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Long term field trials demonstrate sustainable nutrient supply and uptake in rehabilitated bauxite residue

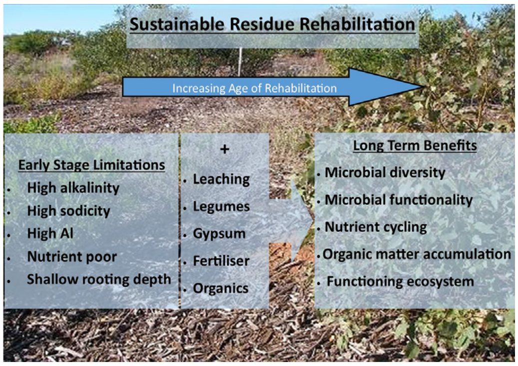
I.R. Phillips [a,b], R. Courtney [c,*]

[a] Department of Agriculture and Fisheries, Queensland Government, Toowoomba, Queensland 4350, Australia
[b] Alcoa of Australia Limited, Pinjarra, Western Australia, Australia
[c] Department of Biological Sciences and Bernal Institute, University of Limerick, Ireland

HIGHLIGHTS

- Bauxite residue rehabilitation is afflicted by high pH, sodicity and poor nutrient content.
- Previous studies have been restricted by short monitoring timeframes.
- Long term performance of vegetation on rehabilitated bauxite residue was assessed.
- Organic carbon and total and mineral nitrogen contents of the rehabilitated residue increased over time.
- 10-year old rehabilitation exhibited characteristics similar to an analogue site.

GRAPHICAL ABSTRACT



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ABSTRACT

Establishing a sustainable vegetation cover is one of the most important steps in progressive rehabilitation and final closure of ore-processing residues and tailings facilities. Sustainable rehabilitation partly depends on establishing and maintaining a supply of plant-available nutrients, but few long term field studies demonstrating the success or failure of rehabilitation of degraded land such as mineral processing tailings have been reported. Bauxite-processing residues are a highly sodic, highly alkaline, nutrient-poor by-product generated from alumina extraction, and pose many challenges for successful rehabilitation. This study investigated long term performance of rehabilitation established on bauxite-processing residue storage areas (RSAs) by comparing the nutrient content of the vegetation cover with nutrient concentrations in the underlying residue sand. Five plant species having diverse physiology were selected from rehabilitation varying in age from 1 to 10 years old; these being: *Hardenbergia comptoniana* – a vigorous growing legume ground cover/creeper), *Acacia cochlearis* and *A. rostellifera* - legume shrubs tolerant of sandy, alkaline conditions, *Grevillea crithmifolia* - a drought-tolerant proteaceous shrub tolerant of alkaline soil, and *Spyridium globulosum - a* robust, fast-growing shrub, commonly found on alkaline coastal soils. Gypsum incorporation reduced the pH and soluble aluminium levels in residue sand, but also acted as a long-term source of nutrients for the vegetation cover. Legume species contained more nitrogen than non-legumes (2.5% N and 1.5% N, respectively), and decomposition of surface litter increased organic carbon and total and mineral nitrogen contents of the residue sand over time. Nutrient cycling maintained a supply of macro- and micro- nutrients for the vegetation cover, and 10-year old rehabilitation exhibited characteristics similar to an analogue site. This study highlighted the importance of organic matter

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* Corresponding author.
E-mail address: ronan.courtney@ul.ie (R. Courtney).

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accumulation, developing a functional microbial community, and a diverse plant species mix on transforming the residue sand characteristics and encouraging nutrient cycling as key mechanisms for establishing a sustainable vegetation cover and functional ecosystem on residue sand embankments.

1. Introduction

Bauxite residue is the by-product generated by the extraction of alumina from bauxite ore via the Bayer Process, and is typically highly alkaline, saline, sodic, nutrient-poor and may contain trace elements at elevated levels (Power et al., 2011; Zhu et al., 2016; Cusack et al., 2018). The alumina industry produces approximately 150 MT of bauxite residue each year with an estimated global stockpile of three billion tonnes (Evans, 2016; Xue et al., 2016). Despite multiple attempts to utilize bauxite processing residue, only 2-3% of this material is currently re-used or further processed (Klauber et al., 2011; Evans, 2016; Ujaczki et al., 2018). Consequently, almost all bauxite-processing residue is stored in land-based bauxite residue disposal areas (RSAs) (Burke et al., 2013), with many facilities having a footprint of several hundred hectares (Di Carlo et al., 2019).

