

Article

Residual Effects of Methods Used to Correct Soil Acidity on Soil Chemical Properties in an Agropastoral System

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Abstract

Surface and subsurface acidity ($\text{pH} < 4.4$) limit nutrient availability, restrict root exploration, and impair crop yields in agricultural and agropastoral systems. Subsurface acidity (0.4–0.8 m layer) is a critical limiting factor for mature tropical soils. Methodologies that provide amelioration of surface and subsurface acidity and improvements in soil chemical fertility are necessary to decrease production costs and increase crop yields. This study evaluated the long-term ability of different methodologies for applying calcium (Ca) compounds (limestone (LS), phosphogypsum (PG), and hydrated lime (HL)) to ameliorate surface and subsurface acidity and improve soil chemical fertility. The results showed that the correction of surface acidity by treatments T2 (no-till/LS + PG), T3 (conventional tillage/LS + PG), T5 (no-till/HL + PG) and T6 (minimum tillage/HL + PG) persisted two years after application, as evidenced by higher pH and base saturation (BS) and lower total acidity in the 0.0–0.2 m layer compared with the control. By contrast, the improvement in acidity in the 0.4–0.8 m layer that was previously observed after subsurface application of HL in the 2017–2018 season (T6 and T7, minimum tillage/HL + PG) was lost. Moreover, the improvements in Ca^{2+} content and Ca^{2+} /cation exchange capacity (CEC) observed after applying LS plus PG persisted in the 0.0–0.1 m layer only. However, the improvements in Mg^{2+} content and Mg^{2+} /CEC after applying HL plus PG were not maintained. In addition, the positive effects of Ca compounds on sulfate-S (S-SO_4^{2-}) content throughout the soil profile (0.0–0.8 m) did not persist. By contrast, after two seasons, Ca compound application had residual positive effects on P content in the 0.1–0.8 m layer and organic matter (OM) content in the 0.2–0.8 m layer, which were previously not observed.

Keywords: intercropping systems; tropical soil management; chemical attributes; soil acidification; inorganic amendments



Academic Editor: Claudio Ciavatta

Received: 10 March 2026

Revised: 23 April 2026

Accepted: 8 May 2026

Published: 12 May 2026

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1. Introduction

Maintaining the long-term production capacity of soil is essential for increasing crop yields to meet global food demand [1], which has motivated global interest in sustainable

soil management systems such as no-till [2,3] and agropastoral systems. These systems enhance soil quality and, in turn, crop yields by improving the chemical, physical and biological attributes of soil [4] and conserving biodiversity [5]. However, in many areas of the world, increases in crop yields are limited by soil acidity (pH CaCl_2 values below 4.4) [6,7].

In Brazil, most agropastoral systems are located in the Cerrado biome (the Brazilian savanna), where soil acidity is the result of leaching of basic ions promoted by high rainfall over many years. This high degree of weathering produces soils with low calcium (Ca), magnesium (Mg), potassium (K), and phosphorus (P) contents [8]; low cation exchange capacity (CEC); low base saturation (BS) [9]; and high levels of elements that are toxic to plants, such as exchangeable aluminum (Al^{3+}) and manganese (Mn) [10–12]. The toxicity caused by high Al^{3+} content, P deficiency and low BS hinders root growth, reduces the absorption of water and nutrients by plants [13], and consequently limits crop yields [14], particularly in dry periods [15]. In addition, low Ca^{2+} content in deeper soil layers may confine root exploration to the surface layer.

Applying limestone (LS), i.e., liming, efficiently increases soil pH and BS, supplies Ca^{2+} and Mg^{2+} , and decreases exchangeable Al^{3+} and Mn [10,16]. However, the mobility of the products of LS dissolution is low and depends on the leaching of organic and/or inorganic salts throughout the soil profile; consequently, LS reactivity is restricted to the site of soil application [16,17]. This is problematic in systems without soil tillage, such as agropastoral systems of the Cerrado, where soil acidity correction is usually carried out by applying LS on the surface without incorporation into the soil [18]. Studies have confirmed that surface-applied LS has low mobility [7,19] and that liming without incorporation corrects acidity only in the 0–0.1 m layer [20].

Soil amendments like phosphogypsum (PG, CaSO_4) can increase the efficiency of LS application [10,12]. PG is more soluble than LS (2.5 g L^{-1}) [21] and leaches to subsurface layers [22]. As it moves down the soil profile, PG increases the supply of Ca^{2+} and sulfate-S (S-SO_4^{2-}) and reduces Al^{3+} activity [15,23]. Once in the soil solution, Ca^{2+} adsorbs to the soil-exchange complex and displaces Al^{3+} , K^+ and Mg^{2+} into the soil solution. These cations react with SO_4^{2-} to form AlSO_4^+ (which is less toxic to plants than Al^{3+}) and the neutral ion pairs K_2SO_4^0 and MgSO_4^0 , which, along with CaSO_4^0 , have high mobility in the soil profile [24]. During soil acidity correction, the carbonate of LS is consumed and is no longer available to accompany Ca^{2+} to deeper soil layers, whereas the sulfate of PG remains available [25]. By improving the soil profile, PG application promotes the development of the crop root system [23,26–28] to explore water and nutrients [29], reducing the adverse effects of drought [21], improving crop tolerance to water stress [30], and increasing crop yields [10], especially in the Cerrado biome.

Another input for improving soil fertility is hydrated lime (HL) [18]. HL ($\text{Ca}(\text{OH})_2$) is a fine powder produced by the hydration of virgin lime by an industrial process and comprising $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ [31,32]. The primary difference in reaction kinetics between hydrated lime and limestone is that HL reacts almost instantly and has high solubility, providing immediate pH elevation, whereas LS has low solubility and slow reaction kinetics, making it a long-term, slow-release amendment [33]. However, there is little information on application methodologies and the long-term effects of HL application, particularly in agropastoral systems.

Among soil conservation tillage techniques that reduce soil disturbance [34], improve the physical attributes of soil, and increase root-system development and crop yields is no-till [34,35]. This system is considered an important management practice for sustainable cropping intensification due the maintenance of high surface-soil coverage, which significantly influences the soil attributes, especially in the surface layer [36,37].

Another type of soil conservation tillage, which combines agricultural, livestock, and forestry activities within the same area, includes the integrated production systems [38]. Among these systems are agropastoral systems. However, in agropastoral systems using no-till shallow soil compaction (high bulk density and low porosity) can happen, due to absence of soil mechanical disturbance [39–41]. It is highlighted that excessive soil compaction in untilled surface layers can cause crop yield decrease, notably in dry years [42,43].

By contrast, there are alternative methodologies for mitigating soil compaction and soil acidity in agropastoral systems under no-till, simultaneously. Minimum tillage is another soil conservation tillage technique [44] that can help rebuild soil structure and have lower fuel consumption [45] compared to conventional tillage (harrow and plows).

Therefore, methodologies that provide long-term amelioration of surface and subsurface acidity and improvements in soil chemical fertility are necessary to decrease production costs and increase the crop yields of farmers in the Cerrado. Refs. [18,46] evaluated different methodologies for applying LS, PG, and HL in a Typic Hapludalf in an agropastoral system in Brazil on soil chemical attributes, soybean (*Glycine max* (L.) Merr.) and maize (*Zea mays* L.) grain yields, and the dry matter yield of palisade grass (*Urochloa brizantha* syn. *Brachiaria brizantha* cultivar Marandu). Ref. [18] found that after three seasons, all methodologies corrected surface acidity (0.0–0.2 m) by increasing pH and BS and reducing total acidity. However, only subsurface application of HL combined with both surface application of PG in the first year and surface application of HL in subsequent years increased pH and BS in the subsurface layer (0.4–0.8 m). Ref. [18] also determined that applying LS or HL plus PG increased S-SO_4^{2-} content throughout the soil profile (0.0–0.8 m); in the 0.0–0.2 m layer, applying LS plus PG increased Ca^{2+} content and $\text{Ca}^{2+}/\text{CEC}$, while applying HL plus PG increased Mg^{2+} content and $\text{Mg}^{2+}/\text{CEC}$. However, the long-term effects of these methodologies in agropastoral systems are unclear. To ameliorate acidity in the surface and subsurface layers and improve soil chemical fertility in the long term, different application methodologies (surface, incorporation by soil tillage, or subsurface) for calcium Ca compounds (limestone, phosphogypsum, and hydrated lime) were evaluated in an agropastoral system. This study tested the following hypotheses: (a) the improvements in soil chemical fertility by increasing pH and BS and reducing total acidity in the 0.0–0.2 m layer produced by different methodologies for applying limestone, phosphogypsum, and hydrated lime, and by increasing pH and BS in the subsurface (0.4–0.8 m layer) by subsurface application of HL plus surface application of PG in the first year and surface application of HL in subsequent two years, observed by Refs. [18,46], persist after two seasons and (b) further changes in soil chemical attributes by different methodologies for applying limestone, phosphogypsum, and hydrated lime can occur after two seasons.

2. Materials and Methods

2.1. Description of Study Area

The experiment was carried out at the Advanced Research and Development Division for Rubber Tree and Agroforestry Systems of the Agronomic Institute (IAC) of the São Paulo Agency for Agribusiness Technology (APTA), Votuporanga, Northwest São Paulo State, Southeastern Region, Brazil (20°20' S, 49°58' W and 510 m altitude), in an area with a slope < 5%. The study site is located in the Cerrado biome.

