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Green, Hannah, Larsen, Peter, Koci, Jack, Edwards, Will, and Nelson, Paul
(2023) *Long-term effects of gypsum on the chemistry of sodic soils*. Soil and
Tillage Research, 233 .

Access to this file is available from:

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Please refer to the original source for the final version of this work:

<https://doi.org/10.1016/j.still.2023.105780>

Long-term effects of gypsum on the chemistry of sodic soils

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Abstract

Soils with high exchangeable sodium contents have structural and hydrological problems that limit agricultural productivity. Gypsum is commonly applied as an ameliorant but there are few field studies into its long-term (> 10 years) effects on soil chemistry, especially at depths greater than 0.4 m, and no long-term validation of the gypsum requirement model. The aim of this study was to address these two knowledge gaps. This was achieved by a) carrying out a field study of the effects of repeated gypsum applications, irrigation, and sugarcane cultivation to 1.25 m depth over a 26-year period in Australia, and b) assessing the ability of the gypsum requirement model to predict changes in exchangeable sodium percentage (ESP) more broadly, using 53 unique cases from 17 field studies (> 1 year). In our field study, the greatest reductions in exchangeable sodium (up to 5.49%; $p < 0.05$) occurred between 0.25 and 1.00 m depth, where initial concentrations were highest. The amount of sodium ($16.47 \text{ cmol}_c/\text{m}^2$), magnesium ($2.49 \text{ cmol}_c/\text{m}^2$), and potassium ($0.65 \text{ cmol}_c/\text{m}^2$) displaced was less than the amount of calcium gained ($36.76 \text{ cmol}_c/\text{m}^2$) over the profile. Most calcium was retained in the application layer (0.00–0.25 m) but some moved down to at least 1.25 m. Reductions in exchangeable sodium were smaller than in all previous long-term studies, possibly due to lower deep drainage rates (39–45 mm/year) and increased pH. Assessment of the gypsum requirement model showed that predicted final ESP deviated widely from measured ESP in many cases (95% of predictions deviated by >10%), presumably due to interactions between pH, clay type, carbonate, climate, management, and cation exchange equilibria. By adjusting two model parameters, the effect of gypsum on ESP was more accurately predicted (20% of predictions were within 10% of measured ESP) making it a useful tool for farmers.

Keywords: Solonetz soils, ion exchange, drainage, gypsum, sulfur, soil management

1. Introduction

As demand for agricultural products increases, it is critical that yield gaps are closed and soils are managed sustainably. In many soils, plant growth is limited by poor physical properties such as low porosity, infiltration rate, plant-available water content, and root penetrability associated with clay dispersion (Rengasamy and Sumner, 1998; Page et al., 2021). Clay dispersion is influenced by many factors, especially sodicity. Soil sodicity can be expressed as exchangeable sodium concentration, the proportion of the cation exchange capacity (CEC) occupied by sodium (exchangeable sodium percentage or ESP), or as the ratio of sodium to calcium and magnesium in soil water extracts (sodium adsorption ratio). The dispersive effects of sodium differ between soils due to complex interactions with other soil properties, including other exchangeable cations, pH, salinity, clay content and mineralogy, and organic matter content and nature (Isbell, 1995; Sumner, 1995; Cook et al., 1997; Nelson and Oades, 1998; Bennett et al., 2016; Page et al. 2021). Sodicity can increase or decrease over time depending on changes in vegetation (Fitzpatrick et al., 1995; Oster and Jayawardane, 1998; Qadir et al., 2001), irrigation (Rengasamy and Olsson, 1995; Sentís, 2014; Filippi et al., 2018; Minhas, et al., 2019), physical disturbance (Oster and Jayawardane, 1998; Nelson, 2001), and amendment application (Oster and Jayawardane, 1998).

Sodicity and related properties have a large impact on agricultural productivity. It is estimated that sodic soils cover up to 618 million ha globally, including 340 million ha in Australia (Intergovernmental Technical Panel on Soils [ITPS], 2015). Resultant losses of wheat yield in Australia are estimated at 0.2–0.4 t/ha, equivalent to \$1,300 million of productivity per year (Orton et al., 2018). Similarly, sugarcane yield losses of 1.5–2.1 t/ha for every 1% increase in ESP in the subsoil have been observed (Spalding, 1983; Nelson and Ham, 2000). Sodic soils are also often saline, where plant growth is adversely affected by high concentrations of soluble salts (Sumner et al., 1998; Rengasamy, 2016). It is estimated that each year salinisation results in the loss 0.3–1.5 million ha of productive farmland and decreases the productivity of another 20–46 million ha (ITPS, 2015).

Ameliorating sodic soils usually involves displacing exchangeable sodium with calcium by applying gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum reduces clay dispersion and improves the structure of sodic soils (Rengasamy and Churchman, 1999), but there are also concerns about negative effects in the long term. For example, saline water tables may rise following gypsum application due to increased deep drainage, especially in

irrigated areas (Dowling et al., 1991; Hulugalle et al., 2010; Petheram et al., 2008; Slavich et al., 1995; Voropaeva et al., 2011). This may eventually lead to soil re-sodification and salinisation. Thus, decisions about ameliorating sodic soils must be made carefully, to minimise environmental and economic costs. This requires cost-benefit analysis and predictions of the effect of ameliorants on the soil profile and groundwater over time.

The amount of gypsum required is normally calculated according to the amount of exchangeable sodium to be displaced to a given depth. To account for inefficiencies in calcium-sodium exchange, it is generally recommended that the calculated requirement be increased by a factor (F) of 1.2-1.5 (Allison et al., 1954; Department of Environment and Resource Management [DERM], 2011; Oster and Frenkel, 1980). The gypsum requirement model, as expressed by Oster and Jayawardane (1998), is:

$$\text{Gypsum required} = 0.086 \times F \times \text{depth} \times BD \times CEC \times (\text{initial ESP} - \text{final ESP}) \quad (1)$$

where *Gypsum required* is in t/ha, F is unitless, *depth* is in meters, BD is in t/m³, and CEC is in cmol_c/kg. Despite having been used extensively across the globe for over 70 years, the gypsum requirement model has not been validated or improved using data from field trials conducted over recent decades highlighting the need to re-evaluate the model using field data across a range of contexts, over time, and to depth.

There has been limited research into the long-term effects of gypsum on sodic soil chemistry, especially in the dry tropics. Since the work in temperate to arid northern America and Europe in the first half of the 20th century (reported by Allison et al. 1954 and FAO/UNESCO, 1973), few field studies have reported changes after ten or more years (Voropaeva et al., 2011; Belić et al., 2012; Bennett et al., 2014; Zhao et al., 2019). Only one long-term study was in the dry tropics, where sodic soils are common and agriculture is expanding. In the dry tropics, temperatures are high and rainfall is intense, so results from previous studies may not be applicable due to differences in the rates of ion movement in the profile, duration and depth of saturation, and the amount of deep drainage that occurs. In previous studies, single gypsum applications of 30 t/ha or more resulted in long-term reductions in soil sodicity, but few studies measured effects deeper than 0.4 m. Little data is available on the effects of repeated smaller gypsum applications

(e.g., less than 10 t/ha), which is common practice in many parts of the world, and few studies have determined the effect of gypsum on deep drainage or groundwater quality (Petheram et al., 2008; Voropaeva et al., 2011). Given the widespread use of gypsum, these are critical knowledge gaps. Hence, more long-term field trials are needed to determine how climate, soil type, gypsum rate and timing, irrigation rate, and other land use practices impact the effect of gypsum, especially below the root zone.

In this study two hypotheses were tested. The first was that the long-term reduction in exchangeable sodium in sodic soil profiles treated with gypsum and low salinity irrigation water in the dry tropics is greatest in the surface layer and decreases with depth as the applied calcium is depleted. This was tested by a paired site comparison between a field under sugarcane cultivation for 26 years and an adjacent uncultivated area. The second hypothesis was that the gypsum requirement model adequately predicts the change in ESP across the range of conditions in which gypsum has been applied. It was tested by examining data from a wide range of gypsum field trials, including the one reported here. Model parameters were adjusted empirically to improve its predictive ability.

2. Materials and methods

2.1 Field study design and sampling

The combined effect of sugarcane, irrigation, and gypsum application was determined by comparing soil properties of a field cleared and brought into cultivation in 1994 with an adjacent uncultivated ('virgin') area. The study site was located near Clare (19.86°S, 147.178°E) in the Burdekin River Irrigation Area (BRIA) of Queensland, Australia (Fig. S1). The climate is dry tropical with a distinct wet season (November to April) and dry season (May to October) and high rainfall variability (Bureau of Meteorology [BOM], 2020). The median annual rainfall is 746 mm (2001–2021) and mean monthly minimum and maximum temperatures are 18.2°C and 29.2°C (1970–2021), respectively (BOM, 2022a; BOM, 2022b). The landform is an alluvial plain with soils classified as Sodosols that are strongly alkaline below 0.3 m, and Vertosols that are hard-setting cracking clays with light to light-medium clay texture (McClurg et al., 1992; Isbell and National Committee on Soil and Terrain, 2021). The vegetation (extant on the virgin portion of the site and pre-clearing on the cultivated portion) is *Eucalyptus platyphylla* and *Corymbia* spp. woodland (Queensland Regional Ecosystem 11.3.7/11.3.9; Queensland Herbarium, 2021).

