



Limestone Reapplication and Tillage System Influence Non-Exchangeable Aluminum in Subtropical Oxisol

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Abstract

Liming reduces aluminum (Al) toxicity in acidic soils, but its effects on non-exchangeable aluminum (Al_{ne}) remain unclear. This study evaluated Al fractions and their relationships with soil chemical properties, soybean (*Glycine max* L. Merr.) and wheat (*Triticum aestivum* L.) yields. The experiment was established in July 2023 in Paraná State, Brazil, on an Oxisol, using a randomized block design in a 4×2 factorial arrangement. Treatments consisted of four limestone reapplication rates (0, 1.0, 1.3, and 1.6 times the rate required to reach 70% base saturation) and two application methods (surface application or incorporation into the 0–0.20 m layer). Nine months after reapplication, soil samples from the 0–0.05, 0.05–0.10, and 0.10–0.20 m layers were analyzed. Liming reduced exchangeable aluminum (Al^{3+}) and increased soil organic matter (SOM) in all layers. Non-exchangeable aluminum decreased only in the 0–0.05 m layer. Conventional tillage reduced SOM and increased Al_{ne} by 18% in the surface layer. Non-exchangeable aluminum was positively correlated with potential acidity (H+Al) and negatively correlated with soil pH and base saturation. Wheat yield was more negatively associated with Al_{ne} than soybean yield. Non-exchangeable aluminum correction remained limited to the surface layer regardless of management. Soil disturbance increased Al extractability, indicating greater exposure of reactive Al forms under conventional tillage. Surface liming and no-till favored SOM stability and moderated Al dynamics in subtropical Oxisols.

Keywords Aluminum fractionation · Conventional tillage · No-till · Potential acidity · Soil organic matter

1 Introduction

Soil acidity is one of the main chemical factors limiting the development of agricultural crops (Fageria and Nascente 2014). In acidic soils, pH values below 5.5 favor the destabilization of Al–O bonds, increasing Al^{3+} solubility and promoting hydrolysis reactions that release additional H^+ , thereby intensifying soil acidity (Sposito 2008; Bissani and Ernani 2023). Liming is widely adopted to neutralize acidity and reduce exchangeable Al (Al^{3+}) toxicity. However, most liming studies focus primarily on Al^{3+} extracted with 1.0 mol L^{-1} KCl, while less attention has been given to non-exchangeable Al fraction (Al_{ne}) (Cunha et al. 2018; Rodrigues et al. 2019; Adaime Gabriel et al. 2024). Soil acidity can be classified into active (H^+ ions in the soil solution) and potential forms (Grando et al. 2025). Potential acidity (H+Al) includes exchangeable Al and H^+ adsorbed to negatively charged sites, as well as non-exchangeable forms associated with mineral and organic colloids (Bissani

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and Ernani 2023). A substantial proportion of potential acidity may be linked to Al_{ne} , which has been reported to represent between 29% and 56% of $H+Al$ (Zambrosi et al. 2007; Campos et al. 2022). Despite this contribution, the dynamics of Al_{ne} under different soil management and liming strategies remain poorly understood.

Soil organic matter plays a central role in regulating Al behavior (Martins et al. 2020; Büyükkeskin et al. 2015). Functional groups such as carboxylic and phenolic sites can form stable complexes with Al, reducing its activity in soil solution (Schnitzer 1978; Martins et al. 2020). Part of this Al is weakly to moderately bonded and can be operationally extracted using $0.5 \text{ mol L}^{-1} \text{ CuCl}_2$, which displaces Al associated with organic functional groups (Juo and Kamprath 1979; Zambrosi et al. 2007). Thus, Al_{ne} is commonly estimated as the difference between Al extracted by CuCl_2 and KCl, representing a potentially reactive fraction associated mainly with SOM.

In no-till, limestone is typically applied to the soil surface (Besen et al. 2021; Minato et al. 2023). However, subsurface acidity may persist due to limited limestone mobility and soil buffering capacity (Brignoli et al. 2024; Li et al. 2019; Rheinheimer et al. 2018). Conventional tillage can enhance limestone redistribution along the profile, potentially improving acidity correction at depth (Auler et al. 2017). Nevertheless, soil mobilization disrupts aggregates and accelerates SOM decomposition, leading to losses of organic carbon (Six et al. 2004; Nguyen et al. 2022). Because Al can be released during SOM decomposition (Bloom et al. 1979), the oxidative degradation of organic ligands promoted by soil disturbance may destabilize Al–organic complexes. The rupture of these bonds can mobilize Al into the soil solution, increasing the concentration of reactive Al forms that may impair root growth (Sposito 2008; Alves et al. 2025).

Although the effects of liming and tillage on Al^{3+} are well documented (Auler et al. 2019; Bellinaso et al. 2021; Brignoli et al. 2024; Delfim et al. 2025), little is known about how limestone reapplication and soil mobilization affect Al_{ne} and its relationship with soil chemical properties and crop performance (Martins et al. 2020; Campos et al. 2022). Understanding these interactions is essential for improving liming strategies. We hypothesized that limestone reapplication reduces the amount of Al_{ne} regardless of management system, and tilling the soil increases Al_{ne} release, negatively impacting soybean (*Glycine max* L. Merr) and wheat (*Triticum aestivum* L.) yields. Therefore, this study aimed to evaluate soil Al fractions under different limestone reapplication rates and management systems, and to assess their relationships with soil chemical properties and crop yield.

2 Materials and Methods

2.1 Site Description, Experimental Design, and Treatments

The experiment was installed at the experimental farm of the COAMO agricultural cooperative in Campo Mourão, Paraná State, southern Brazil ($24^{\circ}02'38''\text{S}$ $52^{\circ}22'40''\text{W}$, 630 m a.s.l.). According to the Köppen classification, the climate is humid subtropical (Cfa), with an average annual rainfall of 1700 mm and an average temperature of 21°C . The soil at the experimental site is an Oxisol (Soil Survey Staff 2014), with 740 g kg^{-1} clay and very clayey texture (Lemos and Santos 1996). Its mineralogical composition is dominated by kaolinite and iron and aluminum oxides (Costa 1996). The total rainfall and average temperature during the experimental period (July 2023 – September 2024) were 1202 mm and 23°C , respectively.

From 1975 to 2008, the area was cultivated under no-till with soybean and maize (*Zea mays* L.) in the summer and wheat, white oat (*Avena sativa*), and second-crop maize in autumn/winter. From 2008 onward, the crop sequence was as follows: oat (2008), maize (2008/2009), oat (2009), soybean (2009/2010), wheat (2010), soybean (2011/2012), and maize (2012).

In 2012, an experiment described by Besen et al. (2021) and Brignoli et al. (2025) was performed to evaluate several soil chemical properties and crop yield up to the 2022/2023 soybean season under limestone (incorporated or surface-applied) and gypsum (surface-applied) management in a no-tillage system. Soil tillage occurred only when limestone was incorporated. Treatments consisted of limestone rates applied to achieve BS of 60%, 70%, and 90%, in addition to two gypsum treatments, one at the recommended rate (3700 kg ha^{-1}) and the other at twice the recommended rate (7400 kg ha^{-1}), according to Sousa et al. (2005).

