

Article

Short- and Long-Term Effects of Lime and Gypsum Applications on Acid Soils in a Water-Limited Environment: 2. Soil Chemical Properties

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Abstract: Soil acidity or aluminum (Al) toxicity is a major limitation to crop production. In this paper, we examine the effects of surface-applied lime and gypsum on soil profile chemical properties that affect Al toxicity in short-term (1 year), medium-term (2 years and 8 months) and long-term (10 years) experiments. Sulfate applied to the soil surface as gypsum was leached rapidly to a depth of 40 cm in the short-term despite relatively low amounts (279 mm) of rainfall. In the medium and long-term experiments, 28–54% of the sulfate applied as gypsum was retained in the 0–50 cm soil layer due to adsorption and precipitation reactions. The combined application of lime and gypsum increased soil calcium, to a depth of 30 cm in the short-term and to a depth of 50 cm in the medium and long-terms. Increases in soil sulfate and calcium were associated with greater electrical conductivity to a depth of 50 cm for all sampling times. Application of lime alone had no impact on soil Al, pH, and calcium in the soil layers below 10 cm in the short and medium terms. In the long-term, increasing the rate of lime application from 2 to 8 t L ha^{−1} increased soil pH in the 10–20 cm soil layer while soil Al decreased to a depth of 30 cm. The combined use of lime and gypsum decreased soil Al in the 30–50 cm soil layer in the medium-term and the 20–30 cm soil layer in the long-term which was more than when only lime was applied. Hence, we recommend the use of lime plus gypsum for treating soils with subsoil Al toxicity. Additionally, soil Al measurements are a more sensitive measurement of the impact of surface application lime and lime plus gypsum than soil pH.

Keywords: aluminum toxicity; calcium; electrical conductivity; pH; soil acidity; sulfate

1. Introduction

Aluminum (Al) present in the soil solution as $\text{Al}(\text{H}_2\text{O})_6^{3+}$ abbreviated, as Al^{3+} , is toxic to root growth [1]. Soil $\text{pH}_{\text{CaCl}_2}$ and soil $\text{Al}_{\text{CaCl}_2}$ (Al and pH measured using 0.01 M CaCl_2) are used to indicate the potential limitations imposed by soil acidity and Al toxicity, respectively [2]. When the subsoil or soil layers below 10 cm contain an $\text{Al}_{\text{CaCl}_2}$ content greater than 2.5 mg Al kg^{−1}, there is a significant reduction in wheat (*Triticum aestivum* L.) grain yield. Lime (L, CaCO_3) applied to Al toxic soils increases soil $\text{pH}_{\text{CaCl}_2}$ and decreases soil $\text{Al}_{\text{CaCl}_2}$ resulting in increased crop grain yields [2,3]. However, due to its comparatively low solubility, L broadcast onto the soil surface can be ineffective at treating subsoil

Al toxicity in the short-term and medium-term [2]. Alternatively, gypsum (G, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has the potential to be more effective in treating subsoil Al toxicity due to its greater solubility (2.1 gm L^{-1} in water) compared to L which is sparingly soluble in water (0.013 gm L^{-1}) [4,5]. The application of G increases the sulfate ($\text{SO}_4\text{-S}$) and calcium (Ca) concentration of the soil solution leading to an increase in soil solution electrical conductivity (EC) [5]. Higher soil solution EC decreases the activity of Al^{3+} in the soil solution meaning plants can tolerate greater levels of Al^{3+} toxicity [4]. Additionally, the increase in soil $\text{SO}_4\text{-S}$ content results in the conversion of toxic Al^{3+} to Al sulfate (Al- SO_4), which is not harmful to plant roots [6–8].

The application of G can either decrease, increase or have no effect on soil $\text{pH}_{\text{CaCl}_2}$ [9]. A decrease in soil $\text{pH}_{\text{CaCl}_2}$ arises when added Ca displaces Al^{3+} and hydrogen ions (H^+) from the cation exchange sites into the soil solution [10]. By contrast, an increase in $\text{pH}_{\text{CaCl}_2}$ happens due to $\text{SO}_4\text{-S}$ sorption resulting in the displacement of hydroxide ions (OH^-) [11]. The net effect of these two reactions will determine the overall impact on $\text{pH}_{\text{CaCl}_2}$ [9]. For soils with high $\text{SO}_4\text{-S}$ sorption capacities, the net effect is to increase soil $\text{pH}_{\text{CaCl}_2}$ [12]. In contrast, for soils with low $\text{SO}_4\text{-S}$ sorption capacities, the net result is to decrease $\text{pH}_{\text{CaCl}_2}$. The $\text{SO}_4\text{-S}$ sorption capacity can be measured using the sulfur buffer index (SBI) [13]. Brazilian studies have shown that soils that have high $\text{SO}_4\text{-S}$ sorption capacity have a greater G requirement to overcome the Al toxicity limitations [14]. In contrast, G application did not affect the soil solution pH of soils of South Western Australia [6] because these soils generally have a low SBI [13].

Leaching of $\text{SO}_4\text{-S}$ from the 0–20 cm soil layer occurs in the medium rainfall zone of South Western Australia [15]. However, retention of this leached $\text{SO}_4\text{-S}$ takes place in the soil layers below 20 cm due to the greater $\text{SO}_4\text{-S}$ adsorption properties [15]. In general, soil layers below 10 cm have a greater capacity to adsorb $\text{SO}_4\text{-S}$ due to the lower carbon, phosphorus, pH, and greater clay content [13]. The rate of $\text{SO}_4\text{-S}$ leaching is related to the water holding capacity of the soil, the amount and frequency of rainfall events, and the $\text{SO}_4\text{-S}$ adsorption properties [15]. Hence, the rate of $\text{SO}_4\text{-S}$ leaching will be less in the low rainfall zone of South Western Australia compared to the rates observed in the medium rainfall zone [15]. Additionally, some soils within the region have net anion exchange capacity, which can reduce the rate of nitrate leaching [16]. The reduction in $\text{SO}_4\text{-S}$ leaching in soil with anion exchange capacity is expected to be greater than that which occurs for nitrate because soils adsorb $\text{SO}_4\text{-S}$ more strongly than nitrate. Calcium (Ca), when applied as G and L, can also be leached into the soil profile. The rate of leaching of G and L derived Ca varies according to the rates applied, reaction time and the soil type [17]. Calcium derived from G is leached at a faster rate than Ca derived from L because of the greater solubility of G compared to L and due to the presence of $\text{SO}_4\text{-S}$ as co-anions of G [17,18]. Additionally, L application increases soil pH and the effective cation exchange capacity (ECEC), which reduces the mobility of Ca due to the increased attraction by the pH-dependent negative charges of the soil particles [17].

In the first paper of this series, we concluded that the application of G is profitable in the low-rainfall, eastern wheat belt region of Western Australia despite the soils having a low capacity to adsorb $\text{SO}_4\text{-S}$ which results in rapid leaching of $\text{SO}_4\text{-S}$ and no self-liming effect [3]. In this paper, we examine the impact of surface application of G and L on soil chemical properties overtime to explain these crop grain yield responses. In this paper, we present changes in soil profile $\text{SO}_4\text{-S}$, Ca, EC, Al, pH and ECEC over time. We hypothesize that measurement of soil Al, as opposed to pH, will provide a more sensitive measurement of the impact of surface-applied L on subsoil chemical properties. Additionally, the combined application of L and G will result in a greater reduction in soil Al than when L is applied alone.