As described previously by Ref. [46], prior to the experiment, the area had been used for grain and seed production under conventional soil tillage. In the 2014–2015 season, castor bean was grown for seed production. During the 2015–2016 growing season, maize was cultivated under NT in the summer followed by sunn hemp (*Crotalaria juncea*) in the winter-spring season. In the 2016–2017 growing season, maize was intercropped with Congo grass (*U. ruziziensis* syn. *B. ruziziensis*) in the summer under NT. The Congo grass

was not grazed but was used as a cover crop before the next crop. Details of the study area are shown in Figure S1 in the Supplemental Material.

2.2. Description of Soil and Climate

The soil in the experimental area is classified as an Arenic Hapludult [47] and will be referred to in this study as an Ultisol with sandy texture. According to Köppen's classification, the regional climate type is Aw (tropical with dry winters). The average annual maximum temperature is 31.2 °C; the average annual minimum temperature is 17.4 °C; and the annual mean temperature is 24 °C. The annual average rainfall is 1328.6 mm. Figure S2 in the Supplemental Material presents monthly rainfall, minimum and maximum relative humidity, and minimum and maximum temperature data for Votuporanga from 1 November 2017 to 31 December 2022 [48].

2.3. Description of Experimental Design

The experimental design was randomized complete blocks with four replications using seven treatments involving three Ca compounds (LS, PG, and HL). Each plot had a size of 0.4 ha.

2.4. Description of Treatments

Seven treatments with different combinations of Ca compounds and application management methodologies were implemented over three growing seasons (2017–2018, 2018–2019, and 2019–2020). Three Ca compounds were used: LS, which contained 42% CaO and 7% MgO; PG, which contained 17% CaO and 14% S (S-SO_4^{2-}); and HL, which contained 40% CaO and 27% MgO. Descriptions of the treatments are presented in Table 1, and descriptions of the treatments in each growing season are presented in Table 2.

Table 1. Description of the treatments.

Treatment	Application Management Methodologies			Ca Compounds		
	No-till	Conventional tillage	Minimum tillage	Limestone	Phosphogypsum	Hydrated lime
T1 (control)						
T2	x			x	x	
T3		x		x	x	
T4		x		x		
T5	x				x	x
T6			x		x	x
T7			x		x	x

Table 2. Description of the treatments in each growing season.

Treatment	2017–2018 Season			2018–2019 Season			2019–2020 Season		
	Limestone (LS)	Phosphogypsum (PG)	Hydrated lime (HL)	LS	PG	HL	LS	PG	HL
	kg ha ^{−1}								
T1 (control)									
T2	SA, 2000 ¹	SA, 2500 ¹		SA, ⁵			SA, ⁵		
T3	I, 1000 ² + I, 1350 ³	SA, 1500 ¹		SA, ⁵	SA, ⁶		SA, ⁵	SA, ⁶	
T4	I, 1000 ² + I, 1350 ³			SA, ⁵			SA, ⁵		
T5		SA, 2500 ¹	SA, 725 ¹		SA, ⁶	SA, ⁵		SA, ⁶	SA, ⁵
T6		SA, 2500 ¹	SSA, 450 ⁴			SA, ⁵			SA, ⁵
T7		SA, 2500 ¹	SSA, 260 ⁴			SA, ⁵			SA, ⁵

¹ Surface application (SA). ² Incorporated (I) with a heavy-duty hydraulic harrow (28" discs) and a leveling harrow (20" discs, two times), (conventional soil tillage system). ³ Incorporated with a moldboard plow up to 0.26 m (conventional soil tillage system). ⁴ Subsurface application (SSA) with a 2-shank subsoiler-fertilizer in the 0.0–0.57 m layer (minimum soil tillage system). ⁵ Surface application of compound to ensure that Ca occupied 65% of CEC in the 0.0–0.2 m layer, Ref. [46]. ⁶ Surface application of compound to ensure that Ca occupied 50% of ECEC in the 0.2–0.4 m layer, Ref. [49].

In **T1**, the control treatment, LS, PG, and HL were not applied, and soil tillage was not performed. In **T2**, LS and PG were surface-applied (NT). In the 2nd and 3rd years, PG was not applied. In **T3** and **T4**, the conventional soil tillage system (CT) was used. In the 1st year, LS was incorporated with a heavy-duty hydraulic harrow (28" discs), and the next day a leveling harrow (20" discs) was used two times to level the ground. After that, LS was incorporated with a moldboard plow up to 0.26 m. In **T3**, PG was incorporated with a leveling harrow. In **T5**, HL and PG were surface-applied (NT) in the 1st year; in the 2nd and 3rd years, HL was surface-applied, and PG was surface-applied. In **T6** and **T7**, a minimum soil tillage system (MT) was used. In the 1st year, HL was applied in the 0.0–0.57 m layer using a 2-shank subsoiler-fertilizer, Kamaq, Araras, São Paulo, Brazil, and PG was surface-applied. In the 2nd and 3rd years, PG was not applied. Details of the treatments are shown in Figure S3 in the Supplemental Material.

In the 2nd and 3rd growing seasons, the dose of LS or HL was calculated based on the results of soil analysis to ensure that Ca occupied 65% of CEC in the 0.0–0.2 m layer according to the methodology of Ref. [46]: $LS/HL \text{ (Mg ha}^{-1}\text{)} = Ca^{2+} \text{ saturation of CEC} \times \text{exchangeable } Ca^{2+} \text{ content in cmol}_c \text{ dm}^{-3} \text{ over a depth of 0.0–0.2 m}$. The CEC at a depth of 0.0–0.2 m was calculated as the sum of the contents of exchangeable cations: $CEC = Ca^{2+} + Mg^{2+} + \text{potassium (K)}^+ + \text{total acidity (hydrogen (H)}^+ + Al^{3+})$. The Ca^{2+} saturation (65%) at a depth of 0.0–0.2 m was calculated as $100 \times Ca^{2+} / CEC$.

The dose of PG in the 2nd and 3rd growing seasons was calculated based on the results of soil analysis to ensure that Ca occupied 50% of effective cation exchange capacity (ECEC) in the 0.2–0.4 m layer, following the methodology of Ref. [49]: $PG \text{ (Mg ha}^{-1}\text{)} = (0.5 \times Ca^{2+} \text{ saturation in ECEC} - \text{exchangeable } Ca^{2+} \text{ content in cmol}_c \text{ dm}^{-3} \text{ at a depth of 0.2–0.4 m}) \times 6.4$. The ECEC at a depth of 0.2–0.4 m was calculated as the sum of the contents of exchangeable cations: $ECEC = Al^{3+} + Ca^{2+} + Mg^{2+} + K^+$. The Ca^{2+} saturation (50%) at a depth of 0.2–0.4 m was calculated as $100 \times Ca^{2+} / ECEC$.

2.5. Crop Management

Descriptions of the crop management schedule in each year are presented in Table 3. The details of soil and crop management in the treatments in the 2017–2018 (1st), 2018–2019 (2nd), and 2019–2020 (3rd) seasons were described previously by Ref. [46] and are presented in Tables S1–S3, respectively, in the Supplemental Material. The details of soil and crop management in the treatments in the 2020–2023 seasons are presented in Table S4 in the Supplemental Material. In brief, the doses of LS, PG, and HL used in the treatments were determined based on the results of soil sampling at the end of the previous season.

Table 3. Description of the crop management schedule in each year.

Month(s)	Year
November December	2017
	soil characterization/straw sampling/application of LS and HL application of PG/soybean sowing
April May October November	2018
	soybean harvest/soil sampling
	sun hemp sowing
	straw sampling
January April June June–October November November–December	2019
	palisade grass sowing ¹
	maize harvest/soil sampling
	introduction of beef cattle
	grazing phase
	application of LS, HL and PG
	grazing phase

Table 3. Cont.

Month(s)	Year
January–April May May–December	2020 grazing phase soil sampling grazing phase
January–December	2021 grazing phase
January–November December	2022 grazing phase soil sampling

¹ Palisade grass (*Urochloa brizantha* syn. *Brachiaria brizantha* cultivar Marandu).

2.6. Sampling and Analysis

Soil Sampling and Analysis

Before applying the treatments, soil was sampled from the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers to determine the initial soil characteristics, fertility Ref. [50] and sediment granulometric characteristics (sand, silt, and clay content). The samples were collected at ten random points of each depth increment (0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers). The ten subsamples were homogenized and pooled to form a composite sample of each depth increment. On 10 April 2018 and 19 April 2019, new soil samples were collected for chemical analysis, determination of fertility Ref. [50], and calculation of the doses of LS, PG, and HL to be reapplied according to the treatments. The samples were collected at five random points in each plot of each depth increment (0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers); thus, five subsamples were collected from each layer of each plot. The five subsamples were homogenized and pooled to form a composite sample of each layer of each plot. Soil was sampled with a metal probe and air-dried before analysis.