The cultivated site has grown furrow-irrigated sugarcane since 1995, except for a three-year period from 2003 to 2007 when irrigated Rhodes grass (*Chloris gayana*) was grown. Between 800 and 1000 mm of irrigation water (mean pH 7.8, 0.21 dS/m, sodium 17.0 mg/L, total dissolved ions 155 mg/L, chloride 18.3 mg/L, alkalinity 75.5 mg/L as CaCO₃) from the Burdekin Dam has been applied annually (Queensland Government, 2021a). Between 1995 and 2015, gypsum was applied to the surface and incorporated to a depth of 0.15 m, prior to each planting of sugarcane (Table 1). A non-saline, non-sodic perched water table has been observed below 1.25 m. Groundwater monitoring bores (screening between 18.1 and 21.1 m deep from 1993 to 2021) indicate that groundwater in the regional aquifer is saline (mean 4.09 dS/m), has a high sodium adsorption ratio (mean 3.83), with the water table around 5 m below ground level adjacent to the trial (Queensland Government, 2021b). In 2016, a trial was established on the sugarcane site to compare the effects of two rates of gypsum (5 and 10 t/ha) and mill by-products (mud and ash) on sugarcane yield. The treatments were applied in four replicates in a randomised block design, with each plot consisting of six rows spaced at 1.65 m (Fig. S2). In total, 24.1 t/ha and 29.1 t/ha of gypsum had been applied to this site (Table 1). The trial did not include a non-gypsum control treatment.

Soil samples were collected in April and May 2021 using a 43.5-mm corer. Samples were taken in 0.25-m increments to a depth of 1.25 m. Eight soil cores were taken from the sugarcane plots with 24.1 t/ha gypsum and eight from the sugarcane plots with 29.1 t/ha gypsum. Eight sets of samples were also taken from the virgin sites, from the same soil map units as those in the trial (2Dya-2Uge, 6Dbh, 2DbA; McClurg et al., 1992), with each set being a composite of 5 cores. Within each sugarcane plot, cores were collected 50 m from the top and bottom of the field in relation to irrigation flow. Cores were taken from the shoulder of the planted mound, approximately 0.15 m from the centre of either the third or fourth row within each plot, avoiding the fertiliser application area in the centre of the row. In the virgin sites, where there was gilgai micro-relief, cores were taken mid-way between the mound and depression. Additional cores were collected at half of the sampling locations to measure dry bulk density (BD) in each of the 0.25-m increments.

Chemical analyses were conducted according to the methods described by Rayment and Lyons (2011). Analyses conducted were: exchangeable calcium, potassium, magnesium, and sodium (ammonium acetate, 15D3), CEC (calculation, 15J1), sulfur (MCP, 10B3), pH 1:5 soil:CaCl₂ (4B4; pH), electrical

conductivity 1:5 soil:water (3A1; EC), chloride (5A2b), clay, sand, and silt (hydrometer), ESP (15N1), and exchangeable aluminium (KCl, 15G1). In cases where EC was greater than 0.3 dS/m, exchangeable cation concentrations were corrected for dissolved cations from relationships between EC (> 0.3 dS/m) and soluble sodium ($R^2 = 0.809$), calcium ($R^2 = 0.420$) and magnesium ($R^2 = 0.359$) measured under sugarcane in the BRIA (So et al., 2006; Nelson and Ham, 2021). ESP and CEC were recalculated using the corrected values for exchangeable cations. Exchangeable aluminium saturation was less than 1.5% throughout, including the virgin topsoil, which had the lowest pH, so it is not reported further.

2.2 Field study statistical analyses

All statistical analyses were performed in R Version 4.0.3 (R Core Team, 2020) and figures produced using the package ggplot2 (Wickham, 2016). A series of multivariate analyses of variance (MANOVAs) were conducted to determine the relevance of position in the sugarcane field (top versus bottom) as a factor in the experimental design. Overall, these analyses found no significant effect of position in the field on profile chemistry. Therefore, this factor was not used in further analyses and subsamples taken from the same plot were treated as independent replicates.

For each soil chemical property, mixed effects analysis was performed to determine whether there were significant differences between the virgin and sugarcane profiles. Non-linear depth profiles were approached using generalised additive mixed modelling (GAMM). These analyses were completed using the glmmTMB function in the glmmTMB package (Brooks et al., 2017) and the gam function in the mgcv package (Wood, 2011). Depth, nested within replicates, was included as a random effect as measurements taken at different depths from the same core are not independent. The best model for the number of parameters was determined using the corrected Akaike Information Criterion (AICc; Akaike, 1973). Models were validated using DHARMA residuals (Hartig, 2022) and all defined contrasts were orthogonal.

2.3 Field study mass balance

The change in the quantity of exchangeable cations (sodium, calcium, potassium, magnesium), chloride and sulfur in each layer of the sugarcane profiles relative to the virgin profiles was determined by calculating a mass balance. Quantities in each depth interval were calculated by multiplying concentration

by depth and BD. These values were then averaged across replicates/soil map units for each treatment. The gain/loss of each element in each depth interval was calculated as the mean amount in the sugarcane sites minus the mean amount in the virgin sites.

The total amounts of sodium, calcium and sulfur applied to the surface were calculated based on irrigation and gypsum application records (Ham, 2005; Queensland Government, 2021a). Four scenarios were calculated to account for uncertain inputs. Gypsum initially applied to the trial site had unknown calcium and sulfur content, but it can be assumed to have been mined from either Winton or Hughenden, and these sources have known quality (Table 1). Similarly, exact irrigation application rate was unknown, so scenarios were run based on the likely lowest and highest total rates. Estimates of plant uptake and removal in harvested material were calculated based on yield and concentrations for harvested sugarcane measured at the site (Wilmar Sugar records). The amount of plant uptake from each depth increment was based on reported proportions of root mass at each depth (Nelson and Ham, 2000). It was assumed that 80% of the irrigation water and 100% of the gypsum applied to the surface were incorporated into the first layer (0.00–0.25 m depth) and 20% of irrigation water was lost as run-off, based on field observations.

Calculations were made sequentially down the soil layers. Excess calcium and sulfur in the first layer, i.e., the difference between the total amount applied, the amount gained, and plant uptake and removal at harvest were assumed to move down to the next layer (0.25–0.50 m) and the calculations were repeated down the profile until the deepest layer sampled (1.00–1.25 m). The amount of calcium and sulfur unaccounted for at the bottom of the measured profile in each scenario was compared using generalised linear modelling using the *glm* function in the stats package (R Core Team, 2020).

2.4 Field study: deep drainage calculation

The average deep drainage rates in the sugarcane profiles throughout the 26 years of cultivation was calculated using an Excel version of the *SODICS* model (Rose et al., 1979). It has been employed previously to estimate deep drainage rates after land use changes (Thorburn et al., 1990; Dowling et al., 1991; Radford et al. 2009; Silburn et al., 2011; Tolmie et al., 2011). The model uses the chloride concentrations of the soil before and after ‘treatment’, as well as irrigation water and rainfall, to estimate water

movement through the soil profile. The maximum chloride value in each layer of the soil profiles from the virgin sites was used as the 'before treatment'. The mean chloride profiles of the sugarcane plots were used as the 'after treatment'. As with the elemental mass balance, two scenarios were run due to uncertainty about the irrigation rate, and 80% infiltration was assumed. Estimates of the drained upper water limit and air-dry moisture content profiles were derived from McClurg et al. (1992).

2.5 Gypsum requirement model assessment and modification

To assess how well the gypsum requirement model (Equation 1) predicts final ESP, data from field trials investigating the effect of gypsum on sodic soil chemistry were used. Those that included all the required data comprised 53 unique cases from around the world, including two from the BRIA trial in this study and 51 from 16 peer-reviewed papers (Table S1). These cases covered a range of climates, land uses, soil types, gypsum rates and lengths of time since application. Trials that had saline or sodic irrigation water or acidic soils were excluded because the effects of those conditions on calcium- sodium exchange are not accounted for in the model.

A two-layer version of the model was used to replicate the *Gypsy* model, which incorporates a sugarcane yield response function, and a cost-benefit analysis for Australian sugarcane growers (Nelson et al., 2000). In *Gypsy*, *depth* is fixed at 0.00–0.25 and 0.25–0.50 m due to the requirements of the empirical relationships used to relate ESP to sugarcane yield. For this analysis, *depth* was allowed to vary, as impact on sugarcane yield was not investigated. The depth of the surface layer in the available cases ranged from 0.075 to 0.35 m. Thirty-six cases included a second depth interval, the lower boundary of which ranged from 0.15 to 0.70 m depth, encompassing the bulk of the root zone.

The gypsum requirement model was reproduced in R (Supplementary Material) and rearranged to predict the *final ESP* in both layers given the gypsum application rate in each case. In *Gypsy*, the ESP in the first layer decreases either until the applied calcium is depleted, or the minimum final ESP is reached. Excess calcium moves into the second layer where the calculation is then repeated. In this study, the *minimum final ESP* was set at 3%, which is the default value in *Gypsy*. This is assumed to be both the non-limiting ESP and the ESP below which no more calcium-sodium exchange occurs due to high hydraulic conductivity

and low exchange efficiency. The parameter F in Equation 1 describes the efficiency of exchange between calcium and sodium (Oster and Frenkel, 1980). This was set at 1.3 (the default value in *Gypsy*) in both layers.

