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Graphical abstract

**Aged biochar alters nitrogen pathways in bauxite-processing residue sand:
Environmental impact and biogeochemical mechanisms**

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Abstract

Low nitrogen (N) content and retention in bauxite-processing residue sand (BRS) disposal areas pose a great challenge to the establishment of sustainable vegetation cover in this highly alkaline environment. The budget and fate of applied N in BRS and its potential environmental impacts are largely unknown. We investigated the effect of combined application of biochars [aged acidic (AC) vs alkaline pine (PC)] and di-ammonium phosphate (DAP) fertiliser on ammonia (NH_3) volatilisation, nitrous oxide (N_2O) emission and N retention in a 116-day glasshouse study. The application of AC to BRS decreased pH (≈ 0.5 units) in BRS, while PC biochar increased pH (≈ 0.3 units). The application of AC reduced NH_3 volatilisation by ca. 80%, while PC by ca. 25%. On the other hand, the AC treatment increased N_2O emission by 5 folds. However, the N loss via N_2O emission in the AC treatment only accounted for ca. 0.4% of applied N. The reduction in BRS pH and increased retention of mineral N due to the presence of oxygen-containing (phenolic and carboxylic) functional groups in AC may be responsible for reduced NH_3 volatilisation and increased N_2O emission. This study has highlighted the potential of biochar (particularly aged biochar) in improving N retention and minimising environmental impacts in highly alkaline environments.

Keywords:

Bauxite-processing residue sand, aged acidic biochar, Nitrogen loss, rehabilitation

1. Introduction

The increasing demand for alumina from fast-growing developing countries has driven the increased production of bauxite in recent years. Australia is the largest producer of bauxite in the world, with annual output of approximately 62 million metric dry tons (McKay et al., 2013). For every tonne of alumina, about two tonnes of highly alkaline and highly saline bauxite-processing residue are produced (Phillips and Chen, 2010). The large-scale deposition of this hazardous 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. Alcoa of Australia (produces approximately 15 Mt of bauxite residue annually) separates its residue into two distinct size fractions; <150 microns (residue mud) and >150 microns (residue sand). Bauxite-processing residue sand (BRS), represents the primary material used for constructing the perimeter walls of Alcoa's residue storage areas (Goloran et al., 2014, 2013) which is progressively rehabilitated as part of refinery closure (Gherardi and Rengel, 2003).

Establishing a vegetation cover on residue sand can be challenging due to its initial characteristics such as low and imbalanced nutrient concentrations, high hydraulic conductivity and low water and nutrient retention capacity, high alkalinity and salinity, and low organic matter content. The sustainability of this vegetation will in part depend on the ability of residue sand to supply nutrients for plant uptake (Jones et al., 2012, 2010; Phillips and Chen, 2010; Thiagarajan et al., 2012). The nitrogen (N) level in bauxite residue sand is very low (total N < 0.03% and available N < 3 mg kg⁻¹) and nutrient deficiencies in the plants growing in bauxite residue have also been reported (Chen et al., 2010; Eastham et al., 2006). Various fertilisers and organic amendments such as composts, poultry manure (Courtney and Mullen, 2009; Jones et al., 2012), sewage sludge (Fuller et al., 1982) and biochar (Chen et al., 2013) have been used for amelioration of bauxite residue. Although organic amendments lead to the development of BRS structure, improved fertiliser-use efficiency and increased BRS water availability (Eastham et al., 2006), their slow decomposition limits fast biomass production (Banning et al., 2014). Inorganic fertilisers such as ammonium-, nitrate- and phosphate-based salts are considered as an effective and economical alternative to organic amendments (Eastham et al., 2006). Currently, 2.7 tons per hectare of di-ammonium phosphate (DAP) is used for the rehabilitation of bauxite residue disposal areas to compensate their poor N availability (Chen et al., 2010). However, this may also cause a significant N loss (up to 85% of applied N) to the environment, mainly through N volatilisation (as NH₃) and leaching (NO₃⁻) processes (Chen et al.,

2010). Limited information is also available on the loss of N from BRS in the forms of nitrous oxide (N_2O) and dinitrogen (N_2) via denitrification process. Therefore, more research is needed to identify the optimum combination of suitable fertiliser types, which would minimise N losses and decrease the need for future supplements.

