New Methodologies for the Surface Application of Limestone and Gypsum in Different Crop Systems

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Abstract: To address the problems of soil acidity (pH values below 4.4) in surface and subsurface soil layers and improve soil chemical fertility, this study evaluated three methodologies for surface application of limestone (LS) (ensuring that calcium (Ca) 2+ occupied 70%, 60% or 50% of cation exchange capacity (CEC) at a depth of 0.0–0.2 m) and gypsum (GP, phosphogypsum) (ensuring that Ca 2+ occupied 60%, 50% or 40% of effective cation exchange capacity (ECEC) at a depth of 0.2–0.4 m). LS and GP were applied in a conventional pasture system (CPS), no-till system (NTS), and agropastoral system (APS) in an Arenic Hapludult in Brazil. Surface application of LS and GP using these three methodologies corrected surface and subsurface acidity and improved soil chemical fertility. Specifically, Ca 2+ content increased in the CPS, NTS, and APS at a depth of 0.0–0.2 m and in the CPS and APS at a depth of 0.2–0.4 m; sulfur (S)-SO 4 2− content and Ca 2+/ECEC increased in the CPS, NTS, and APS at a depth of 0.2–0.4 m; base saturation (BS) increased and aluminum (Al) 3+ content decreased in the NTS and APS at depths of 0.0–0.2 m and 0.2–0.4 m; and pH, magnesium (Mg) 2+ content, CEC, Ca 2+/CEC, and Mg 2+/CEC increased and total acidity decreased in the NTS and APS at a depth of 0.0–0.2 m.

Keywords: soil fertility; soil acidity; conventional pasture system; no-till system; agropastoral system

1. Introduction

Conservation management systems aim to prevent soil erosion or degradation and are widely used in agriculture. No-till systems (NTSs) eliminate the practice of turning the soil and allow plant material to accumulate on the surface for the sowing or planting of the next crop [1]. Agropastoral systems (APSs) incorporate pasture, which takes advantage of the soil correction and residual fertilizer applied to the previous crop. In turn, the successive crop benefits from the physical conditioning of the soil and straw production by the pasture [2]. In these conservation management systems, soil acidity is typically corrected by applying limestone (LS) on the soil surface without incorporation. The low mobility of the dissolution products of surface-applied LS limits its efficiency in reducing acidity in subsurface layers of the soil, resulting in variable loads that depend on the leaching of organic and/or inorganic salts through the soil profile [3]. Surface liming (LS application) creates a soil acidity correction front in the soil that is proportional to dose and time [4,5]. Several studies have shown that the positive effects of superficial liming are most pronounced in the surface layers of the soil [5–11].
Subsoil acidity limits agricultural productivity by restricting root growth and the absorption of water and nutrients by crops [12–14]. Improving soil conditions below the surface layers can increase and/or stabilize crop yield, especially in regions with dry winters that are subject to dry spells. One such region is the Cerrado biome in Brazil, which is also characterized by Ca deficiency in the soil subsurface, frequently in association with Al toxicity [15]. An interesting option for improving the subsurface soil layers in NTSs is the application of gypsum (GP), which has been used in acidic soils as a complement to LS [16,17]. The high mobility of GP has been attributed to its greater solubility and the presence of a stable sulfate anion (SO\text{4}^{2–}) [18]. In Europe, the anticipated expansion of soil salinization due to climate change is expected to increase the demand for GP as a soil amendment [19,20].

Surface application of GP in NTSs reduces exchangeable Al\text{3+} levels, increases Ca\text{2+} and S-SO\text{4}^{2–} levels and, in some cases, indirectly raises pH values in subsurface soil layers [6,7,21–25]. Positive effects of GP application after 24 months have been reported [6], and these effects persisted at 36 months after application [7]. In another study, increased pH was observed at depths of 0.2–0.4 m at 8 months and 0.4–0.6 m at 20 and 32 months after surface application of GP [26]. GP has also been found to increase pH and Ca\text{2+} and S-SO\text{4}^{2–} levels and reduce exchangeable Al\text{3+} levels in the soil up to 18 months after application [20]. The authors attributed this effect to a ligand exchange reaction on the surface of soil particles that involved partial neutralization of acidity [27]. Other studies have observed increases in Ca\text{2+} levels in the soil profile and Mg\text{2+} lixiviation [24,26,28,29] and decreases in exchangeable Al\text{3+} [22,23,30] due to surface application of GP.

There is a need to test new LS and GP dosing methodologies, as surface application of LS does not effectively correct subsurface acidity and the optimal dosage of GP remains unclear. To contribute to solving the problems of acidity in the surface and subsurface layers and improving soil chemical fertility in conventional pasture systems (CPSs), NTSs, and APSs, in this study we tested the following hypothesis: surface application of LS (ensuring that Ca\text{2+} occupies 70%, 60%, or 50% of CEC at a depth of 0.0–0.2 m) and surface application of GP (ensuring that Ca\text{2+} occupies 60%, 50%, or 40% of ECEC at a depth of 0.2–0.4 m) can correct surface and subsurface acidity and improve soil chemical fertility.

2. Materials and Methods

2.1. Site, Soil, Climate, and Treatments

The experiment was carried out at the Advanced Research Center and Development for Rubber and Agroforestry Systems of the Agronomic Institute (IAC) of the São Paulo Agency for Agribusiness Technology (APTA), which is located in the Cerrado biome in the municipality of Votuporanga, São Paulo State, Brazil (20°20′S, 49°58′W and 510 m altitude). The soil in the experimental area is classified as an Arenic Hapludult (USDA soil classification system) [31], hereafter referred to as Ultisol, with a sandy texture. Each plot was 5 m long and 5 m wide, with a total area of 25 m². The climate in the region is tropical with dry winters (Aw-type according to Köppen’s classification). The average annual maximum, minimum, and mean temperatures are 31.2 °C, 17.4 °C, and 24 °C, respectively, and the annual average rainfall is 1328.6 mm. Monthly data on potential evapotranspiration (PET), rainfall (R), and average temperature (T) in Votuporanga from 1 November 2017 to 29 February 2020 are shown in Figure 1. Data on PET for January and February 2020 were not available from the data source used.

The experimental design was randomized complete blocks with four replications and four treatments involving LS and GP application. The details of the LS and GP applications in each treatment are provided in Table 1.
Figure 1. Data on PET, R, and T in Votuporanga, São Paulo State, Brazil, from November 2017 to February 2020. Source: [32].

Table 1. Treatment details.

| Treatment | LS | GP |
|-----------|----|----|
| T1        | surface applied to ensure that Ca\(^{2+}\) occupied 70% of CEC at a depth of 0.0–0.2 m | surface applied to ensure that Ca\(^{2+}\) occupied 60% of ECEC at a depth of 0.2–0.4 m |
| T2        | surface applied to ensure that Ca\(^{2+}\) occupied 60% of CEC at a depth of 0.0–0.2 m | surface applied to ensure that Ca\(^{2+}\) occupied 50% of ECEC at a depth of 0.2–0.4 m |
| T3        | surface applied to ensure that Ca\(^{2+}\) occupied 50% of CEC at a depth of 0.0–0.2 m | surface applied to ensure that Ca\(^{2+}\) occupied 40% of ECEC at a depth of 0.2–0.4 m |
| T4        | not applied | not applied |

The LS contained 31% CaO and 21% MgO, and the GP contained 17% CaO and 14% S (S\(\text{SO}_4\)). To calculate the required amount of LS, the following equation was used according to the methodology of [33]:

\[
\text{LS amount (Mg ha}^{-1}\text{)} = \text{Ca}^{2+} \text{ saturation in CEC} - \text{exchangeable Ca}^{2+} \text{ content in cmol}_c \text{ dm}^{-3} \text{ at a depth of 0.0–0.2 m}
\]