From 2023 onward, a new treatment design was adopted: gypsum treatments were removed, and a limestone treatment was introduced. The current study reports the results of the experiment conducted from 2023. The experiment was established in July 2023 using a randomized complete block design with a 4×2 factorial scheme and four replications per treatment. The soil chemical properties (0–0.20 m) prior to the beginning of the experiment are presented in Table 1. Treatments included four limestone rates: 0 (unlimed control) and rates calculated to raise theoretical BS to 70%, 90%, and 110%. The rate required to reach 70% BS was considered the recommended rate ($1\times$), according to SBCS/NEPAR (2019). The higher rates were calculated proportionally as $90/70$ ($1.3\times$) and $110/70$ ($1.6\times$) of the recommended rate, resulting in increasing limestone rates.

Table 1 Initial soil chemical properties (0–0.20 m layer) in July 2023 and corresponding limestone rates (LR) used in the reapplication

Treatment	pH CaCl ₂	Al ³⁺ cmol _c dm ⁻³	Ca ²⁺	Mg ²⁺	K ⁺	CEC _{pH7.0}	BS	Al saturation	LR
							%		Mg ha ⁻¹
NT ₀	5.0	0.10	4.42	1.02	0.39	11.35	51	1.25	-
CT ₀	4.7	0.00	3.79	0.78	0.40	9.84	51	0.00	-
NT ₁	5.3	0.00	4.93	1.14	0.47	11.59	57	0.00	1.86
CT ₁	4.9	0.04	3.74	1.20	0.36	10.52	51	0.75	2.47
NT _{1.3}	4.9	0.01	4.81	1.07	0.51	11.27	57	0.25	4.59
CT _{1.3}	4.9	0.21	3.29	1.03	0.34	10.01	47	2.25	5.31
NT _{1.6}	5.3	0.01	4.61	1.43	0.40	11.07	58	0.25	7.11
CT _{1.6}	5.2	0.00	4.48	1.43	0.34	11.20	56	0.00	7.47

CEC_{pH7.0} cation-exchange capacity at pH 7.0, BS base saturation, NT no till, CT conventional till. The subscript values 0, 1, 1.3, and 1.6 represent fractions of the recommended lime rate to achieve 70% BS

Limestone rates (LR) were calculated using the BS method (SBCS/NEPAR 2019), which considers cation-exchange capacity at pH 7.0 ($\text{CEC}_{\text{pH7.0}} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{H} + \text{Al}$) and BS ($\text{BS} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+) / \text{CEC}_{\text{pH7.0}} \times 100$). The LR, expressed in Mg ha^{-1} , was determined using the equation: $\text{LR} = (\text{BS}_2 - \text{BS}_1) \times \text{CEC}_{\text{pH7.0}} / \text{RNV}$, where RNV is the relative neutralizing value of the limestone product, BS_2 is the target BS of each treatment (70%, 90%, or 110%), and BS_1 is the initial soil BS. The rates corresponding to each treatment are presented in Table 1. The applied dolomitic limestone had an RNV of 81%, containing 26% CaO and 22% MgO. Limestone was applied manually and, in treatments with incorporation management, subsequently incorporated into the 0–0.20 m soil layer using a moldboard plow followed by a harrower (20 discs, 0.51 m in diameter). Each experimental unit measured 84 m² (12 × 7 m).

2.2 Crop Management

White oat, soybean, and wheat were grown during the experimental period using the cultivars and fertilizers listed in Table 2. Oat seeds were sown on July 4, 2023, and desiccated on October 5, 2023, followed by roller crimper management, with residues left in the field as ground cover. Soybean crops were sown on November 16, 2023, and harvested on March 25, 2024. Wheat was sown on June 5, 2024, and harvested on September 23, 2024. Pest and disease management followed the technical recommendations for the region. Grain moisture was corrected to 130 g kg⁻¹ and crop yield converted to kg ha⁻¹.

2.3 Soil Sampling and Chemical Analysis

Soil samples were collected at 9 months after limestone application (April 2024). Collection was carried out using a cutting shovel at depths of 0–0.05, 0.05–0.10, and 0.10–0.20 m in the inter-row region of the last crop (soybean). Two samples were collected from each experimental unit and combined to obtain a composite sample, as described by Besen et al. (2021). The samples were dried in a forced-air oven at 45 °C and sieved through 2 mm (10-mesh) sieves.

Soil pH was determined in 0.01 mol L⁻¹ CaCl₂ solution using a soil/solution ratio of 1:2.5. pH-SMP was determined based on the equilibrium pH between the soil and a solution containing K₂CrO₄, Ca(CH₃COO)₂, CaCl₂·2H₂O, triethanolamine, and 4-nitrophenol, adjusted to pH 7.5 (Shoemaker et al. 1961). Potential acidity was estimated from pH-SMP using the equation $\ln(\text{H} + \text{Al}) = 6.068 - 0.744 \times \text{pH-SMP}$, as described by Pavan et al. (1992). Potassium (K⁺) was extracted with Mehlich-1 solution (0.0125 mol L⁻¹ H₂SO₄ + 0.05 mol L⁻¹ HCl) using a soil/solution volumetric ratio of 1:10. Exchangeable calcium, Mg²⁺, and Al³⁺ contents, used for BS calculation, were extracted using 1.0 mol L⁻¹ KCl. Exchangeable potassium was quantified by flame photometry, Ca²⁺ and Mg²⁺ by atomic absorption spectrometry, and Al³⁺ by titration with 0.025 mol L⁻¹ NaOH. Soil organic carbon was determined according to Quaggio and Raij (1979), through colorimetric measurement of the green color produced by Cr (III) ions reduced by organic carbon, extracted using a soil/solution volumetric ratio of 1:10. The extraction solution consisted of 0.667 mol L⁻¹

Table 2 Agronomic information and rates of N, P, and K in seeding and broadcast fertilization for oat, soybean, and wheat crops in Campo Mourão, Paraná State, Brazil

Crop (season)	Cultivar	Seeding fertilization (kg ha ⁻¹)			Broadcast fertilization (kg ha ⁻¹)		
		N	P	K	Stage	N	K
Oat (2023)	IPR Andrômeda	24	16	20	Tillering	50	-
Soybean (2023/2024)	M-SOY 6101	6	18	35	-	-	-
Wheat (2024)	TBIO Astro	30	20	25	Tillering	50	-

$\text{Na}_2\text{Cr}_2\text{O}_7$ and $5.0 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. Organic carbon content was converted to SOM using a factor of 1.724, based on the assumption that SOM contains approximately 58% C. Soil organic matter was expressed as a percentage, according to SBCS/NEPAR (2019).

2.4 Aluminum Fractionation

Exchangeable and non-exchangeable Al were extracted simultaneously with $0.5 \text{ mol L}^{-1} \text{CuCl}_2$ solution, whereas Al^{3+} was selectively extracted with $1.0 \text{ mol L}^{-1} \text{KCl}$ solution. The difference between the CuCl_2 -extracted fraction and the Al^{3+} fraction was treated as the Al fraction complexed to organic matter (Al_{ne}). Analytical procedures followed the method of Juo and Kamprath (1979), with adaptations by Zambrosi et al. (2007).

