Accelerating Bauxite Residue Remediation with Microbial Biotechnology

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Abstract

Biological neutralisation of pH, driven by the microbial fermentation of added organic carbon substrates such as glucose, has recently emerged as a promising technique for remediation of bauxite residue, dropping pH from >11 to <8 in five days. Here, we report on a glasshouse experiment combining this novel microbially-driven pH neutralisation technology with other existing (abiotic) remediation approaches, including addition of gypsum, sewage sludge, and irrigation. Scaling up the bioremediation treatment by three orders of magnitude from previous laboratory trials to these glasshouse trials was successful. Adding bioremediated residue (5 cm thick) at the residue surface significantly enhanced pH neutralisation to depth, decreasing pH from 13 to ~10 as far as 25 cm below the residue surface. Increasing irrigation and tillage frequency accelerated salt removal. Combining our microbial bioneutralisation treatment with fortnightly tillage and daily irrigation provided the best opportunity to rapidly decrease pH and salinity, and is currently being trialled at field scale.

Keywords

Biotechnology • Bioneutralisation • Tillage • Salinity • pH

Introduction

Bauxite residue is an alkaline, saline by-product of alumina refining, with current annual global production rates averaging around 120 MT, adding to the estimated 3 GT already held in residue storage areas [5]. The closure of these residue storage areas has historically relied upon installation of a cap or cover system to provide a medium for plant growth (i.e. soil), and isolate the underlying bauxite residue from further rainfall (creating leachate) and interactions with the vegetation cover (e.g. [7]). Cap and cover systems usually contain a capillary break or water-impermeable layer (e.g. high density polyethylene) to prevent pore water from the alkaline, saline residue moving upwards into the soil through capillary rise and in turn to prevent excess rainfall leaching into the residue [6]. This is then overlain by imported clean fill to provide sufficient soil depth for plant roots and water balance management, and finally, an imported high quality topsoil to supply plant nutrients and support vegetation (Fig. 1). However, cap and cover systems do not provide a true 'walk-away' solution to closure of residue storage areas, as the geochemical and physical properties of the residue remain unchanged, and the cap system requires ongoing monitoring and maintenance [6].

In situ remediation, that is, relying on natural processes or addition of amendments to shift the properties of bauxite residue towards those of a natural soil, provides an opportunity to transform the residue itself, and hence avoid some of the typical challenges posed by a cap or cover system.

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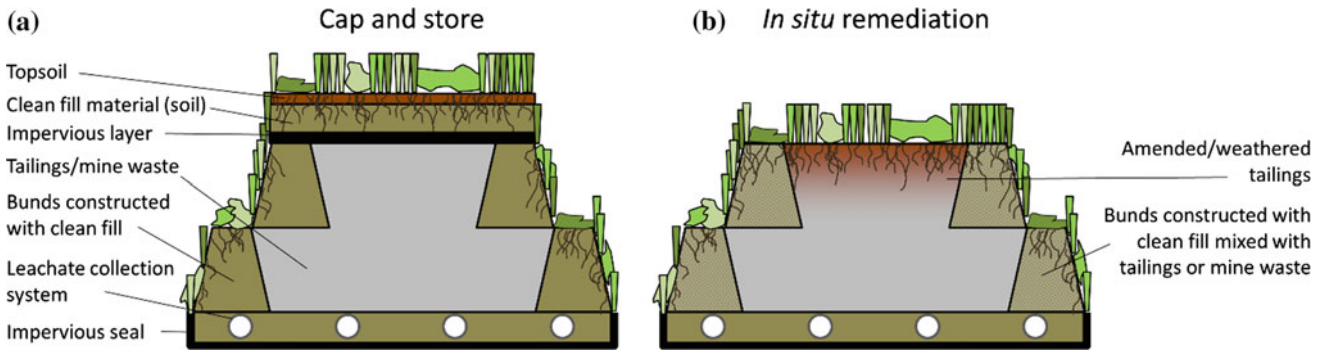

Fig. 1 Schematic diagrams of **a** cap and store, and **b** in situ remediation approaches to tailings management. Diagrams not to scale. Figure from Santini and Banning [6]