CEC was calculated as the sum of the contents of exchangeable cations:

\[
\text{CEC} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{potassium (K)}^+ + \text{total acidity (hydrogen (H)}^+ + \text{Al}^{3+}) \text{ at a depth of 0.0–0.2 m}
\]

Ca\(^{2+}\) saturation (70%, 60%, and 50%) was calculated as:

\[
100 \times \frac{\text{Ca}^{2+}}{\text{CEC}} \text{ at a depth of 0.0–0.2 m}
\]

To calculate the required amount of GP, the following equation was used according to the methodology of [34]:

\[
\text{GP amount (Mg ha}^{-1}\text{)} = \text{Ca}^{2+} \text{ saturation in ECEC} - \text{exchangeable Ca}^{2+} \text{ content in cmol}_c \text{ dm}^{-3} \text{ at a depth of 0.2–0.4 m} \times 6.4
\]

ECEC was calculated as the sum of the contents of exchangeable cations:

\[
\text{ECEC} = \text{Al}^{3+} + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ \text{ at a depth of 0.2–0.4 m}
\]

Ca\(^{2+}\) saturation (60%, 50%, and 40%) was calculated as:

\[
100 \times \frac{\text{Ca}^{2+}}{\text{ECEC}} \text{ at a depth of 0.2–0.4 m}
\]

Three crop systems were used: CPS, NTS, and APS. The total area of each system was approximately 1.0 ha. In the T1, T2 and T3 treatments, LS and GP were broadcast...
(manually) on the soil surface (superficial application) on 22 November 2017 (spring), 30 August 2018 (winter), and 12 September 2019 (winter), in all crop systems. The three crop systems are shown in Figures 2–4.

**Figure 2.** Conventional pasture system (CPS), 12 September 2019.

**Figure 3.** No-till system (NTS), 12 September 2019.
Figure 4. Agropastoral system (APS), 12 September 2019.

2.2. Crop Systems

The CPS was implemented in an area of recovered pasture cultivated with millet (*Pennisetum glaucum*) (fall-winter season 2008/09), soybean (*Glycine max* L.) (spring-summer season 2009/10), sunn hemp (*Crotalaria juncea*) (fall-winter season 2009/10), and maize intercropped with palisade grass (*Urochloa brizantha* syn. *Brachiaria brizantha* cultivar Marandu) (spring-summer season 2010/11). Beginning in September 2011, newly weaned beef cattle were introduced into the area and remained until slaughter, and the pasture was not restructured thereafter. A continuous grazing system was used with a stocking rate of 1–2 animal units ha\(^{-1}\) (one animal unit is equal to a live weight of 450 kg) according to the forage offered. The animals were allowed to move freely about the pasture. The cattle were grazed to a certain weight and removed, and a new set of cattle were introduced and grazed to a certain weight. LS (29% CaO and 20% MgO) was surface applied at a dose of 300 kg ha\(^{-1}\) on 3 February 2016.

The NTS was implemented in the 2009/10 season in an area that was previously used for grain production in a conventional soil tillage system. The crops used in the NTS were soybean, maize, sunn hemp, grain sorghum (*Sorghum bicolor*), and a sorghum-sudangrass hybrid (*S. bicolor × S. sudanense*) intercropped with palisade grass and Congo grass (*U. ruziziensis* syn. *B. ruziziensis*). In the 2016/17 season, soybean and sunn hemp were grown in the spring-summer and fall-winter seasons, respectively.

The APS was implemented in the 2010/11 season in an area that had been previously used for grain production in a conventional soil tillage system. The crop rotation used in this system was soybean (spring-summer season), sunn hemp (after soybean; fall-winter season), and maize intercropped with palisade grass (after sunn hemp; spring-summer season). In this system, newly weaned beef cattle were introduced sixty days after the harvest of maize intercropped with palisade grass. The cattle remained in the area for 14 months. The area was then closed for thirty days, and the grass was desiccated with glyphosate (a broad-spectrum systemic herbicide). Next, soybean was sown in an NTS on the palisade grass straw. The grazing system was continuous, and the stocking rate was 2–4 animal units ha\(^{-1}\) according to the forage offered. The animals were allowed to
move freely about the pasture, and different generations of animals were pastured on the same area.

2.3. Crop Management
2017/18 season

The treatment schedule in the 2017/18 season with details of soil and crop management is shown in Table 2.

Table 2. Treatment schedule in the 2017/18 season.

| Date       | Activity                                      | CPS | NTS | APS |
|------------|-----------------------------------------------|-----|-----|-----|
| 10/30/2017 | soil characterization                          | x   | x   | x   |
| 11/03/2017 | straw sampling                                | x   | x   | x   |
| 11/22/2017 | surface application of LS and GP              | x   | x   | x   |
| 11/24/2017 | maize sowing                                  | x   | x   | x   |
| 12/11/2017 | first topdressing †                           | x   | x   | x   |
| 12/14/2017 | palisade grass sowing                         | x   | x   | x   |
| 12/18/2017 | second topdressing ‡                          | x   | x   | x   |
| 03/27/2018 | maize harvest                                 | x   | x   | x   |
| 04/16/2018 | soil sampling                                 | x   | x   | x   |

† first topdressing fertilization of maize. ‡ second topdressing fertilization of maize.

In the NTS and APS, the maize hybrid Dow AgroSciences 2B587 Power Core™ was sown mechanically on a straw of sunn hemp under no-till, at a row spacing of 0.8 m and density of 6.0 seeds m$^{-1}$ (0.0167 m plant spacing). Basic fertilization was performed, sowing at a dose of 315 kg ha$^{-1}$ of 08-28-16 fertilizer (8% N, 28% P$_2$O$_5$, and 16% K$_2$O), with 1.7% Ca and 3.6% S-SO$_4^2$-. The first topdressing fertilization of maize was carried out using 20-00-20 fertilizer (20% N and 20% K$_2$O) at a dose of 270 kg ha$^{-1}$. The second topdressing fertilization of maize was carried out using ammonium sulfate (20% N and 22% S-SO$_4^2$-) at a dose of 250 kg ha$^{-1}$.

Palisade grass was sown mechanically in the NTS and APS using 10 kg ha$^{-1}$ of forage seeds with a cultural value of 50% mixed with simple superphosphate fertilizer (18% P$_2$O$_5$, 16% Ca, and 8% S-SO$_4^2$-; common practice) at a dose of 60 kg ha$^{-1}$. Two rows were sown between rows of the maize crop. The cultural value of seed indicates seed quality and is calculated according to the following formula: cultural value = (%germination × %purity)/100.

Sampling and analysis

Soil samples were collected at depths of 0.0–0.2 and 0.2–0.4 m before the application of the treatments to determine the initial soil characteristics and fertility [35]. The samples were collected at 10 random points in each crop system at depths of 0.0–0.2 and 0.2–0.4 m; thus, 10 subsamples were collected at each depth of the crop system. The 10 subsamples were homogenized and pooled to form a composite sample for each depth of each crop system. Soil was sampled with a metal probe and air-dried before analysis.

pH was evaluated in 0.01 M CaCl$_2$ 2H$_2$O solution, and total acidity (H$^+$ + Al$^{3+}$) was determined by titration using 1 N calcium acetate (C$_4$H$_6$CaO$_4$) solution, pH 7.0. S-SO$_4^{2-}$ content was determined by the calcium phosphate (Ca$_3$(PO$_4$)$_2$) method, and the levels of P, K$^+$, Ca$^{2+}$, and Mg$^{2+}$ in the soil were determined by extraction with ion-exchange resin [35]. These results were used to calculate the base saturation (BS) based on the relationship between the content of exchangeable bases in the soil (Ca$^{2+}$, Mg$^{2+}$, and K$^+$) and the cation exchange capacity (CEC) in cmol$_c$ dm$^{-3}$, as well as the percentage ratios of K$^+$/CEC, Ca$^{2+}$/CEC, and Mg$^{2+}$/CEC.
On 16 April 2018, new soil samples were collected for chemical analysis, determination of fertility [35], and calculation of the doses of LS and GP to be reapplied according to the treatments. The samples were collected at five random points in each plot at depths of 0.0–0.2 and 0.2–0.4 m; thus, five subsamples were collected from each depth of each plot. The five subsamples were homogenized and pooled to form a composite sample of each depth of each plot. Soil was sampled with a metal probe and air-dried before analysis.