A 2.0 g aliquot of soil was used for both extractions. For determination of the CuCl_2 -extracted fraction, soil samples were stirred in polyethylene tubes containing 20 mL of $0.5 \text{ mol L}^{-1} \text{CuCl}_2$ for 1 h at 150 rpm. The suspension was centrifuged for 5 min at 2000 rpm ($850 \times g$) and filtered through a $2 \mu\text{m}$ quantitative filter. Aluminum- CuCl_2 contents were determined by atomic emission spectroscopy using a microwave plasma atomic emission spectrometer (Agilent MP-AES 4200) at 396.15 nm. Exchangeable Al contents were determined by titration with $0.025 \text{ mol L}^{-1} \text{NaOH}$ using phenolphthalein as indicator.

2.5 Statistical Analysis

Data were tested for normality and homoscedasticity using the Shapiro–Wilk and Bartlett tests, respectively. Variables that did not exhibit a normal distribution were square-root-transformed according to Zimmermann (2014) and tested again for normality. Subsequently, means were subjected to analysis of variance (ANOVA) using the *F*-test. When significant, means were compared between tillage management systems by the *t*-test (minimum significant difference), and polynomial regression models were constructed to analyze limestone rates. Each soil layer was analyzed individually. Relationships between Al_{ne} content and soil chemical properties in each layer were assessed by regression analysis. The best-fitting model was selected based on the Akaike information criterion and the coefficient of determination. Pearson's correlation analysis was performed between soil chemical properties and soybean and wheat yields. Statistical significance was set at $p < 0.05$ for all analyses.

3 Results

3.1 Effects of Management System and Liming on Al Fractions and SOM

No interaction was observed between limestone rate and management system (Table 3). In all layers, Al_{ne} content was significantly higher than Al^{3+} content. Significant effects of limestone rate and management system on Al_{ne} content were detected only in the 0–0.05 m layer, with Al_{ne} decreasing by $0.527 \text{ cmol}_c \text{ kg}^{-1}$ for each unit increase in limestone rate (Fig. 1a). In the 0–0.05 m layer, Al_{ne} was 18% higher ($0.53 \text{ cmol}_c \text{ kg}^{-1}$) under soil tillage than under no-till (Fig. 1b). In the 0.05–0.10 m and 0.10–0.20 m layers, mean Al_{ne} contents were 3.37 and $3.43 \text{ cmol}_c \text{ kg}^{-1}$, respectively, with no significant differences among limestone rates or application methods (Fig. 1c–f).

Liming reduced Al^{3+} content in all layers (Fig. 2a, c, and e), but effects were more pronounced in the 0.10–0.20 m layer ($0.367 \text{ cmol}_c \text{ kg}^{-1}$ reduction per unit of limestone rate applied) (Fig. 2e). Management system exerted significant main effects on the 0–0.05 m layer, with conventional tillage increasing Al^{3+} content by $0.15 \text{ cmol}_c \text{ kg}^{-1}$ (Fig. 2b). In the 0.05–0.10 and 0.10–0.20 m layers, mean Al^{3+} contents were 0.23 and $0.57 \text{ cmol}_c \text{ kg}^{-1}$, respectively (Fig. 2d and f).

Soil organic matter increased with liming across all evaluated layers (Fig. 3a, c, and e). The increase was more pronounced in the 0–0.05 m layer and gradually decreased with depth, as indicated by the angular coefficient of 0.239 (Fig. 3a). Conventional tillage reduced SOM only in the 0–0.05 m layer (Fig. 3b). Mean SOM contents in the

Table 3 Analysis of variance results (*p*-values) for exchangeable aluminum (Al^{3+} , $\text{cmol}_c \text{ kg}^{-1}$), non-exchangeable aluminum (Al_{ne} , $\text{cmol}_c \text{ kg}^{-1}$), and soil organic matter (SOM, %) as a function of limestone rate and management system (conventional tillage and no-till)

Variable	Rate (R)	Management (M)	$R \times M$	Mean
<i>0–0.05 m layer</i>				
Al^{3+} ($\text{cmol}_c \text{ kg}^{-1}$)	0.0082*	0.0028*	0.1090	0.19
Al_{ne} ($\text{cmol}_c \text{ kg}^{-1}$)	0.0218*	0.0169*	0.2205	3.19
SOM (%)	0.0133*	0.0000*	0.5090	2.87
<i>0.05–0.10 m layer</i>				
Al^{3+} ($\text{cmol}_c \text{ kg}^{-1}$)	0.0062*	0.2061	0.0554	0.23
Al_{ne} ($\text{cmol}_c \text{ kg}^{-1}$)	0.1817	0.4538	0.5233	3.37
SOM (%)	0.0253*	0.4346	0.9217	2.42
<i>0.10–0.20 m layer</i>				
Al^{3+} ($\text{cmol}_c \text{ kg}^{-1}$)	0.0240*	0.4553	0.8258	0.57
Al_{ne} ($\text{cmol}_c \text{ kg}^{-1}$)	0.4770	0.7949	0.2418	3.43
SOM (%)	0.0002*	0.0018*	0.8479	2.01