Table 1 Initial properties of bauxite residue, and target values for remediation

Parameter	Unamended bauxite residue[a]	Remediation target
pH	11.3	5.5–9
EC (mS cm^{-1}; 1:5 extract)	7.4	≤ 4
Exchangeable sodium percentage (%)	69	≤ 9.5
Organic C (wt%)	0.3	≥ 0.5
Bulk density (g cm^{-3})	2.5	≤ 1.6
Microbial community composition	Low diversity, dominated by (*Gamma-*) *Proteobacteria*, *Firmicutes*, *Actinobacteria*, *Bacteroidetes*, *Ascomycota*, *Basidiomycota*	High diversity, including typical soil phyla *Acidobacteria*, *Gemmatimonadetes*, and *Planctomycetes*

Amended from Graefe and Klauber [4], Santini and Banning [6], Santini et al. [11]
[a]Values for all except microbial community composition are average values reported in the literature

Application of amendments at the surface of existing bauxite residue storage areas avoids importation of soil and cap materials; expensive excavation, treatment, and replacement of residue; and harnesses natural environmental drivers (e.g. rainfall, evaporation) to minimise amendment costs and accelerate timeframes [6]. In situ remediation goals for bauxite residue include decreasing pH, salinity, and sodicity, decreasing bulk density by increasing aggregation, and establishing a compositionally and functionally diverse microbial community [4, 9] (Table 1). Application of gypsum, combined with tillage and irrigation, addresses several remediation goals simultaneously, by providing a source of Ca^{2+} to displace Na^{+}, as well as facilitating export of alkaline, saline-sodic pore water [4, 13, 14], and development of stable soil structure [13]. Organic amendments such as hay, compost, and sewage sludge have also been successful in improving soil properties and encouraging the development of microbial and plant biomass [1, 3, 13]. Until recently, microbial communities had been regarded as passive responders to remediation, rather than having the capacity to play active roles in meeting remediation targets [9, 11]. Investigation of how microbial communities in globally distributed bauxite residues, amended with various materials and aged for varying lengths of time, highlighted the potential for these communities to actively contribute to remediation [9, 11]. Microbial fermentation of a simple glucose substrate has since been demonstrated in laboratory-based batch trials to decrease residue pH from >11 to <8 in five days [10], with simultaneous increases in aggregation through the exudation of extracellular polymeric substances (EPS). Glucose is a readily available and relatively low-cost substrate for fermentation, and this microbially-driven pH neutralisation ('bioneutralisation' or 'bioremediation') therefore provides an additional tool to combine with existing amendments for in situ remediation of bauxite residue. The next logical step is to test this microbially-driven approach for pH neutralisation at larger (glasshouse) scale, in combination with abiotic amendments [10].

Bringing the bauxite residue, microbial inoculant, and glucose together can be performed in one of two ways: treating residue in a bioreactor, or applying a spray-on

approach similar to hydromulching. Bioreactors, relying on either a static batch treatment or a continuous flow treatment system, offer a high level of control over discharged residue quality; however, the remote location of some residue sites requires the development of passive, low-infrastructure alternatives. A spray-on approach (whereby a solution containing the microbial inoculant suspended in nutrient media is distributed across the barren residue surface through existing dust suppression sprinklers or water trucks) is a promising alternative [9]. Comparing the efficacy of both approaches necessitates glasshouse trials to evaluate depth effects, that are not possible at laboratory scale, and the effects of variable field environmental conditions (e.g. evaporation, sunlight, etc.) [9, 11]. The objectives of this glasshouse study were to:

(a) Demonstrate that microbially-driven pH neutralisation could be successfully scaled up from laboratory to glasshouse trials (involving a three orders of magnitude increase in bioreactor size); and
(b) Identify the optimal combination of existing abiotic (irrigation, tillage, and organic matter) amendments and microbial (bioreactor, and spray-on) amendments to rapidly meet multiple remediation goals.