For the BRIA cases, the model was run with gypsum rates of 24.1 and 29.1 t/ha, using the ESP from the virgin sites as *initial ESP* values. Two scenarios for each rate were run to account for uncertainty in gypsum quality (Table 1). In all other cases, unless specified, the default *gypsum quality* (14% sulfur) and *BD* (1.3 and 1.4 g/cm³ in the surface and second layers respectively) in *Gypsy* were used. Additionally, if the soil was saline (EC > 0.3 dS/m) and salts were not removed prior to analysis, *CEC* and *initial ESP* were corrected using EC and chloride concentration as per *Gypsy*, assuming the charge of chloride is balanced by dissolved sodium.

The predicted *final ESP* was plotted against the final ESP measured in the field trials and a linear regression determined using the *lm* function in the stats package (R Core Team, 2020). A two-sided t-test was undertaken to determine whether the slope of this line was significantly different ($\alpha < 0.05$) to $y = x$. Exploratory plots were produced to determine whether any of the measured soil properties accounted for the difference between the predicted and measured values (Fig. S3). Based on these plots, adjustments were made to model parameters to improve its accuracy, specifically *minimum final ESP* and F . Linear regressions were fit to the results of the adjusted models, and they were compared to those of the original model to determine if there was a significant improvement in the slope of the linear regression. This was done using the *anova* function in the stats package (R Core Team 2020) and the *lstrends* function in the package *emmeans* (Lenth, 2022). Fisher's r-to-z test was also used to determine if there was a significant improvement in correlation between predicted and measured final ESP with each iteration. This was done using the *paired.r* function in the *psych* package (Revelle, 2021).

3. Results

3.1 Field study: Effect of gypsum application, irrigation and sugarcane on profile chemistry

Mean ESP was lower at all depths in the sugarcane plots, and mean exchangeable sodium and potassium were lower at all depths except 1.00–1.25 m. The greatest differences were at 0.25–0.50 m (Fig. 2–4).

Compared to the virgin sites, mean profile ESP was 5.11% and 5.49% lower in the 24.1 t/ha ($t = -3.43$, $p < 0.001$) and 29.1 t/ha gypsum plots ($t = -3.56$, $p < 0.001$, adjusted $R^2 = 0.451$), respectively. In the 24.1 t/ha gypsum plots, mean profile exchangeable sodium and potassium were 1.31 ($t = -3.49$, $p < 0.001$, adjusted $R^2 = 0.485$) and 0.044 cmol_c/kg lower ($t = -3.58$, $p < 0.001$, adjusted $R^2 = 0.349$) than the virgin sites, respectively. In the 29.1 t/ha gypsum plots, they were 1.25 ($t = -3.21$, $p = 0.002$) and 0.043 cmol_c/kg lower ($t = -3.33$, $p = 0.001$), respectively. The mean concentration of exchangeable magnesium down the profile did not significantly differ between the sugarcane plots and the virgin sites ($p > 0.05$, adjusted $R^2 = 0.228$).

Mean exchangeable calcium was 2.33 and 2.57 cmol_c/kg greater in the 24.1 ($t = 4.38$, $p < 0.001$) and 29.1 t/ha gypsum plots ($t = 4.84$, $p < 0.001$, adjusted $R^2 = 0.275$) respectively, compared to the virgin sites. Mean exchangeable calcium was greater in the sugarcane plots in all layers except for the 0.50–0.75 m layer (Fig. 5). The largest differences between the sugarcane plots and the virgin sites were in the 0.00–0.25 m layer, followed by the 1.00–1.25 m layer. Furthermore, the GAMM indicated that the relationship between exchangeable calcium and depth was significantly non-linear in the virgin sites (edf = 3.95, $F = 3.91$, $p < 0.001$) but constant in the sugarcane plots (edf_{24.1/29.1} = 0.00, $F_{24.1/29.1} = 0.00$, $p_{24.1} = 0.790$, $p_{29.1} = 0.600$).

Mean chloride concentration down the whole profile was 71.29 and 76.85 mg/kg in the 24.1 t/ha ($t = -2.52$, $p = 0.012$) and 29.1 t/ha gypsum plots ($t = -2.33$, $p = 0.020$), respectively, and 199.84 mg/kg in the virgin sites ($t = 18.29$, $p < 0.001$). The best GAMM fit used a gaussian distribution (log link). Mean EC was 0.36 and 0.39 dS/m in the 24.1 t/ha ($t = -2.60$, $p < 0.011$) and 29.1 t/ha gypsum

plots ($t = -1.99$, $p = 0.049$), respectively, and 0.453 dS/m in the virgin sites ($t = -7.68$, $p = < 0.001$, adjusted $R^2 = 0.318$). The best fit GAMM used a gamma distribution (log link).

The greatest difference between treatments for both mean chloride and EC was in the $0.75\text{--}1.00 \text{ m}$ layer, with values in the sugarcane plots less than half those of the virgin sites (Fig. 6–7). In contrast, in the $0.00\text{--}0.25 \text{ m}$ layer, mean chloride and EC were greater in the sugarcane plots than in the virgin sites. Below 0.25 m depth, chloride concentration was less spatially variable in the sugarcane plots than the virgin site.

Mean sulfur concentration was 38.10 and 44.04 mg/kg in the 24.1 t/ha gypsum plots ($t = 4.73$, $p < 0.001$) and 29.1 t/ha gypsum plots ($t = 5.10$, $p < 0.001$), respectively, and 5.83 mg/kg in the virgin sites ($t = 6.27$, $p < 0.001$). The best GAMM fit to the data used a gamma distribution (log link). Mean sulfur concentration was greater in the sugarcane plots in all layers including in the $1.00\text{--}1.25 \text{ m}$ layer, with the largest difference between at $0.25\text{--}0.50 \text{ m}$ (Fig. 8). For all treatments, mean sulfur concentrations were lowest in the $0.00\text{--}0.25$ and $1.00\text{--}1.25 \text{ m}$ layers.

For pH, the greatest difference between treatments was in the $0.00\text{--}0.25 \text{ m}$ layer, where mean pH was 1.22 and 1.27 units greater in the 24.1 and 29.1 t/ha gypsum plots than the virgin site, respectively (Fig. 9). Differences were smaller below 0.25 m . Bulk density and clay content were similar between the sugarcane and the virgin profiles. Mean BD was 1.51 , 1.53 and 1.52 g/cm^3 in the virgin, 24.1 t/ha gypsum, and 29.1 t/ha gypsum sites, respectively. Similarly, mean proportion of clay was 37% , 38% , and 40% in the virgin, 24.1 t/ha gypsum, and 29.1 t/ha gypsum sites, respectively.

3.2 Field study: Effect of gypsum application, irrigation and sugarcane on elemental mass balance

On average, over 90% of the calcium applied was accounted for in the top 1.25 m of soil plus the amount taken up by the crop (Table 2). Gypsum application rate did not significantly affect the amount of calcium unaccounted for under any of the four scenarios ($p > 0.05$). In contrast, around 85% of applied sulfur was not detected in the measured soil profile (Table 3). Significantly more sulfur was unaccounted for where higher rates were applied, due to differences in application rate ($t = 3.15$, $p = 0.002$) and initial gypsum quality ($Z = 2.51$, $p = 0.012$).

The amount of exchangeable calcium gained by the soil was significantly greater than the total amount of other exchangeable cations lost in some layers of the profile (Fig. 10). In the 0.00–0.25 m layer, the mean amount of calcium gained by the profiles under sugarcane cultivation was over 10 times greater than the mean amount of exchangeable sodium lost. On average, more exchangeable magnesium than sodium was lost from this layer, although at least $12 \text{ mol}_c/\text{m}^2$ more exchangeable calcium was gained than the two combined. The mean amount of calcium gained and sodium lost were similar in the 0.25–0.50 and 0.75–1.00 m layers in both the 24.1 and 29.1 t/ha gypsum-treated plots. In these layers, CEC changed minimally indicating that the gain in exchangeable calcium was balanced by a loss of other exchangeable cations. In contrast, CEC changed substantially in the other layers. In the 1.00–1.25 m layer, in both sugarcane treatments, mean CEC increased by over $14 \text{ mol}_c/\text{m}^2$ due to a gain in all exchangeable cations. Down the profile, the changes in potassium were an order of magnitude less than all other exchangeable cations. Loss of exchangeable cations was likely balanced by movement of chloride, nitrate, and sulfate ions e.g., unaccounted-for sulfur (Table 3). Dissolved sodium was lost from all layers of the profile under both gypsum-treated sets of plots, except in the 0.00–0.25 m layer where dissolved sodium was not calculated ($\text{EC} < 0.3 \text{ dS/m}$).

3.3 Field study: Effect of gypsum application, irrigation and sugarcane on deep drainage

At 1.25 m, the estimates of average deep drainage were highest in the 24.1 t/ha gypsum plots under both irrigation rate scenarios. The highest estimate of deep drainage was 44.9 mm/year under the high irrigation rate scenario. The lowest deep drainage estimate was 38.7 mm/year in the 29.1 t/ha gypsum plots under the low irrigation rate scenario.

3.4 Gypsum requirement model assessment and modification

In the surface layer (0.00 to 0.075–0.35 m), the slope of the linear regression between predicted and measured final ESP ($\beta = 0.370$, $t = 2.87$, $p = 0.006$) was significantly less than 1 ($t = 4.88$, $df = 57$, $p < 0.001$; Fig. 11a). The proportion of the variation in predicted final ESP explained by the model was low ($R^2 = 0.126$). Variance increased with ESP, violating the assumption of homogeneity of variance for the regression model. In very few cases (3 out of 59) was predicted final ESP within 10% of the measured final ESP. Final ESP was overestimated in 20 cases and underestimated in 36 cases, with 32 of those having a predicted final ESP of 3% (the *minimum final ESP*).