There has been an increasing interest in biochar research, due to its beneficial effects on plant growth in harsh environmental conditions. Biochar application can also modify N_2O emissions by improving soil microbial activity (Lan et al., 2017; Lehmann et al., 2011), regulating the available N and C supplies (Gonzalez-Perez et al., 2004; Prendergast-Miller et al., 2011), and changing soil pH and aeration conditions (Enders et al., 2012; Kinney et al., 2012). Although beneficial effects of biochar application on N retention and reducing N loss have been observed in previous investigations (Esfandbod et al., 2017b; Goloran et al., 2014, 2013), little is known about the underlying biogeochemical mechanisms of this complicated process, particularly for rehabilitation performance in BRS.

Therefore, the main objectives of this study were to: (1) assess the effect of acidic and alkaline biochars on the N budget and fate of applied N fertiliser in BRS; (2) evaluate the effectiveness of biochar on improving N bioavailability and plant growth in BRS; and (3) understand the dynamics of NH_3 volatilisation and N_2O emission in response to biochar-amended relative to fertiliser-amended BRS in the presence of growing plants. The underlying hypotheses were: (a) pH and biochemical characteristics of different biochars would affect bauxite residue sand N dynamic, NH_3 volatilisation and N_2O emission differently; (b) Biochar application to bauxite residue sand may improve N retention and plant growth by increasing N use efficiency and consequently reducing N loss to the environment.

2. Materials and Methods

2.1. Bauxite-processing residue sand and biochars

“Fresh” (unweathered and untreated) BRS was collected from Alcoa’s Kwinana Refinery residue storage area (32° 11' S, 115° 49' E), Western Australia. Field samples were air-dried prior to sieving, with the <2 mm size fraction retained for this experiment. The BRS contained 98% sand, 1% silt and 1% clay with initial pH of 11.3 (1:5 water), EC of 34 dS cm⁻¹, and water holding capacity (WHC) of 254 g kg⁻¹ (Table 1). To simulate Alcoa’s current rehabilitation prescription, the BRS was amended with gypsum (1% w/w basis), rewetted to 60% WHC and incubated for two weeks to allow reaction. After incubation, the 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 was undertaken to remove much of the pore-water salinity and alkalinity, and involved five leaching events (i.e. 152 mm per event).

Two biochars with different physicochemical characteristics, namely aged acidic 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 NH₄⁺ adsorption capacity. The PC biochar was produced at 700 °C with the final resident time of 1 hour under an oxygen free condition. The resulting biochar exhibited a pH of 8.6 and high NO₃⁻ adsorption capacity (Table 1). The NH₄⁺ and NO₃⁻ adsorption capacity of biochars were determined using the sorption isotherms method (Esfandbod et al., 2017b).

2.2. Growth chamber preparation and experimental design

The growth chambers consisted of a cylindrical polyethylene base (12 cm diameter and 12.5 cm height) and two detachable transparent polyethylene gas chambers specially designed for measuring

N₂O emission and NH₃ volatilisation (SI Fig. 1). The base chamber was designed to be a waterproof pot. The upper chambers were connected to the base using an elastic rubber band and high vacuum silicon grease to ensure an airtight gap between the chambers during sampling. The study employed four treatments with six replicates; namely (1) Control (CK): BRS (1580 g pot⁻¹) without adding N fertiliser and biochar; (2) DAP: BRS + 177.2 mg N pot⁻¹, equivalent to 574.2 kg N ha⁻¹ as Di-ammonium phosphate; (3) DAP+AC: BRS + Di-ammonium phosphate + AC (26.33 g pot⁻¹ AC, equivalent to 85.0 ton ha⁻¹ AC in the top 30 cm); and (4) DAP+PC: BRS + Di-ammonium phosphate + PC (13.17 g pot⁻¹ PC, equivalent to 42.5 ton ha⁻¹ PC in the top 30 cm).

The AC and PC biochars 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 hours. The moisture content of each treatment was adjusted to 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 per pot containing 235 mg L⁻¹ K, 200 mg L⁻¹ Ca, 31 mg L⁻¹ P, 64 mg L⁻¹ S, 48 mg L⁻¹ Mg, 0.5 mg L⁻¹ B, 5 mg L⁻¹ Fe, 0.5 mg L⁻¹ Mn, 0.05 mg L⁻¹ Zn, 0.02 mg L⁻¹ Cu and 0.01 mg L⁻¹ Mo, without N source); the latter to provide essential nutrients for plant growth (Hoagland and Arnon, 1950). Treated samples were then pre-incubated for one week at 25 °C, after which the moisture content of each sample adjusted to 50% WHC. Distilled water and DAP solution were used as the solutions for control and fertilised treatments, respectively. The pre-treated samples were transferred to growth chambers and 20 *Wimmera rigid* ryegrass (*Lolium rigidum*) seeds, which had been soaked in distilled water overnight, sown in each chamber. During the experiment, the chambers were maintained at 50% WHC by adding small volumes of distilled water every three days, and at a near-constant temperature of 22 ± 2°C. The experiment was terminated after 116 days, and at this time, the plants were harvested.

