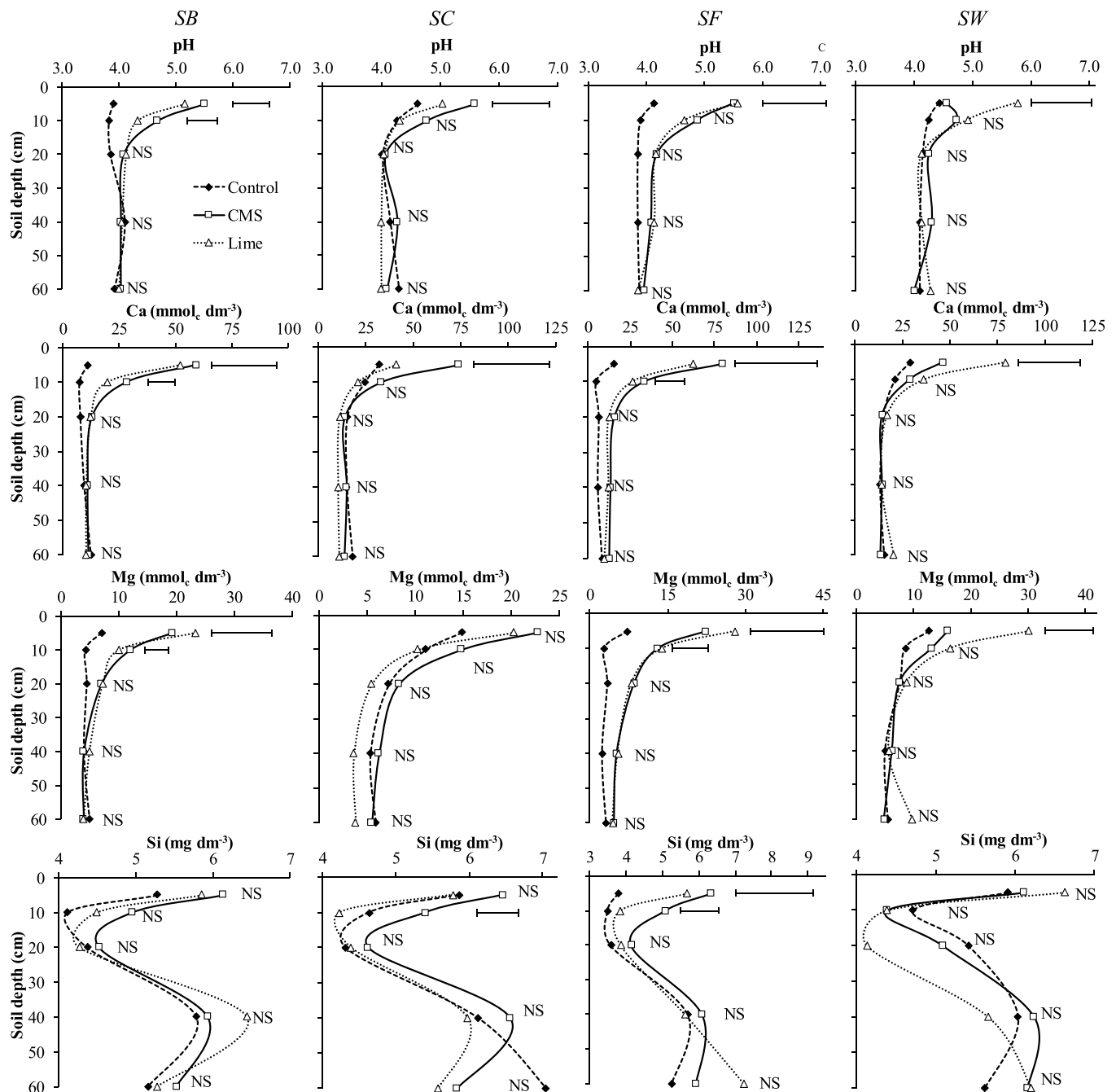
Fig. 3. pH, Ca, Mg, and Si within the soil profile after the application of soil pH amendments — Control, Dolomitic lime (Lime), and Calcium-magnesium silicate (CMS) — at four cropping-systems (*SB*, *SC*, *SF*, and *SW*). Points are the average of replicates ($n = 4$). Horizontal bars indicate the Least Significant Difference (LSD) at $p \leq 0.05$. NS: not significant. Please note the different scales in the *x-axis* of graphs.

