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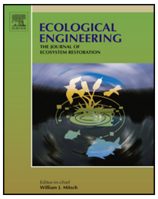

Selecting a nitrogen availability index for understanding plant nutrient dynamics in rehabilitated bauxite-processing residue sand

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ABSTRACT

Understanding nutrient dynamics in non-typical soil materials such as bauxite-processing residue sand ($pH > 10$; $EC > 30\,dS\,m^{-1}$) is critical for developing fertilizer strategies and evaluating ecological restoration performance. Indices relating nitrogen (N) concentration in soil to plant N uptake are well-established for natural soils but their application to non-typical soils has received little attention. This study investigated a range of soil-based methods [i.e. 2 M KCl extractable inorganic N (NH_4^+, NO_3^-), potentially mineralizable nitrogen (PMN), and 0.01 M $CaCl_2$ extractable N] to identify their suitability for describing soil–plant N relations in highly alkaline bauxite-processing residue sand. Nitrogen availability indices were measured under laboratory (pot trial) and field conditions. Pot trial was established using residue sand that had been amended (10%, v/v, basis) with various organic (greenwaste compost, biochar and biosolids) and inorganic (zeolite) materials. Both the field study and pot trial showed that 2 M KCl extractable NO_3^--N was most highly correlated with plant biomass N compared with the other N availability indices. Findings from this study suggest that 2 M KCl extractable NO_3^--N can be used as a soil quality indicator in developing fertilizer management strategies and assessing ecological status of the residue storage areas.

1. Introduction

Large quantities of residue materials are produced at alumina refineries through the Bayer process (Phillips and Chen, 2010). Alcoa World Alumina Australia employs a "dry-stacking" method of residue storage, which involves separating the residue into coarse (>150 μm) and fine (<150 μm) fractions. The coarse fraction (hereafter referred to as bauxite-processing residue sand, BRS) is used to construct the outer perimeter walls of residue storage areas (RSAs). The outer embankments are progressively vegetated as part of Alcoa's commitment to progressive closure of its RSAs. Thus, BRS represents the primary growth medium for establishing a vegetation cover, and the sustainability of this vegetation will in part depend on the ability of residue sand to supply nutrients for plant uptake (Gherardi and Rengel, 2003; Thiyagarajan et al., 2009; Phillips and Chen, 2010; Jones et al., 2010; Jones and Haynes, 2011).

Establishing a sustainable plant cover system in BRS poses significant challenges due to its inherently hostile characteristics, such as high pH ($pH > 10$), high electrical conductivity ($EC > 30\,dS\,m^{-1}$), high Exchangeable Sodium Percentage ($EPS > 70\%$), high hydraulic conductivity, high soluble Al content, low levels of 2 M KCl extractable N ($<3\,mg\,kg^{-1}$) and poor nutrient availability [available $P < 3\,mg\,kg^{-1}$; organic carbon (C) 0.05–0.13%; EDTA extractable $Mn < 0.8\,mg\,kg^{-1}$, $Cu < 0.4\,mg\,kg^{-1}$ and $Fe > 200\,mg\,kg^{-1}$] (Gherardi and Rengel, 2003; Thiyagarajan et al., 2009; Chen et al., 2010; Jones et al., 2010; Phillips and Chen, 2010; Anderson et al., 2011; Courtney and Kirwan, 2012). Therefore, selection and application of appropriate fertilisers are critical for successfully establishing long-term vegetation covers in RSAs.

Currently, Alcoa applies 2.7 tons ha^{-1} of diammonium phosphate-based fertilizer (DAP) as part of its rehabilitation protocol. This rate was partly established based on the high P sorption properties of residue (Bendfeldt et al., 2001; Courtney and Harrington, 2010), but previous studies have identified that these properties can markedly affect N availability, which is significantly influenced by gypsum addition in the residue (Alcoa's current practice). Gypsum supplies readily available Ca^{2+} that promotes high P adsorption capacities in the residue (Summers et al., 1996) while at the same time depresses the retention of NH_4^+ due to increased competition between NH_4^+ and Ca^{2+} for the limited exchange sites (Phillips, 1998). It was reported that up to 95% of N fertilizer applied to BRS could be lost via volatilization

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within one week due to its high pH (Chen et al., 2010). Previous studies indicated nutrient deficiencies in BRS even after addition of fertilizer due to extreme alkalinity and sodicity of the residue (Bell et al., 1997; Jasper et al., 2000; Eastham and Morald, 2006; Thiyagarajan et al., 2009). However, the addition of organic and inorganic amendments has been found to improve the chemical, microbial and physical properties of BRS as a plant growth medium (Courtney and Harrington, 2010, 2012; Jones et al., 2011; Courtney and Kirwan, 2012). While previous studies have shown the limitations of BRS as a potential growing medium, information on nutrient performance indices in this material is scarce (Courtney and Harrington, 2010).

Performance indices are critical guides for evaluating ecological restoration performance and therefore its long term likelihood of developing into a sustainable ecosystem. Soil N availability indices have been incorporated in classifying ecological conditions in soils due to N influence on plant growth performance and species compositions (Taylor, 1991; Binkley and Hart, 1989). Thus, the use of a suitable soil N index that fully reflects its ecological significance is crucial (Wilson et al., 2005). Although there are various methods for obtaining a nutrient availability index for natural soils, little information is available on whether these methods are appropriate for non-typical soils such as BRS. For example, plant nutrient extraction techniques that employ a buffered solution may over- or under-estimate availability for those nutrients that are pH-sensitive (e.g. N, P and trace elements). Moreover, the hostile environment of BRS (i.e. highly alkaline and high leaching), may negatively affect the performance of the chemical based extraction methods as they fail to account for soil mineral N loss mechanisms such as leaching and denitrification (Sharifi et al., 2007), and even volatilization (highly alkaline substrate) due to effects of environmental conditions.