2. Materials and Methods

2.1. Field Experimental Sites

The short-term (ST, 1 year), and medium-term (MT, 2 years and 8 months) experiments were located near the town of Burracoppin ($-31^{\circ}30'9''$ S latitude, $118^{\circ}38'50''$ E longitude) and had a total of $2\text{--}4\text{ t L ha}^{-1}$ applied in the previous 15 years before the commencement of the experiment. The third was a long-term (LT, 10 years) experiment located near the town of Bonnie Rock ($-30^{\circ}37'3''$ S latitude, $118^{\circ}14'9''$ E longitude) and had no history of L application. The experiments are located in the low rainfall region of the South Western Australian grain belt. Long term (1980–2018) average rainfall for the Bonnie Rock and Burracoppin sites are 309 mm (range 158–453 mm) and 364 mm (range 315–414 mm) respectively. While Bonnie Rock and Burracoppin are in the same rainfall zone, rainfall amount and distribution can differ, for example, annual rainfall at Bonnie Rock was 296 mm compared Burracoppin of 400 mm in 2015 [3]. Crop grain yield and nutrient concentration and measured soil chemical properties from the control treatment are presented by [3]. In summary, G application was profitable at the MT experiment where deep ripping had removed the subsoil compaction constraint. In contrast, the most profitable treatment at the LT experiment was where L and G were applied together. The soils at the experimental sites are classified as Tenosols [19]. At the LT site, the gravel content increased from 5% in 0–10 cm to 56% in 30–50 cm, which reduces the water holding capacity.

In the ST experiment, we top-dressed the G and L treatments on 31 March 2017. The treatments consisted of: a control (C), 2.5 t L ha^{-1} (L2.5), $2.5\text{ t gypsum ha}^{-1}$ (G2.5) and, 2.5 t L ha^{-1} plus $2.5\text{ t gypsum ha}^{-1}$ (L2.5 + G2.5). The MT experiment consisted of the same L and G treatments as the ST experiment, plus additional treatments comprising 5.0 t L ha^{-1} (L5.0) and 5.0 t L ha^{-1} plus 2.5 t G ha^{-1} (L5.0 + G2.5). In this experiment, we broadcasted the L and G treatments on 31 July 2015, which was followed by deep ripping and cultivation. The LT experiment treatments consisted of: a control (C) 2.0 t L ha^{-1} (L2), 4.0 t L ha^{-1} (L4), 8.0 t L ha^{-1} (L8), 2.0 t G ha^{-1} (G2), and 4.0 t L ha^{-1} plus 2.0 t G ha^{-1} (L4 + G2). We broadcasted half (1, 2, and 4 t L ha^{-1} , and 1 t G ha^{-1}) of the L and G rates in March of 2008 and in March of 2013. We used three treatments replication in all experiments. The distance of the experiment site for L sources was 370–380 km compared for the G source of 140–200 km. The L source consisted of 80–93% CaCO_3 while the G source contained $175\text{--}178\text{ g S kg}^{-1}$ and $214\text{--}224\text{ g Ca kg}^{-1}$ [3].

Crops grown at the MT experiments were canola (*Brassica napus* L. cv Bonito) in 2016, wheat (cv Calingiri) in 2017, and barley (*Hordeum vulgare* cv Spartacus CL) in 2018. The same crops were grown at the ST experiment in 2017 and 2018. Wheat was grown at the LT experiment in 2008, 2010, 2011, 2013, 2014, 2015, and 2016. Seeding occurred with farmer equipment for the ST and MT experimental sites and plot cone seeder for the LT site in May. We used a small plot header to harvest the plots in November of each year.

2.2. Soil Measurements

We collected four 5 cm diameter soil cores in depth increments of 10 cm to 50 cm from each plot in March 2018 which was 1 year (ST), 2 years and 8 months (MT), and 10 years (LT) after the application of L and G treatments. The four cores were bulked to provide soil profile samples for each plot. In this paper, treatment effects on $\text{pH}_{\text{CaCl}_2}$ and $\text{Al}_{\text{CaCl}_2}$ were measured using a 1:5 soil to 0.01 M CaCl_2 solution extraction and electrical conductivity (EC) using the same soil to solution ratio but with water [20]. The extractable sulfur content of the soil profile was measured using 0.25 M KCl heated for 3 h at $40\text{ }^{\circ}\text{C}$ (S_{KCl40}) [21]. Soil buffer index (SBI) was measured to assess the S-SO_4 adsorption properties of the soil using the procedure of [13] in the control treatments [3]. Exchangeable cations, Al (Al_{Ex}), Ca (Ca_{Ex}), potassium (K_{Ex}), magnesium (Mg_{Ex}) and sodium (Na_{Ex}), were extracted using an unbuffered solution of 0.1 M ammonium chloride and barium chloride at 1:10 soil to solution ratio with cation concentration measured by ICP-AES [20]. The ECEC value is calculated as the sum of the cations, Al_{Ex} , Ca_{Ex} , K_{Ex} , Mg_{Ex} and Na_{Ex} [20]. The percentage of cation occupied by $\text{Al}_{\text{Ex}}\%$ and $\text{Ca}_{\text{Ex}}\%$ is Al_{Ex} or Ca_{Ex} divided by ECEC multiplied by 100. Other soil nutrient measurements included ammonium

and nitrate, Colwell phosphorus and potassium, phosphorus buffering index, organic carbon, DTPA extractable copper, manganese, and zinc, and hot boron are summarized by [3].

2.3. Lime and Gypsum Recovery

Calculated $\text{SO}_4\text{-S}$ and Ca recovered from applied G is the difference between S_{KCl40} (mg S kg^{-1}) and Ca_{Ex} (mg Ca kg^{-1}) content of each soil layer between the G and the C treatment. In the calculation, we used a bulk density of 1.7 gm cm^3 multiplied by the sampling depth (10 cm) to convert mg kg^{-1} to kg ha^{-1} . The difference for each soil layer is then summed to give the amount of G or L recovered in the 0–50 cm soil layer of the three experimental sites [3]. Percent L or G recovered is then the summed amount divided by the amount applied. In doing the calculation, we used the measured Ca and S content of the G and the CaCO_3 content of the L sources. Gravel content for the LT experiment, reduced S_{KCl40} and Ca_{Ex} content when expressed in the units of kg ha^{-1} .

2.4. Statistical Analysis

For individual soil layers, analysis of variance was done using a treatment structure of treatments and a block structure of replicates to determine the significance of amendment treatment main effects at each soil depth using Genstat® [22]. Differences between treatments were then determined using the Duncan multiple range test. Throughout the paper, the least significant difference values, were determined at $p \leq 0.05$. The exception where $p \leq 0.07$ was used to denote significance because of the high variability in some measurements. These exceptions were, in the ST experiment for calculated $\text{SO}_4\text{-S}$ recovery from the applied G (Table 1), in the MT experiment for $\text{Al}_{\text{CaCl}_2}$, Al_{Ex} and the LT experiment for $\text{pH}_{\text{CaCl}_2}$. In retrospect, to account for the high variability, we should have collected more than four soil profile cores per plot. Regression equations for comparison between soil measurements were determined using the regression SigmaPlot® 12.5 analysis regression wizard [23].