In the deeper layer (lower bound of 0.15–0.70 m), the slope of the linear regression between predicted and measured final ESP ($\beta = 1.47$, $t = 11.2$, $p < 0.001$) was also significantly less than 1 ($t = -3.57$, $df = 38$, $p = 0.001$; Fig. 11b), but the proportion of the variation in predicted final ESP explained by the model was higher than in the surface layer ($R^2 = 0.766$). In 3 of the 40 cases that reported a deeper layer, predicted final ESP was within 10% of the measured final ESP. Predicted final ESP was overestimated in 17 cases and underestimated in 20 cases. In seven cases ESP was predicted not to change in the second layer because the calcium applied in gypsum was fully retained in the surface layer. In only one of these cases was the predicted final ESP (i.e., the initial ESP) within 10% of the measured final ESP.

Exploratory plots were produced to find a *minimum final ESP* value that would reduce the underestimation of predicted final ESP in the surface layer and overestimation in the deeper layer. The measured final ESP in the field was strongly correlated with measured initial ESP, corrected for soluble sodium content (Fig. S4). Therefore, *minimum final ESP* was set to the *final ESP* calculated by the regression equation, forced through the origin to prevent final ESP being greater than initial ESP:

$$\text{Final ESP} = 0.541 \times \text{Initial ESP} \quad (t = 21.13, p < 0.001, R^2 = 0.820) \quad (2)$$

Further exploratory plots revealed that adjusting the F parameter in each layer affected the slope and R^2 values of the linear regression between predicted and measured final ESP. F values of 2 in the surface

layer and 1 in the deeper layer were chosen as optimum values. The accuracy of the model improved in the surface layer after *minimum final ESP* and *F* were adjusted as described (Fig. 11c). The slope of the linear regression between predicted and measured final ESP for the adjusted model was greater than the original model ($\beta = 0.742$, $t = 0.503$, $p < 0.001$) and not significantly different to 1 ($t = 1.76$, $p = 0.085$). Furthermore, the proportion of variation in predicted final ESP explained by the model was significantly greater than the original model ($R^2 = 0.308$, $Z = 1.92$, $p = 0.05$). In 47.5% of cases, the adjusted model more accurately predicted the final ESP after amelioration and in 20% of cases, the prediction was within 10% of the measured final ESP including all four cases from the BRIA. Of the cases where the predictions of final ESP were less accurate after adjustments were made, five were worse by 10% or more, including three from the same field trial (Abrol and Bhumbla, 1979).

The model accuracy also improved in the deeper layer after the adjustments described above (Fig. 11d). The slope of the linear regression was less than in the original model ($\beta = 1.24$, $t = 10.1$, $p < 0.001$) and was not significantly different to 1 ($t = -1.93$, $p = 0.0605$). Furthermore, in 75% of cases, the adjusted model more accurately predicted the final ESP ($n = 24$) or was within 2.5% of the original estimate ($n = 6$). In 12.5% of cases, the prediction was within 10% of the measured final ESP. Of the cases where predictions were less accurate after adjustments were made, three were worse by 10% or more and like in the surface layer, all were from the same field trial (Abrol and Bhumbla, 1979).

4. Discussion:

4.1 Effect of long-term gypsum application, irrigation, and sugarcane cultivation on sodic soil chemistry in the dry tropics

In this study, the soil profile chemistry of a Sodosol and a sodic Vertosol in the dry tropics were substantially improved compared to their virgin state following 26 years of sugarcane cultivation, including irrigation and repeated applications of gypsum. The greatest reductions in ESP and exchangeable sodium occurred between 0.25 and 1.00 m depth (Fig. 2–3), not in the surface layer as hypothesised. The greatest reductions in exchangeable sodium occurred in parts of the profile where initial concentrations were highest, aligning with trends found in our assessment of the gypsum requirement model (Fig. S4; Eq. 2). Over the whole profile (0.00–1.25 m), 36.76 cmol_c/m² of calcium was gained, and 16.47

cmol_c/m² of sodium, 2.49 cmol_c/m² of magnesium and 0.65 cmol_c/m² of potassium were lost. The quantity of exchangeable calcium gained was approximately equal to the quantity of exchangeable sodium, potassium and magnesium lost, only in the 0.25–0.50 and 0.75–1.00 m layers under the higher gypsum rate (Fig. 10). Most calcium from the applied gypsum was retained in the layer to which it was applied (0.00–0.25 m; Fig. 5) but some moved down to at least 1.25 m, similar to previous findings (Kelley and Brown, 1934; Loveday, 1976; Greene and Ford, 1985; Mehanni, 1987; Belić et al., 2012). Overall, long-term gypsum application reduced soil sodicity under sugarcane cultivation in the dry tropics, however, less sodium was displaced than expected based on the amount of gypsum applied.

Lack of sodium displacement may be the result of repeated low application rates. Reductions in ESP and exchangeable sodium were less than other long-term (> 10 years) studies, for example, Zhao et al. (2019), Greene and Ford (1985), and Kelley and Brown (1934). Higher rates of gypsum were applied in a single year in these studies than was applied in four applications over 26 years in our study. The latter reported that ESP decreased from 70 to 5% in the 0.00–0.30 m layer, and from 35 to 19% in the 0.91–1.22 m layer 10 years after a single application of gypsum at 37 t/ha. Higher total applied gypsum increases available calcium while higher gypsum rate per application creates a steeper calcium concentration gradient at the surface-solution interface, increasing the rate of displacement of sodium from exchange sites (Oster and Frenkel, 1980). However, in their meta-analysis of flue gas desulphurisation gypsum use in China, Wang et al. (2021) found that ESP decreased by $37.4\% \pm 9.6\%$ regardless of the amount applied, soil type and depth, climate, and management practices, although the actual application rates were not reported. Across the cases used in our assessment of the gypsum requirement model, the amount of sodium displaced was approximately equivalent to the amount of calcium added where over 10 t/ha of gypsum was applied, and more variable results occurred at lower application rates (Fig. S3). Thus, under low gypsum application rates, other soil processes and/or site specific effects may significantly impact calcium-sodium exchange efficiency.

Changes in soil pH may explain patterns in cation distribution throughout the soil profile in this study. Large gains in exchangeable calcium and CEC in the 0.00–0.25 and 1.00–1.25 m layers corresponded with substantial increases in pH (1.2 and 0.3 units, respectively; Fig. 9). Based on the mean CEC-to-clay ratio (CCR; 0.40–0.46 across the treatments), the surface layer of soil is dominated by variable-charge colloids

such as kaolinite and organic matter, whose CEC increase with pH (Weil and Brady, 2016; Stace et al., 1968). The pH in the 0.00–0.25 m layer of the sugarcane plots (approximately 6–7) also suggests some precipitation of calcium as carbonate. In contrast, as mean pH increased above 8.5 in the 1.00–1.25 m layer, substantial precipitation of calcium and sodium carbonates would have occurred. The CCR in this layer (mean of 0.62 across the treatments) indicates a higher proportion of permanent charge colloids, so less change in CEC per unit change in pH would be expected than in the 0.00–0.25 m layer. As such, the increase in CEC may have been partially an artifact due to extraction of cations from the carbonates. Interestingly, the calcium that moved below the root zone and accumulated at 1.00–1.25 m appears to have moved through the 0.50–0.75 m layer without displacing sodium and magnesium (Fig. 5). Exchangeable calcium did not exceed more than 65% of the CEC in any of the layers, suggesting that there is a limit to the amount of calcium that can be held on the cation exchange complex. This may be due to soil pH being greater than 8.0 below 0.50 m depth (Fig. 9) which would change the equilibrium between cations on the exchange complex and the soil solution due to the precipitation of carbonates (Oster and Frenkel, 1980). In their review of gypsum use in agriculture, Zoca and Penn (2017) found that pH could increase or decrease following gypsum application but that changes were usually small (0.2–0.3 units). In their meta-analysis, Wang et al. (2021) found consistent decreases in pH, with larger magnitude changes in more sodic soils. Additionally, all long-term field trials that measured pH found that it significantly decreased (Kelley and Brown 1934; Belić et al., 2012; Zhao et al., 2019), often by more than one unit. As such, reasons behind the large increases in pH seen in this study must be explored further.

Reduction of sulfur may be responsible for large increases in pH following gypsum application and irrigation. Sulfur was leached to 1.25 m, more than twice the depth recorded in other long-term field trials (Zhao et al., 2019), and a proportion of the unaccounted-for sulfur (Table 3) may have been leached even deeper. However, low deep drainage estimates suggest an additional loss mechanism. It is possible that sulfur was lost from the soil profile as H_2S due to temporary anaerobic soil conditions following irrigation events. Oxygen (O_2), nitrate (NO_3^-), manganese (Mn^{4+}), iron (Fe^{3+}), and sulfate (SO_4^{2-}) are sequentially reduced by microbial activity during anaerobic conditions, alkalising the soil (Inglett et al., 2005). The highest rates of sulfate reduction likely occurred in the 0.00–0.25 m layer where the soil was saturated for the longest time (due to irrigation and low permeability), organic matter content was highest, and sulfate concentration was initially highest (being the gypsum application zone). This is also the layer where the difference in pH between the sugarcane plots and the virgin sites was greatest (1.2 units higher in the

sugarcane plots; Fig. 9). Critically, this has not been noted in other studies, in fact, Zhang et al. (2022) found decreasing pH with increasing gypsum and irrigation rates due to leaching of bicarbonates. Alkalinity from irrigation water may also have contributed to changes in soil pH in our study. Although mean irrigation water alkalinity was within an acceptable range it varied, with carbonate concentrations reaching 155 mg/L at times (Queensland Government, 2021a). However, mean bicarbonate concentration in the irrigation water applied at the trial of Kelley and Brown (1934) was similarly high yet pH decreased. These larger than expected changes in this study and others, and the importance of such pH changes for crop nutrition, indicate that further investigation into the long-term effect of gypsum on pH, particularly via desulfurisation under irrigated crop production on clay soils, is necessary.