2018/19 season

The treatment schedule in the 2018/19 season with details of soil and crop management is shown in Table 3.

Table 3. Treatment schedule in the 2018/19 season.

| Date          | Activity                        | CPS | NTS | APS |
|---------------|---------------------------------|-----|-----|-----|
| 08/30/2018    | surface application of LS and GP| x   | x   | x   |
| 11/27/2018    | palisade grass mowing           | x   | x   | x   |
| 04/17/2019    | soybean sowing                  | x   | x   | x   |
| 04/24/2019    | soil sampling                   | x   | x   | x   |
| 04/29/2019    | sunn hemp sowing                | x   | x   | x   |

Soybean sowing was carried out mechanically under no-till on the palisade grass straw using the soybean cultivar 74HO112TP IPRO Paranaiba. Seeds were sown at a row spacing of 0.5 m and density of 14 seeds m$^{-1}$ (0.0714 m plant spacing). Fertilization was applied at sowing at a dose of 300 kg ha$^{-1}$ of 04-20-20 fertilizer (4% N, 20% P$_2$O$_5$, and 20% K$_2$O) with 4.9% Ca, 3.6% S-SO$_4$, 0.05% B, 0.06% Mn and 0.27% Zn.

Sunn hemp was sown on soybean straw in the NTS at a row spacing of 0.5 m and density of 25 seeds m$^{-1}$ (0.04 m plant spacing) under no-till.

Sampling and analysis

On 24 April 2019, new soil samples were collected for chemical analysis, determination of fertility [35], and calculation of the doses of LS and GP to be reapplied according to the treatments following the same methodologies used in the previous year.

2019/20 season

The treatment schedule in the 2019/20 season with details of soil and crop management is shown in Table 4.

Table 4. Treatment schedule in the 2019/20 season.

| Date          | Activity                        | CPS | NTS | APS |
|---------------|---------------------------------|-----|-----|-----|
| 09/09/2019    | sunn hemp harvest†              | x   | x   | x   |
| 09/10/2019    | sunn hemp mowing                | x   | x   | x   |
| 09/12/2019    | surface application of LS and GP| x   | x   | x   |
| 11/12/2019    | palisade grass sowing           | x   | x   | x   |
| 11/12/2019    | soybean sowing                  | x   | x   | x   |
| 11/13/2019    | maize sowing                    | x   | x   | x   |
| 11/27/2019    | first topdressing‡              | x   | x   | x   |
| 12/02/2019    | second topdressing§             | x   | x   | x   |
| 03/09/2020    | maize harvest                   | x   | x   | x   |
| 03/11/2020    | soybean harvest                 | x   | x   | x   |
| 06/16/2020    | soil sampling                   | x   | x   | x   |

† sunn hemp harvest for seed production. ‡ first topdressing fertilization of maize. § second topdressing fertilization of maize.
In the NTS, on 12 November 2019, palisade grass was sown in a broadcast system (manually) at a density of 1000 points of cultural value ha\(^{-1}\).

In the APS, soybean was sown mechanically under no-till on the palisade grass straw using the soybean cultivar 74HO112TP IPRO Paranaiba. Seeds were sown at a row spacing of 0.5 m and density of 16.75 seeds m\(^{-1}\) (0.0597 m plant spacing). Fertilization was applied at sowing at a dose of 300 kg ha\(^{-1}\) of 04-20-20 fertilizer (4% N, 20% \(\text{P}_2\text{O}_5\), and 20% \(\text{K}_2\text{O}\)) with 4.9% Ca, 3.6% S-\(\text{SO}_4\), 0.05% B, 0.06% Mn, and 0.27% Zn.

In the NTS, the maize hybrid Forseed FS533 PWU was sown mechanically on sunn hemp straw under no-till at a row spacing of 0.5 m and density of 4 seeds m\(^{-1}\) (0.25 m plant spacing). Basic fertilization was performed, sowing at a dose of 250 kg ha\(^{-1}\) of 08-28-16 fertilizer (8% N, 28% \(\text{P}_2\text{O}_5\), and 16% \(\text{K}_2\text{O}\)), with 1.7% Ca and 3.6% S-\(\text{SO}_4\). The first topdressing fertilization of maize was carried out using 20-00-20 fertilizer (20% N and 20% \(\text{K}_2\text{O}\)) at a dose of 250 kg ha\(^{-1}\). The second topdressing fertilization of maize was carried out using ammonium sulfate (20% N and 22% S-\(\text{SO}_4\)) at a dose of 250 kg ha\(^{-1}\).

**Sampling and Analysis**

On 16 June 2020, new soil samples were collected for chemical analysis and determination of fertility [35] following the same methodologies used in the previous year.

2.4. Statistical Analysis

The data of soil chemical attributes at each soil depth (0.0–0.2 and 0.2–0.4 m) in each season (2017/18, 2018/19, and 2019/20) were submitted to ANOVA (F test), and the averages were compared by the Tukey test (\(p < 0.05\)) using the software Assisstat Version 7.7, [36], Campina Grande, Brazil. The standard errors of the means of significant changes in soil chemical attributes were also analyzed in graphical format using the software Microsoft Excel (2016).

3. Results

In the 2017/18 season, there was 7920 kg ha\(^{-1}\) and 7070 kg ha\(^{-1}\) of straw dry matter on the soil in the NTS and APS, respectively. In the NTS, the palisade grass was mowed on 27 November 2018, to facilitate soybean sowing, as the average green matter was 18,840 kg ha\(^{-1}\). Table 5 presents the initial soil characteristics.

### Table 5. Initial characteristics of the soil in 2017 at depths of 0.0–0.2 and 0.2–0.4 m.

| Characteristics | Crop Systems | Depth (m) |
|-----------------|--------------|-----------|
|                 | CPS NTS APS  | CPS NTS APS |
| P (resin), mg dm\(^{-3}\) | 4 34 22 2 9 15 |
| S-\(\text{SO}_4\)^2\(^{-}\), mg dm\(^{-3}\) | 3 3 4 4 4 5 |
| Organic matter, g dm\(^{-3}\) | 5.2 4.3 4.5 5.3 4.1 4.1 |
| pH (1:2.5 soil/0.01 M \(\text{CaCl}_2\) suspension) | 5.2 4.3 4.5 5.3 4.1 4.1 |
| \(\text{K}^+\), cmol\(_c\) dm\(^{-3}\) | 0.1 0.28 0.21 0.18 0.27 0.25 |
| \(\text{Ca}^{2+}\), cmol\(_c\) dm\(^{-3}\) | 1.4 1.0 0.7 1.3 0.8 0.5 |
| \(\text{Mg}^{2+}\), cmol\(_c\) dm\(^{-3}\) | 1.1 0.6 0.7 0.8 0.4 0.4 |
| \(\text{Al}^{3+}\), cmol\(_c\) dm\(^{-3}\) | 0.0 0.4 0.2 0.0 0.5 0.6 |
| Total acidity pH 7.0 (\(\text{H}^+ + \text{Al}^{3+}\)), cmol\(_c\) dm\(^{-3}\) | 1.6 3.1 2.5 1.6 2.8 2.8 |
| Base saturation, % | 62 38 39 59 34 29 |
| CEC pH 7.0, cmol\(_c\) dm\(^{-3}\) | 4.2 5.0 4.1 3.9 4.3 4.0 |
| \(\text{K}^+ /\text{CEC}\), % | 2 6 5 5 6 6 |
| \(\text{Ca}^{2+} /\text{CEC}\), % | 33 20 17 34 18 13 |
| \(\text{Mg}^{2+} /\text{CEC}\), % | 25 12 17 21 9 10 |