Table 1. Recovery (%) of the applied $\text{SO}_4\text{-S}$ as calculated by the difference in S_{KCl40} between the G and C treatments for the short-term (ST), medium-term (MT) and long-term (LT) experiments using soil samples collected in March 2018.

Depth (cm)	ST		MT		LT		
	G2.5	L2.5 + G2.5	G2.5	L2.5 + G2.5	L5.0 + G2.5	G2.0	L4 + G2
0–10	NA	NA	10	13	29	30	6
10–20	34	41	9	10	23	9	6
20–30	17	18	4	6	11	7	8
30–40	7	9	2	7	12	6	7
40–50	1	2	3	8	8	3	5
Total	NA	NA	28	31	54	26	27

L is the lime treatments. NA Recoveries are greater than 100% due to the insufficient number of soil cores collected to account for site variation.

3. Results

3.1. Sulphur

Soil S_{KCl40} in the ST experiment for the C treatment increased from 14–22 mg S kg^{-1} in the 0–10 cm to 28–61 mg S kg^{-1} in the 40–50 cm soil layer (Figure 1a). In the ST experiment, G application increased soil S_{KCl40} , from 22 to 537–676 mg S kg^{-1} in the 0–10 cm soil layer which was equivalent to more than the amount of $\text{SO}_4\text{-S}$ applied (Table 1). In contrast, the application of L had no effect on soil S_{KCl40} in the ST. In the MT, the L5.0 + G2.5 treatment increased soil S_{KCl40} by 526–551% in the 0–20 cm soil layer and by 53–157% in the 20–50 cm soil layer compared to the C treatment (Figure 1b). In the MT, these increases accounted for 28–54% of the applied $\text{SO}_4\text{-S}$ (Table 1). In the LT, G alone increased S_{KCl40} by 415% in the 0–10 cm soil layer (Figure 1c), while S_{KCl40} was 56–144% greater for the G treatments

compared to the C treatment in the 10–50 cm soil layers. In the LT, these increases in S_{KCl40} only accounted for 26–27% of applied SO_4 -S (Table 1).

3.2. Calcium

Soil Ca_{Ex} decreased from 1.96–3.23 $cmol\ kg^{-1}$ in the 0–10 cm to 0.23–0.35 $cmol\ kg^{-1}$ in the 40–50 cm soil layer for the ST and MT experiments (Figure 1d,e). Soil Ca_{Ex} was lower for the LT experiment, but the content also decreased with increasing soil depth from 0.81 $cmol\ kg^{-1}$ in the 0–10 cm to 0.49 $cmol\ kg^{-1}$ in the 40–50 cm soil layer (Figure 1f).

In the ST, the L2.5 + G2.5 treatment increased soil Ca_{Ex} relative to the C treatment by 96–122% in the 0–20 cm soil layer and by 77–99% in the 20–40 cm soil layer (Figure 1d). In comparison, the G and L alone treatments increased Ca_{Ex} by 49–72% compared to the C treatment in the 0–10 cm soil layer. In the MT, soil Ca_{Ex} for the L5.0 + G2.5 treatment was greater than the C by 46–141% in the 0–50 cm soil layer, (Figure 1e). In contrast, the G and L alone treatments had no significant effect on Ca_{Ex} . In the LT, the L4, L8, and L4 + G2 treatments increased Ca_{Ex} by 131–249% in the 0–20 cm soil layer and for the L4 + G2 treatment by 94% in the 20–50 cm soil layer compared to the C treatment (Figure 1f). At the same time, soil Ca_{Ex} content for the L2 treatment was greater by 139% in the 0–10 cm soil layer and by 77% in the 10–20 cm soil layer than the C treatment (Figure 1e). For the G2 treatment in the LT experiment, Ca_{Ex} content was not significantly greater than the C treatment in the 0–20 cm soil layer.

Calcium recovery, as indicated by the increase in Ca_{Ex} was low (–2–31%) for all L treatments across the 3 three experiments (Table 2). In contrast, Ca recovery for the G treatments was high (82–92%) in the ST and MT but relatively low (48%) in the LT while Ca recovery was low (23–37%) for the L + G treatments for the three experiments.

Table 2. Recovery (%) of the applied Ca from the L and G application as calculated by the difference in Ca_{Ex} between the L and G treatments compared to the C treatment for the ST, MT, and LT experiments using soil samples collected in March 2018.

Depth (cm)	ST			MT					LT				
	L2.5	G2.5	L2.5 + G2.5	L2.5	L5	G2.5	L2.5 + G2.5	L5.0 + G2.5	L2	L4	L8	G2.0	L4 + G2
0–10	19	43	19	–1	–2	15	6	9	20	15	9	20	15
10–20	7	20	10	0	3	33	5	11	6	5	5	14	9
20–30	3	15	5	0	1	9	4	4	1	1	1	6	4
30–40	2	8	3	–1	0	12	5	4	0	1	1	3	2
40–50	1	6	1	1	1	13	4	4	0	0	0	4	1
Total	31	92	37	–2	3	82	23	31	28	22	15	48	30

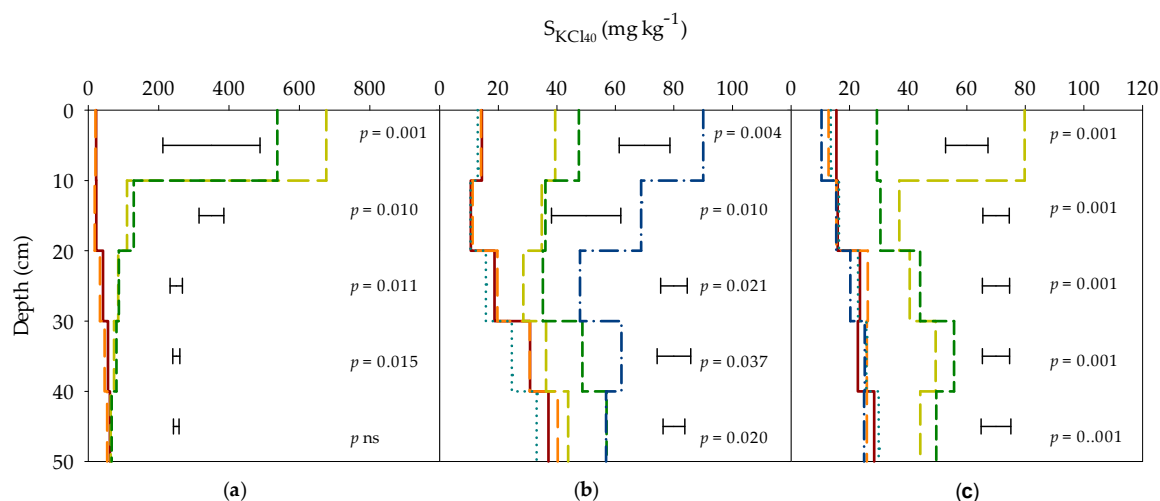


Figure 1. Cont.