Low deep drainage rates may also explain lower reductions in sodium compared to other long-term field trials. Estimated rates of deep drainage in our study were low for salt affected areas of Queensland, which range from 2 to 150 mm/year depending on rainfall, evapotranspiration, and hydraulic conductivity (DERM, 2011). Although evapotranspiration rates are around 1000 mm/year (BOM, 2016), deep drainage is still expected to be high given the high rates of irrigation and rainfall received at the study site. Indeed, another study in the BRIA estimated deep drainage rates of up to 98 mm/year at 1.0 m depth in similarly managed soils (Dowling et al., 1991). Dowling et al. (1991) estimated that one year after 20 t/ha of gypsum was applied, deep drainage rates increased to 140–380 mm/year; at least three times greater than in this study. Critically, Dowling et al. (1991) expected deep drainage to decrease as calcium was leached from the profile, however, this does not explain the low drainage rates in our study, as a high proportion of calcium from gypsum was accounted for in the soil profile (Table 2). This result is more likely because EC approximately halved to almost non-saline levels below 0.50 m due to leaching of dissolved sodium and chloride (Fig. 7), while ESP decreased very little, staying well within the sodic range (Fig. 2; Isbell, 2021). Saline-sodic soils tend to be more stable than non-saline sodic soils as high ionic strength compresses the diffuse double layer, decreasing the tendency of clay to disperse (Weil and Brady, 2016). Additionally, the sandy loam soils in the long-term trials of Zhao et al. (2019) and Kelley and Brown (1934) would have had higher infiltration rates and experienced more effective leaching of sodium than the clay soils in this study based on texture alone. Mao and Li (2023) found a significant linear relationship between gypsum application rate (15–60 t/ha) and ESP reduction after one year where clay content was low (9.80%) but no effect of application rate where clay content was high (39.8%). Hence, soil texture and climate must both be considered when determining calcium-sodium exchange efficiency.

4.2 Assessment of gypsum requirement model

The ability of the gypsum requirement model to predict ESP following application of gypsum to a range of neutral-alkaline sodic soils was initially poor, using an F value of 1.3 and *minimum ESP* of 3. In many cases, the model predicted a final ESP of 3%, but that rarely occurred in the field (Fig. 11a). The accuracy of prediction was least in cases where initial ESP was greater than 30%, pH was greater than 9.5, clay percentage was less than 30%, and time since gypsum application was <5 years (Fig. S3). There was also a significant relationship between model accuracy and CCR (Fig. S3) indicating that exchange depends on clay mineralogy. Furthermore, the model often incorrectly predicted that calcium from applied gypsum was completely consumed in amelioration of the surface layer and that no improvement in ESP would occur in the next layer (Fig. 11b). This may not occur in reality if there are preferred pathways through which gypsum and other solutes move down the profile without coming in contact with exchange surfaces. Movement of water through preferred pathways has been demonstrated in many soils and is particularly pronounced in cracking clays (Shainberg et al., 1989). Inaccuracies may also be due to the chloride-based correction for dissolved sodium, which probably results in an underestimate of ESP in some cases. In specific examples excluded from the analysis (Batarseh, 2017; Zhao et al., 2018), the corrected ESP was less than zero, likely due to these locations having significant quantities of salts other than sodium chloride. As such, in soils with high EC that have not been pre-leached before analysis, it may be better to correct ESP and CEC values for dissolved sodium, calcium, and magnesium using measured relationships as was done for the results of the BRIA trial. Furthermore, the model does not account for the combined effects of salinity and sodicity on hydraulic conductivity and solute movement. Error in the predictions may also result from treatment of soils as discrete homogeneous layers. The model assumed displaced exchangeable sodium moves out of the 0.00–0.25 m layer but did not account for it moving into the 0.25–0.50 m layer. Although no specific examples of sodium accumulation shallower than 0.60 m were found in our study or others, it is possible under certain conditions this may occur, causing gypsum to be less effective than predicted. Finally, it should be noted that the measured final ESP may also have errors involved, due to spatial variations and analytical errors.

Simple adjustments to the gypsum requirement model (i.e., changes to *minimum final ESP* and F) significantly improved the accuracy of predictions across the broad range of situations examined.

Furthermore, the new approach for determining the final ESP better reflects the equilibrium nature of the cation exchange process than the original model. In the adjusted model, predicted ESP was within $\pm 10\%$ of measured ESP in 11 of 59 cases from 8 of 17 sites (mostly sub-tropical and tropical), including all cases from the BRIA trial. This could be considered reasonable as a decision support tool, demonstrating the capability and utility of a simple tipping bucket type model. Other methods for calculating gypsum requirement are either: empirical and thus specific to one soil type and site, untested in the field, require additional chemical analyses (e.g., sulfur, exchangeable magnesium, dissolved cations, clay content), or significantly overestimate the effectiveness of gypsum at ameliorating sodicity (Greene and Ford, 1985; Zoca and Penn, 2017). Many of the cases used in this analysis applied 100% of the gypsum theoretically required to fully ameliorate the soil, but few achieved this. The main exception was the study of Abrol and Bhumbra (1979), which was the only trial to have installed drainage. Drainage may have facilitated flushing of sodium from the soil profile. Oster and Frenkel (1980) found that the F parameter depended on the amount of calcium present (impacted by the rate of gypsum applied and the initial soil concentration), and the equilibrium of carbonate precipitation and dissolution. The latter is most likely the reason for variations we found in the accuracy of predictions in cases with high pH. Modelling precipitation/exchange equilibria, as done by *UNSATCHEM* (Simunek et al., 1996) and *HYDRUS* (Simunek et al., 2018), is complex as it requires knowledge of partial pressures of carbon dioxide, which depends on organic matter, respiration, and gas diffusion, as well as pH, physical size and surface area of precipitated calcium carbonate nodules, and temperature. The simple gypsum requirement model could be improved by determining F values appropriate to the soils in question. Indeed, it has been previously recommended that F should be higher for the subsoil than surface soil (DERM, 2011). Improvements may also be made by adjusting CEC based on the empirical relationship found between model accuracy and approximate clay percentage (Fig. S3).

5. Conclusions

The long-term effect of gypsum application, irrigation, and sugarcane cultivation on the chemistry of sodic clayey soils in the dry tropics involved several processes that varied with depth. Substantial retention of calcium in the topsoil (0.00-0.25 m depth) was associated with an increase in pH, possibly related to sulfate reduction, and consequent increase in CEC , with a relatively small reduction in exchangeable sodium. In the subsoil (0.25-1.00 m depth), the added calcium displaced a substantial and equivalent amount of exchangeable sodium, displacing it to >1 m depth. Although there was a large reduction in

exchangeable sodium and dissolved salts over the whole profile (to 1.25 m depth), the lack of change in ESP in the deepest layer, coupled with the reduction in EC at that depth, resulted in low deep drainage rates through the whole profile. These long-term changes mean that the root zone conditions have been improved, but sodicity deep in the profile still influences hydrology. Although the processes involved in amelioration of sodic soils are complex and vary greatly depending on soil, climate and management factors, assessment of a wide range of field trial data gave confidence that the simple gypsum requirement model, with empirical adjustments suggested here, can be a useful tool for predicting long-term effects of gypsum application across a range of conditions.

Acknowledgements

We are grateful to Chloe Lai for providing advice on the Gypsy model, Mark Silburn for providing the SODICS model and assistance with running it, Nutrient Advantage laboratory for undertaking chemical analysis, Leroy Chung for his immense efforts assisting with field work, and Gary Ham for sharing his knowledge and experience.

Funding

This work was supported by funding from James Cook University and Wilmar Sugar.