Methods

Glasshouse Leaching Column Design

Glasshouse leaching columns were constructed from 55 cm lengths of 100 mm diameter PVC pipe, with a cap attached and sealed at the base with PVC cement (Fig. 2). Three (3) mm PVC tubing connected a central drainage hole at the base of the columns to a sealed leachate collection container. Freely draining conditions were established by placing a 3-cm deep layer of acid-washed, sterilised sand in the base of each column, over which a circle of nylon mesh was placed to avoid washing out of fines. The interior of the columns were sterilised with a sodium hypochlorite solution before filling with bauxite residue from Alcoa of Australia Limited's Kwinana refinery.

Residue and Amendment Preparation, and Trial Establishment

Bauxite residue was amended with 5 wt% gypsum, evenly mixed into the bauxite residue on arrival at the glasshouse. Leaching columns were packed with 50 cm of bauxite

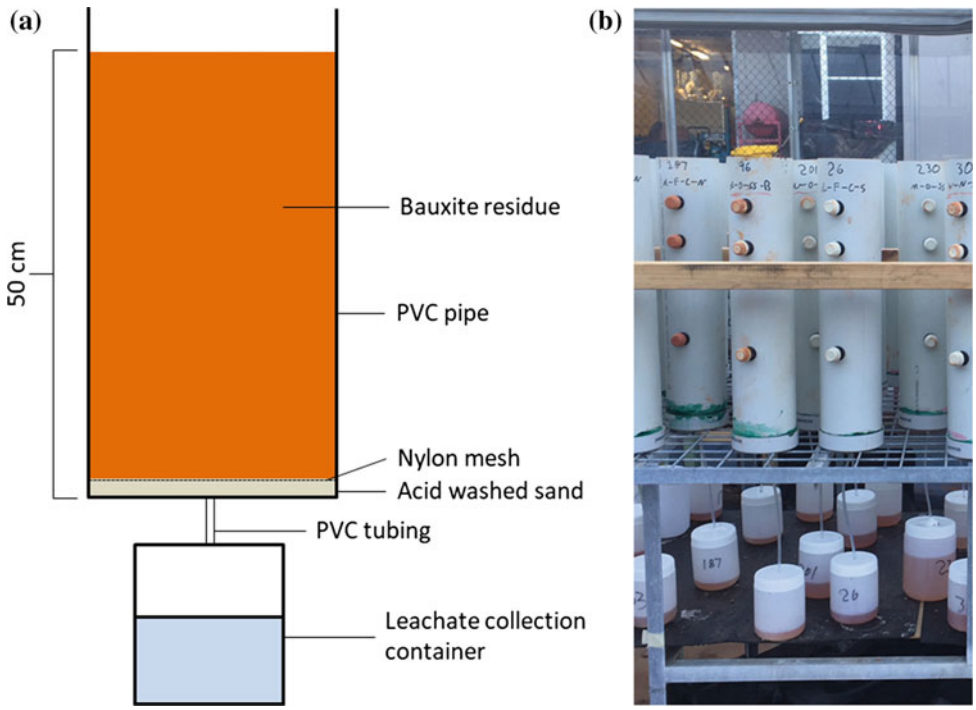

Fig. 2 **a** Design of glasshouse leaching columns (diagram not to scale); and **b** side photograph of some of the leaching columns during trials

residue, weighed and tamped at 5 cm depth intervals to maintain consistent bulk density across all columns. Experimental factors being compared were:

(a) microbial inoculant—levels: bioreactor cap, spray-on inoculum, none
(b) irrigation, totalling 1490 mm/year, applied at differing frequencies—levels: daily (32 mL/day), weekly (224 mL/week), monthly (897 mL/month)
c) tillage—fortnightly, once at commencement, none
(d) organic matter—sewage sludge (pH 6.49, EC 8.06 mS cm^{-1}), compost (pH 5.73, EC 4.33 mS cm^{-1}), none.

To create the bioreactor-neutralised residue, a subsample of the gypsum-amended residue (60 kg) was then combined with 15 wt% glucose, 1.25 wt% peptone, 1 wt% yeast extract, and 20% garden soil, and split across 4 × 30 L plastic tubs. These were incubated in the glasshouse until residue pH in all tubs was ≤ 7. The bioreactor-neutralised residue was then homogenised in one large container, and applied to columns by removing the upper 5 cm of residue and replacing it with bioreactor-neutralised residue (forming a bioreactor 'cap'). The spray-on microbial inoculum was prepared by combining glucose, yeast extract, peptone, and garden soil in the same ratios as above for the bioreactor-neutralised residue, but replacing residue with deionised water, and stirring the solution in a 4 L conical flask until suspension pH was ≤ 8. The suspension was then applied with a plastic transfer pipette to the surface of each column receiving this treatment.

