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Micro-Water Harvesting and Soil Amendment Increase Grain Yields of Barley on a Heavy-Textured Alkaline Sodic Soil in a Rainfed Mediterranean Environment

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Abstract: This paper focuses on the adverse effects of soil sodicity and alkalinity on the growth of barley (*Hordeum vulgare* L.) in a rainfed environment in south-western Australia. These conditions cause the accumulation of salt (called 'transient salinity') in the root zone, which decreases the solute potential of the soil solution, particularly at the end of the growing season as the soil dries. We hypothesized that two approaches could help overcome this stress: (a) improved micro-water harvesting at the soil surface, which would help maintain soil hydration, decreasing the salinity of the soil solution, and (b) soil amelioration using small amounts of gypsum, elemental sulfur or gypsum plus elemental sulfur, which would ensure greater salt leaching. In our experiments, improved micro-water harvesting was achieved using a tillage technique consisting of exaggerated mounds between furrows and the covering of these mounds with plastic sheeting. The combination of the mounds and the application of a low rate of gypsum in the furrow (50 kg ha^{-1}) increased yields of barley grain by 70% in 2019 and by 57% in 2020, relative to a control treatment with conventional tillage, no plastic sheeting and no amendment. These increases in yield were related to changes in ion concentrations in the soil and to changes in apparent electrical conductivity measured with the EM38.

Keywords: electromagnetic induction; EC$_{1:5}$; EM38; gypsum; plastic mulch; sodicity; elemental sulfur; transient salinity

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1. Introduction

This paper focuses on the growth of barley (*Hordeum vulgare* L.) on a sodic alkaline soil (Vertic Calcic Calcisol) affected by transient salinity and the ability of micro-water harvesting and soil amendment with combinations of gypsum and elemental sulfur to increase yield.

Soil sodicity is a constraint of global significance. It has recently been estimated that sodicity, expressed as an exchangeable sodium percentage (ESP) greater than 6%, occurs in surface soils (0–30 cm) in at least 75% of years on approximately 9.2 Mkm^2 of land, with the most severely affected continents being Asia, Africa and Australia [1]. Soil alkalinity is also important in semi-arid landscapes. Global-scale soil surveys show that the predominant factor determining soil pH is climate; in general, there is an abrupt transition from acid to alkaline pH values at the point where mean annual precipitation falls below mean annual potential evapotranspiration [2].

Sodicity [3,4] and alkalinity [5,6] both increase soil dispersion, but for different reasons. In many Australian soils, the dominant clay is kaolinite [7], which consists of platelet-like crystals approximately 390–560 nm in diameter and 60–120 nm in thickness [8]. The faces of these platelets are negatively charged. However, at neutral pH, their edges are positively charged [9]. When kaolinitic particles cluster together, they flocculate; there are two mechanisms for this: lamellar ('face to face') flocculation, and 'edge-to-face' flocculation [9]. Lamellar flocculation requires the repulsive forces of the clouds of cations occupying the space between adjacent clay faces to be overcome: this can be achieved by increasing the electrolyte concentration and by increasing concentrations of divalent calcium ions in this space [10]. 'Edge-to-face' flocculation depends on the electrostatic attraction of negatively charged platelet faces with positively charged edges; however, when the soil becomes alkaline, the positive charges on the edges become surrounded by hydroxyl ions, the net positive charges on the edges are lost, 'edge-to-face' flocculation ceases, and the clay disperses [11].

One consequence of dispersion in the sodic and alkaline dispersive soils of semi-arid landscapes is the accumulation of salt ("transient salinity") in the profile [5,12]. The adverse effects of soil dispersion on crop growth may in fact be caused by transient salinity. Given sufficient concentration, salts in a soil will adversely affect the growth of all agricultural crops [13,14]. However, the factor that actually decreases crop yield in saline soils is not the salt concentration of the soil but the salinity of the soil solution, which is the ratio of salt to water in the soil [12]. Elevated salinities of the soil solution adversely affect crop growth by decreasing the osmotic potential of the soil solution and by increasing the concentration of toxic ions in the soil solution [12,15,16]. The degree of stress is proportional to the concentration of salt in the soil, but also increases exponentially as the concentration of water in the soil declines [17–19]. We therefore considered it likely that the adverse effects of transient salinity on crop growth could be ameliorated by increasing soil hydration (using micro-water harvesting) and by decreasing, through leaching, salt concentrations in the soil (using amendment with gypsum or elemental sulfur) c.f. [20–26].

The salts associated with transient salinity either fall in the rain [27,28] or derive from the weathering of high-sodium rocks [12] and increase in concentration in the root zone in soils that disperse [5,12]. Based on measurements of the concentration of Cl^- in rainwater and average annual rain statistics, it has been estimated that the salt stored in the upper 1 m of a typical sodic alkaline soil in Western Australia would have taken approximately 1300 years to accumulate [5].

It seems likely that the independent effects of sodicity and alkalinity on salt accumulation are caused by effects of dispersion on saturated hydraulic conductivity (K_s). In column experiments with a kaolinitic soil perfused with an electrolyte solution of 50 mmol L^{-1} of charge and a Sodium Adsorption Ratio (SAR) of 20, increasing the pH from 6 to 8 caused a 43% decrease in K_s. However, when the SAR was increased to 40 at the same electrolyte concentration, increasing the pH from 6 to 8 caused an 97% decrease in K_s [29]. Results such as these suggest that sodicity and alkalinity interact in their adverse effects on soils.

The work described in the present paper is based around three themes: firstly, the ability of surface water harvesting and soil amendment to improve crop growth and yield, secondly the impacts of these treatments on transient salinity and soil chemistry, and thirdly relationships between variation in soil apparent electrical conductivity, grain yield and soil chemistry.

Regarding Theme 1 (improving crop growth and grain yield), we have been experimenting with approaches that address the issues of soil hydration and salt leaching in sodic alkaline soils using: (a) exaggerated soil mounding and plastic sheeting to increase surface water harvesting and improve the water content of the soil, and (b) the application of soil amendments (such as gypsum and elemental sulfur) that reverse dispersion. The present work marks the convergence of these two approaches in a field trial. We hypothesized that the grain yield of barley would be improved by micro-water harvesting at the soil surface

(H1), and by soil amendment with small rates of application of gypsum, elemental sulfur, or gypsum plus elemental sulfur (H2).

Regarding Theme 2 (effects of treatments on transient salinity and soil chemistry), previous work has shown that the salinity of the soil ($EC_{1:5}$) is affected by soil sodicity and soil pH [5,6]. However, it is not actually known which ions are most associated with transient salinity, how soil amendments affect these ions, and how these changes correlate with grain yield. We hypothesized (H3) that micro-water harvesting and soil amendment would affect crop yield because they decreased ion concentrations in the soil profile.

Regarding Theme 3 (relationships between variation in soil apparent electrical conductivity, grain yield and soil chemistry), electromagnetic induction (measured with instruments such as the Geonics EM38 or DualEM) has been used to survey variation in soil salinity at the landscape scale since the 1980s [30]. Readings, referred to as measures of the apparent electrical conductivity (EC_a), are known to respond positively to increasing solute concentration in soils, and also respond to soil water and clay contents [31]. Surveys on sodic alkaline soils with electromagnetic induction have shown spatial variation in apparent electrical conductivity at the paddock scale [5]. We used the EM38 to survey our plots in the spring of each year. We hypothesized that readings would be affected by amendment and tillage treatments (H4), be correlated with grain yield (H5), and be correlated with soil chemistry (H6).

2. Materials and Methods

2.1. Location

The trial was sown on a sandy clay Calcic Calcarosol (Australian Soil Classification) [32] or Vertic Calcic Calcisol (Sodic) (World Reference Base) [33] on Merredin Research Station (−31°30′25′′ S, 118°13′04′′ E) in 2019; there was a repeat application of treatments with sowing over the same plots in 2020. There is strong patterning of apparent electrical conductivity (EC_a) measured with the DualEM 1S at the paddock scale in alkaline sodic soils in this area [5]. To locate our trial site, we conducted a DualEM 1S survey across six paddocks at the Research Station on 9 April 2019 (Figure 1). A number of locations with high EC_a were identified from this survey and we selected the site for the trial at the place indicated in Figure 1.

2.2. Trial Design and Management

The trial had a factorial design, with two tillage treatments (conventional tillage or tillage with a 'mounded' interrow with plastic sheeting over the top of the mounds), four amendment treatments (nil, application of gypsum (G), application of elemental sulfur (ES), or application of gypsum plus elemental sulfur (G+ES)), and four replicates. The plots were laid out in 8 ranges (running east–west), with 4 plots per range (running north–south). Running east–west, every two adjacent ranges either had conventional cultivation or the mounded tillage treatment. Running north–south, adjacent pairs of plots within pairs of ranges had the same amendment (nil, G, ES or G+ES). Amendments were applied to the 4 pairs of tillage combination (running east–west) and the 4 plots (running north–south) using a Latin square design.