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Figures and tables

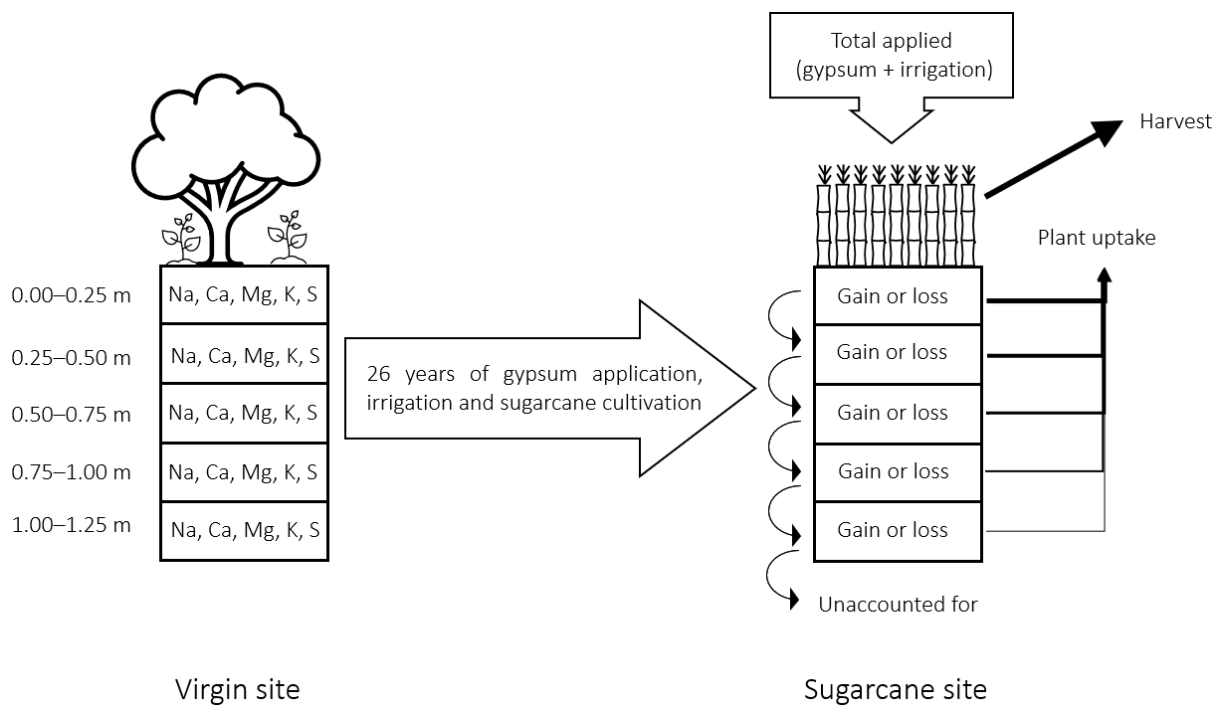


Fig. 1. Diagram of mass balance calculation for soil sodium, calcium, potassium, magnesium, and sulfur over 26 years of gypsum application, irrigation, and sugarcane cultivation.

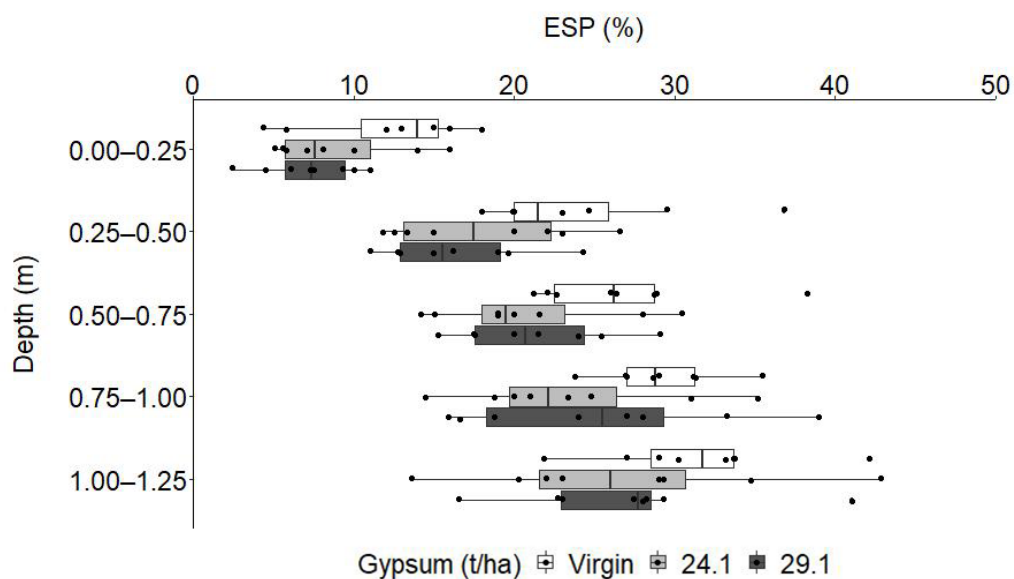


Fig. 2. Exchangeable sodium percentage (ESP) depth profile for each treatment. Points represent measured values, boxes represent the interquartile range, the vertical line within boxes represents the median, and the whiskers extend to the last point within 1.5 x interquartile range.

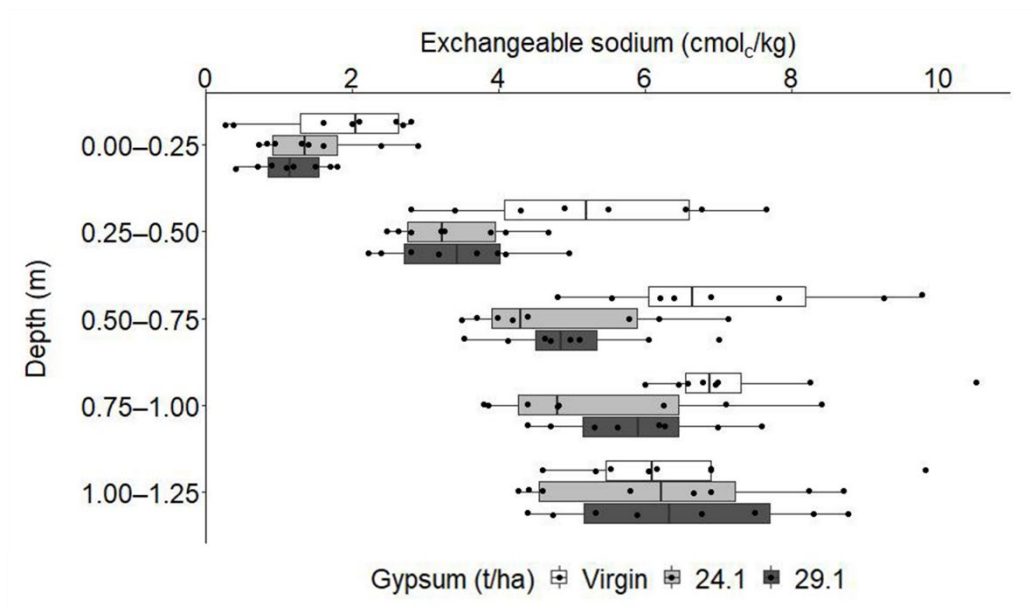


Fig. 3. Exchangeable sodium concentration depth profile for each treatment. Points represent measured values.

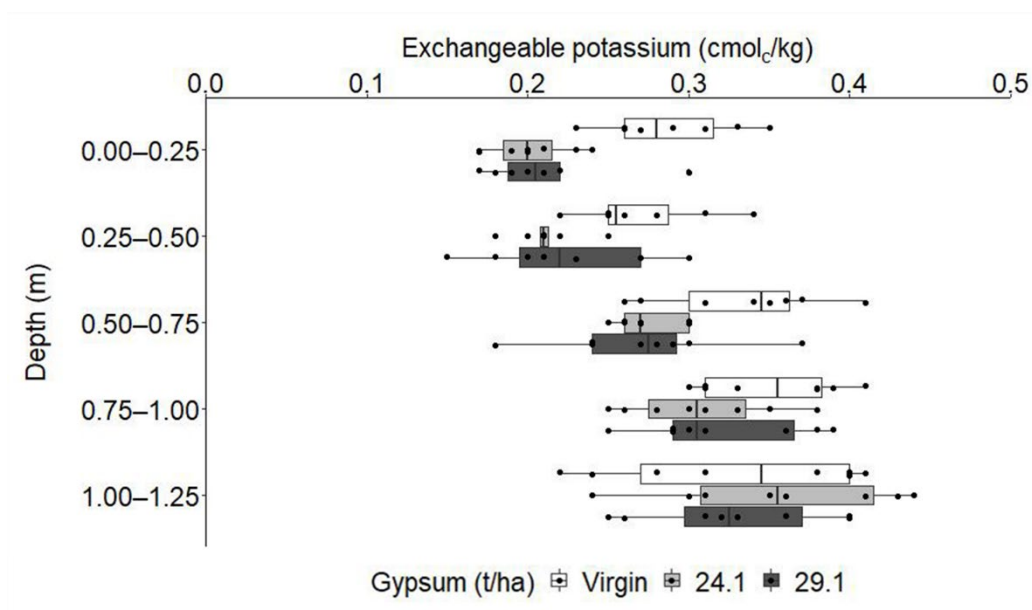


Fig. 4. Exchangeable potassium concentration depth profile for each treatment. Points represent measured values.

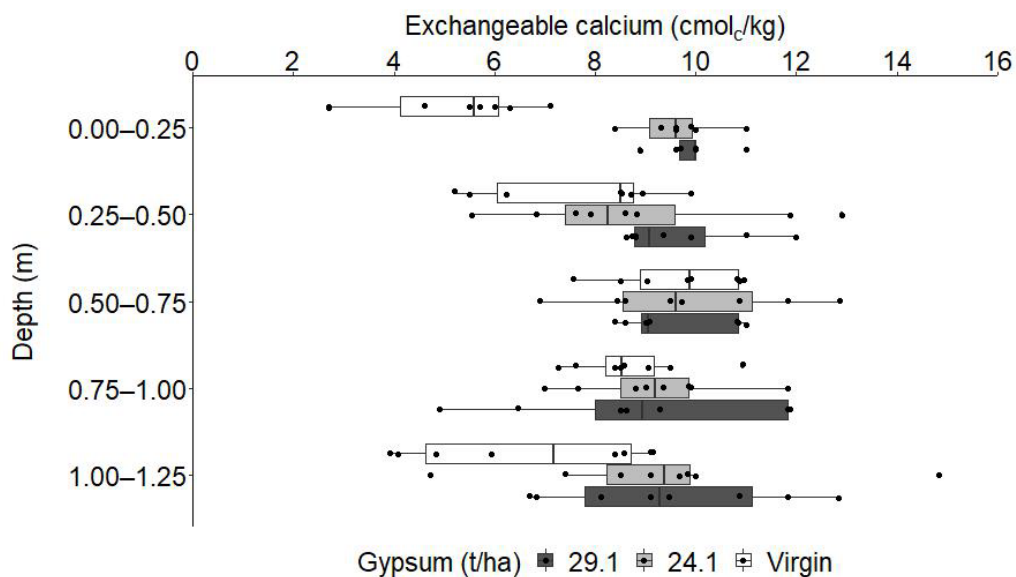


Fig. 5. Exchangeable calcium concentration depth profile for each treatment. Points represent measured values.