Organic matter (40 T/ha) was applied as a thin layer to the surface of residue, after sieving to <2 mm. Tillage was performed manually with a screwdriver, following a fixed agitation pattern. Irrigation (equivalent to 1490 mm/year) was applied with either a spray bottle (daily) or beaker (fortnightly and monthly).

After packing and application of microbial inocula and organic matter, columns were irrigated to field capacity. Leaching tubes were sealed and all columns were capped for a five day equilibration period, after which tillage and irrigation were applied. Tillage and irrigation treatments continued to be applied throughout the five month experiment.

Sample Collection and Analysis, and Data Analysis

Leachate samples were collected weekly for pH and electrical conductivity (EC). At the end of the experiment, columns were destructively sampled, with solids collected at 0–5, 5–10, and 25–30 cm below the residue surface in each column. Solids from all treatments were dried at 40 °C and analysed for pH and EC [8]. A four-way ANOVA was used to identify significant differences between treatments, followed by a post hoc Tukey test to separate treatment means. A significance level of $\alpha = 0.05$ was used unless otherwise stated.

Results and Discussion

Microbial pH Neutralisation in Glasshouse Bioreactors

One of the major aims of this study was to demonstrate successful scale up from laboratory (40 mL) to glasshouse (30 L) bioreactors, involving a three orders of magnitude increase in bioreactor size. Compared to previous laboratory trials using residue with similar initial pH and similar carbon and nutrient dose rates [10], the glasshouse bioreactors took a longer time to reach their inferred maximum acid generation rate (laboratory: day 4; glasshouse: day 9; Fig. 3) and minimum pH $\leq$ 7 (laboratory: day 10; glasshouse: day 14; Fig. 3). However, the minimum pH in the laboratory and glasshouse experiments were not different (laboratory: pH 7.05 ± 0.05; glasshouse: pH 7.17 ± 0.12). Overall, this demonstrated successful scale up from the laboratory to the glasshouse.

pH and Salinity in Solids and Leachates After 5 Months

pH

Adding a 5 cm thick layer of microbially-neutralised bauxite residue, treated in the glasshouse bioreactors, to the surface of the bauxite residue significantly improved pH neutralisation in the bulk residue beneath, to a depth of 25 cm below the surface (Fig. 4). At 0–5 cm and 10–15 cm depth, residue pH was significantly lower in treatments receiving the

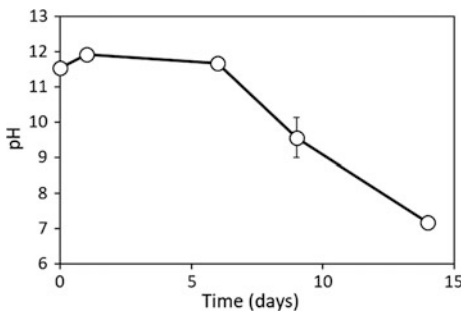

Fig. 3 Residue pH in glasshouse bioreactors (30 L tubs, four replicates) during pH neutralisation. Values displayed are the mean of four replicates; error bars (where visible) indicate ±1 standard error of the mean

