



## Research article

# Biochar amendment and water stress alter rhizosphere carbon and nitrogen budgets in bauxite-processing residue sand under rehabilitation



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## ABSTRACT

Nitrogen (N) bioavailability is one of the main limiting factors for microbial activity and vegetation establishment in bauxite-processing residue sand (BRS). Although beneficial effects of biochar on reducing N loss in the early stages of BRS rehabilitation have been observed previously, the underlying mechanisms of this complicated process, particularly the interactions between applied biochar and the plant rhizosphere is largely unknown. This glasshouse study (116 days), investigated the coupled effects of biochar and water stress on N bioavailability in the rhizosphere of ryegrass (*Lolium rigidum*) grown in BRS amended with di-ammonium phosphate (DAP) fertiliser (at rates of 0 or 2.7 t ha<sup>-1</sup>) with and without biochar amendment. The applied biochar was characterised as either aged acidic (AC) or alkaline pine (PC) and was mixed with BRS at a rate of 5% v/v under four moisture regimes (50%, 40%, 20% and 7.5% water holding capacity). Amending BRS with AC and PC biochars increased NH<sub>4</sub><sup>+</sup> retention and decreased cumulative NH<sub>3</sub> volatilization within both the rhizosphere and root-free zones compared with fertiliser only treatment. These effects were more pronounced for the AC than PC biochar, suggesting that aged acidic biochar has the great potential for use in rapid establishment of vegetation in BRS disposal areas. The biochar amendment increased cumulative nitrous oxide emissions compared with DAP only treatment, with no significant differences among different moisture regimes. The Control and 20% water holding capacity (WHC) treatment showed the highest dissolved organic carbon (DOC) concentrations compared with other treatments and moisture regimes in the ryegrass rhizosphere, while the highest dissolved organic N concentration were observed in the DAP + AC treatment. Reducing moisture levels below 20% WHC generally decreased microbial biomass carbon (MBC) concentrations and activity in both the rhizosphere and root-free zones of all treatments, while total N generally decreased as moisture levels decreased from 50% to 7.5% WHC. Plant took up more N in the DAP + AC treatment compared with DAP + PC and DAP only treatments, while increasing water stress generally resulted in decreased aboveground biomass.

## 1. Introduction

Fast development of alumina industry in recent years has resulted in a global bauxite residue inventory of 3.4 billion tons, with an increase of approximately 120 million tons each year (Kong et al., 2017; Xue et al., 2016). The large-scale deposition of bauxite residue in close distance from the alumina refineries would cause potential environmental risks due to the sensitivity of bauxite residue disposal areas to wind and water erosion. Problematic physicochemical properties of unweathered bauxite-processing residue sand (BRS) such as high alkalinity, salinity and sodicity, low water holding properties, poor nutrient retention, high leaching potential, and negligible microbial activity, are well-known to restrict plant growth in this harsh environment (Gherardi and

Rengel, 2003; Goloran et al., 2014b; Jones et al., 2010; Menzies et al., 2004). Rehabilitation of bauxite-processing residue storage areas often occurs on embankments constructed using BRS. Given the limitations of this material as a growth medium, establishing a sustainable ecosystem requires a detailed understanding of soil-water-plant nutrient dynamics (Goloran et al., 2014a; Gwenzi et al., 2011). Incorporation of inorganic (fertiliser) and organic (biosolids, manure, compost and biochar) amendments with BRS can supply essential nutrients for plant growth in the short term, but nutrient deficiencies still occur in the longer term causing deterioration of rehabilitation performance (Goloran et al., 2014b; Thiagarajan et al., 2011, 2009). Organic amendments can also improve the water holding capacity (Courtney et al., 2009; Munshower, 1994) and microbial activity (Jones et al., 2010) of rehabilitated BRS;

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however, the coupled interactions of water and nutrient resulting from organic amendments within the plant rhizosphere has received very little attention in rehabilitation.