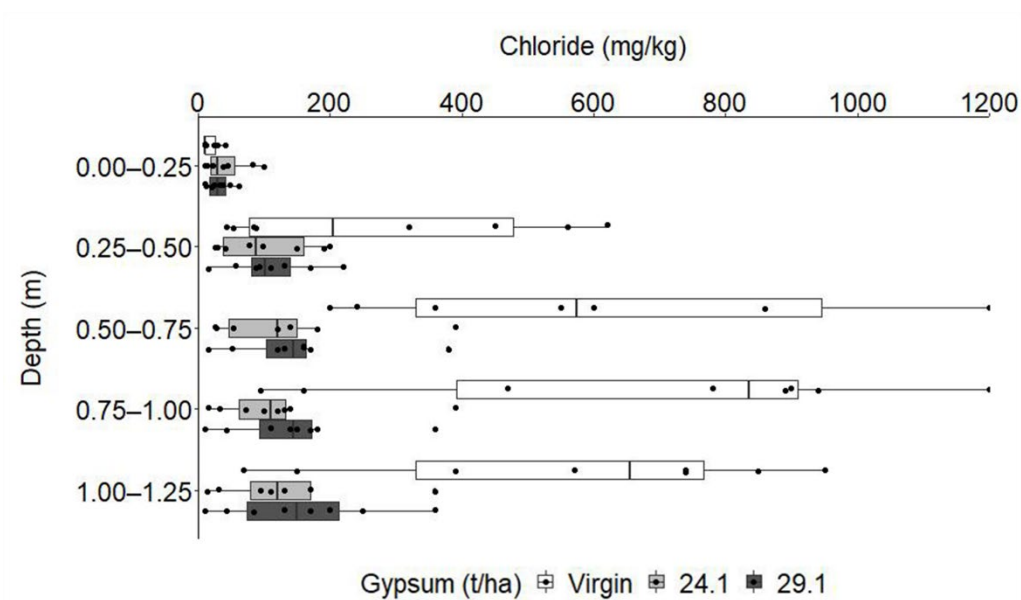


Fig. 6. Chloride concentration depth profile for each treatment. Points represent measured values.

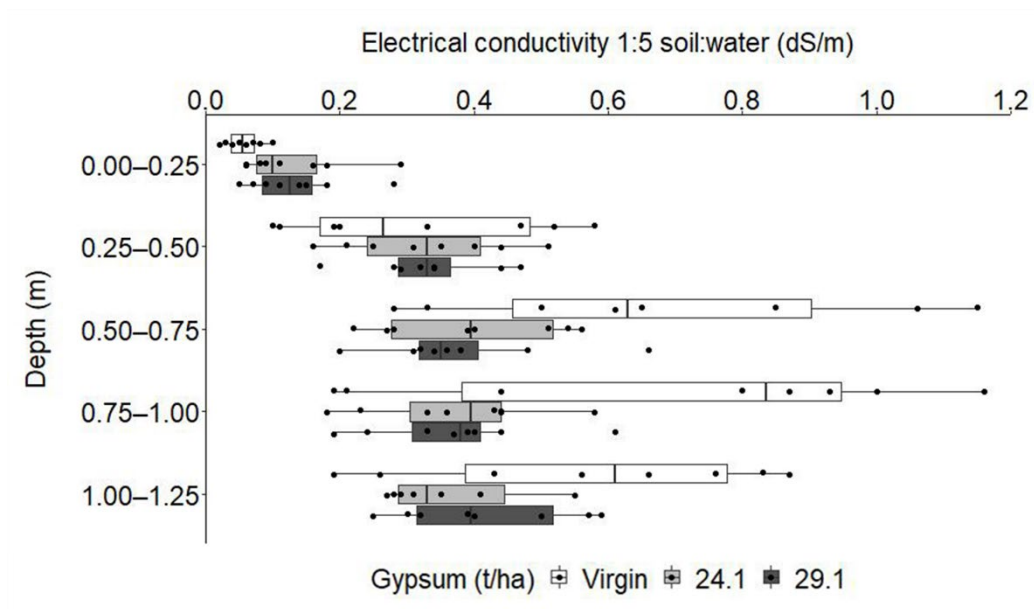


Fig. 7. Electrical conductivity depth profile for each treatment. Points represent measured values.

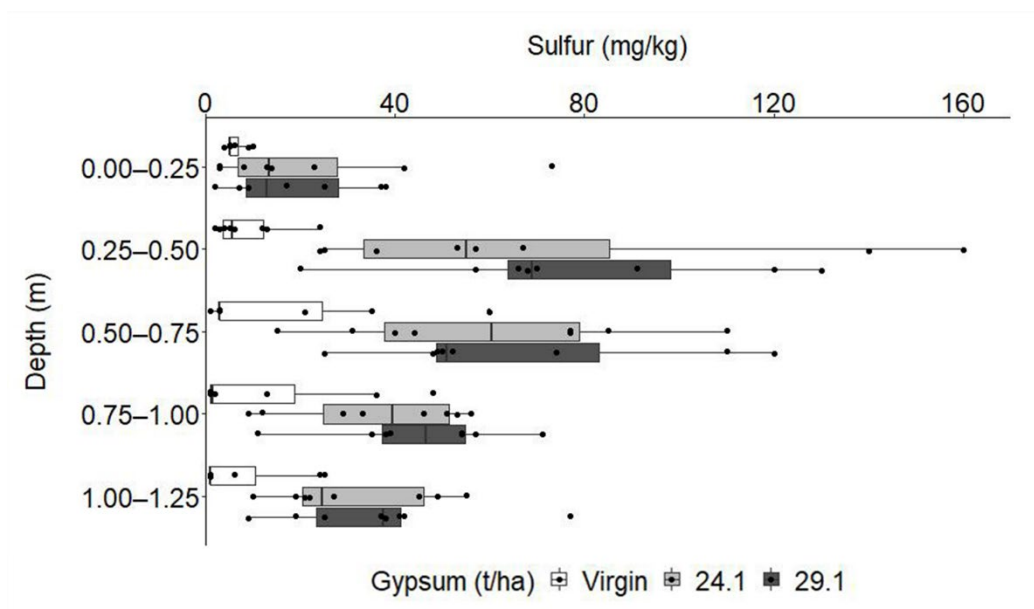


Fig. 8. Sulfur concentration depth profile for each treatment. Points represent measured values.

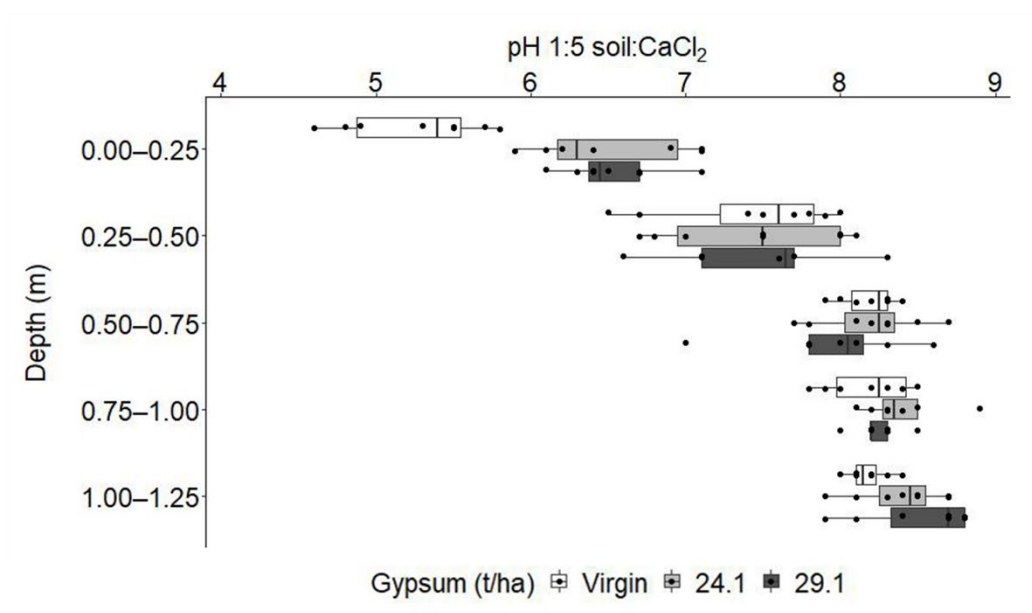


Fig. 9. pH depth profile for each treatment. Points represent measured values.