2.3. Measurement of NH₃ volatilisation

Ammonia (NH_3) volatilisation was measured using the modified sponge trap method (Chen et al., 2010). The sponges used to trap NH_3 were prepared by rinsing with distilled water until the leachate contained negligible N, and then dried. The sponges were then uniformly moistened with 10 ml of trapping solution (173 ml L^{-1} concentrated sulfuric acid and 60 ml L^{-1} glycerol) and placed inside the trap (He et al., 1999). The sponges were sampled after 1, 4, 7, and 14 days, respectively. After this initial two weeks, NH_3 volatilisation was monitored on the 2nd and 5th days of each week for the remainder of the experiment (chamber closure time of 16 h). Ammonia captured by the sponge trap was extracted using 2 M KCl (1:10 ratio). The NH_4^+ -N concentration in the supernatant was determined using a SmartChem®200 Discrete Chemistry Analyser (WESTCO Scientific Instruments Inc.).

2.4. Measurement of N_2O emission

Gas sampling was undertaken every 1 to 7 days depending on the expected levels of emitted N_2O . For each sampling event, gas samples were collected from the growth chamber headspaces for three of the six replicates. Gas samples were collected one hour after closure of the chambers, to allow “equilibrium” gaseous compositions to develop, using a 25 mL gas-tight syringe. The content of the syringe was immediately transferred to a pre-evacuated 12 mL glass vial (Exetainer, Labco Ltd, High Wycombe, UK) prior to N_2O analysis using a gas chromatograph (Shimadzu GC-2010 Plus). The linearity test on N_2O concentration increases were performed on several sampling events during the study by sampling gas concentrations every 30 minutes for 1.5 hours after the chamber closure (Rezaei Rashti et al., 2015). The N_2O emission from all treatments showed linear trends during the measurement period. The N_2O values for days without sampling were estimated by arithmetic mean of the measurements on the two closest days (Rezaei Rashti et al., 2016). The cumulative N_2O emission for each treatment was calculated by summing the daily emissions.

2.5. Biomass harvest and plant and bauxite residue sand analysis

The above- and below- ground biomass of the ryegrass plants were measured at the end of experiment. Root lengths were estimated by a modified line intersect method (Tennant, 1975). Total carbon (TC) and nitrogen (TN) contents of the ryegrass, as well as the residual C and N in BRS, were measured in all treatments by dry combustion using a LECO CN analyser (TruMac NO. 830-300-400). The pH and EC values were measured in a 1:5 volumetric suspension of BRS in distilled water (Rayment and Lyons, 2011). Mineral N (NH_4^+ and NO_3^-) of BRS was extracted with 2 M KCl at a 1:4 ratio using an end-over-end shaker for 1 hour and filtering through Whatman 42 paper (Rayment and Lyons, 2011). After filtering the samples, the extraction process was repeated for the second time, and the two extracts bulked as a single sample. The NO_3^- -N and NH_4^+ -N concentrations in the extracts were determined by a SmartChem®200 Discrete Chemistry Analyser (WESTCO Scientific Instruments Inc.). Total extractable mineral N was calculated as the sum of NO_3^- -N and NH_4^+ -N concentrations. The BRS and plant analysis included three replicates from each treatment and the results were expressed on an oven-dry basis.

2.6. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was carried out to identify characteristics of functional groups on biochars obtained from different feedstocks and temperatures. Both of investigated biochars were air dried and then heated at 550 °C for 4 h to enhance their crystallinity. The FTIR spectra of the biochars were obtained using Perkin Elmer (PEFT-IR C94249) and were collected in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans per sample using a

SpectraTech Microcup DRIFT accessory. The samples were prepared as KBr pellet (1:300 sample-KBr mixture) in an agate mortar (Biniak et al., 1997).

2.7. Data processing and statistical analysis

The values of residual N in different fertilised treatments were calculated by subtracting total N contents of treatments from their mineral N concentrations at the end of experiment. The results were then modified based on each biochar's N content to allow biochar amended treatments to be comparable with the DAP treatment. The reported value for N_2 loss from each treatment was not measured directly but estimated from the difference between total N budget and other measured N pathways.

Statistical analysis was performed by univariate analysis of variance using the IBM SPSS Statistics 23 software package. All data were tested for the normality of distribution using Kolmogorov-Smirnov test prior to statistical analysis. The differences at $P \leq 0.05$ between treatments using LSD test considered statistically significant.