and -Si, varied significantly but inversely proportional to each other as a function of soil pH amendments (Table 3 and Fig. 4). Overall, the application of lime or CMS resulted in comparable decreases in exchangeable Al levels especially in the upper layers, indicating that pH elevation plays a great role in depleting Al^{3+} activity in tropical soils under long-term NT conditions. Interestingly, the SC and SW cropping-systems exhibited a slightly different effect of acidity correction even in the topsoil, which might be related to greater competition from the rotation crops for $Al(H_2O)_6^{3+}$ uptake. In this context, it is well-known that *T. aestivum* is a strong Al accumulator (Delhaize et al., 1993) thus complexes formed within these plants presumably facilitate Al transport to lower horizons, and surprisingly the same can be applied to the *C. spectabilis*, then resulting in the comparatively large depletion of

exchangeable Al observed for the SC and SW cropping-systems (Fig. 4). By contrast, acidity correction for the SF and SB cropping-systems caused Al^{3+} to decrease from $10 +$ to 0 mmol$_c$ dm^{-3} in the 0–5 cm layer, mostly for lime as in the case of SF. This indicates that pH elevation plays a greater role in depleting Al^{3+} activity under these soil conditions than the formation of aluminosilicates, which disagrees with the findings of Castro and Crusciol (2013) who found an inverse relationship between Al and Si levels. In our study, no significant relationship was found between those elements (*data not shown*).

Potential acidity H+Al exhibited an identical pattern as exchangeable Al, except that significant differences were found for the SW cropping-system in the uppermost soil layer as well (Fig. 4).

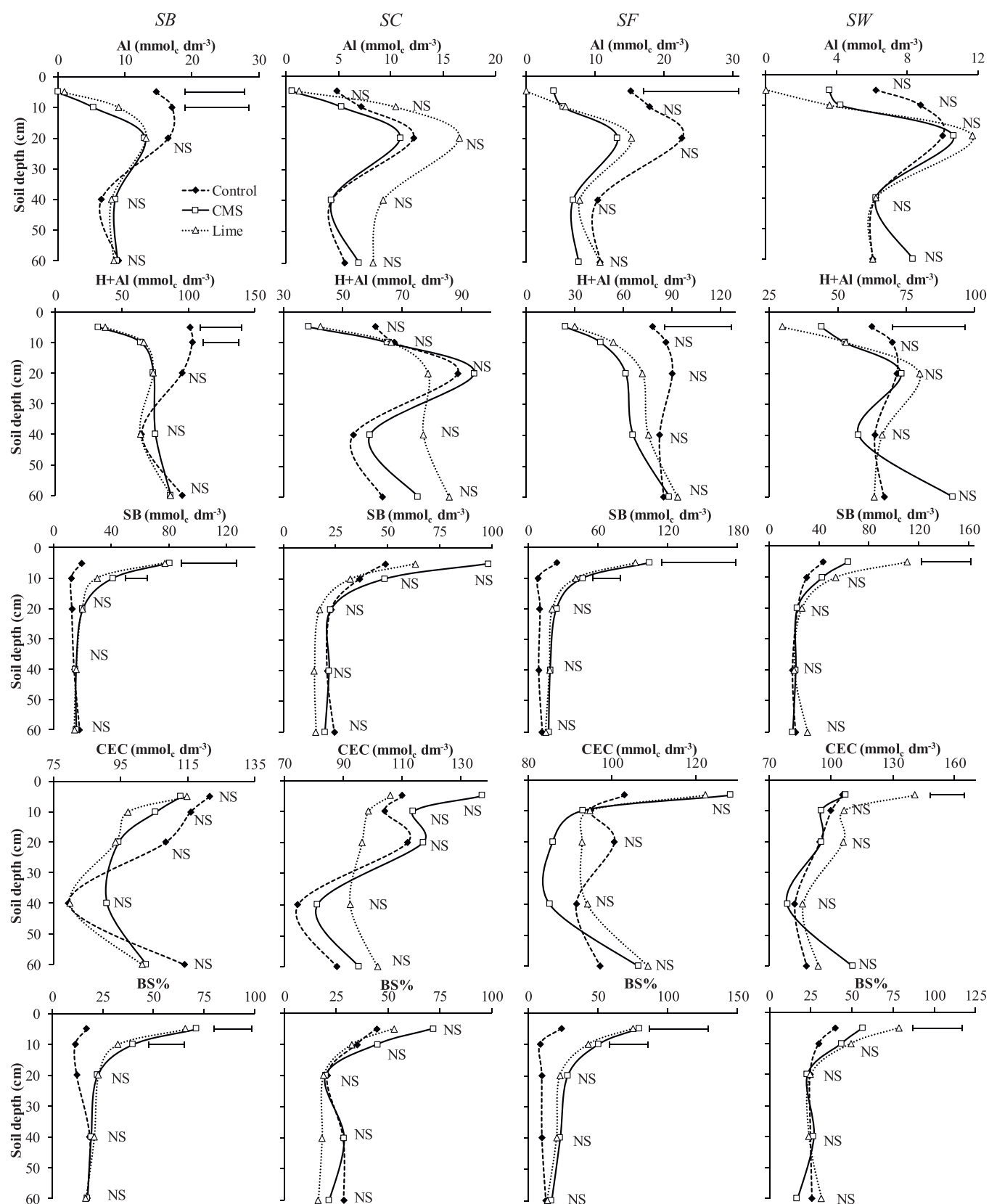**Sum of base (SB)** behaved as a reflection of the exchangeable-Ca and