The pH (1:2.5 soil/0.01 M CaCl₂ suspension) and total acidity pH 7.0 (H⁺ + Al³⁺) were determined by the methodology of Ref. [50]. Total acidity was determined by titrimetry and was extracted from the soil using 1 mol L^{−1} calcium acetate (C₄H₆CaO₄) pH 7, a buffered solution that removes Al³⁺ and undissociated H from the soil Ref. [50]. The S-SO₄^{2−} content was determined by the calcium phosphate (Ca₃(H₂PO₄)₂) method Ref. [51], and the levels of P, K⁺, Ca²⁺, and Mg²⁺ in the soil were determined by extraction with ion-exchange resin [50]. The Ca₃(PO₄)₂ method is based on the extraction of S-SO₄^{2−} from soil samples by a solution of 0.01 mol L^{−1} Ca(H₂PO₄)₂ [50]. Quantification is performed by turbidimetry, which detects barium sulfate (BaSO₄) formed by the reaction of barium chloride dihydrate (BaCl₂·2H₂O) with S-SO₄^{2−} extracted from soil samples [50]. Extraction with ion-exchange resin allows the evaluation of so-called labile phosphorus by gradual dissolution of phosphate compounds from the solid phase of the soil and transfer of orthophosphate ions to the ion-exchange resin [50]. Furthermore, as the extraction is carried out with a mixture of cationic and anionic exchange resins saturated with sodium bicarbonate, the exchangeable cations are also largely transferred from the soil to the resin, especially if the levels are not too high [50]. An advantage of using sodium bicarbonate is that the bicarbonate ions buffer the medium at a pH close to neutrality, which is favorable for the dissolution of phosphates from the soil, while the sodium ions saturate the cationic resin, allowing the removal of exchangeable cations from the soil [50]. The Ca²⁺ and Mg²⁺ were determined by atomic absorption spectrophotometry, and K⁺ was determined by flame photometry [50]. These results were used to calculate the values of BS through the relationship between the content of exchangeable bases in the soil (Ca²⁺, Mg²⁺, and K⁺) and CEC and ECEC in cmolc dm^{−3} as well as the percentage ratios of K⁺/CEC, Ca²⁺/CEC, Mg²⁺/CEC, and Ca²⁺/ECEC [50].

To assess the long-term effects of the methodologies used to apply Ca compounds in the 2017–2020 seasons, soil samples were collected on 12 December 2022, for chemical analysis and determination of fertility. Soil was sampled with a metal probe and air-dried before analysis. The samples were collected at five random points of each depth increment (0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers) in each plot. The five subsamples from each layer were homogenized and pooled to form a composite sample of the layer. The chemical attributes of the samples were analyzed using the same methodology described previously Ref. [50].

2.7. Statistical Analysis

Before analyzing the data to evaluate the residual effect of the treatments applied in the 2017–2018, 2018–2019, and 2019–2020 growing seasons, the normality and homoscedasticity of the data were analyzed by the Shapiro–Wilk and Bartlett tests, respectively, both at 0.05 probability. Differences in soil chemical attributes in each soil layer (0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m) in the 2022–2023 season were analyzed by ANOVA (F test). Averages were compared by Tukey’s test ($p \leq 0.05$) in Assistat [52].

3. Results

The initial chemical characteristics and the sediment granulometric characteristics of the soil are shown in Table S5 in the Supplemental Material. Tables 4–7 present the chemical attributes of the soil in the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers, respectively, in the 2022–2023 season. Al^{3+} content was below the method detection/quantification limit in all samples from the four layers and thus was excluded from statistical analysis.

Table 4. Characteristics of the 0.0 to 0.1 m soil layer.

Attribute							Treatment ⁶								F Test	LSD ⁷	CV ⁸	SE ⁹
	T1		T2		T3		T4		T5		T6		T7					
P (resin), mg dm ^{−3}	31.00	c ¹⁰	50.00	ab	35.50	bc	31.50	c	57.00	a	46.00	abc	43.50	abc	8.64 **	15.63	15.92	2.05
S-SO ₄ ^{2−} , mg dm ^{−3}	4.00	ab	3.25	b	3.50	ab	4.50	a	3.00	b	3.25	b	3.00	b	5.16 **	1.15	14.06	0.12
OM, g dm ^{−3} ¹	14.00	bc	14.75	abc	17.00	a	13.00	c	15.75	ab	14.75	abc	16.50	ab	5.82 **	2.72	7.71	0.32
pH ²	5.50	e	6.13	bcd	6.55	a	6.00	cd	6.48	ab	6.28	abc	5.80	de	17.97 **	0.41	2.88	0.07
K ⁺ , cmol _c dm ^{−3}	0.35	a	0.24	bc	0.13	cd	0.10	d	0.2425	ab	0.2375	b	0.30	ab	13.85 **	0.11	20.94	0.02
Ca ²⁺ , cmol _c dm ^{−3}	1.10	c	2.65	ab	3.40	a	1.85	bc	3.38	a	2.35	ab	1.60	bc	10.84 **	1.24	22.85	0.18
Mg ²⁺ , cmol _c dm ^{−3}	0.90	b	1.00	ab	1.50	a	0.95	b	1.30	ab	1.38	ab	1.20	ab	4.50 **	0.51	18.50	0.05
Total acidity ³	1.50	a	1.08	bc	0.95	c	1.10	bc	0.98	c	1.03	c	1.20	b	33.00 **	0.15	5.86	0.03
BS, % ⁴	61.0	c	78.0	ab	84.0	a	69.5	bc	83.0	a	78.8	ab	72.0	b	13.08 **	10.59	6.03	1.61
CEC, cmol _c dm ^{−3} ⁵	3.85	b	4.96	ab	5.98	a	4.00	b	5.89	a	4.99	ab	4.30	b	6.29 **	1.60	14.09	0.19
K ⁺ /CEC, %	9.09	a	4.74	c	2.09	d	2.45	d	4.15	c	4.82	c	6.85	b	45.92 **	1.68	14.77	0.45
Ca ²⁺ /CEC, %	29.0	d	53.3	ab	56.5	ab	45.5	bc	57.0	a	46.0	abc	37.0	cd	18.99 **	11.18	10.34	1.99
Mg ²⁺ /CEC, %	23.0	ab	20.0	b	25.0	ab	22.5	ab	22.0	ab	28.0	a	28.0	a	4.55 **	6.70	11.92	0.70

¹ Organic matter. ² pH (1:2.5 soil/0.01 M CaCl₂ suspension). ³ Total acidity pH 7.0 ($\text{H}^+ + \text{Al}^{3+}$), cmol_c dm^{−3}. ⁴ Base saturation = 100 ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+/\text{CEC}$ pH 7.0). ⁵ Cation exchange capacity (CEC) pH 7.0 = $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{total acidity}$ ($\text{H}^+ + \text{Al}^{3+}$). ⁶ See Table 1 for details of the treatments. ⁷ LSD: least significant difference. ⁸ CV: coefficient of variation. ⁹ SE: standard error. ¹⁰ Within rows, means followed by the same letter are not significantly different according to Tukey’s test (0.05). ** Significant at the 0.01 probability level.

Table 5. Characteristics of the 0.1 to 0.2 m soil layer.

Attribute	Treatment ⁶														F Test	LSD ⁷	CV ⁸	SE ⁹
	T1		T2		T3		T4		T5		T6		T7					
P (resin), mg dm ^{−3}	17.00	d ¹⁰	35.00	b	27.50	c	31.00	bc	47.25	a	36.25	b	34.50	b	66.78 **	5.26	6.91	1.65
S-SO ₄ ^{2−} , mg dm ^{−3}	3.00		3.25		3.50		3.00		3.25		3.25		3.50		1.31	0.83	10.96	0.07
OM, g dm ^{−3} ¹	11.00	bc	11.75	abc	12.50	ab	10.00	c	11.50	bc	12.25	abc	14.00	a	6.30 **	2.34	8.45	0.28
pH ²	5.40	c	5.85	ab	6.20	a	6.20	a	6.10	a	5.98	a	5.55	bc	14.23 **	0.39	2.84	0.06
K ⁺ , cmol _c dm ^{−3}	0.29		0.28		0.20		0.37		0.38		0.34		0.30		1.76	0.22	30.14	0.02
Ca ²⁺ , cmol _c dm ^{−3}	1.20		1.93		1.90		1.40		1.95		1.70		1.20		3.45 *	0.85	22.63	0.08
Mg ²⁺ , cmol _c dm ^{−3}	0.60	b	0.60	b	1.00	a	0.60	b	0.78	ab	1.03	a	0.75	ab	5.61 **	0.36	20.41	0.04
Total acidity ³	1.50	a	1.18	b	1.00	c	1.10	bc	1.13	bc	1.20	b	1.25	b	20.60 **	0.16	5.81	0.03
BS, % ⁴	58.0	c	70.3	ab	75.5	a	68.0	ab	73.3	a	70.5	ab	64.0	bc	10.35 **	8.58	5.36	1.21
CEC, cmol _c dm ^{−3} ⁵	3.59		3.98		4.10		3.47		4.23		4.27		3.50		2.77 *	0.97	10.77	0.09
K ⁺ /CEC, %	8.08		6.89		4.88		10.66		9.06		8.21		8.58		2.47	5.36	28.52	0.49
Ca ²⁺ /CEC, %	33.0	b	48.8	a	46.5	ab	40.0	ab	45.8	ab	38.0	ab	34.0	b	4.63 **	13.61	14.26	1.42
Mg ²⁺ /CEC, %	17.0	bc	14.8	c	24.5	a	17.0	bc	18.3	abc	24.0	ab	21.0	abc	5.45 **	7.49	16.45	0.87

¹ Organic matter. ² pH (1:2.5 soil/0.01 M CaCl₂ suspension). ³ Total acidity pH 7.0 ($\text{H}^+ + \text{Al}^{3+}$), cmol_c dm^{−3}. ⁴ Base saturation = 100 ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+/\text{CEC}$ pH 7.0). ⁵ cation exchange capacity (CEC) pH 7.0 = $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{total acidity}$ ($\text{H}^+ + \text{Al}^{3+}$). ⁶ See Table 1 for details of the treatments. ⁷ LSD: least significant difference. ⁸ CV: coefficient of variation. ⁹ SE: standard error. ¹⁰ Within rows, means followed by the same letter are not significantly different according to Tukey’s test (0.05). ** Significant at the 0.01 probability level. * Significant at the 0.05 probability level.