* $p < 0.05$

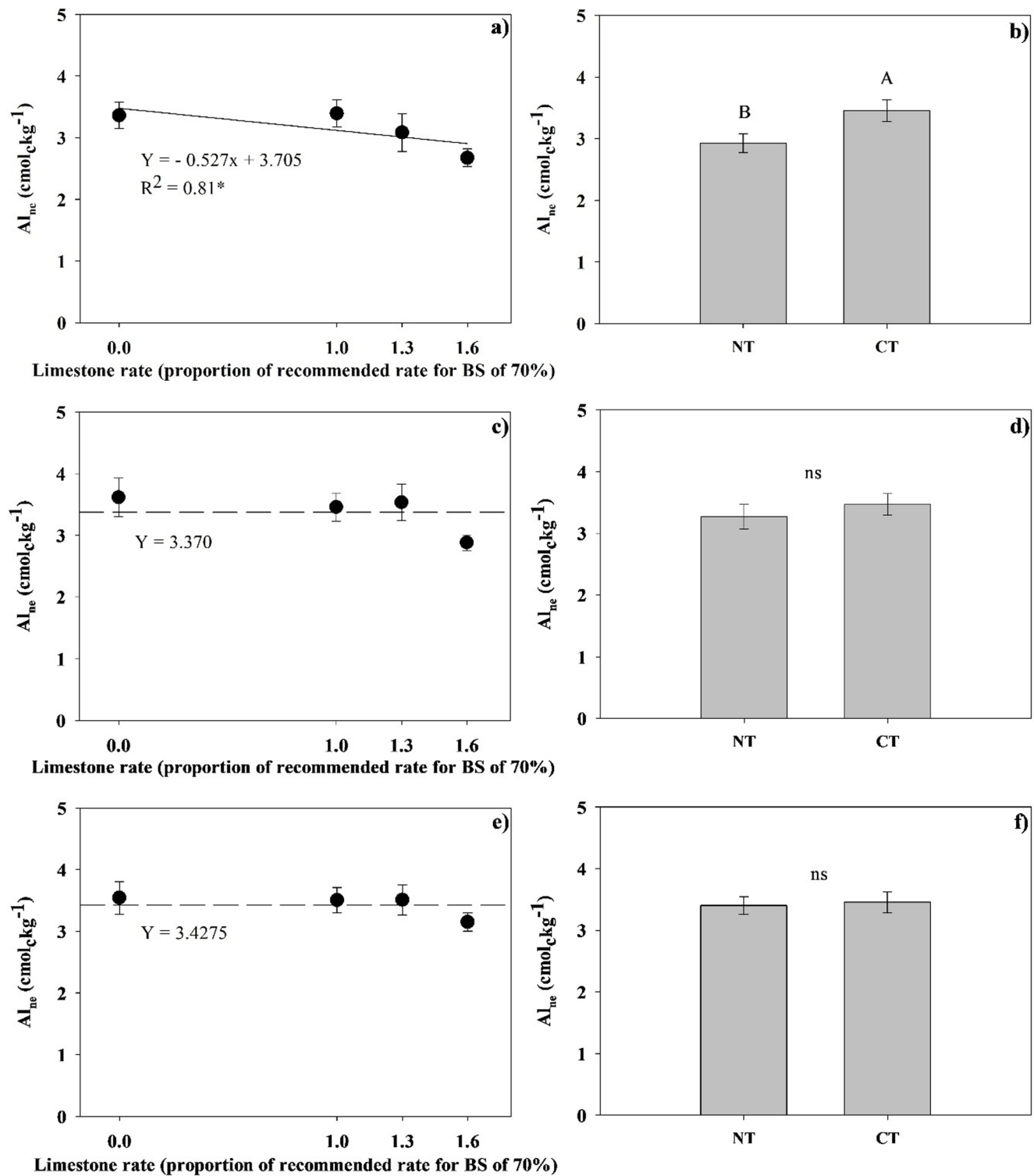


Fig. 1 Non-exchangeable aluminum (Al_{ne} , cmol_c kg⁻¹) content as a function of limestone rate (proportion of recommended rate for base saturation [BS] of 70%) and management system in the (a, b) 0–0.05 m, (c, d) 0.05–0.10 m, and (e, f) 0.10–0.20 m layers. Different

letters indicate significant differences between management systems by the *t*-test ($p < 0.05$). * $p < 0.05$; ns, not significant; NT, no-till; CT, conventional till. Vertical bars represent the standard error of the mean

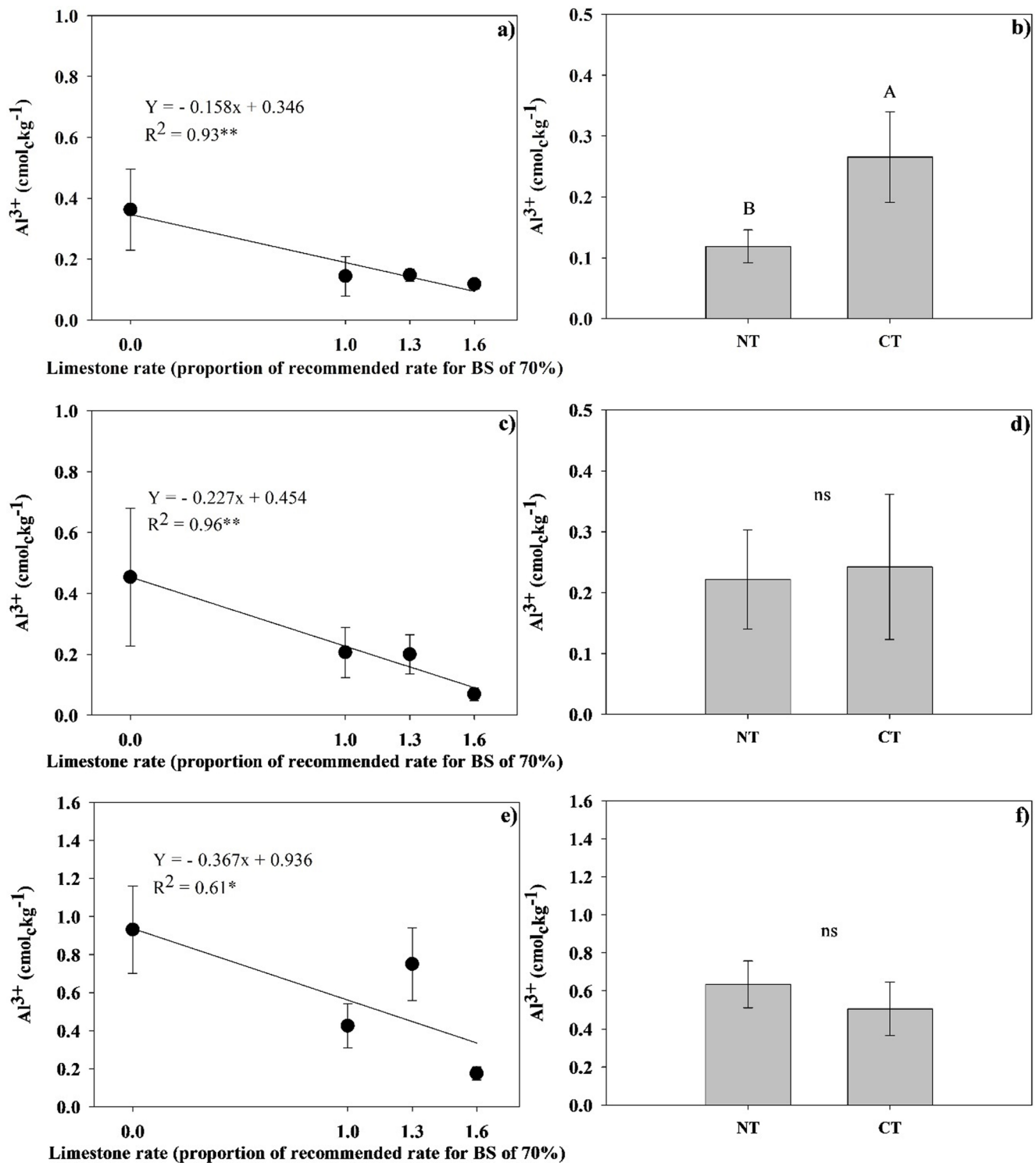


Fig. 2 Exchangeable aluminum (Al^{3+} , cmol_c kg⁻¹) content as a function of limestone rate (proportion of recommended rate for base saturation [BS] of 70%) and management system in the (a, b) 0–0.05 m, (c, d) 0.05–0.10 m, and (e, f) 0.10–0.20 m layers. Different letters indi-

cate significant differences between management systems by the *t*-test ($p < 0.05$). * $p < 0.05$; ns, not significant; NT, no-till; CT, conventional till. Vertical bars represent the standard error of the mean

