Amelioration of Subsurface Acidity in Sandy Soils in Low Rainfall Regions. II. Changes to Soil Solution Composition Following the Surface Application of Gypsum and Lime

C. D. A. McLay, G. S. P. Ritchie, W. M. Porter and A. Cruse

Abstract

Two field trials were sampled to investigate the changes to soil solution chemical properties of a yellow sandplain soil with an acidic subsoil following the application of gypsum and lime to the soil surface in 1989. The soils were sandy textured and located in a region of low annual rainfall (300–350 mm). Soil was sampled annually to a depth of 1 m and changes in soil solution composition were estimated by extraction of the soil with 0.005 M KCl.

Gypsum leaching caused calcium (Ca), sulfate (SO₄) and the ionic strength to increase substantially in both topsoil and subsoil by the end of the first year. Continued leaching in the second year caused these properties to decrease by approximately one-half in the topsoil. Gypsum appeared to have minimal effect on pH or total Al (Al₄⁺), although the amount of Al present as toxic monomeric Al decreased and the amount present as non-toxic AlSO₄²⁻ ion pairs increased. Magnesium (Mg) was displaced from the topsoil by gypsum and leached to a lower depth in the subsoil. In contrast, lime caused pH to increase and Al to decrease substantially in the topsoil, but relatively little change to any soil solution properties was observed in the subsoil. There was an indication that more lime may have leached in the presence of gypsum in the first year after application at one site.

Wheat yields were best related to the soil acidity index Al₄⁺/EC (where EC is electrical conductivity of a 1:5 soil:water extract), although the depth at which the relationship was strongest in the subsoil varied between sites. The ratio Al₄⁺/EC was strongly correlated with the activity of monomeric Al species (i.e. the sum of the activities of Al³⁺, AlOH²⁺ and Al(OH)₂⁺) in the soil solution. An increase in the concentration of sulfate in the subsoil solution (which increased the ionic strength, thereby decreasing the activity of Al³⁺, and also increased the amount of Al present as the AlSO₄²⁻ ion pair) was probably the most important factor decreasing Al toxicity to wheat. The results indicated that gypsum could be used to increase wheat growth in aluminium toxic subsoils in sandy soils of low rainfall regions and that a simple soil test could be used to predict responses.

Introduction

Subsurface acidity has been shown to be the most important soil factor causing low crop yields in soils in many areas of the world (Reeve and Sumner 1972; Ritchey et al. 1980; Shainberg et al. 1989), including a large area of
yellow sandplain soils in the eastern wheatbelt of Western Australia (Carr et al. 1991). Recent research has indicated that, in many agricultural farming systems, surface-applied gypsum is the most economically viable method for increasing crop yields on soils with subsurface acidity, due to its ability to leach rapidly to the required depth, whereas lime is only effective if incorporated into the subsoil because of its low mobility (Sumner et al. 1986; Farina and Channon 1988; Shainberg et al. 1989).

Even though surface applications of gypsum increase crop yields (Reeve and Sumner 1972; Hammel et al. 1985; Sumner et al. 1986; Farina and Channon 1988; McCray et al. 1991), the actual mechanisms by which amelioration has occurred remain poorly understood. Several suggestions have been made to explain how gypsum ameliorates Al toxicity: self-liming, i.e. sulfate displacing hydroxide off soil surfaces into the soil solution (Reeve and Sumner 1972); a decrease in Al$^{3+}$ activity in the soil solution due to an increase in ionic strength (Ritchie 1989); the formation of non-toxic AlSO$_4^{2-}$ ion pairs (Pavan et al. 1982) or precipitation of aluminium hydroxy sulfate minerals out of the soil solution (Nordstrom 1982); displacement of Al$^{3+}$ off soil colloids and subsequent leaching of Al$^{3+}$ from the soil (Oates and Caldwell 1985); and a decrease in the ratio of Al:Ca (Ritchey et al. 1980). In all of the proposed mechanisms, it is essential that gypsum leaches from the surface into the subsoil for amelioration to occur.