Fig. 4. Exchangeable-aluminum (Al^{3+}), H+Al, SB (sum of base), CEC (cation exchange capacity), and BS (base saturation) within the soil profile after the application of soil pH amendments — Control, Dolomitic lime (Lime), and Calcium-magnesium silicate (CMS) — at four cropping-systems (*SB*, *SC*, *SF*, and *SW*). Points are the average of replicates ($n = 4$). Horizontal bars indicate the Least Significant Difference (LSD) at $p \leq 0.05$. NS: not significant. Please note the different scales in the *x-axis* of graphs.

-Mg discussed previously since it is the summation of those elements and K, which also had a stratification pattern within the soil profile (Table 3, and Figs. 2, 3, and 4). Variations of soil pH and mobility of basic cations down the profile strongly depend on the absence of acid cations in the upper layers. Thus, the mobility of basic cations (K^+, Ca^{2+}, and Mg^{2+}) is favored at pH_{CaCl2} 4.6–4.9 (Rheinheimer et al., 2000). At this low pH, any subsurface movement is hindered by the cations' adsorption to variable negative charges, which are increased as pH increases beyond 4.9 (Caires et al., 2006). Therefore, mobility may have been disfavored by the strong reaction of soil amendments in the soil surface causing the stratification of basic cations, thus the SB, within the profile (Figs. 3 and 4).

Effective cation exchange capacity (CEC) is calculated by taking into account the last two parameters (Sum of base [SB] and potential acidity [H+Al]). However, no significant trends were observed for any of the factors analyzed or their interactions (Table 3 and Fig. 4). A reason for this might be attributed to the potential acidity (H+Al) occupying the majority of the soil exchangeable sites as will be discussed next for the base saturation, the parameter used to recommend rates of soil acidity ameliorators.