* base saturation (BS) = 100(\(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ /\text{CEC}\) pH 7.0). ‡ cation exchange capacity (CEC) pH 7.0 = \(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{total acidity (H}^+ + \text{Al}^{3+}\)).
Tables 6–8 show the values of the F test for the chemical attributes of the soil at depths of 0.0–0.2 and 0.2–0.4 m in the CPS, NTS, and APS, respectively, in the 2017/18, 2018/19, and 2019/20 seasons.

**Table 6.** Values of the F test for changes in soil chemical attributes in the CPS at depths of 0.0–0.2 and 0.2–0.4 m in the 2017/18, 2018/19, and 2019/20 seasons.

| Attribute          | 2017/18 | 2018/19 | 2019/20 | 2017/18 | 2018/19 | 2019/20 |
|--------------------|---------|---------|---------|---------|---------|---------|
| Depths (m)         | 0.0–0.2 | 0.2–0.4 |
| P                  | 1.3232  | 0.9465  | 3.1220  | 1.2295  | 0.8594  | 0.7805  |
| S-SO₄²⁻             | 1.0730  | 25.5578 | 7.0000  | 0.2898  | 21.4809 | 131.8000 |
| OM †               | 0.2365  | 0.2104  | 1.2127  | 0.3555  | 1.2209  | 0.1648  |
| pH                 | 1.0151  | 2.0222  | 1.2127  | 0.3555  | 1.2209  | 0.1648  |
| K⁺                  | 1.9412  | 1.9282  | 1.4934  | 0.0070  | 1.2581  | 0.6129  |
| Ca²⁺               | 0.0497  * | 1.0157  | 115.8571 ** | 0.7241  | 1.6686  | 10.7692 ** |
| Mg²⁺               | 0.4688  | 8.4178 ** | 1.0730  | 0.2898  | 21.4809 | 131.8000 ** |
| H⁺ + Al³⁺           | 0.3600  | 4.4043 * | 1.8299  | 0.3750  | 1.8132  | 0.5191  |
| Al³⁺                | 0.0000  | 3.0000  |
| BS ‡                | 0.3160  | 1.7484  | 2.0514  | 0.7700  | 0.5413  | 2.3932  |
| CEC §               | 0.3163  | 0.4971  | 0.3221  | 1.5353  | 0.2269  | 1.2589  |
| K⁺/CEC              | 1.1240  | 2.1404  | 3.8082  | 0.2785  | 1.1422  | 1.4007  |
| Ca²⁺/CEC            | 0.0406  | 3.0826  | 6.0526 * | 0.3560  | 2.2604  | 4.8044 * |
| Mg²⁺/CEC            | 2.2720  | 21.6231 ** | 1.1740  | 0.8633  | 2.1860  | 5.8961 * |
| Ca²⁺/ECEC ¶         | 0.3957  | 3.7224  | 16.1574 ** | 0.7700  | 0.5413  | 2.3932  |

† organic matter. ‡ base saturation (BS) = 100(Ca²⁺ + Mg²⁺ + K⁺)/CEC pH 7.0. § cation exchange capacity (CEC pH 7.0 = Ca²⁺ + Mg²⁺ + K⁺ + total acidity (H⁺ + Al³⁺)). ¶ effective cation exchange capacity (ECEC) = Al³⁺ + Ca²⁺ + Mg²⁺ + K⁺. * Significant at the 0.05 probability level. ** Significant at the 0.01 probability level.

The Al³⁺ content was 0.0 cmol dm⁻³ in several samples collected at depths of 0.0–0.2 and 0.2–0.4 m in the 2018/19 and 2019/20 seasons in the CPS and 0.0–0.2 m in the 2019/20 season in the NTS and APS. Consequently, no statistical analysis of Al³⁺ content was performed.

**Table 7.** Values of the F test for changes in soil chemical attributes in the NTS at depths of 0.0–0.2 and 0.2–0.4 m in the 2017/18, 2018/19, and 2019/20 seasons.

| Attribute          | 2017/18 | 2018/19 | 2019/20 | 2017/18 | 2018/19 | 2019/20 |
|--------------------|---------|---------|---------|---------|---------|---------|
| Depths (m)         | 0.0–0.2 | 0.2–0.4 |
| P                  | 7.3658 ** | 1.1621 | 31.6567 ** | 8.7581 ** | 7.5869 ** | 1.4235 |
| S-SO₄²⁻             | 8.6522 ** | 1.0238 | 0.8351  | 23.4000 ** | 4.0958 ** | 30.9710 ** |
| OM †               | 1.3607  | 1.4211 | 23.2909 ** | 0.4091  | 0.5044  | 4.0000  |
| pH                 | 1.6524  | 9.5647 ** | 38.6000 ** | 0.6960  | 0.8359  | 1.8201  |
| K⁺                  | 4.9884 * | 5.9600 * | 3.8082  | 0.2785  | 1.1422  | 1.4007  |
| Ca²⁺/CEC            | 1.7542  | 15.5659 ** | 39.5879 ** | 2.3276  | 2.3775  | 4.8044 * |
| Mg²⁺               | 3.3529  | 7.4568 ** | 124.3846 ** | 3.5961  | 1.4876  | 14.4348 ** |
| H⁺ + Al³⁺           | 1.0722  | 2.336  | 43.0000 ** | 0.1142  | 0.0040  | 2.9091  |
| Al³⁺                | 3.6000  | 3.0000  |
| BS ‡                | 0.1184  | 34.8448 ** | 196.5373 ** | 1.6576  | 3.9020 * | 47.8000 ** |
| CEC §               | 1.1439  | 3.9993 * | 44.3686 ** | 0.2677  | 1.1944  | 1.1088  |
| K⁺/CEC              | 5.3352 * | 8.3639 ** | 4.3792  | 6.5985 * | 2.7297  | 3.2166  |
| Ca²⁺/CEC            | 2.9247  | 8.0877 ** | 32.2683 ** | 1.4342  | 2.5277  | 18.4197 ** |
| Mg²⁺/CEC            | 4.2055 * | 4.9776 * | 207.3810 ** | 5.3718 * | 3.0494 ** | 35.3308 ** |
| Ca²⁺/ECEC ¶         | 7.6258 ** | 0.6277  | 12.3096 ** | 5.0000 * | 5.0000 * | 5.0000 * |

† organic matter. ‡ base saturation (BS) = 100(Ca²⁺ + Mg²⁺ + K⁺)/CEC pH 7.0. § cation exchange capacity (CEC pH 7.0 = Ca²⁺ + Mg²⁺ + K⁺ + total acidity (H⁺ + Al³⁺)). ¶ effective cation exchange capacity (ECEC) = Al³⁺ + Ca²⁺ + Mg²⁺ + K⁺. * Significant at the 0.05 probability level. ** Significant at the 0.01 probability level.
Figures 5–7 show the changes in the chemical attributes of the soil at depths of 0.0–0.2 and 0.2–0.4 m in the CPS, NTS, and APS in the three seasons (2017/18, 2018/19, and 2019/20).

