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# Short- and Long-Term Effects of Lime and Gypsum Applications on Acid Soils in a Water-Limited Environment: 1. Grain Yield Response and Nutrient Concentration

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**Abstract:** Surface (0–10 cm) and subsoil (soil layers below 10 cm) acidity and resulting aluminum (Al) toxicity reduce crop grain yields. In South Western Australia (SWA), these constraints affect 14.2 million hectares or 53% of the agricultural area. Both lime (L, CaCO<sub>3</sub>) and gypsum (G, CaSO<sub>4</sub>) application can decrease the toxic effect of Al, leading to an increase in crop grain yields. Within the region, it is unclear if G alone or the combined use of L and G has a role in alleviating soil acidity in SWA, due to low sulfate S (SO<sub>4</sub>-S) sorption properties of the soil. We present results from three experiments located in the eastern wheatbelt of SWA, which examined the short-term (ST, 2 growing seasons), medium-term (MT, 3 growing seasons), and long-term (LT, 7 growing seasons over 10 years) effects of L and G on grain yield and plant nutrient concentrations. Despite the rapid leaching of SO<sub>4</sub>-S and no self-liming impact, it was profitable to apply G, due to the significant ST grain yield responses. The grain yield response to G developed even following relatively dry years, but declined over time due to SO<sub>4</sub>-S leaching. At the LT experimental site had received no previous L application, whereas, at the ST and MT sites, L had been applied by the grower over the previous 5–10 years. For the LT site, the most profitable treatment for wheat (*Triticum aestivum* L.) grain yield, was the combined application of 4 t L ha<sup>-1</sup> with 2 t G ha<sup>-1</sup>. At this site, the 0–10 cm soil pH<sub>CaCl2</sub> was 4.6, and Al<sub>CaCl2</sub> was greater than 2.5 mg kg<sup>-1</sup> in the 10–30 cm soil layer. In contrast, at the ST and MT sites, the pH<sub>CaCl2</sub> of 0–10 cm soil layer was ≥5.5; it was only profitable to apply G to the MT site where the soil compaction constraint had been removed by deep ripping. The use of L increases soil pH<sub>CaCl2</sub>, resulting in the improved availability of anions, phosphorus (P) in the LT and molybdenum (Mo) at all sampling times, but reduced availability of cations zinc (Zn) in the LT and manganese (Mn) at all sampling. The application of G reduced Mo concentrations, due to the high SO<sub>4</sub>-S content of the soil.

**Keywords:** aluminum toxicity; wheat; barley; canola; phosphorus; molybdenum; manganese; nutrient concentration; soil acidity; zinc

## 1. Introduction

In South Western Australia (SWA), soil acidity affects about 14.2 million hectares or 53% of the agricultural area [1]. Soil acidity in SWA develops across a range of soil types, including Tenosols and Chromosols [2] in the 10–30 cm layer, due to soil acidification [3,4]. Rates of acidification range within 10–11 kg CaCO<sub>3</sub> yr<sup>-1</sup> for these soil types due to product removal [3,4]. Higher acidification rates 17–48 kg CaCO<sub>3</sub> yr<sup>-1</sup> can occur in legume by cereal rotations due to different rates of nitrate leaching [4]. Subsoil Al toxicity in wheat happens when Al<sub>CaCl2</sub> (extractable soil Al measured using a 0.01 M CaCl<sub>2</sub> solution) is greater than 2.5–4.5 mg kg<sup>-1</sup> in the subsoil [5]. Lime (L, CaCO<sub>3</sub>) is applied to the soil surface to increase pH<sub>CaCl2</sub> (soil pH measured using a 0.01 M CaCl<sub>2</sub> solution) and decrease subsoil Al<sub>CaCl2</sub>. The resulting increased crop grain yield can be attributed to an increase in root growth, leading to greater uptake of water and nutrients [6–9].

The amount of organically bound Al is dependent on soil solution dissolved organic matter (DOM), Al concentration, and pH [10]. In the surface soil layer (0–10 cm), soil organic matter actively binds soluble Al, due to the soil having relatively high DOM compared to subsoil layers [11]. In contrast, organically bound Al is important soil profiles that have relatively high DOM content in the subsoil [12]. Topdressed or broadcasted L can reduce subsoil Al toxicity when sufficient L is applied to maintain the surface soil layer pH<sub>CaCl2</sub> ≥ 5.5 [13–15], provided it is anthropologically incorporated by cultivation to increase L dissolution [13]. Growers in the SWA region have adopted the practice of applying L to increase surface pH<sub>CaCl2</sub> at sufficient rates, to decrease subsoil Al<sub>CaCl2</sub> [5]. However, surface-applied L moves slowly into the subsoil [16,17]. Hence, surface-applied L rates of 2–4 t L ha<sup>-1</sup> only increased subsoil pH<sub>CaCl2</sub> by greater than 0.3 units in 39% of the observations, in a database of L experiments conducted in SWA [5]. Coastal deposits of L are very cost-effective in treating both surface and subsoil acidity within 200–250 km of the L source. Within this zone, growers are tending to use high L rates (6–10 t ha<sup>-1</sup>) applied over several years to treat subsoil acidity [18]. The high transport costs or distances of greater than 250 km make this approach less cost-effective for the eastern regions of the SWA. Hence, growers of the Eastern wheatbelt region are looking for alternative ways of managing subsoil Al toxicity.

Gypsum (G, CaSO<sub>4</sub>) deposits which are located near salt lakes in the eastern wheatbelt region, have significantly reduced transport cost compared to transporting L from the coastal deposits. Moreover, G can be effective in treating subsoil Al toxicity, due to its greater solubility (2.0–2.5 gm L<sup>-1</sup>) [19] compared to L, which is sparingly soluble in water (0.013 gm L<sup>-1</sup>) [20]. Lime also stops dissolving when the soil pH surrounding the L particle reaches a pH of 7.1 [21]. The soil pH restriction on L dissolution, combined with its low solubility means that L application can have a limited impact on subsoil [5]. In contrast, G dissolves much more quickly in the soil resulting in high concentrations of SO<sub>4</sub>-S and calcium (Ca), which can be leached rapidly into the soil profile [22–25]. The increase in SO<sub>4</sub>-S and Ca content also increases the soil's electrical conductivity (EC) [22–25]. Hence, the application of G has a greater potential to increase root growth in the subsoil than L application, because the increase in SO<sub>4</sub>-S results in the precipitation of aluminum sulfate (Al-SO<sub>4</sub>) and the increase in EC which reduces Al<sup>3+</sup> activity [25,26]. In Australia, yield responses to G application for treating subsoil Al<sup>3+</sup> limitations have been reported on Tenosols in Western Australia [22,27] and Chromosols in New South Wales [28] and Victoria [29]. In contrast, on heavier textured soils (twelve sites with L and G treatments), only three were responsive to G application, while nine were responsive to the L application [30]. Hence, there is a need for further research to identify soils with Al toxicity limitations that are likely to be responsive to G and to define the optimum rate and timing of G application [31]. The soil chemical changes when G is applied to soil are very complex [25]. In general, soil with low SO<sub>4</sub>-S adsorption capacity, which occurs for some soils of SWA [25], have no self-liming effect of G application [23] and applied SO<sub>4</sub>-S is rapidly leached into the soil profile [32].

The application of L increases soil pH, resulting in a decrease in anion adsorption and an increase in cation adsorption and cation exchange capacity of the soil [33]. Hence, L application can increase the plant's tissue P concentration [33–35] and Mo concentration [36–38], but decrease Zn

concentration [34,38–40] and Mn concentration [34,39–41]. Improved root growth due to L application that alleviates the Al toxicity limitation can also be a factor that contributes to increasing P uptake [42]. Molybdenum is an essential nutrient for plant growth, with Mo deficiency appearing on acid soil [37]. In contrast, G application results in a high  $\text{SO}_4\text{-S}$  content of the soil and a decrease in Mo uptake [37]. Plants take up molybdate through  $\text{SO}_4\text{-S}$  transporters [43], because the two anions have similar chemical properties. Hence, they may compete for the binding sites on the same transporters [44].

We hypothesize for soils that have a low capacity to adsorb  $\text{SO}_4\text{-S}$  as measured by the sulfate buffer index method [45], G applied alone can still be profitable due to the short to medium term grain yield responses. At the same time, G used with low rates of L ( $\leq 4 \text{ t ha}^{-1}$ ) can be more profitable than using L alone at  $>4 \text{ t ha}^{-1}$ .

## 2. Materials and Methods

### 2.1. Field Experimental Sites

The field experiments consisted of three sites that were monitored over the short term (ST) (2 growing seasons), medium term (MT) (3 growing seasons), and long term (LT) (7 growing seasons over 10 years). The ST and MT experiments were located at  $-31^\circ 30' 9''$  S latitude,  $118^\circ 38' 50''$  E longitude, and were in the same paddock near the town of Burracoppin, which is 304 km east of Perth. The location of the LT trial was at  $-30^\circ 37' 3''$  S latitude,  $118^\circ 14' 9''$  E longitude near the town of Bonnie Rock, which is 370 km northeast of Perth. The soils at the sites are classified as yellow Tenosols [2]. A total of  $2\text{--}4 \text{ t L ha}^{-1}$  had been applied in the previous 15 years to the ST and MT experimental sites, with a grower application rate of  $1\text{--}2 \text{ t L ha}^{-1}$  in the year of application. The LT trial site had no prior history of L application.