Establishing a sustainable vegetation cover is one of the most important steps in progressive and final closure of ore-processing residues and tailings facilities (e.g. Tordoff et al., 2000; Ye et al., 2002; Xue et al., 2016). A vegetation cover provides not only a method of maintaining structural integrity of the engineered facility, but also an improved visual environment and the initiation of a new ecosystem for local flora and fauna (Cortina et al., 2011; Zhu et al., 2016). Like many ore-processing residues, successful rehabilitation of bauxite residues is under-pinned by not only establishing the most-suitable vegetation species, but importantly on developing the most-appropriate growing medium. In many cases, where good quality soil (topsoil or sub-soil) is not available, additions of amendments (e.g. compost, composted manures and/or gypsum; Courtney and Timpson, 2005; Eastham et al., 2006, Eastham and Morald, 2006; Goloran et al., 2015a, 2015b, 2015c; Bray et al., 2018; Xue et al., 2018; Courtney and Xue, 2019) and/or fertilizers (Eastham et al., 2006; Eastham and Morald, 2006) is often required. In this respect, successful rehabilitation is a combination of both selection of plant species most suited to the environmental conditions with management of the (chemical, physical and microbial) properties of the growing medium (Banning et al., 2010, 2014; Jones et al., 2010, 2011, 2012; Huang et al., 2012; Courtney et al., 2013; Phillips, 2014, 2015; Torgersrud et al., 2019). In the long term, sustainable vegetation of mine tailings represents one of the most cost-effective and efficient methods of reducing potential ongoing environmental impacts following mine closure (Di Carlo et al., 2019).

The importance of a functioning soil medium for sustainable rehabilitation and ecosystem development on tailings facilities has long been recognized (Jones and Haynes, 2011; Banning et al., 2010, 2014; Cross et al., 2019). Considerable time is typically required to transform substrates capable of supporting a vegetation, particularly for bauxite residue which exhibits inherently hostile characteristics (high alkalinity, high salinity, high sodicity and low fertility; Khaitan et al., 2010; Jones and Haynes, 2011; Power et al., 2011; Santini and Fey, 2013). However, published literature on long term rehabilitation performance trajectories for diverse and extreme growth medium characteristics are scarce (Cortina et al., 2011), particularly for bauxite residue. This lack of information represents a major knowledge gap in designing rehabilitation protocols to obtain a sustainable vegetation cover (Torgersrud et al., 2019).

Numerous studies have investigated nutrient dynamics in bauxite residue (Thiyagarajan et al., 2009, 2011, 2012; Chen et al., 2009a, 2009b; Chen et al., 2013; Banning et al., 2010, 2014; Goloran et al., 2013; Goloran et al., 2014a, 2014b, 2014c, Goloran et al., 2015a, 2015b, 2015c; Goloran et al., 2017; Jones et al., 2010, 2011, 2012, 2015; Kaur et al., 2016). Many of these studies highlighted the importance of nutrient addition (organic and inorganic forms) to both establishing and sustaining a vegetation cover. Nitrogen contents of unamended bauxite residues are low, ranging from trace (Krishna et al., 2005) to 0.02% (Wong and Ho, 1993; Goloran et al., 2015a, 2015b). Cation nutrient imbalances can arise due to the dominance of sodium (Na) and aluminium, coupled with an abundance of calcium (Ca) resulting from gypsum amendment (Courtney and Timpson, 2005; Eastham et al., 2006, Eastham and Morald, 2006. Anderson et al., 2011) The dominance of Na, Al and Ca can induce deficiencies in other key nutrients such as magnesium (Mg) and potassium (K) unless supplements are added (Courtney and Timpson, 2005). Conversely, plant Na content in residue rehabilitation can decline following gypsum amendment (Courtney and Harrington, 2012) and age (Courtney and Kirwan, 2012; Di Carlo et al., 2020), primarily due to cation exchange (Ca:Na exchange) and/or subsequent leaching as the mobile species Na_2SO_4 and NaCl (Jones et al., 2015). The presence of amorphous Fe and Al oxides can limit plant nutrient availability due to specific adsorption mechanisms (e.g. phosphorus (P), copper (Cu), zinc (Zn), boron (B)) (Apak et al., 1998; Snars et al., 2004; Phillips and Chen, 2010). Therefore, in the absence of efficient nutrient cycling between the soil-water-plant systems, past research has suggested regular applications of fertiliser macro- and micro- nutrients may be required for sustained plant growth and recruitment in rehabilitated bauxite residue (Eastham et al., 2006; Courtney and Harrington, 2012).