3. Results

3.1. Surface functional groups on aged acidic and alkaline biochars

FTIR analysis showed the highest intensity of surface functional groups in AC followed by BRS and PC, respectively (Fig. 1). The PC biochar spectra only showed a narrow band in ranges of 850 – 900 cm^{-1} (C–H bend, alkenes; phenyl ring) and the BRS spectra indicated a few narrow bands at 750 – 850 cm^{-1} (C–Cl stretch, alkyl halides; S–S disulphide), and 900 – 1050 cm^{-1} (=C–H bend, alkenes; P–OR esters). However, AC biochar spectra showed broad interval bands between 665 and 1500

cm⁻¹ (Esfandbod et al., 2017b). These observed peaks may be attributed to the N–H (primary and secondary amines), C=N stretch (aliphatic and aromatic amines), N–O asymmetric and symmetric stretch (nitro compounds) and N–H bend (primary amines) vibration (Likhacheva et al., 2002). Moreover, the observed peaks at 1710 – 1730 cm⁻¹, 1550 – 1610 cm⁻¹ and 3000 – 3650 cm⁻¹ in AC biochar (Fig. 1), may be associated with the special vibration of C=O carboxylic, C–H phenolic following with the antisymmetric stretching vibration of –COC– from aromatic hydrocarbons, and –OH and –NH₂ stretching vibration, respectively. As a result, the AC biochar may have greater capacity for adsorbing NH₄⁺ due to the presence of these groups.

3.2. Effects of biochar amendment on pH and EC

The application of DAP to BRS slightly reduced the pH ($\approx$ 0.1 unit) compared with CK treatment (pH = 8.3) at the end of experiment (Fig. 2); however the differences were not statistically significant. On the other hand, by the end of experiment, the DAP+PC and DAP+AC treatments significantly ($P < 0.05$) increased ($\approx$ 0.3 units) and decreased ($\approx$ 0.5 units) the pH of BRS when compared with the CK and DAP treatments, respectively. There was no significant difference in EC among the treatments although the CK and DAP treatments tended to have higher EC than the DAP+AC and DAP+PC treatments by the end of experiment.

3.3. Dynamics of N₂O emission and NH₃ volatilisation

The highest daily N₂O emission was observed at different stages of the experiment for different treatments. While N₂O emission in the DAP+AC treatment reached its peak around day 45, the CK, DAP and DAP+PC treatments displayed maximum N₂O fluxes between 80 to 95 days after the start of the experiment (Fig. 3). However, the N₂O emissions were very low due to limited microbial

activity (data not reported) in BRS. The daily NH_3 volatilisation reached its highest level within the first day of study in all fertilised treatments (but 18 days for CK) and gradually declined to levels similar to those in the CK treatment by the third week of the experiment.

The DAP+AC treatment increased cumulative N_2O emission ($P < 0.05$) compared with the DAP and DAP+PC treatments (Fig. 4). The cumulative N_2O emission in DAP+PC was slightly higher than DAP, while the difference between these treatments was not statistically significant. Both DAP+AC and DAP+PC treatments decreased cumulative NH_3 volatilisation ($P < 0.05$) compared with the DAP treatment. However, the results showed a significant reduction in NH_3 volatilisation ($P < 0.05$) after the addition of acidic biochar rather than alkaline pine biochar to BRS. The cumulative N_2O emission and NH_3 volatilisation values for CK treatment were negligible in comparison with the fertilised treatments.

3.4. The pathways of N loss in bauxite-processing residue sand

The highest estimated value of N_2 emission was observed in the DAP+AC treatment (Table 2), which indicated the significantly higher activity of denitrifying microorganisms in this treatment than DAP and DAP+PC treatments. Approximately 9% of the applied N fertiliser was lost as N_2 emission for the DAP+AC treatment, while N_2 loss from the DAP and DAP+PC treatments were less than 2.5% of the applied N fertiliser (Fig. 5). Of all the N fertilised treatments, only DAP+AC exhibited significant adsorption capacity for mineral N, and fixed around 37% of applied N within the BRS profile by the end of the experiment (i.e. residue N). While residue N accounted for the largest N pool in DAP+AC treatment, it made a negligible contribution when calculating the overall N budget for DAP and DAP+PC treatments.

