



Article

Short- and Long-Term Effects of Lime and Gypsum Applications on Acid Soils in a Water-Limited Environment: 3. Soil Solution Chemistry

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Abstract: Aluminum (Al) toxicity imposes a significant limitation to crop production in South Western Australia. This paper examines the impact of surface-applied lime and gypsum on soil solution chemistry in the short term (1 year) and the long-term (10 years) in water limited environments. In the experiments, we measured soil solution chemistry using a paste extract on soil profile samples collected to a depth of 50 cm. We then used the chemical equilibrium model MINTEQ to predict the presence and relative concentrations of Al species that are toxic to root growth (Al associated with Al^{3+} and $AlOH^2$ or Toxic-Al) and less non-toxic forms of Al bound with sulfate, other hydroxide species and organic matter. A feature of the soils used in the experiment is that they have a low capacity to adsorb sulfate. In the short term, despite the low amount of rainfall (279 mm), sulfate derived from the surface gypsum application is rapidly leached into the soil profile. There was no self-liming effect, as evidenced by there being no change in soil solution pH. The application of gypsum, in the short term, increased soil solution ionic strength by 524–681% in the 0–10 cm soil layer declining to 75–109% in the 30–40 cm soil layer due to an increase in soil solution sulfate and calcium concentrations. Calcium from the gypsum application displaces Al from the exchange sites to increase soil solution Al activity in the gypsum treatments by 155–233% in the short term and by 70–196% in the long term to a depth of 40 cm. However, there was no effect on Toxic-Al due to Al sulfate precipitation. In the long term, sulfate leaching from the soil profile results in a decline in soil solution ionic strength. Application of lime results in leaching of alkalinity into the soil profile leading to a decreased Toxic-Al to a depth of 30 cm in the long term, but it did not affect Toxic-Al in the short term. Combining an application of lime with gypsum had the same impact on soil solution properties as gypsum alone in the short term and as lime alone in the long term.

Keywords: aluminum species; calcium; ionic strength; pH; soil acidity; soil solution; sulfate



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1. Introduction

Aluminum (Al) toxicity results in reduced crop yields when subsoil layers, layers below 10 cm, have 0.01 M $CaCl_2$ extractable Al (Al_{CaCl_2}) concentrations greater than 2.5–4.5 mg Al kg^{-1} [1]. The use of lime (L, $CaCO_3$) and gypsum (G, $CaSO_4$) applications reduces subsoil Al toxicity resulting in increased crop grain yield [2–5]. Gypsum use can be more profitable than L application in overcoming subsoil Al toxicity in the South Western Australia agricultural region's low rainfall zone in the short term. This is due to G having comparatively higher solubility than L and the low sulfate (SO_4-S) sorption properties of some soils in this region [5]. The limited SO_4-S sorption combined with high June and July

rainfall results in rapid leaching of applied $\text{SO}_4\text{-S}$ and no appreciable self-liming effect on soil pH [6–8].

The current recommendation for managing subsoil Al toxicity is to apply sufficient L to maintain the $\text{pH}_{\text{CaCl}_2}$ (pH measured using 0.01 M CaCl_2) in the 0–10 cm layer greater than 5.5 [9]. However, the surface L application only creates a relatively small pool of alkalinity in the 0–10 cm layer because L stops dissolving at a pH of 7.1 [10], resulting in slow leaching of dissolved L into the subsoil [11]. Gypsum is more soluble than L (2.1 gm G L^{-1} compared to 0.013 gm L L^{-1} [12,13]. Hence, $\text{SO}_4\text{-S}$ and calcium (Ca) derived from G are leached more rapidly into the subsoil than alkalinity derived from L [8,14]. The greater $\text{SO}_4\text{-S}$ and Ca content of the soil results in higher ionic strength (IS), which lessens the soil Al toxic effect on root growth [15]. In soil, solution studies express Al toxicity as Al activity (Al_{Act}) as opposed to the concentration of Al in solution (Al_{Soln}) to account for the impact of other solution ions [16]. The reduction in subsoil Al toxicity has been shown to increase crop grain yields, often within the G application year [2,3,5]. However, the leaching of $\text{SO}_4\text{-S}$ below the Al toxicity layer reduces the effectiveness of G over time [5,8].

The application of G increases soil solution Ca concentration (Ca_{Soln}), which can result in the displacement of Al^{3+} and H^+ from the exchange sites leading to an increase in Al soil solution concentrations (Al_{Soln}) [16,17]. In contrast, we observed no increase in $\text{Al}_{\text{CaCl}_2}$ extraction when G was applied to the soil due to the lower sensitivity of the $\text{Al}_{\text{CaCl}_2}$ measurement compared to the soil solution measurement [8]. Application of G results in two possible reactions that can change soil pH [18]. First, the increase in soil solution $\text{SO}_4\text{-S}$ concentration ($\text{SO}_4\text{-S}_{\text{Soln}}$) increases $\text{SO}_4\text{-S}$ sorption resulting in the displacement of OH^- , which produces an associated increase in soil pH and cation exchange capacity (CEC) [19]. Second, G application can decrease soil pH due to the release of H^+ (or adsorption of OH^-) as a result of surface charge increase through the effects of increased IS_{Soln} [20].

The soil solution's chemical composition is used to determine L and G's impact on Al species distribution [21–23] using chemical equilibrium models such as MINTEQ [24,25]. The speciation of Al_{Act} is dependent on soil solution pH_{Soln} , chemical equilibrium reactions in the soil solution, and surface dissolution reactions of the soil minerals [26]. The model MINTEQ can undertake these calculations because stability constants for modelling Al–inorganic complexes are well characterized [22,27]. In soils, the most plant toxic Al species is $\text{Al}(\text{H}_2\text{O})_6^{3+}$, which is often abbreviated to Al^{3+} [28,29]. Depending on the soil pH, Al^{3+} undergoes hydrolysis which breaks the H–O bond leading to the release of hydrogen ion and the formation of the amorphous Al hydroxide species, including AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$ [22,23]. Below $\text{pH}_{\text{CaCl}_2}$ of 5.0, Al^{3+} , AlOH^{2+} , and AlSO_4^+ are present, while $\text{Al}(\text{OH})_2^+$ occurs at low concentrations and neither $\text{Al}(\text{OH})_4^-$ nor $\text{Al}(\text{OH})_3$ are present [21]. The toxic Al species (Toxic-Al) for root growth are Al^{3+} and AlOH^{2+} [30,31]. In contrast, the non-toxic species are $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, AlSO_4^+ , $\text{Al}(\text{SO}_4)_2^-$, and AlHSO_4^+ [30,31]. Application of L, which results in soil pH increasing above 5.0, will remove Toxic-Al. In contrast, at soil pH below 5.0, G application results in a portion of the Toxic-Al forming non-toxic $\text{SO}_4\text{-Al}$ [2,6,32].

Aluminum can form complexes in solution with fluoride, phosphate, and dissolved organic carbon (DOC_{Soln}) which are not toxic to plants [22,23,33,34]. An empirical equation can calculate the organically bound Al (Org-Al) concentration based on measured values for DOC_{Soln} , Al_{Soln} , and pH_{Soln} [35]. While MINTEQ version 3.1 can provide a more accurate soil solution prediction, organically bound Al [24] than the empirical equation of [35], which is limited to a narrow pH range [24]. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used to measure Al in soil extraction solutions. Due to the very high temperatures in the plasma of an ICP-AES, the method measures total Al in the solution, including both inorganic and organically bound Al [36]. Therefore, inorganic Al concentration in the soil solution (Al_{Inorg}) is equal to Al_{Soln} measured by ICP-AES minus Org-Al. The Al_{Act} critical value range or Al_{Act} associated with 90% of relative plant growth is 40–150 $\mu\text{mol L}^{-1}$ for surface soils [36] and 10–90 $\mu\text{mol L}^{-1}$ for subsoils [30,37]. For more tolerant crops such as maize, the reduction in root and shoot biomass growth happens

when the Al_{Act} is greater than $480 \mu\text{mol L}^{-1}$ [38], while for less tolerant crops, there is a lower critical value of $100 \mu\text{mol L}^{-1}$ for mung bean [39] and for $9\text{--}15 \mu\text{mol L}^{-1}$ for white clover [40].

The paper aims to examine the impact of a factorial combination of L and G applications on soil solution chemical properties and Al speciation in the short term (ST, one year) and the long term (LT, 10 years). The soil profiles have a low $SO_4\text{-S}$ adsorption capacity or a sulfate buffer index (SBI) of <35 [5,6]. Previous papers in this series have highlighted the impact of these treatments on crop grain yield, nutrient concentration and soil chemical properties [5,8]. We hypothesize that soil solution measurements will provide greater insight into the soil chemical reactions than soil test measurements, which occur due to G and L application to soils with a low SBI and hence explain the crop yield responses observed by [5].