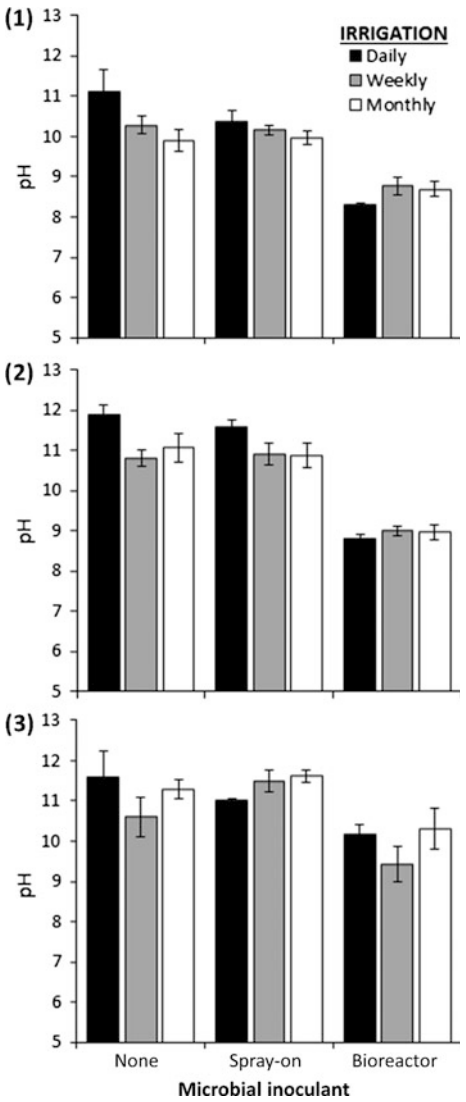

Fig. 4 pH in bauxite residue solids in leaching columns after 5 months, at (1) 0–5 cm depth; (2) 10–15 cm depth; (3) 20–25 cm depth. Results for two factors only, microbial inoculant and irrigation, are shown in the interests of brevity. Values displayed are the mean of three replicates; error bars indicate ±1 standard error of the mean

bioreactor cap than the spray-on inoculant or no inoculant. Residue pH in treatments receiving the bioreactor cap was also lower than those receiving the spray-on inoculant or no inoculant at 20–25 cm depth. At this depth, interactions with organic matter and tillage diminished the significance of the effect of microbial inoculants on pH. Downward leaching of excess organic acids and dissolved $CO_{2(g)}$ and in situ fermentation of organic carbon by microbial communities were the likely mechanisms of pH neutralisation in the residue to depth below the bioreactor caps.

Microbial inoculants also affected leachate pH; however, this effect was moderated by that of irrigation frequency. Leachate pH from treatments receiving the bioreactor-neutralised residue cap was significantly lower than that of the other microbial treatments where weekly or monthly irrigation was applied, but did not have a significant effect on leachate pH where daily irrigation was applied (Fig. 5). Total leachate volume was significantly lower in treatments receiving daily irrigation than weekly or monthly irrigation (data not shown), and therefore it is likely that the break-through point of neutralised pore water reporting to leachates was not reached in treatments under daily irrigation.

Salinity (EC)

Given the promising pH neutralisation results observed in the bioreactor cap treatments, the subsequent discussion will focus on how best to combine the bioreactor cap with other treatments to achieve multiple remediation goals. Due to the release of salts during neutralisation, electrical conductivity (EC, as a measure of salinity) was significantly higher in solids from treatments receiving a bioreactor cap, compared to no microbial inoculant. However, several other factors showed potential to address the higher salt load in these neutralised residues. Increased EC from pH neutralisation under bioreactor caps was partially offset by increasing the frequency of tillage and irrigation, both of which enhanced salt export. Tillage also enhanced salt export in other treatments, with fortnightly tillage significantly decreasing EC in the upper 0–15 cm compared with once-off tillage (data not shown) and also significantly increasing leachate EC (Fig. 7). Leachate EC was higher under fortnightly tillage than less frequent tillage (Fig. 6). Increased leachate EC under fortnightly tillage is consistent with the decreased solids EC observed within this tillage level, and reflecting enhanced salt export, likely through reducing aggregate size and increasing surface area.

Irrigation frequency also influenced residue and leachate EC. In treatments receiving the bioreactor-neutralised residue cap, increasing irrigation frequency to daily significantly decreased residue solids EC at 0–5 cm depth, compared with weekly or monthly irrigation (Fig. 6). At 10–15 and 20–25 cm depth, increasing irrigation frequency significantly decreased solids EC across all microbial inocula (data not shown). In general, daily tillage and fortnightly irrigation