Provision of adequate nutrients is essential as a residue rehabilitation goal (Grafe and Klauber, 2011) but published literature on long term monitoring of rehabilitation performance is scarce (Courtney et al., 2013; Bray et al., 2018; Courtney and Xue, 2019; Torgersrud et al., 2019). Consequently, understanding the magnitude and rate of changes in characteristics of both soil/residue growth medium and vegetation survival and succession is limited. This lack of understanding is compounded because soil and vegetation performance are often coupled. Therefore, establishing long term monitoring of rehabilitation performance, coupled with establishing quality criteria, is critical (Huang et al., 2012). Methodologies such as ecosystem function analysis to assess soil nutrient status in conjunction with plant performance for rangelands have been developed (Tongway and Hindley, 2004). This approach has been applied to ecosystem assessment through monitoring rehabilitated mine sites over time with target performance criteria established from analogue sites. However, identifying appropriate analogue sites is often difficult, particularly for long term monitoring (Tongway and Hindley, 2004). Therefore, studies with the capacity to study long term changes in rehabilitation performance criteria such as nutrient dynamics in association with an appropriate analogue site are essential for understanding ecosystem sustainability of degraded land.

The aims of this study were to quantify nutrient concentrations in rehabilitated bauxite-processing residue storage facilities of varying age, and to determine if nutrient deficiencies are limiting long term sustainability of the vegetation cover. This study targeted five key plant species (*Hardenbergia comptoniana*, *Acacia cochlearis*, *Acacia rostellifera*, *Grevillea crithmifolia* and *Spyridium globulosum*) and related plant nutrient contents to that of the residue sand to assess whether temporal changes in residue sand nutrient contents are limiting or favouring rehabilitation performance.

2. Materials and methods

2.1. Site description

Samples of bauxite-processing residue sand (BRS) and plant material were collected from Alcoa's Kwinana (KW; 32°12′04.73″S 115°49′08.60″E) and Pinjarra (PJ; 32°37′57.51″S 115°55′30.30″E) refineries in Western Australia. An analogue site, representing the Bassendean Dune System (AN; 32°12′40.78″S 115°49′14.64″E) was sampled from undisturbed bushland adjacent to the Kwinana RSA (McArthur and Bettenay, 1960). This site was selected based on similarities in general soil physical and chemical characteristics and climate between residue sand embankments and the natural environment of the coastal plain of south-west Western Australia. Previous studies found plant species native to the sandy soils of the coastal plain could establish and grow in gypsum-amended residue sand (Jasper et al., 2000; Outback Ecology, 2005). The vegetation of the areas sampled are characterized by Open Heath (≤1.7 m in height) of *Acacia rostellifera*, *Olearia axillaris, Melaleuca systena*, and *Spyridium globulosum* over open mixed herbs and sedges (Outback Ecology, 2005). The study region experiences a Mediterranean-type climate with a mean annual rainfall of 760 mm, which mainly falls during the winter months, and a mean annual temperature range of 10–29 °C.