Each plot was 8 m in length, the width between plot centers was 2.4 m, and there were 5 rows per plot at 375 mm spacings. Measurements were made on the inner 3 rows of each plot. The mounding was achieved with a specially designed mechanical seeder that produced a mound with a slope of 25° approximately 9 cm in height and 30 cm in width. After sowing, each mound was covered with strips of clear polythene sheeting, 0.5 mm in thickness, 8 m in length and 30 cm in width. Seed of barley (*Hordeum vulgare*, cv Spartacus) was sown at a rate of 70 kg ha^{-1}. In each year, the gypsum and elemental sulfur amelioration treatments were applied as part of the seeding operation at the time of sowing to the area of the furrow (7.5 cm in width) at rates of 50 and 77 kg ha^{-1}, respectively, (or 10 and 15.4 kg ha^{-1}, respectively, assuming that the furrow accounted for 20% of the soil surface area). The gypsum was applied with the seed; the elemental sulfur was applied approximately 5 cm deeper with the fertilizer. The soil sulfate concentration was greater than 3.1 mg S kg^{-1} in the 0–30 cm range, indicating that the soil is not responsive to sulfur fertilizer application [34]. A basal S fertilizer was therefore not applied to the experiment.

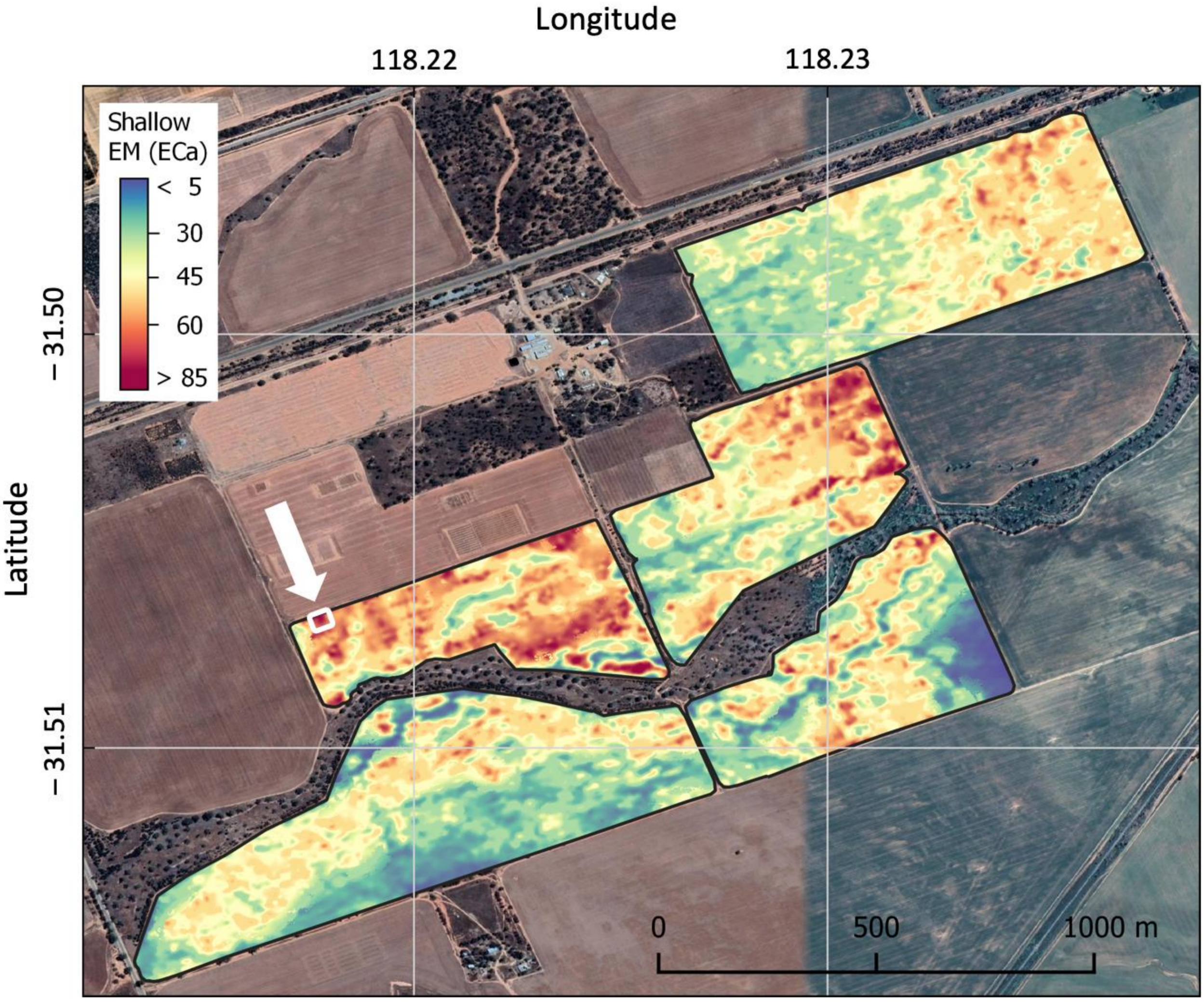

Figure 1. Variation in apparent electrical conductivity (EC$_a$) measured at the paddock scale with a DualEM (the 50 cm dipole) at Merredin Research Station on 9 April 2019. The trial was located in the white square indicated by the arrow.

The trial was sown on 17 June 2019 and again on 21 May 2020. In both years, monoammonium phosphate with copper and zinc (11.6% N, 3% S, 21% P, 0.05% Cu, 0.10% Zn) was applied at seeding at 40 kg ha^{-1}. Later surface applications of N occurred as urea in 2019 on 9 August (13.8 kg N ha^{-1}), and in 2020 on 2 July (13.8 kg N ha^{-1}), 3 August (18.4 kg N ha^{-1}) and 14 August (9.2 kg N ha^{-1}).

Green leaf cover was estimated at approximately two weekly intervals throughout each growing season by photographing each plot at three locations; the images were processed using the Canopeo method [35] to determine the areal percentage of green in the photo. The images were processed in MATLAB (MathWorks, Natick, MA, USA).

Biomass cuts (1 m of row at three locations within each 8 m plot) were taken when the crop was at anthesis on 23 September 2019 and 2 September 2020, and final harvest cuts (also 1 m of row at three locations) were taken on 19 November 2019 and 27–28 October 2020. Measurements were made of total shoot biomass at anthesis and final harvest, total grain yield, 1000 grain weight and the number of tillers with heads.

2.3. Soil Sampling and Analysis

Soil was sampled with a percussion drill rig (1 hole per plot) on three occasions: 18 July 2019 (31 days after sowing in the first year), 29 April 2020 (22 days before sowing in the second year) and 13 August 2020 (84 days after sowing in the second year). On the first occasion, the soil was sampled to 70 cm (10 cm intervals to 30 cm and 20 cm intervals to 70 cm). The sampled soil was oven dried, finely ground and analyzed by a commercial laboratory (CSBP Soils Laboratory, Bibra Lake, Australia). The methods of the analyses conducted are summarized in Table 1. Measurements were made of pH_{H2O}, $EC_{1:5}$, SO_4^{2-} and boron. On the second occasion the soil was sampled to 70 cm (also 10 cm intervals to 30 cm and 20 cm intervals to 70 cm), these variables were measured again and exchangeable cations were also determined. On the third occasion, the soil was sampled to 120 cm (20 cm intervals to 60 cm and 30 cm intervals to 120 cm), and measurements were made of pH_{H2O}, $EC_{1:5}$, a range of cations and anions were determined in water extracts, and measurements were also made of soil water. For the first and third surveys, a hole was dug over the central furrow in each plot either near the plot center (first survey) or near the north end (third survey). This enabled correlations to be made between soil chemistry and grain yield.

Table 1. Soil data collected at the three times of sampling.

Analysis	First Sampling	Secon Sampling	Third Sampling	Method
pH_{H2O}; $EC_{1:5}$	✓	✓	✓	Soil extracted in deionised water at a ratio of 1:5, stirring for one hour. pH and EC of extract measured using a pH and conductivity electrode [36] (Methods 4A1 and 3A1).
SO_4^{2-}	✓	✓	✓	Soil extracted in 0.25 M KCl. S content of extract analysed by inductively coupled plasma (ICP) spectroscopy [36] (Method 10D1).
Boron	✓	✓	-	Soil extracted in 0.01 M $CaCl_2$, in ratio of 1:4. Mixture heated to 90 °C and extract read for boron using ICP spectroscopy [36] (Method 12C2).
Exchangeable cations	-	✓	-	Soil extracted using a mixture of 0.1 M NH_4Cl and $BaCl_2$ in ratio of 1:10. Exchangeable cations in extract determined using ICP spectroscopy [36] (Method 15E1).
Soluble cations	-	-	✓	Water soluble cations determined in a 1:5 soil: water extraction. Cations in extract determined using ICP spectroscopy [36] (Method 5A4).
Chloride	-	-	✓	Water soluble chloride determined in a 1:5 soil:water extraction. Chloride concentration in extract determined colorimetrically [36] (Method 5A2b).

2.4. Electromagnetic Induction Surveys

Electromagnetic induction surveys were conducted at the plot scale with an EM38 (Geonics Limited) in the horizontal orientation in the spring of each year (10 October 2019 and 21 September 2020). Each plot was surveyed over the middle furrow at three locations—the north end of the plot, the middle of the plot and the south end of the plot. In each year, one-third of these readings therefore overlapped with a soil survey position.

2.5. Other Data Sources

Rainfall and reference evapotranspiration (ET_o) data were accessed from the Scientific Information for Land Owners (SILO) database [37] for the Merredin Bureau of Meteorology weather station [38] located approximately 7 km east of the trial site.