Ammonia volatilisation accounted for the largest proportion of the N budget for DAP and DAP+PC (79.9% and 59.0%, respectively) treatments, but only accounted for 15.5% of the N budget for the DAP+AC treatment. The highest mineral N content was observed for the DAP+PC treatment, being 32.5% of the added N fertiliser, followed by DAP+AC and DAP treatments, respectively. Mineral N contents in biochar amended treatments were almost two times higher than the DAP treatment by the end of study, but only the DAP+AC treatment showed significantly ($P < 0.05$) higher plant N uptake compared with the DAP treatment. There were no significant differences in NH_4^+ concentrations among the treatments during the study; however, DAP+AC and DAP+PC treatments significantly ($P < 0.05$) increased NO_3^- concentration compared with DAP and CK treatments. The DAP treatment also showed significantly ($P < 0.05$) higher NO_3^- concentration than the CK treatment.

3.5. Effects of biochar amendment on N recovery by plants

The addition of DAP to BRS increased ryegrass shoot biomass, however the differences between CK and DAP treatments were not significant (Table 3). Biochar amendment in the DAP+AC and DAP+PC treatments significantly ($P < 0.05$) increased plant shoot biomass when compared with the CK and DAP treatments, while no significant differences were detected between ryegrass root biomass between treatments. The DAP+AC treatment showed the maximum root length and shoot / root biomass ratio, while the minimum root length and shoot / root biomass ratio observed at DAP and CK treatments, respectively. The application of N fertiliser (DAP) significantly ($P < 0.05$) increased ryegrass N concentration and uptake compared with the CK treatment. The ryegrass N concentration and uptake in the DAP+AC treatment was also significantly ($P < 0.05$) higher than DAP and DAP+PC treatments.

4. Discussion

4.1. Effect of aged acidic and alkaline biochars on NH_3 volatilisation and N_2O emission

Biochar addition was found to significantly decrease NH_3 volatilisation in BRS (DAP+AC; DAP+PC) compared with the DAP treatment (Figs. 3, 4). Furthermore, acidic biochar appeared to reduce NH_3 volatilisation relative to alkaline biochar. Most of the N loss as NH_3 (up to 85%) occurred during the very early stage of the experiment (i.e. within 24 hours to 7 days). Trends in NH_3 volatilisation may be ascribed to biochar-induced shifts in BRS pH and $\text{NH}_3/\text{NH}_4^+$ adsorption capacity. Application of AC reduced soil pH (from pH 8.3 in CK to 7.8 in DAP+ AC treatments), which was consistent with the reduction in NH_3 volatilisation (Figs. 2, 3, 4). Chen et al (2010) reported that 95% of N applied as DAP to BRS was lost via NH_3 volatilisation within one week due to highly alkaline pH. Biochar has also been found to increase the adsorption of $\text{NH}_3/\text{NH}_4^+$, possibly due to the presence of functional groups on biochar surface (Esfandbod et al., 2017b; Taghizadeh-Toosi et al., 2012a, 2012b). In this study, the higher intensity of functional groups on the AC surface appear to have made a significant contribution to the higher adsorption of $\text{NH}_3/\text{NH}_4^+$ compared with the PC and BRS (Fig. 1) and consequently reduced NH_3 volatilisation (Figs. 3, 4). On the other hand, despite the increase in pH for the DAP+PC treatment (≈ 0.3 units) compared with the CK (Fig. 2), the DAP+PC treatment displayed less NH_3 volatilisation than the DAP treatment (Fig. 4). This is likely to be due to the presence of functional groups on the PC surface, which has been reported to have relatively high cation sorption capacity (Esfandbod et al., 2017a).

Lee et al., (2006) and Ullah et al., (2008) reported that pH has a negative correlation with N_2O production, and acidic environments tend to have higher N_2O emissions than alkaline environments (Rochester, 2003). pH affects the activity of N_2O -reductase and hence the production of N_2O and N_2 through denitrification process (Weier and Gilliam, 1986). Therefore, the higher N_2O emission in the DAP+AC treatment in comparison with DAP+PC and DAP treatments may have been regulated by

its lower pH and higher mineral N availability for denitrification. The reduction in BRS pH by 0.5 units after AC application may have caused the higher activity of denitrifying bacteria (Lan et al., 2019), which may explain the significant role of denitrification in the fate of applied N as DAP fertiliser in BRS, especially at the high moisture content (50% WHC) employed in the current experiment. Biochar amendment also has an indirect effect on denitrification by reducing oxygen availability and stimulating the soil moisture effect on N₂O emission. Increased microbial activity in response to biochar addition to BRS, combined with high moisture retention capacity of biochar, could reduce oxygen availability in BRS microsites. Consequently, this may encourage the formation of anaerobic conditions, thereby facilitating denitrification and N₂O emission. Although N₂O emission in DAP+AC treatment was 5 times higher than DAP treatment, total N₂O emission only accounted for less than 0.4% of the applied N fertiliser in all treatments. This value is in the lower level of Intergovernmental Panel on Climate Change (IPCC) guideline of 1% (from 0.3 to 3%) of applied N fertiliser (IPCC, 2013).