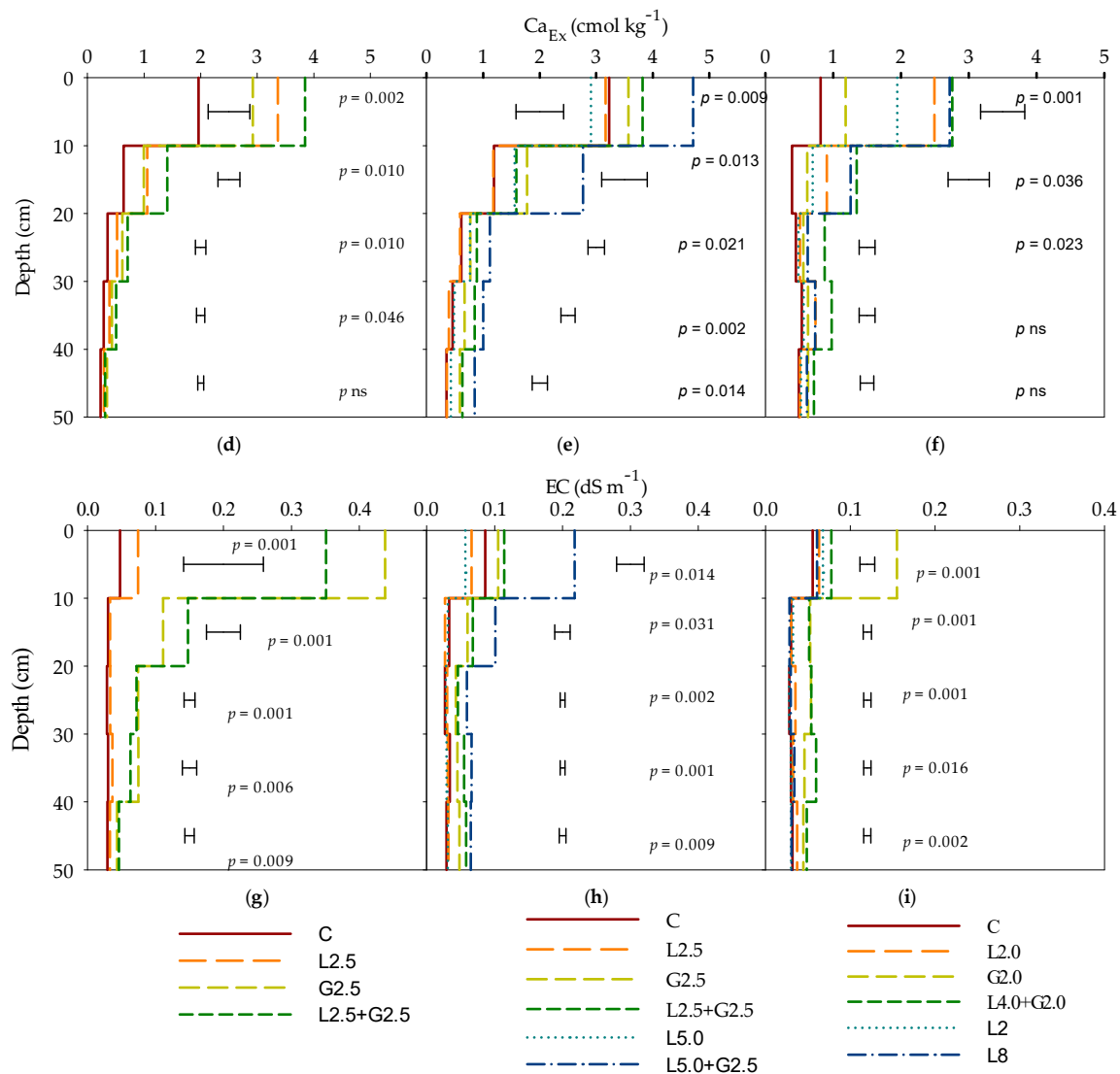


Figure 1. (a–c) Soil S_{KCl40} , (d–f), Ca_{Ex} , and (g–i) EC (a,d,g) in the ST for C, L2.5, G2.5, L2.5 + G2.5 treatments (b,e,h), in the MT for C, L2.5, G2.5, L2.5 + G2.5, L5.0, and L5.0 + G2.5 treatments and; (c,f,i) in the LT for C, L4, G2, L4 + G2, L2, and L8 treatments. Error bars represent least significant difference values at $p = 0.05$, $n = 3$ for each depth with ns denoting $p > 0.05$.

3.3. Electrical Conductivity

The application of L did not affect soil EC in the three experiments (Figure 1g–i). In contrast, the use of G resulted in a substantial increase in EC in the surface soil layers in the ST, and to lesser extents in the MT and LT. In the ST, the highest increase for the G treatments compared to the C and L2.5 treatments was in the 0–10 cm soil layer (636–490%) declining to a 67–98% increase in the 30–40 cm soil layer (Figure 1g). There was also an increase of 28% for the L5.0 + G2.5 compared to the C treatment in the 40–50 cm soil layer. In the MT, EC values of the L5.0 + G2.5 treatment were 64–154% greater than the C in the 0–50 cm soil layer (Figure 1h). In the LT, soil EC value for the L4 + G2 treatment was 178% greater than the C treatment in the 0–10 cm soil layer while for the G2 and L4 + G2 treatments EC was 41–93% greater than the C in the 10–50 cm soil layer (Figure 1i).

3.4. Aluminum and pH

For the C treatment, soil $\text{Al}_{\text{CaCl}_2}$ in the ST and MT experiments increased from 0.1–0.2 mg Al kg⁻¹ in the 0–10 cm to 15.4–22.2 mg Al kg⁻¹ in the 40–50 cm (Figure 2a,b). In the LT experiment, the highest soil $\text{Al}_{\text{CaCl}_2}$ for the C treatment was 11.1–11.2 mg Al kg⁻¹ in the 10–30 cm (Figure 2c).

The L treatments decreased $\text{Al}_{\text{CaCl}_2}$, while G alone treatment had no impact on $\text{Al}_{\text{CaCl}_2}$. The extent and depth to which L application reduced on $\text{Al}_{\text{CaCl}_2}$ varied with time, L rate, and G application. In both the ST and MT experiment L, $\text{Al}_{\text{CaCl}_2}$ is near zero in the 0–10 cm soil layers and hence was not lowered further by L application. In the ST, L G, and L + G application decreased $\text{Al}_{\text{CaCl}_2}$ compared to the C treatment by 48–69% in the 10–20 cm soil layer (Figure 2a).

In the MT, $\text{Al}_{\text{CaCl}_2}$ was again near-zero and not lowered further by L application in 0–30 cm soil layer (Figure 2b). In contrast, $\text{Al}_{\text{CaCl}_2}$ was 74–91% lower for the L5.0 + G2.5 treatment compared to the C treatment in the 30–50 cm soil layer with the difference significant at $p = 0.054$ for the 30–40 cm soil layer. In the LT, soil $\text{Al}_{\text{CaCl}_2}$ content for the L treatments was lower than the C treatment by 91–92% in the 0–10 cm (Figure 2c). In the 10–20 cm soil layer, $\text{Al}_{\text{CaCl}_2}$ content was 55% lower for the L4 treatment, and 77–95% lower for the L4, L4 + G2, and L8 treatments than the C treatment. In the 20–30 cm soil layer, the L4 + G2 treatment had a 70% lower $\text{Al}_{\text{CaCl}_2}$ than the C treatment.

Soil Al_{Ex} in the ST and MT experiments, for the C treatment, increased with increasing soil depth from 0.09–0.10 cmol kg⁻¹ in the 0–10 cm to 0.53–0.81 cmol kg⁻¹ in the 40–50 cm soil layer (Figure 2d,e). In the LT experiment, the highest soil Al_{Ex} for the C treatment of 0.36–0.45 cmol kg⁻¹ occurred in the 10–30 cm soil layer (Figure 2f).