Aluminium toxicity in the 15–25 cm depth layer has been identified as the major soil factor limiting plant growth in the yellow sandplain soils in the low rainfall regions of Western Australia (Carr et al. 1991). The soils have a low water holding capacity (5–10%), are freely drained and are commonly sown with wheat and lupins in a 2:1 rotation. McLay et al. (1994) reported that gypsum (at rates of 3 t ha$^{-1}$ or higher) increased wheat yields by up to 45% in the first 2 years following application to the surface. In contrast, the application of lime to the surface increased yields by up to only 15% in the second year. The highest yields (up to 77% increase) were achieved when gypsum and lime were added together. Even though yields increased, it was not known which of the above mechanisms were operating. Identification of mechanisms by which surface applied gypsum ameliorates subsoil acidity is necessary to predict wheat responses and model the longevity of amelioration. It is not possible to predict the operative mechanisms from gypsum research published previously because different soils, climates and crop types were used and the actual mechanisms of amelioration in those studies remained fairly poorly understood. Previous work has mainly been conducted on soils with higher clay contents and water holding capacity than the yellow sandplain soils of Western Australia (Gillman et al. 1989; Shainberg et al. 1989). The higher rainfall of most regions where gypsum has been investigated for subsoil acidity (750–2000 mm) is also considerably higher than the eastern wheatbelt of Western Australia (300–350 mm). Only one previous study investigating gypsum considered wheat growth (Bruce et al. 1988; Shainberg et al. 1989), whereas others have often not even included plants (e.g. Gillman et al. 1989) and have often been conducted under laboratory conditions or by using artificial rainfall. In some studies, Ca deficiency has been the major factor limiting plant growth rather than Al toxicity (Shainberg et al. 1989). The high rates of application that are often used (commonly in excess of 10 t ha$^{-1}$) would not be economically feasible in all cropping systems, particularly in the
low rainfall region of the eastern wheatbelt of Western Australia. In addition, the extractants used to measure changes to soil chemical properties in previous work have not necessarily been appropriate for correlation with plant growth or for following changes in soil solution composition.

The aims of this paper are to report changes to soil solution composition following the surface application of gypsum and lime to sandy soils with Al toxic subsoils in a low annual rainfall environment, to relate changes in soil solution chemical properties to wheat yields in the field, and to identify possible mechanisms by which gypsum ameliorates subsurface acidity in the field.

Materials and Methods

The sites, soil, treatments and field trial design and management have been described in detail in a previous paper (McLay et al. 1994). In summary, field trials were established on a deep yellow sandplain soil with a highly acidic subsoil in two different regions of Western Australia (Carrabin and Trayning). The trials were an incomplete factorial design containing different rates (1, 3 and 9 t ha\(^{-1}\)) and sources (fine lakeside gypsum (FL); coarse lakeside gypsum (CL); phosphogypsum (PG)) of gypsum and different rates of lime (2 and 4 t ha\(^{-1}\)). Wheat was grown in the first two years after establishment and lupins were grown in the third year in accordance with the local district practice. At Carrabin, all treatments were sampled for soil analysis. At Trayning, only the following 10 treatments were sampled: FL 1, FL 3 and FL 9 t ha\(^{-1}\); CL 3 t ha\(^{-1}\); PG 3t ha\(^{-1}\); lime 2 and 4 t ha\(^{-1}\); FL 3+lime 2 t ha\(^{-1}\); FL 3+lime 4 t ha\(^{-1}\); control.

Soil Sampling

Soil samples were taken to a depth of 1 m using a 5 cm diameter percussion auger in late April 1990 and 1991 (i.e. 1 and 2 years respectively after the initial application of lime and gypsum to the soil surface) and separated into the following depth increments: 0–5, 5–10, 10–15, 15–25, 25–40, 40–60 and 60–100 cm. Previous studies on yellow sandplain soils (Carr and Ritchie 1993) had shown that late summer was the best time for sampling for prediction of crop yields in the approaching season. Soil chemical properties were not measured immediately after application of amendments to the soil surface in 1989 and it is assumed, therefore, that the gypsum or lime remained predominantly within the topsoil until the first significant rains fell after the crops were sown.

Three soil samples were taken from each of the four replicate plots for each treatment and bulked and a subsample was taken for chemical analysis (i.e. four replicate samples for each treatment were retained). All samples were air-dried and sieved (<2 mm) and stored in polythene bags for analysis.

Chemical Analyses

Soil was extracted in deionized water and 0·005 \(\text{M} \) KCl by shaking on an end over end shaker for 17 h at a soil:extractant ratio of 1:5 (4 g of soil plus 20 mL extractant). The ionic strength of the soil solution at field capacity was estimated from the electrical conductivity of the water extract by using the equation of Gillman and Bell (1978). All other analyses were conducted on the 0·005 \(\text{M} \) KCl extracts which had previously been shown to provide good relationships between soil acidity properties and plant growth on unamended yellow sandplain soils (Carr et al. 1991). The majority of the Al extracted by 0·005 \(\text{M} \) KCl is from the soil solution because the ionic strength of the KCl solution is similar to that of the soil solution in unamended soils and hence minimizes disturbance of the equilibrium between soluble and solid phase ions (Dolling and Ritchie 1985; Gillman 1991). Samples were filtered through a millipore 0·45 \(\mu\text{M} \) filter following extraction. The pH was measured with an Orion 940E pH meter with a combined glass electrode. Total aluminium (\(\text{Al}_\text{T}\)) was measured by the colorimetric pyrocatechol violet method (Dougan and Wilson 1974) with spectrophotometer readings made on a Pye Unicam SP8–150 UV/Vis spectrophotometer at 580 nm wavelength. Calcium, magnesium and sodium were measured on a Perkins–Elmer 403 atomic absorption spectrophotometer. Sulfate and nitrate were measured by ion-exchange chromatography using
an HPLC Waters Action Analyser with a borate/gluconate (pH 8.5) eluent. Nitrate was only measured on samples in 1991. The activities of various aluminium species (Table 1) in the 0.005 M KCl extracts of selected treatments from Carrabin in 1990 and 1991 were estimated using the chemical speciation program TITRATOR (Cabaniss 1987). It was assumed the presence of organic anions was negligible due to the extremely low organic content of the subsoil (McLay et al. 1994). The ionic strength used in the program was determined from the EC of the water extracts as described above. The concentrations of ions used were from the 0.005 M KCl extracts. Formation constants used for the aluminium species are given in Table 1. Activities were calculated using the mean concentration for a treatment and not each replicate of the treatment. The total activity of monomeric aluminium (\(\Sigma A_{\text{mono}}\)) was calculated as the sum of the activities of \(A_{\text{OH}}^{2+}\), \(A_{\text{OH}}^{-}\) and \(A_{\text{OH}}^{+}\) in the extracts.