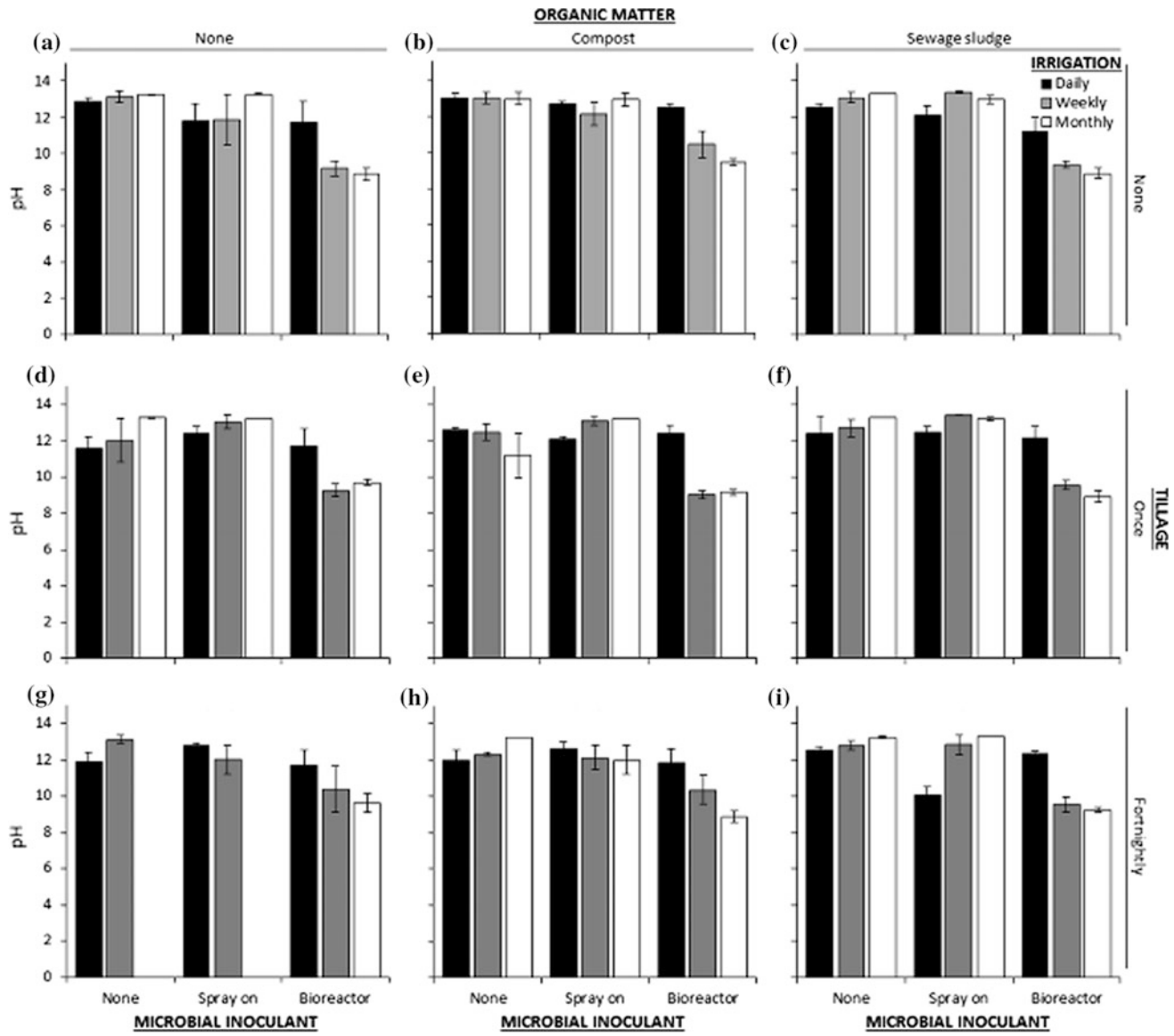

Fig. 5 pH in bauxite residue leachate samples, collected from glasshouse leaching columns five months after trial commencement. Text in capital letters, bold, and underline indicates factors within the experimental design. Treatments are as follows: **a** No organic matter, no tillage; **b** compost, no tillage; **c** sewage sludge, no tillage; **d** no organic matter, tillage once; **e** compost, tillage once; **f** sewage sludge, tillage once; **g** no organic matter, tillage fortnightly; **h** compost, tillage fortnightly; **i** sewage sludge, tillage fortnightly. Values displayed are the mean of three replicates; error bars indicate ±1 standard error of the mean