Nitrogen (N) bioavailability is considered a major limitation for biological activities and vegetation establishment in highly alkaline (unweathered) BRS. Nitrogen is known to be rapidly lost from BRS either by ammonia ( $\text{NH}_3$ ) volatilization or nitrate ( $\text{NO}_3^-$ ) leaching (Chen et al., 2010; Phillips and Chen, 2010). Goloran et al. (2014b) found biochar incorporation into BRS enhanced N retention due to its ability to resist decomposition compared with other commonly used organic materials. Biochar may also assist in establishing a sustainable microbial community in the early stages of BRS rehabilitation process (Zhu et al., 2016).

The presence of growing plants can markedly affect the intensity of chemical and biological processes in the soil-plant root zone. Currently, little information is available regarding the interactions between biochar amended BRS and the plant rhizosphere. Therefore, the aim of this study was to investigate the coupled effects of nutrient and water stress on ryegrass (*Lolium rigidum*) growth in unweathered BRS. The main objectives were to investigate the role of the rhizosphere in overall ryegrass performance, and evaluate the effectiveness of biochar amendment on N bioavailability and plant growth in BRS, under different moisture regimes. The underlying hypotheses of this study were the physicochemical interactions between applied mineral N and biochars and consequently plant growth rate in BRS disposal areas would be affected by different moisture regimes; and biochar biochemical characteristics would reduce chemically driven N losses, such as  $\text{NH}_3$  volatilization, but may not significantly affect microbial driven N losses through nitrification and denitrification processes.

## 2. Materials and methods

### 2.1. Bauxite-processing residue sand and biochar physicochemical properties

“Fresh” (unweathered and untreated) BRS was collected from Alcoa of Australia (Alcoa) Kwinana Residue Storage Area (32° 11' S, 115° 49' E), Western Australia. Field samples were air-dried and sieved (< 2 mm) prior to conducting all experiments and analyses. The BRS contained 98% sand, 1% silt and 1% clay with initial pH of 11.3 (1:5 water), EC of 34 (dS  $\text{cm}^{-1}$ ), and water holding capacity (WHC) of 254  $\text{g kg}^{-1}$  (Table 1). To simulate Alcoa's rehabilitation prescription, the BRS was amended with gypsum at 1% (w/w basis), rewetted to 60% WHC and incubated for two weeks. After incubation, gypsum amended BRS was transferred to a leaching chamber and slowly leached with a volume of distilled water equivalent to average annual rainfall of the Kwinana area (i.e. 758 mm). Leaching (five leaching events) was undertaken to remove much of the pore-water salinity and alkalinity, with the pH and EC values measured before and after each leaching event.

Two biochars with different physicochemical characteristics, namely acidic aged eucalyptus biochar (AC) and alkaline pine biochar (PC), were selected for this experiment. The AC biochar was produced during a wildfire in 1969 at Peachester State Forest (26° 50'S, 152°53'E), Sunshine Coast hinterland of Queensland, Australia, with a pH of 3.1 and high  $\text{NH}_4^+$  adsorption capacity (Esfandbod et al., 2017).

**Table 1**  
Selected initial properties of BRS and applied biochars.

	Pyrolysis temperature (°C)	Moisture (%)	BET ( $\text{m}^2 \text{g}^{-1}$ )	$\rho_b$ ( $\text{g cm}^{-3}$ )	pH (1:5 water)	EC (dS $\text{cm}^{-1}$ )	Total C (%)	Total N (%)	$\text{NH}_4^+$ -N (mg $\text{kg}^{-1}$ )	$\text{NO}_3^-$ -N (mg $\text{kg}^{-1}$ )
AC	350–550	4.4	108	0.54	3.1	0.11	51.7	0.16	19.94	1.12
PC	700	7.5	382	0.27	8.6	0.32	81.6	0.16	0.11	0.61
BRS	ND	4.5	ND	1.70	11.3	34.00	0.1	0.01	ND	ND

BRS = bauxite-processing residue sand; AC = acidic aged biochar; PC = pine biochar; BET = BET surface area;  $\rho_b$  = bulk density; ND = not detectable.

The PC biochar was produced at 700 °C with the final resident time of 1 h under an oxygen free condition. The resulting biochar exhibited a pH of 8.6 and high  $\text{NO}_3^-$  adsorption capacity (Table 1).