2.2. Sampling protocol

Sampling at Kwinana was undertaken on residue sand embankments rehabilitated in 2004, 2006, 2008 and 2012, representing rehabilitation ages of 10, 8, 5 and 1 years, respectively. Sampling at Pinjarra was undertaken on embankments rehabilitated in 2004, 2006 and 2008, representing rehabilitation ages of 10, 8 and 5 years, respectively. The variation in age of rehabilitation arises because not all refineries had areas under rehabilitation across all years of investigation. Samples of gypsum, di-ammonium phosphate-based fertiliser and surface mulch were also collected due to the potential for these materials to supply plant nutrients in the short- and long- term. A sample of “freshly-deposited” residue sand was collected from each Refinery to highlight the initial properties of the growing medium prior to rehabilitation. Sampling at the analogue site was undertaken on the existing soil and vegetation and is assumed to represent nutrient concentrations typical of the native vegetation under long term growth.

2.2.1. Plant sampling

Five species of plants common to the analogue and RSA sites were selected for nutrient investigation. These were *Hardenbergia comptoniana* (*Harcom;* Fabaceae family), *Acacia cochlearis* (*Acacoc;* Mimosaceae family), *Acacia rostellifera* (*Acaros*; Mimosaceae family), *Grevillea crithmifolia* (*Grecri;* Proteaceae family), and *Spyridium globulosum* (*Spyglo;* Rhamnaceae family). These species were chosen to reflect the more common plant forms found in long term rehabilitation at Alcoa's RSAs, and plants having diverse physiology (Bell et al., 2008; Daws and Phillips, 2013). *Hardenbergia comptoniana* is a vigorous growing legume ground cover/creeper, *Acacia cochlearis* and *Acacia rostellifera* are both legume shrubs tolerant of sandy, alkaline conditions, *Grevillea crithmifolia* is a drought-tolerant proteaceous shrub that can grow in alkaline soil, and *Spyridium globulosum* is a robust, fast-growing shrub, commonly found on alkaline coastal soils.

A minimum of six plants of each selected species were identified for sampling at each location. Twenty-five recently matured leaf blades were sampled for each individual plant species (Reuter and Robinson, 1997), oven-dried at 60 °C and milled prior to nutrient analysis. The elemental composition of the leaf material was analysed for aluminium (Al), boron (B), copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), molybdenum (Mo), phosphorus (P) and sulfur (S) following digestion (aqua regia) using ICP-AES. Plant carbon (C) and nitrogen (N) were determined using a LECO combustion analyser.

2.2.2. Soil sampling

Residue sand was collected from embankments that had been rehabilitated following Alcoa's standard rehabilitation prescription: (1) incorporation of gypsum ($CaSO_4$) at 225 t/ha to approximately 1.5 m depth to reduce pH and sodicity, (b) incorporation of di-ammonium phosphate fertiliser (DAP at 2.7 t/ha) and micro-nutrients (copper, manganese, zinc, molybdenum) to approximately 0.2 m depth, (3) broadcasting of a seed mix containing 55 plant species native to the coastal plain (Bassendean Dune) ecosystems of Western Australia, (4) application of wood mulch to produce a surface layer of 0.1 m to provide dust suppression, and (5) planting of native seedlings known to not establish from the native seed mix. The five species selected in this study were established from seed (Banning et al., 2010).

Approximately 500 g of BRS were collected at depth intervals of 0–2 and 2 - 10 cm directly below plant canopies (Fig. S1). Soil samples were air-dried (25 °C for 48 h) and sieved (<2 mm) prior to analysis. Soil extractions were completed using the methods outlined by Rayment and Lyons (2011) for: total N (Dumas high-temperature combustion), mineral N (2 M KCl-extractable NH_4 and NO_3; measured colorimetrically using flow injection analysis); total P (sodium carbonate fusion); available P (0.5 M $NaHCO_3$ at pH 8.5), available S (0.25 M KCl at 40 °C); organic carbon (Dumas high-temperature combustion); EC (1:5 soil to water extract); pH (1:5 soil to water extract); DTPA extractable Cu, Zn, Fe and Mn (0.005 M DTPA); exchangeable Al (1 M KCl), Ca, Mg, Na and K (1 M ammonium chloride at pH 7, pre-treated for soluble salts). The effective cation exchange capacity was calculated as the sum of exchangeable cations.