2.6. Statistical Analyses

Statistical analyses (ANOVAs and regressions) were conducted using Genstat (18th edition, VSN International). ANOVAs were used to determine the significance of tillage and amendment treatments. Soil chemical parameters were analyzed in ANOVAs with tillage and amendment as variables and depth as a repeating measure. The following codes have been adopted indicating statistical significance: ns = not significant; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

3. Results

3.1. Rainfall and Reference Evapotranspiration

Rainfall and reference evapotranspiration (ET_o) data for 2019 and 2020 are reported in Table 2. The site has a typical Mediterranean climate, with wet winters of low evaporative demand and dry summers with high evaporative demand. In general, 2019 had less rainfall for crop growth than 2020, although plants were constrained by lack of moisture late in the growing season in each year. In 2019, there was 29 mm of pre-seasonal (February–April) rain, and 186 mm of seasonal rain (May–October), of which 23 mm fell in the period between anthesis and harvest. In 2020, there was 58 mm of pre-seasonal rain, and 212 mm of seasonal rain, of which 16 mm fell in the period between anthesis and harvest. In each year, ET_o values were approximately 1.5 mm day^{-1} in mid-winter (early July), rising to approximately 3–4 mm day^{-1} during crop maturation (early October).

Table 2. Total monthly rainfall (mm) and reference evapotranspiration (ET_o) for 2019 and 2020.

Month	Rain (mm)		ET_o (mm)	
	2019	2020	2019	2020
January	0.6	0.2	210	201
February	0	44	178	155
March	6.4	9.7	150	130
April	22.8	3.8	95	102
May	5.8	64.8	71	66
June	67.2	41.6	45	51
July	37	36.1	50	49
August	52	48.6	66	61
September	3.6	19.9	106	90
October	20.6	1.2	144	141
November	2.2	48.2	189	147
December	0.2	13.2	225	200
Total	215.4	269.7	1526	1393

Data from weather station at Merredin (−31°28′32″ S, 118°16′44″ E) [37,38].

3.2. Theme 1—Improving Crop Growth and Grain Yield

The effects of tillage and amendment treatments on barley grain yield in the two seasons are summarized in Table 3 Part A (data for 2019) and Part B (data for 2020). In overview, the combination of best treatments (mounding plus G amendment) increased grain yield by 70% in 2019 and by 57% in 2020 relative to the conventional plus nil amendment control (Table 3). The tillage by amendment interaction was not significant, indicating that the amendment treatments followed the same trend for the two tillage practices.

Table 3. Effect on the grain yield and yield components of barley (*H. vulgare*) from tillage and amendment treatments in: (A) the 2019 growing season, and (B) the 2020 season. Values are the average of four measurements, with the standard error of the mean given in brackets. A statistical summary is given at the foot of each table.

Tillage	**Amendment**	**Grain Yield (t ha^{-1})**	**Shoot Dry Mass (t ha^{-1})**	**Heads (Number m^{-1} row)**	**1000 Grain Weight (g)**	**Anthesis Biomass (t ha^{-1})**
Part A. 2019 Growing Season						
Mound	G	3.12	8.35	225.1	29.90	9.28
	G+ES	3.09	8.06			8.38
	ES	2.54	7.60			8.79
	nil	2.23	7.04			8.21
Conventional	G	2.55	6.66	198.1		6.99
	G+ES	2.36	6.44			7.22
	ES	2.26	6.49			6.77
	nil	1.84	5.60			6.27
p-values						
Main effect tillage		***	***	***	ns	***
Main effect amendment		***	***	ns	ns	*
Tillage x amendment		ns	ns	ns	ns	ns
LSD$_{0.05}$						
Main effect tillage		0.20	0.32	10.0	-	0.44
Main effect amendment		0.28	0.46	-	-	0.62
Tillage x amendment		-	-	-	-	-
Part B. 2020 growing season						
Mound	G	3.77	9.05	254.8	30.28	7.35
	G+ES	3.59			29.04	
	ES	3.38			27.58	
	nil	3.23			27.28	
Conventional	G	2.98	7.31	216.7	27.82	5.61
	G+ES	2.65			27.20	
	ES	2.51			26.24	
	Nil	2.40			25.48	
p-values						
Main effect tillage		***	***	***	***	***
Main effect amendment		*	ns	ns	***	ns
Tillage x amendment		ns	ns	ns	ns	ns
LSD$_{0.05}$						
Main effect tillage		0.26	0.59	13.5	0.92	0.37
Main effect amendment		0.37	-	-	1.30	-
Tillage x amendment		-	-	-	-	-

Amendments were: nil, gypsum (G), elemental sulfur (ES), and gypsum plus elemental sulfur (G+ES). The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E). Statistical significance is as follows: ns = not significant; * $p < 0.05$; *** $p < 0.001$.

There were highly significant ($p < 0.001$) main effects of tillage, with the mounded treatment having higher growth than the conventional tillage treatment. Average values for the mounded treatment in 2019 and 2020 were 22% and 33% higher, respectively, for grain yield, 23% and 24% higher, respectively, for shoot dry mass (DM) at harvest, 14% and 18% higher, respectively, for heads per meter of row, and 27% and 31% higher, respectively, for shoot DM at anthesis. In addition, the 1000-grain weight was 7% higher with the mounding tillage than the conventional tillage in 2020.

There were also significant ($p < 0.05$ or $p < 0.001$) main effects of soil amendment, with the gypsum (G) amendment having higher growth, decreasing in the order G > G+ES >E S > nil. Average grain yields of the G compared to nil treatment were 28% and 20% higher in 2019 and 2020, respectively. Average grain yields of the ES compared to nil treatment were 18% higher in 2019. In addition, in 2019, the shoot DM at harvest and the shoot DM at anthesis were 19% and 12% higher, respectively, with the G amendment than the nil treatment, and in 2020 the 1000-grain weight was 10% higher with the G amendment than nil treatment.

A correlation of grain yields in 2019 (three samples per plot) with grain yields in 2020 (three samples per plot) was significant with a positive simple line of best fit ($p < 0.001$; $r^2 = 0.281$) (Figure 2).

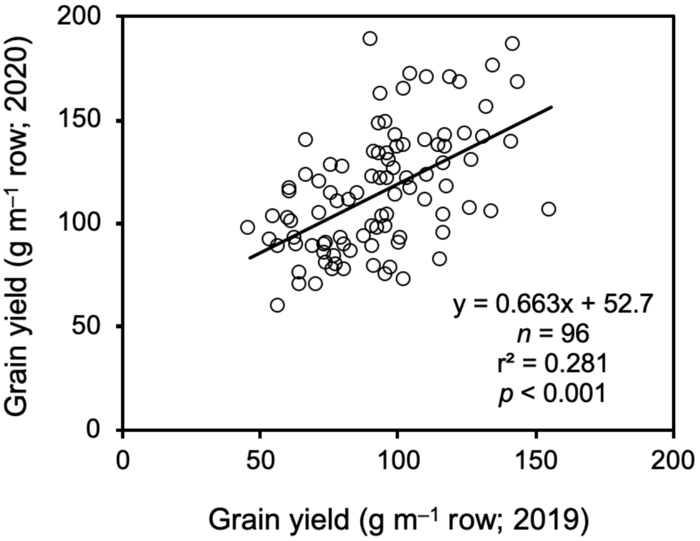

Figure 2. Correlation between grain yield data in 2019 and 2020. There were three points per plot. The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

The effects of tillage and amendment on green leaf cover during the 2019 and 2020 growing seasons are summarized in Figure 3A,B and Figure 3C,D, respectively. Green cover became measurable within a few weeks of sowing and reached a maximum in early September; it then declined as the leaves senesced. In each year, there were significant effects of tillage from the earliest dates of green cover measurement (Figure 3A,C). In contrast, with amendment, the impacts on green cover became most significant at the end of the growing season (Figure 3B,D). In both years, at the end of the growing season, the application of the gypsum amendment delayed leaf senescence.

3.3. *Theme 2—Effects of Treatments on Transient Salinity and Soil Chemistry*

3.3.1. Overview

The effects of soil depth, tillage and amendment treatments on the soil variables measured at the first, second and third times of sampling are summarized in the Supplementary Materials (Tables S1–S3, respectively).

A soil is considered saline if the electrical conductivity of the saturation extract (EC_e) is above 4 dS m^{-1} [39]. For a sandy clay, this equates to an $EC_{1:5}$ of approximately 0.47 dS m^{-1}, based on the conversion factor of Slavich and Petterson [40]. In overview (Table 4), the soil analyses showed that the soil was sodic (ESP values greater than 6%) [41], alkaline (pH_{H2O} values greater than 7), and affected by salinity at depth ($EC_{1:5}$ values greater than 0.47 dS m^{-1}).

For each of the series of samplings, there were two factors of overall importance. The most impressive aspect of soil chemistry was that for all ions measured, there was a highly significant ($p < 0.001$) effect of depth in the soil profile. At the first time of sampling (Supplementary Materials—Table S1), with $EC_{1:5}$, SO_4^{2-} and boron, average values increased 3.8–5.5 fold as depth increased from 0–10 to 50–70 cm. At the second time of sampling (Supplementary Materials—Table S2), with $EC_{1:5}$, SO_4^{2-}, boron and Na^+_{exch}, average values increased 2.6–6.6 fold as depth increased from 0–20 to 50–70 cm. At the third time of sampling (Supplementary Materials—Table S3), with Na^+, SO_4^{2-}, and Cl^-, average concentrations were 7.9–10.2 fold higher at 90–120 cm than at 0–0 cm, and Mg^{2+}, K^+, the $EC_{1:5}$ and Ca^{2+} were 2.5–5.3 fold higher at 90–120 than at 0–10 cm.