Base saturation (BS%) reflected the effects of soil acidity correction on exchangeable-Ca and -Mg and potential acidity (H+Al) where significant variations were found down to 10 cm at most (Fig. 4). Lime did not differ from CMS at the uppermost soil layer where the amendments differed from the control (Fig. 4). These results agreed with the findings of Corrêa et al. (2007) and Castro and Crusciol (2013) who did not observe differences between silicate-based products and lime after 18 months of their surface application under NT, same interval period between the last application of acidity ameliorators and soil sampling in our study (18–24 months, Table 2). Conversely, Deus et al. (2020) found slight differences between lime- and CMS-based products after 23 months of application; however, their soil pH amendments were incorporated. This implies that CMS-based products to correct acidity faster in the subsurface depend on whether they are incorporated or not even if they are more water-soluble than lime products.

3.4. Relationship between stratified soil chemical attributes and soybean yield

Undoubtedly, the application of lime or CMS contributed to increased soybean yield in year-8 when the yield was evaluated, and this was fully explored and exhausted in the work of Antonangelo et al. (2022). The current work aimed to evaluate if soil chemical attributes from stratified soil layers would be as impactful for soybean yields as those collected from 0 to 20 cm only. For this, a Heatmap comprising the Pearson correlations between soil chemical attributes and soybean yield for the 0–20 cm and stratified soil layers was plotted (Fig. 5). Significant relationships were found for the same soil chemical attributes and soybean yield when looking into the 0–20 and 0–5 cm soil layers, to a lesser extent for the 5–10 cm, and almost absent for the 10–20 cm. Unsurprisingly, soil layers collected from 20 + cm did not satisfy any relationship between soil chemical attributes and soybean yield (Fig. 5).

The soil chemical attributes most affecting soybean yield, as seen for the 0–20 and 0–5 cm soil layers, were pH, Ca, Mg, Si, SB, BS% (positively impact) and exchangeable Al and potential acidity – H+Al (negatively impact). Moreover, the overall relationships were greater for the 0–5 than for the 0–20 cm, and neither layers showed any relationship between P and K with soybean yield (Fig. 5) because P and K were not influenced by soil amendments used. Soil amendments affected soybean yield to a greater extent than that of cropping-systems. Concerning sulfur (S), the positive relationship between the 0–20, 5–10, and 10–20 cm soil layers with soybean yield, in contrast to the non-relationship found for the 0–5 cm soil layer (Fig. 5), is because S might influence significantly the soybean yield (Borja Reis et al., 2021) mainly at the subsurface root system since such element, as well as the adequate N:S ratio, are important for soybean yield increment (Crespo
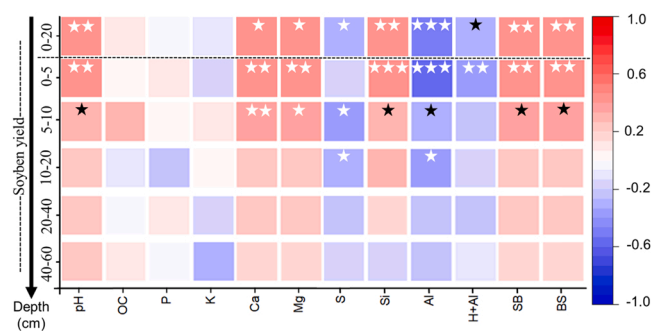

Fig. 5. Heatmap of Pearson correlation coefficient between soybean yield and soil chemical attributes at each soil layer studied ($n = 48$ comprising both cropping-systems and soil amendments). The 0–20 cm soil layer (top) represents the averaged soil chemical attributes over the 0–5, 5–10 and 10–20 cm soil layers. BS (base saturation) = (SB / CEC) × 100 %, where CEC (cation exchange capacity) = SB + (H+Al), and SB (sum of base concentrations) = Ca + Mg + K. Exact values can be seen in Supplementary Table S1. ***: $p < 0.001$; **: $p < 0.01$; *: $p < 0.05$; colored squares with no stars means relationships are not significant ($p > 0.05$).

et al., 2021). And clearly, S values increased as soil depth increased as discussed previously (Fig. 2). It remains to be known how effective is the soybean root system at soil layer 5 + cm as far as S uptake is concerned. The exact values of Person correlation coefficients can be found in Supplementary Table S1.