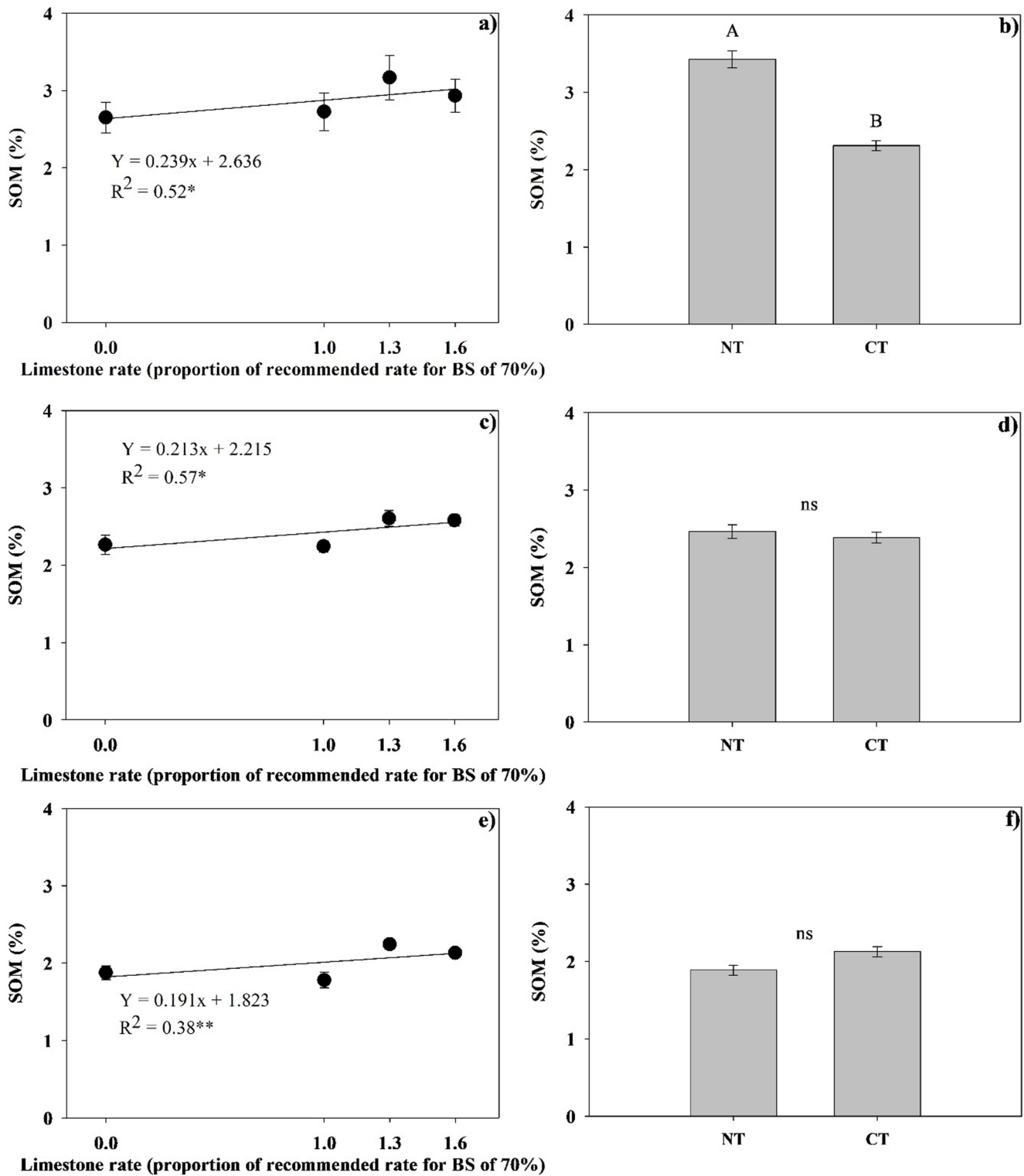


Fig. 3 Soil organic matter (SOM, %) as a function of limestone rate (proportion of recommended rate for base saturation [BS] of 70%) and management system in the (a, b) 0–0.05 m, (c, d) 0.05–0.10 m, and (e, f) 0.10–0.20 m layers. Different letters indicate significant differences

between management systems by the *t*-test ($p < 0.05$). * $p < 0.05$; ns, not significant; NT, no-till; CT, conventional till. Vertical bars represent the standard error of the mean

0.05–0.10 and 0.10–0.20 m layers were 2.42% and 2.01%, respectively (Fig. 3d and f).

3.2 Relationships Between Al_{ne} and Soil Chemical Properties

Based on the regression analyses presented in Figs. 4, 5 and 6, no significant linear or quadratic relationship was detected between Al_{ne} and Al^{3+} or SOM. In all studied layers, Al_{ne} increased linearly with increasing H+Al (Figs. 4 and 5, and 6). There was a linear reduction in Al_{ne} with increasing BS and soil pH in the 0–0.05 m layer (Fig. 4). In the 0.05–0.10 m layer, a quadratic response was observed for BS and soil pH (Fig. 5c and e). The highest Al_{ne} contents were estimated to be achieved at 48% BS (3.71 cmol_c kg⁻¹) and pH 5.0 (3.84 cmol_c kg⁻¹). Similar patterns were observed for the 0.10–0.20 m layer (Fig. 6), in which Al_{ne} contents were estimated to increase up to 52% BS (4.72 cmol_c kg⁻¹) and pH 5.0 (3.91 cmol_c kg⁻¹).

3.3 Correlations Between Al Fractions, Soil Chemical Properties, and Crop Yield

The Al_{ne} was negatively correlated with SOM only in the 0–0.05 m layer (Fig. 7a). However, in all layers, Al_{ne} showed a negative correlation with pH and wheat yield. Additionally, Al_{ne} was positively correlated with H+Al in all layers and negatively correlated with BS and soybean yield in the first two layers. The Al^{3+} showed a negative correlation with SOM, BS, pH, and soybean yield across all layers, except for SOM in the 0.10–0.20 m layer (Fig. 7c). In the 0.00–0.05 and 0.05–0.10 m layers, SOM showed a positive correlation with BS, pH, and soybean yield, except for soybean in the 0.05–0.10 m layer (Fig. 7b). Base saturation was negatively correlated with H+Al in all layers, positively correlated with pH in all layers, and positively correlated with soybean yield in the 0.00–0.05 and 0.05–0.10 m layers. A negative relationship was also observed between H+Al and pH in all layers, and between H+Al and soybean yield in the 0.00–0.05 and 0.05–0.10 m layers. Soil pH was positively correlated with soybean yield in all layers.

4 Discussion

Previous studies have reported higher levels of Al_{ne} than Al^{3+} in soils (Campos et al. 2022; Martins et al. 2020; Zambrosi et al. 2007; Godsey et al. 2007). This pattern is commonly attributed to the greater extractive capacity of CuCl₂ compared with KCl (Juo and Kamprath 1979). Copper ions exhibit strong affinity for carboxylic (–COOH) and phenolic (–OH) functional groups, potentially displacing Al

associated with SOM, including inner-sphere complexes (Hargrove and Thomas 1984). In contrast, K⁺ from KCl is monovalent and has a larger hydrated radius, which limits its ability to displace more strongly bound Al forms, being primarily effective in extracting electrostatically retained Al^{3+} . However, under the acidic conditions of CuCl₂ extraction (pH 3.1–3.7 in the present study), the solubilization of inorganic Al forms may also occur, including Al–OH polymers and low-crystallinity Al hydroxides (Zambrosi et al. 2007; Urrutia et al. 1995; Cunha et al. 2015). Therefore, Al_{ne} should not be interpreted strictly as organically complexed Al, but rather as an operationally defined fraction obtained from the difference between CuCl₂ and KCl extractable Al, which may include contributions from both organic complexes and reactive inorganic Al forms.