4.2. The influence of biochar amendment on N budget in bauxite-processing residue sand

Biochar can potentially affect the rates of N cycling in BRS through changes in conditions controlling nitrification and/or denitrification processes, and also improve the adsorption of ammonia by increasing the cation exchange capacity (Clough et al., 2010). The CK treatment had the lowest residue N and mineral N concentrations, which may be a consequence of the lack of organic matter, coupled with the limited capacity to supply and/or retain N (Courtney et al., 2009; Jones et al., 2010). Addition of organic amendments such as biochar can increase the N content of BRS (Clough et al., 2010; Lehmann et al., 2011) as evident in this study, where AC and PC biochars greatly elevated the amount of mineral N and residue N in BRS (Fig. 5).

324 The FTIR spectral analysis showed that PC had just a narrow band in ranges of 850 - 900 cm^{-1} (C–H
 325 bend, alkenes; phenyl ring), which may explain the lower NH_4^+ sorption capacity in DAP+PC in
 326 comparison with DAP+AC treatment. This behaviour of PC was consistent with the very low residue
 327 N content in the DAP+PC treatment. In contrast, spectral analysis predicted significant electrostatic
 328 interactions between NH_4^+ and the activated functional groups on the surfaces of AC as NH_4^+ has a
 329 high coordination affinity to oxygen- and nitrogen-bearing functional groups. For example, the
 330 vibration peaks at 665 and 1500 cm^{-1} indicated that their adsorption can be related to coordination
 331 through N–H (primary and secondary amines), C=N stretch (aliphatic and aromatic amines), N–O
 332 asymmetric and symmetric stretch (nitro compounds) and N–H bend (primary amines) groups that
 333 exist on the surface of AC (Harlov et al., 2001). The AC, as an aged biochar, showed a specific band
 334 in ranges of 3000 – 3400 cm^{-1} on its surface which is related to phenolic –OH and –NH₂ stretching
 335 vibrations, resulting in a stronger conjugate and diffusion effect on NH_4^+ sorption. This is in
 336 agreement with the findings of Wang et al. (2015) reporting that sorption of NH_4^+ was greatly related
 337 to acidic functional groups (phenolic –OH and carboxyl C=O). The presence of oxygen-containing
 338 functional groups on the AC surface resulted in effective exchangeable sites for the NH_4^+ sorption.
 339 Therefore, the higher residual N content in the DAP+AC in comparison with the DAP+PC treatment
 340 can be attributed to the presence of oxygen-containing functional groups on the AC, which are
 341 complexed and intercalated with NH_4^+ on the surface or between layers via hydrogen being bonded
 342 to oxygen containing group (Bernal and Lopez-Real, 1993). While this study has demonstrated the
 343 benefits of acidic biochar as an amendment to BRS, it has also provided critical information on the
 344 suitability of DAP as an N fertiliser in rehabilitation on alkaline plant growth mediums such as BRS.
 345 The findings of this study indicated that pH is one of the main regulating factors of N availability and
 346 plant uptake as well as growth response by ryegrass in the early stages of BRS rehabilitation. The
 347 application of AC biochar with low pH (Table 1) revealed better N availability, leaf N uptake and
 348 dry matter yield (Tables 2, 3 and Fig. 5) than alkaline PC biochar. Given these results, mechanisms

that would reduce the alkalinity of BRS should be given a priority in developing rehabilitation protocols, and in particular, fertiliser applications should be timed to coincide with BRS pH values which maximise N retention and plant N availability (Goloran et al., 2014).