### Table 1. Equilibrium constants used in calculation of Al species

<table>
<thead>
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<th>Reaction product</th>
<th>(\log K^0)</th>
<th>Reaction product</th>
<th>(\log K^0)</th>
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<tr>
<td>(MgSO_4)</td>
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</table>

**Statistical Analyses**

Changes to soil chemical properties at each depth were analysed by analysis of variance for an incomplete factorial design using Genstat (Lawes Agricultural College, Rothamsted). A high amount of variability (coefficients of variation of 10-50%) was commonly recorded between replicate plots; therefore few significant differences were recorded at the 5% level of significance for many soil chemical properties.

Linear and non-linear regression analysis was used to correlate wheat grain yields with various soil chemical properties and soil acidity indices from the different treatments. Soil chemical data had not been collected in 1989 and correlations with yield in 1989 cannot therefore be established. The negative response of lupins to gypsum application (McLay et al. 1994) was not due to Al toxicity and therefore lupin yields in 1991 were not correlated with soil acidity indices.

**Results**

The fine lakeside source of gypsum (FL) is used to represent the changes to soil chemical properties that occurred down the soil profile following gypsum application, as few differences were recorded between sources, particularly in the subsoil. Although differences in some soil chemical properties existed between rates of gypsum application and, to a lesser extent, lime application, only rates of application of 3 t ha\(^{-1}\) gypsum and 2t ha\(^{-1}\) lime are presented in this paper to represent the changes that occurred.

**Changes to Soil Solution Chemical Properties**

In unamended soil, pH was highest at the surface and decreased with depth at both Carrabin and Trayning (Figs 1a-d). At both sites, gypsum application resulted in no changes to pH down the soil profile in 1990 and 1991 (\(P < 0.05\)) (Figs 1a, b). No differences were recorded in pH between different rates or sources of gypsum at any depth (Table 2).
Fig. 1. The pH measured in 0·005 M KCl extracts v. depth for four representative treatments at Carrabin and Trayning in 1990 and 1991. Amendments were applied to the soil surface in 1989. Bars indicate the least significant difference ($P < 0.05$) for all the treatments in the trial design for a particular depth.

Lime increased the pH substantially up to a depth of 10 cm in 1990 and to a depth of 15 cm in 1991 at both sites (Figs 1a–d). No differences in subsoil pH were recorded between the two rates of lime application, although a higher pH was recorded at the surface ($P < 0.05$) with the 4 than the 2 t ha$^{-1}$ rate of lime application (Table 2). The application of gypsum plus lime caused increases in pH near the surface (0–15 cm) similar to the application of lime alone, and at Carrabin in 1990 resulted in higher pH (up to 0.5 of a pH unit) in the subsoil (15–60 cm). A higher pH was not recorded in the subsoil at Trayning, following the application of gypsum plus lime.

Aluminium

Total aluminium concentration was lowest at the surface and increased with depth in unamended soil (Figs 2a,b) and was generally at a higher concentration in the subsoil at Carrabin than Trayning. Both gypsum and lime amendments appeared to lower Al$_T$ throughout the soil at Carrabin in both 1990 and 1991 (Figs 2a,b), although most of these differences were not significant due to the high variability. The concentration of Al$_T$ at Carrabin was lower in plots which received gypsum plus lime than the other treatments up to a depth of 25 cm (Figs 2a,b). The application of amendments generally did not change Al$_T$ in the subsoil at Trayning although a slightly higher concentration of Al$_T$ was recorded in gypsum plots at a depth of 25–40 cm in 1990 and at 40–60 cm in
Table 2. Effect of rate and source of gypsum application, and rate of lime application on changes to soil chemical properties at selected soil depths at Carrabin in 1990 and 1991
(Rates: 1, 3 and 9 t ha\(^{-1}\); Sources: fine lakeside, coarse lakeside and phosphogypsum; Lime+gypsum rate: lime+1 t ha\(^{-1}\); Lime+3 t ha\(^{-1}\))