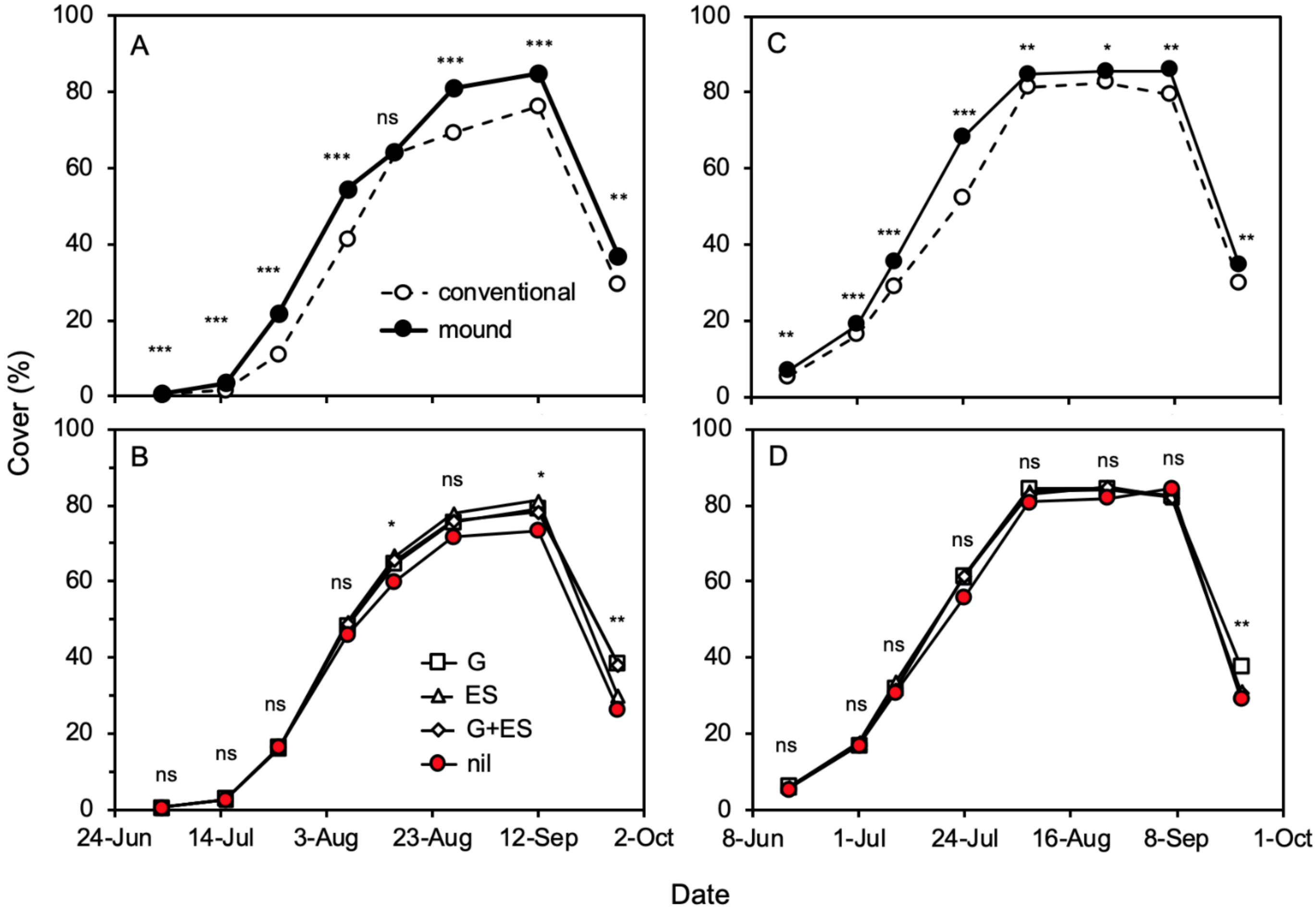

Figure 3. Effect on green leaf cover by barley of tillage (**A**,**C**) and amendment (**B**,**D**) in the 2019 growing season (**A**,**B**), and the 2020 season (**C**,**D**). Each point is the average of 16 (**A**,**C**) or 8 values (**B**,**D**). The significance of treatment comparisons is indicated at each date. Amendments were: nil, gypsum (G), elemental sulfur (ES), and gypsum plus elemental sulfur (G+ES). The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E). Statistical significance is as follows: ns = not significant; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

Table 4. Selected properties (based on average values across all treatments) at the three times of soil sampling. The data for these samplings are given in the Supplementary Materials, Tables S1–S3.

Variable	**Time of Sampling**		
	First	**Second**	**Third**
ESP > 6%	ND	All depths	ND
$pH_{H2O} > 7$	All depths	All depths	All depths
$EC_{1:5} > 0.47$ dS m^{-1}	No depths to 70 cm	50–70 cm	Depths ≥ 40 cm

Exchangeable sodium percentage (ESP); ND = not determined.

Secondly, there was a group of ions were positively correlated with each other. The first survey had three measures of ion concentration—the $EC_{1:5}$, and concentrations of SO_4^{2-} and boron. These were significantly ($p < 0.001$) correlated with r^2 values between 0.421 and 0.774. The second sampling included measures of the $EC_{1:5}$, SO_4^{2-}, boron and four exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}). Of these, $EC_{1:5}$, SO_4^{2-}, boron and exchangeable Na^+ were most significantly ($p < 0.001$) correlated with r^2 values between 0.243 and 0.820. The third sampling included measures of the $EC_{1:5}$, SO_4^{2-}, Cl^- and four soluble cations (Na^+, K^+, Ca^{2+} and Mg^{2+}). Of these, $EC_{1:5}$, SO_4^{2-}, Na^+ and Cl^- were most significantly ($p < 0.001$) correlated with r^2 values between 0.661 and 0.906.

3.3.2. Effects of Treatments

Treatments had greatest effect at the first time of sampling (Supplementary Materials—Table S1). With $EC_{1:5}$, and SO_4^{2-} there were significant main effects of amendment ($p < 0.01$) and a significant interaction between depth and amendment ($p < 0.001$). There had been 54 mm of rain and 47 mm of potential evapotranspiration (ET_o) in the 31 days since sowing (the day of implementation of the amendment treatments). Relative to 'nil', the amendments (G, ES and G+ES) were all associated with substantial decreases in the $EC_{1:5}$ and SO_4^{2-} concentration at all soil depths measured (Figure 4). At an average soil depth of 60 cm, these decreases were approximately 40% for $EC_{1:5}$ and approximately 60% for SO_4^{2-} concentration (Figure 4A,B, respectively). Although a salt ($CaSO_4$) had been applied to these soils with the G and G+ES amendments, the $EC_{1:5}$ and the SO_4^{2-} concentrations were lower than the nil controls, indicating that there had been a net flux of salt below 70 cm in the 31 days since sowing.

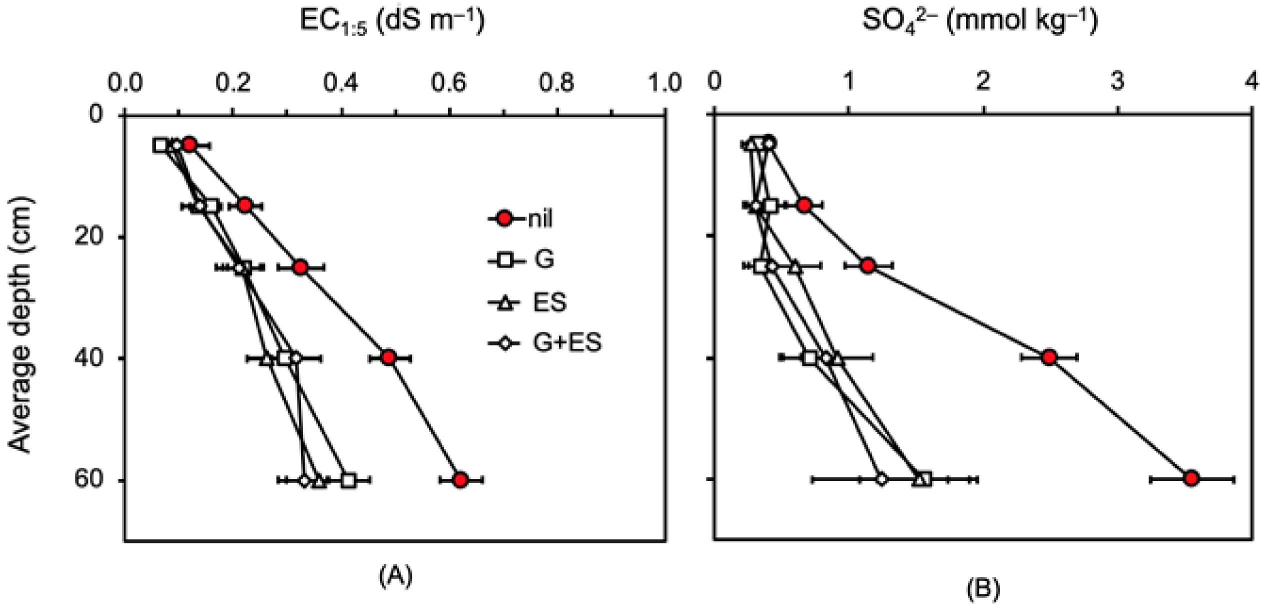

Figure 4. Effects (at 31 days after sowing) of depth and amendment (nil, G, ES, or G+ES) on: (**A**) $EC_{1:5}$, and (**B**) SO_4^{2-} concentration. Points are the average of four replicates. Error bars indicate the standard error of the mean. In each case, there was a significant effect of depth ($p < 0.001$), a significant main effect of amendment ($p < 0.01$) and a significant interaction between depth and amendment ($p < 0.001$). Amendments were: nil, gypsum (G), elemental sulfur (ES), and gypsum plus elemental sulfur (G+ES). The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