In the ST, the L and G treatments decrease Al_{Ex} by 29–49% in the 10–20 cm soil layer (Figure 2d). In the MT, soil Al_{Ex} was 48–62% lower for the G5.0 + L5.0 treatment than the C treatment in the 30–50 cm soil layer, with the difference significant at $p = 0.062$ in the 40–50 cm soil layer (Figure 2e). In the LT, soil Al_{Ex} for the L and L + G treatments was 72–86% lower in the 0–10 cm soil layer than the C treatment (Figure 2f). In the 10–20 cm soil layer, the L4, L4 + G2, and L8 treatments decreased Al_{Ex} content by 53–72% compared to the C treatment. For the L4 + G2 treatment, Al_{Ex} content was 46–47% lower in the 20–30 cm soil layer compared to the C treatment. Application of G2 did not affect Al_{Ex} in the 0–50 cm soil layer.

Soil $\text{pH}_{\text{CaCl}_2}$ in the ST and MT experiments, for the C treatment, decreased with increasing soil depth from 5.5–6.6 in the 0–10 cm to 4.2–4.7 in the 40–50 cm soil layer (Figure 2g,h). In the LT experiment, soil profile $\text{pH}_{\text{CaCl}_2}$ ranged between 4.5–4.7 (Figure 2i). In the ST and MT, neither L nor G application altered $\text{pH}_{\text{CaCl}_2}$ in any soil layers (Figure 2g,h). In the LT, soil $\text{pH}_{\text{CaCl}_2}$ ranged between 6.0–6.4 for the L4, L8, and L4 + G2 treatments compared to 4.6 for the C treatment in the 0–10 cm soil layer (Figure 2i). Additionally, $\text{pH}_{\text{CaCl}_2}$ for the L8 treatment was greater at 5.1 compared to 4.5 for the C treatment in the 10–20 cm soil layer at $p = 0.066$.

The relationships between $\text{pH}_{\text{CaCl}_2}$ and $\text{Al}_{\text{CaCl}_2}$ were similar for the three experimental sites (Figure 3). In the LT experiment, the L treatments decreased $\text{Al}_{\text{CaCl}_2}$ from 11.3 to 2.8 mg Al kg⁻¹ with the associated change in $\text{pH}_{\text{CaCl}_2}$, ranging from 4.4 to 4.6. The lowest $\text{pH}_{\text{CaCl}_2}$ and greatest $\text{Al}_{\text{CaCl}_2}$ occurred in the 20–50 cm soil layer for the ST experiment, in the 30–50 cm soil layer for the MT experiment, and in the 10–30 cm soil layer for the LT experiment (Figure 2). Soil $\text{pH}_{\text{CaCl}_2}$ and $\text{Al}_{\text{CaCl}_2}$ were both related to Al_{Ex} (Figure 4). The relationships and equations used to convert $\text{Al}_{\text{CaCl}_2}$ to Al_{Ex} are presented in Figure 4.

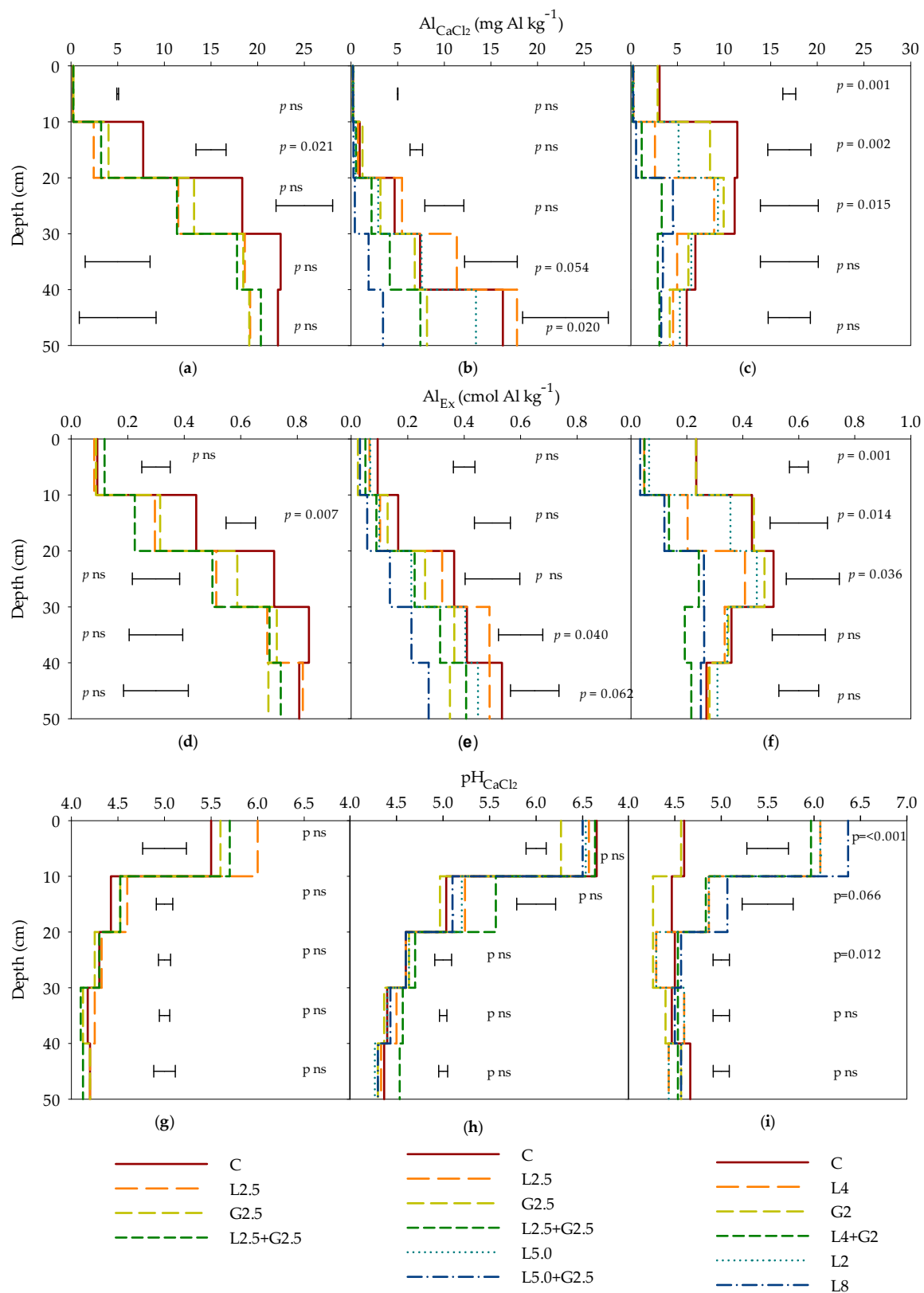


Figure 2. (a–c) Soil Al_{CaCl_2} , (d–f) Al_{Ex} , and (g–i) pH_{CaCl_2} (a,d,g) in the ST for C, L2.5, G2.5, L2.5 + G2.5 treatments (b,e,h), in the MT for C, L2.5, G2.5, L2.5 + G2.5, L5.0, and L5.0 + G2.5 treatments; and (c,f,i) and in the LT for C, L4, G2, L4 + G2, L2, and L8 treatments. Error bars represent least significant difference values at $p = 0.05$, $n = 3$ for each depth with ns denoting $p > 0.05$. The exceptions were in (e) for the 40–50 cm where $p = 0.062$ and (i) for the 10–20 cm where $p = 0.066$.