The non-significant relationships between soybean yields with cation exchange capacity (CEC) and micronutrients are presented in Supplementary Table S2. Non-significant relationships between soybean yields and soil CEC are due to most of CEC is occupied by H+Al. In this work, the distribution of micronutrients within the soil profile for the soil amendments and cropping-systems studied were not fully explored given the lack of consistent relationship among those factors and the availability of the micronutrients analyzed (Table 3). Also, as presented in Supplementary Table S2, no relationship was found between soybean yields and micronutrients. Briefly, the depth distribution for all micronutrients followed a similar pattern of decreasing concentration with increasing soil depth beyond the first 5 cm in the soil profile (*data not shown*). Higher micronutrient levels in the topsoil layers relative to subsurface soils are likely a result of greater decomposition of soil organic matter and crop residues (Wright et al., 2005), as most residues decompose within a few months after harvesting (Zibilske and Materon, 2005), releasing inorganic nutrients and contributing to accumulation in the topsoil. Iron (Fe) and Cu were negatively related to soil pH ($r = -0.37$ and -0.23, respectively, both at $p < 0.001$ with $n = 240$), consistent with Wright et al. (2007) in a similar field trial. On the other hand, Zn was positively related to soil pH ($r = 0.46$ at $p < 0.001$ with $n = 240$) while Mn exhibited no relationship. This shows that no consistent pattern of micronutrient distribution across the soil profile was found as a consequence of soil pH amendment application.

Soil chemical attributes related to soil acidity and soil pH correction most influenced soybean yield as highlighted in this work and, quantitatively, in previous works of Antonangelo et al. (2022) and Deus et al. (2020), where soybean yields increased, respectively, by 40 % and 33 % when compared to the control. Thus, either under long-term NT or in the NT implementation, surface application of lime or CMS-based products ameliorates soil acidity and improves nutrient availability and yield of the soybean crop. In this context, it is important to know whether the stratified soil sampling from 0 to 5 cm or common soil sampling from the arable layer of 0–20 cm would recommend different rates of soil pH amendment for the optimum yield. If so, it could cause a potential economic impact since those amendments are expensive in most areas.

To verify this, we regressed the lime rate calculated when soil is sampled from 0 to 20 cm against that calculated from the results when soil is sampled from 0 to 5 cm (Fig. 6). Recommendations for soil acidity
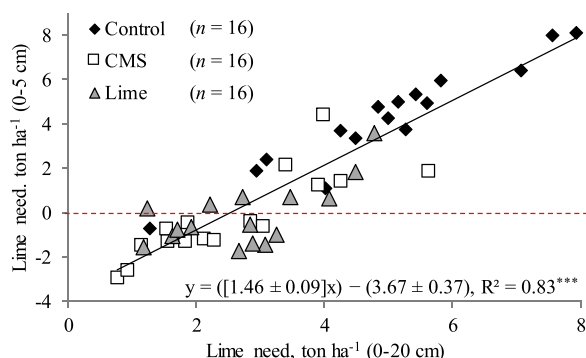
Fig. 6. Relationship between lime need for soils sampled from 0 to 20 and 0–5 cm ($n = 48$). The 0–20 cm soil layer represents the averaged values over the 0–5, 5–10 and 10–20 cm soil layers. Lime need was calculated based on the method of raising the percentage of base saturation (BS): Lime need (t ha^{-1}) = ([(BS2 − BS1) × CEC] / [(10 × ECCE)]), where BS2 = 70 % (target BS); BS1 = actual BS from soil analysis = (SB / CEC) × 100 %, where CEC (cation exchange capacity) = SB + (H+Al), and SB (sum of base concentrations) = Ca + Mg + K; ECCE = effective CaCO$_3$ equivalence (assumed to be 100 % for calculations). Negative values below the red dashed line indicate no need for liming when soil is sampled from 0 to 5 cm. *** : $p < 0.001$.