Table 6. Characteristics of the 0.2 to 0.4 m soil layer.

Attribute	Treatment ⁶											F test	LSD ⁷	CV ⁸	SE ⁹
	T1	T2	T3	T4	T5	T6	T7								
P (resin), mg dm ⁻³	11.00	29.25	21.00	21.00	28.25	35.75	33.00	16.62 **	9.74	16.28	1.63				
S-SO ₄ ²⁻ , mg dm ⁻³	4.00	3.50	3.50	3.50	3.00	3.00	3.00	3.79 *	0.91	11.57	0.10				
OM, g dm ⁻³ ¹	8.50	10.50	10.50	11.00	10.00	10.25	11.00	9.07 **	1.32	5.53	0.18				
pH ²	5.50	5.70	6.00	6.05	5.75	5.90	5.70	2.68 *	0.55272	4.08	0.05				
K ⁺ , cmol _c dm ⁻³	0.14	0.35	0.28	0.27	0.32	0.32	0.31	2.84 *	0.19	28.60	0.02				
Ca ²⁺ , cmol _c dm ⁻³	1.20	1.50	1.25	1.85	1.48	1.40	1.20	2.90 *	0.63	19.23	0.06				
Mg ²⁺ , cmol _c dm ⁻³	0.45	0.43	0.65	1.20	0.68	0.63	0.55	15.87 **	0.30	19.94	0.05				
Total acidity ³	1.25	1.25	1.15	1.15	1.25	1.18	1.25	0.56	0.31	10.93	0.02				
BS, % ⁴	59.0	64.5	65.5	74.5	65.8	66.8	62.0	4.29 **	10.82	7.08	1.11				
CEC, cmol _c dm ⁻³ ⁵	3.04	3.52	3.33	4.47	3.72	3.52	3.31	8.97 **	0.71	8.51	0.09				
K ⁺ /CEC, %	4.52	9.79	8.41	5.94	8.70	9.31	9.33	2.45	5.93	31.76	0.53				
Ca ²⁺ /CEC, %	39.5	42.5	38.0	41.5	38.5	39.3	36.0	0.96	10.34	11.27	0.83				
Mg ²⁺ /CEC, %	14.79	12.01	19.49	26.86	18.27	17.53	16.6	7.64 **	7.84	18.72	0.98				
Ca ²⁺ /ECEC, % ^c	67.20	65.93	57.44	55.82	58.41	59.53	58.31	6.57 **	8.00	5.68	0.10				

¹ Organic matter. ² pH (1:2.5 soil/0.01 M CaCl₂ suspension). ³ Total acidity pH 7.0 (H⁺ + Al³⁺), cmol_c dm⁻³. ⁴ Base saturation = 100 (Ca²⁺ + Mg²⁺ + K⁺/CEC pH 7.0). ⁵ Cation exchange capacity (CEC) pH 7.0 = Ca²⁺ + Mg²⁺ + K⁺ + total acidity (H⁺ + Al³⁺). ⁶ See Table 1 for details of the treatments. ⁷ LSD: least significant difference. ⁸ CV: coefficient of variation. ⁹ SE: standard error. ¹⁰ Within rows, means followed by the same letter are not significantly different according to Tukey's test (0.05). ** Significant at the 0.01 probability level. * Significant at the 0.05 probability level.

Table 7. Characteristics of the 0.4 to 0.8 m soil layer.

Attribute	Treatment ⁶												F Test	LSD ⁷	CV ⁸	SE ⁹		
	T1		T2		T3		T4		T5		T6						T7	
P (resin), mg dm ⁻³	2.00	c ¹⁰	8.00	b	9.00	b	9.00	b	6.50	b	7.00	b	15.00	a	31.31 **	3.24	17.17	0.72
S-SO ₄ ²⁻ , mg dm ⁻³		3.00		4.25		4.00		4.00		3.25		5.00		3.50	2.10	2.18	24.17	0.20
OM, g dm ⁻³ ¹	7.00	c	8.00	b	8.50	ab	8.00	b	8.25	ab	8.25	ab	9.00	a	13.89 **	0.76	4.02	0.12
pH ²	5.60	b	5.63	b	6.00	ab	6.20	a	5.98	ab	5.75	ab	5.60	b	4.61 **	0.52	3.81	0.05
K ⁺ , cmol _c dm ⁻³	0.08	d	0.125	cd	0.205	b	0.34	a	0.1525	bcd	0.1575	bcd	0.16	bc	23.54 **	0.07925	19.47	0.02
Ca ²⁺ , cmol _c dm ⁻³		1.00		1.13		1.05		1.10		1.15		1.05		0.90	2.39	0.26	10.41	0.02
Mg ²⁺ , cmol _c dm ⁻³		0.50		0.40		0.50		0.50		0.55		0.50		0.45	1.13	0.21	18.43	0.02
Total acidity ³	1.20	a	1.18	a	1.10	ab	1.00	b	1.08	ab	0.02	ab	1.15	ab	4.38 **	0.15	5.75	0.02
BS, % ⁴	57.0	ab	58.3	b	61.0	ab	66.0	a	63.3	ab	60.3	ab	57.0	b	5.96 **	6.42	4.55	0.73
CEC, cmol _c dm ⁻³ ⁵	2.78	ab	2.83	ab	2.86	ab	2.94	a	2.93	ab	2.83	ab	2.66	b	2.71 *	0.27	4.05	0.02
K ⁺ /CEC, %	2.88	c	4.43	bc	7.18	b	11.56	a	5.26	bc	5.54	bc	6.06	b	19.46 **	2.91	20.30	0.55
Ca ²⁺ /CEC, %		36.0		40.0		36.5		37.0		39.3		37.0		33.5	2.43	6.42	7.42	0.58
Mg ²⁺ /CEC, %		18.0		14.3		17.5		17.0		18.8		17.5		17.0	0.93	6.84	17.08	0.52

¹ Organic matter. ² pH (1:2.5 soil/0.01 M CaCl₂ suspension). ³ Total acidity pH 7.0 (H⁺ + Al³⁺), cmol_c dm⁻³. ⁴ Base saturation = 100 (Ca²⁺ + Mg²⁺ + K⁺/CEC pH 7.0). ⁵ Cation exchange capacity (CEC) pH 7.0 = Ca²⁺ + Mg²⁺ + K⁺ + total acidity (H⁺ + Al³⁺). ⁶ See Table 1 for details of the treatments. ⁷ LSD: least significant difference. ⁸ CV: coefficient of variation. ⁹ SE: standard error. ¹⁰ Within rows, means followed by the same letter are not significantly different according to Tukey's test (0.05). ** Significant at the 0.01 probability level. * Significant at the 0.05 probability level.

3.1. Soil Chemical Properties by Layer

Table 4 presents the characteristics of the surface (0.0–0.1 m) layer of soil. Compared with T1 (control), total acidity was 0.3–0.55 cmol_c dm⁻³ lower, and Ca²⁺/CEC was 17.0–23.0 percentage points higher in the treatments in which Ca compounds were applied (T2–T7). In T2–T6, pH was 0.5–1.05 units higher than in T1. In T2, T3, T5 and T6, Ca²⁺ content was 1.25–2.3 cmol_c dm⁻³ higher than in T1, and BS was 17.0–23.0 percentage points higher than in T1. In the surface layer, T3 provided a pH of 6.55, while the value of pH in T1 was 5.5. In T2, T4, T5 and T6, the pH was 6.13, 6.0, 6.48 and 6.28, respectively. According to [6], soil pH (CaCl₂) values below 4.4 increase the availability of Al, whereas a pH range of 5.4–6.4 ensures the availability of most nutrients essential for crops. In addition, high Al³⁺ content (Al toxicity) affects root growth, restricting the capacity of plants to absorb water and nutrients [53]. These results signify a highly successful soil improvement.

Table 5 presents the characteristics of the 0.1–0.2 m soil layer. The total acidity was 0.25–0.5 cmol_c dm⁻³ lower, and P content was 10.5–30.25 mg dm⁻³ higher in T2–T7 than in T1. In T2–T6, pH was 0.45–0.8 units higher than in T1, and BS was 10.0–17.5 percentage points higher than in T1.

Table 6 presents the characteristics of the 0.2 to 0.4 m soil layer. In T2–T7, P content and OM were 10.0–24.75 mg dm⁻³ and 1.5–2.5 g dm⁻³ higher than in T1, respectively. No significant differences ($p > 0.05$) in any soil chemical attributes were observed between the treatments with HL (T5, T6, and T7).

The characteristics of the 0.4 to 0.8 m soil layer are shown in Table 7. In T2–T7, P content and OM were 4.5–13.0 mg dm^{−3} and 1.0–2.0 g dm^{−3} higher than in T1, respectively. These results corroborate those of Ref. [54], whose authors observed lasting benefits of liming for total acidity, P availability, and OM content for at least three years after application.