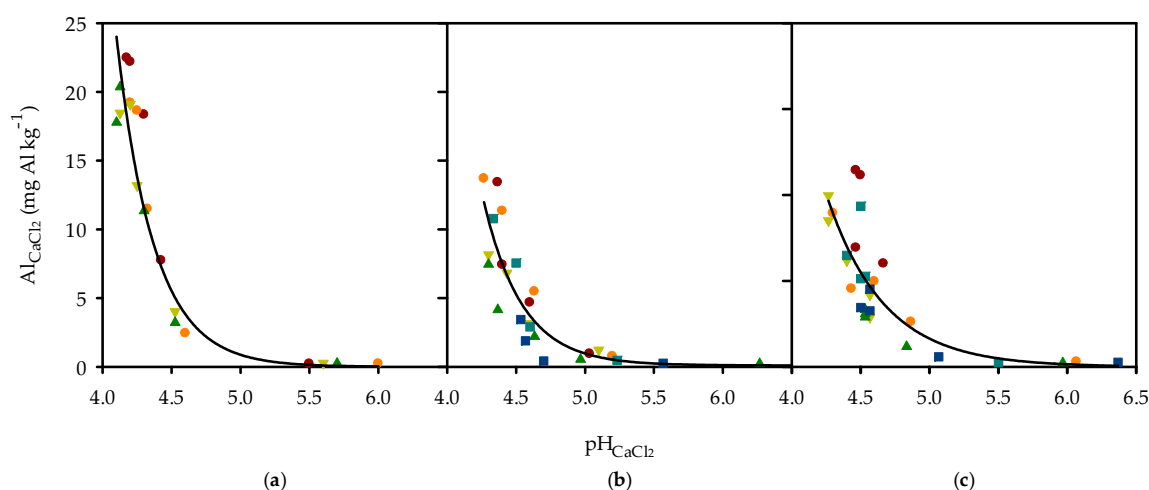


Figure 3. (a) Relationship between $\text{pH}_{\text{CaCl}_2}$ and $\text{Al}_{\text{CaCl}_2}$ (mg Al kg^{-1}) across sampling depths for the ST ($\text{Al}_{\text{CaCl}_2} = (85,221,378 \times \exp(-3.67 \times \text{pH}_{\text{CaCl}_2}))$, $r^2 = 0.94$; (b) MT ($\text{Al}_{\text{CaCl}_2} = 0.09 + (47,860,313 \times \exp(-3.56 \times \text{pH}_{\text{CaCl}_2}))$, $r^2 = 0.78$); and (c) LT ($\text{Al}_{\text{CaCl}_2} = 0.001 + (292,525 \times \exp(-2.41 \times \text{pH}_{\text{CaCl}_2}))$, $r^2 = 0.60$) experiments for the various L and G treatments measured in March 2018. The ST, MT, and LT; L and G treatments are C (●), L2.5 (▼), G2.5 (▲), and L2.5+G2.5 (◆). The additional treatments in the MT are; L5.0 (■) and L5.0+G2.5 (■); and in the LT are L2 (■) and L8 (■).

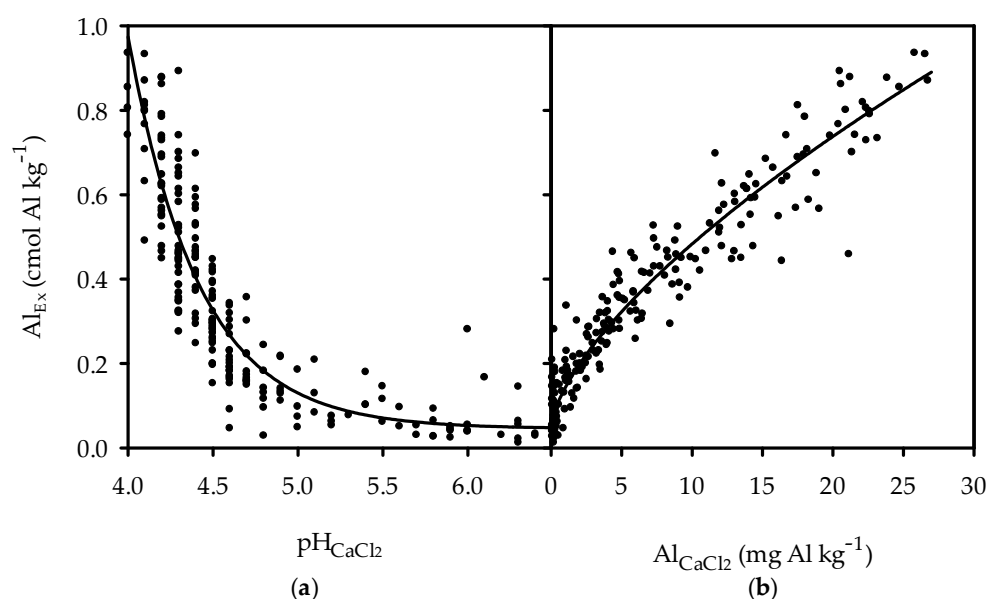


Figure 4. (a) Relationship between $\text{pH}_{\text{CaCl}_2}$ and Al_{Ex} : $\text{Al}_{\text{Ex}} = 0.04 + (13,648 \times \exp(-2.40 \times \text{pH}_{\text{CaCl}_2}))$, $r^2 = 0.82$; and (b) $\text{Al}_{\text{CaCl}_2}$ and Al_{Ex} , $\text{Al}_{\text{Ex}} = 0.05 + (0.093 \times (\text{Al}_{\text{CaCl}_2})^{0.668})$, $r^2 = 0.93$.

3.5. Effective Cation Exchange Capacity

Soil ECEC of the soil profile, in the three experiments, decreased with increasing soil depth from 1.51–2.40 cmol kg^{-1} in the 0–10 cm to 1.07–1.15 cmol kg^{-1} in the 40–50 cm soil layer (Figure 5). In the ST, soil ECEC for the L and G treatments was 44–87% greater than the C treatment in the 0–10 cm soil layer while ECEC was 16–50% greater for the L2.5 + G2.5 treatment was than the C in the 10–30 cm soil layer. In the MT, ECEC of the L5.0 + G2.5 treatment was greater than the C, L2.5, and L5.0 treatments by 27–96% in the 0–50 cm soil layer (Figure 5b). In the LT, ECEC for the L2 treatment was 56–65% greater in the 0–20 cm soil layer compared to the C treatment (Figure 5c). For the L4, L8, and L4 + G2 treatments ECEC was 90–148% greater in the 0–20 cm soil layer compared to the C treatment. Soil ECEC for the G2 treatment was the same as the C treatment.