2. Materials and Methods

2.1. Field Experimental Sites

This paper reports soil solution chemistry obtained from the ST and LT, which have received a factorial combination of L and G application presented by [5]. The first experiment was a ST trial located near South Burracoppin ($-31^{\circ}30'9''$ S latitude, $118^{\circ}38'50''$ E longitude), which had $2\text{--}4 \text{ t L ha}^{-1}$ applied in the 15 years prior to the experiment. At Bonnie Rock ($-30^{\circ}37'3''$ S latitude, $118^{\circ}14'9''$ E longitude), the second experiment was a LT experiment on a site with no previous L use. The soil type for both sites was a Tenosol according to the Australia Soil Classification System or Arenosols under the World Reference Base for Soil Resources [41]. At the Bonnie Rock site, the gravel content increased with increasing soil depth [5]. Both experiments consisted of small plots of 1.8 m by 20 m arranged in a complete randomized block design with three replications.

2.2. Soil Measurements

We measured soil solution chemical properties on soil samples collected to a depth of 50 cm, in increments of 10 cm on 20–22 March 2018. For the ST experiment, we collected soil samples from the control (C), 2.5 t L ha^{-1} (L2.5), 2.5 t G ha^{-1} (G2.5), $2.5 \text{ t L + G ha}^{-1}$ (L2.5 + G2.5) treatments applied on 31 March 2017. For the LT experiment, we used the control (C), 4 t L ha^{-1} (L4), 2 t G ha^{-1} (G2), and $4 \text{ t L ha}^{-1} + 2 \text{ t G ha}^{-1}$ (L4 + G2) treatments with half of these rates (2 t L ha^{-1} and 1 t G ha^{-1}) in March 2008 and the other half in March 2013. When we present the two experimental sites, the factorial treatment abbreviations used are C, L, G, and L + G. More details of the soil sampling procedures are given in [5,8].

Previous researchers extracted soil solution from air-dry soil that had been wet to a tension of 0.1 bar and centrifuged at a force $9009 \times g$ for 45 min [42]. Our initial aim was to remove the soil solution using this approach. However, we were only able to extract a small volume of soil solution, which was insufficient to undertake all of the measurements. Also, we had a limited amount of soil sample available to do the soil solution extractions. Hence, we used a saturated paste extract with a solution to soil ratios (ml water to g soil) of 0.4:1.0 for the 0–10 and 10–20 cm layers and 0.35:1.0 for the other sampling three depths between 20 and 50 cm. We used different ratios due to greater water retention by the 0–20 cm samples compared to the 20–50 cm samples. We acknowledge the best method to extract soil solution is provided by [42]. However, we note other Al_{Soln} chemical species studies have used water extracts using a range of solution to soil ratios of 1:1, 0.40:1, 0.20:1, and 0.10:1 [42–44] because it is difficult to measure the true soil solution [42].

The water extraction procedure involved weighing 200 g of soil into a 500 mL beaker. We then added 80 gm of Milli-Q[®] water to the 0–10 and 10–20 cm and 70 gm to the below 30 cm soil samples. We then covered the beakers with glad wrap to stop evaporation loss and incubated them for 16 h at 25°C . We then extracted the soil solution by centrifuging the soil for 10 min at $9223 \times g$, followed by filtration using a $0.45 \mu\text{m}$ cellulose membrane.

We then measured the following chemical properties of the saturated paste extract solution which from this point onwards we refer to as the “soil solution”. The solution’s

alkalinity (Alk_{Soln}) is the amount of acid (mg L^{-1}) required to lower $\text{pH}_{\text{CaCl}_2}$ to 4.3 [45]. We used ICP-AES, which measures the total concentration (mg L^{-1}) of the following ions in solution; Al_{Soln} , Ca_{Soln} , iron, potassium, magnesium, sodium, phosphate, $\text{SO}_4\text{-S}_{\text{Soln}}$, silicon. We measured redox potential (mV), pH_{Soln} , and fluoride concentration using an ion-specific electrode. Nitrogen concentration (mg L^{-1}) as ammonium and nitrate was measured colorimetrically [45]. Dissolved organic carbon in the soil solution (DOC_{Soln}) concentration (mg L^{-1}) was determined using a modified [46] method for soil solution using a sample size of 5 mL. We have compared soil solution measured (pH_{Soln} , Al_{Act} , Ca_{Soln} and $\text{SO}_4\text{-S}_{\text{Soln}}$) to the corresponding soil chemical measurements $\text{pH}_{\text{CaCl}_2}$, $\text{Al}_{\text{CaCl}_2}$, (pH and Al extracted by 0.01 M CaCl_2) and exchangeable Al_{Ex} and Ca_{Ex} measured by [47], and $\text{SO}_4\text{-S}$ removed by 0.25 M KCl heated at 40 °C for three hours (S_{KCl40}) [48].

Using a greater solution to soil ratios than the method recommended by [42] dilutes the extracted ion's concentration. In acidic soils, water stress resulted in the greater appearance of Al toxicity symptoms in roots than for the treatments without water stress [43], suggesting a rapid increase in the Al concentration in the soil solutions with decreasing soil water [49]. We confirmed this observation in a small incubation experiment using five solutions to soil ratios ranging from 0.2:1.0 to 0.5:1.0 decrease Al concentration from 1.6 to 0.9 mg L^{-1} . Hence, we calculated ion concentrations at a water content of 0.14 L kg^{-1} for the 0–10 cm layer and 0.10 L kg^{-1} for the layers below 10 cm, or the drainage-upper limit observed in Tenosols [50].

2.3. Ionic Strength

The IS_{Soln} (mmol L^{-1}) was calculated from the electrical conductivity (EC) measurements using the formula of [42]:

$$\text{IS}_{\text{Soln}} = ((0.0446 \times \text{EC}) - 0.000173) \times 1000, \quad (1)$$

where EC is the electrical conductivity (dS m^{-1}) measured in a 1:5 soil to water solution.

Al concentration is expressed in soil solution studies as the Al ion activity in the soil solution [51]. The activity of Al in the soil solution (Al_{Act}) is the product between Al_{Soln} and activity coefficient (y_i):

$$\text{Al}_{\text{Act}} = \text{Al}_{\text{Soln}} \times y_i, \quad (2)$$

Debye-Huckel's equation is used to calculate the activity coefficient (y_i) [27]:

$$\text{Log}(y_i) = -A \times Z_i^2 \times \mu^{1/2}, \quad (3)$$

where $A = 0.509$ for pure water at 25 °C; Z_i = ion valency charge; $\mu = \text{IS}_{\text{Soln}}$.

2.4. Aluminum Species

The measured values for DOC_{Soln} , Alk_{Soln} , pH_{Soln} , Al_{Soln} , Ca_{Soln} , and $\text{SO}_4\text{-S}_{\text{Soln}}$ were used as inputs for the chemical equilibrium model, MINTEQA2 version 3.1 to predict the composition of chemical species [25]. Since soil solution Al was measured using an ICP-AES, it represents the total concentration in the soil solution (Total- Al) or inorganic Al (Inorg- Al) plus organic Al (Org- Al) [36]. To account for this effect, we calculated Org- Al using the equation of [35]. We then calculated Inorg- Al as Total- Al minus Org- Al . We then entered Inorg- Al into MINTEQA2, as the input Al concentration input and used the Gaussian dissolved organic matter model to calculate Org- Al [25,52]. The model inputs predicted a charge balance difference of less than 10%, indicating that MINTEQA2 provides an accurate prediction of Al species. The Al species, Org- Al , Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, AlSO_4^+ , $\text{Al}(\text{SO}_4)_2^-$, and AlHSO_2^+ were generated from the MINTEQA2 model. We then grouped these species as follows: (1) Org- Al , (2) Toxic- Al as Al^{3+} (3) OH- Al as AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and (4) $\text{SO}_4\text{-Al}$ as AlSO_4^+ , $\text{Al}(\text{SO}_4)_2^-$, and AlHSO_2^+ . We present the results as Al species activities ($\mu\text{mol L}^{-1}$). The fluoride and phosphate concentrations were below the detection limits. We did not use the concentration

(mg L^{-1}) of iron, potassium, magnesium, sodium, ammonium, nitrate, and silicon to run the model because these ions are not associated with Al species and including these measurements resulted in a charge difference of greater than 10%. We then present Org-Al, Toxic-Al, OH-Al, and SO_4 -Al species in the paper's Results and Discussion sections.

2.5. Statistical Analysis

Analysis of variance (ANOVA) to determine the significance of treatments effects on the soil solution chemical properties within soil layers of the soil profile to a sampling depth of 50 cm was done using Genstat[®] [53]. We report treatment responses if the treatment resulted in a change in the soil solution measurement of greater than the least significant difference values determined at $p = 0.05$.

We used the SigmaPlot[®] version 12.5 [54] regression wizard to define relationships between soil and soil solution measures. Linear equation ($y = a + [b \times x]$) were fitted for most relationships. The exception was the use of exponential equations to define the relationship between S_{KCl40} and $\text{SO}_4\text{-S}_{\text{Soln}}$ ($\text{SO}_4\text{-S}_{\text{Soln}} = a + b \times [1 - \exp[-c \times S_{\text{KCl40}}]]$) and between $\text{pH}_{\text{CaCl}_2}$ and Al_{Soln} ($\text{Al}_{\text{Soln}} = a + b \times \exp(-c \times \text{pH}_{\text{CaCl}_2})$).