Figures 1 and 2 illustrate the chemical attributes of the soil in the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers in the 2022–2023 season, including P (Figure 1a); S (Figure 1b); organic matter (OM) (Figure 1c); pH (Figure 1d); Ca²⁺ (Figure 1e); Mg²⁺ (Figure 1f); H⁺ + Al³⁺ (Figure 2a); BS (Figure 2b); Ca²⁺/CEC (Figure 2c); and Mg²⁺/CEC (Figure 2d).

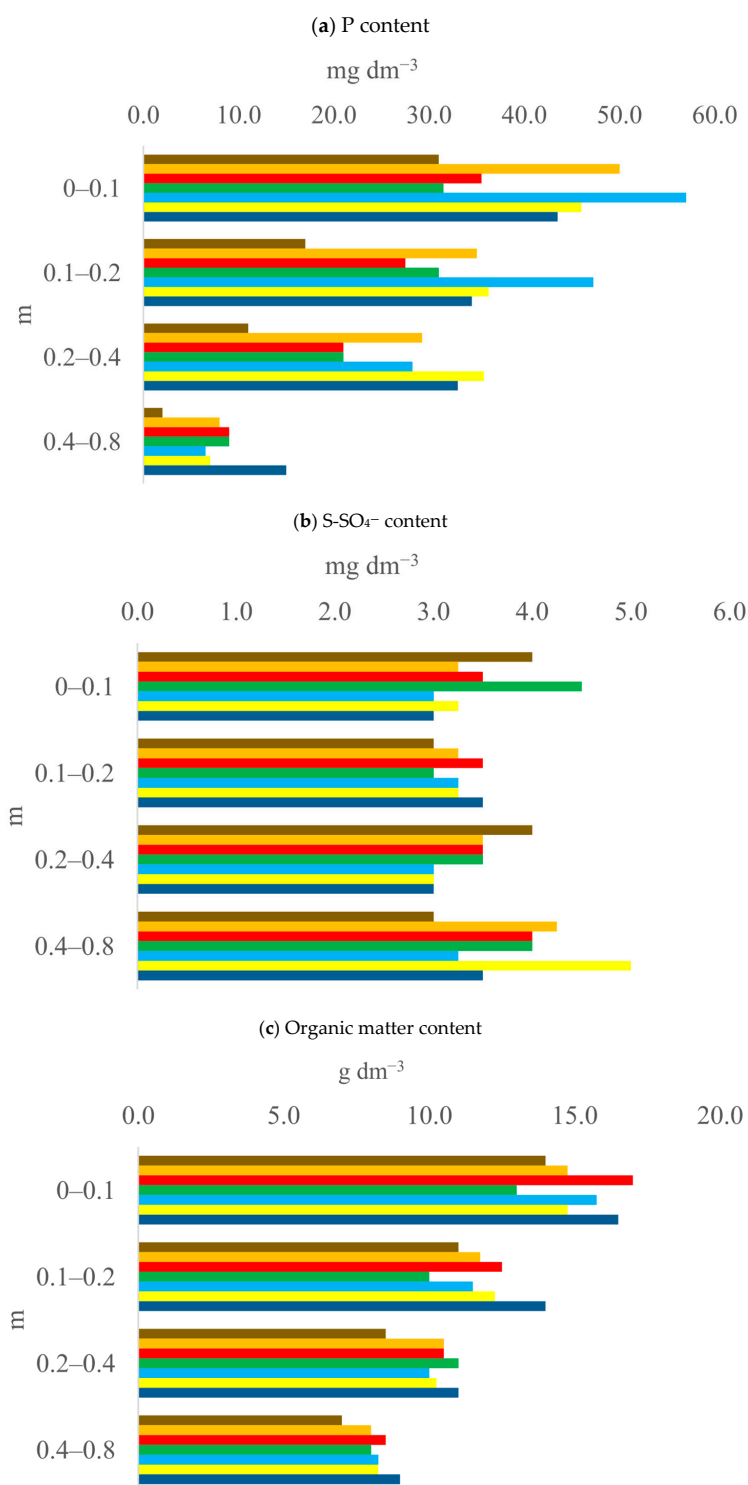


Figure 1. Cont.

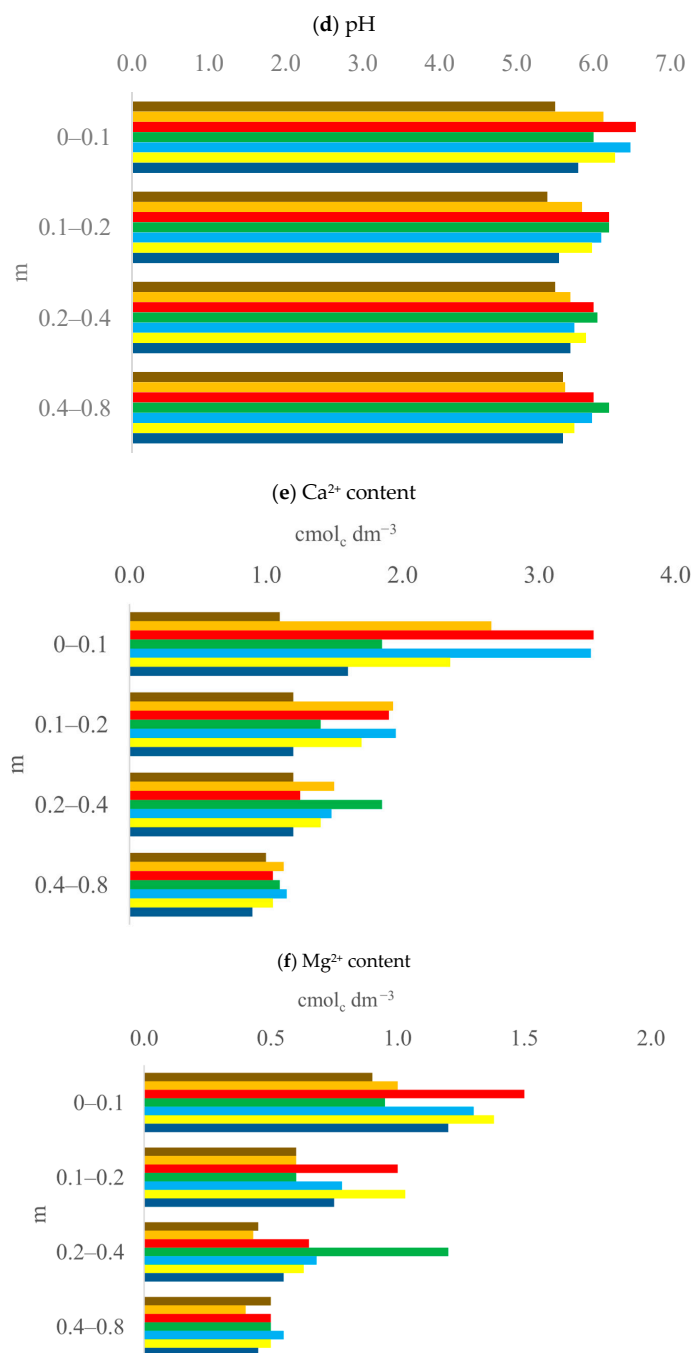


Figure 1. Average values of soil chemical attributes (horizontal axis) in the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers (vertical axis) in the 2022–2023 season. Treatments: T1—control (brown); T2 (orange); T3 (red); T4 (green); T5 (blue); T6 (yellow); and T7 (dark blue).

3.2. Trends of Soil Characteristics by Layer and Treatment

In the surface layer, $\text{Ca}^{2+}/\text{CEC}$ ranged from 29% in T1 to 57% in T5; however, none of the treatments provided 65% of Ca^{2+} in CEC. Similarly, in the 0.1–0.2 m layer, $\text{Ca}^{2+}/\text{CEC}$ ranged from 33% in T1 to 49% in T5.

In the 0.2–0.4 m layer, every treatment provided 50% of Ca^{2+} in ECEC. In the 0.4–0.8 m layer, pH, BS, and CEC were highest in T4, whereas total acidity was lowest in this treatment.

The increases in Ca^{2+} content and $\text{Ca}^{2+}/\text{CEC}$ achieved by applying LS plus PG (T2 and T3) were maintained in the surface layer but not in the 0.1–0.2 m layer, corroborating the findings of Ref. [53].