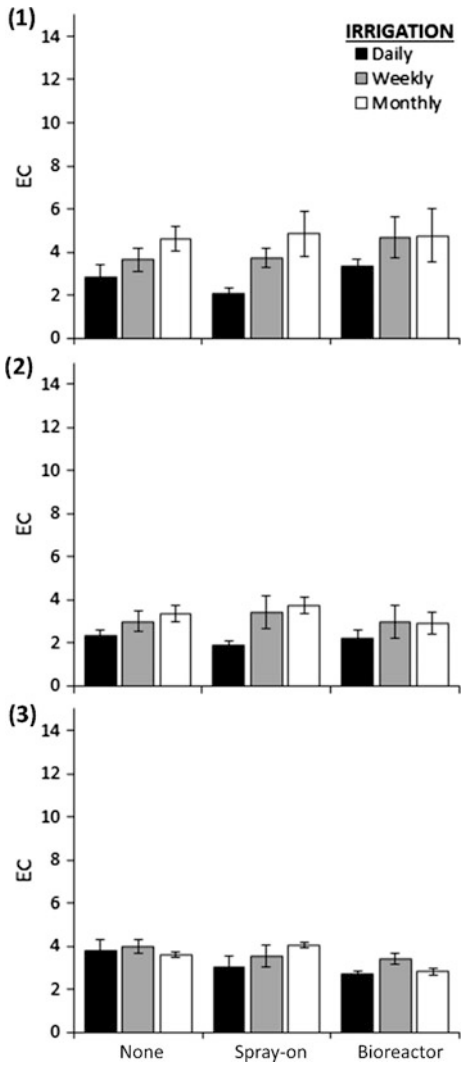

Fig. 6 EC (electrical conductivity) in bauxite residue solids in leaching columns after 5 months, at (1) 0–5 cm depth; (2) 10–15 cm depth; (3) 20–25 cm depth. Results for two factors only, microbial inoculant and irrigation, are shown in the interests of brevity. Values displayed are the mean of three replicates; error bars indicate ±1 standard error of the mean

also increased leachate EC; although these effects were moderated by interactions with microbial inoculant and organic matter.

Residue and leachate pH and EC were significantly affected by organic matter through interactions with tillage and microbial inocula only. These interactions affected variables including leachate total weight and EC, and residue solids pH and EC at 20–25 cm. Future work will focus on quantifying the contributions of organic matter additions to nutrient accumulation (e.g. organic C, total N, extractable P and K), for which sewage sludge and compost have been previously demonstrated to provide substantial benefit [1, 2, 12].

Conclusions and Implications for Field Trials

This study demonstrated successful scale up of microbial fermentation of organic carbon for pH neutralisation, as a promising biotechnological pathway for enhancing bauxite residue remediation in concert with other (abiotic) amendments, from laboratory to glasshouse. Further, the advance of a pH neutralisation front below the depth of application of a microbially-neutralised (bioreactor) residue cap indicated downwards leaching of acidic metabolites (organic acids, $CO_{2(g)}$) which enhanced residue remediation. The factorial study design enabled identification of the optimal treatment combination to meet multiple remediation targets, including both residue and leachate pH and salinity. Fortnightly tillage and daily irrigation counteracted the increased EC in treatments receiving the microbially-neutralised (bioreactor) residue cap. Combining the microbially-neutralised (bioreactor) residue cap to neutralise pH with fortnightly tillage and daily irrigation to remove salts was therefore identified as the optimal combination of amendments at the glasshouse scale. Further work will also explore the role of organic matter in increasing nutrient concentrations, and recommend the best level of this treatment to be combined with the optimal treatment combination for decreasing pH and EC.