3. Results

3.1. Soil Solution Measurement

The C treatment's soil profile $\text{SO}_4\text{-S}_{\text{Soln}}$ values decreased with increasing depth in both the ST and LT experiments (Figure 1a,b). In the ST experiment, $\text{SO}_4\text{-S}_{\text{Soln}}$ declined from 137 mg L^{-1} in the 0–10 to 36 mg L^{-1} in the 40–50 cm layer. In the LT experiment, $\text{SO}_4\text{-S}_{\text{Soln}}$ values decreased from 61 mg L^{-1} in the 0–10 to 15 mg L^{-1} in the 40–50 cm layer. Only where G was applied was there an increase in $\text{SO}_4\text{-S}_{\text{Soln}}$ in these experiments. In the ST, G2.5 application increased $\text{SO}_4\text{-S}_{\text{Soln}}$ by 859–1329% in the 0–20 cm layer but only by 92–118% in the 40–50 cm layer (Figure 1a). In the LT, the G2 treatment increased $\text{SO}_4\text{-S}_{\text{Soln}}$ by 681% in the 0–10 cm layer, which was 123% greater than $\text{SO}_4\text{-S}_{\text{Soln}}$ for the L4 + G2 treatment (Figure 1b). The G2 and L4 + G2 treatments also increased $\text{SO}_4\text{-S}_{\text{Soln}}$ by 244–408% in the 10–30, which declined to 92–118% in the 40–50 cm layer. $\text{SO}_4\text{-S}_{\text{Soln}}$ was lower for the L + G treatment than the L treatment in the 0–10 cm layer.

For the C treatment, Ca_{Soln} decreased with increasing depth for both the ST and LT experiments (Figure 1c,d). Ca_{Soln} declined from 288 mg L^{-1} in the 0–10 cm to 41 mg L^{-1} in the 40–50 cm layer in the ST experiment. In the LT experiment, Ca_{Soln} decrease from 197 mg L^{-1} in the 0–10 cm to 43 mg L^{-1} in the 40–50 cm layer. Only G application increased Ca_{Soln} in these experiments. In the ST, G2.5 application increased Ca_{Soln} by 493–1124% in the 0–20 cm layer, but only by 84–120% in the 40–50 cm layer (Figure 1c). In the LT, G2.0 application increased Ca_{Soln} by 493–1124% in the 0–20, and by 208–244% in the 30–40 cm layer (Figure 1d).

The C treatment's IS_{Soln} values were $2.3\text{--}2.5 \text{ mmol L}^{-1}$ in the 0–10 cm layer and $1.1\text{--}1.5 \text{ mmol L}^{-1}$ in the 10–50 cm layer in both the ST and LT experiments (Figure 1e,f). Only G application increased IS_{Soln} in these experiments. In the ST, IS_{Soln} was greater for the G2.5 treatments than the C by 524–681% in the 0–10 cm layer, declining to a 75–109% increase in the 30–40 cm layer (Figure 1e). The IS_{Soln} for the L2.5 ($1.4\text{--}3.1 \text{ mmol L}^{-1}$) was the same as the C treatment for all layers. In the LT, IS_{Soln} for the G2 treatment was 192% greater than the C in the 0–10 cm layer (Figure 1f). The IS_{Soln} for the G2 and L4 + G2 treatments was 41–99% greater than the C in the 10–50 cm layer. For the L4 treatment, IS_{Soln} was the same as the C treatments in all layers.

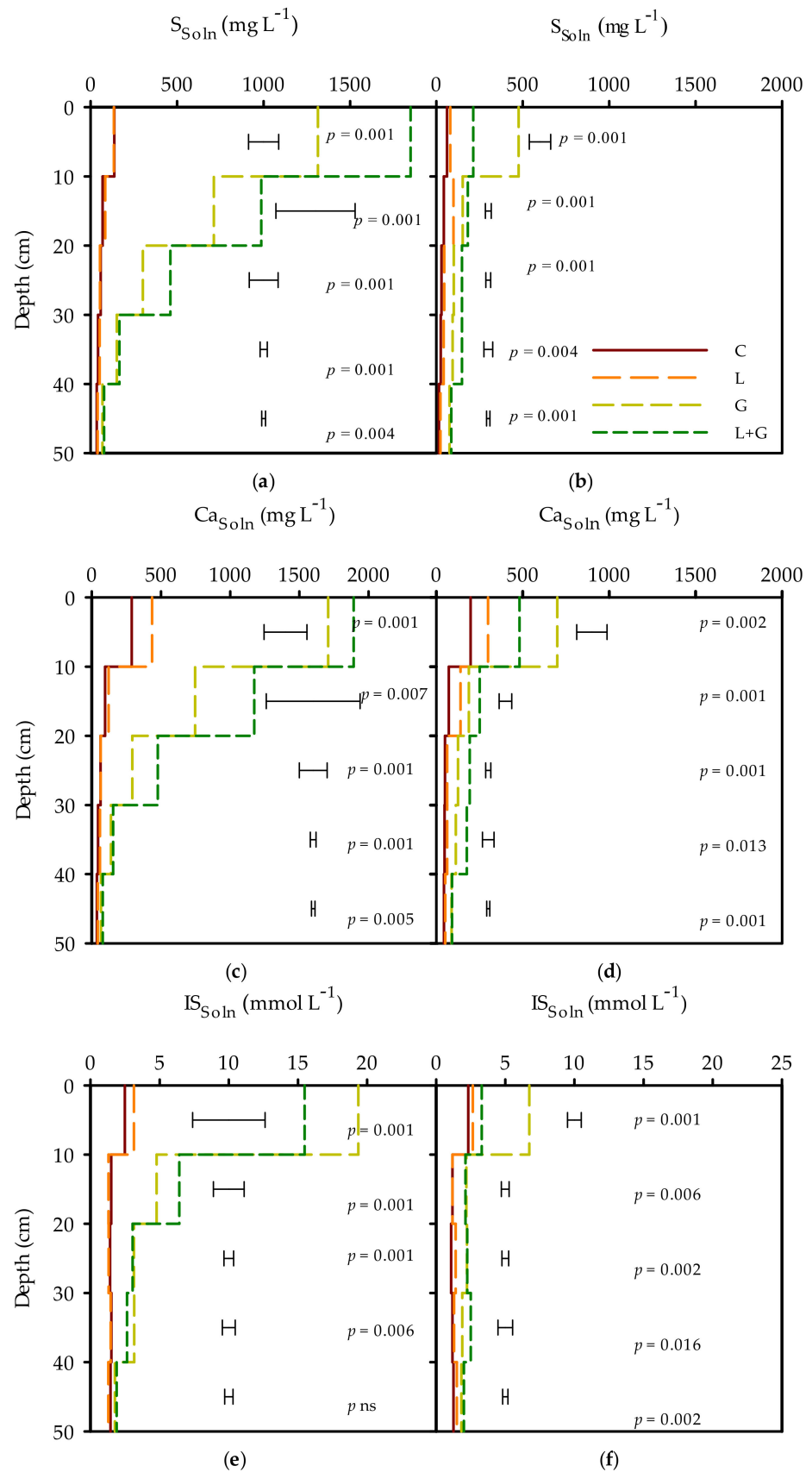


Figure 1. (a,b) The soil solution sulfate ($\text{SO}_4\text{-S}_{\text{Soln}}$ mg L^{-1}), (c,d), calcium (Ca_{Soln} , mg L^{-1}), and (e,f) ionic strength (IS_{Soln} mmol L^{-1}), (a,c,e) in the ST (b,d,f) and LT (b,d,f) for the C, L, G, and L + G treatments. The error bars represent least significant difference values at $p = 0.05$, $n = 3$ for each depth with ns denoting $p > 0.05$.

In the ST experiment, Al_{Act} for the C treatment was $4 \mu\text{mol L}^{-1}$ in the 0–10 cm but much greater ($65\text{--}83 \mu\text{mol L}^{-1}$) in the 10–50 cm layer (Figure 2a). In the LT experiment, the highest soil Al_{Act} for the C treatment of $65 \mu\text{mol L}^{-1}$ occurred in the 10–20 cm layer (Figure 2b). Al_{Act} was also relatively high ($36\text{--}33 \mu\text{mol L}^{-1}$) in the 0–10 and 20–30 cm layer but lower ($13 \mu\text{mol L}^{-1}$) in the 30–50 cm layer. The application of G increased Al_{Act} in both the ST and LT, while L application resulted in a decrease in Al_{Act} in the LT. In the ST, Al_{Act} for the G2.5 treatment was 233% greater than the C in the 20–30 cm layer (Figure 2a). Also, Al_{Act} for the G2.5 and L2.5 + G2.5 treatments was 155–157% greater than the C in the 30–40 cm layer. In the LT, Al_{Act} for the L4 and L4 + G2 treatments was 67–96% lower than the C treatment in the 0–20 cm layer. In contrast, for the G2 treatment, Al_{Act} was greater by 70–89% in the 0–20 cm layer and by 100–196% in the 20–40 cm layer (Figure 2b). Al_{Act} for the L4 + G2 treatment was the same as the L4 treatments in the 0–50 cm layer.