Table 8. Values of the F test for changes in soil chemical attributes in the APS at depths of 0.0–0.2 and 0.2–0.4 m in the 2017/18, 2018/19, and 2019/20 seasons.

| Attribute          | Seasons                                                                 |
|--------------------|-------------------------------------------------------------------------|
|                    | 2017/18       | 2018/19       | 2019/20       | 2017/18       | 2018/19       | 2019/20       |
| Depths (m)         | 0.0–0.2       | 0.2–0.4       | 0.0–0.2       | 0.2–0.4       | 0.0–0.2       | 0.2–0.4       |
| P                  | 6.1386 *      | 15.0799 **    | 8.0542 **     | 22.5918 **    | 33.0626 **    | 16.7379 **    |
| S-SO$_4^{2-}$      | 39.7059 **    | 10.1264 **    | 23.1998 **    | 164.0284 **   | 33.7664 **    | 103.8148 **   |
| OM *               | 0.4500        | 0.4648        | 1.0322        | 0.3402        | 1.3902        | 0.7850        |
| pH                 | 0.4853        | 4.9960 *      | 16.4907 **    | 0.2967        | 2.6614        | 3.2550        |
| K                  | 5.8170 *      | 2.6770        | 21.2525 **    | 1.0090        | 2.7255        | 0.3122        |
| Ca$^{2+}$          | 6.0750 *      | 6.4847 *      | 36.8554 **    | 1.1333        | 0.7850        | 1.8595        |
| Mg$^{2+}$          | 1.5106        | 12.3541 **    | 23.6917 **    | 0.6418        | 1.3349        | 3.6882        |
| H$^+$/Al$^{3+}$    | 1.4118        | 47.1176 **    | 28.8480 **    | 9.4918 **     | 30.0612 **    | 3.6882        |
| BS ‡               | 1.6183        | 20.7994 **    | 11.0210 **    | 2.3113        | 10.0000 **    | 14.8062 **    |
| CEC §              | 2.2514        | 14.9161 **    | 4.8664 *      | 1.3448        | 10.0000 **    | 14.8062 **    |
| K$^+/CEC$          | 6.7761 *      | 5.9735 *      | 85.3023 **    | 0.8427        | 3.7631        | 0.3788        |
| Ca$^{2+}$/CEC      | 5.1432 *      | 42.8508 **    | 32.6592 **    | 11.7964 **    | 36.9013 **    | 48.1899 **    |
| Mg$^{2+}$/CEC      | 14.8537 **    | 2.3988        | 6.3730 *      | 2.2952        | 2.2952        | 2.2952        |
| Ca$^{2+}$/ECEC ¶   | 4.2804 *      | 23.4731 **    | 22.3599 **    | 1.2897        | 2.2952        | 2.2952        |

† organic matter. ‡ base saturation (BS) = 100(Ca$^{2+}$ + Mg$^{2+}$ + K$^+$/CEC pH 7.0). § cation exchange capacity (CEC) pH 7.0 = Ca$^{2+}$ + Mg$^{2+}$ + K$^+$ + total acidity (H$^+$ + Al$^{3+}$). ¶ effective cation exchange capacity (ECEC) = Al$^{3+}$ + Ca$^{2+}$ + Mg$^{2+}$ + K$^+$. * Significant at the 0.05 probability level. ** Significant at the 0.01 probability level.

Figure 5. Averages and standard errors of soil characteristics in the CPS in the 2017/18 (blue), 2018/19 (red), and 2019/20 (green) seasons: (a, b) Ca$^{2+}$ content at a depth of 0.0–0.2 m (a) or 0.2–0.4 m (b); S-SO$_4^{2-}$ at a depth of 0.2–0.4 m (c).
Figure 6. Cont.
Figure 6. Averages and standard errors of soil characteristics in the NTS in the 2017/18 (blue), 2018/19 (red), and 2019/20 (green) seasons: Ca$^{2+}$ content at a depth of 0.0–0.2 m (a); S-SO$_4^{2-}$ content at a depth of 0.2–0.4 m (b); pH at a depth of 0.0–0.2 m (c); BS at a depth of 0.0–0.2 m (d); Ca$^{2+}$/CEC at a depth of 0.0–0.2 m (e).

Figure 7. Cont.
Figure 7. Cont.
Figure 7. Averages and standard errors of soil characteristics in the APS in the 2017/18 (blue), 2018/19 (red), and 2019/20 (green) seasons: (a,b) Ca$^{2+}$ content at depths of 0.0–0.2 m (a) and 0.2–0.4 m (b); Mg$^{2+}$ content at a depth of 0.0–0.2 m (c); S-$\text{SO}_4^{2-}$ at a depth of 0.0–0.2 m (d); H$^+$ + Al$^{3+}$ at a depth of 0.0–0.2 m (e); Al$^{3+}$ at a depth of 0.2–0.4 m (f); (g,h) BS at depths of 0.0–0.2 m (g) and 0.2–0.4 m (h); Ca$^{2+}$/CEC at a depth of 0.0–0.2 m; (i) Ca$^{2+}$/ECEC at a depth of 0.2–0.4 m (j).
2017/18 season

In the CPS, there were no differences (p < 0.05) in soil chemical attributes at depths of 0.0–0.2 and 0.2–0.4 m among the treatments, despite the significant values of F for Ca\(^{2+}\) content and Ca\(^{2+}\)/CEC at a depth of 0.0–0.2 m.

In the NTS, at a depth of 0.0–0.2 m, P content increased by 8.5 mg dm\(^{-3}\) in T3 compared with T1, but S-SO\(_4^{2-}\), K\(^+\), K\(^+\)/CEC, and Mg\(^{2+}\)/CEC did not differ (p < 0.05) among the treatments in which LS and GP were applied (T1, T2, and T3). At a depth of 0.2–0.4 m, P content increased by 5.25–6.25 mg dm\(^{-3}\) in T3 compared with T2 and T1; S-SO\(_4^{2-}\) content increased by 12.5–20.25 mg dm\(^{-3}\) in T1, T2, and T3 compared with the control (T4); and Ca\(^{2+}\)/ECEC increased by 11.82–15.5 percentage points in T1, T2, and T3 compared with the control. By contrast, compared with the control, K\(^+\) content decreased by 0.06–0.09 cmol\(_c\) dm\(^{-3}\) in T1, T2, and T3. K\(^+\)/CEC and Mg\(^{2+}\)/CEC did not differ (p < 0.05) among T1, T2, and T3.

In the APS, at a depth of 0.0–0.2 m, Ca\(^{2+}\)/CEC increased by 12.34 percentage points in T1 compared with the control (T4). In addition, S-SO\(_4^{2-}\) content increased by 10.5 mg dm\(^{-3}\) in T1 and by 4.0–4.5 mg dm\(^{-3}\) in T2 and T3 compared with the control; P content increased by 9.5 mg dm\(^{-3}\) in T3 compared with T2; and Ca\(^{2+}\) content increased by 0.53 cmol\(_c\) dm\(^{-3}\) in T1 compared with the control. Mg\(^{2+}\) and K\(^+\) content and Mg\(^{2+}\)/CEC did not differ (p < 0.05) among T1, T2, and T3. By contrast, compared with the control, K\(^+\)/CEC decreased by 0.89–1.05 percentage points in T1, T2, and T3. At a depth of 0.2–0.4 m, S-SO\(_4^{2-}\) content increased by 26.25 mg dm\(^{-3}\) in T1 and by 5.5–7.5 mg dm\(^{-3}\) in T2 and T3 compared with the control; P content increased by 9.75–11.5 mg dm\(^{-3}\) in T1 and T3 compared with T2; Ca\(^{2+}\)/CEC increased by 8.42 and 7.24 percentage points in T1 and T2, respectively, compared with the control; Mg\(^{2+}\)/CEC increased by 2.65 percentage points in T2 compared with T3; and Ca\(^{2+}\)/ECEC increased by 16.88 percentage points in T1 compared with the control.