The distinct responses of Al fractions to limestone application indicate that exchangeable and non-exchangeable Al differ in their reactivity and sensitivity to acidity correction. Limestone reduced Al^{3+} down to the 0.10–0.20 m layer, whereas Al_{ne} decreased only in the 0–0.05 m layer. Exchangeable Al, which is electrostatically retained on the exchange complex, can be readily neutralized by OH[–] ions released during limestone dissolution. In contrast, Al_{ne} represents Al associated with more stable complexes, particularly with SOM, which do not dissociate as readily as exchangeable Al^{3+} (Alleoni et al. 2010). Previous studies suggest that the reduction of Al associated with SOM may occur only at higher pH values than those required to neutralize exchangeable Al^{3+} (Zambrosi et al. 2007; Stevenson 1994). As soil pH increases, dissociation of organic functional groups may weaken Al–organic associations, increasing the likelihood of Al displacement and subsequent precipitation as Al hydroxides. Additionally, higher limestone rates provide greater Ca²⁺ and Mg²⁺ inputs, which may compete with Al for binding sites on organic ligands and contribute to displacement reactions (Campos et al. 2022). This mechanism is consistent with our results, in which Al_{ne} decreased at limestone rates exceeding the recommendation for 70% BS. Because Al_{ne} contributed substantially to potential acidity in the surface layer, higher limestone inputs may be required to reduce total acidity where this fraction is significant. The slower movement of the alkalization front reported by Pauletti et al. (2014) and Minato et al. (2023) further supports the persistence of Al_{ne} in subsurface layers.

In addition to limestone rate, soil disturbance also altered Al dynamics in the surface soil. Conventional tillage increased both Al^{3+} and Al_{ne} contents in the 0–0.05 m layer, suggesting that soil mobilization enhanced the extractability of reactive Al forms. This effect may be associated with the destabilization of Al–organic associations caused by aggregate disruption and enhanced oxidation of SOM (Loss et al. 2016). In the present study, conventional tillage reduced

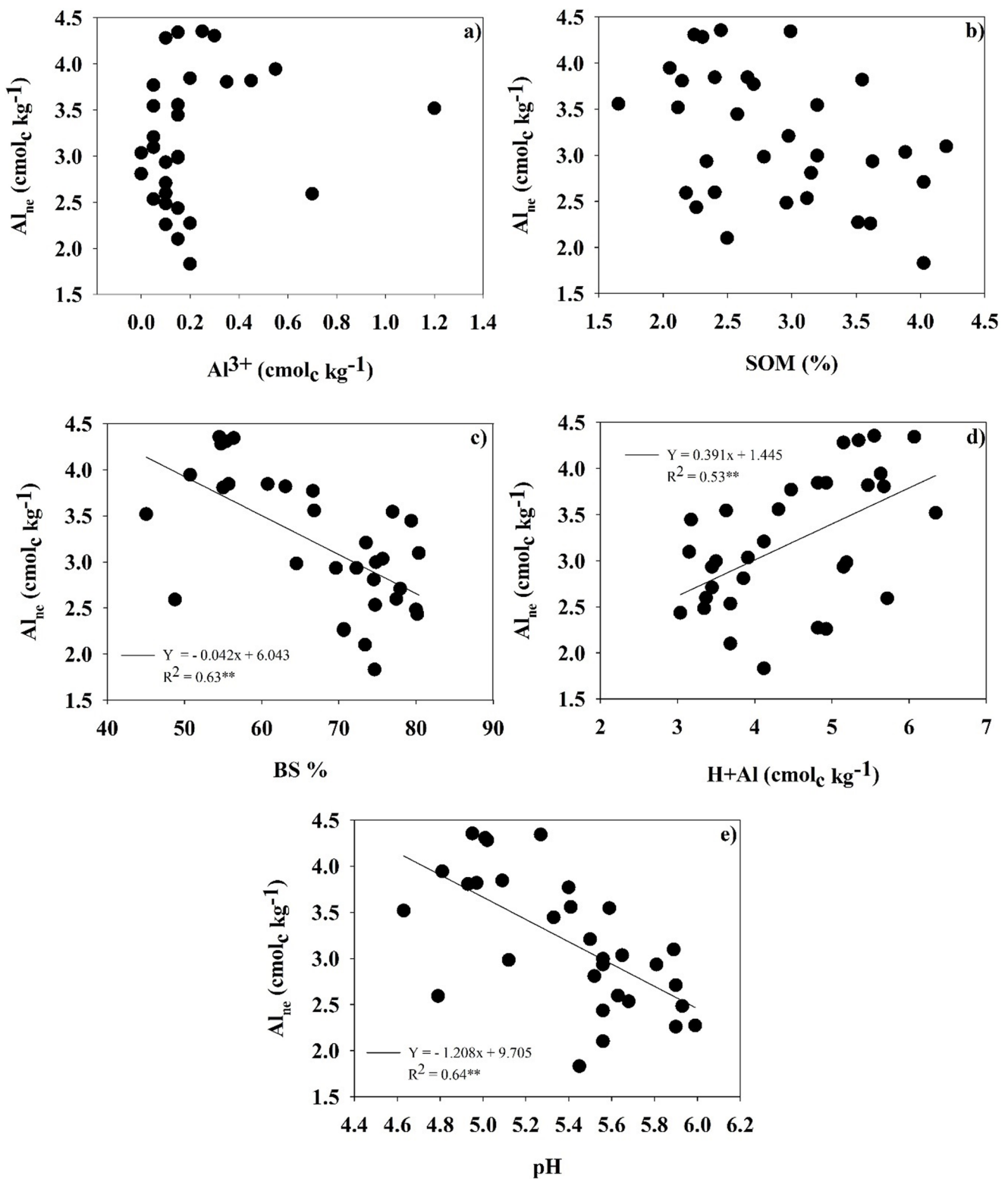


Fig. 4 Relationships between non-exchangeable aluminum (Al_{ne}) content and soil chemical properties in the 0–0.05 m layer. * $p < 0.05$; ** $p < 0.01$; Al^{3+} , exchangeable aluminum; BS, base saturation; SOM, soil organic matter; H+Al, potential acidity