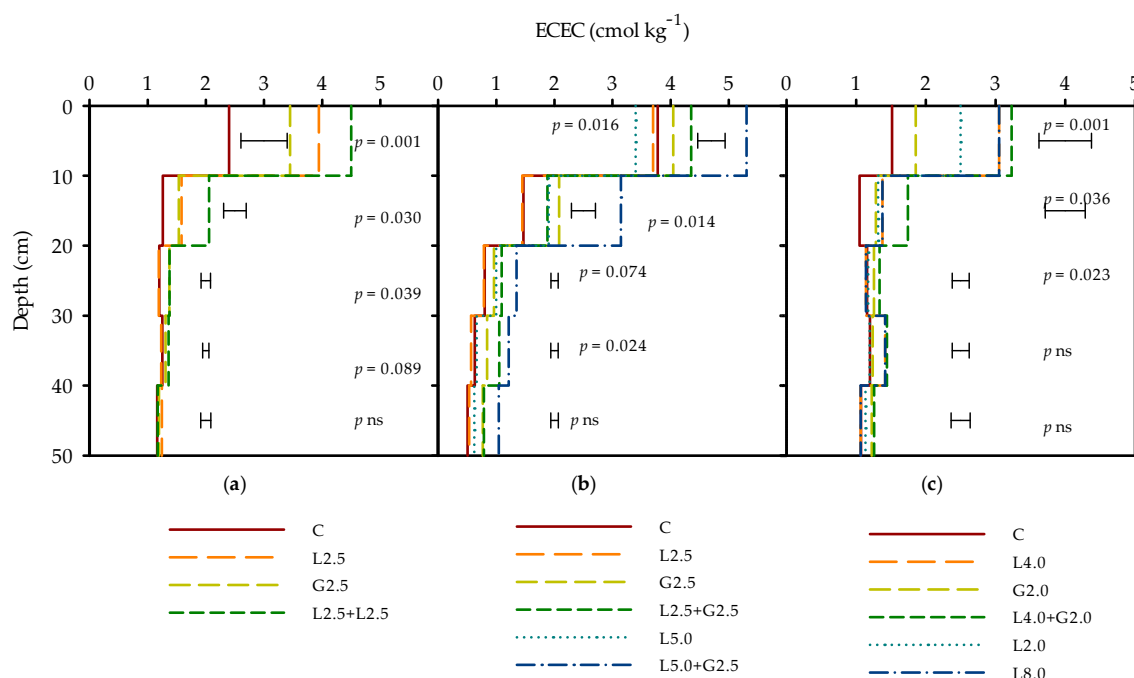


Figure 5. (a) Soil ECEC in the ST for C, L2.5, G2.5, L2.5 + G2.5 treatments, (b) in the MT for C, L2.5, G2.5, L2.5 + G2.5, L5.0, and L5.0 + G2.5 treatments; and (c) in the LT for C, L4, G2, L4 + G2, L2, and L8 treatments. Error bars represent least significant difference values at $p = 0.05$, $n = 3$ for each depth with ns denoting $p > 0.05$.

4. Discussion

4.1. Sulfate

Leaching of soil $\text{SO}_4\text{-S}$ occurs in light texture soils of South Western Australia due to the low water holding capacity of the soil profile, high June and July rainfall and limited adsorption of $\text{SO}_4\text{-S}$ [15]. The soil profile for the LT experiment had SBI of 10–14, indicating the soil has a low capacity to adsorb $\text{SO}_4\text{-S}$ [13]. The soil profiles at the other two experimental sites had a greater ability to adsorb $\text{SO}_4\text{-S}$, especially in the soil layers below 10 cm with SBI of 9–36. Due to this combination of rainfall, water holding capacity of the soil, and $\text{SO}_4\text{-S}$ adsorbing capacity, $\text{SO}_4\text{-S}$ derived from G was readily leached into and through the soil profile. In the ST experiment, $\text{SO}_4\text{-S}$ was leached rapidly into the soil profile, as measured by the increase $S_{\text{KCl}40}$ content, even after a relatively low rainfall (279 mm) growing season (Figure 1a). The increase in $S_{\text{KCl}40}$ was associated with increased EC (Figure 1g) and Al- SO_4 [24], leading to an increasing canola grain yield in the first year after application [3]. In retrospect, in the ST, to cope with the variation observed following a recent application of G, we should have collected more soil cores to define the G effect on $S_{\text{KCl}40}$ measurement accurately. In the MT and LT, the effectiveness of G declines [3] because $\text{SO}_4\text{-S}$ is leached below the 50 cm sampling depth as indicated by the low recovery of the applied $\text{SO}_4\text{-S}$ (28–54%) (Table 1).

The leaching of $\text{SO}_4\text{-S}$ can also occur within 3.5 years, even for soils with high $\text{SO}_4\text{-S}$ adsorption capacities [12]. In the LT, G application increased $S_{\text{KCl}40}$ content resulting in the retention of 26–27% of the applied $\text{SO}_4\text{-S}$ within 0–50 cm soil layer (Table 1). Retention of $\text{SO}_4\text{-S}$ was also observed in the subsoil 13 years after the G application due to the high $\text{SO}_4\text{-S}$ adsorption capacity [12]. Soils retain $\text{SO}_4\text{-S}$ by the processes of adsorption and precipitation [25]. The precipitation of Al- SO_4 is more critical in soils with high Al content which occurs in soil with $\text{pH}_{\text{CaCl}_2}$ less than 4.5 [26]. Soil with greater $\text{pH}_{\text{CaCl}_2}$ has a lower ability to adsorb $\text{SO}_4\text{-S}$ due to decreases in anion exchange capacity on variable charge surfaces [27]. Hence, L application which increases soil pH results in lower retention of $\text{SO}_4\text{-S}$ or lower $S_{\text{KCl}40}$ content in the 0–20 cm for the LT experiment (Figure 1c). We have confirmed the retention

of $\text{SO}_4\text{-S}$ as Al-SO_4 for these experiments using soil solution and modelling approach [24]. However, in the LT, the lower wheat grain yield response to the G treatment occurs over time is attributed to the leaching of $\text{SO}_4\text{-S}$ below the Al^{3+} toxic layer (10–40 cm) [3].

4.2. Calcium

In general, the effect of the application of L and G is to increase Ca_{Ex} (Figure 1d–f), and decrease Al_{Ex} (Figure 2d–f) with the net result an increase in ECEC (Figure 5a–c) [28]. Leaching of Ca derived from G and L varies according to application rates, time of contact with the soil and soil properties [17]. In these experiments, we applied Ca at different rates of L and G, and it was not possible to directly compare the leaching rates of the two Ca sources. Nevertheless, in the LT experiment, the application of L and G together resulted in an increase in soil Ca_{Ex} to a depth of 30 cm compared to only 20 cm when only L8 or G was applied (Figure 1f). Similarly, the combined application of L and G increased Ca_{Ex} to a greater depth than the use of only L or G on soils in southern Brazil [17].