2018/19 season

In the CPS, at a depth of 0.0–0.2 m, S-SO\(_4^{2-}\) content increased by 10.67 mg dm\(^{-3}\) in T1 compared with T2 and T3; Mg\(^{2+}\) content increased by 0.78 cmol\(_c\) dm\(^{-3}\) in T3 compared with T1; and Mg\(^{2+}\)/CEC increased by 9.75 percentage points in T2 and 12.25 percentage points in T3 compared with T1. Despite a significant F value, total acidity did not differ (p < 0.05) among the treatments. At a depth of 0.2–0.4 m, S-SO\(_4^{2-}\) content increased by 8.67 and 7.5 mg dm\(^{-3}\) in T3 compared with T1 and T2, respectively.

In the NTS, at a depth of 0.0–0.2 m, pH increased by 0.4–0.58, Ca\(^{2+}\) content increased by 0.98–1.33 cmol\(_c\) dm\(^{-3}\), BS increased by 14.83–21.33 percentage points, and Ca\(^{2+}\)/CEC increased by 12.0–16.0 percentage points in T1, T2, and T3 compared with the control. Mg\(^{2+}\) content increased by 0.51 cmol\(_c\) dm\(^{-3}\) in T1 compared with T3, and Al\(^{3+}\) content and Mg\(^{2+}\)/CEC did not differ (p < 0.05) among T1, T2, and T3. By contrast, K\(^+\) content decreased by 0.18–0.2 cmol\(_c\) dm\(^{-3}\) in T1, T2, and T3 compared with the control. CEC increased by 1.27 cmol\(_c\) dm\(^{-3}\) in T1 compared with the control, and K\(^+\)/CEC decreased by 3.27–3.95 percentage points. At a depth of 0.2–0.4 m, S-SO\(_4^{2-}\) content increased by 9.25 mg dm\(^{-3}\) in T1 compared with the control; P content increased by 8.0 mg dm\(^{-3}\) in T2 compared with T1; Al\(^{3+}\) decreased by 0.23–0.34 cmol\(_c\) dm\(^{-3}\) in T1 and T3 compared with T2; and Mg\(^{2+}\)/CEC increased by 0.4–0.5 cmol\(_c\) dm\(^{-3}\) percentage points in T3 and T1 compared with T2. Despite a significant F value, BS did not differ (p < 0.05) among the treatments.

In the APS, at a depth of 0.0–0.2 m, Ca\(^{2+}\) content increased by 1.16–1.46 cmol\(_c\) dm\(^{-3}\), total acidity decreased by 0.65–0.85 cmol\(_c\) dm\(^{-3}\), and Al\(^{3+}\) decreased by 0.18–0.25 cmol\(_c\) dm\(^{-3}\) in T1, T2, and T3 compared with the control. In addition, P content was 17.0, 10.5, and 8.5 mg dm\(^{-3}\) higher in T2, T1, and T3, respectively, than in the control, and BS increased by 27.0, 22.5, and 13.0 percentage points, respectively. Ca\(^{2+}\)/ECEC increased by 25.75, 24.5, and 17.25 percentage points in T1, T2, and T3, respectively, compared with the control. Compared with the control, S-SO\(_4^{2-}\) content increased by 1.92 and 3.25 mg dm\(^{-3}\) in T1 and T3, respectively; pH increased by 0.93, Mg\(^{2+}\) content increased by 0.73 cmol\(_c\) dm\(^{-3}\), and CEC increased by 8.42 and 7.24 percentage points in T1 compared with T3.
increased by 1.9 percentage points in T2. K+/CEC did not differ (p < 0.05) among T1, T2 and T3. At a depth of 0.2–0.4 m, S-SO$_4^{2-}$ content increased by 6.5–9.5 mg dm$^{-3}$ in T1, T2, and T3 compared with the control; Ca$^{2+}$ content increased by 0.58–0.8 cmol$_c$ dm$^{-3}$, Al$^{3+}$ decreased by 0.3–0.38 cmol$_c$ dm$^{-3}$, BS increased by 9.5–15.5 percentage points, Ca$^{2+}$/CEC increased by 14.75, 19.25, and 15.25 percentage points, respectively, and Ca$^{2+}$/ECEC increased by 23.96–26.18 percentage points.

2019/20 season

In the CPS, at a depth of 0.0–0.2 m, S-SO$_4^{2-}$ content increased by 2.67 mg dm$^{-3}$ in T3 compared with the control; Ca$^{2+}$ content increased by 0.67 cmol$_c$ dm$^{-3}$ in T2 and by 0.27–0.3 cmol$_c$ dm$^{-3}$ in T1 and T3 compared with the control; and Ca$^{2+}$/CEC increased by 17.33 percentage points in T2 compared with the control. At a depth of 0.2–0.4 m, Ca$^{2+}$ content increased by 0.3–0.43 cmol$_c$ dm$^{-3}$ and Ca$^{2+}$/ECEC increased by 10.75–20.54 percentage points in T1, T2, and T3 compared with the control. In addition, S-SO$_4^{2-}$ content increased by 3.66 mg dm$^{-3}$ in T3 and by 1.33 mg dm$^{-3}$ in T1 and T2 compared with the control, and Mg$^{2+}$ content increased by 0.3 cmol$_c$ dm$^{-3}$ in T1 compared with T3. Ca$^{2+}$/CEC and Mg$^{2+}$/CEC did not differ (p < 0.05) among T1, T2, and T3.

In the NTS, at a depth of 0.0–0.2 m, pH increased by 1.2–1.5 in T1, T2, and T3 compared with the control; Ca$^{2+}$ content increased by 1.65–2.05 cmol$_c$ dm$^{-3}$, total acidity decreased by 0.1–1.3 cmol$_c$ dm$^{-3}$, BS increased by 35.33–42.0 percentage points, CEC increased by 17.57–22.4 percentage points, and Ca$^{2+}$/CEC increased by 19.0–26.67 percentage points. In addition, Mg$^{2+}$ content increased by 0.15, 0.13, and 0.11 cmol$_c$ dm$^{-3}$ in T1, T2, and T3, respectively, compared with the control, and Mg$^{2+}$/CEC increased by 19.0–21.0 percentage points in T1 and T2 and 15.5 percentage points in T3. OM content increased by 6.5 g dm$^{-3}$ in T2 compared with the control. Despite a significant F value, P content did not differ (p < 0.05) among the treatments. At a depth of 0.2–0.4 m, S-SO$_4^{2-}$ content increased by 3.67 and 9.17 mg dm$^{-3}$ in T2 and T3, and Ca$^{2+}$/ECEC increased by 6.5–11.33 percentage points in T1, T2, and T3 compared with the control. In addition, compared with the control, BS increased by 16.67 percentage points in T2 and 8.0–9.0 percentage points in T1 and T3; Mg$^{2+}$/ECEC increased by 3.5–7.67 percentage points in T1 and T2; Ca$^{2+}$ content increased by 0.6 cmol$_c$ dm$^{-3}$, Mg$^{2+}$ content increased by 0.4 cmol$_c$ dm$^{-3}$, and Al$^{3+}$ content decreased by 0.2 cmol$_c$ dm$^{-3}$ in T2.