3.3.3. Correlations between Soil Chemistry and Grain Yield

The soil at the first and third times of sampling was taken immediately over a furrow; we were therefore able to correlate grain yields from that immediate location with soil chemistry. Tables S4 and S5 in the Supplementary Materials summarize the outcomes of linear correlations between different soil chemical variables and grain yield for the 2019 and 2020 growing seasons, respectively. For 2019 (Table S4–Supplementary Materials), the most important single variables associated with decreasing grain yield were SO_4^{2-} and $EC_{1:5}$ at 30–50 cm ($p < 0.001$; r^2 values of 0.472 and 0.337, respectively). Graphs of these relationships show that grain yield decreased by approximately 40% as the SO_4^{2-} concentration increased from 0.5 to 3.5 mmol kg^{-1} (Figure 5A) and as the $EC_{1:5}$ increased from 0.1 to 0.6 dS m^{-1} (Figure 5B).

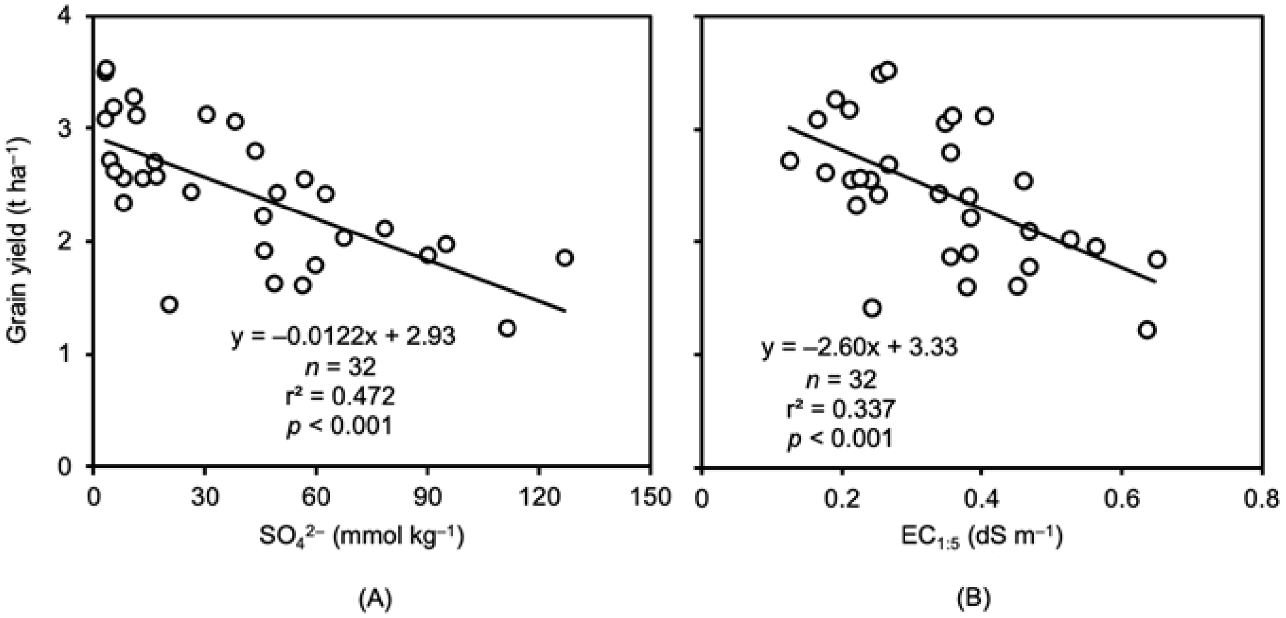

Figure 5. Best correlations between grain yield (2019) and soil chemistry (first time of sampling): (**A**) SO_4^{2-} at 30–50 cm, and (**B**) $EC_{1:5}$ at 30–50 cm. The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

In 2020 (the wetter year), a wider range of soil factors were measured, including soluble ions and soil water. Most of the soil parameters measured did not have significant effects on grain yield (Supplementary Materials, Table S5). However, simultaneous measures of ions and soil water provided us with the opportunity to calculate ion concentrations in the soil solution by assuming that the ion measured was dissolved in the soil water. Concentrations measured in this way are more sensitive indicators of plant stress than concentrations on a soil weight basis because it is the salinity of the soil solution (not the soil) that impacts on plant growth [12]. For 2020 (data summarized in Table S5–Supplementary Materials), the most important single variables associated with decreasing grain yield were gravimetric water at 20–40 and 40–60 cm ($p < 0.001$; r^2 values of 0.500 and 0.408, respectively) and SO_4^{2-} in the soil solution at 90–120 cm ($p < 0.01$; $r^2 = 0.270$). Graphs of these relationships show that grain yield decreased by 40–50% as the soil water content at 20–40 and 40–60 cm decreased from approximately 17 to 12% dry soil (Figure 6A), and by 40% as the SO_4^{2-} concentration in the soil solution at 90–120 cm increased from approximately 20 to 60 mM (Figure 6B).

3.4. Theme 3—Relationships between Variation in Soil Apparent Electrical Conductivity, Grain Yield and Soil Chemistry

3.4.1. EM38 Readings, Treatments and Grain Yield

EM38 surveys of apparent electrical conductivity in the horizontal orientation (EC_{ah}) were conducted at three locations in each plot in the spring of 2019 and at the same locations in 2020. In 2019, EC_{ah} values varied (5th percentile to 95th percentile) from 51 to 84 mS m^{-1}; in 2020 values varied from 43 to 77 mS m^{-1}. However, correlations of readings between 2019 and 2020 showed that the spatial variation in EC_{ah} was consistent between years; values collected at the same locations in the spring of 2019 and the spring of 2020 were significantly linearly correlated (Figure 7; $p < 0.001$; $r^2 = 0.58$).

The impacts of tillage and amendment treatments on EM38 readings (EC_{ah}) and the relationships between EC_{ah} and grain yield are summarized in Figure 8. In 2019, there were significant effects of amendment treatments ($p < 0.001$) and tillage ($p < 0.01$) on EC_{ah}, but no interaction. In 2020, the effect of amendment was also significant ($P < 0.001$) but there was no significant effect of tillage or interaction. In each year, the G, ES and G+ES amendments had 12–18% lower EC_{ah} readings than the nil control (Figure 8A,C). In

2019, the mounding plus plastic sheeting treatment had 8% lower EC_{ah} readings than the conventional treatment (Figure 8A).

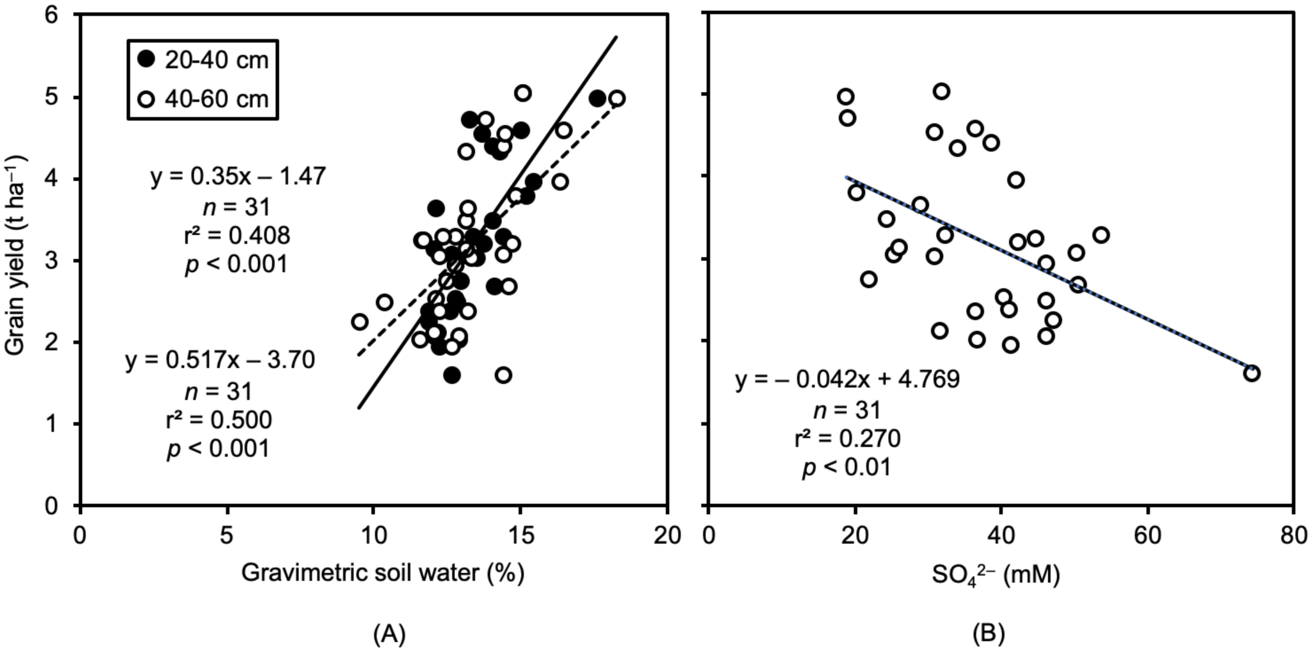

Figure 6. Best correlations between grain yield and gravimetric soil water or soil chemistry in 2020 (third time of sampling): (**A**) soil water at 20–40 cm and 40–60 cm, and (**B**) SO_4^{2-} in the soil solution at 90–120 cm. The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