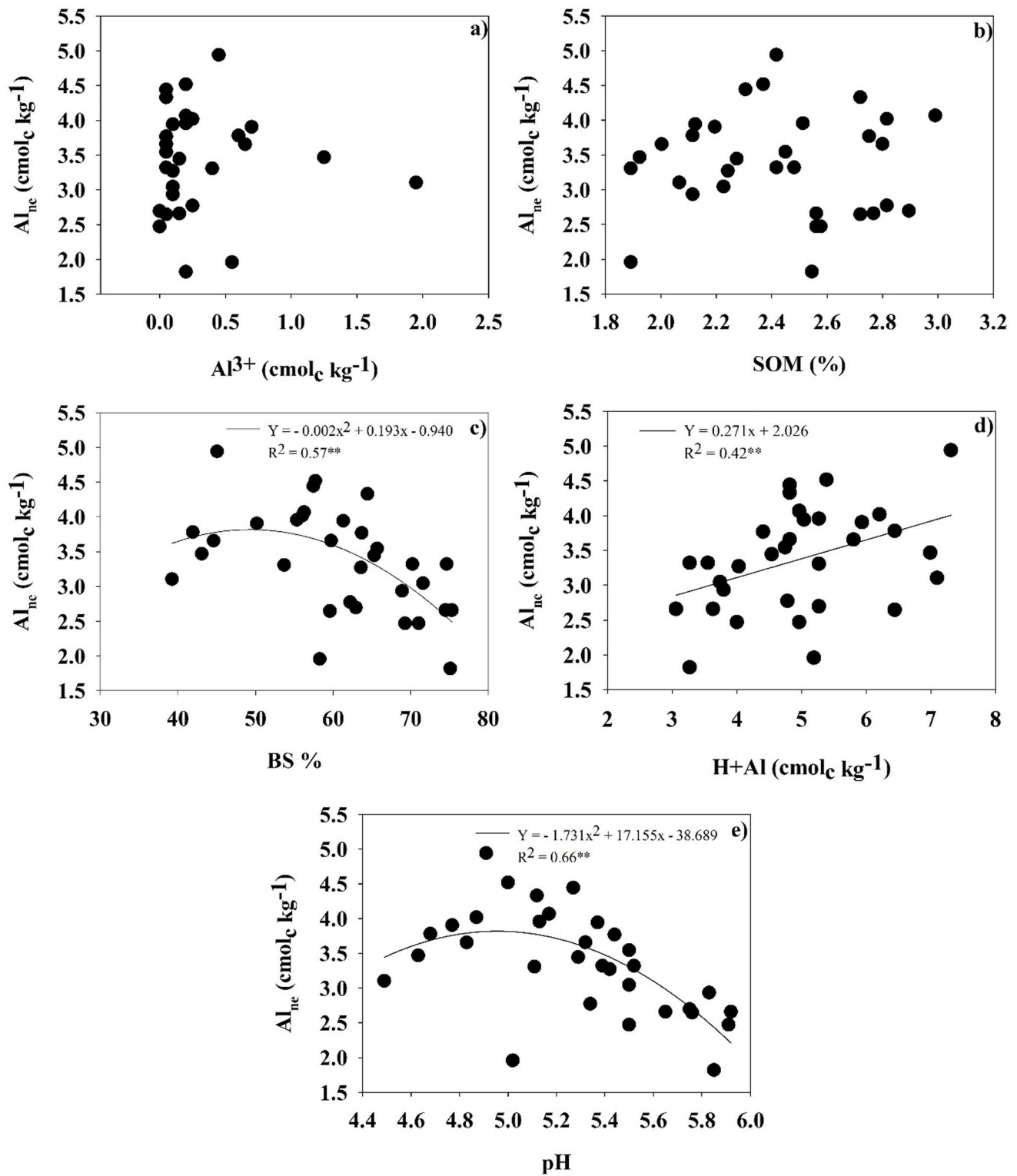


Fig. 5 Relationships between non-exchangeable aluminum (Al_{ne}) content and soil chemical properties in the 0.05–0.10 m layer. * $p < 0.05$; ** $p < 0.01$; Al^{3+} , exchangeable aluminum; BS, base saturation; SOM, soil organic matter; H+Al, potential acidity

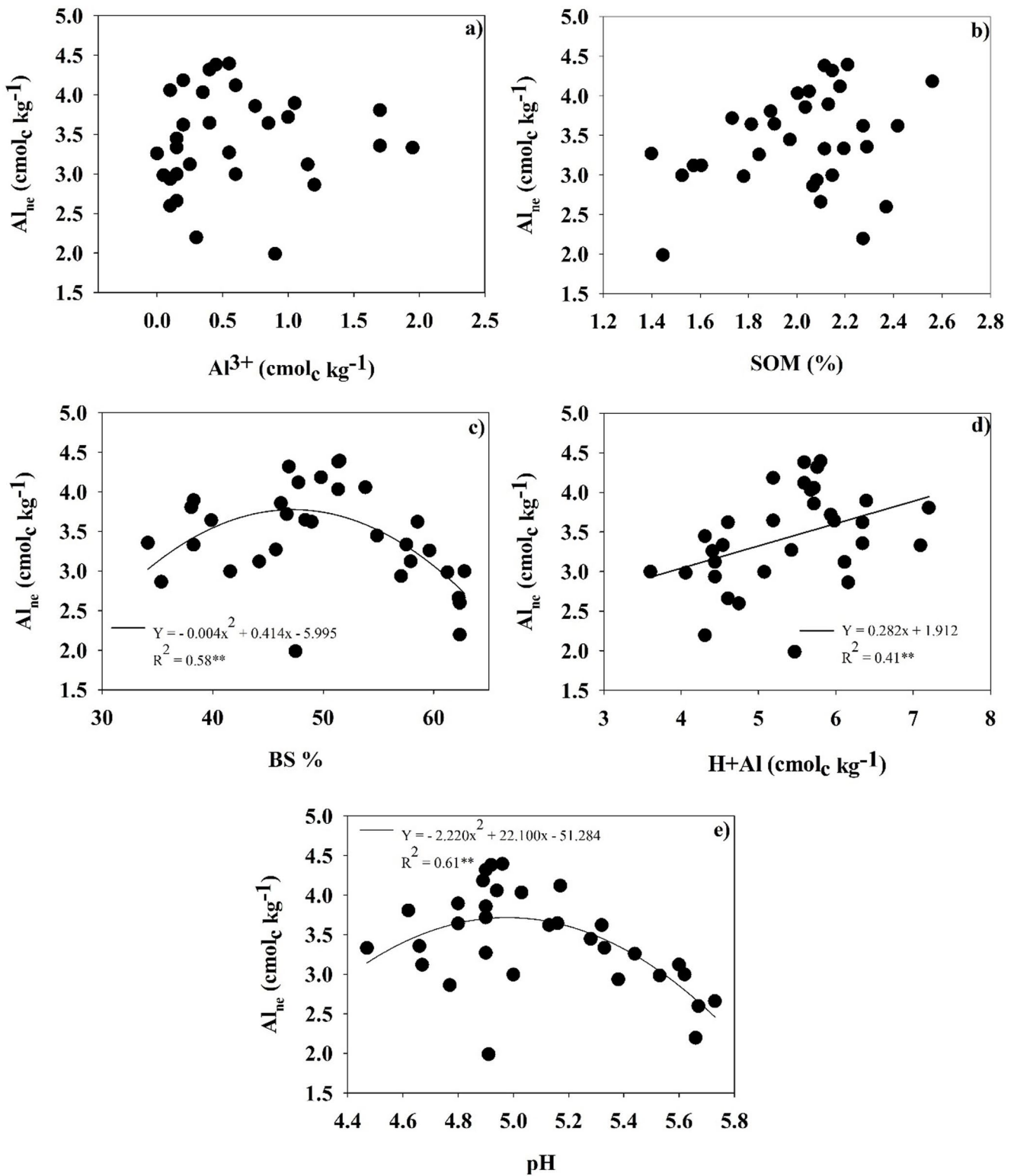
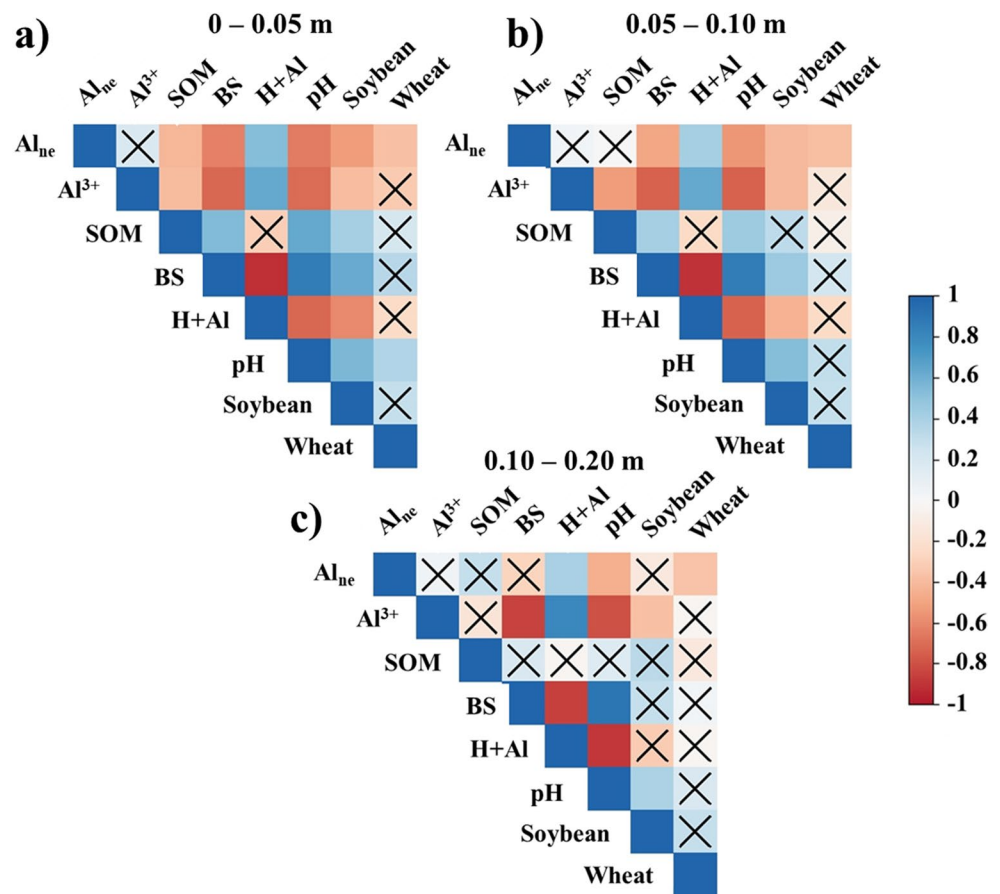