### 2.2. Soil Measurements

Soil samples were collected using a 5 cm diameter soil corer from the control plots of the LT experiment, at depths of 0–10 and 10–30 cm in March 2008, and at depths of 0–10, 10–30, and 30–50 cm at the three experimental sites in March 2018. Four soil cores were collected per plot, and bulked for each layer. Mean soil chemical values for each experiment are presented in Table 1.

Soil  $\text{pH}_{\text{CaCl}_2}$  and soil  $\text{Al}_{\text{CaCl}_2}$  was measured using a 1:5 soil to 0.01 M  $\text{CaCl}_2$  solution ratio. Electrical conductivity (EC) was measured using the 1:5 soil to solution ratio using water. Exchangeable cations Al ( $\text{Al}_{\text{Ex}}$ ), Ca ( $\text{Ca}_{\text{Ex}}$ ), potassium ( $\text{K}_{\text{Ex}}$ ), magnesium ( $\text{Mg}_{\text{Ex}}$ ), and sodium ( $\text{Na}_{\text{Ex}}$ ) were measured using a mixture of 0.1M ammonium chloride and barium chloride at 1:10 soil to solution ratio. Details of these procedures are provided by [46]. Calculated effective cation exchange capacity (ECEC) is the sum of the cations  $\text{Al}_{\text{Ex}}$ ,  $\text{Ca}_{\text{Ex}}$ ,  $\text{K}_{\text{Ex}}$ ,  $\text{Mg}_{\text{Ex}}$ , and  $\text{Na}_{\text{Ex}}$ . Percentage cation saturation ( $\text{Al}_{\text{Ex}}\%$  and  $\text{Ca}_{\text{Ex}}\%$ ) is  $\text{Al}_{\text{Ex}}$  or  $\text{Ca}_{\text{Ex}}$  divided by ECEC multiplied by 100. Sulfur (S) content was measured using 0.25 M KCl, heated for 3 h at  $40^\circ \text{C}$  ( $\text{S}_{\text{KCl40}}$ ) [47]. Sulfate sorption capacity was measured using the sulfate buffer index (SBI) [45]. Other soil macro-nutrient measurements included ammonium and nitrate, Colwell phosphorus ( $\text{P}_{\text{Col}}$ ), and potassium ( $\text{K}_{\text{Col}}$ ), phosphate buffer index (PBI), organic carbon (C) [46]. Micro-nutrient measurements included DTPA extractable copper ( $\text{Cu}_{\text{DTPA}}$ ), manganese ( $\text{Mn}_{\text{DTPA}}$ ) and zinc ( $\text{Zn}_{\text{DTPA}}$ ) and hot water extractable boron ( $\text{B}_{\text{Hot}}$ ) [46].

At the LT site, the gravel content by weight increased from 5% in 0–10 cm to 12%, in 10–30 cm, 16% in 20–30 cm, and 56% in 30–50 cm soil depths (data not presented). Key soil chemical properties of the 0–10 cm soil layer were  $\text{pH}_{\text{CaCl}_2}$  (4.4–6.6),  $\text{Al}_{\text{CaCl}_2}$  (0–4  $\text{mg kg}^{-1}$ ), EC (0.05–0.09  $\text{dS m}^{-1}$ ), SBI 9–20,  $\text{Al}_{\text{Ex}}$  (0.09–0.16  $\text{cmol kg}^{-1}$ ),  $\text{Ca}_{\text{Ex}}$  (0.72–3.23  $\text{cmol kg}^{-1}$ ) (Table 1). In the soil layers below 10 cm, the range in  $\text{pH}_{\text{CaCl}_2}$  was 4.2–4.8,  $\text{Al}_{\text{CaCl}_2}$  was 3–22  $\text{mg kg}^{-1}$ , EC was 0.03–0.04  $\text{dS m}^{-1}$ ,  $\text{Al}\%$  was 21–69%, and SBI was 12–35. Soil  $\text{K}_{\text{Col}}$  at the LT experimental site was 27% less in the 0–10 cm soil layer and 47% less in the 10–30 cm soil layer, in 2018 compared to 2008. Similarly, soil  $\text{K}_{\text{Ex}}$  at the LT experimental site was 33% less in the 0–10 cm soil layer, and 48% less in the 10–30 cm soil layer in 2018 compared to 2008. In contrast, there were only small differences in  $\text{pH}_{\text{CaCl}_2}$ ,  $\text{Al}_{\text{CaCl}_2}$ , and  $\text{Al}_{\text{Ex}}$  between the 2008 and 2018 measurements. Other main chemical properties of the soil layers below 10 cm are presented in Table 1.

**Table 1.** Selected soil properties at the beginning of the long term (LT) field study in March 2008 at two soil depth increments (0–10 and 10–30 cm), and in March 2018 at three depth increments (0–10 and 10–30 and 30–50 cm), for the short term (ST), medium term (MT) and LT experiments in March 2018.

Property	ST 2018			MT 2018			LT 2008			LT 2018		
	Soil Depth (cm) †			Soil Depth (cm) †			Soil Depth (cm) †			Soil Depth (cm) †		
	0–10	10–30	30–50	0–10	10–30	30–50	0–10	10–30	0–10	10–30	30–50	
pH <sub>AlCl2</sub>	5.5	4.4	4.2	6.6	4.8	4.4	4.4	4.2	4.6	4.5	4.6	
Al <sub>CaCl2</sub> (mg kg <sup>-1</sup> )	0.0	13.0	22.0	0.0	3.0	10.0	4.0	11.0	3.0	11.0	6.5	
EC dS m <sup>-1</sup>	0.05	0.03	0.03	0.09	0.03	0.03	0.07	0.03	0.06	0.04	0.04	
P <sub>Col</sub> (mg kg <sup>-1</sup> )	14	4	5	12	6	2	32	10	29	8	3	
PBI	24	31	44	NA	NA	NA	31	40	29	47	62	
K <sub>Col</sub> (mg kg <sup>-1</sup> )	41	28	27	29	16	15	70	59	51	33	35	
S <sub>KCl40</sub> (mg kg <sup>-1</sup> )	22.0	32.0	58.0	14.0	15.0	34.0	11.0	12.0	15.0	20.0	24.5	
SBI	20	21	35	9	26	31	NA	NA	13	12	13	
Carbon (%)	0.8	0.5	0.3	0.8	0.5	0.3	0.8	0.5	0.7	0.4	0.3	
Cu <sub>DTPA</sub> (mg kg <sup>-1</sup> )	0.2	0.1	0.1	0.3	0.3	0.2	NA	NA	0.3	0.2	0.3	
Mn <sub>DTPA</sub> (mg kg <sup>-1</sup> )	0.6	0.2	0.1	1.1	0.5	0.3	NA	NA	3.3	1.3	1.0	
Zn <sub>DTPA</sub> (mg kg <sup>-1</sup> )	0.1	0.1	0.0	0.2	0.1	0.1	NA	NA	0.3	0.1	0.1	
B <sub>Hot</sub> (mg kg <sup>-1</sup> )	0.5	0.5	0.5	0.5	0.5	0.5	0.8	0.8	0.5	0.5	0.6	
Al <sub>Ex</sub> (cmol kg <sup>-1</sup> )	0.10	0.58	0.82	0.09	0.27	0.47	0.16	0.36	0.14	0.35	0.29	
Ca <sub>Ex</sub> (cmol kg <sup>-1</sup> )	1.96	0.50	0.26	3.23	0.90	0.41	0.72	0.50	0.81	0.42	0.52	
Mg <sub>Ex</sub> (cmol kg <sup>-1</sup> )	0.25	0.09	0.07	0.41	0.17	0.11	0.19	0.04	0.31	0.16	0.21	
K <sub>Ex</sub> (cmol kg <sup>-1</sup> )	0.07	0.05	0.05	0.08	0.04	0.03	0.15	0.12	0.10	0.06	0.07	
Na <sub>Ex</sub> (cmol kg <sup>-1</sup> )	0.03	0.01	0.01	0.06	0.03	0.02	0.06	0.03	0.06	0.03	0.03	
ECEC (cmol kg <sup>-1</sup> )	2.40	1.23	1.20	3.87	1.40	1.04	1.28	1.04	1.51	1.10	1.12	
Al%	4%	48%	69%	2%	21%	45%	13%	35%	15%	40%	28%	
Ca%	82%	40%	21%	83%	63%	39%	56%	48%	54%	38%	46%	

† Values presented are means ( $n = 3$ ), NA indicates measurement is not available.

### 2.3. Rainfall

At Burracoppin, annual rainfall was 400 mm in 2015, 414 mm in 2016, 315 mm in 2017, and 330 mm in 2018 (Table 2). Growing season rainfall (1 May to 31 October) was 200 mm in 2015, 206 mm in 2016, 182 mm in 2017, and 222 mm in 2018. Fallow season rainfall (1 November to 30 April) was 116 mm in 2015, 269 mm in 2016, 141 mm in 2017, and 100 mm in 2018. At the Bonnie Rock LT site, annual rainfall ranged between 150 mm in 2010 to 461 mm in 2016. Growing season rainfall ranged between 122 mm in 2001 to 326 mm in 2016. Fallow season rainfall was 19 mm in 2010, and greater than 92 mm for the other years of the experimental period.