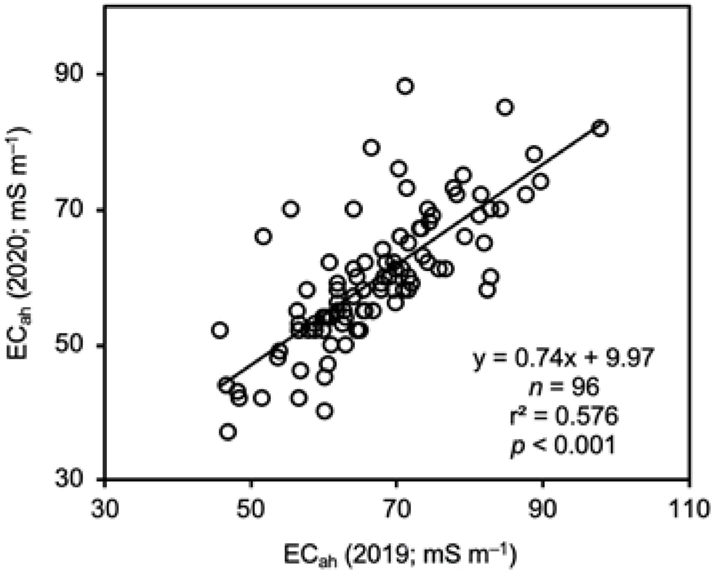

Figure 7. Correlations of EM38 readings in the horizontal orientation (EC_{ah} values) collected on 10 October 2019 and, at the same plot locations, on 21 September 2020. The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

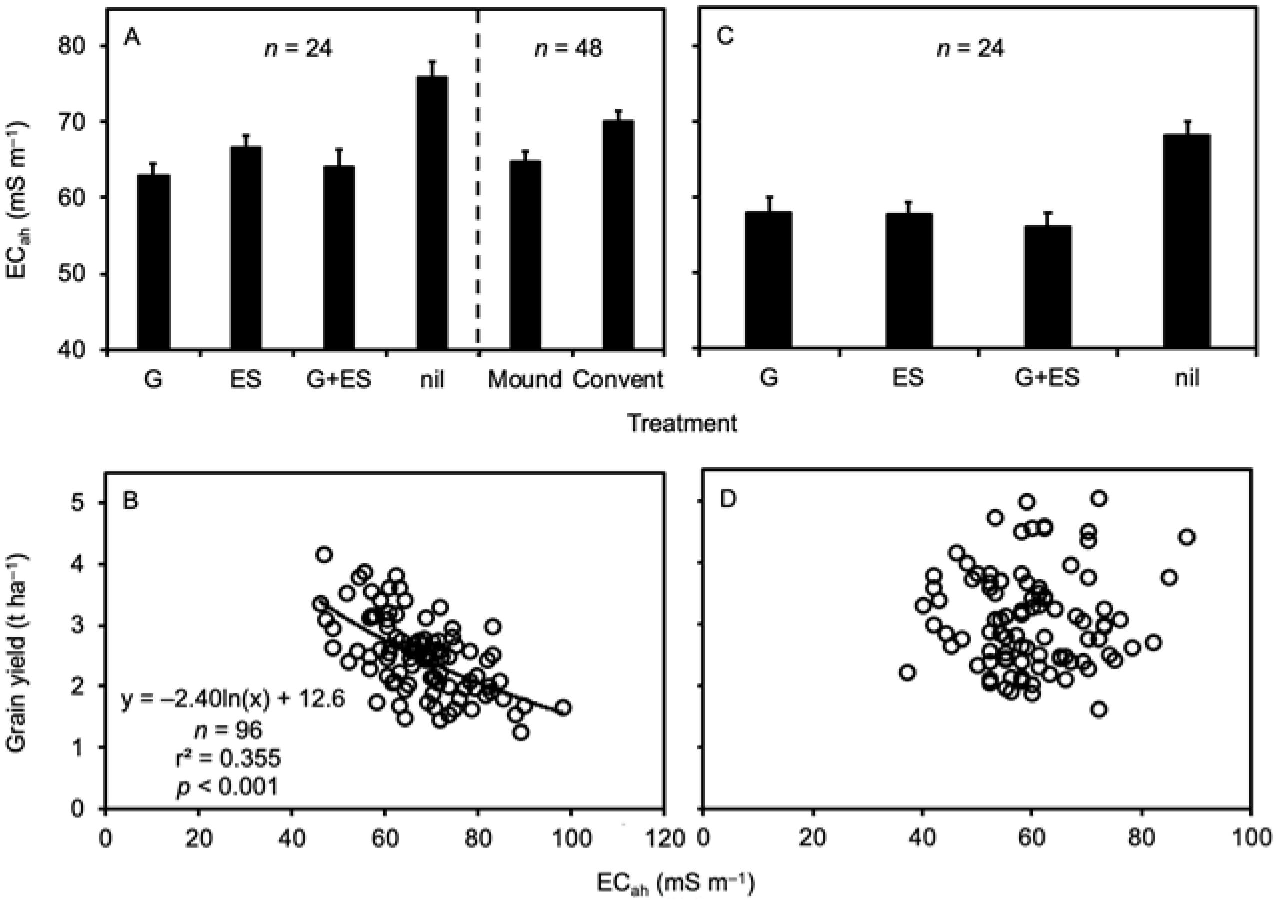

Figure 8. Effects of tillage and amendment treatments on average EM38 readings in the horizontal orientation (EC$_{ah}$) (**A**,**C**) and the relationship between EC$_{ah}$ and grain yield (**B**,**D**). Data were collected in 2019 (**A**,**B**) and 2020 (**C**,**D**). EC$_{ah}$ data were collected with the EM38 in the horizontal orientation. Amendments were: nil, gypsum (G), elemental sulfur (ES), and gypsum plus elemental sulfur (G+ES). The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

Figure 8B,D shows the relationship between EC$_{ah}$ readings and grain yield in each year. In 2019, there was a significant logarithmic relationship (r^2 = 0.35; $p < 0.001$) between increasing EC$_{ah}$ and declining grain yield. Based on the line of best fit, grain yields were approximately 3.2 t ha^{-1} at an EC$_{ah}$ of 50 mS m^{-1}, but declined to approximately 1.5 t ha^{-1} at an EC$_{ah}$ of 100 mS m^{-1} (Figure 8B). In 2020, there was no significant relationship between EC$_{ah}$ and grain yield (Figure 8D).

3.4.2. EM38 Readings and Soil Chemistry

EM38 readings could be related to soil chemistry because in 2019, one-third of measurements were taken near the holes of the first time of soil sampling; and in 2020, one-third of measurements were taken near the holes of the third time of sampling (n = 32 in each case). A statistical summary of the relationships (simple linear correlations) between EM38 readings and soil chemistry for each year are given in the Supplementary Materials Table S6, and Figure 9 shows the strongest relationships. In 2019, EC$_{ah}$ readings were most significantly ($p < 0.001$) correlated with EC$_{1:5}$ values at 50–70 cm (r^2 = 0.470; Figure 9A), but were also correlated with EC$_{1:5}$ at all depth intervals between 10 and 50 cm, and with SO_4^{2-} at all depth intervals between 20 and 70 cm (Supplementary Materials Table S6). In 2020, EC$_{ah}$ readings were most significantly ($p < 0.001$) correlated with EC$_{1:5}$ values at 90–120 cm (r^2 = 0.595; Figure 9B), but were also correlated with EC$_{1:5}$ at all depth intervals between 20 and 90 cm, with SO_4^{2-} at all depth intervals between 40 and 120 cm, and with Cl^- at all depth intervals between 20 and 120 cm (Supplementary Materials Table S6). Based on the lines of best fit, in 2019, EC_{ah} values increased by 44% as the $EC_{1:5}$ at 50–70 cm increased from 0.15 to 0.75 dS m^{-1} (Figure 9A); and in 2020, EC_{ah} values increased by 54% as the $EC_{1:5}$ at 90–120 cm increased from 0.6 to 1.2 dS m^{-1} (Figure 9B).