4.3. Effect of biochar application on plant growth and N dynamics

Understanding nutrient dynamics in non-typical soil materials such as bauxite-processing residue sand ($\text{pH} > 10$; $\text{EC} > 30 \text{ dS m}^{-1}$) is critical for developing fertilisation or organic amendment strategies, and in evaluating ecological restoration performance. The application of biochars (AC and PC) to BRS in the presence of mineral N fertiliser produced higher dry matter, leaf N concentration and N uptake by ryegrass than CK and DAP treatments, suggesting the great potential of biochar in providing stability of applied N fertiliser in BRS. In addition, our findings suggested that biochar amendment to BRS not only increased ryegrass growth, but also improved the N supplying capacity of BRS. This would be highly beneficial for achieving sustainable vegetation covers and subsequent ecosystems in mine closure and rehabilitation. It is concluded that AC and PC amendment in combination with sufficient inorganic fertiliser (such as DAP) may significantly improve plant growth performance and provide a sustainable source of N for vegetation establishment in bauxite-residue storage areas. The results also indicated that total bioavailable N was strongly associated with N uptake by ryegrass, with highest residual and mineral N contents found in the DAP+AC treatment. Consequently, the highest plant biomass N content was also found in this treatment. This finding could be attributed to the predominance of NH_4^+ adsorption to AC surface, which becomes the main source of N uptake by ryegrass. This is supported by findings of Tagliavini et al. (1995), Clarkson and Warner (1979), and Watson (1987), which reported ryegrass preference for NH_4^+ uptake under solution culture and pot trial studies.

Previous studies have indicated the significance of NH_3 volatilisation from inorganic fertilisers such as DAP in alkaline environments (Ali and Stroehlein, 1991; Devine and Holmes, 1964; Fenn et al., 1978). The AC biochar application significantly improved the bioavailability of N in BRS by increasing the sorption and retention of NH_4^+ in its exchange sites. As a result, the DAP+AC treatment showed significantly higher residual N content than other treatments by the end of experiment, followed by DAP+PC, DAP and CK treatments. The growth response of ryegrass observed in this study was consistent with the findings of Bowman (2003) who reported a substantial increase in shoot biomass and a decrease in root biomass of ryegrass with increasing residual N rate. The highest plant biomass observed in the DAP+AC treatment may be a response of ryegrass to uptake more available soil N due to manipulation of BRS alkaline environment by application of aged acidic biochar (Chen et al., 2004, 2003). The amendment of BRS by both AC and PC biochars resulted in higher plant biomass when compared with CK and DAP treatments. This finding indicates the efficiency of biochar application as an amendment to provide more sustainable N availability for optimum plant growth in highly alkaline BRS environment. It can also be concluded that combined application of AC biochar and NH_4^+ based mineral fertilisers (such as DAP) has a great potential to alleviate N deficiency in BRS storage areas by improving sustainable N availability for plants growth due to retaining more NH_4^+ in the surface exchange sites.

5. Conclusions

This study has shown that incorporation of biochar (alkaline and acidic) into alkaline BRS significantly modified the N availability and its pathways in BRS. The addition of aged acidic biochar decreased NH_3 volatilisation but increased N_2O emission, while alkaline biochar amendment resulted in higher NH_3 volatilisation and lower N_2O emission compared with the acidic biochar treatment. These biochar-induced changes in the dynamics of N in BRS could be accounted for by

the shifts in acid-base reaction and adsorption capacity of NH_4^+ due to application of biochars with different physicochemical characteristic. Acidic biochar resulted in lower pH, while alkaline biochar increased the pH value in BRS. In addition, acidic biochar had a larger quantity of oxygen-containing functional groups on its surface compared with the alkaline pine biochar, contributing greatly to the higher adsorption of NH_4^+ . This study has provided critical information on the effects of different biochars on the dynamics of N in alkaline growing mediums such as bauxite-processing residue sand. The findings of this study would also provide an excellent baseline information for selecting and timing of the inorganic fertilisers' application, susceptible to loss through volatilisation and denitrification, and should be considered in planning rehabilitation prescriptions for bauxite-processing residue sand.

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Fig. 1. FTIR spectra analysis of bauxite-processing residue sand (BRS), aged acidic biochar (AC) and pine biochar (PC) used in this study.

Fig. 2. Bauxite-processing residue sand pH and EC values of different treatments at the end of experimental period. Vertical bars are standard error of three replicates. CK = Control (without amendments of DAP or biochar); DAP = Di-ammonium phosphate; DAP + AC = Di-ammonium phosphate + acidic aged biochar; DAP + PC = Di-ammonium phosphate + pine biochar. Means of the treatments by the same letter are not different at the 5% level of significance.

Fig. 3. Daily NH_3 volatilisation, N_2O emission and $\text{NH}_3 / \text{N}_2\text{O}$ ratio of different treatments during the experimental period. Vertical bars are standard error of three replicates. SDW = soil dry weight; CK = Control (without amendments of DAP or biochar); DAP = Di-ammonium phosphate; DAP + AC =

Fig. 4. Cumulative NH_3 volatilisation (a) and N_2O emission (b) of different treatments during the experimental period. Vertical bars are standard error of three replicates. SDW = soil dry weight; CK = Control (without amendments of DAP or biochar); DAP = Di-ammonium phosphate; DAP + AC = Di-ammonium phosphate + acidic aged biochar; DAP + PC = Di-ammonium phosphate + pine biochar.