A number of soil extraction methods have been widely used for evaluating soil N availability (Houba et al., 1990; Sparks et al., 1996; Khan et al., 2001; Mulvaney et al., 2001). These include the extractions of soils with water, 2 M potassium chloride (KCl) and 0.01 M calcium chloride ($CaCl_2$) solutions. Concentrations of NH_4^+-N, NO_3^--N and organic N were determined in these extracts as indicators of available N in soils (Houba et al., 1990; Sparks et al., 1996; Chen et al., 2005; Burton et al., 2007). The use of 2 M KCl is one of the conventional methods for inorganic N extraction by measuring both solution and adsorbed NH_4^+-N, NO_3^--N and dissolved organic N (DON), and has been universally adopted (Sparks et al., 1996; Chen et al., 2005). Meanwhile, 0.01 M $CaCl_2$ has been proposed as a multi-nutrient soil extractant, which includes inorganic N for all types of soils (Houba et al., 1990; Jones, 1998). This extractant is proposed to mimic the ionic strength of naturally-occurring soil solutions as a means to extract most available N (Houba et al., 1990). The dominance of organic N in soil prompted the use of incubation methods such as PMN (potentially mineralizable N) to measure N availability, which has gained wide acceptance since the 1950s (Jin et al., 2007). PMN as soil N indicator does not only measure organic N but also provides indication on the capacity of soil or microbes to convert organic nitrogen into mineral forms (Gugino et al., 2009).

Each of these methods – 2 M KCl for extractable NH_4^+ and NO_3^- (Nayyar et al., 2006; Akhtar et al., 2011), 0.01 M $CaCl_2$ (Quemada and Diez, 2007) and PMN (Bushong et al., 2007; Jin et al., 2007) – have been used for determining the N supplying capacity in alkaline and calcareous soils. However, their suitability in alkaline BRS is not known. The objective of this study was to evaluate which of these extraction methods is the best index of N availability in BRS by linking the concentrations of plant available N (i.e. NH_4^+, NO_3^- and mineralizable N) measured by abovementioned N indices to plant N uptake using both the pot trial and field survey.

2. Materials and methods

2.1. Pot trial

Bauxite-processing residue sand was sourced from Alcoa's Kwinana Refinery in south-west Western Australia (latitude 32°11′54.22″ South and longitude 115°49′31.93″ East). Samples were collected from freshly deposited (unweathered and untreated) stockpiles, and from rehabilitated embankments ranging in age from 5, 7 and 15 years old. Samples were air-dried, and the <2 mm size fraction retained for pot tria. To simulate Alcoa's current protocol for remediating BRS, phosphogypsum (<1 mm) was added to freshly deposited BRS at a rate of 1% (w/w), rewetted to 60% water holding capacity and incubated for 2 weeks. After incubation, samples of phosphogypsum amended fresh BRS were leached with the equivalent amount of the average annual rainfall at Kwinana RSAs (758 mm). Phosphogypsum was not added to the older BRS samples as these had already received gypsum as part of the rehabilitation prescription.

Samples of the phosphogypsum amended fresh BRS were mixed with a range of organic and inorganic amendments at a rate of 10% (v/v); these included greenwaste compost (GC), biochar (BC), zeolite (ZL), and biosolids (BS). These amendments were air-dried and sieved (2 mm) before being added to the BRS. The combination of amendments and BRS produced a total of 5 different BRS growth media such as BRS without amendment (BRSNA), BRS with Greenwaste compost (BRSGC), BRS with Biochar (BRSBC), BRS with Zeolite (BRSZL) and BRS with Biosolids (BRSBS). In addition to this, BRS growth media from the older rehabilitated areas were included as growth media in this study. These were 5 Year Rehab BRS (5YRRH BRS), 7 Year Rehab BRS (7YRRH BRS) and 15 Year Rehab BRS (15YRRH BRS). All growth media were air-dried prior to the addition of fertilizer solution (NH_4NO_3 plus $Ca(H_2PO_4)_2$). This was to allow adjustment of BRS water-holding capacity to 60% even after addition of fertilizer solution. The fertilizer solution was added at a rate of 0, 83.4, 125.1, 166.8, 208.5, 250.1, 333.5 and 416.1 mg pot^{-1}, which is equivalent to fertilizer levels 0, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 tons ha^{-1} DAP in the field, respectively. Altogether, there were eight (8) types of BRS growth media, one (1) grass species, eight (8) N fertilizer levels with three (3) replicates. A total of 192 pots were observed for this experiment and were arranged in a complete randomized design.

BRS growing media were placed in plastic pots made from 250 mL containers (SARSTEDT Australia Pty Ltd.), and covered with aluminum foil in order not to expose plant roots to light throughout the growing period. The total mass of BRS growing media ranged from 248 to 285 g pot^{-1}, as it varied due to added organic/inorganic amendments. Wimmera ryegrass (*Lolium rigidum*) was planted due to its ability to grow in highly alkaline soil, and because this is the primary grass species planted at Alcoa's RSAs. Each pot was planted with 25 pre-germinated ryegrass seeds, and plants were harvested after a three month growing period. The above-ground parts were cut at the BRS surface and the root systems were retrieved and washed using distilled water. Both roots and the above-ground parts were dried at 60 °C and weighed for measurement of dry matter. A subsample of plant materials was taken for chemical analysis. BRS growth media from each pot were all collected (as one composite sample), mixed well and divided into two portions. One portion (desired amount per extraction procedure) was used for immediate chemical extraction of plant available N and for measuring PMN. The other portion was air-dried and analyzed for total N and other extractable elements.