**Table 2.** Monthly and annual rainfall (mm) at the ST and MT experimental sites (Burracoppin) over the three years (2015–2018) and the LT trial site (Bonnie Rock) over the 10 years (2008–2018).

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Annual
Burracoppin													
2015	0	1	86	29	19	40	105	29	4	3	52	32	400
2016	39	3	81	63	45	60	43	37	16	4	1	21	414
2017	45	65	6	2	34	8	43	49	32	16	8	6	315
2018	39	35	7	5	18	39	53	69	7	35	21	2	330
Bonnie Rock													
2008	8	142	22	57	3	25	87	11	42	19	10	0	426
2009	50	10	15	18	25	32	51	35	17	7	7	6	271
2010	3	0	1	1	23	19	29	32	12	7	4	18	150
2011	53	25	37	17	29	19	54	43	20	48	16	81	442
2012	13	11	17	1	8	52	13	17	20	1	38	49	240
2013	22	10	36	6	20	15	26	33	25	14	11	11	230
2014	22	30	33	52	27	9	32	12	26	6	11	4	261
2015	0	1	66	11	6	26	105	34	4	1	38	4	296
2016	27	4	65	28	39	88	147	23	24	6	1	10	461
2017	32	65	12	0	15	4	37	28	23	4	18	2	240
2018	59	29	5	4	5	17	47	28	6	44	7	2	253

### 2.4. Treatments

The L and G treatments were top-dressed onto the soil surface in all experiments. The plots (1.8 m by 20 m) were arranged in a randomized complete block design, with three replications. The ST experiment treatments consisted of a control (C), 2.5 t L ha<sup>-1</sup> (L2.5), 2.5 t G ha<sup>-1</sup>, (G2.5), 2.5 t L, and G ha<sup>-1</sup> (L2.5 + G2.5), applied on 31 March 2017. In the case of L + G application, L and G were applied separately on the same day. The MT experiment consisted of the same treatments and the additional treatments of 5.0 t L ha<sup>-1</sup> (L5.0) and 5.0 t L ha<sup>-1</sup> plus 2.5 t G ha<sup>-1</sup> (L5.0 + G2.5), applied on 31 July 2015. Penetrometer measurements found subsoil compaction, greater than 3.0 MPa, within the 15–25 cm soil layer. Hence, the MT experimental site was ripped to a depth of 40 cm using an Agrowplow<sup>®</sup> the day after the application of the L and G treatments. On the same day the site was then cultivated to a depth of 10 cm using a Grizzly<sup>®</sup> tandem offset disc to incorporate the applied L and G. The deep ripping and cultivation took place the day after the application of L and G treatment. The location of the ST experiment was in an un-ripped area of the paddock. Moreover, there was no incorporation of the L and G after application. The G rate of 2.5 t ha<sup>-1</sup> was selected based on [27]. The use of high L rates was to obtain a pH<sub>CaCl<sub>2</sub></sub> of greater than 5.5 in the 0–10 soil layer [15].

The ST and MT experiments were sown and managed using farmer equipment with canola (*Brassica napus* L. cv Bonito) sown at 4.0 kg seed ha<sup>-1</sup> on 7 April 2016, wheat (cv Calingiri) sown at 50 kg ha<sup>-1</sup> on 23 April 2017, and barley (*Hordeum vulgare* L. cv Spartacus CL) seeded at 60 kg ha<sup>-1</sup> on 20 April 2018. Crop harvest with a small plot header occurred in November.

The LT experiment treatments comprised: control (C), 2.0 t L ha<sup>-1</sup> (L2), 4.0 t L ha<sup>-1</sup>, (L4), 8.0 t L ha<sup>-1</sup>, (L8), 2.0 t G ha<sup>-1</sup> (G2) and 4.0 t L ha<sup>-1</sup> plus 2.0 t G ha<sup>-1</sup> (L4 + G2). Half (1, 2, and 4 t L ha<sup>-1</sup>

and 1 t G ha<sup>-1</sup>) of the L and G rates were top dressed in March of 2008 and in March of 2013. The experimental site had not been deep ripped, nor was tillage used to incorporate the treatments.

Lime sourced for these three experiments came from Lancelin (−31°02′52″ S latitude 115°21′15″ E longitude). Distance from Lancelin to Bonnie Rock is 370 km, and to South Barracoppin is 380 km. The L consisted of 55–57% within the particle size range <250 µm diameter, with 80–87% CaCO<sub>3</sub> content and 40–42% within the particle size range 250–500 µm with 86–93% CaCO<sub>3</sub> content. The G came from Lake Hillman (−30°17′60″ S, 117°10′0″ E) for the ST and MT experiments, and contained 175 g S kg<sup>-1</sup> and 214 g Ca kg<sup>-1</sup>. The G for the LT experiment came from Lake Cowcowing (−33°55′44″ S, 117°23′4″ E), and contained 178 g S kg<sup>-1</sup> S and 22.4 g Ca kg<sup>-1</sup>. Distance from Lake Cowcowing to Bonnie Rock is 140 km, and to South Barracoppin is 200 km.

At the LT experiment, wheat was grown in 2008, 2010, 2011, 2013, 2014, 2015, and 2016. Lupin (*Lupinus angustifolius* L.) was grown but not harvested, due to crop failure in 2009, and chemically fallowed to control weeds in 2012. Fertilizer application included 3 kg N ha<sup>-1</sup>, 4.5 kg P ha<sup>-1</sup> and 1.5 kg S ha<sup>-1</sup> at seeding with an additional 10 kg N ha<sup>-1</sup> applied post-seeding in 2015. The site was sown in May of each year, using an experimental plot cone seeder, with knife points on 22 cm spacings, and harvested with a small plot header to measure grain yield in November of each year.

Relative grain yield percentage (RY%) equals the grain yield of the control treatment (GY<sub>C</sub>), divided by the maximum grain yield achieved for all treatments (GY<sub>Max</sub>) multiplied by 100,  $RY\% = GY_C / GY_{Max} \times 100$ . Treatment relative grain yield response equals the grain yield of the treatment minus the grain yield of the control treatment, divided by the grain yield of the control multiplied by 100.

The calculated economics of applying L and G used grower costs, which were \$44 t<sup>-1</sup> L and \$30 t<sup>-1</sup> G for the purchase and transport to the experimental site location in 2008. The cost of spreading L and G is \$8 ha<sup>-1</sup>. These costs had increased to \$60 t<sup>-1</sup> L, \$38 t<sup>-1</sup> G, and spreading cost of \$10 ha<sup>-1</sup> in 2018. Wheat grain prices (APW) were 230 t<sup>-1</sup> in 2008, 310 t<sup>-1</sup> in 2010, 250 t<sup>-1</sup> in 2011, 310 t<sup>-1</sup> in 2013, 265 t<sup>-1</sup> in 2014, 275 t<sup>-1</sup> in 2015, 255 t<sup>-1</sup> in 2016 and 241 t<sup>-1</sup> in 2017. The canola price was \$580 t<sup>-1</sup> in 2016, and the barley price was \$255 t<sup>-1</sup> in 2018. Grower costs of seeding, managing, and harvest of the crop were \$170 ha<sup>-1</sup> in 2008. The grower costs increased at a rate of \$10 ha<sup>-1</sup> yr over the period 2008 to 2018, such that it cost \$250 ha<sup>-1</sup> in 2018. The calculated profit (\$ ha<sup>-1</sup>) is grain yield multiplied by price, minus the cost of production. Calculated net present value (NPV) assumes an interest rate of 5%. The calculated treatment NPV is the total NPV for the treatment minus total NPV for the control.

## 2.5. Plant Measurements

Whole top plant tissue concentration of nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg), boron (B), copper (Cu), zinc (Zn) manganese (Mn) sodium (Na) and molybdenum (Mo) concentrations followed the method of [48]. Collection of these samples happened 6–8 weeks after seeding in the LT experiment 2008–2016, and in early September for the trials sampled in 2018. The study presents Mo concentrations from the ST experiment measured in 2018, and the LT experiment measured in 2010, 2011, and 2018. Additionally provided are P, K, S, Ca, Zn, and Mn concentrations from the LT experiment measured in 2008 and 2010–2016. Nutrient critical values were determined using [49]. Plant nutrient data not presented includes N, Mg, B, Cu, Fe, and Na from the LT experiment and other nutrient data from the ST experiment, because the L and G treatments did not affect these concentrations. Similarly, L had no consistent effect on N and Mg concentrations [34].

## 2.6. Statistical Analysis

Analysis of variance (ANOVA) to determine significant treatment response for grain yield and nutrient concentration was conducted in Genstat® [50], using a treatment structure of soil amendment treatments and a block structure of replicates. The paper reports grain yield and nutrient concentration responses at  $p \leq 0.05$ . For a measurement year, the significant difference among treatments was determined by Duncan multiple comparison tests, with treatment values followed by different letters being significantly different at ( $p \leq 0.05$ ). The limitation of Al toxicity within the 0–30 cm soil layer was



calculated by taking the maximum soil  $\text{Al}_{\text{CaCl}_2}$  measured within the three 10 cm increment layers of the 0–30 cm soil layer [5]. The relationship between P and N concentrations were determined using the linear regression analysis of Genstat® [50].