Fig. 5. Nitrogen budget (%) and fate of different forms of N for different treatments over the entire experimental period. The different letters within boxes with the same colour indicate significant differences between the treatments at $P < 0.05$. The reported values for N_2 loss were not measured directly but estimated from the difference between total N budget and other measured N pathways. The residue N values of treatments calculated by subtracting total N contents from mineral N concentrations at the end of experiment, and modified based on each biochar's N content for biochar amended treatments. DAP = Di-ammonium phosphate; DAP + AC = Di-ammonium phosphate + acidic aged biochar; DAP + PC = Di-ammonium phosphate + pine biochar.

Table 1: Selected initial properties of bauxite-processing residue sand (BRS) and applied biochars

	Pyrolysis temperature (°C)	Moisture (%)	BET (m ² g ⁻¹)	pb (g cm ⁻³)	pH (1:5)	EC (dS m ⁻¹)	Total C (%)	Total N (%)	NH ₄ ⁺ -N (mg kg ⁻¹)	NO ₃ ⁻ -N (mg kg ⁻¹)
AC	350 - 550	4.4	108	0.54	3.1	0.11	51.7	0.16	19.9	1.1
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	0.07	0.01	ND	ND

AC = acidic aged biochar; PC = pine biochar; BET = BET surface area; pb = bulk density; ND = not detectable.

Table 2: Nitrogen (N) pools in bauxite-processing residue sand (BRS) for different treatments

Treatment	NH ₃ -N loss (mg kg ⁻¹)	N ₂ O-N loss (mg kg ⁻¹)	N ₂ loss (mg kg ⁻¹)	NH ₄ ⁺ -N (mg kg ⁻¹)	NO ₃ ⁻ -N (mg kg ⁻¹)	Residue-N* (mg kg ⁻¹)
CK	0.36 a**	0.01 a	0.00 a	7.27 a	0.26 a	0.00 a
DAP	87.30 b	0.07 b	1.13 b	9.41 a	19.68 b	0.00 a
DAP + AC	17.12 c	0.36 c	9.90 c	7.86 a	44.73 c	27.51 b
DAP + PC	65.61 d	0.14 b	2.55 bc	8.58 a	49.04 c	0.02 a

* The residue-N reported according to the remaining of applied N fertiliser in BRS without including biochar N pools. ** Means followed by different letters within a column indicate significant differences between the treatments at $P < 0.05$. The reported values for N₂ loss were not measured directly but estimated from the difference between total N budget and other measured N pathways. CK = Control; DAP = Di-ammonium phosphate; DAP + AC = Di-ammonium phosphate + acidic aged biochar; DAP + PC = Di-ammonium phosphate + pine biochar.

Table 3: Plant biomass and N uptake for different treatments at the end of experiment

Treatment	Shoot* biomass (mg pot ⁻¹)	Root biomass (mg pot ⁻¹)	Shoot / Root biomass ratio	Root length (m pot ⁻¹)	Plant biomass / Root length (mg m ⁻¹)	Plant N concentration (mg g ⁻¹)	Plant N uptake (mg pot ⁻¹)
CK	191 a**	71 a	2.7 a	22.8 a	11.5 a	13.2 a	3.4 a
DAP	233 a	52 a	4.5 ab	14.8 a	19.3 b	29.2 b	8.2 b
DAP + AC	402 b	51 a	7.9 b	22.8 a	19.9 b	34.2 c	15.5 c
DAP + PC	321 b	51 a	6.3 b	22.1 a	16.8 ab	29.5 b	10.8 b

* The data reported according to plant dry weight. ** Means followed by different letters within a column indicate significant differences between the treatments at $P < 0.05$. CK = Control (without amendments of DAP or biochar); DAP = Di-ammonium phosphate; DAP + AC = Di-ammonium phosphate + acidic aged biochar; DAP + PC = Di-ammonium phosphate + pine biochar.

Highlights

- 1) Effects of biochar and mineral fertiliser studied on nitrogen fate in bauxite residue
- 2) Aged acidic biochar decreased, while alkaline pine biochar increased pH of residue
- 3) Aged biochar showed high oxygen-containing functional groups and adsorption capacity
- 4) Added biochar decreased ammonia volatilization while increased nitrous oxide emission
- 5) Aged biochar increased nitrogen retention, plant nitrogen concentration and uptake