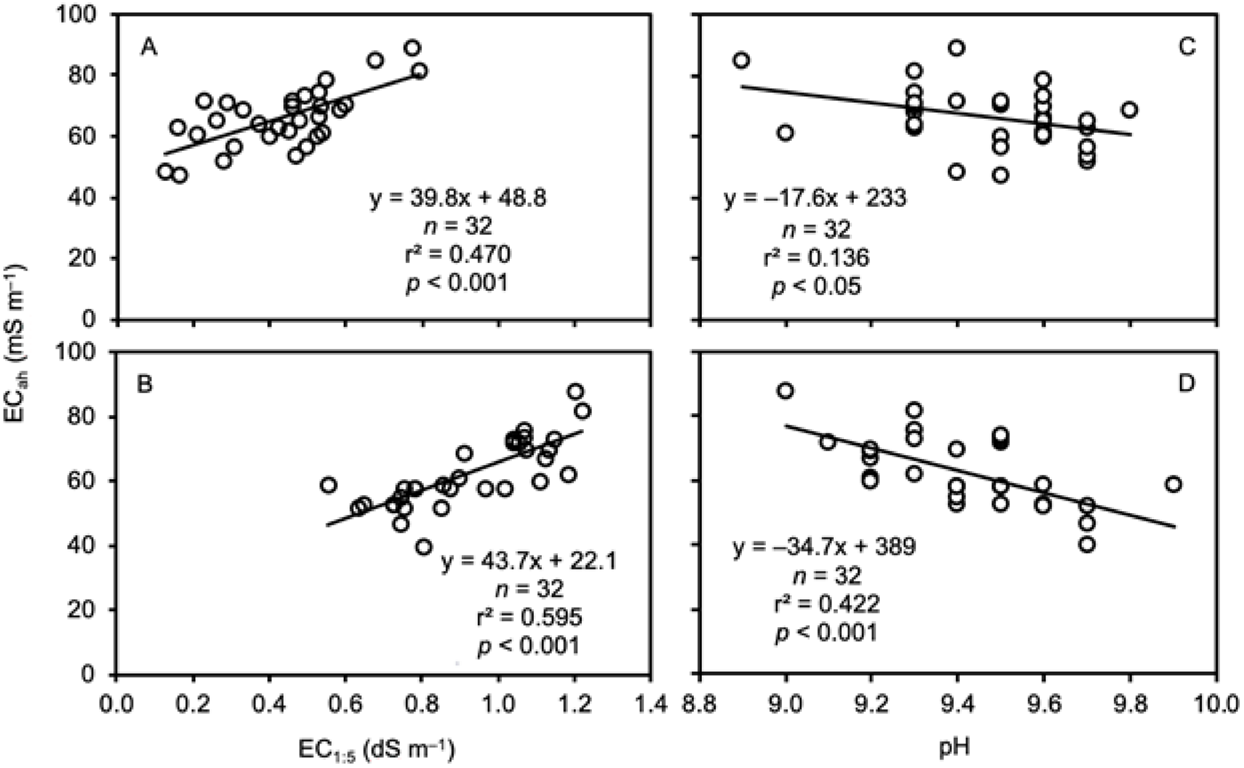

Figure 9. Correlations between EM38 readings in the horizontal orientation (EC_{ah}) and other soil variables: (**A**) EC_{ah} and $EC_{1:5}$ at 50–70 cm (2019), (**B**) EC_{ah} and $EC_{1:5}$ at 90–120 cm (2020), (**C**) EC_{ah} and pH at 50–70 cm (2019); (**D**) EC_{ah} and pH at 90–120 cm (2020). The soil was a Vertic Calcic Calcisol located on Merredin Research Station (−31°30′25″ S, 118°13′04″ E).

Interestingly, in both 2019 and 2020, there were negative relationships between EC_{ah} and pH at 50–70 cm (2019; $p < 0.05$; Figure 9C) and 90–120 cm (2020; $p < 0.001$; Figure 9D). Based on the lines of best fit, in 2019, EC_{ah} values decreased by 19% as the pH at 50–70 cm increased from 9.0 to 9.8 (Figure 9A); and in 2020, EC_{ah} values decreased by 36% as the pH at 90–120 cm increased from 9.0 to 9.8 (Figure 9B). Why was this so? It may have been because of the relationship between pH and $CaCO_3$. It has been previously shown that the concentration of $CaCO_3$ in soils in this region increases in an exponential manner as the pH of soil increases over the pH range from 7.9 to 9.7 [5]. The presence of substantial concentrations of $CaCO_3$ (an insoluble salt) would presumably decrease the proportion of more conductive material in the soil profile. In 2020, there was also a significant ($p < 0.01$) negative relationship between increasing $CaCO_3$ at 90–120 cm and EC_{ah} (Supplementary Materials, Table S6).

4. Discussion

This research was conducted to determine the impacts of micro-water harvesting and soil amendment on the grain yield of barley in a sodic alkaline soil. In accord with our six hypotheses (H1 to H6), we found that the grain yield of barley was improved by micro-water harvesting at the soil surface (H1), and by soil amendment with small amounts of gypsum, elemental sulfur or gypsum plus elemental sulfur (H2). Soil amendment with gypsum and ES was associated with decreased $EC_{1:5}$, and $SO_4{}^{2-}$ concentrations in the soil (H3) and with decreased EM38 readings (H4). Elevated EM38 readings were correlated with decreased grain yield in 2019 (the drier year), but not in 2020 (the wetter year) (H5), and were also correlated with elevated $EC_{1:5}$ and SO_4^{2-} values (H6). One of the striking features of this work was that we found these effects in barley, a relatively salt-tolerant cereal [42]; the effects of soil desalinization due to soil amendment might have been even stronger if we had used a more salt-sensitive field crop such as field peas or wheat c.f. [14,42] as our test species.

This discussion has four parts, focusing on each of the three themes and finally on the implications of our work for industry.

4.1. Theme 1—Improving Crop Growth and Grain Yield

Our results showed significant effects of tillage and amendment on crop yield. These effects are discussed separately.

4.1.1. Tillage

Plastic sheeting is widely used in many areas of the world as a mulch to decrease soil evaporation, increase soil temperatures and decrease the leaching of fertilizers; see recent reviews [43,44]. Our use of mounding with plastic sheeting to increase micro-water harvesting on soils affected by transient salinity was primarily as a 'proof of concept' treatment. In our research, the beneficial effects of mounding and plastic sheeting were discernible in terms of green cover measurements from the start of each growing season (Figure 3A,C); and at the end of each growing season, there were increases in grain yield of 22% and 33% in 2019 and 2020, respectively, compared with conventional cultivation (Table 3). These yield gains were of a similar order of magnitude to those that have been made with annual crops elsewhere. For example, in a meta-analysis of 474 comparisons published in China, the average yield improvement in wheat through the use of plastic mulch compared to no-mulch was approximately 21% [45].

4.1.2. Amendment

Measures of green cover showed that the beneficial effects of amendment became most significant towards the end of each growing season (Figure 3B,D). Nevertheless, at the end of each growing season, there were increases in grain yield of 28% and 20% in 2019 and 2020, respectively, compared with nil amendment (Table 3). Our yield gains with gypsum were consistent with those achieved in earlier studies under rainfed conditions. In 10 trials at 5 locations in Western Australia between 1983 and 1987, gypsum at 2.5 t ha^{-1} increased cereal yields by 16–38% in 6 trials, but the application was non-significant in the others [46]. In New South Wales, at three sites, gypsum at 1.25, 2.5 and 12.5 t ha^{-1} increased wheat yields by a median of 30, 53 and 67% over the following 2–5 years [47]. However, in all of these studies, the rates of gypsum application (1.25–12.5 t ha^{-1}) were far higher than used by us (50 kg ha^{-1} placed within the furrow). We are aware of only one study (conducted on a sodic soil under irrigated conditions) in Pakistan where increases in grain production have been achieved with low rates of gypsum application. In an irrigated experiment on a silty clay loam soil with an $EC_{1:1}$ of 4.9 dS m^{-1} ($EC_{1:5}$ of ~1.0 dS m^{-1}), application of gypsum at the rate of 213 kg ha^{-1} produced a 26% increase in wheat yield [48].

One of the curious features of our work is that there were also benefits to grain yield from soil amendment with S (18% increase in 2019). This effect could have also been mediated by the synthesis of gypsum. Elemental S has one major role as a soil amendment: soil acidification [25,26]. Acidithiobacillus bacteria oxidize the applied ES in the soil to form sulfuric acid, but in calcareous soils this can react with carbonate to form gypsum ($CaSO_4 \cdot 2H_2O$). The critical reactions are:

$$2S + 3O_2 + 2H_2O = 2H_2SO_4 \quad (1)$$

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2 \quad (2)$$

4.2. Theme 2—Effects of Treatments on Transient Salinity and Soil Chemistry

Under rainfed conditions, gypsum is dissolved and leached from soils at the rate of approximately 1 t ha^{-1} for every 120–130 mm of rainfall [49]. How is it that a rate of gypsum application in the furrow of 50 kg ha^{-1} (leachable based on this rule of thumb by approximately 6 mm of rain) was able to have such a strong effect on crop yield? We suggest that in the sodic alkaline soils of semi-arid Australia, transient salinity can be a major factor limiting grain yield. This creates an osmotic stress to plants after anthesis as the soils dry out and the salinity of the soil solution increases, impacting on crop water relations particularly late in the growing season. The application of a low rate of gypsum might establish a brief 'electrolyte effect' in the soil [50], re-orientating the clay platelets and unblocking soil pores for enough days to restore soil hydraulic conductivity (K_s) and allow the movement of salt deeper into the soil profile. The removal of salt from the shallow soil would enable the crop to better manage the adverse water relations of the drying soil during maturation. In the present work, this view is supported by the effects of amendment on measures of soil salinity (Figure 4A,B), and the significant correlations between measures of soil salinity and grain yield (Figures 5 and 6B). Therefore, the effect of the gypsum on K_s might be ephemeral, but the legacy of even a brief increase in K_s can persist until the end of the season.