In the ST experiment, pH_{Soln} for the C treatment was 6.7 in the 0–10 cm. The pH_{Soln} was lower (4.4–4.9) in the 10–50 cm layer (Figure 2c). In the LT experiment, pH_{Soln} for the C treatment ranged within 4.3 to 4.6 in the 0–50 cm layer with the lowest pH_{Soln} existing in the 10–30 cm layer (Figure 2d). Only L application increased pH_{Soln} in these experiments. The L and L + G treatments increased pH_{Soln} from 5.4 to 6.9–7.4 in the ST and from 4.6 to 6.9 in the LT (Figure 2c,d). In the LT, pH_{Soln} in the 10–20 cm layer for the L4 and L4 + G2 treatments was 5.7 compared 4.3 for the C treatment, which not significant due to the high variability in pH_{Soln} observed for this layer. In contrast, G2 application did not affect pH_{Soln} in either experiment.

The Alk_{Soln} value for the C treatment was 3.3 mg L^{-1} in the 0–10 cm layer for the ST experiment. Lower Alk_{Soln} values ($0.2\text{--}0.6 \text{ mg L}^{-1}$) existed in the 10–50 cm layers of the ST experiment and the 0–50 cm layers of the LT experiment (Figure 2e,f). In these experiments, L and L + G application increased Alk_{Soln} . In the ST, the Alk_{Soln} for the L2.5 and L2.5 + G2.5 treatments was 275–388% greater in the 0–10 cm layer than the C treatment (Figure 2e). In the LT, Alk_{Soln} for the L4 and L4 + G2 treatments was 275–388% greater than the C treatment in the 0–10 cm layer (Figure 2f). In contrast, G application alone did not affect Alk_{Soln} in either experiment.

The highest DOC_{Soln} ($14\text{--}31 \text{ mg L}^{-1}$) appeared in the 0–10 cm layer with lower ($4\text{--}9 \text{ mg L}^{-1}$) DOC_{Soln} in the 10–50 cm layer for both experiments (Figure 3a,b). Application of L and G increased in DOC_{Soln} in the ST experiment. In the ST, the L2.5 and G2.5 treatments increased DOC_{Soln} by 65% in the 0–10 cm layer, while the L2.5 + G2.5 treatment increased the DOC_{Soln} by 110% compared to the control treatment (Figure 3a). In the LT, the L4, G2, and L4 + G2 treatments may have increased DOC_{Soln} in the 0–20 cm layer, but this difference was not significant due to the large variation in DOC_{Soln} at the site (Figure 3b).

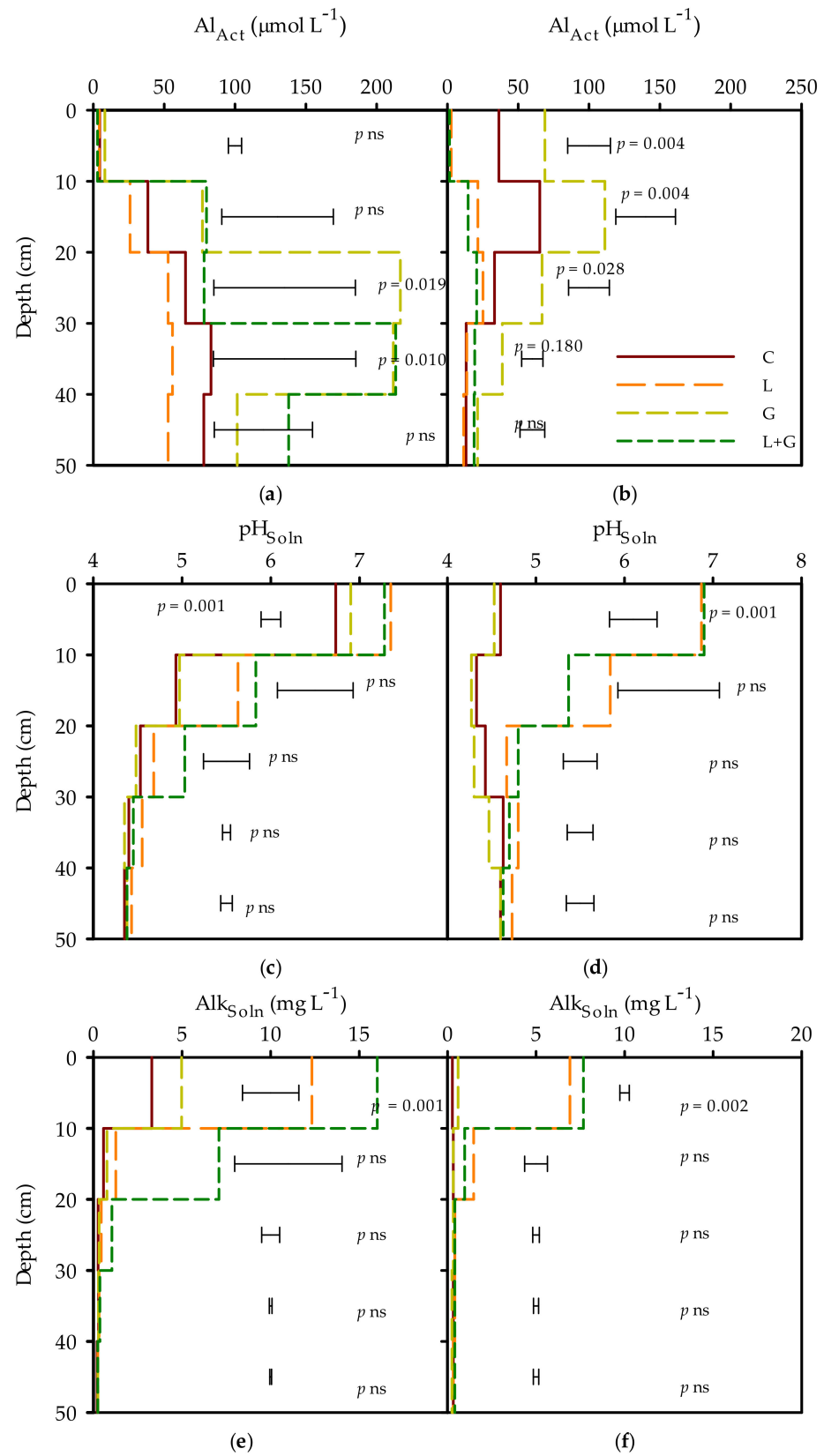


Figure 2. (a,b) The soil solution Al activity (Al_{Act}) ($\mu mol L^{-1}$), (c,d), pH (pH_{Soln}), and (e,f) alkalinity (Alk_{Soln}) ($mg L^{-1}$), (a,c,e) in the ST (b,d,f) and LT (b,d,f) for the C, L, G, and L + G treatments. The error bars represent the least significant difference values at $p = 0.05$, $n = 3$ for each depth with ns denoting $p > 0.05$.

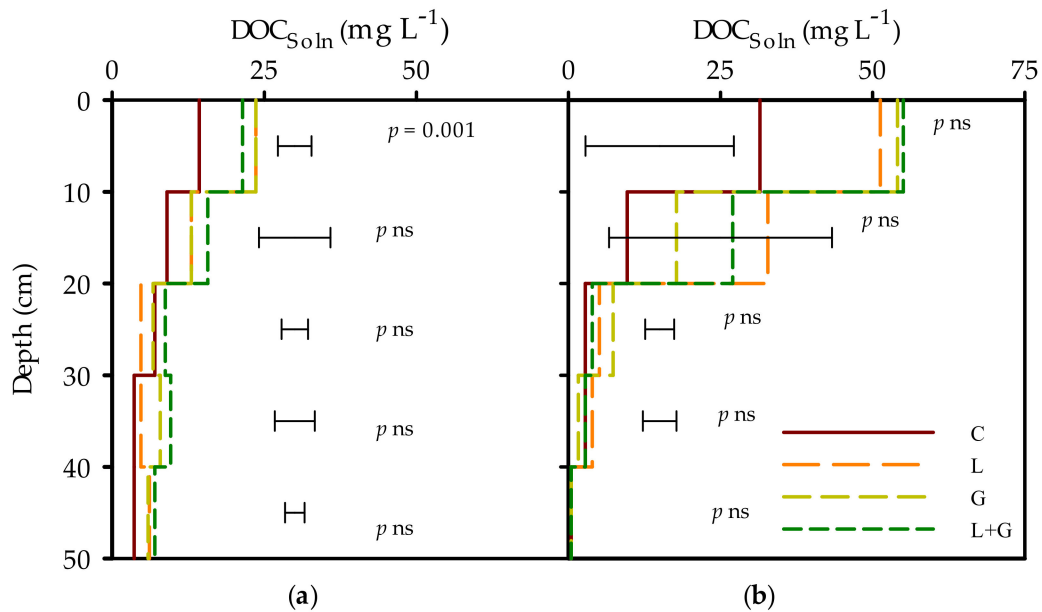


Figure 3. (a) The soil solution dissolved organic carbon (DOC_{Soln}) (mg L^{-1}) in the ST (b) and LT for the C, L, G, and L + G treatments. The error bars represent the least significant difference values at $p = 0.05$, $n = 3$ for each depth with ns denoting $p > 0.05$.