<table>
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<th>Soil property</th>
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<th>Gypsum source</th>
<th>Lime rate</th>
</tr>
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<td>n.s.</td>
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<tr>
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<td>n.s.</td>
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</tr>
<tr>
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<td>***</td>
<td>**</td>
<td>n.s.</td>
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<tr>
<td>Ca</td>
<td>***</td>
<td>***</td>
<td>n.s.</td>
</tr>
<tr>
<td>Mg</td>
<td>***</td>
<td>***</td>
<td>n.s.</td>
</tr>
<tr>
<td>SO(_4)</td>
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0-5 cm

| pH            | n.s.         | n.s.           | n.s.      | n.s.      | n.s.  | n.s. |
| Al\(_T\)      | n.s.         | n.s.           | n.s.      | n.s.      | n.s.  | n.s. |
| EC            | ***          | ***            | n.s.      | n.s.      | *     | n.s. |
| Ca            | **           | ***            | n.s.      | n.s.      | *     | n.s. |
| Mg            | n.s.         | ***            | n.s.      | n.s.      | n.s.  | n.s. |
| SO\(_4\)      | ***          | ***            | n.s.      | *         | n.s.  | n.s. |

15-25 cm

| pH            | n.s.         | n.s.           | n.s.      | n.s.      | n.s.  | n.s. |
| Al\(_T\)      | n.s.         | n.s.           | n.s.      | n.s.      | n.s.  | n.s. |
| EC            | ***          | ***            | n.s.      | n.s.      | *     | n.s. |
| Ca            | **           | ***            | n.s.      | n.s.      | *     | n.s. |
| Mg            | n.s.         | ***            | n.s.      | n.s.      | n.s.  | n.s. |
| SO\(_4\)      | ***          | ***            | n.s.      | *         | n.s.  | n.s. |

40-60 cm

| pH            | n.s.         | n.s.           | n.s.      | n.s.      | n.s.  | n.s. |
| Al\(_T\)      | n.s.         | n.s.           | n.s.      | n.s.      | n.s.  | n.s. |
| EC            | ***          | **             | n.s.      | *         | n.s.  | n.s. |
| Ca            | **           | *              | n.s.      | n.s.      | n.s.  | n.s. |
| Mg            | n.s.         | *              | n.s.      | n.s.      | n.s.  | n.s. |
| SO\(_4\)      | ***          | ***            | n.s.      | *         | n.s.  | n.s. |

* \(P < 0.05\); ** \(P < 0.01\); *** \(P < 0.001\); n.s., not significant.

1991 (Figs 2c,d). At both sites, different rates or sources of gypsum or lime application did not affect \(\text{Al}_T\) in the subsoil (Table 2).

In control and treatment plots at Carrabin, the variation of \(\Sigma(\text{Al}_{\text{mono}})\) with depth followed a similar trend to \(\text{Al}_T\) (Figs 3a,b). The application of all amendments resulted in lower \(\Sigma(\text{Al}_{\text{mono}})\) throughout the profile. In the 15-25 cm layer, there was a bigger difference in \(\Sigma(\text{Al}_{\text{mono}})\) between the control and the amended soils in 1991 than in 1990. The lowest \(\Sigma(\text{Al}_{\text{mono}})\) was recorded with lime plus gypsum at depths below 40 cm in 1990 and there was generally less difference between treatments in 1991.

The activity of the \(\text{AlSO}_4^+\) ion pair was substantially lower than \(\Sigma(\text{Al}_{\text{mono}})\) throughout the profile at Carrabin (Figs 3c,d). It was highest in plots which received gypsum and was maximal at 15-40 cm depth in 1990, and 25-60 cm depth in 1991. Limed plots, in contrast, resulted in either similar or slightly lower (\(\text{AlSO}_4^+\)) to control plots down the soil profile. An increase in the rate of gypsum applied increased (\(\text{AlSO}_4^+\)) at depths up to 40 cm in 1990 and 60 cm in 1991 (data not shown).

**Electrical Conductivity of Water Extracts**

The EC of the water extracts in unamended soil near the surface was similar at both sites (Figs 4a-d) and equivalent to an ionic strength of approximately
Fig. 2. Concentration of total aluminium in 0.005 M KCl extracts v. depth for four representative treatments at Carrabin and Trayning in 1990 and 1991. Bars indicate the least significant difference ($P < 0.05$) for all the treatments in the trial design for a particular depth.

0.002 in the soil solution. At Carrabin, the unamended subsoil had a similar EC to the surface. At Trayning, the EC was similar to the surface at depths down to 25 cm, and then increased with depth to a maximum at 60–100 cm which had an EC equivalent to an ionic strength of 0.005.