In the APS, at a depth of 0.0–0.2 m, pH increased by 1.1–1.33, Ca$^{2+}$ content increased by 1.58–1.9 cmol$_c$ dm$^{-3}$, total acidity decreased by 1.13–1.33 cmol$_c$ dm$^{-3}$, BS increased by 32.5–36.5 percentage points, and Ca$^{2+}$/CEC increased by 27.75–28.5 percentage points in T1, T2, and T3 compared with the control. In addition, compared with the control, P content increased by 4.75 mg dm$^{-3}$ in T2; S-SO$_4^{2-}$ content increased by 2.33 and 4.58 mg dm$^{-3}$ in T1 and T2, and Ca$^{2+}$/CEC increased by 0.9, 0.78, and 0.5 in T1, T3, and T2, respectively; Mg$^{2+}$ content increased by 0.15, 0.13, and 0.11 cmol$_c$ dm$^{-3}$ in T1, T2, and T3 compared with the control. In addition, compared with the control, BS increased by 16.67 percentage points in T2 and 8.0–9.0 percentage points in T1 and T3; Mg$^{2+}$/ECEC increased by 3.5–7.67 percentage points in T1 and T2; Ca$^{2+}$ content increased by 0.6 cmol$_c$ dm$^{-3}$, Mg$^{2+}$ content increased by 0.4 cmol$_c$ dm$^{-3}$, and Al$^{3+}$ content decreased by 0.2 cmol$_c$ dm$^{-3}$ in T2.

Effects of the treatments on S-SO$_4^{2-}$ content

LS and GP application increased S-SO$_4^{2-}$ content at depths of 0.0–0.2 m (T1 and T2 in the NTS and T1, T2, and T3 in the APS in the 2017/18 season; T1 in the CPS and T1 and T3 in the APS in the 2018/19 season; and T3 in the CPS and T1 and T2 in the APS in the 2019/20 season) and 0.2–0.4 m (T1, T2, and T3 in the NTS and APS in the 2017/18 and 2018/19 seasons and T1, T2, and T3 in the CPS, NTS, and APS in the 2019/20 season).
**Effects of the treatments on pH**

The application of LS and GP increased pH at a depth of 0.0–0.2 m (T1, T2, and T3 in the NTS and T2 in the APS in the 2018/19 season and T1, T2, and T3 in the NTS and APS in the 2019/20 season).

**Effects of the treatments on Ca\(^{2+}\) content**

LS and GP application increased Ca\(^{2+}\) content at depths of 0.0–0.2 m (T1 in the APS in the 2017/18 season; T1, T2, and T3 in the NTS and APS in the 2018/19 season; and T1, T2 and T3 in the CPS, NTS, and APS in the 2019/20 season) and 0.2–0.4 m (T1, T2, and T3 in the APS in the 2018/19 season and T1, T2, and T3 in the CPS and APS and T2 in the NTS in the 2019/20 season).

**Effects of the treatments on Mg\(^{2+}\) content**

At a depth of 0.0–0.2 m, LS and GP application increased Mg\(^{2+}\) content in T1 in the NTS and T2 in the APS in the 2018/19 season and in T1, T2, and T3 in the NTS and APS in the 2019/20 season. At a depth of 0.2–0.4 m, LS and GP application increased Mg\(^{2+}\) content in T2 in the NTS in the 2019/20 season.

**Effects of the treatments on Al\(^{3+}\) content**

LS and GP application decreased Al\(^{3+}\) content at depths of 0.0–0.2 m (T1 and T2 in the NTS and T1, T2, and T3 in the APS in the 2018/19 season) and 0.2–0.4 m (T1 and T3 in the NTS and T1, T2, and T3 in the APS in the 2018/19 season and T2 in the NTS and T1, T2, and T3 in the APS in the 2019/20 season).

**Effects of the treatments on K\(^{+}\) content**

The application of LS and GP decreased K\(^{+}\) content at a depth of 0.0–0.2 m in T1, T2, and T3 in the NTS in the 2018/19 season and the APS in the 2019/20 season. At a depth of 0.2–0.4 m, LS and GP decreased K\(^{+}\) content in T1, T2, and T3 in the NTS in the 2017/18 season.

**Effects of the treatments on total acidity**

LS and GP application decreased the total acidity at a depth of 0.0–0.2 m in T1, T2, and T3 in the APS in the 2018/19 season and in T1, T2, and T3 in the NTS and APS in the 2019/20 season.

**Effects of the treatments on BS**

LS and GP increased BS at depths of 0.0–0.2 m (T1, T2, and T3 in the NTS and APS in the 2018/19 and 2019/20 seasons) and 0.2–0.4 m (T1, T2, and T3 in the APS in the 2018/19 season and T1, T2, and T3 in the NTS and APS in the 2019/20 season).

**Effects of the treatments on CEC**

The application of LS and GP increased CEC at a depth of 0.0–0.2 m in T1 in the NTS and T2 in the APS in the 2018/19 season and in T1, T2, and T3 in the NTS and T1 in the APS in the 2019/20 season.

**Effects of the treatments on Ca\(^{2+}\)/CEC**

The application of LS and GP increased Ca\(^{2+}\)/CEC at a depth of 0.0–0.2 m (T1, T2, and T3 in the NTS and APS in the 2018/19 and 2019/20 seasons and T2 in the CPS in the 2019/20 season).

**Effects of the treatments on Mg\(^{2+}\)/CEC**

LS and GP increased Mg\(^{2+}\)/CEC at depths of 0.0–0.2 m (T1 in the NTS in the 2018/19 season and T1, T2, and T3 in the NTS and T1 and T3 in the APS in the 2019/20 season) and 0.2–0.4 m (T1 and T2 in the NTS in the 2019/20 season).
Effects of the treatments on $K^+$/CEC

The application of LS and GP decreased $K^+$/CEC at a depth of 0.0–0.2 m in T1, T2, and T3 in the NTS in the 2018/19 season and in the APS in the 2019/20 season.

Effects of the treatments on $Ca^{2+}$/ECEC

The application of LS and GP increased $Ca^{2+}$/ECEC content at a depth of 0.2–0.4 m (T1, T2, and T3 in the NTS and APS in the 2017/18 season; T1, T2, and T3 in the APS in the 2019/20 season; and T1, T2, and T3 in the CPS and APS in the 2019/20 season).

4. Discussion

Effects of the treatments on S-SO$_4^{2-}$ content

The increases in S-SO$_4^{2-}$ content illustrate the importance of combining GP amendment with LS application to improve S-SO$_4^{2-}$ content at depths of a 0.0–0.4 m layer in CPSs, NTSs, and APSs. GP was previously reported to improve the availability of exchangeable SO$_4^{2-}$ in the entire soil profile [24,37,38]. In addition, several studies have found that the tandem application of LS and GP provides nutrients and is an alternative strategy for improving the root environment in the early years of cultivation, when the effects of LS have not yet reached the subsurface layers due to its poor solubility and mobility [26,39].

Effects of the treatments on pH

Combining LS and GP provided better conditions for LS to act on the soil solution and increase pH [40]. Liming is the most efficient methodology for increasing pH [29], particularly in the surface layer (depth of 0.0–0.1 m) [41,42]. GP indirectly corrects soil pH in deeper layers in the soil because it contains SO$_4^{2-}$, which displaces OH$^-$ from soil colloids into solution [26].