Transient salinity (the salinity of dispersive soils) can be expected to impact most in dry years, when soil moisture is low, so the salinity of the soil solution is high; it will impact least in wet years when soil moisture is high so the salinity of the soil solution is low. The levels of salinity stress at the present site can be illustrated using the data on soluble ion concentrations and soil water reported in the Supplementary Materials Table S3. At the time of the third soil sampling, at a depth of 0–20 cm, the soil had concentrations of soluble Na^+, Mg^{2+}, K^+ and Ca^{2+} of approximately 8.1, 4.7, 4.3 and 2.4 mmol kg^{-1} DM, respectively. If we assume that these ions were dissolved in the soil water (14.4% DM), then their concentrations in the soil water would have been approximately 56, 33, 30 and 17 mM, respectively, providing us with a total cation concentration of 136 mM. Seawater has a cation concentration of approximately 550 mM [51], so at this water content, the soil had an average salinity in the soil solution of 25% seawater. Using the same method of calculation, at 20–40 cm depth the total cation concentration would have been 314 mM (57% seawater), and at 40–60 cm the total cation concentration would have been 602 mM (109% seawater). If the water content at each of these soil depths had halved towards the end of the growing season, then the salinities would have doubled.

4.3. Theme 3—Relationships between EM38 Readings, Grain Yield and Soil Chemistry

Electromagnetic induction has been widely used to survey soil salinity at the landscape and paddock scales [31] and has also been used to account for variation in soil salinity at the plot scale [19,52]. With other spatial techniques such as radiometric analysis and yield mapping, electromagnetic induction has the advantage of being able to survey variation in soils remotely and relatively cheaply [53,54]. The use of electromagnetic induction on cropland in Western Australia is relatively recent [5,55]. The data contained in Figure 1 are from the largest survey with a DualEM yet conducted at the Research Station. Using these data, we were able to identify a number of locations of high apparent electrical conductivity; our work at one of these showed that crop growth and yield could be increased through the application of low rates of gypsum and elemental sulfur.

With respect to EM38 readings, our work has had three main outcomes. Firstly, there is reproducible patterning in the variation in EC_{ah} measurements between years: at the scale of our trial site (an area of approximately 20 × 40 m) plots that had low and high readings in 2019, had similar low and high readings in 2020 (Figure 8). This mirrored the patterning in grain yield in the plots between years: plots that had low and high grain yield in 2019 also had similar low and high grain yields in 2020 (Figure 2). This suggests that much of the variation in apparent electrical conductivity and grain yield is caused by underlying spatial variation. Secondly, there were significant decreases in EC_{ah} with soil amendment (2 years) and with mounding with plastic sheeting (1 year) (Figure 9). With the EC_{ah}, approximately half the reading is influenced by the upper 40 cm of the soil profile: the balance is from deeper in the profile [56]. It therefore appeared that our treatments affected the bulk of the soil profile accessible to cereal roots. Thirdly, salinity ($EC_{1:5}$) and $SO_4{}^{2-}$ values (from drill samples) were positively correlated with EC_{ah} ($p < 0.001$), and pH and $CaCO_3$ concentrations in the subsoil (particularly 90–120 cm) were negatively correlated with EC_{ah} ($p < 0.001$ and $p < 0.01$, respectively). Variation in EC_{ah} values was correlated with variation in yield in the dry year (2019) but not the wet year (2020). The explanation for this effect is not yet clear, but we note that there were strong relationships between $EC_{1:5}$, and Cl^- and $SO_4{}^{2-}$ concentrations in the soil and grain yield in 2019 but not in 2020. It may be that the higher rainfall in 2020 maintained high levels of soil hydration that masked much of the adverse effect of transient salinity on crop yield.

4.4. Implications for Industry

Salinity in Australia has two principal causes [12]: it can be associated with shallow water tables (water table-induced salinity) and it can be associated with dispersive soils (transient salinity). Shallow water table salinity often causes such severe salinity in soils that the land is only suited to the growth of halophytes [57,58]. In contrast, soils affected by transient salinity are often cropped [12]. Our data suggest that transient salinity can impact on crop yields in semi-arid environments.

Our trial was based on the philosophy that maintaining soil heterogeneity at the scale of the distance between a furrow and mound could have advantages in semi-arid environments in better focusing water around plant roots. We applied G and ES amendments to overcome soil dispersion only in the furrow. Compared to conventional practice, the rate of application of gypsum used in our trial was exceptionally low, 10 kg ha^{-1}, but focused into the furrow, where the rate there would have been closer to 50 kg ha^{-1}. This is a much lower gypsum application rate than those used in past studies to ameliorate sodic soils: e.g., 2.5 t ha^{-1} [46], 12 t ha^{-1} [20] and 15 t ha^{-1} [59]. As for S, the amount applied (15.4 kg ha^{-1}, or 77 kg ha^{-1} in the furrow) was calculated to be sufficient (once oxidized) to break down approximately 20% of $CaCO_3$ present in the upper 20 cm of the soil profile. Why should such exceptionally low rates of soil amendment be now yielding benefits to grain yield? Thirty to forty years ago, when most of the gypsum amendment studies cited here were conducted, crops were generally fertilized using single superphosphate, which contained approximately 50% $CaSO_4$ [60]. A traditional superphosphate application rate of approximately 1 bag per acre (125 kg ha^{-1}) would therefore have supplied approximately 63 kg ha^{-1} of $CaSO_4$. Since the 1980s, crop fertilization strategies have moved strongly towards the use of compound fertilizers that do not contain gypsum. This practice may have moved heavy-textured sodic alkaline soils towards a state of long-term 'gypsum deficiency'.

Our discoveries that sites susceptible to transient salinity can be identified using electromagnetic induction, that the application of low rates of gypsum can cause substantial leaching of salt from these in the year of application, and that such decreases can increase grain yields, could be important in the management of these soils. Farmers and their advisers have tended to regard the application of gypsum to soils as a substantial capital investment, requiring the application of many tonnes per hectare. However, our results suggest a less capital-intensive method of application: small amounts could be applied each year. An efficient method of delivering such small amounts each year might be through the use of compound fertilizers containing gypsum.

5. Conclusions

Our work has had a number of highly novel elements. For the first time, research into soil amendment (with gypsum and elemental sulfur) has been joined to micro-water harvesting as a method of increasing crop production on sodic soils. This combination of treatments increased crop yield by 70% in 2019 and by 57% in 2020. Our use of micro-water harvesting to overcome transient salinity by better hydrating sodic soils is novel. Our use of exceptionally low rates of gypsum application to improve crop growth under field conditions is novel. Our demonstration of improved crop yields in response to a decrease in transient salinity is novel. Our use of EM technologies to pinpoint where in the landscape soil treatments should be applied is also novel.

One of the recurring themes of agronomic research conducted in non-irrigated semi-arid landscapes throughout the world is that crop productivity is most limited by rainfall [61,62]. It is now recognized that in many landscapes, this production will also be adversely impacted by climate change [63]. Plant breeders have set themselves the task of increasing grain yields by improving crop water use efficiency, but the rates of progress have been slow; over the period 1960–2010, average crop yields in rainfed environments have increased by less than 1% per year, with much of these yield increases also being attributable to improved agronomy [62]. Therefore, where will the next major leap in productivity come from? The research conducted in this paper and other papers in this special edition [64,65] suggest that major increases in crop yield may come from overcoming soil constraints such as soil sodicity, alkalinity and acidity.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agronomy11040713/s1, Table S1. Variation in selected soil variables (averaged by depth) at the first time of sampling (18 July 2019). Table S2. Variation in selected soil variables including exchangeable cations averaged with depth at the second time of sampling (29 April 2020). Table S3. Variation in selected soil variables including soluble ions averaged with depth at the third time of sampling (13 August 2020). Table S4. Summary statistics for linear correlations between grain yield in 2019 and soil chemical variables at the first time of sampling (18 July 2019). Table S5. Summary statistics for simple linear correlations between grain yield in 2020 and pH, $EC_{1:5}$, $CaCO_3$, water and ion concentrations in the soil solution. Table S6. Summary statistics for simple linear correlations between EC_{ah} readings and soil chemistry in 2019 and 2020.

Author Contributions: Conceptualization, D.H., E.G.B.-L. and D.M. based on an original idea of C.W.; methodology, E.G.B.-L., G.R. and D.M.; formal analysis, E.G.B.-L.; investigation, D.M., R.M., L.W., E.G.B.-L. and G.R.; data curation, E.G.B.-L., D.M. and R.M.; writing—original draft preparation, E.G.B.-L.; writing—review and editing, D.H., G.R. and R.M.; supervision, E.G.B.-L. and D.H.; project administration, D.H.; funding acquisition, D.H. All authors have read and agreed to the published version of the manuscript.

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