3.2. Soil Relationships with Solution Properties

Figure 4a presents the relationship between soil $\text{pH}_{\text{CaCl}_2}$ and pH_{Soln} . As $\text{pH}_{\text{CaCl}_2}$ increased, the difference between $\text{pH}_{\text{CaCl}_2}$ and pH_{Soln} increased, as indicated by the linear regression slope, which was equal to 1.54 (Table 1).

Table 1. Regression coefficients for the relationship between soil and soil solution measurements of pH, $\text{SO}_4\text{-S}$, Al and Ca across the control (C), lime (L), gypsum (G) and L + G treatments in the short term (ST) and long-term (LT). The soil measurements examined were pH, and Al were measured using 0.01 M CaCl_2 ($\text{pH}_{\text{CaCl}_2}$ and $\text{Al}_{\text{CaCl}_2}$), exchangeable Al (Al_{Ex}) and $\text{SO}_4\text{-S}$ extracted by 0.25 M KCl heated for 3 h at 40 °C. The soil solution measurements using a paste extract to measure pH (pH_{Soln}), $\text{SO}_4\text{-S}$ ($\text{SO}_4\text{-S}_{\text{Soln}}$), Ca (Ca_{Soln}), and Al activity (Al_{Act}). See Figure 4 for plotted relationships.

| Comparison | Period Time | Treatments | Relationship | Regression Coefficients | | | r^2 |
|--|-------------|------------|--------------|-------------------------|----------|--------|-------|
| | | | | a | b | c | |
| $\text{pH}_{\text{CaCl}_2}$ vs. pH_{Soln} | ST & LT | All | Linear | −2.07 | 1.54 | | 0.83 |
| $\text{S}_{\text{KCl}40}$ vs. $\text{SO}_4\text{-S}_{\text{Soln}}$ | ST & LT | All | Exponential | −48.6 | 1616 | | 0.59 |
| $\text{pH}_{\text{CaCl}_2}$ vs. Al_{Act} | ST & LT | All | Exponential | 0.0001 | 56098362 | 0.0039 | 0.42 |
| $\text{Al}_{\text{CaCl}_2}$ vs. Al_{Act} | ST & LT | C and L | Linear | 5.56 | 3.21 | −3.14 | 0.71 |
| Al_{Ex} vs. Al_{Act} | ST & LT | C and L | Linear | −3.96 | 96.41 | | 0.67 |
| Ca_{Ex} vs. Ca_{Soln} | ST & LT | C and L | Linear | 8.19 | 125.2 | | 0.87 |

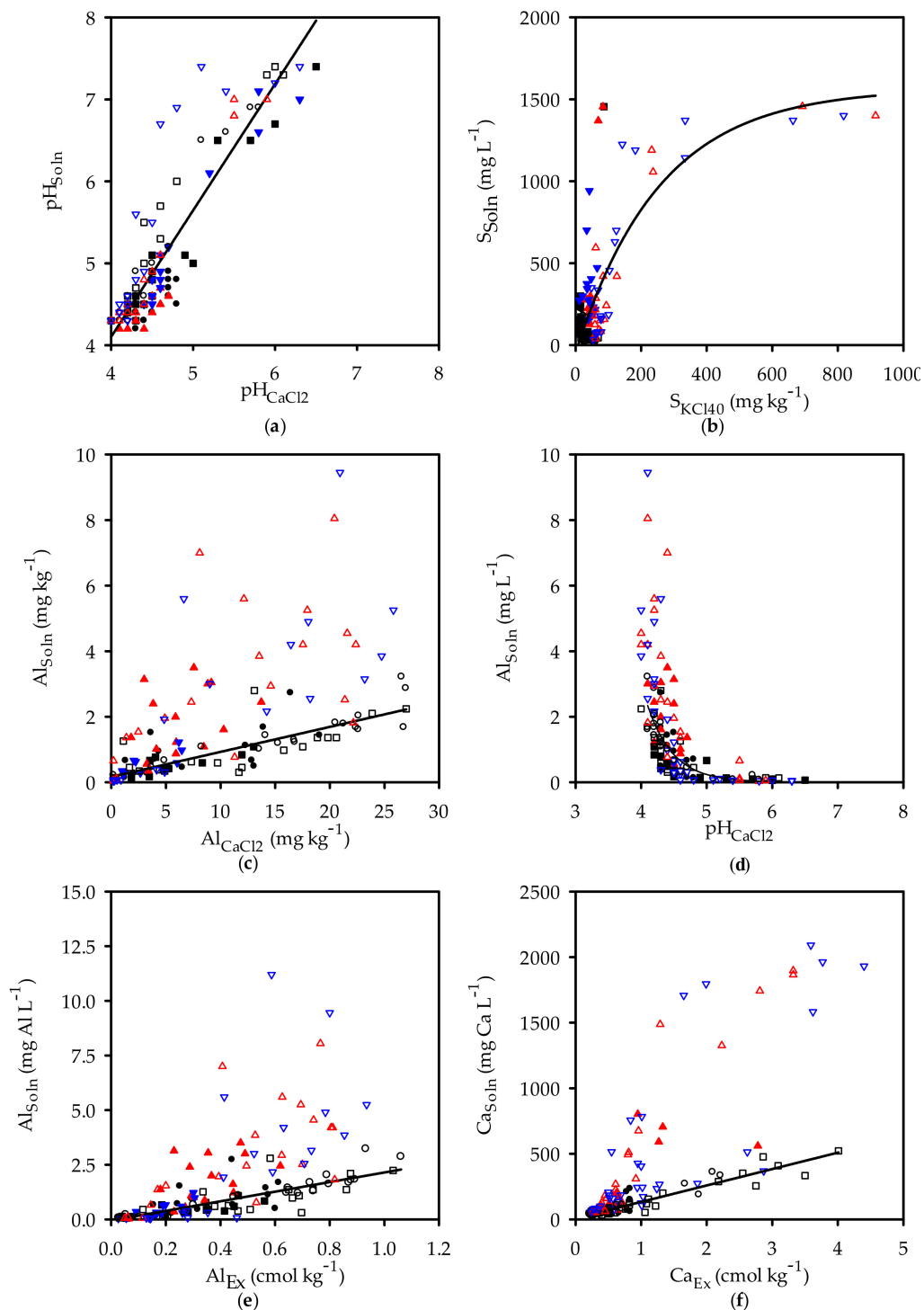


Figure 4. Relationship between soil and solution measurements for (a) $\text{pH}_{\text{CaCl}_2}$ versus pH_{Soln} , (b) $S_{\text{KCl}_{40}}$ versus $\text{SO}_4\text{-S}_{\text{Soln}}$, (c) $\text{Al}_{\text{CaCl}_2}$ versus Al_{Act} , (d) $\text{pH}_{\text{CaCl}_2}$ versus Al_{Act} , (e) Al_{Ex} vs. Al_{Act} , and (f) Ca_{Ex} vs. Ca_{Soln} . For the (a,c,e) ST experiment treatments C (○), L2.5 (□), G2.5 (△), and L2.5 + G2.5 (▽) (b,d,f), and the LT experiment treatment C (●), L4.0 (■), G2.0 (▲), and L4.0 + G2.0 (▼). See Table 1 for regression equations for fitted lines.

In the ST, for the L2.5 + G2.5 treatment, $\text{pH}_{\text{CaCl}_2}$ was lower with an associated greater pH_{Soln} compared to the other treatments. Soil $S_{\text{KCl}_{40}}$ was related to $\text{SO}_4\text{-S}_{\text{Soln}}$ ($r^2 = 0.59$) for both experiments across all treatments (Figure 4b). Soil $\text{Al}_{\text{CaCl}_2}$ was related to Al_{Act} ($r^2 = 0.71$), but only for the C and L treatments (Figure 4c). Al_{Act} concentrations were greater for the L2.5 + G2.5 and L4 + G2 treatments compared to the C treatment in both experiments. There was a poor relationship between soil $\text{pH}_{\text{CaCl}_2}$ and Al_{Act} ($r^2 = 0.42$)

across all treatments with the highest Al_{Act} observed for the ST trial for the G2 treatments (Figure 4d). Soil Al_{Ex} was related to Al_{Act} ($r^2 = 0.64$), but only for the C and L treatments (Figure 4e). The Al_{Act} concentration for a measured Al_{Ex} was greater for the L2.5 + G2.5 and L4 + G2 treatments than the C and L treatments in both experiments. Soil Ca_{Ex} was related to Ca_{Soln} ($r^2 = 0.87$) for the C and L treatments with greater concentrations occurring for the G2.5 treatment in the ST experiment (Figure 4f).

3.3. Soil Solution Al Species

In the ST, Org-Al ranged within 0 to $16 \mu\text{mol L}^{-1}$ in the 0–50 cm layer of all treatments (Figure 5a). The L2.5, G2.5, and L2.5 + G2.5 treatments had 48–75% lower Org-Al than the C treatment in the 10–30 cm layer. Org-Al was variable among treatments ($8\text{--}15 \mu\text{mol L}^{-1}$) in the 30–50 cm layer. The OH-Al decreased with increasing depth from $4 \mu\text{mol L}^{-1}$ in the 0–10 cm layer to $1 \mu\text{mol L}^{-1}$ in the 20–50 cm layer (Figure 5b). The treatments did not affect OH-Al in 0–50 cm layer. The Toxic-Al increased with increasing depth from $0 \mu\text{mol L}^{-1}$ in the 0–10 cm layer to $9 \mu\text{mol L}^{-1}$ in the 30–50 cm layer regardless of treatments (Figure 5c). There was no $SO_4\text{-Al}$ in the 0–10 cm layer of all treatments (Figure 5d). Application of G increased $SO_4\text{-Al}$ by 174–1039%, 432–666%, and 299–301% in the 10–20, 20–30, and 30–40 cm layers, respectively, compared to the C and L2.5 treatments.