Effects of the treatments on $Ca^{2+}$ content, $Ca^{2+}$/CEC, and $Ca^{2+}$/ECEC

Increasing $Ca^{2+}$ content at soil depths of 0.0–0.2 m and 0.2–0.4 m is important due to the role of $Ca^{2+}$ in root growth [13], including cell division [43], and because plants absorb $Ca^{2+}$ almost exclusively via the roots [44]. $Ca^{2+}$ absorbed by superficial roots cannot meet the needs of deep roots located in environments with poor levels of this nutrient [45]. The continuity of channels in NTSs [46] promotes the descent of $Ca^{2+}$ [47], and no soil turning was performed in the crop systems in the present study. LS application has previously been reported to increase $Ca^{2+}$ content [45,48], as has GP application [24,29,47,49,50]. Moreover, previous studies have shown that combined application of LS and GP can increase $Ca^{2+}$ content [40,51,52]. The combined application of LS and GP enhances the descent of $Ca^{2+}$ and Mg$^{2+}$, which are added by liming, in the soil profile [53,54] via the formation of ionic pairs with SO$_4^{2-}$ [55] dissociated from GP. This ion descends easily in the soil profile, carrying K$^+$, Mg$^{2+}$, and, mainly, $Ca^{2+}$ along with it [47,56,57]. Increasing and redistributing $Ca^{2+}$, Mg$^{2+}$, and K$^+$ at greater depths in NTSs is important for alleviating the chemical impairment of root development and for promoting water deficit resistance in maize and soybean crops [42]. In addition, the presence of grazing cattle in the CPS and APS increased the effects of surface application of LS at greater depths by promoting $Ca^{2+}$ and Mg$^{2+}$ leaching in the soil profile through the formation of low-molecular-weight organic acids. These organic acids are released during the decomposition of animal waste, mainly feces, or are exuded by pasture plants during grazing [58]. Grazing of palisade grass leads to a higher regrowth rate, as this grass is characterized by a voluminous fasciculated root system. The greater regrowth of tillers after grazing increases the volume of pores in the soil, allowing the movement of cations within the soil profile.

Effects of the treatments on Mg$^{2+}$ content and Mg$^{2+}$/CEC

Mg$^{2+}$ and $Ca^{2+}$ compete for negative charges in soil, and $Ca^{2+}$ is preferred in exchange sites [59]. As LS contains a high percentage of Ca (31% CaO), it provides a high $Ca^{2+}$ concentration in the soil, which promotes the displacement of Mg$^{2+}$ from exchange sites.
Mg\textsuperscript{2+} is less strongly retained due to its greater hydrated radius and lower electronegativity. This displacement allows greater movement of Mg\textsuperscript{2+} within the profile and formation of the MgSO\textsubscript{4}\textsuperscript{0} ion pair \[24,60\]. Movement of Mg\textsuperscript{2+} within the soil profile is also promoted by water-soluble compounds originating from the residues of previous crops \[61\]. Compared with the initial content of Mg\textsuperscript{2+} in the soil, LS and GP increased Mg\textsuperscript{2+} content at a depth of 0.0–0.2 m by 1.0 and 0.53 cmol\textsubscript{c} dm\textsuperscript{−3} in the NTS and APS, respectively. These results are consistent with previous studies that have found increases in Mg\textsuperscript{2+} content with the application of GP \[42\]. However, another study found that GP improved soil fertility in the soil profile but that Mg\textsuperscript{2+} migrated down over a period of three years, regardless of application \[38\]. GP application reduces Mg\textsuperscript{2+} in the surface layers, leading to accumulation in the subsurface layers \[26\]. Thus, the methodology used in this study to apply LP and GP promotes a more uniform distribution of Mg\textsuperscript{2+} along the soil profile.

**Effects of the treatments on Al\textsuperscript{3+} content**

Once in the soil solution, the ion Ca\textsuperscript{2+} can react in the soil exchange complex, shifting Al\textsuperscript{3+}, K\textsuperscript{+}, and Mg\textsuperscript{2+} to the soil solution. In turn, these ions can react with SO\textsubscript{4}\textsuperscript{2−} to form AlSO\textsubscript{4}\textsuperscript{+} (which is less toxic to plants) and the neutral pairs K\textsubscript{2}SO\textsubscript{4}, MgSO\textsubscript{4}, and CaSO\textsubscript{4}, which have great mobility in the soil profile \[62\]. The dissociation of GP releases Ca\textsuperscript{2+}, which binds to organic carbon, making SO\textsubscript{4}\textsuperscript{2−} available in the soil solution to replace OH\textsuperscript{−}. These chemical changes in the soil solution also interfere with the increase in pH and reduction of acidity by Al\textsuperscript{3+} \[22\].

**Effects of the treatments on K\textsuperscript{+} content**

The decreases in K\textsuperscript{+} content and K\textsuperscript{+}/CEC at a depth of 0.0–0.2 m in the NTS and APS due to LS and GP application are related to K\textsuperscript{+} lixiviation within the soil profile, which is promoted by GP \[51\]. By contrast, GP application did not promote K\textsuperscript{+} lixiviation in the CPS, corroborating previous findings \[45,47,52,63\]. The absence of an effect of GP application on K\textsuperscript{+} lixiviation can be explained by the low formation of the K\textsubscript{2}SO\textsubscript{4} ionic pair (0.2% of total solubility) \[64\].

**Effects of the treatments on total acidity**

The reduction in total acidity in the NTS and APS may have been due to the movement of fine particles of LS through the continuous pores within the soil profile (which are the result of root system decomposition) \[10\] and the formation of ionic pairs between sulfate or nitrate and Ca\textsuperscript{2+} and Mg\textsuperscript{2+} from LS \[65\]. Decreasing total acidity is important to avoid restrictions on the expansion of the root system, which would impair access to water and nutrients found in the deepest layers of the soil \[32\]. The reduction in total acidity may also be related to the formation of complexes of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} with soluble organic compounds released by the decomposition of plant biomass deposited on the soil surface (carboxylic and phenolic radicals) \[66,67\]. In the present study, all cultivations were carried out under no-till on the residues of the previous crops, as the NTS was established in the 2009/10 season and the APS was established in the 2011/12 season.

**Effects of the treatments on BS**

The increases in BS and CEC in the NTS and APS were promoted by the supply of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} by LS, which contained 31% CaO and 21% MgO, and GP, which contained 17% CaO, and by the movement of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} in the soil profile. Previous studies have reported that combining GP with LS enhances the vertical movement of Ca\textsuperscript{2+} in the soil profile \[40,54,68,69\]. GP application has also been shown to increase BS \[45,49,50\]. In addition, changes in BS are always greatest after the grazing season (winter) \[70\]. However, this improvement in BS is temporary because the decomposition of plant residues increases soil acidity, which was minimized in the present study by the use of three applications of LS \[71\].
5. Conclusions

In the present study, three methodologies for the surface application of LS and GP in CP5s, NTSs, and APSs were evaluated. Surface application of LS (ensuring that Ca$^{2+}$ occupies 70%, 60%, or 50% of CEC at a depth of 0.0–0.2 m) and GP (ensuring that Ca$^{2+}$ occupies 60%, 50%, or 40% of ECEC at a depth of 0.2–0.4 m) corrected surface and subsurface acidity and improved soil chemical fertility. Ca$^{2+}$ content increased in the CPS, NTS, and APS at a depth of 0.0–0.2 m and in the CPS and APS at a depth of 0.2–0.4 m; S-SO$_4^{2–}$ content and Ca$^{2+}$/ECEC increased in the CPS, NTS, and APS at a depth of 0.2–0.4 m; BS increased and Al$^{3+}$ content decreased in the NTS and APS at depths of 0.0–0.2 m and 0.2–0.4 m; and pH, Mg$^{2+}$ content, CEC, Ca$^{2+}$/CEC, and Mg$^{2+}$/CEC increased and total acidity decreased in the NTS and APS at a depth of 0.0–0.2 m.

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