2.2.3. Gypsum, fertiliser, “fresh” residue sand and mulch

Samples of gypsum, di-ammonium fertiliser, “freshly-deposited” residue sand, and wood mulch were collected from stockpiles at the Kwinana (KW) and Pinjarra (PJ) RSAs. Approximately 500 g of each material were randomly collected from within the stockpiles and composited to obtain a representative sample. The chemical composition of gypsum was determined by dissolving 0.2 g of gypsum in 100 mL of Milli-Q water (>18 MΩ) and analysing the filtrate (<0.45 μm) (Rayment and Lyons, 2011). Sodium (Na), magnesium (Mg), aluminium (Al), phosphorus (P), sulphate (SO_4), potassium (K), calcium (Ca), iron (Fe), boron (B), manganese (Mn), copper (Cu) and zinc (Zn) were determined using ICP-AES. Ammonium (NH_4) and nitrate (NO_3) were determined colorimetrically, and bicarbonate (HCO_3) and carbonate (CO_3) by titration to pH 4.5. Electrical conductivity (EC) and pH were measured using appropriate meters. The chemical composition of di-ammonium phosphate fertiliser and wood mulch were determined following digestion using aqua regia (Rayment and Lyons, 2011). The resulting solution was analysed for sodium (Na), magnesium (Mg), phosphorus (P), sulfur (S), potassium (K), calcium (Ca), iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) by ICP-AES. Total N was determined by combustion (950 °C in oxygen as the carrier gas) using a LECO FP- 428 Nitrogen Analyser.

Physical and chemical properties of “fresh” bauxite-processing residue sand have been reported previously (e.g. Chen et al., 2009a, 2009b) and can be summarised as: well-graded angular sand, extremely alkaline (pH >10), extremely saline (EC >11 dS/m), having poor nutritional value (total $N < 0.02\%$, total P ≈ 11 mg/kg, mineral nitrogen <2 mg/kg, EDTA- Cu, Zn and Mn <1 mg/kg, available P ≈ 4 mg/kg, available S ≈ 10 mg/kg) due to a very low organic carbon (organic C < 0.06%) content, a low CEC (<4 cmol/kg) dominated by Na (ESP = 69%), with lesser concentrations of Ca (30%) and Mg plus K (≈ 1%), and a P Buffering Index of ≈800 L/kg. Concentrations of nutrients in the pore water (saturated paste extract) and solid phases are provided for the “fresh” residue sand and the Kwinana analogue site (Tables 1 and 2).

2.3. Statistical analysis

Correlations between measured parameters were tested using Pearson's correlation ($p < 0.05$) and linear regression analysis using

Table 1
Pore-water nutrient concentrations in "fresh" residue sand, native sand (Analogue), and gypsum.

Parameter	Fresh residue sand	Analogue	Gypsum
Na (mg/L)	2357.7 ± 1042.2	46 ± 0	22.23 ± 16.94
Mg (mg/L)	6.71 ± 10.69	33.730 ± 0.31	1.21 ± 1.02
Al (mg/L)	12.75 ± 14.27	6.07 ± 0.455	0.92 ± 0.66
P (mg/L)	4.69 ± 4.75	47.65 ± 2.515	0.29 ± 0.3
SO_4 (mg/L)	769.28 ± 810.89	0.38 ± 0.091	592 ± 10.2
Cl (mg/L)	21.91 ± 6.88	9.27 ± 0.615	0.21 ± 0.34
K (mg/L)	30.29 ± 25.55	58.66 ± 0.560	1.25 ± 0.17
Ca (mg/L)	51.08 ± 121.56	5.94 ± 0.968	431 ± 14
Fe (mg/L)	4.14 ± 4.15	20.25 ± 1.77	0.09 ± 0.14
NH_4-N (mg/L)	0.34 ± 0.201	21.10 ± 0.655	0.09 ± 0.03
NO_3-N (mg/L)	0.86 ± 1.108	5.58 ± 1.47	0.01 ± 0.01
EC (mS/m)	5904.02 ± 5843.86	0.017 ± 0.014	224 ± 3
pH	9.17 ± 0.851	6.22 ± 0.11	6.6 ± 0.13
HCO_3 (mg/L)	468.6 ± 226.9	30.54 ± 1.273	27.44 ± 1.32
CO_3 (mg/L)	10,860 ± 10,070	7.18 ± 3.90	0.01 ± 0.01
B (mg/L)	nm	nm	0.13 ± 0.02
Mn (mg/L)	nm	nm	0.25 ± 0.01
Cu (mg/L)	nm	nm	0.15 ± 0.02
Zn (mg/L)	nm	nm	0.25 ± 0.01

nm = not measured.