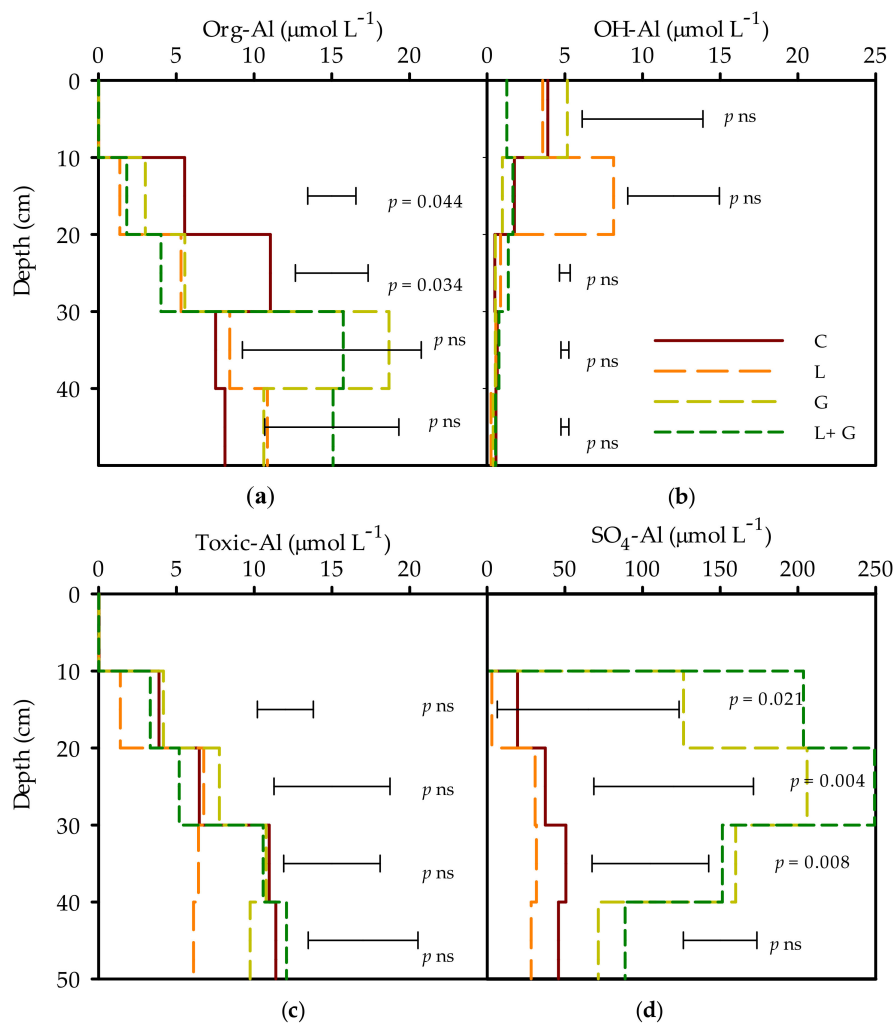


Figure 5. The ST effect on (a) Org-Al, (b) OH-Al, (c) Toxic-Al, and (d) $SO_4\text{-Al}$ ($\mu\text{mol L}^{-1}$) for the C, L2.5, G2.5 and L2.5 + G2.5 treatments. Error bars represent the least significant difference. The abbreviation ns denotes not significant at $p \leq 0.05$, $n = 3$.

In the LT, the L4 and L4 + G2 treatments had 100% lower Org-Al than the C treatment in the 0–10 cm layer (Figure 6a). Org-Al was 258–405% greater for the L2 and G2 treatments than the C treatment in the 10–20 cm layer. Org-Al was low (1–7 $\mu\text{mol L}^{-1}$) for all treatments in the 30–50 cm layer. The L and G treatments did not affect OH-Al with concentrations ranging between 0.2–2.5 $\mu\text{mol L}^{-1}$ in the 0–20 cm layer (Figure 6b). The Toxic-Al was lower for the L4 and L4 + G2 treatments by 100%, and 87–90% (at $p = 0.053$) and 32–33% in the 0–10, 10–20, 30–40 cm layers, respectively, than the control treatment (Figure 6c). In contrast, Toxic-Al was the same in the soil profile for the C and G2 treatments. The application of G2 resulted in greater $\text{SO}_4\text{-Al}$ by 330%, 137%, 188%, and 397% in the 0–10, 10–20, 20–30, 30–40 cm layers, respectively, compared to the C treatment (Figure 6d). $\text{SO}_4\text{-Al}$ was lower for the L4 + G2 treatment than the G2 treatment by 90–100% in the 0–20 and by 52–71% in the 20–40 cm soil layer.

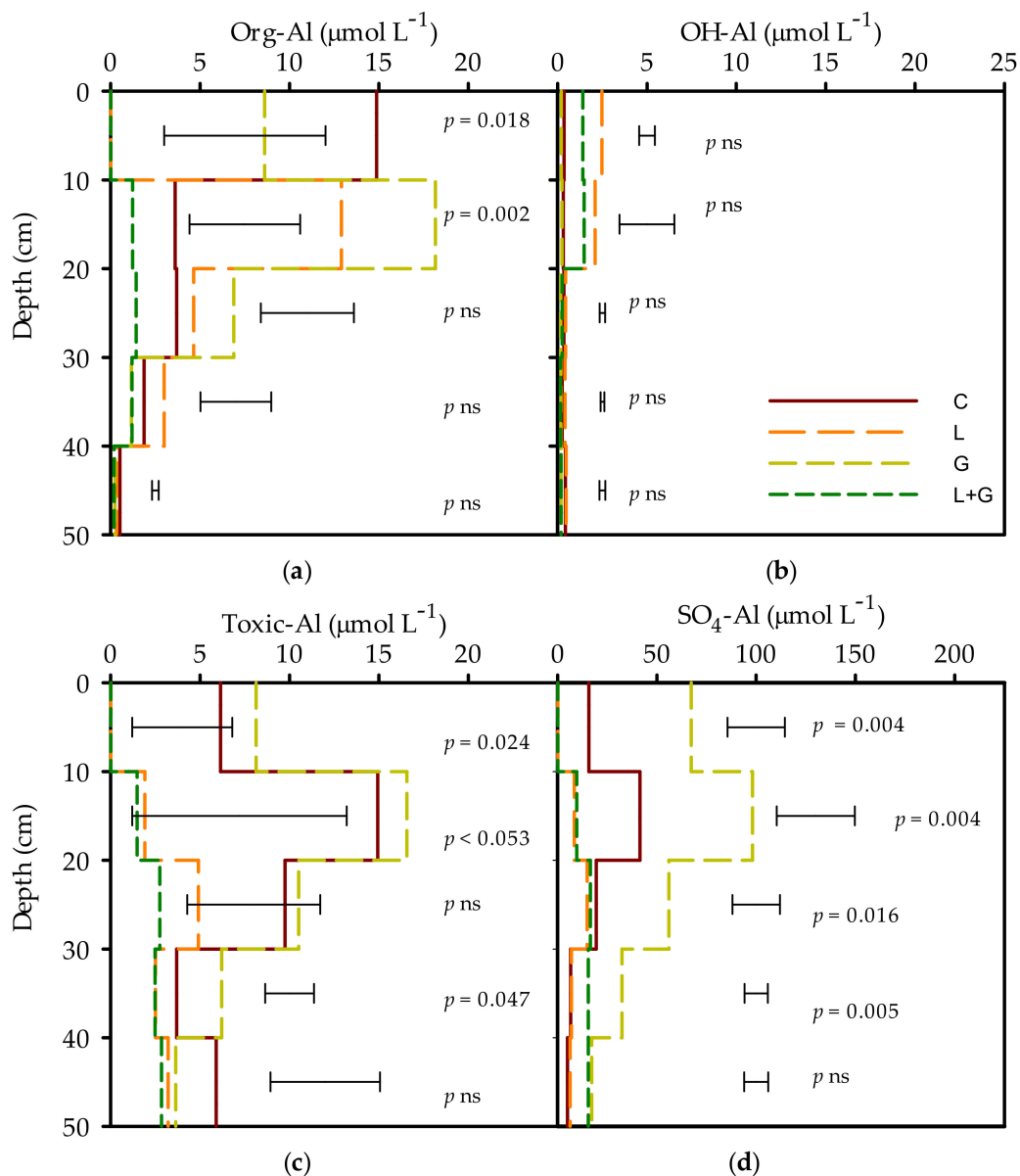


Figure 6. The LT effect on (a) Org-Al, (b) OH-Al, (c) Toxic-Al, and (d) $\text{SO}_4\text{-Al}$ ($\mu\text{mol L}^{-1}$) for the treatments C, L4, G2 and L4 + G2 application. Error bars represent the least significant difference. The abbreviation ns denotes not significant at $p \leq 0.05$, $n = 3$.