Significant changes to EC in the subsoil in 1990 were recorded up to 40 cm depth only for plots which received gypsum, with or without lime. At Carrabin, the largest change to EC down the profile in both 1990 and 1991 occurred with the application of gypsum plus lime (Figs 4a, b). However, at Trayning the increase in EC down the profile was similar for both gypsum and gypsum plus lime (Figs 4c, d). The resulting EC at the surface and in the subsurface (15–25 cm) at Carrabin in 1990 following the addition of gypsum was equivalent to an ionic strength of 0.018 and 0.006 respectively. The ionic strength at the same depths at Trayning in 1990 was 0.013 and 0.005 respectively. The
EC decreased substantially in the topsoil (0–15 cm) and decreased slightly at 15–25 cm between 1990 and 1991 for most treatment plots (Table 2). There was a linear relationship between gypsum application rate and the EC of the soil solution at 15–25 cm at Carrabin in both 1990 and 1991 (equations 1 and 2 respectively):

\[
EC = 28.6 \text{ (gypsum rate)} + 35.1\quad (r^2 = 0.90), \quad (1)
\]
\[
EC = 12.0 \text{ (gypsum rate)} + 47.8\quad (r^2 = 0.98).
\]

The less intensive sampling regime at Trayning prohibited the relationship being substantiated at the site. Below 25 cm depth, there was little change to EC. At both sites, EC increased \((P < 0.001)\) throughout the soil profile as the rate of gypsum application increased (Table 2). A lower EC \((P < 0.05)\) was recorded at 40–60 cm with phosphogypsum than the lakeside sources of gypsum in 1991 (Table 2).
Fig. 4. Electrical conductivity in water extracts v. depth for four representative treatments at Carrabin and Trayning in 1990 and 1991. Bars indicate the least significant difference (P < 0.05) for all the treatments in the trial design for a particular depth.

Lime caused the EC to increase up to a depth of only 10 and 5 cm at Carrabin and Trayning respectively in the first year after application (i.e. 1990). In 1991, the EC increased down to a depth of 15 cm in limed plots at both sites. The only difference in EC recorded between the different rates of lime application was recorded at the surface in 1990 when 4 t ha\(^{-1}\) lime resulted in a higher EC than 2 t ha\(^{-1}\) lime (Table 2).

**Calcium**

The calcium concentration generally followed a similar trend to EC following the application of amendments (Figs 5a-d). At Carrabin, the increase in concentration of Ca at depths near the soil surface as a result of application of the different amendments followed the order: control < lime < gypsum < gypsum plus lime. The Ca concentration in the lime plus gypsum plots in 1990 was slightly less than the sum of the Ca concentrations from both the gypsum and lime plots individually. At Trayning, Ca in soil near the surface was highest in plots which received gypsum. The concentration of Ca at depths close to the surface decreased by approximately half from 1990 to 1991 for both the gypsum and gypsum plus lime treatments at Carrabin, whereas only small changes were observed at Trayning.
In the subsoil, Ca increased \((P < 0.05)\) at depths up to 25 cm in 1990, and 40 cm in 1991 at both sites following gypsum application. Lime caused only small increases in the Ca concentration at both sites, although Ca appeared to increase at greater depths at Carrabin than Trayning. The Ca concentration increased throughout the profile at both sites as the rate of gypsum application increased, but no differences were observed between soils amended with different gypsum sources or lime application rates (Table 2).

**Sulfate**

Sulfate concentrations also followed a similar trend to EC (Figs 6a-d). Sulfate concentrations in both the surface and subsurface increased substantially throughout the profile in plots which received gypsum \((P < 0.05)\). The concentration of \(\text{SO}_4\) decreased considerably throughout the profile in gypsum treated plots at Carrabin from 1990 to 1991, but only small changes in \(\text{SO}_4\) concentration were observed at Trayning. Lime, in contrast, did not affect \(\text{SO}_4\) concentrations in the soil \((P < 0.05)\). At Carrabin in 1990, \(\text{SO}_4\) concentrations were similar in plots which had received gypsum plus lime to those which had only received...
In 1991, plots which received gypsum plus lime had lower concentrations of SO$_4$ than where gypsum alone had been applied up to 10 cm depth, but the reverse was true below 10 cm depth. At Trayning, lower SO$_4$ concentrations were measured in plots which received gypsum plus lime than gypsum alone up to 10 cm depth in 1990 and 25 cm depth in 1991. Below these depths, similar SO$_4$ concentrations were measured in both years.

Sulfate in the profile increased significantly as the rate of gypsum increased (Table 2). No differences in SO$_4$ concentration were observed between plots amended with different gypsum sources or lime rates, however. The only difference between the different sources was recorded at the surface in 1991, where SO$_4$ concentrations were higher with coarse lakeside gypsum than the other sources, and at 40–60 cm where SO$_4$ was lower with phosphogypsum than the other sources. The 4 t ha$^{-1}$ lime rate resulted in a higher SO$_4$ concentration at 15–25 cm than the 2 t ha$^{-1}$ lime rate (Table 2).