ameliorators are based on commercially available lime, and CMS could be calculated based on equal amount of ECCE. However, the difference of costs between different soil acidity amendments may vary drastically. According to the equation presented in Fig. 6, the overall need for lime is 2.21-ton ha^{-1} lower for soils sampled from 0 to 5 cm when compared to the 0–20 cm soil sampling. Negative values below the red dashed line indicate no need for liming when soil is sampled from 0 to 5 cm (Fig. 6). When negative values are turned into zero (0), intercept and slope from equation and linear model are still highly significant ($p < 0.001$) and the need for liming is 1.07-ton ha^{-1} lower according to the equation: y = ([1.19 ± 0.09]x) − (2.26 ± 0.34), $R^2 = 0.80$***. It is important to underline that such results are a consequence of the previous soil amendment application, thus the 0−5 cm sampling would surely require a higher rate of soil pH corrective in fields under NT because of surface acidification in the short-term when no amendment was applied previously. On the other hand, the subsequent liming application rate may be reduced if the uppermost soil layer is sampled and if the soil chemical attributes from such a layer, affected by prior lime addition, are still consistently related to the yield of the cash crop. Consequently, in the framework of our study, sampling depth is important in determining the amount of amendment needed to correct soil acidity under NT especially with prior application of amendments.

Another reason behind the reduced levels of H+Al in the upper layers when soil is sampled from 0 to 5 cm, and thus a decreased need for liming, is likely a consequence of Al–OC-based complexes lowering the Al toxicity. The organic acid secretion is an effective Al defense mechanism for many plants (Kopittke et al., 2016) so does the organic matter decomposition, which are enhanced under long-term NT systems. As such, NT has the potential to ameliorate toxic Al in acidic topsoil through the augmented formation of Al-DOC (dissolved organic carbon) complexes (Paul, 1991). Such Al–OC complexes enhancement in the upper layers of tropical soils under NT has been proven to be true in the work of Antonangelo et al. (2022) while investigating the same experimental site as this study.

The OC levels for all cropping-systems and pH control regimes decreased sharply with increased soil depth: dropping by ~15 % between the 0–5 and 5–10 cm layers, ~25 % between the 0–5 and 10–20 cm layers, and by 40–45 % between the 0–5 cm and 20–60 cm layers (Fig. 1). Thus, NT is an efficient soil management system that enhances the accumulation of soil organic matter (SOM) and improves the quality of humid tropical and subtropical soils (Briedis et al., 2012), e.g., by reducing Al activity in the uppermost soil layer thus causing the

stratification of soil chemical attributes, which might lead to distinguished, mostly reduced, liming recommendation rates. Further studies must focus on stratifying the depth at which the root system of cash crops is more active in soils under NT to verify the need for fertilizers and soil amendments according to such depth and compare with the requirements resulting from the common arable layer (0–20 cm).

4. Conclusions

- The NT system caused the stratification of all soil chemical attributes studied regardless of the cropping-systems and soil pH amendments used.
- Application of lime or CMS in the acid soil significantly decreased exchangeable Al and H+Al, and increased pH, Ca, Mg, Si, SB, BS% in the upper soil layers (0–10 cm) for most cropping-systems studied.
- The effects of CMS on soil chemical attributes did not differ from those of lime at any stratified layer 24 months after their application in the tropical soil under NT.
- Soil acidity parameters from 0 to 5 cm were significantly related to soybean yield, and the stratification of potential acidity (H+Al) led to a reduced estimation for soil amendment when soil is sampled from 0 to 5 cm in comparison to the sampling at 0–20 cm. Therefore, sampling depth should be consistent with the depth used for lime recommendation calculation for NT systems.
- The stratification pattern of soil chemical attributes under long-term NT is well explored in our study and shows that the different soil management practices related to the addition of soil amendments have the potential to increase stratification of important agronomic parameters. Thus the increased availability of nutrients in the uppermost soil layer (e.g., if the soil is sampled from 0 to 5 cm) may lead to a reduced need for fertilizer and/or lime application in the subsequent amendment addition under long-term NT agricultural lands. Thus, it is important to keep monitoring long-term experiments towards the evaluation of stratified soil attributes as related to the yields of crops.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.still.2022.105522.

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