Soil S_{KCl40} is related to per cent of Al_{Act} as SO_4 -Al (SO_4 -Al%) ($r^2 = 0.59$) (Figure 7a). In contrast, there was no relationship between SO_4 - S_{Soln} and SO_4 -Al% (Figure 7b). In comparison, Toxic-Al was related to pH_{Soln} more than pH_{CaCl_2} (Figure 8a,b), but not related to either Al_{CaCl_2} or Al_{Soln} (data not presented).

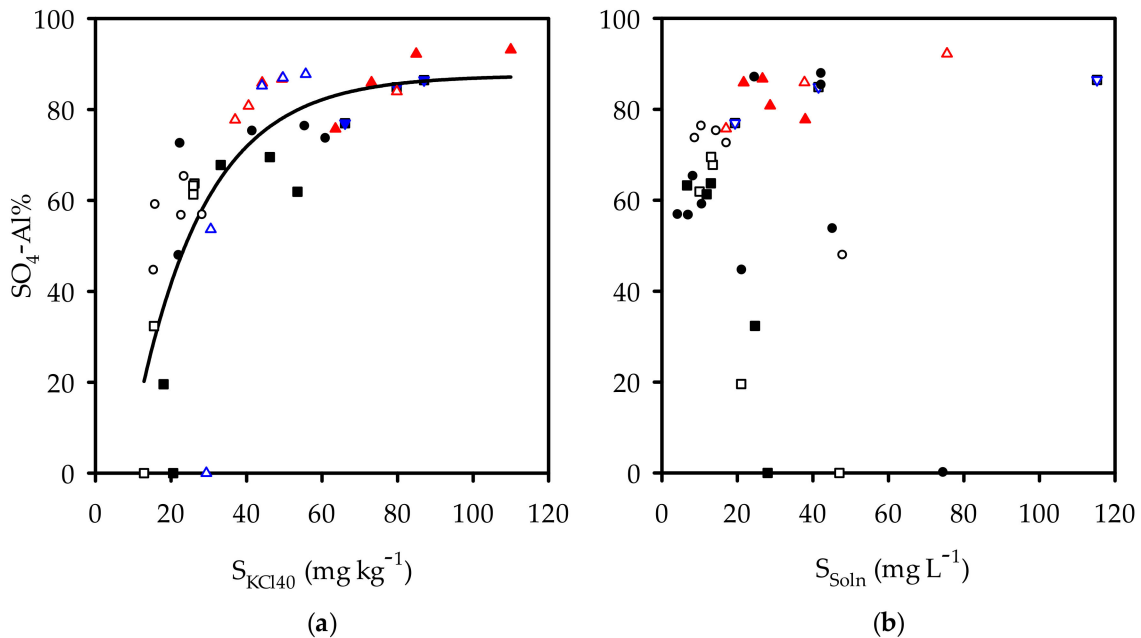


Figure 7. Relationship between SO_4 -Al% and (a) S_{KCl40} ($SO_4 - Al\% = -46.4 + 133.9 \times (1 - \exp(-0.05 \times S_{KCl40}))$, $r^2 = 0.56$) and (b) S_{Soln} for the ST experiment treatments C (\circ), L (\square), G (\triangle), and L + G (∇), and for the LT experiment treatments C (\bullet), L (\blacksquare), G (\blacktriangle), and L + G (\blacktriangledown).

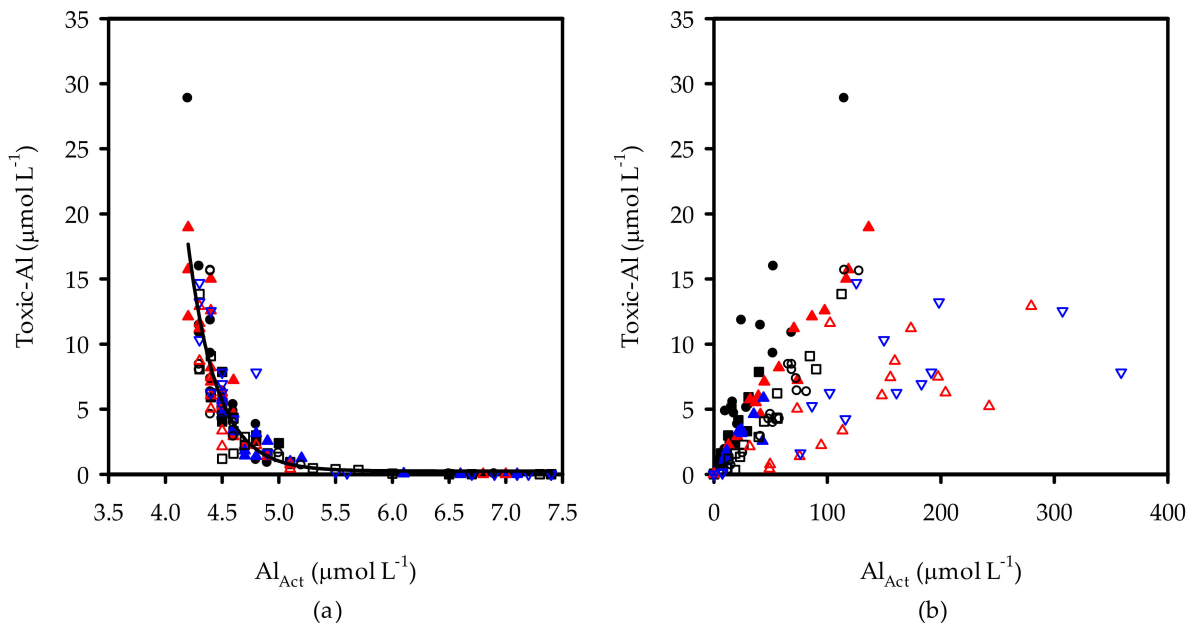


Figure 8. Relationship between Toxic-Al (a) pH_{Soln} ($Toxic - Al = 0.25 + 2.29 \times 10^8 \times \exp(-3.90 \times pH_{Soln})$, $r^2 = 0.81$) and (b) Al_{Soln} ST experiment treatments C (\circ), L (\square), G (\triangle), and L + G (∇), and for the LT experiment treatments C (\bullet), L (\blacksquare), G (\blacktriangle), and L + G (\blacktriangledown).

4. Discussion

The Al species likely to be present when the soil pH_{Soln} is below 5.0 are Org-Al, Toxic-Al, and $\text{SO}_4\text{-Al}$ [21,32]. The MINTEQ-predicted Toxic-Al activity in the soil profiles was up to $16 \mu\text{mol L}^{-1}$ in the sublayers (Figures 5c and 6c), which is above the critical range for harmful Al toxicity effects on Al sensitive plant growth [40]. In the LT, the application of L alone or in combination with G reduced Toxic-Al to a depth of 30 cm resulting in increased crop grain yield [5].

Changes in soil solution properties ($\text{SO}_4\text{-S}_{\text{Soln}}$, Ca_{Soln} , Al_{Act} , and $\text{SO}_4\text{-Al}$) due to the application of G provide greater insight into the behaviour of soil Al and its effects on crop yield than the measured changes in soil chemical properties (S_{KCl40} , Ca_{Ex} , $\text{Al}_{\text{CaCl}_2}$, Al_{Ex} , and $\text{SO}_4\text{-Al}$) [8]. In the ST, application of G2.5 increased the soil solution measurement $\text{SO}_4\text{-S}_{\text{Soln}}$ (Figure 1a), Ca_{Soln} (Figure 1c), IS_{Soln} (Figure 1e), Al_{Act} (Figure 2a), and $\text{SO}_4\text{-Al}$ (Figure 5d). The increase in Ca_{Soln} results in the Ca^{2+} displacing Al^{3+} from the exchange site increasing Al_{Act} , which in turn decreases pH_{Soln} due to the associated release of H^+ from the cation exchange sites into the soil solution [15,17,18]. We did not identify this reaction using the soil measurements [8]. Instead, we observed G application increased S_{KCl40} , Ca_{Ex} , and ECEC resulting in a small decrease in $\text{Al}_{\text{CaCl}_2}$ and no change in Al_{Ex} [8]. However, complexation of Al^{3+} as $\text{SO}_4\text{-Al}$ also takes place, as predicted by MINTEQ. The G treatment's overall effect was to have the same Toxic-Al concentration as the control treatment (Figure 5c) with pH_{Soln} closely related to Toxic-Al (Figure 8a). The formation of $\text{SO}_4\text{-Al}$ appears to be sufficient to overcome the rise in Al toxicity associated with the greater Al_{Act} when G is applied [55]. Therefore, the soil solution measurements confirm that the mechanism for the greater crop grain yield observed for the G treatments in the ST [5] is due to the greater $\text{SO}_4\text{-S}_{\text{Soln}}$ and Ca_{Soln} or greater S_{KCl40} and Ca_{Ex} increasing IS_{Soln} or EC resulting in the amelioration of the Al toxicity effect [15]. Simultaneously, the $\text{SO}_4\text{-Al}$ complexation plays an essential role in maintaining toxic-Al in the soil solution [2] at the same concentrations as the C treatment (Figures 5c and 8b). The ability of $\text{SO}_4\text{-S}$ to form $\text{SO}_4\text{-Al}$ is dependent on the $\text{SO}_4\text{-S}_{\text{Soln}}$ concentration [31]. However, in this study, $\text{SO}_4\text{-Al}\%$ was more related to S_{KCl40} (Figure 7a) than $\text{SO}_4\text{-S}_{\text{Soln}}$ (Figure 7b) because of low $\text{SO}_4\text{-Al}\%$ relative to $\text{SO}_4\text{-S}_{\text{Soln}}$ for the C and L treatments in the LT experiment (Figure 7b).