### 3. Results

#### 3.1. Grain Yield

The greater grain yield at the MT experiment compared to the ST experiment was due to a deep ripping removing subsoil compaction (Table 3). In both the ST and MT experiments, there was no significant response to the L alone treatments (L2.5 and L5.0). In the MT experiment, G2.5, L2.5 + G2.5, and L5.0 + G2.5 treatments increased canola and wheat grain yield by 15–20%, compared to the C treatment in 2016 and 2017. In the ST experiment, G2.5 and L2.5 + G2.5 treatments increased wheat grain yield by 18–26%, compared to the C treatment in 2017. Barley grain yield response to G treatments was not significant in the MT experiment, but significant for the G2.5 and L2.5 + G2.5 treatments (18–26%), in the ST experiment in 2018. Total grain yield was 13–15% greater for the G2.5, L2.5 + G2.5, and L5.0 + G2.5 treatments in the MT experiment and 19–22% greater for the G2.5 and L5.0 + G2.5 treatments in the ST experiment, compared to the C treatment.

**Table 3.** Grain yields ( $\text{t ha}^{-1}$ ) of canola in 2016, wheat in 2017, and barley 2018, observed at the MT (3 growing seasons, 2017–2018), and the ST (2 growing seasons, 2016–2018) experiments. The total represents the sum of the grain yields over the study period. Treatments were applied once on 31 July 2015 for the MT experiment, and 31 March 2017 for the ST experiment. Treatments included control (C),  $2.5 \text{ t L ha}^{-1}$  (L2.5),  $5 \text{ t L ha}^{-1}$  (L5.0),  $2.5 \text{ t G ha}^{-1}$  (G2.5), and  $2.5 \text{ t L ha}^{-1}$  plus  $2.5 \text{ t G ha}^{-1}$  (L2.5 + L2.5). For each year, different lower case letters indicate a significant difference between means at  $p \leq 0.05$ . The LSD values are presented at  $p \leq 0.05$ .

Treatment and Year	MT				ST		
	2016	2017	2018	Total	2017	2018	Total
C	2.05 <sup>b</sup>	2.14 <sup>c</sup>	1.74 <sup>a</sup>	5.93 <sup>c</sup>	1.29 <sup>b</sup>	0.73 <sup>c</sup>	2.01 <sup>b</sup>
L2.5	2.12 <sup>b</sup>	2.13 <sup>c</sup>	1.89 <sup>a</sup>	6.14 <sup>b,c</sup>	1.34 <sup>b</sup>	0.82 <sup>b,c</sup>	2.16 <sup>b</sup>
L5.0	2.21 <sup>a,b</sup>	2.21 <sup>b,c</sup>	1.84 <sup>a</sup>	6.26 <sup>b</sup>	NA	NA	NA
G2.5	2.36 <sup>a</sup>	2.46 <sup>a,b</sup>	1.87 <sup>a</sup>	6.68 <sup>a</sup>	1.54 <sup>a</sup>	0.86 <sup>a,b</sup>	2.40 <sup>a</sup>
L2.5 + G2.5	2.39 <sup>a</sup>	2.51 <sup>a</sup>	1.87 <sup>a</sup>	6.77 <sup>a</sup>	1.53 <sup>a</sup>	0.92 <sup>a</sup>	2.45 <sup>a</sup>
L5.0 + G2.5	2.38 <sup>a</sup>	2.57 <sup>a</sup>	1.89 <sup>a</sup>	6.84 <sup>a</sup>	NA	NA	NA
LSD ( $p \leq 0.05$ )	0.19	0.27	0.12	0.31	0.11	0.09	0.16

NA indicates treatment not applied. For each term period and year, different lower-case letters indicate a significant difference between means at  $p \leq 0.05$ .

In the MT experiment, the high cost of the L treatments and the non-significant effect on grain yield resulted in negative treatment NPV of  $-\$100$  to  $-\$209 \text{ ha}^{-1}$  (Table 4). In contrast, the cost and associated grain yield increases for the G2.5 treatment resulted in positive treatment NPV of  $\$157 \text{ ha}^{-1}$ . In the ST experiment, the low treatment grain yield increases resulted in negative treatment NPV, ranging between  $-\$24$  to  $-\$179 \text{ ha}^{-1}$ .

In the LT experiment, wheat grain yields ( $\text{t ha}^{-1}$ ) ranged from  $0.67 \text{ t ha}^{-1}$  in 2014 to  $2.15 \text{ t ha}^{-1}$  in 2011 for the C treatment due to variation in growing season rainfall (Table 5). Low June rainfall in 2014 resulted in a delay in crop emergence resulting in low wheat grain yield and a non-significant response for all treatments. The L2 treatment increased wheat grain yield compared to the C treatment by 20% in 2016. The L4 treatment increased wheat grain yield compared to the C treatment by 10–24% in 2008, 2011, and 2016. The L8 treatment increased wheat grain yield compared to the C treatment by 15–27%, in sampling years other than 2014. The difference between the L4 and L8 treatments was not significant. The G treatment increased wheat grain yield compared to the C treatment, but the magnitude declined over time from 17–22% in 2008–2010, to non-significant in 2011. The re-application of G in 2013 gave

a non-significant wheat grain yield response in 2013, 2015, and 2016. In contrast, wheat grain yield response for L8 treatment compared to the C treatment increased over time, from 14% in 2008 to 27% in 2016. Finally, the L4 + G2 treatment increased wheat yield by 17–25% in all sampling years other than 2014. Treatment increased total grain yield over the 7 sampling years compared to the C treatment by 14–23% for L2, L4, L8, and G2 treatments and 26% for L4 + G2.

**Table 4.** Profit (\$ ha<sup>-1</sup>) is calculated for canola in 2016, wheat in 2017, and barley in 2018, at the MT (3 growing seasons, 2017–2018), and the ST (2 growing seasons, 2016–2018) experiments. The total net present value (NPV) was calculated over the study period. Treatment NPV is the total NPV for the treatment minus total NPV of the control. Treatments were applied once at the MT experiment in July 2015, and at the ST experiment in March of 2017.

Treatment	MT					ST			
	2016	2017	2018	Total NPV	Treatment NPV	2017	2018	Total NPV	Treatment NPV
C	\$959	\$308	\$194	\$1360		\$89	-\$64	\$27	
L2.5	\$825	\$303	\$232	\$1261	-\$100	-\$73	-\$41	-\$107	-\$134
L5.0	\$702	\$324	\$219	\$1151	-\$209	NA	NA	NA	NA
G2.5	\$1019	\$387	\$227	\$1518	\$157	\$33	-\$31	\$3	-\$24
L2.5 + G2.5	\$861	\$400	\$227	\$1379	\$19	-\$145	-\$15	-\$152	-\$179
L5.0 + G2.5	\$700	\$415	\$232	\$1244	-\$116	NA	NA	NA	NA

NA indicates treatment not applied.

**Table 5.** The LT experiment wheat grain yields (t ha<sup>-1</sup>) observed for the 7 sampling years, between 2008–2016. The total represents the sum of the grain yields over the study period. Treatments were applied twice, in March of 2008 and 2013. Treatments were defined as the total amount of L or G used, and included control (C), 2 t L ha<sup>-1</sup> (L2), 4 t L ha<sup>-1</sup> (L4), 8 t L ha<sup>-1</sup> (L8), 2 t G ha<sup>-1</sup> (G2) and 2 t L ha<sup>-1</sup> plus 1 t G ha<sup>-1</sup> (L4 + G2). For each year, different lower case letters indicate a significant difference between means at  $p \leq 0.05$ . LSD values are presented at  $p \leq 0.05$ .

Treatment	2008 <sup>†</sup>	2010	2011	2013 <sup>†</sup>	2014	2015	2016	Total
C	1.89 <sup>b</sup>	1.08 <sup>b</sup>	2.15 <sup>c</sup>	1.48 <sup>c</sup>	0.65 <sup>a</sup>	1.64 <sup>c</sup>	1.59 <sup>b</sup>	10.49 <sup>c</sup>
L2	2.07 <sup>a,b</sup>	1.31 <sup>a,b</sup>	2.34 <sup>b,c</sup>	1.59 <sup>b,c</sup>	0.78 <sup>a</sup>	1.87 <sup>b,c</sup>	1.98 <sup>a</sup>	11.93 <sup>b</sup>
L4	2.19 <sup>a</sup>	1.20 <sup>a,b</sup>	2.39 <sup>a,b</sup>	1.57 <sup>b,c</sup>	0.78 <sup>a</sup>	1.88 <sup>b,c</sup>	2.10 <sup>a</sup>	12.11 <sup>a,b</sup>
L8	2.19 <sup>a</sup>	1.39 <sup>a</sup>	2.59 <sup>a</sup>	1.74 <sup>a,b</sup>	0.83 <sup>a</sup>	2.00 <sup>a,b</sup>	2.17 <sup>a</sup>	12.91 <sup>a,b</sup>
G2	2.29 <sup>a</sup>	1.39 <sup>a</sup>	2.22 <sup>b,c</sup>	1.71 <sup>a,b,c</sup>	0.84 <sup>a</sup>	1.87 <sup>b,c</sup>	1.67 <sup>b</sup>	11.99 <sup>b</sup>
L4 + G2	2.29 <sup>a</sup>	1.43 <sup>a</sup>	2.59 <sup>a</sup>	1.84 <sup>a</sup>	0.89 <sup>a</sup>	2.18 <sup>c</sup>	1.97 <sup>a</sup>	13.20 <sup>a</sup>
LSD ( $p \leq 0.05$ )	0.21	0.22	0.22	0.20	0.21	0.27	0.27	1.05

<sup>†</sup> The treatments applied in March. For each element and year, different lower-case letters indicate a significant difference between means at  $p \leq 0.05$ .