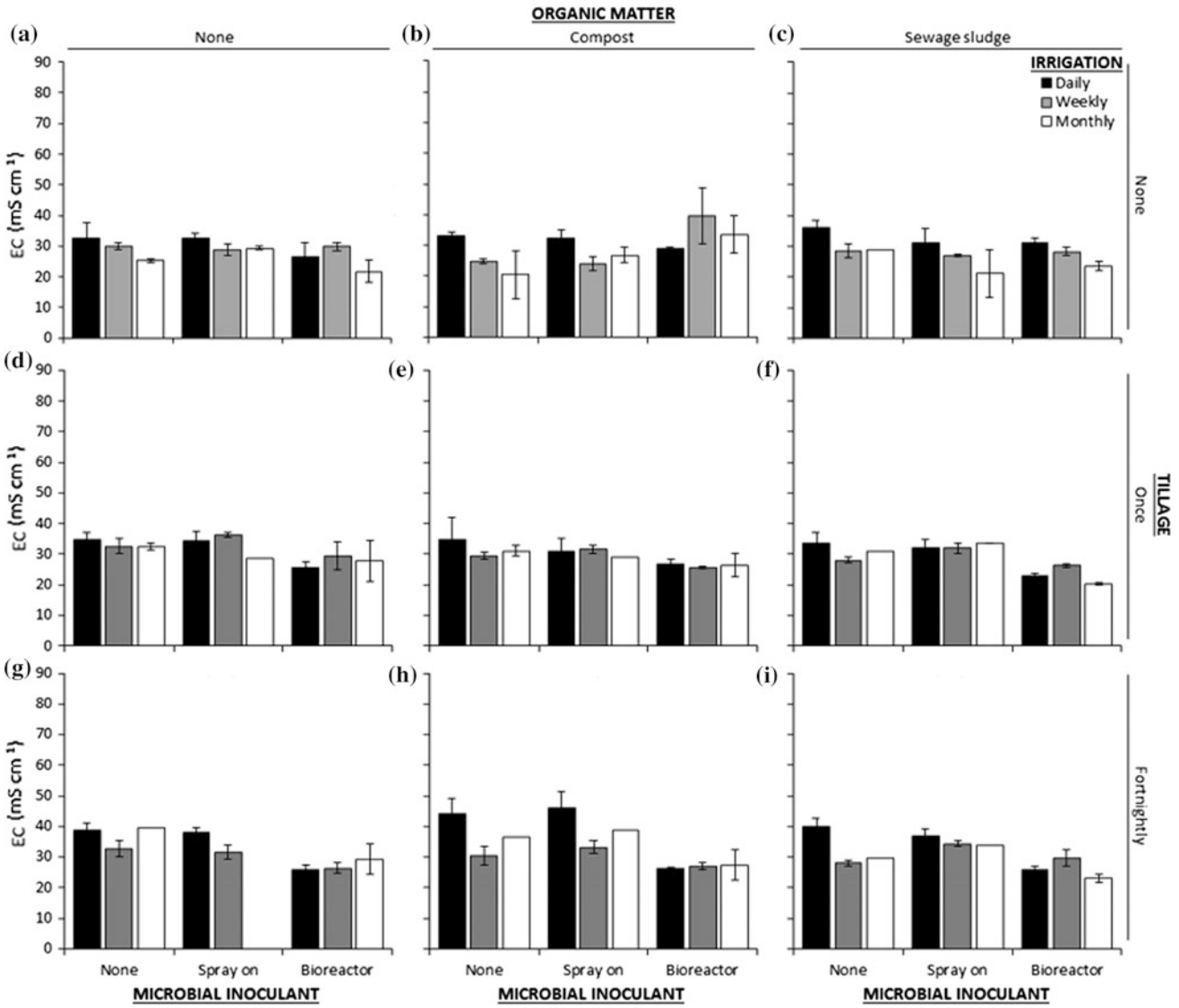

Fig. 7 EC in bauxite residue leachate samples, collected from glasshouse leaching columns five months after trial commencement. Text in capital letters, bold, and underline indicates factors within the experimental design. Treatments are as follows: **a** No organic matter, no tillage; **b** compost, no tillage; **c** sewage sludge, no tillage; **d** no organic matter, tillage once; **e** compost, tillage once; **f** sewage sludge, tillage once; **g** no organic matter, tillage fortnightly; **h** compost, tillage fortnightly; **i** sewage sludge, tillage fortnightly. Values displayed are the mean of three replicates; error bars indicate ±1 standard error of the mean

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