**Magnesium**

Magnesium concentrations were lower in the top 10 cm of soil, and substantially higher in the subsoil (below 15 cm depth) at both sites in plots which received...
gypsum (Figs 7a-d). This effect was more pronounced as the rate of gypsum increased (Table 2). Lime application tended to increase Mg concentrations slightly throughout the profile and higher Mg concentrations were measured at the surface with the 4 than the 2 t ha\(^{-1}\) rate of lime application (Table 2). The result of adding gypsum plus lime together was to decrease Mg concentrations near the surface, but to a lesser extent than had occurred when gypsum alone was applied, and increase Mg concentrations in the subsoil to similar concentrations that had been measured from gypsum application alone.

**Sodium and Nitrate**

The monovalent ions measured (Na and NO\(_3\)) tended to be less affected by gypsum and lime applications (data not presented). Small increases in Na concentrations and small decreases in NO\(_3\) concentrations (measured in 1991 only) were observed throughout the profile for both gypsum and/or lime amendments.
Relationship of Yield to Soil Chemical Properties

Wheat yields in plots which had received gypsum were generally higher in the first 2 years after application than in plots which did not receive any gypsum (McLay et al. 1994). No correlation was observed between the yield of wheat and simple soil solution properties such as pH or AIT down the soil profile. Instead, the best correlation was recorded with the soil acidity index AIT/EC at both sites, although the type of relationship and depth at which the best correlation was obtained differed between the two sites. At Carrabin, the best correlation ($r^2 = 0.51$) was obtained with a logarithmic relationship between yield and AIT/EC at a depth of 15-25 cm (Fig. 8a). At Trayning, yields were linearly related to AIT/EC at a depth of 25-40 cm ($r^2 = 0.96$) (Fig. 8b). Linear regression analyses revealed that at Carrabin in 1990, EC at 15-25 cm depth was best correlated with the 0.005 M KCl-extractable SO4 concentration (equation 3), whereas at Trayning, EC at 25-40 cm depth was best correlated with the 0.005 M KCl-extractable Ca concentration (equation 4):

\[ EC = 66.1 + 0.17 \times (SO_4) \quad r^2 = 0.75, \quad (3) \]
\[ EC = -13.5 + 0.27 \times (Ca) \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 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Discussion

Gypsum leached quickly, despite the low rainfall, and resulted in changes to soil solution composition down to 1 m depth after the first year. In contrast, relatively little lime leaching occurred and, after 2 years, lime had only affected soil solution properties in the top 15 cm of soil. Gypsum resulted in large increases in Ca, SO₄ and ionic strength but little change to pH or Al₇ was recorded. Changes to chemical properties in treatments where gypsum plus lime were applied together were generally different to the application of either of these treatments separately. Wheat yields appeared to be best correlated with the soil acidity index Al₇/EC, and the increase in ionic strength of the soil solution following gypsum application appeared to be an important mechanism of amelioration.

Effect of Amendments on Soil Solution Composition

Gypsum generally had little effect on pH and Al₇ although a trend towards slightly lower Al₇ was apparent in the soil at Carrabin. Previous studies have shown that the application of gypsum may either increase, decrease or cause no change to soil pH (Reeve and Sumner 1972; Pavan et al. 1982; Hammel et al. 1985; Hue et al. 1985; Sumner et al. 1986; Farina and Channon 1988; Shainberg et al. 1989). It has been suggested that, in highly weathered soils with low exchangeable acidity, an increase in pH should be observed but can probably only be detected if measured in water (Farina and Channon 1988; Shainberg et al. 1989). Others (e.g. Bruce et al. 1988) have reported a decrease in soil pH measured in water at a rate of gypsum application that was calculated to increase the Ca saturation of the ECEC to 20%. The general lack of change reported here is probably a result of the ‘salt effect’ counterbalanced by displacement of hydroxide ions off soil surfaces by sulfate ions.

Gypsum substantially increased the ionic strength of the soil solution and the concentration of Ca and SO₄ in both the topsoil and subsoil. At both sites, leaching of gypsum into the subsoil within the first year resulted in a large increase in EC, Ca and SO₄ at depths below 15 cm in 1990. Therefore, the low rainfall of the region (about 300 mm) did not prevent a surface application of gypsum from leaching to the depth that was required to decrease the severity of subsoil acidity in the eastern wheatbelt of Western Australia. The rainfall at Carrabin and Trayning is considerably lower than the rainfall in other regions of the world where gypsum has been successfully used to ameliorate subsoil acidity. However, the Mediterranean climate of the region results in 80% of the rainfall occurring in the 6 months of the growing season and therefore maximizes the amount of leaching which can occur. The possibility of extensive leaching was supported by a bromide tracer leaching study at Carrabin (data not presented) which showed that a conservative tracer such as bromide could leach beyond 100 cm depth in one growing season. Continued leaching of gypsum in the second year after application caused EC, Ca and SO₄ to be substantially lower in the topsoil at both sites in 1991 compared with 1990, particularly at the Carrabin site. The lack of a concomitant increase in these soil properties in the subsoil in 1991 indicated that the leaching of ions from the topsoil into the subsoil was balanced by either leaching of ions below 100 cm depth, uptake of solutes...
by plants from the subsoil or transformation to less soluble forms. Leaching of gypsum in the second year (i.e. the growing season of 1990) was a probable cause of the lack of response of wheat to the lowest rate of gypsum application (1 t ha$^{-1}$) at the two sites because it resulted in only low concentrations of the gypsum constituents involved in amelioration remaining in the soil.