The RY% values for the C treatment was 68% in the year of low rainfall of 2010 compared to 83% in 2011, which had the highest October rainfall for the study period. The order of decreasing treatment RY was L4 + G2 (90–100%), followed by L8 (86–100%), then L4 (82–94%), then G2 (80–100%), and finally, L2 (81–91%).

In the LT experiment, the high grain yield response resulted in a positive treatment NPV for all treatments. The greatest treatment NPV of \$332 ha<sup>-1</sup> occurred for the L4 + G2 treatment (Table 6). The order of decreasing treatment NPV was L4 + G2, then G2 (\$277 ha<sup>-1</sup>), then L2 (\$219 ha<sup>-1</sup>), then L4 (\$145 ha<sup>-1</sup>), and finally L8 (\$134 ha<sup>-1</sup>).



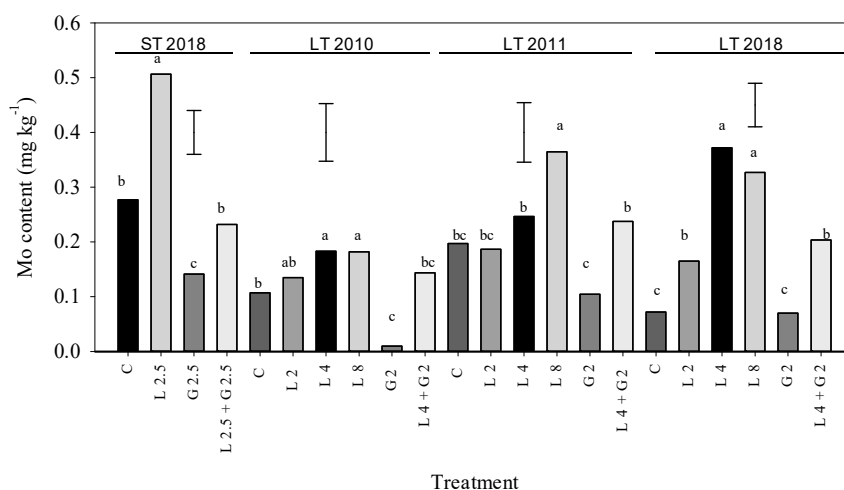
**Table 6.** Profit (\$ ha<sup>-1</sup>) calculated from the LT experiment, for the 7 sampling years 2008–2016. The total net present value (NPV) was calculated over the study period. Treatment NPV is the total NPV for the treatment minus total NPV of the control. Treatments were applied twice, in March of 2008 and 2013.

Treatment	2008 †	2010	2011	2013 †	2014	2015	2016	Total	Treatment
								NPV	NPV
C	\$265	\$155	\$348	\$259	−\$38	\$231	\$175	\$1173	
L2	\$202	\$226	\$395	\$293	−\$3	\$294	\$275	\$1392	\$219
L4	\$126	\$192	\$408	\$287	−\$3	\$297	\$306	\$1318	\$145
L8	−\$82	\$251	\$458	\$339	\$10	\$330	\$323	\$1307	\$134
G2	\$281	\$251	\$365	\$330	\$13	\$294	\$196	\$1450	\$277
L4 + G2	\$73	\$263	\$458	\$370	\$26	\$380	\$272	\$1505	\$332

† The treatments applied in March.

### 3.2. Shoot Nutrient Concentrations

In the ST experiment, the Mo concentration of the plant tissue was affected by the L2.5 and G2.5 treatments measured in 2018 (Figure 1). The L2.5 treatments increased the shoot Mo concentration compared to the C treatment by 83%, while G2.5 application resulted in a 49% decrease in Mo concentration. The Mo concentration for the L2.5 + G2.5 treatments was not significantly different from the C.



**Figure 1.** Mo concentration (mg kg<sup>-1</sup>) response for the treatments control (C), 2.5 t L ha<sup>-1</sup> (L2.5), 2.5 t G ha<sup>-1</sup> (G2.5), 2.5 t L ha<sup>-1</sup> plus 2.5 t G ha<sup>-1</sup> (L2.5 + G2.5) measured at the ST experiment in 2018 and for the treatments control (C), 2.0 t L ha<sup>-1</sup> (L2), 4.0 t L ha<sup>-1</sup> (L4), 8.0 t L ha<sup>-1</sup> (L8), 2.0 t G ha<sup>-1</sup> (G2), 4.0 t L ha<sup>-1</sup> plus 2.0 t G ha<sup>-1</sup> (L4 + G2) at the LT experiment in 2010, 2011 and 2018. For each year, bars sharing the same letter were not significantly different at ( $p \leq 0.05$ ). Error bar represents LSD ( $n = 3$ ).

In the LT experiment, the application of L increased Mo concentration by up to 71% in 2010, 85% in 2011, and 416% in 2018. In contrast, G2 application decreased Mo concentration by 91% in 2010, with the effect being not significant in 2011 and 2018. The L4 + G2 treatment had similar Mo concentrations as the C treatment in 2010 and 2011, but a 182% greater Mo concentration in 2018.

In the LT, the application of L increased P concentration, but decreased the Zn and Mn concentration in wheat shoots (Table 7).

**Table 7.** Wheat shoot Mn (mg kg<sup>-1</sup>), P (g kg<sup>-1</sup>), K (g kg<sup>-1</sup>), Zn (mg kg<sup>-1</sup>), Ca (g kg<sup>-1</sup>), and S (g kg<sup>-1</sup>) measured at the LT experiment among years for the treatments control (C), 2 t L ha<sup>-1</sup> (L2), 4 t L ha<sup>-1</sup> (L4), 8 t L ha<sup>-1</sup> (L8), 2 t G ha<sup>-1</sup> (G2) and 2 t L ha<sup>-1</sup> plus 1 t G ha<sup>-1</sup> (L4 + G2). The LSD values are for the means,  $n = 3$  at  $p \leq 0.05$ .