### 2.2. Growth chamber preparation and experimental design

The cylindrical polyethylene growth chamber specially designed for this experiment was 12 cm in diameter and 12.5 cm in height. Each chamber comprised of three concentric compartments that effectively separated (but not isolated) the BRS into either a rooting zone or a non-rooting zone. The rooting zone (rhizosphere) comprised of the inner circle with the radius extending from the centre to 3 cm out (i.e. 0–3 cm radius). The non-rooting zone was separated into two sections of root-free zone 1 (3–4 cm radius) and root-free zone 2 (4–6 cm radius). Each zone was separated using weaved stainless steel frames covered with 40  $\mu\text{m}$  polyethylene mesh (Fig. S1). Detachable transparent polyethylene gas chambers were also specially designed for measuring  $\text{NH}_3$  volatilization and greenhouse gas emissions (carbon dioxide ( $\text{CO}_2$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) emissions from total growth chamber and root zone areas) during the experimental period. The base chamber was designed to be a waterproof pot, while upper chambers were connected to the base using an elastic rubber band and high vacuum silicon grease to ensure an airtight gap between the upper and lower chambers during gas sampling events.

The study employed four moisture regimes (50%, 40%, 20% and 7.5% water holding capacity), coupled with four amendment treatments in three replicates; these being (1) CK: BRS (1580  $\text{g pot}^{-1}$ ) without adding N fertiliser and biochar; (2) DAP: BRS (1580  $\text{g pot}^{-1}$ ) + 177.2 mg N  $\text{pot}^{-1}$ , equivalent to 574.2  $\text{kg N ha}^{-1}$  as Di-ammonium phosphate; (3) DAP + AC: BRS (1580  $\text{g pot}^{-1}$ ) + Di-ammonium phosphate + AC (the same N rate of DAP plus 26.33  $\text{g pot}^{-1}$ , equivalent to 85.0  $\text{ton ha}^{-1}$  AC in the top 30 cm); and (4) DAP + PC: BRS (1580  $\text{g pot}^{-1}$ ) + Di-ammonium phosphate + PC (the same N rate of DAP plus 13.17  $\text{g pot}^{-1}$ , equivalent to 42.5  $\text{ton ha}^{-1}$  PC in the top 30 cm). The AC and PC biochars (passed through 2 mm sieve) were added to BRS at a ratio of 1:20 (i.e. 5% on a v/v basis) and mixed thoroughly by end-over-end shaking for 24 h.

The moisture content of each treatment was adjusted to about 25% WHC (WHC = 25.4% moisture for BRS, 29.1% moisture for BRS + AC and 30.3% moisture for BRS + PC) using distilled water and Hoagland solution (120.4 ml  $\text{pot}^{-1}$  containing 235  $\text{mg L}^{-1}$  K, 200  $\text{mg L}^{-1}$  Ca, 31  $\text{mg L}^{-1}$  P, 64  $\text{mg L}^{-1}$  S, 48  $\text{mg L}^{-1}$  Mg, 0.5  $\text{mg L}^{-1}$  B, 5  $\text{mg L}^{-1}$  Fe, 0.5  $\text{mg L}^{-1}$  Mn, 0.05  $\text{mg L}^{-1}$  Zn, 0.02  $\text{mg L}^{-1}$  Cu and 0.01  $\text{mg L}^{-1}$  Mo, without N source); the latter to provide essential nutrients for plant growth. Considering that biochar amendment has changed the WHC of fresh BRS, different treatments would have slightly different moisture content (25%–30% moisture) while the percentage of WHC remain the same in all treatments. Treated samples were pre-incubated for one week at 25 °C, after which the moisture content of each sample was re-adjusted to 50% WHC. Distilled water and di-ammonium phosphate solutions were used for control and fertiliser applied treatments, respectively. The pre-treated samples were transferred to growth chambers (50% W/W in the root zone, 17% W/W in root-free zone 1 and 33% W/W in root-free zone 2), and 30 Wimmera rigid ryegrass (*Lolium rigidum*) seeds, pre-soaked for 16 h in distilled water, were sown in the

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