4.3. Electrical Conductivity

The EC of Tenosols of South Western Australia is generally less than 0.11 dS m^{-1} due to the highly weathered and leached nature of the soil [29]. EC is an important measurement when examining subsoil Al toxicity limitations because soils with greater EC decreases Al^{3+} activity and increases ion paring, which together makes the solution Al^{3+} less toxic [30]. For example, soils with greater EC have a lower critical $\text{Al}_{\text{Ex}}\%$ value [31]. In the three present experiments, EC was less than 0.07 dS m^{-1} in the soil profile (Figure 1g–i). The critical range for tolerant wheat cultivars to achieve 90% of maximum grain yield is between 21–32 $\text{Al}_{\text{Ex}}\%$, which is equivalent to $\text{Al}_{\text{CaCl}_2}$ of 3.9–7.0 mg Al kg^{-1} (Figure 4b). For the three experimental sites, $\text{Al}_{\text{Ex}}\%$ for the sampling depth 10–30 cm ranged between 10–59% indicating Al toxicity at levels that would reduce wheat grain yield. In these experiments, the application of G increased soil EC to $\geq 0.07 \text{ dS m}^{-1}$ in the 0–30 cm soil layer in the ST (Figure 1g). This increase in EC reduced the critical range 13–21 $\text{Al}_{\text{Ex}}\%$, which is equivalent to $\text{Al}_{\text{CaCl}_2}$ of 2.0–3.9 mg kg^{-1} and is more consistent with the critical range observed by [2]. The increase in EC due to G application is, therefore, likely to have contributed to reducing the adverse effects of subsoil Al^{3+} toxicity and increased grain yield [3].

4.4. Aluminum and pH

Leaching of alkalinity derived from dissolved L occurs when $\text{pH}_{\text{CaCl}_2}$ of the 0–10 cm soil layer is greater than 5.5 [32]. When L is applied, both Ca, and Mg cations are leached, suggesting the ions are moving as Ca and Mg bicarbonate [12]. Once $\text{pH}_{\text{CaCl}_2}$ of the 0–10 cm soil layer has achieved a $\text{pH}_{\text{CaCl}_2}$ of 7.1, L will stop dissolving [33,34]. Due to this restriction on L dissolution, the pool of alkalinity available to be leached into the subsoil is insufficient for the L application to have an impact on subsoil pH [2,32,35,36]. In the ST and MT experiments, $\text{pH}_{\text{CaCl}_2}$ in the 0–10 cm soil layer was greater than 5.5, and the application of additional L resulted in no impact on subsoil $\text{pH}_{\text{CaCl}_2}$ over the sampling period of two years and eight months. In the LT, a high rate of L application ($4\text{--}8 \text{ t ha}^{-1}$) increased $\text{pH}_{\text{CaCl}_2}$ in the 10–20 cm soil layer while 2 t L ha^{-1} did not affect subsoil $\text{pH}_{\text{CaCl}_2}$ (Figure 2i). This observation is consistent with other studies that have shown L application can be slow or in some cases, ineffective in increasing subsoil $\text{pH}_{\text{CaCl}_2}$ [2,35,36].

There are a diverse array of chemical reactions that can arise when G is applied, resulting in a change in soil pH [37]. In soils with a high capacity for $\text{SO}_4\text{-S}$ sorption, the net effect is an increase in soil $\text{pH}_{\text{CaCl}_2}$ [12]. In contrast, the LT experiment soil profile has an SBI of 10–14, indicating a low ability to sorb $\text{SO}_4\text{-S}$, [3]. Hence, the net effect of G application on the low SBI was no significant impact on soil $\text{pH}_{\text{CaCl}_2}$ in the 10–30 cm soil layer (Figure 2i). Nevertheless, small changes in the $\text{pH}_{\text{CaCl}_2}$ within the range of 4.3–4.5 can result in significant changes in $\text{Al}_{\text{CaCl}_2}$ (Figure 4). However, in this case, G application did not affect $\text{Al}_{\text{CaCl}_2}$ compared to the C treatment in the 10–20 cm soil layer (Figure 2c).

Application of L to the soil surface resulted in a more significant decline in soil Al values (Al_{CaCl_2} and Al_{Ex}) than the increase in pH_{CaCl_2} in the soil layers below 10 cm because there is an exponential relationship between pH_{CaCl_2} and these soil Al measurements (Figures 3 and 4a). Hence, for small changes in pH_{CaCl_2} below 4.5, there is a greater change in Al_{CaCl_2} and Al_{Ex} . Therefore, both Al_{CaCl_2} and Al_{Ex} are a more sensitive measurement of the impact of L application on soil properties than pH_{CaCl_2} . For example in the LT experiment, L8 resulted in a 50–92% decrease in the Al_{CaCl_2} content to a depth of 40 cm (Figure 2c) compared to pH_{CaCl_2} which only increased from 4.6 to 5.1 in the 10–20 cm soil layer (Figure 2i). Furthermore, in the MT experiment, the L2.5 + G2.5 treatment resulted in a 54–84% reduction in soil Al_{CaCl_2} in the soil layers 20–50 cm (Figure 2e) and no effect subsoil pH_{CaCl_2} (Figure 2h). These observations are consistent with other experiments that observed the application of L decreased Al_{Ex} to a greater depth than the decrease in pH_{CaCl_2} [38–40]. For example, in an experiment monitored over time, application of 6 t L ha⁻¹ increased pH_{CaCl_2} in the 10–20 cm soil layer by 0.2–0.4 pH units after 2.5 years with the effect remaining constant over time while Al_{Ex} decrease by 55% after 2.5 years and to 68% after ten years [41]. However, reductions in Al_{CaCl_2} and Al_{Ex} observed for the L8 treatment did not increase crop grain yield compared to the L2 treatment [3].

An effective LT strategy is to apply sufficient L to maintain the soil pH_{CaCl_2} of the 0–10 cm greater than 5.5 because it will maximize the impact that a surface L application will have on the subsoil Al toxicity content [32]. In the LT experiment, 4–8 t L ha⁻¹ resulted in a pH_{CaCl_2} of greater than 6.1 in the 0–10 cm soil layer measured in March 2018, but the treatments did not affect pH_{CaCl_2} in the 20–30 cm soil layer (Figure 2c). In contrast, L and G have a synergistic effect on soil Al toxicity by increasing alkalinity leaching as indicated by a more significant decline in Al_{CaCl_2} and Al_{Ex} in the MT (Figure 2b,e). In retrospect, to account for the high variability, we should have collected more soil cores than 4 to define this effect better. In the LT experiment, the L4 + G2 treatment resulted in a greater and deeper decline in Al_{CaCl_2} and Al_{Ex} compared to the L4 treatment (Figure 2c,f). Other researchers have also hypothesized the combined application of L and G could have a synergistic effect in improving soil chemical properties and crop grain yields as observed by for highly acidic subsoil [6,42,43]. However, the response was not consistent between sampling years at another experiment conducted located near the ST experimental site [6]. Additionally, in high rainfall subtropical region, the combined use of L and G had no synergistic effect in improving soil chemical properties and crop grain yields [44]. In that agricultural system and soil, surface application of L was effective in increasing pH measured using water as the extracting solution to a depth of 60 cm within the first year. In contrast, in the South Western Australia agricultural region L application can be ineffective in increasing subsoil pH_{CaCl_2} [2]. Hence, the synergistic L and G effect in improving soil chemical properties and crop grain yields could play a significant role in South Western Australia. However, further research is required to examine the combination of soil and growing environments where this effect occurs.

5. Conclusions

The combined application of lime and gypsum is more effective than applying lime alone in managing subsoil Al constraints for crop production in the short-term (1 year) due to the increased soil sulfate, calcium and electrical conductivity of the subsoil with the application of gypsum even following relatively dry year (279 mm). Use of lime and gypsum together in the medium-term (two years and eight months) and long-term (ten years) lead to a decrease in soil Al, to a greater depth than the application of lime only. The impact of broadcast lime plus gypsum and lime alone resulted in changes in subsoil Al measurements to a greater depth than changes in soil pH, indicating soil Al measurements are more sensitive than soil pH measurements.

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