Nutrient	Treatment	2008 †	2010	2011	2013 †	2014	2015	2016	2018
Mn	C	188 <sup>b,c</sup>	328 <sup>a</sup>	323 <sup>a</sup>	338 <sup>a</sup>	282 <sup>b</sup>	285 <sup>a</sup>	246 <sup>a</sup>	61 <sup>a</sup>
	L2	173 <sup>c</sup>	270 <sup>b</sup>	265 <sup>b</sup>	242 <sup>b</sup>	187 <sup>c</sup>	191 <sup>b</sup>	156 <sup>b</sup>	32 <sup>b</sup>
	L4	203 <sup>b,c</sup>	262 <sup>b</sup>	220 <sup>c</sup>	197 <sup>b</sup>	167 <sup>c</sup>	175 <sup>b</sup>	118 <sup>c</sup>	28 <sup>b</sup>
	L8	191 <sup>b,c</sup>	244 <sup>b</sup>	214 <sup>c</sup>	175 <sup>b</sup>	181 <sup>c</sup>	155 <sup>b</sup>	101 <sup>c</sup>	32 <sup>b</sup>
	G2	251 <sup>a</sup>	362 <sup>a</sup>	345 <sup>a</sup>	364 <sup>a</sup>	361 <sup>a</sup>	282 <sup>a</sup>	244 <sup>a</sup>	59 <sup>a</sup>
	L4 + G2	225 <sup>b,c</sup>	267 <sup>b</sup>	231 <sup>b,c</sup>	223 <sup>b</sup>	222 <sup>a</sup>	185 <sup>b</sup>	116 <sup>c</sup>	36 <sup>b</sup>
	LSD ( $p \leq 0.05$ )	38	38	69	77	58	68	32	16
P	C	1.5 <sup>b</sup>	2.3 <sup>a</sup>	3.9 <sup>a</sup>	3.4 <sup>b</sup>	2.2 <sup>c</sup>	3.7 <sup>c</sup>	4.0 <sup>c</sup>	1.7 <sup>c</sup>
	L2	1.5 <sup>b</sup>	2.3 <sup>a</sup>	4.2 <sup>a</sup>	3.3 <sup>b</sup>	2.5 <sup>b,c</sup>	3.9 <sup>b</sup>	5.0 <sup>b</sup>	2.0 <sup>a</sup>
	L4	1.7 <sup>a,b</sup>	2.2 <sup>a</sup>	3.9 <sup>a</sup>	3.7 <sup>a,b</sup>	2.7 <sup>a,b</sup>	4.0 <sup>b</sup>	5.2 <sup>b</sup>	2.1 <sup>a</sup>
	L8	1.5 <sup>a,b</sup>	2.5 <sup>a</sup>	4.3 <sup>a</sup>	4.2 <sup>a</sup>	2.9 <sup>a</sup>	4.4 <sup>a</sup>	6.2 <sup>a</sup>	2.0 <sup>a,b</sup>
	G2	1.6 <sup>a,b</sup>	2.5 <sup>a</sup>	4.0 <sup>a</sup>	3.8 <sup>a,b</sup>	2.7 <sup>a,b</sup>	3.6 <sup>b,c</sup>	4.5 <sup>b,c</sup>	1.8 <sup>b,c</sup>
	L4 + G2	1.7 <sup>a,b</sup>	2.8 <sup>a</sup>	4.3 <sup>a</sup>	4.2 <sup>a</sup>	2.8 <sup>a,b</sup>	3.9 <sup>b</sup>	5.4 <sup>b</sup>	2.1 <sup>a</sup>
	LSD ( $p \leq 0.05$ )	0.2	0.6	0.5	0.6	0.3	0.5	0.8	0.2
K	C	19 <sup>a,b</sup>	20 <sup>a</sup>	27 <sup>a</sup>	29 <sup>a</sup>	18 <sup>a</sup>	25 <sup>a</sup>	19 <sup>a,b</sup>	14 <sup>b</sup>
	L2	20 <sup>a</sup>	20 <sup>a</sup>	26 <sup>a</sup>	29 <sup>a</sup>	19 <sup>a</sup>	27 <sup>a</sup>	18 <sup>a,b</sup>	19 <sup>a,b</sup>
	L4	19 <sup>a,b</sup>	17 <sup>a</sup>	25 <sup>a</sup>	26 <sup>a</sup>	19 <sup>a</sup>	27 <sup>a</sup>	20 <sup>a</sup>	22 <sup>a</sup>
	L8	16 <sup>c</sup>	18 <sup>a</sup>	25 <sup>a</sup>	29 <sup>a</sup>	17 <sup>a</sup>	24 <sup>a</sup>	16 <sup>a,b</sup>	17 <sup>a,b</sup>
	G2	18 <sup>b,c</sup>	20 <sup>a</sup>	27 <sup>a</sup>	32 <sup>a</sup>	19 <sup>a</sup>	27 <sup>a</sup>	16 <sup>a,b</sup>	16 <sup>a,b</sup>
	L4 + G2	20 <sup>a</sup>	21 <sup>a</sup>	25 <sup>a</sup>	29 <sup>a</sup>	30 <sup>a</sup>	25 <sup>a</sup>	14 <sup>b</sup>	21 <sup>a</sup>
	LSD ( $p \leq 0.05$ )	2	3	3	6	3	4	5	6
Zn	C	22 <sup>a</sup>	27 <sup>a,b</sup>	35 <sup>a</sup>	36 <sup>a</sup>	19 <sup>a</sup>	24 <sup>a</sup>	22 <sup>a</sup>	18 <sup>a</sup>
	L2	26 <sup>a</sup>	25 <sup>a,b</sup>	35 <sup>a</sup>	33 <sup>a</sup>	17 <sup>a</sup>	22 <sup>a,b</sup>	19 <sup>a,b</sup>	12 <sup>b</sup>
	L4	29 <sup>a</sup>	24 <sup>b</sup>	28 <sup>b</sup>	32 <sup>a</sup>	17 <sup>a</sup>	22 <sup>a,b</sup>	17 <sup>b</sup>	12 <sup>b</sup>
	L8	23 <sup>a</sup>	25 <sup>a,b</sup>	33 <sup>a,b</sup>	35 <sup>a</sup>	16 <sup>a</sup>	21 <sup>b</sup>	17 <sup>b</sup>	10 <sup>c</sup>
	G2	28 <sup>a</sup>	28 <sup>a,b</sup>	37 <sup>a</sup>	36 <sup>a</sup>	24 <sup>a</sup>	24 <sup>a</sup>	22 <sup>a</sup>	18 <sup>a</sup>
	L4 + G2	29 <sup>a</sup>	32 <sup>a</sup>	34 <sup>a,b</sup>	41 <sup>a</sup>	18 <sup>a</sup>	22 <sup>a,b</sup>	18 <sup>a,b</sup>	13 <sup>b</sup>
	LSD ( $p \leq 0.05$ )	4	3	3	4	2	1	2	1
Ca	C	2.7 <sup>b</sup>	5.8 <sup>b</sup>	6.4 <sup>c</sup>	5.4 <sup>c</sup>	5.4 <sup>b</sup>	5.3 <sup>b</sup>	7.1 <sup>b</sup>	2.5 <sup>a</sup>
	L2	3.3 <sup>a</sup>	7.2 <sup>a</sup>	7.6 <sup>b</sup>	5.9 <sup>b</sup>	5.6 <sup>b</sup>	5.9 <sup>a,b</sup>	7.3 <sup>b</sup>	2.9 <sup>a</sup>
	L4	3.4 <sup>a</sup>	7.8 <sup>a</sup>	8.0 <sup>b</sup>	7.3 <sup>b</sup>	5.9 <sup>a,b</sup>	6.0 <sup>a,b</sup>	8.3 <sup>a,b</sup>	3.1 <sup>a</sup>
	L8	3.3 <sup>a</sup>	7.6 <sup>a</sup>	7.9 <sup>b</sup>	7.1 <sup>b</sup>	6.9 <sup>a</sup>	6.7 <sup>a</sup>	8.9 <sup>a</sup>	3.3 <sup>a</sup>
	G2	3.8 <sup>a</sup>	7.7 <sup>a</sup>	8.2 <sup>b</sup>	7.5 <sup>a,b</sup>	6.9 <sup>a</sup>	5.7 <sup>a,b</sup>	8.6 <sup>a,b</sup>	3.2 <sup>a</sup>
	L4 + G2	3.6 <sup>a</sup>	7.8 <sup>a</sup>	8.8 <sup>a</sup>	7.8 <sup>a</sup>	6.8 <sup>a</sup>	6.9 <sup>a</sup>	8.6 <sup>a,b</sup>	3.2 <sup>a</sup>
	LSD ( $p \leq 0.05$ )	0.6	0.8	1.2	1.0	1.0	1.2	1.4	0.8
S	C	1.8 <sup>a</sup>	3.0 <sup>a</sup>	3.5 <sup>a</sup>	3.4 <sup>a,b</sup>	2.3 <sup>a</sup>	3.8 <sup>a,b</sup>	3.8 <sup>a</sup>	1.7 <sup>a</sup>
	L2	1.9 <sup>a</sup>	3.4 <sup>a</sup>	3.6 <sup>a</sup>	3.0 <sup>b</sup>	2.2 <sup>a</sup>	3.5 <sup>c</sup>	3.9 <sup>a</sup>	1.8 <sup>a</sup>
	L4	1.9 <sup>a</sup>	3.4 <sup>a</sup>	3.5 <sup>a</sup>	3.4 <sup>a,b</sup>	2.3 <sup>a</sup>	3.8 <sup>c</sup>	3.9 <sup>a</sup>	1.8 <sup>a</sup>
	L8	1.9 <sup>a</sup>	3.2 <sup>a</sup>	3.6 <sup>a</sup>	3.5 <sup>a,b</sup>	2.6 <sup>a</sup>	3.6 <sup>b,c</sup>	3.9 <sup>a</sup>	1.7 <sup>a</sup>
	G2	2.0 <sup>a</sup>	3.4 <sup>a</sup>	3.8 <sup>a</sup>	4.0 <sup>a</sup>	2.5 <sup>a</sup>	3.6 <sup>b,c</sup>	4.3 <sup>a</sup>	1.9 <sup>a</sup>
	L4 + G2	2.0 <sup>a</sup>	3.4 <sup>a</sup>	3.8 <sup>a</sup>	3.7 <sup>a,b</sup>	2.4 <sup>a</sup>	3.5 <sup>a</sup>	4.2 <sup>a</sup>	1.9 <sup>a</sup>
	LSD ( $p \leq 0.05$ )	0.4	0.4	0.4	0.6	0.3	0.2	0.5	0.3

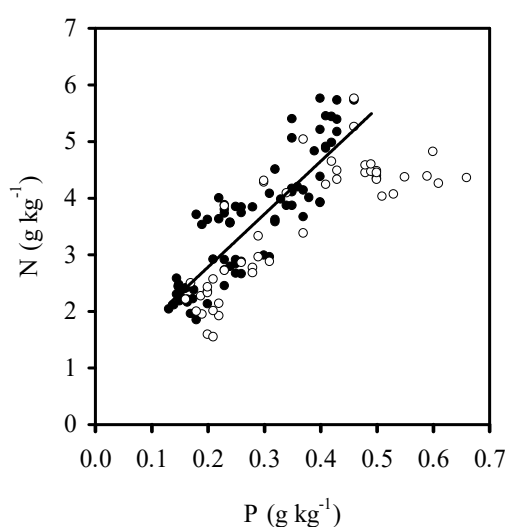
† The treatments applied in March. For each term period and year, different lower-case letters indicate a significant difference between means at  $p \leq 0.05$ .

The Mn concentration for the L2, L4, L8, and L4 + G2 treatments was 18–59% lower than the C treatment for wheat grown over the period 2010–2016 (Table 7). For barley grown in 2018, Mn

concentration was lower compared to wheat grown in the previous years, but Mn concentration was still 48–54% less for the L treatments compared to the C treatment. In contrast, in the G2 treatment Mn concentration was 28–34% greater than the C treatment in 2008 and 2014.