The larger decreases in EC, Ca and SO$_4$ in the topsoil of gypsum plots at the Carrabin site from 1990 to 1991 than at the Trayning site indicated that more extensive leaching of amendments probably occurred at Carrabin than Trayning. As the total amount and distribution of rainfall at the two sites was similar, we suggest that the better plant growth (and subsequently higher grain yields) that occurred at Trayning than Carrabin (McLay et al. 1994) could have resulted in more rapid drying of the soil following rainfall, hence less dissolution of amendments at the surface and less leaching of solutes by water.

The general lack of differences between gypsum sources was probably due to their similar chemical composition (McLay et al. 1994). An increase in fluoride concentration in solutions may decrease Al toxicity to plants (Cameron et al. 1986) but no yield increases were evident in phosphogypsum plots compared with plots which received the other gypsum sources. Although the fluoride content of the phosphogypsum (3800 mg kg$^{-1}$) was substantially higher than that of the lakeside sources of gypsum (<16 mg kg$^{-1}$), it is likely that any fluoride released from the gypsum would react rapidly with soil near the surface and not reach the subsoil to effect amelioration. The lack of differences between fine or coarse lakeside gypsum is attributed to sufficient solubility of the coarser gypsum under the environmental conditions.

The displacement of Mg by gypsum from the topsoil to lower in the profile has previously been reported (Farina and Channon 1988; Shainberg et al. 1989) and has important implications for the Mg nutrition of plants in the long term where gypsum is applied. The Mg concentration in plant tissues in the field trial was lowest in plants from gypsum plots (McLay et al. 1994), indicating that supplementary Mg would probably be required in gypsum plots in the longer term. Few reports exist on the fate of Na and NO$_3$.

Lime caused EC, Ca and pH to increase in the topsoil, but had little effect on any soil solution chemical properties in the subsoil; this indicates that direct incorporation of lime into the subsoil would be necessary for liming to be effective in the short term. The large increase in pH measured in the topsoil following lime application, even at the lower 2 t ha$^{-1}$ rate (pH increased from approximately pH 5.5 to 7.3 in the 0–5 cm layer), reflected the low pH buffering capacity of the soil due to its low organic matter and clay content (McLay et al. 1994). The high pH may necessitate regular monitoring of plant nutrient status to ensure that deficiency of other nutrients such as Mn and P is not induced when lime is applied.

In contrast to gypsum, the movement of lime was very limited in the soil at both sites. At the end of the first year after application, the changes to pH, EC and Ca suggested that lime had remained predominantly in the 0–10 cm depth of incorporation. A slight downward movement of lime was indicated by an increase in these soil properties in the 10–15 cm layer at the end of the second year. The lack of differences in the depth of lime movement between the two lime rates suggested that over-liming is unlikely to result in more extensive leaching of lime.
in this soil. More extensive leaching of lime may have occurred in the presence of gypsum in the first year at Carrabin because the pH at depths greater than 15 cm in plots which received gypsum plus lime was higher than that in the plots which only received lime. This implied either greater solubility of lime in the presence of gypsum, which is contrary to what the ‘common-ion’ effect would predict (Vogel 1961), or less adsorption of hydroxide ions in the topsoil (which is unlikely because of the higher ionic strength). The Ca concentrations in the soil solution were higher in the lime plus gypsum treatments than in the lime treatments (Figs 5a,b) and it is possible, therefore, that the higher ionic strength in the presence of gypsum decreased the activity of Ca$^{2+}$, enabling more lime to dissolve, which more than counter-balanced the common ion effect. The higher pH at depth only occurred at one site and in one year, and its longer term significance is uncertain at this stage.

Possible Mechanisms of Amelioration of Subsoil Acidity

Decreasing the proportion of soluble Al that was toxic to wheat appeared to be an important mechanism by which gypsum ameliorated the acidic subsoil. This apparently was achieved by decreasing the activity of toxic monomeric Al species by increasing the ionic strength of the soil solution and partly by Al$\text{SO}_4$ complexing. The extent to which it occurred depended on the application rate of gypsum, the concurrent presence of lime and the rate and extent of leaching.