the software package *Statistix* version 10 (Analytical Software, 2020). Concentrations of nutrients for leaf, residue sand and natural sand samples were statistically analysed using analysis of variance (General linear model; *Statistix* version 10). Significant differences between the main treatments were separated using least significant differences (LSD $p < 0.05$) to test if (a) leaf nutrient concentrations varied significantly ($p < 0.05$) between site, plant species and age (i.e. *Site* x Rehabilitation Age x Plant species), and (b) nutrient concentrations of 10-year old rehabilitation were significantly ($p < 0.05$) to those of the analogue site.

3. Results

3.1. Properties of "fresh" residue sand, native sand (analogue), and gypsum

Pore-water extracted from "fresh" residue sand was extremely saline and alkaline, and dominated by Na, CO_3, HCO_3 and SO_4, with minor contributions from Al, Cl, K and Ca (Table 1). In contrast, pore-water for soil from the analogue site exhibited relatively low salinity and alkalinity, was dominated by Na, Mg, P, K, HCO_3, and contained nearly 30 mg/L of mineral N, primarily as the NH_4 species.

Gypsum was slightly acidic (pH 6.6) and dominated by Ca and SO_4, with lesser amounts of Na and HCO_3, and, albeit at low concentrations, P, Mn, Zn, Cu and B (Table 1). The presence of P is a consequence of this material being a by-product from superphosphate fertiliser manufacturing and is more commonly referred to as phosphogypsum. Di-ammonium phosphate-based fertiliser was dominated by N, P, K and S (Table 2), along with significant amounts of trace elements (i.e. Cu, Zn, B, Mo and Mn). Surface mulch contained approximately 0.25 and 0.03% total N and total P, respectively (Table 2).

The C:N ratio tended to decrease with age (i.e. C:N ≈ 167 for mulch <1 year old, and ≈64 for mulch 10 years old), due to a decrease in total C and a slight increase in total N. Changes in other macro-nutrients such as P, K, S, Cl, Ca, Mg and Na were more variable, for example, K, Cl and Na tended to decline with age, while Ca increased.

Table 2
Mean (n = 2) chemical composition of mulch of varying age and di-ammonium based fertiliser (DAP).

	Mulch age (years)				DAP
	0.1	5	8	10	
Total C (%)	44.3 ± 0.8	30.8 ± 3.0	20.8 ± 1.9	24.6 ± 3.6	nm
Total N (%)	0.26 ± 0.30	0.24 ± 0.03	0.10 ± 0.06	0.39 ± 0.40	9.98 ± 0.1
Total P (%)	0.03 ± 0.04	0.03 ± 0.01	0.02 ± 0.01	0.04 ± 0.04	12.11 ± 0.28
K (%)	0.20 ± 0.26	0.06 ± 0.01	0.04 ± 0.01	0.05 ± 0.04	10.95 ± 2.05
S (%)	0.05 ± 0.04	0.16 ± 0.02	0.05 ± 0.01	0.08 ± 0.06	8.20 ± 1.13
Cl (%)	0.14 ± 0.16	0.04 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	nm
Ca (%)	0.98 ± 1.24	1.06 ± 0.34	0.77 ± 0.23	1.34 ± 1.54	1.07 ± 0.63
Mg (%)	0.07 ± 0.07	0.05 ± 0.01	0.05 ± 0.02	0.06 ± 0.04	1.02 ± 0.59
Na (%)	0.07 ± 0.08	0.05 ± 0.01	0.02 ± 0.01	0.03 ± 0.02	0.21 ± 0.01
Al (%)	0.67 ± 0.09	3.25 ± 1.13	4.85 ± 1.91	5.60 ± 3.26	nm
B (mg/kg)	9.1 ± 8.4	15.2 ± 0.7	15.5 ± 0.7	25.5 ± 4.9	300 ± 56
Cu (mg/kg)	4.1 ± 0.9	7.1 ± 3.1	6.7 ± 1.9	16.5 ± 10.6	750 ± 354
Mn (mg/kg)	19.5 ± 4.9	48.5 ± 19.1	59.5 ± 2.1	84.5 ± 10.6	850 ± 215
Mo (mg/kg)	3.4 ± 0.9	5.5 ± 2.1	5.5 ± 0.7	15.8 ± 12.7	25.6 ± 2.5
Zn (mg/kg)	15.1 ± 16.8	17.0 ± 3.5	16.6 ± 2.8	25.1 ± 7.1	1000 ± 90

nm = not measured.