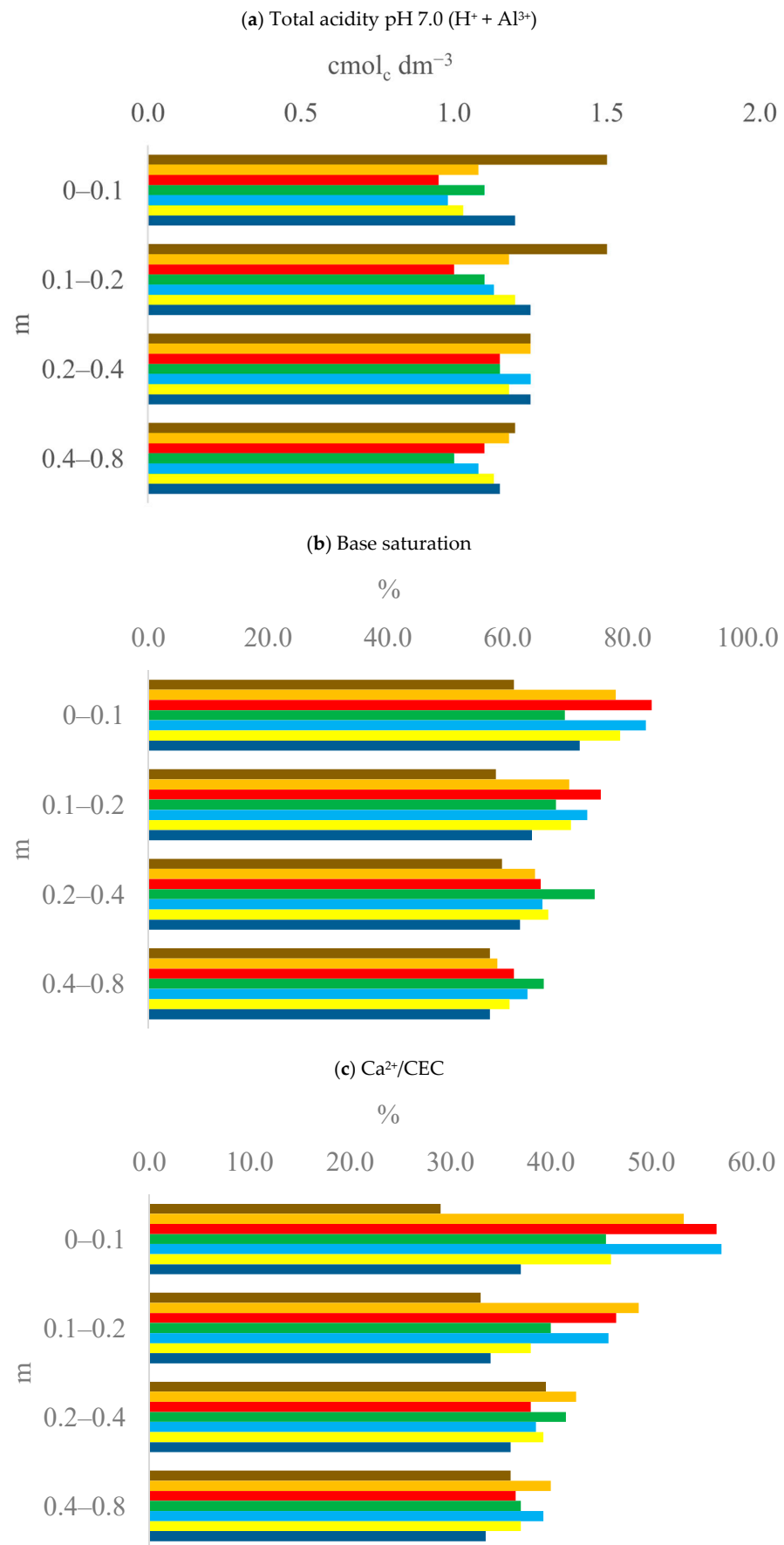


Figure 2. Cont.

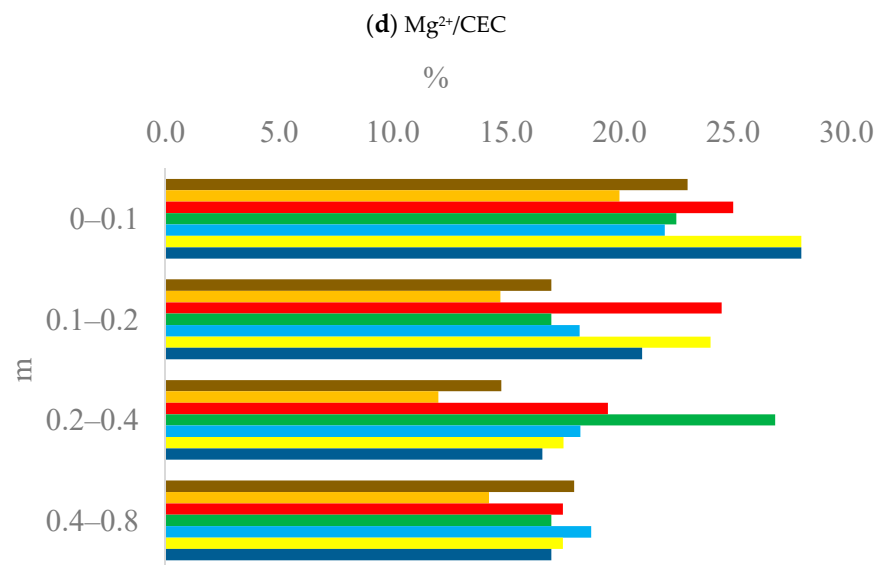


Figure 2. Average values of soil chemical attributes (horizontal axis) in the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers (vertical axis) in the 2022–2023 season. Treatments: T1—control (brown); T2 (orange); T3 (red); T4 (green); T5 (blue); T6 (yellow); and T7 (dark blue).

The increases in Mg^{2+} content and $\text{Mg}^{2+}/\text{CEC}$ observed after applying HL plus PG (T6) were maintained in the 0.1–0.2 m layer but not in the 0.0–0.1 m layer. These results corroborate those of Ref. [54], who found that PG application promoted a decrease in Mg^{2+} content in the surface layer and an increase in deeper layers. By contrast, these increases did not persist in T5 and T7.

4. Discussion

This study confirms that treatments T2, T3, T5 and T6 (methodologies for applying Ca compounds for surface and subsurface acidity correction) had residual effects on surface acidity at depths of 0.0 to 0.2 m in this agropastoral system by increasing pH and BS and reducing total acidity. These findings are consistent with those of Ref. [54], in a tropical soil (sandy clay loam kaolinitic and thermic Typic Haplorthox) with a no-till maize and Congo grass intercropping system, which reported long-term positive effects of LS and PG amendment on P content; Ref. [55], in a tropical soil (medium texture Haplustox) with liming carried out four months before planting the an orchard of mango cultivar Palmer, observed residual effects of liming, including increased P content and reduced total acidity, and Ref. [56], in a tropical soil (Red Oxisol) with a no-till maize-soybean rotation, left fallow in the fall/winter, determined that total acidity in the 0.0–0.3 m layer was reduced two years after liming. By contrast, residual effects of subsurface application of HL combined with both surface application of PG in the first year and surface application of HL in subsequent years (T6 and T7) were not observed; these treatments had initially increased pH and BS in the subsurface layer (0.4–0.8 m).

The positive effects of applying LS or HL plus PG on S-SO_4^{2-} content throughout the soil profile (0.0–0.8 m) were not maintained. This reflects the high forage dry matter biomass production in the palisade grass pasture (ranging from 11,272 to 18,084 kg ha⁻¹ on 12 February 2020) [46], which increased S absorption [57], which ranged from 1.09 to 1.82 g kg⁻¹ [46].

By contrast, after two seasons, Ca-compound application had residual positive effects on P content in the 0.1–0.8 m layer and OM content in the 0.2–0.8 m layer that were not previously observed. Similar to the present study, Ref. [58], in a tropical soil (clay texture typical dystrophic Red Oxisol) with the succession of wheat and soybean crops,

and with residual effect of PG evaluated 33 months after its application, along with the effects of P doses, observed residual positive effects of PG application on P content and attributed these effects to the presence of P residues in the PG itself. The higher OM content in the subsurface layer in T2–T7 was due to the residual positive effects of Ca compounds on fertility throughout the soil profile, which included increases in P and K^+ contents, BS, and K^+ / CEC . These improvements were reflected in the dry matter yield of palisade grass forage, consistent with previous studies reporting positive effects of PG on soil chemical properties and root-dry-mass density of sugarcane Ref. [59], in a tropical soil (dystrophic Red Latosol) in an area kept under spontaneous vegetation with a predominance of grasses (*U. decumbens* syn. *B. decumbens* and *Andropogon gayanus*), with PG applied on the soil surface after sugarcane planting, and on black oat (*Avena strigosa*) biomass, Ref. [60], in a tropical soil (very clayey Typic Hapludox) with PG and N rates on black oat regrowth and on succeeding soybean under no-till, with PG application, even up to 44 and 55 months earlier.

The higher Mg^{2+} content, CEC, and Mg^{2+} / CEC in the 0.2–0.4 m layer and K^+ content and K^+ / CEC in the 0.4–0.8 m layer in T4 compared with the other treatments were due to the slow effect of LS. Ref. [61] observed effects of LS only at approximately 18 months after application, and Ref. [62], in a soil belonging to the Dystrudepts group in Mexico, with maize used as an indicator crop in an area of variable fertility and scarce organic matter, observed increased Mg^{2+} content two years after the application of LS without PG. The factors that influence the reaction time and residual effect of LS in the soil include soil buffer power, degree of homogenization during LS incorporation [63], and LS particle size Ref. [55]. LS acts most quickly the bigger its total relative neutralizing power, a crucial index in agriculture that indicates the efficiency of a soil amendment in neutralizing soil acidity, and when incorporated into soils with low buffer capacity, whereas its effect is slowest when applied as coarse particles on the surface of highly buffered soils without incorporation. Total relative neutralizing power, often measured as relative neutralizing value or effective Ca carbonate equivalent, is a metric for LS quality that combines chemical purity and particle size (fineness); it calculates how effectively a material can raise soil pH compared to pure Ca carbonate Ref. [64]. By contrast, in the surface layer, T4 provided lower Ca^{2+} and Mg^{2+} contents and lower BS compared with the other methodologies for applying Ca compounds for surface and subsurface acidity correction. Notably, PG was not used in this treatment. Although PG does not directly affect soil pH, it increases Ca^{2+} content and CEC [54], and BS and CEC are related ($BS = 100 (Ca^{2+} + Mg^{2+} + K^+ / CEC \text{ pH } 7.0)$).