The L4 + G2 treatment in the LT experiment increased P shoot concentration compared to the C treatment by 5–35%, over the period 2008–2018 (Table 7). The P concentration for the L8 treatment was 24% greater than the C treatment first in 2013, and it remained 19–55% greater between 2014–18. The P concentration for the L4 treatment was 23% greater than the C treatment in 2014, and remained 24–30% greater between 2016–18. Finally, the P concentration for the L2 treatment was 18–25% greater than the C treatment between 2016–18.

Wheat shoot P and N concentration are related when the L treatments had no effect on P concentration (Figure 2). For treatments where L and L + G application increased P concentration, P concentration was relatively greater compared to N concentration, especially for the 2016 growing season, where P concentration was relatively high compared to the other growing seasons (Table 7).



**Figure 2.** Relationship between P and N ( $\text{g kg}^{-1}$ ) for observations where the L application had no impact on P ( $\text{g kg}^{-1}$ ) (●) and when L and L + G treatment increase P ( $\text{g kg}^{-1}$ ) (○). Regression equation for the relationship for ● observations is  $N (\text{g kg}^{-1}) = 0.8 + 10.0 \times P (\text{g kg}^{-1})$ ,  $r^2 = 0.78$  ( $p < 0.0001$ ) and for all observations is  $N (\text{g kg}^{-1}) = 1.4 + 7.0 \times P (\text{g kg}^{-1})$ ,  $r^2 = 0.63$ , line not presented.

The L4 and L4 + G2 treatment increased K concentration by 49–50% compared to the C treatment in 2018 (Table 7). The wheat tissue Zn concentration ( $\text{mg kg}^{-1}$ ) for the L8 treatments was lower than the control in 2015 (13%), 2016 (23%) and 2018 (44%). The Zn concentration ( $\text{mg kg}^{-1}$ ) for the L2 and L4 treatments was 33% lower than the C treatment in 2018.

The Ca concentration was 9–35% greater for the L2 and L4 treatments than the C treatment, over the period 2008–2013. The Ca concentration was 8–41% greater for the L8 treatment than the C treatment over the period 2008–2016. The G2 treatment had 28–41% high Ca concentration than the C treatment over the period 2010–2014. The L4 + G2 treatment had 26–38% greater Ca concentration than the C treatment over the period 2008–2015.

The S concentration was not affected by the L and G treatments, but varied between years, ranging between 1.8–4.3  $\text{g kg}^{-1}$ . The exception was for the G2 treatment, which increased S concentration by 18% in 2013, while the L2 and L4 + G2 treatments decreased S concentration in 2015.

In the LT experiment, N, Cu, and B concentrations were not affected by the L and G treatments (data not presented).

## 4. Discussion

### 4.1. Grain Yield

The occurrence of the wheat grain yield response to L or G application is dependent on their impact on  $\text{pH}_{\text{CaCl}_2}$ , EC and the concentration of toxic  $\text{Al}^{3+}$  in the root zone [23,26]. Whereas L has a significant impact on the soil  $\text{Al}_{\text{CaCl}_2}$  and  $\text{pH}_{\text{CaCl}_2}$ , G affects EC and Al species composition in the soil solution [23,26]. For soils with subsoil  $\text{Al}_{\text{CaCl}_2}$  greater than 2.5–4.5  $\text{mg kg}^{-1}$  [5], a response to the L application developed in the LT (Table 5) because the L application reduces subsoil  $\text{Al}_{\text{CaCl}_2}$  below the critical values [23], leading to increased root growth and access to soil water [8,39]. The nutrient co-benefits of L include the reduced potential for Mn toxicity in the ST, increased shoot Mo concentration in both the ST and LT, increased uptake of Ca in the ST and MT, and increased uptake of P in the LT. In contrast, L application decreased reduced shoot Zn concentration in the LT (Table 7).

For Tenosols of SWA, the acidification process results in reduced pH within the 10–30 cm soil layer [2]. Hence, Tenosols often have toxic Al concentrations in the 10–30 cm, as illustrated by the  $\text{Al}_{\text{CaCl}_2}$  soil profile at the LT experimental site [23]. By contrast, other acid soils have increased severity of Al toxicity with increasing soil depth, as illustrated by the  $\text{Al}_{\text{CaCl}_2}$  soil profile at the ST and MT [23] experimental sites. These differences in the distribution of the Al toxicity constraint within the soil profile will have an impact on the ability of L and G applications to treat the limitation. When the Al toxicity constraint is within the 10–30 cm soil layer, G provided a grain yield response over the period 2008–2010, during which there was 1520 mm of rainfall (Table 4). The decline in the effectiveness of the G application over time can be attributed to the leaching of  $\text{SO}_4\text{-S}$  through this soil layer [23].

Crop grain yield increased for two years after G application in the ST and MT experiments (Table 3), when the  $\text{pH}_{\text{CaCl}_2}$  in the 0–10 cm layer was greater than 5.5, and the  $\text{Al}_{\text{CaCl}_2}$  content of the soil layer below 10 cm was greater than 2.5  $\text{mg kg}^{-1}$  (Table 1). The G treatment was profitable in the MT experiment, but not in the ST experiment, where the removal of subsoil compaction constraint had a larger effect on yield than the G treatment (Table 4). In contrast, the application of L did not affect grain yield in the short to medium term on these soils, where the  $\text{pH}_{\text{CaCl}_2}$  in the 0–10 cm layer was greater than 5.5. Similarly, when the soil  $\text{pH}_{\text{KCl}}$  was greater than 5.0 in the 0–10 cm soil layer, and the subsoil  $\text{Al}_{\text{KCl}}$  (soil pH and Al measured using a 0.005 M KCl solution) was greater than 2.0  $\text{mg kg}^{-1}$  [22], G application increased wheat grain yield, while L application had no effect [27].

At the LT experiment, L, G and L + G application resulted in an increase in wheat grain yield in most years (Table 3), because the soil had a  $\text{pH}_{\text{CaCl}_2}$  value of 4.6 in the 0–10 cm soil layer and the  $\text{Al}_{\text{CaCl}_2}$  content of the soil layer below 10 cm was greater than 2.5–4.5  $\text{mg kg}^{-1}$  (Table 1). The short-term effect of L application was due to L application, overcoming the acidity limitation in the surface soil layer, because L moves slowly into the subsoil layers [5]. Due to the large increase in grain yield observed, the L2 and L4 treatments were profitable, even in the first year after application, while the greater cost of the L8 treatments resulted in a small loss (Table 6). In contrast, the ST effect of the G application was due to the G treating subsoil Al toxicity limitation, due to the rapid leaching of  $\text{SO}_4\text{-S}$  into the soil layers below 10 cm, increasing  $\text{S}_{\text{KCl40}}$  and EC [23] and the formation of  $\text{Al-SO}_4$  [26].

The most effective and profitable treatment in the LT experiment was L4 + G2 treatment, which resulted in treatment RY% values near 100% (94–100%) (Table 3) and a treatment NPV of \$332  $\text{ha}^{-1}$  for the 7 cropping seasons. The order of declining agronomic effectiveness of the other treatments was L8, followed by L4, followed by G2, and finally L2. In contrast, the order of declining profitable was G2 (\$277  $\text{ha}^{-1}$ ), followed by L2 (\$219  $\text{ha}^{-1}$ ), followed by L4 (\$145  $\text{ha}^{-1}$ ), and finally L8 (\$134  $\text{ha}^{-1}$ ) for the 7 crops grown over 9 years. Hence, the small increase in grain yield observed by increasing L application from 2 to 8 t L  $\text{ha}^{-1}$  (Table 5) was not sufficient to cover the greater costs. The rates of acidification are in the order of 10–11  $\text{kg CaCO}_3 \text{ yr}^{-1}$  [3,4]. Moreover, there is no change in either  $\text{pH}_{\text{CaCl}_2}$  or  $\text{Al}_{\text{CaCl}_2}$  over the study period of the LT experiment (Table 1). Hence, L treatments will provide grain yield response greater than the LT study period, which will increase the profitability of the L treatments. The length of time the L response will last is illustrated in other L experiments

from the region, which have been monitored for up to 18 years [5]. For example, an experiment, which had a subsoil  $Al_{CaCl_2}$  content of  $7 \text{ mg kg}^{-1}$ , gave a 20% response to  $4 \text{ t L ha}^{-1}$  16 years after the initial application.

The application of L4 + G2 was the most agronomically effective and profitable treatment, because the L application acts to increase the soil  $pH_{CaCl_2}$  and decrease  $Al_{CaCl_2}$  in the 0–10 cm soil layer [23] and the G application acts to increase the  $S_{KCl40}$  and EC [23]. Furthermore, subsoil  $Al_{CaCl_2}$  declined more when both L and G are used, compared to when only L is used in the MT and LT [23]. Similarly, highest grain yields arise when G and L are applied together, and the application of G resulted in a greater grain yield than when only L was applied [27,51]. The response to G application develops because it increases soil solution EC, and results in the formation of  $Al-SO_4$  [22]. The application of L resulted in an increase in soil  $pH_{KCl}$  and a decrease in soil  $Al_{KCl}$  in the 0–10 cm soil layer. The combined application of L and G resulted in L increasing  $pH_{KCl}$  to a greater depth than when L alone is applied at one site.