A good relationship between plant yield and the ratio $\text{Al}_1/\text{EC}$ in the subsoil at both sites indicated that the increase in ionic strength of the soil in the Al toxic layer was an important factor in increasing yields following gypsum application. The ratio $\text{Al}_1/\text{EC}$ at 15–25 cm depth was linearly correlated ($r^2 = 0.86$) with the activity of monomeric Al that was calculated to be present in the soil solution of plots which received gypsum. Hence, the ratio $\text{Al}_1/\text{EC}$ recognizes that it is the activity of Al$^{3+}$ rather than the concentration of total Al that is toxic to plants (Adams and Lund 1966). Carr et al. (1991) have suggested a similar relationship ($\text{Al}/\text{Na}$, where Na is an indicator of ionic strength of unamended soils) can be used for predicting the severity of Al toxicity to wheat growth in unamended yellow sandplain soils of Western Australia. Soil solution EC and ionic strength have also been suggested for use in predicting the activity of Al$^{3+}$ in soil solutions of an Oxisol and Ultisol in Puerto Rico (Brenes and Pearson 1973) and a range of soils from Queensland (Bruce et al. 1989). However, the relationships reported in those studies did not apply to the yellow sandplain soils we studied because the Al concentration measured did not increase with the increase in ionic strength following gypsum application. The ratio $\text{Al}_1/\text{EC}$ is a simple soil test that can be easily measured and does not require the use of chemical speciation programs or more complicated analytical techniques for estimating ‘toxic’ aluminium. The good relationship between gypsum application rate and EC at 15–25 cm depth for the 2 years indicates that it should be possible to model changes to EC for different application rates over time, making it possible to predict changes to the ionic strength in the subsoil and therefore wheat responses to gypsum application on soils similar to the yellow sandplain soils.

The different type of relationship between $\text{Al}_1/\text{EC}$ and wheat grain yield at the two sites could be attributed to the wider range of $\text{Al}_1/\text{EC}$ values which were recorded from the various treatments at Carrabin. The log relationship at
Carrabin was influenced strongly by a single Al$_T$/EC value which corresponded to the control treatment (Fig. 8a). However, this value was important as the application of all amendments at Carrabin decreased the Al$_T$/EC ratio to an extent that no values were recorded close to the control. At Trayning, the soil solution inherently contained a higher ionic strength than Carrabin; hence, the Al$_T$/EC ratio for the control was lower and closer to the ratio for the amended soil, and therefore no plateau in the curve would be expected. The differences in the relationship between the two sites suggests that when the soil is amended with gypsum, a small increase in ionic strength of the soil solution in the Al toxic layer is likely to increase wheat yields more at Trayning than at Carrabin when $0.2 < \text{Al}_T/\text{EC} < 0.5$. However, the absolute increase in yield at Carrabin would be higher if the increase in ionic strength was large enough to decrease Al$_T$/EC to less than 0.2 in the Al$_T$ toxic layer. The values of Al$_T$/EC in amended plots at Carrabin were lower than at Trayning probably because of the greater amount of leaching of solutes into the layer that required amelioration. The lack of response of wheat to gypsum, observed in the first year at Trayning, (McLay et al. 1994), was probably a result of the greater depth to the Al-toxic layer, along with the extent of leaching which was probably lower than at Carrabin.

The good correlation between SO$_4$ and ionic strength at Carrabin (equation 3), and Ca and ionic strength at Trayning (equation 4), indicated that leaching of gypsum components was predominantly responsible for the increase in ionic strength in the Al toxic layer at the respective sites in 1990. The reason for the difference in the component which was best correlated with EC between the sites in 1990 is unclear. It was expected that SO$_4$ would leach more rapidly from the topsoil (and be correlated with ionic strength in the subsoil) than Ca, as observed at Carrabin. Sulfate, however, was better correlated than Ca with EC at Trayning in 1991. As well as contributing to an increase in ionic strength, an increase in SO$_4$ concentration in the soil solution following gypsum application also increased the activity of AlSO$_4^-$ ion pairs which have previously been suggested to decrease the amount of Al which is toxic to plants (Pavan et al. 1982; Singh 1984; Cameron et al. 1986).

The lack of correlation between yield and pH or total aluminium concentration in the soil solution indicated that the mechanism of amelioration could not simply be explained by changes in pH or Al$_T$. Previous mechanisms which have been proposed such as a pH increase by self-liming (Reeve and Sumner 1972; Farina and Channon 1988), a decrease in the concentration of Al$^{3+}$ in solution by precipitation of Al hydroxy sulfate minerals (Adams and Rawajfih 1977; Nordstrom 1982; Hue et al. 1985) or leaching of Al$^{3+}$ out of the soil (Kotze and Deist 1975; Oates and Caldwell 1985) were not evident from the measurements made. Estimates of Al$^{3+}$ activity in the soil extracts of the subsoil indicated that they were under-saturated with respect to the dissolution of alunite, jurbanite or basaluminite.

Conclusions

Gypsum was able to increase yields of wheat grown on soils with acidic subsoils in a low rainfall region because the soils were well drained, enabling sulfate to leach to the acidic layer where it decreased Al toxicity by increasing ionic strength and possibly through Al complexation with SO$_4$. The soil test, Al$_T$/EC, has
potential as a simple soil test to predict wheat responses to gypsum applications because of its correlation with yield and because of the relationship between EC at 15–25 cm and gypsum application rate.

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References