3.2. Effect of age on residue rehabilitation

3.2.1. Residue sand properties

3.2.1.1. Nutrient content. Total C generally increased with age of rehabilitation, although the magnitude of increase was often not significant ($p < 0.05$; Fig. 1). Values increased from about 0.6% in 1-year old rehabilitation to ≈1% for older (≥8-year old) rehabilitation in the 0–2 cm depth, but remained ≈0.2% in the 2–10 cm depth across all ages of rehabilitation.

Total N in residue sand followed similar trends to total C (Fig. 1). Values increased from ≈0.02% in 1-year old rehabilitation to 0.04–0.05% for older rehabilitation (≥8 years old) in the 0–2 cm layer, with smaller increases observed in the 2–10 cm layer. Changes in total C and total N were reflected in the C:N ratio, which decreased from about 40 for 1-year old rehabilitation to 21 for 10-year old rehabilitation in the 0–2 cm depth, and from 34 to 14, respectively, in the 2–10 cm depth.

Mineral N (NH_4 and NO_3) as a function of rehabilitation age displayed similar trends to total N (Fig. 1). In the early stage of rehabilitation (≤5 years old), NH_4 concentrations were not significantly ($p < 0.05$) different between the 0–2 and 2–10 cm depths; however, for older rehabilitation NH_4 concentrations were higher in the surface layer, although the differences between means were not significant. Nitrate concentrations were typically low for all ages of rehabilitation, ranging from 0.5 to 2 mg/kg. Although NO_3 concentrations suggested this nutrient was increasing with age of rehabilitation, the magnitude of increase was not statistically significant ($p < 0.05$).

Total P concentrations increased significantly ($p < 0.05$) in 5-year old rehabilitation compared with 1-year old rehabilitation (Fig. 1). In older rehabilitation, total P significantly declined to concentrations not significantly ($p < 0.05$) different to concentrations measured in 1-year old rehabilitation. This behaviour was observed in both the 0–2 and 2–10 cm depths.

Available P displayed similar trends to that observed for total P, although concentrations were about an order of magnitude lower (Fig. 1). Available P concentrations were not significantly different between the two depth intervals, which is not unexpected given the method of P incorporation as fertiliser and as a component of gypsum.

Residue sand pH and EC displayed little variation with age, with values in the range of 7.5–8.4 (pH) and 0.5–2 dS/m (EC) (Fig. 2). Available S concentrations declined with age of rehabilitation, decreasing from >1000 mg/kg to <200 mg/kg over the 10-year age period (Fig. 2). The concentrations of exchangeable cations (Ca, Mg, K, Na and Al) remained relatively constant with rehabilitation age for both depth intervals (Fig. 3). The ECEC was dominated by Ca with only minor contributions from the remaining cations.

Micro-nutrient (Cu, Zn, Mn, B and Fe) concentrations remained relatively constant with rehabilitation age for both depth intervals (Fig. 4).

Pearson correlation coefficients show total C was positively correlated ($p < 0.05$) with many key nutrients, in particular total and mineral