Soil solution Al only accounts for less than 1% of Al_{Ex} [56]. Similarly, in this study, soil solution, Al accounted on average for only 0.47% of the Al_{Ex} . Hence, Al_{Ex} acts as a reserve of Al to buffer Al_{Soln} from changes when G is applied to the soil [56]. However, Al_{Act} is poorly correlated with Al_{Ex} [56] and $\text{Al}_{\text{CaCl}_2}$ when examined across all treatments (Figure 4c,e). The highest regression correlation of $r^2 = 0.41$ across all treatments occurred for the relationship between pH_{Soln} and Al_{Act} (Figure 4d), which is consistent with the observations of [56]. Mineral phase reactions can control Al_{Act} [27]. For example, for a group of Queensland soils with G application, the equation for the relationship between pH_{Soln} and $\log(\text{Al}_{\text{Act}})$ is the same as the theoretical values for gibbsite dissolution ($\log(\text{Al}_{\text{Act}}) = 8.04 - (3.00 \times \text{pH}_{\text{Soln}})$) [56]. However, for the LT experiment, $\log(\text{Al}_{\text{Act}})$ the C and G treatments were greater than the theoretical values for gibbsite dissolution. Also, the lime treated soils of the ST experiment had high $\log(\text{Al}_{\text{Act}})$ for the measured pH_{Soln} because L application can result in the formation of trace quantities of more soluble Al minerals that subsequently controlled Al_{Act} [57]. Hence, Al_{Act} for Western Australian soils result from several mineral phase retention and release reactions [26].

The IS_{Soln} values for the experimental sites were low, less than 2.5 mmol L^{-1} (Figure 1e,f), which is consistent with other measurements conducted on highly weathered soils from Queensland and the South Western Australia wheatbelt [42,58]. Hence, these soils have a high expression of Al toxicity due to the low IS_{Soln} and EC. In the ST, G2.5 application increased IS_{Soln} to 16.9 mmol L^{-1} in the 0–10 cm layer and $3.2\text{--}4.9 \text{ mmol L}^{-1}$ in the subsoil (Figure 1e). The effect is to decrease the Al activity leading to a 14–19% increase in crop grain yield [5,15]. The immediate impact of G on these soil solution properties is illustrated by the leaching of $\text{SO}_4\text{-S}_{\text{Soln}}$ (Figure 1a), and Ca_{Soln} (Figure 1c), increasing IS_{Soln} (Figure 1e) to

the depth of 40 cm even after only 279 mm of rainfall over the period March 2017 to March 2018 [5].

In the LT, $\text{SO}_4\text{-S}$ and Ca applied as G is retained within the 50 cm layer as indicated by greater $\text{SO}_4\text{-S}_{\text{Soln}}$ (Figure 1b), Ca_{Soln} (Figure 1d), S_{KCl40} and Ca_{Ex} [8]. However, $\text{SO}_4\text{-S}_{\text{Soln}}$ was leached below the 50 cm [8], decreasing the effectiveness of the G2 treatment on crop yield increase overtime in the LT experiment [5]. There was an initial grain yield response of 16–23% in the LT experiment in the first year after application declining to 4–9% four years after the G2 application [5]. The Al toxicity limitation in the ST trial occurs below 10 cm while in the LT experiment, it exists in the 0–30 cm layer (Figures 5c and 6c). Because water flow from rainfall decreases with depth, the benefit of applying G to sites which have Al toxicity below 30 cm (ST experiment) should last longer compared to when Al toxicity exists in the 0–30 cm layer (LT experiment). In South Western Australia, for moderately acidic soils, Al toxicity in the 0–30 cm layer is widespread due to Tenosols' acidification process [59]. Indeed, for very acidic soils, longer-term acidification can result in Al toxicity appearing to a depth of 80 cm as illustrated by the soil profile presented by [60].

In both the ST and LT, G application increased the percentage of Al_{Act} in the form of $\text{SO}_4\text{-Al}$ (Figures 5d and 6d). At the same time, there was no effect on pH_{Soln} (Figure 2a,b) suggesting limited additional $\text{SO}_4\text{-S}$ sorption and release of OH^- . There was no relationship between Al_{Act} and $\text{Al}_{\text{CaCl}_2}$ or Al_{Ex} across all treatments (Figure 4c,e). In contrast, Al_{Act} was related to pH_{Soln} with the G treatments from the ST experiment having the highest concentration of Al_{Act} (Figure 4d), but there was no impact of the G treatments on the relationship between Al_{Act} and pH_{Soln} of the ST experiment. Hence, G application increases Ca_{Soln} and displaces Al^{3+} and H^+ from the exchange sites [15,17]. However, there is no net effect on pH_{Soln} because increased $\text{SO}_4\text{-S}_{\text{Soln}}$ resulted in some $\text{SO}_4\text{-S}$ sorption and OH^- displacement from the exchange sites [61].

In the LT, we observed the L treatments' effectiveness increased over time with grain yield response of 10–18% in the year of application rising to 20–36% in subsequent years [5]. Lime solubility is lower than G [11,12], resulting in no change in Al_{Act} (Figure 2b) and pH_{Soln} (Figure 2d) in the layers below 10 cm in the ST. In contrast, G application increases in $\text{SO}_4\text{-S}_{\text{Soln}}$ (Figure 1a), Ca_{Soln} (Figure 1c) and IS_{Soln} (Figure 1e) to a depth of 50 cm in the first year after application. In the LT, the L4 treatment affected soil solution properties Al_{Act} to a depth of 30 cm but pH_{Soln} only in the 0–10 cm soil layer (Figure 2b,d). Similarly, L decreased $\text{Al}_{\text{CaCl}_2}$ to a depth of 30 cm, while $\text{pH}_{\text{CaCl}_2}$ and Ca_{Ex} only increased to a depth of 20 cm [8]. This observation is consistent with the previous publications which have shown the application of L sometimes has a small impact on the layers below 10 cm due to its low solubility and limited ability to be leached into the soil profile [1,8,11,62].

DOC_{Soln} can form complexes with Al_{Soln} that are not influenced by L application [63]. However, in both experiments, applied L increased DOC_{Soln} (Figure 3b) because it increases organic matter solubility, microbial activity, production of soluble molecules and displacement of the previously adsorbed dissolved organic matter by other anions [64]. In agricultural soils, DOC_{Soln} can range within 0 to 74 mg L^{-1} [64]. In soils with $\text{DOC}_{\text{Soln}} < 60 \text{ mg L}^{-1}$, such as those presented here (Figure 3), up to 80% of Al_{Soln} can be bounded by DOC_{Soln} for soil with $\text{pH} < 5.0$ [34,65]. In the ST experiment, which has a history of L application pH_{Soln} was greater than 5.5 and Al_{Act} was low with all of the Al_{Act} calculated to be in the form of OH-Al (Figure 5b). In contrast, in the LT experiment, which has no L use history, pH_{Soln} was 4.6, with only 45% of Al_{Act} calculated to be associated with Org-Al in the 0–10 cm layer (Figure 6a). Hence, Toxic-Al was likely to be limiting wheat production, given the greater wheat yield in the first year where L had been applied [5]. The increase in Ca_{Soln} can reduce DOC_{Soln} due to increasing microbial consumption or adsorption by cation bridging [66]. However, at the LT, G application increased DOC_{Soln} by 42% in the 0–10 cm layer, possibly due to $\text{SO}_4\text{-S}$ sorption desorbing DOC [66].

5. Conclusions

These soil solution measurements provide greater insight into the chemical reactions involved when lime and gypsum are applied to soils with an Al toxicity limitation for crop production than soil chemical measurements. In the short term, surface-applied gypsum increases soil solution sulfate and calcium to a depth of 50 cm despite low amounts of rainfall (279 mm). The increase in soil solution calcium resulted in the displacement of Al from the exchange sites leading to an increasing soil solution Al activity. However, there is no impact on Toxic-Al concentrations because this increase in Al activity is associated with Al sulfate formation, which is not harmful to root growth. The increase in soil solution sulfate, calcium and ionic strength together corrected the subsoil Al toxicity limitation.

In the long term, sulfate is leached from the soil profile resulting in a decline in the soil solution ionic strength and its effect on soil Al toxicity. Alkalinity from 4 t lime ha⁻¹ leached into the soil profile reducing Al toxic forms to a depth of 30 cm. In the long term, gypsum gave no additional benefit over lime in terms of Toxic-Al but did maintain higher IS within the profile to 50 cm.

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