4.1. Effects of the Treatments on pH and Total Acidity

Consistent with the results of this study, Refs. [56,65], in a tropical soil (sandy loam Oxisol) under no-till using the following crops over a period of 72 months, black oat, maize, wheat and soybean, observed residual effects of the surface application of LS and PG under NT on pH, with increases in the 0.0–0.1 and 0.1–0.2 m layers. The combined application of LS and/or HL with PG provided better conditions for LS and/or HL to act on the soil solution and increase pH. Increased pH is the result of (1) physical downward movement of fine LS particles through the continuous porosity in the soil profile formed after the decomposition of dead roots or by soil organisms; (2) the formation of ionic pairs between NO_3^- or SO_4^{2-} (released from fertilizer or mineralized OM) and Ca^{2+} and Mg^{2+} from the amendment; or (3) the formation of water-soluble CaL^0 or CaL-type complexes between plant residues on the soil surface (carboxylic and phenolic radicals) and Ca^{2+} or Mg^{2+} , which involves the incorporation of hydrophilic groups, such as sulfonated or charged substituents, onto the ligand (L) and subsequent metal ion coordination Refs. [56,66]. In addition, PG can indirectly increase soil pH in deeper layers as the $S-SO_4^{2-}$ from the PG

displaces OH^- from soil colloid surfaces into the soil solution Ref. [14]. In agropastoral systems under no-till, low-molecular-weight organic acids released during the decomposition of animal waste, mainly feces, or exuded by pasture residues Ref. [67] can increase the effects of surface application of LS and/or HL at greater depths by favoring the downward movement of Ca^{2+} and Mg^{2+} in the soil profile.

Residual effects of T3, T4, T6 and T7 on pH and total acidity were not observed, indicating that repeated application may be necessary when these management practices are used. One reason for the lack of a decrease in total acidity ($\text{H}^+ + \text{Al}^{3+}$) in the 0.2–0.4 and 0.4–0.8 m layers in T2–T7 was due the use of 10-10-10 fertilizer in topdressing fertilization of palisade grass, which contained urea as the N source. Urea contains N-NH_3 Ref. [20], which rapidly oxidizes to nitrate in the soil, releasing H^+ Ref. [68]. Another reason is that the decomposition of organic residues originating from soybean, maize and palisade grass acidified the soil, decreasing pH and increasing total acidity Ref. [69].

In T2, residual effects were not observed in the 0.4–0.8 m layer, corroborating previous findings by Ref. [66], in a tropical soil (Rhodic Paleudult) followed by no-till soil cultivation, without LS incorporation, and under conventional tillage, with incorporation into the soil, that verified that positive effects of surface liming are most pronounced in the surface layers of the soil. Basic anions from the dissolution of LS (OH^- and HCO_3^-) move by mass flow to the deeper layers of the soil, where they react with acidic cations (H^+ , Fe^{2+} , Al^{3+} , and Mn^{2+}), preventing further alkalization reactions Ref. [70]. In addition, the reaction of LS is generally limited to the site of soil application, and it does not reduce subsoil acidity quickly [16]. Moreover, when LS is applied to the surface, the low mobility of its products of dissolution restricts the efficiency of this soil conditioner in reducing acidity in subsurface layers of the soil with variable loads, which depends on the leaching of organic and/or inorganic salts throughout the soil profile Ref. [17]. Ref. [23] reported that Ca^{2+} and Mg^{2+} concentrations in the acidic subsoil of an Oxisol were related to the downward movement of S-SO_4^{2-} .

4.2. Effects of the Treatments on Base Saturation

T2–T7 had residual positive effects on BS in the 0.0–0.1, 0.1–0.2, and 0.2–0.4 m layers. Reaction of Ca^{2+} in the soil solution with the soil-exchange complex displaces K^+ and Mg^{2+} into the soil solution, where these cations react with SO_4^{2-} to form the neutral ionic pairs K_2SO_4^0 and MgSO_4^0 , which, along with CaSO_4^0 , have great mobility in the soil profile Ref. [24]. Ca^{2+} , K^+ , and Mg^{2+} compete for some of the same adsorption sites in the soil Ref. [71]. Therefore, increasing Ca^{2+} , K^+ , and Mg^{2+} contents in the soil profile also increases BS.

4.3. Effects of the Treatments on P Content

The residual effects on P content can be attributed to the formation of compounds between Ca and P due to the dissociation of compounds containing Ca and S in the presence of water, which releases Ca^{2+} and SO_4^{2-} ions. Ca^{2+} subsequently reacts with P, reducing the latter's solubility according to Refs. [14,72], in a tropical soil (dystrophic Clay Rhodic Hapludox) with surface application and incorporated into the soil of LS, using soybean cultivation in the summer and barley (*Hordeum distichum* L.) /wheat cultivation in the winter, and Ref. [10], in a tropical soil (clayey, kaolinitic, thermic Rhodic Hapludox) with maize and soybean cultivation and LS applied to the soil surface or incorporated into the topsoil, and PG applied to the surface, also observed increases in P content in the surface layer after the application of high doses of PG. As expected, P content in the 0.0–0.1 and 0.1–0.2 m layers was higher under NT (T5 and T2) than under conventional soil tillage (T3 and T4). This occurred because a lack of soil turnover promotes nutrient accumulation in the surface

layers Ref. [14] and because of the immobility of P in soil, Refs. [73,74], in a tropical soil (Typic Hapludox) using three cover crop residues: pearl millet (*Pennisetum glaucum* L.), oats (*A. sativa* L.) and Gigantic guinea sorghum (*Guinea sorghum*), interacting with doses of P, applied over straw mulch, observed similar results and concluded that P adsorption capacity decreases as the soil concentration of P increases. By contrast, under no-till, the constant supply of organic material increased organic P in deeper layers, which increased the fertility of the soil after mineralization. Ref. [75], in a tropical soil (Red-Yellow Cambic Argisol) with soil being cultivated with annual crops and submitted to six tillage systems (no-till, disc plow, moldboard plow, heavy disc harrow, and heavy disc harrow + moldboard plow), showed that a few years after the establishment of no-till, the chemical, physical and biological properties of the surface layer differed from those in an intensive tillage system that included regular moldboard plowing with secondary tillage.

4.4. Effects of the Treatments on K^+ Content

The higher dry matter yield of palisade grass forage in T2 than in T1 in the 2019–2020 season (as shown in Ref. [46]) explains the higher K^+ content in the 0.2–0.4 m layer in T2 compared with T1 two years later. K is the most abundant cation in plant tissues due to its extensive absorption by roots as K^+ ions from the soil solution Ref. [76]. In addition, K is required in large quantities by crops, equaling the amount of N required, and accumulates in residues at levels three or four times higher than P Ref. [77]. Forage grasses such as palisade grass have very extensive and constantly renewed root systems, which, when combined with their high dry matter production potential, enable rapid changes in soil OM and nutrient levels [78]. In addition, by absorbing nutrients from subsurface layers of the soil and subsequently releasing them to the surface layer upon decomposition of its residues, palisade grass can restore considerable amounts of nutrients to crops. Refs. [79,80], in two tropical soils (Oxisols) with soybean and maize in rotation with cover crops (grain sorghum—*Sorghum bicolor*, pearl millet, Sudan grass—*S. sudanense*, grain sorghum $\times$ Sudan grass hybrid, and Congo grass), observed an average increase in K^+ content of $0.23 \text{ cmol}_c \text{ dm}^{-3}$ two seasons after planting Congo grass, another forage grass of the genus *Urochloa*.

In T2–T7, the application of Ca compounds for three seasons resulted in downward movement of K^+ from the surface layer to the 0.2–0.4 and 0.4–0.8 m layers, corroborating the results of Ref. [56]. In addition, due to the thermodynamics of ion exchange and the properties of Ca^{2+} , PG can potentially increase leaching losses of Mg^{2+} and K^+ to deep layers Ref. [22]. The CaSO_4 in PG reduces Al^{3+} activity, decreasing subsurface acidity effects and redistributing basic cations such as Mg^{2+} and K^+ from the surface to subsurface layers Refs. [26,60].

4.5. Effects of the Treatments on Ca^{2+} Content and $\text{Ca}^{2+}/\text{CEC}$

The residual positive effects of Ca compounds on Ca^{2+} content and $\text{Ca}^{2+}/\text{CEC}$ were restricted to the surface layer due to the lower mobility of Ca^{2+} in the soil profile Ref. [16], as Ca^{2+} is retained by negatively charged clays and OM Ref. [81]. Ca^{2+} was also consumed by the increase in palisade grass forage yield, as Ca^{2+} is important for root growth Ref. [15] and cell division Ref. [82].

4.6. Effects of the Treatments on Mg^{2+} Content and $\text{Mg}^{2+}/\text{CEC}$

The increases in Mg^{2+} content and $\text{Mg}^{2+}/\text{CEC}$ in the 0.1–0.2 m layer in T6 were due to the movement of Mg^{2+} in the soil profile. The supply of Ca^{2+} by PG solubilization promotes the substitution of Mg^{2+} from the exchange complex to the soil solution and the formation of the ionic pair MgSO_4^0 . This ionic pair is more easily leached in the soil by water infiltration, promoting the movement of Mg^{2+} in the soil profile Refs. [3,21,22]. A

high concentration of Ca^{2+} in the soil favors the displacement of Mg^{2+} from exchange sites. The displaced Mg^{2+} can form an ion pair with SO_4^{2-} or be leached in the form of Mg^{2+} ions, which is the preferred form of displacement in the profile Ref. [83]. In addition, Mg^{2+} mobility was promoted by the formation of complexes with soluble organic compounds released by the decomposition of crop biomass deposited on the soil surface (carboxylic and phenolic radicals) and by the release of low-molecular-weight organic acids from root exudates under the influence of grazing and from the decomposition of animal waste, mainly feces Refs. [67,83]. Mg^{2+} was also consumed by palisade grass forage yield because Mg is a component of chlorophyll and participates in the transfer of energy for the process of photosynthesis Ref. [84].