Seasonal conditions have a significant effect in determining the size of the L response. More significant crop production responses develop when water stress happens during the growing season [6,17,40,52,53]. For example, the highest grain yield response tends to be found under seasons when water stress take place during the vegetative stage and just after anthesis [17]. Similarly, in the LT experiment, grain yield response to L and L + G treatments was more pronounced when the crop was more reliant on subsoil water. For example, lowest RY% (68%) exists in the driest year (2010) because the crop is more reliant on subsoil water. In contrast, the highest RY% (83%) occurred in the year with the wettest October (2011), because the crop is less reliant on subsoil water. Similarly, low RY% arise in years when high fallow season rainfall (228–320 mm) was followed by low growing season rainfall (<140 mm) [5]. For the MT and LT experiment, the measured RY% was consistent with the  $Al_{CaCl_2}$  soil–wheat L response relationship, defined by [5]. In contrast, for the ST experiment, the measured RY% was greater than the RY% value determined by the equation defined by [5]. This suggests that the G treatment did not fully overcome the Al toxicity limitation.

#### 4.2. Nutrition

The application of G to the soil reduces Mo concentration in plant tissue, as was observed in both the ST and LT experiments (Figure 1). This is because plants take up molybdate through  $SO_4-S$  transporters [43], and the presence of high  $SO_4-S$  concentrations in the soil solution decrease molybdate uptake, due to competition for absorption by the same anion transporters [44]. By contrast, the application of L to soils increases soil pH, leading to a decrease in Mo adsorption and increase plant availability of soil Mo [37]. This resulted in greater plant tissue Mo concentrations for the L treatments, both in the ST and LT experiments. The Mo response to L application increased from 26–32% in 2010 to 27–147% in 2011, to 129–416% in 2018 in the LT experiment (Figure 1). The critical Mo concentration range in wheat tissue is  $0.08\text{--}0.10 \text{ mg kg}^{-1}$  [49]. For the C treatment, in the LT experiment, Mo concentration ranged between  $0.07\text{--}0.15 \text{ mg kg}^{-1}$  and was  $0.28 \text{ mg kg}^{-1}$  for the ST experiment. The lowest Mo concentration ( $0.05 \text{ mg kg}^{-1}$ ) occurred for the G2 treatment at the LT in 2010, which is below the wheat critical Mo concentration range of  $0.09\text{--}0.18 \text{ (mg kg}^{-1})$  [37]. However, the G2 treatment was observed to increase the grain yield in 2010 (Table 3) indicating the effect of G on soil Al toxicity was more important than the effect of G on Mo uptake (Figure 1). Nevertheless, in conducting G experiments in the future, it is recommended to apply Mo to all treatments, to reduce the risk of Mo deficiency developing on the G treatments.

The application of L increases the soil  $pH_{CaCl_2}$ , which results in decreased P precipitation [54,55] and greater Zn adsorption [38,56]. Moreover, the application of L can remove the  $Al^{3+}$  toxicity, which increases the ability of wheat roots to uptake P [42,57,58]. In the case of P, increased P concentration in wheat shoots developed at the LT six years (2013), after the initial application of L (Table 7). The application L did not affect the N concentration of crop shoots. Hence, the shoot P concentration was related to N concentration for the sampling times where L application had no effect on P concentration

(Figure 2) is consistent with the observation of [59]. Furthermore, the L treatment gave a greater P concentration relative to N concentration, only in 2016 (Table 7). Phosphorus uptake was greater in 2016 because of the relatively wet June and July since P uptake is greater when the soil has greater water content [59], and because of the increased soil availability of P due to the liming (Table 7). However, the increase in P concentration was unlikely to increase wheat grain yield, because the experiment received an annual application of P fertiliser ( $4.5 \text{ kg P ha}^{-1}$ ), and the soil test and shoot P concentration values indicate adequate P availability [49,60].

There are conflicting reports of the impact of lime application on K nutrition. The application of L has been reported to both decrease [42] and increase K concentration in plants [39,58,61,62]. In the LT experiment, there was no treatment effect on shoot K concentration over the period 2008 to 2016, but the L4 and L4 + G2 treatments increased K concentration by 49–50% in 2018 (Table 7). For the C treatment, the K concentration treatment varied over time ( $18\text{--}29 \text{ g kg}^{-1}$ ), when plants were sampled 6–8 weeks after seeding, over the period 2008–2016. These shoot K concentrations are close to the critical value of  $23 \text{ g kg}^{-1}$  for 54-day-old wheat plants [63]. Crop removal of K over the experimental period (2008 to 2018) reduced the  $K_{\text{Col}}$  of the soil from 70 to  $51 \text{ mg kg}^{-1}$  in the 0–10 cm soil layer (Table 1), which is within the critical range for 90% of maximum production for wheat  $37\text{--}58 \text{ mg kg}^{-1}$  [64]. Hence,  $K_{\text{Col}}$  has declined to marginal levels for wheat production later in the LT term experiment. Nevertheless, in the LT experiment, wheat grain yield was increased by 24–36%, by the L2, L4, L8 and L4 + G2 treatments. This indicates that soil acidity or Al toxicity was limiting wheat production more than marginal  $K_{\text{Col}}$  status of the soil.

Gypsum contains Ca and  $\text{SO}_4\text{-S}$ , hence, the application of G to soils is likely to increase the Ca concentration and S concentration in plant tissue. An increase in nutrient concentration can result in greater plant growth if the nutrient concentration is lower than the critical value for crop growth, and the G application increases the plant uptake of the limiting nutrient. The wheat shoot S concentration was greater than the critical of  $2.9 \text{ g kg}^{-1}$  [65], in 2010, 2011, 2013, 2015, and 2016, but lower than this value in 2008, 2014 and 2018 (Table 7). In years where S concentration was below the critical value, G application did not increase the S concentration compared to the control. Furthermore, the high  $S_{\text{KCl40}}$ ,  $14\text{--}28 \text{ mg kg}^{-1}$ , in both the 0–10 cm and the 0–30 cm soil layers, is above the critical value for wheat growth [66]. Hence, it is unlikely that the increase in grain yield resulting from G application is due to improved S nutrition.

Both L and G application increased Ca concentration in crops (Table 7). An increase in Ca concentration can be important when growing plants on acidic soils [67]. However, in these experiments, Ca concentration for the C treatments was greater than the critical range of  $1.8\text{--}2.1 \text{ g kg}^{-1}$  [49], indicating that the plants contained adequate Ca for plant growth. Similarly, the soil had a sufficient level of soil Ca with all soil layers sampled having  $\text{Ca}_{\text{Ex}}$  greater than the critical value of 10% of ECEC (Table 1) [68,69]. When acidic soils are deficient in Ca, or  $\text{Ca}_{\text{Ex}}$  per cent is lower than 10%, the impact of Ca can be more important than the effect of soil Al [68].

In the case of Zn, the increase in soil pH due to L application can reduce Zn uptake, due to an increase in Zn precipitation [38,56], or reduce Zn uptake due to an increase in Ca uptake [70]. In the LT experiment, L application reduced wheat shoot Zn concentration [71] (Table 7). However, reduced Zn concentration is unlikely to have resulted in a decrease in wheat grain yields, because the Zn concentration remained above the wheat shoot Zn critical range of  $16\text{--}20 \text{ mg kg}^{-1}$  in 2015 and 2016 [49]. However, it could be Zn deficient in 2018, because shoot Zn concentration were below this critical concentration ( $10\text{--}12 \text{ mg kg}^{-1}$ ) for the L treatments. Also, G application did not affect the Zn concentration, even though the Ca concentrations in the wheat shoots had increased to the same amount as for the L treatments. This suggests that reduced shoot Zn concentration when L is applied is because of increased Zn adsorption [38,56], and not due to increased Ca uptake [70].

Increases in soil pH due to L application reduces  $\text{Mn}^{2+}$  availability, and hence plant uptake of Mn. The critical concentration in wheat shoots is  $9\text{--}13 \text{ mg kg}^{-1}$  for Mn deficiency and  $380 \text{ mg kg}^{-1}$  for Mn toxicity [49]. In the LT experiment, L application decreased the Mn concentration in all years. However,



Mn deficiency is unlikely to develop because the Mn concentration remained much greater than the critical values (Table 7). The Mn wheat shoot concentration for the C treatment ranged between 188–328 mg kg<sup>-1</sup> and with G application increasing Mn concentration to 251–361 mg kg<sup>-1</sup>. These values are below the critical value for Mn toxicity in wheat. Nevertheless, the results highlight the benefit of L application in reducing the risk of Mn toxicity developing.

## 5. Conclusions

The most profitable treatment for wheat production in the LT was to apply 4 t L ha<sup>-1</sup> in combination with the application of 2 t G ha<sup>-1</sup>. At this site, soil pH<sub>CaCl2</sub> in the 0–10 cm soil layer was equal to 4.6 and Al<sub>CaCl2</sub> was greater than 2.5 mg kg<sup>-1</sup> in the 10–30 cm soil layer. In contrast, when the pH<sub>CaCl2</sub> of 0–10 cm was >5.5, due to previous L use history, and the subsoil Al<sub>CaCl2</sub> content was greater than 2.5 mg kg<sup>-1</sup>, it was only profitable to apply G in the ST and MT. The use of G was profitable in the ST and MT, and with L application in the LT, even though the soil studied had a low capacity to adsorb SO<sub>4</sub>-S, which results in the rapid leaching of SO<sub>4</sub>-S and no self-liming effect.

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