Fig. 6 Relationships between non-exchangeable aluminum (Al_{ne}) content and soil chemical properties in the 0.10–0.20 m layer. * $p < 0.05$; ** $p < 0.01$; Al^{3+} , exchangeable aluminum; BS, base saturation; SOM, soil organic matter; H+Al, potential acidity

Fig. 7 Pearson correlation matrix between soil chemical properties and soybean (2023/2024) and wheat (2024) yields in the (a) 0–0.05 m, (b) 0.05–0.10 m and (c) 0.10–0.20 m layers. The “x” represents non-significant correlations ($p > 0.05$). Al_{ne} , non-exchangeable aluminum; Al^{3+} , exchangeable aluminum; BS, base saturation; SOM, soil organic matter; H+Al, potential acidity



SOM in the surface layer, indicating that soil mobilization may have weakened the stability of Al–organic complexes and increased the extraction of reactive Al forms by both KCl and $CuCl_2$ (Ernani 2016). The magnitude of these effects may depend on soil mineralogy, climate, residue management, and tillage intensity (Blanco-Canqui and Wortmann 2020). In highly weathered and clay-rich soils, part of the SOM may remain physically protected within aggregates, limiting carbon losses even under disturbance (Brignoli et al. 2024). However, aggregate disruption may still expose reactive Al associated with organic and mineral phases.

The contribution of mineral-associated Al may also help explain the increase in extractable Al fractions under conventional tillage. Under acidic extraction conditions, $CuCl_2$ may solubilize reactive Al associated with poorly crystalline hydroxides or mineral surfaces (Cunha et al. 2015; Urrutia et al. 1995). Previous characterization of this soil reported the presence of 2:1-type clay minerals (Costa 1996). These minerals may occur as hydroxy-Al interlayered vermiculites or smectites, formed by the insertion of hydroxy-Al polymers into the interlayer space of 2:1 clay minerals. Under acidic conditions, part of this interlayered Al may become solubilized and contribute to the release of reactive Al forms

into the soil solution (Bissani and Ernani 2023). Therefore, soil disturbance may influence not only exchangeable Al^{3+} , but also non-exchangeable Al fractions associated with SOM and reactive mineral phases.

The relationships observed between Al fractions and soil chemical properties reinforce the importance of acidity correction in controlling Al dynamics. In all evaluated layers, both Al_{ne} and Al^{3+} showed negative correlations with soil pH and base saturation (BS). Increasing soil pH promotes the development of negative charges on soil colloids, which are occupied by cations such as Ca^{2+} , Mg^{2+} , and K^+ , thereby increasing BS (Ernani 2016). Simultaneously, higher pH conditions reduce Al activity in the soil solution by favoring the precipitation of reactive Al forms as $Al(OH)_3$ (Zambrosi et al. 2007). The positive correlation between Al_{ne} and H+Al indicates that Al associated with the organic phase represents a substantial reserve contributing to soil potential acidity (Campos et al. 2022). Together, these results indicate that acidity correction directly decreases the availability and extractability of reactive Al forms in the soil.

Improved soil chemical conditions were also associated with greater SOM accumulation and better crop performance. The positive correlation between SOM, pH, and BS suggests that acidity correction may favor microbial

activity, humic substance formation, plant biomass production, and subsequent carbon inputs into the soil (Paradelo et al. 2015). Another possible explanation is the formation of Ca–organic matter bridges, which enhance microaggregate stability and contribute to increased carbon stocks following Ca^{2+} input from limestone (Briedis et al. 2012). The presence of Al^{3+} is one of the main limitations for root development (Brignoli et al. 2023), directly affecting water and nutrient uptake (Fageria and Nascente 2014). Although soybean is generally considered less sensitive to Al toxicity due to greater exudation of organic acids and larger root volume, wheat yield showed a negative correlation with Al_{ne} , whereas no significant correlation was observed with Al^{3+} . This pattern suggests that Al_{ne} may represent a reserve pool of potentially reactive Al capable of influencing crop performance under certain conditions. Although the release of Al_{ne} into soil solution during the crop cycle was not directly assessed, the results indicate that both soil acidity and soil disturbance play important roles in regulating Al forms and their potential effects on crop development.

5 Conclusion

Limestone reapplication reduced Al^{3+} throughout the soil profile, whereas the reduction in Al_{ne} was restricted to the surface layer, partially rejecting the hypothesis that limestone reapplication would decrease Al_{ne} regardless of management system. In contrast, conventional tillage increased both Al^{3+} and Al_{ne} contents in the topsoil, supporting the hypothesis that soil disturbance enhances the release of reactive Al forms. These findings demonstrate that no-till provide benefits beyond erosion control, water retention, and soil structural improvement, also contributing to the stabilization of Al in less reactive forms associated with SOM. Soil mobilization may destabilize these associations and increase the potential release of Al forms with toxic effects on grain crops, particularly in highly weathered clay-rich soils.

The results also highlight the importance of considering Al_{ne} as a relevant component of soil acidity dynamics and a potential contributor to crop responses under acidic conditions. From a practical perspective, maintaining soil conservation practices and minimizing mechanical disturbance may improve the efficiency of long-term acidity management in subtropical Oxisols. A limitation of the present study is that Al_{ne} was operationally defined by chemical extraction methods, which do not allow precise differentiation between Al associated with SOM and minerals. Future studies combining selective extractors with spectroscopic techniques may improve the identification

of the origin and reactivity of Al_{ne} fractions in tropical soils.

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Declarations

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

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