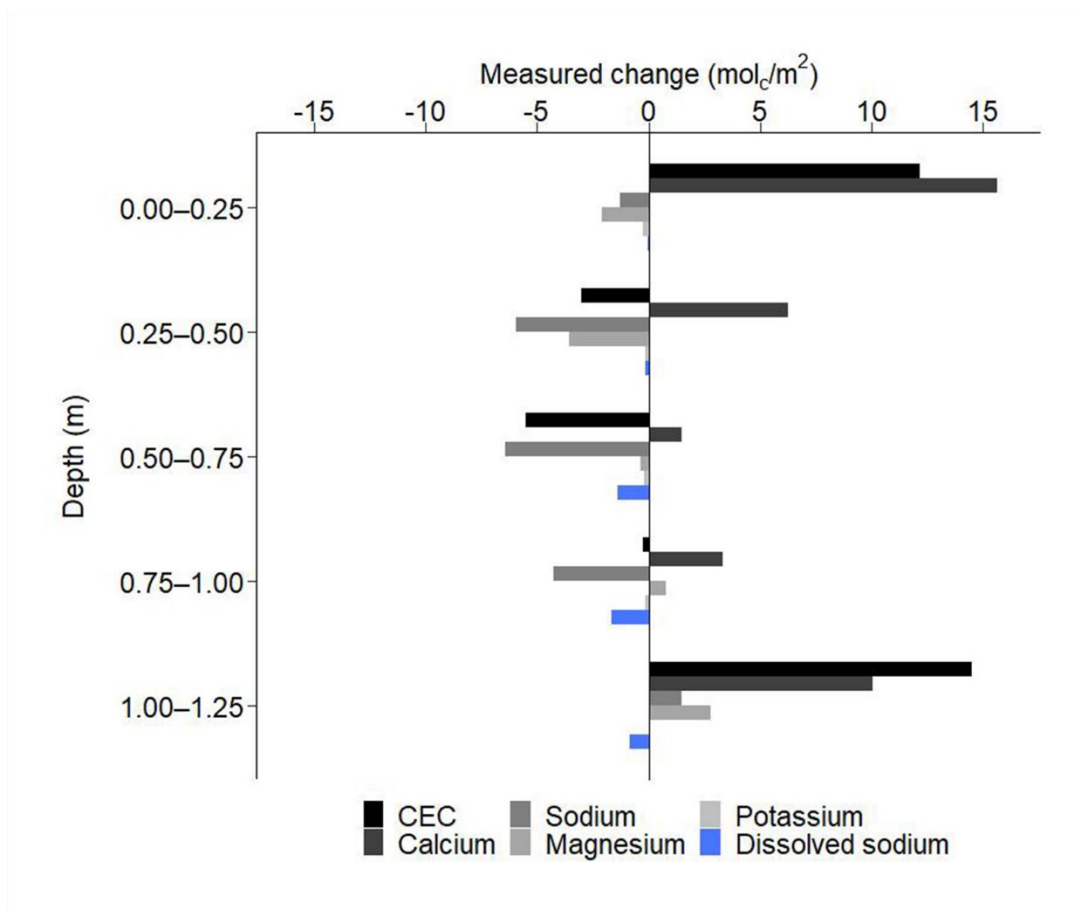


Fig. 10. Calculated changes in the amount of exchangeable cations and CEC in each layer of the profile. That is the difference between the mean amount of each cation or CEC in the sugarcane plots and the virgin [colour image].

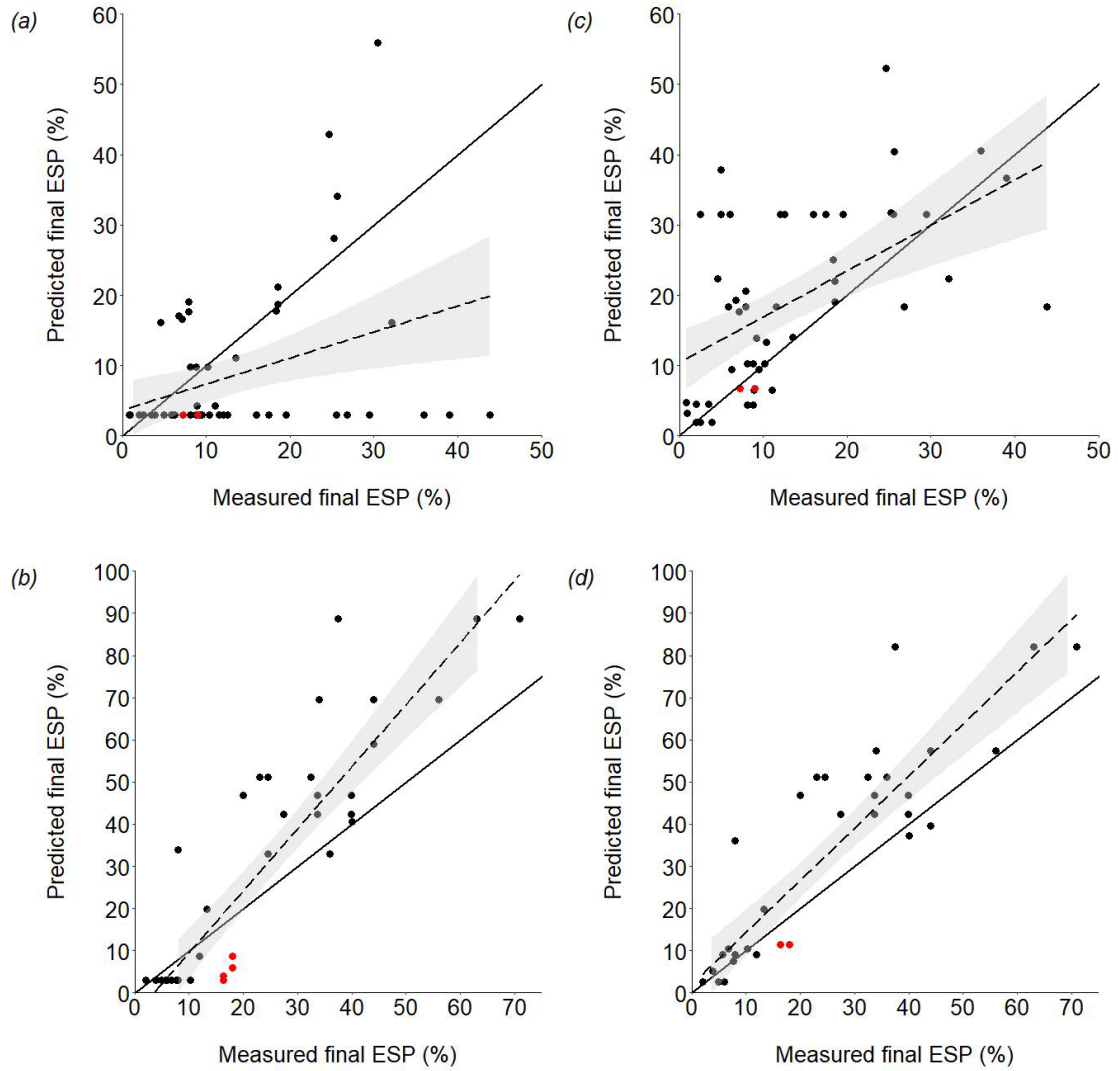


Fig. 11. Final ESP predicted by (a, b) the original gypsum requirement model with $F = 1.3$ in both layers and *minimum final ESP* = 3%, and (c, d) the adjusted version of gypsum requirement model with $F = 2$ in the top layer and 1 in the next layer and *minimum final ESP* calculated according to Equation 2, plotted against measured final ESP. Each black point is a unique case from the literature. The red points are cases from the BRIA trial. Results are shown for (a, c) the surface and (b, d) the deeper layer reported. The solid line is $y = x$ and the dashed line is the linear regression fit to the data and its 95% confidence interval. The equations of the linear regressions are (a) $y = 0.370x + 3.67$ ($R^2 = 0.126$), (b) $y = 1.47x - 5.21$ ($R^2 = 0.766$), (c) $y = 0.742x + 9.83$ ($R^2 = 0.308$), and (d) $y = 1.23x - 1.99$ ($R^2 = 0.730$) [colour image].

Table 1. Gypsum origin, composition, and application rates to sugarcane at the experimental site.

Year	Gypsum origin	Calcium (%)	Sulfur (%)	Low gypsum rate (t/ha)	High gypsum rate (t/ha)
1995–2003	Unknown	Unknown	Unknown	5	5
2008	Winton	22.7	16.9	6.4	6.4
2012	Hughenden	15.2	9.10	7.7	7.7
2016 (trial)	Winton	22.7	16.9	5	10
Total				24.1	29.1

Table 2. Calcium mass balance for the top 1.25 m of soil at the two gypsum application rates, 24.1 and 29.1 t/ha, as an amount (mol/m²) and as a proportion of the total amount applied (%).

Mass balance variable	24.1 t/ha		29.1 t/ha	
	mol/m ²	%	mol/m ²	%
Total applied	37.4	100	43.1	100
Soil gain	33.2	88.7	37.0	85.8
Plant uptake and removal	1.64	4.39	1.64	3.81
Unaccounted for	2.60	6.95	4.49	10.4

Table 3. Sulfur mass balance for the top 1.25 m of soil at the two gypsum application rates, 24.1 and 29.1 t/ha, as an amount (kg/m²) and as a proportion of the total amount applied (%).

Mass balance variable	24.1 t/ha				29.1 t/ha			
	Hughenden		Winton		Hughenden		Winton	
	kg/m ²	%	kg/m ²	%	kg/m ²	%	kg/m ²	%
Total applied	0.376	100	0.429	100	0.460	100	0.514	100
Soil gain	0.066	17.6	0.066	15.4	0.074	16.1	0.074	14.4
Plant uptake and removal	0.059	15.7	0.059	13.8	0.059	12.8	0.059	11.5
Unaccounted for	0.251	66.8	0.305	71.1	0.327	71.1	0.381	74.1