4.7. Effects of the Treatments on Organic Matter Content

The oldest stems and stalks of palisade grass forage have high C/N ratios and high levels of lignin and polyphenols, which results in slow decomposition Ref. [85] and favors increases in OM throughout the soil profile Ref. [86]. In the soil solution, CaSO_4 (Ca sulfate) is hydrolyzed to $\text{Ca}^{2+} + \text{SO}_4^{2-} + \text{CaSO}_4^0$ Ref. [58]. The Ca^{2+} ions react with the soil-exchange complex and displace Al^{3+} , K^+ and Mg^{2+} to the soil solution, where they react with sulfate (SO_4^{2-}) to form AlSO_4^+ (a form of Al that is less toxic to plants) and the neutral ionic pairs K_2SO_4^0 , MgSO_4^0 and CaSO_4^0 , which have high mobility Ref. [87]. These ionic pairs move to deeper layers, improving the soil profile, crop root-system development, water absorption through plant roots Refs. [27,53], and, ultimately, crop yields Ref. [88]. Residual effects of LS and PG on soil fertility, including increases in OM content and BS and decreases in total acidity, and on aboveground and root biomass and maize and soybean yields, also were observed by Refs. [10,54–56,65].

4.8. Considerations

Several studies have reported limitations of surface application of LS in systems without soil tillage (no-till): Ref. [16]—maize response to LS and PG applications at the installation of no-till in a tropical soil (Clay Rhodic Hapludox); Ref. [17]—surface and incorporated application of LS in a tropical soil (clayey, kaolinitic, thermic Rhodic Hapludox) with cropping sequence: soybean, barley, soybean, wheat, soybean, maize, and soybean; and Ref. [18]. The low mobility of the products of LS dissolution restricts the efficiency of this soil-liming agent in reducing acidity in subsurface layers of the soil and results in variable loads, also known as pH-dependent loads. This variability is characteristic of the highly weathered soils common in tropical regions such as Brazil and results in leaching of organic and/or inorganic ion pairs deeper into the soil Ref. [17]. To contribute to methods for ameliorating surface and subsurface acidity and improving soil chemical fertility in agropastoral systems under no-till, we established this study of the residual effects of different application methodologies (surface, incorporation by soil tillage, or subsurface) for Ca compounds (LS, PG, and HL) that were implemented during the 2017–2020 seasons. In contrast to our expectations, the improvements in soil chemical attributes throughout the soil profile (0.0–0.8 m) after the incorporation of LS and subsurface application of HL in the 2017–2018 season did not persist in subsequent seasons. The surface application of LS and HL reduces energy (fuel) costs compared with application under tillage Ref. [89]. Because the positive effects of applying LS plus PG and applying HL plus PG on soil fertility in the 0.0–0.2 m layer were maintained, T2 and T5 are good options for correcting soil acidity in agropastoral system. These two treatments also increased P content in the 0.1–0.8 m layer and OM content in the 0.2–0.8 m layer, which may promote crop root-system development and plant water and nutrient absorption, thereby reducing the adverse effects of drought, improving crop tolerance to water stress, and increasing crop yields, especially in the Cerrado biome.

In relation to initial soil total acidity in 2017 (Table S5), the combined application of LS and/or HL with PG provided a reduction in total acidity throughout the soil profile in 2022. This reduction ranged from 0.6 to 0.85, 0.65 to 0.9, 0.35 to 0.45, and 0.32 to 0.5 $\text{cmol}_c \text{ dm}^{-3}$ in the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers, respectively. This occurred due to the complete neutralization of the acidic cations (H^+ , Fe^{2+} , Al^{3+} , and Mn^{2+}), which occurs at a pH above 5.6 Ref. [65]. In T2–T7, the pH ranged from 5.8 to 6.7, 5.6 to 6.2, 5.7 to 6.1, and 5.6 to 6.2 in the 0.0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m layers, respectively. This shows that there was no loss of subsurface acidity correction over time, corroborating the results of Ref. [90], in tropical soil (sandy loam kaolinitic, thermic Typic Haplorthox) under no-till and with the following crop rotations: rice in the summer and black oat in the fall; bean in the summer and black oat in the fall; peanut in the summer and oat in the fall; and maize intercropped with Congo grass, which reported that reductions in surface and subsurface soil acidity due to superficial liming with or without PG under no-till were maintained 5 years after application.

In addition, Ref. [91], in a Goldsboro loamy sand (fine-loamy, siliceous, thermic, Aquic Kandiudult), with growing soybean double cropped with wheat for 3 years and after 3 years of continuous maize, observed a vertical stratification of plant nutrients in the soil profile under conservation tillage, especially no-till, in contrast to an accumulation of P, Ca^{2+} , K^+ , and Mg^{2+} near the surface under conventional tillage. However, we observed this stratification under all three soil tillage practices (no-till, conventional tillage, and minimum tillage). In addition, in T2–T7, P and K^+ contents in the 0.0–0.1, 0.1–0.2, and 0.2–0.4 m layers were average according to Ref. [50]. By contrast, in T1, P and K^+ contents in the 0.2–0.4 m layer were low according to Ref. [50].

5. Conclusions

The present study evaluated the residual effects of different methodologies for applying Ca compounds in an agropastoral system in an Ultisol with sandy texture two seasons after the last application.

Some of the improvements in surface acidity and surface and subsurface soil chemical fertility produced by the different methodologies for applying LS, PG, and HL persisted after two seasons. In the 0.0–0.2 m layer, the correction of surface acidity via increased pH and BS and reduced total acidity was maintained. Moreover, the improvements in Ca^{2+} content and $\text{Ca}^{2+}/\text{CEC}$ after applying LS plus PG and Mg^{2+} content and $\text{Mg}^{2+}/\text{CEC}$ after applying HL plus PG were preserved in the surface layer. Finally, Ca-compound application had residual positive effects on P content in the 0.1–0.8 m layer and OM content in the 0.2–0.8 m layer. By contrast, the improvement in acidity in the 0.4–0.8 m layer previously observed after the incorporation of LS and subsurface application of HL in the 2017–2018 season was not maintained. In addition, the positive effects of these amendments on S-SO_4^{2-} content throughout the soil profile (0.0–0.8 m) disappeared. However, the combined application of LS and/or HL with PG provided a reduction in total acidity throughout the soil profile in relation to the initial soil total acidity observed five years earlier, before applying the treatments.

Because increasing the soil contents of Ca and P enables greater root exploration in deeper layers, the present findings have implications for the adoption of practices that minimize surface and subsurface acidity and increase crop productivity.

Thus, due to maintenance in Ca^{2+} and Mg^{2+} contents and in $\text{Ca}^{2+}/\text{CEC}$ and $\text{Mg}^{2+}/\text{CEC}$ after applying LS or HL plus PG in the surface layer, and reduction in total acidity throughout the soil profile, these methodologies for applying Ca compounds in agropastoral systems with soil sandy texture are the most recommended.

Evaluations of the long-term effects of different methodologies for mitigating soil acidity are therefore encouraged.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agronomy16100966/s1>, Figure S1: Details of the experimental area; Figure S2: Monthly rainfall (R), maximum relative humidity (MaxRH), minimum relative humidity (MinRH), maximum temperature (MaxT), and minimum temperature (MinT) data for Votuporanga, São Paulo State, Brazil, from November 2017 to December 2022. Source: [48]. Figure S3: Details of treatments; Table S1: Treatment schedule in the 2017–2018 season; Table S2: Treatment schedule in the 2018–2019 season; Table S3: Treatment schedule in the 2019–2020 season; Table S4: Treatment schedule in the 2020–2023 season; Table S5: Initial soil chemical characteristics by soil layer, 2017.

Author Contributions: Conceptualization, W.L.B.B., M.A. and J.L.H.; methodology, W.L.B.B., M.A. and J.L.H.; formal analysis, M.A.; investigation, W.L.B.B., L.C.P.d.C., D.Y.O.d.O., J.F.B. and L.d.C.S.; writing—original draft preparation, W.L.B.B. and M.A.; project administration, W.L.B.B. and J.L.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Votorantim Cimentos—ViterAgro and Agronelli Indústria e Comércio de Insumos Agropecuários Ltda by the Fundação de Apoio à Pesquisa Agrícola—FUNDAG, grant number 6467.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We are grateful to the staff of Divisão Avançada de Pesquisa e Desenvolvimento de Seringueira e Sistemas Agroflorestais for support for this research, and to Dawn M. Schmidt, ELS for English editing.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

BS	Base saturation
HL	Hydrated lime
LS	Limestone
LSD	Least significant difference
MaxRH	Maximum relative humidity
MaxT	Maximum temperature
MinRH	Minimum relative humidity
MinT	Minimum temperature
OM	Organic matter
PG	Phosphogypsum
R	Rainfall

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