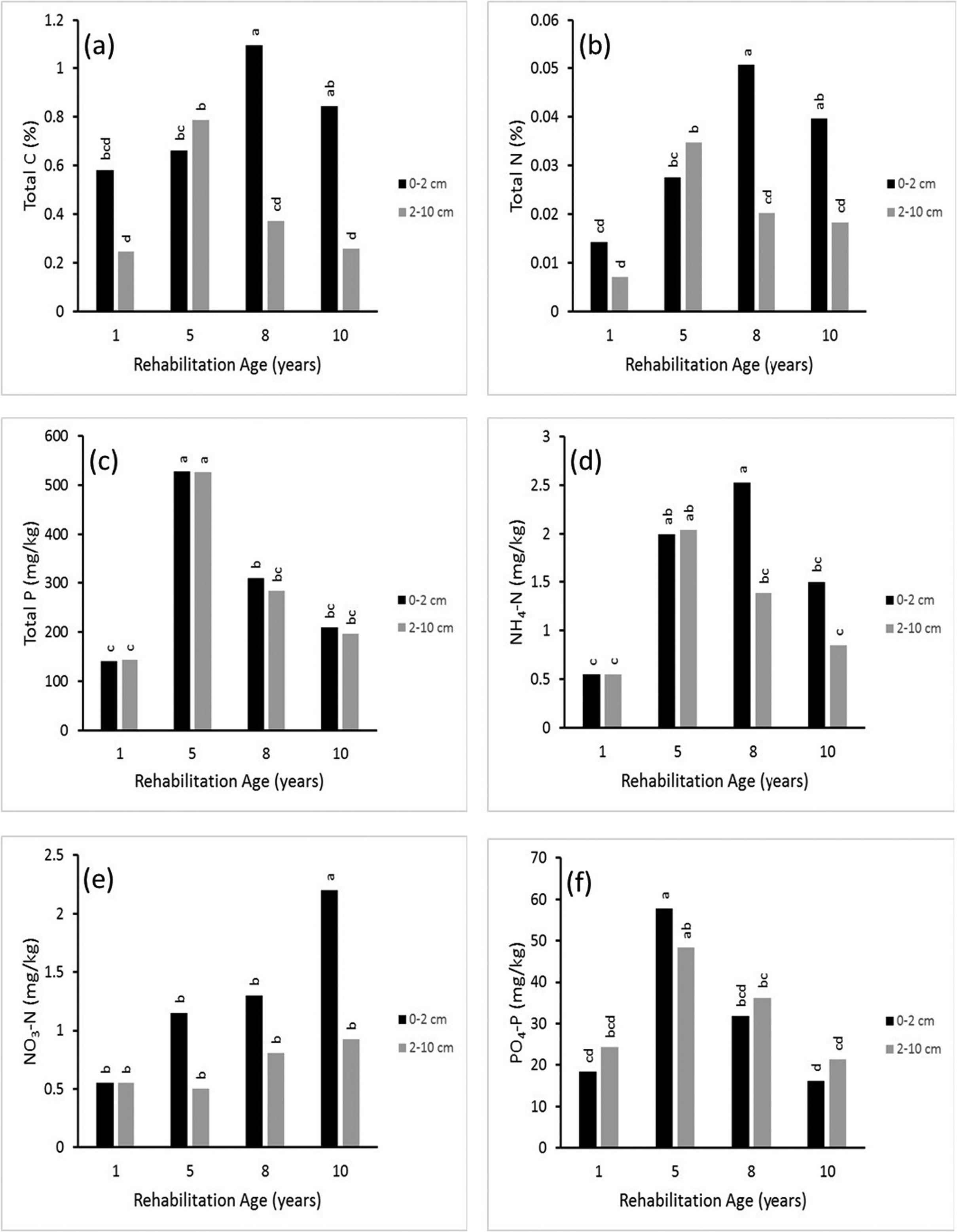

Fig. 1. Effect of age of rehabilitation on (a) total C, (b) total N, (c) total P, (d) NH_4-N, (e) NO_3-N and (f) PO_4-P concentrations in residue sand. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

N, total P, basic cations, and micro-nutrients, and negatively correlated with pH (Supporting Information Table S1). Available P was positively correlated with available S, exchangeable Ca and micro-nutrients B, Cu, Zn and Mn. Since DAP also contained elevated concentrations of micro-nutrients, positive correlations with Cu, Zn, Mn, and Fe are not unexpected.

3.2.1.2. Comparing 10 year old rehabilitation with analogue site. The analogue site contained significantly ($p < 0.05$) higher levels of total C and total N than 10-year old rehabilitation for both the 0–2 and 2–10 cm depths (Table 3). Mineral N concentration however was very similar between sites. In contrast, total P, available P, and available S concentrations

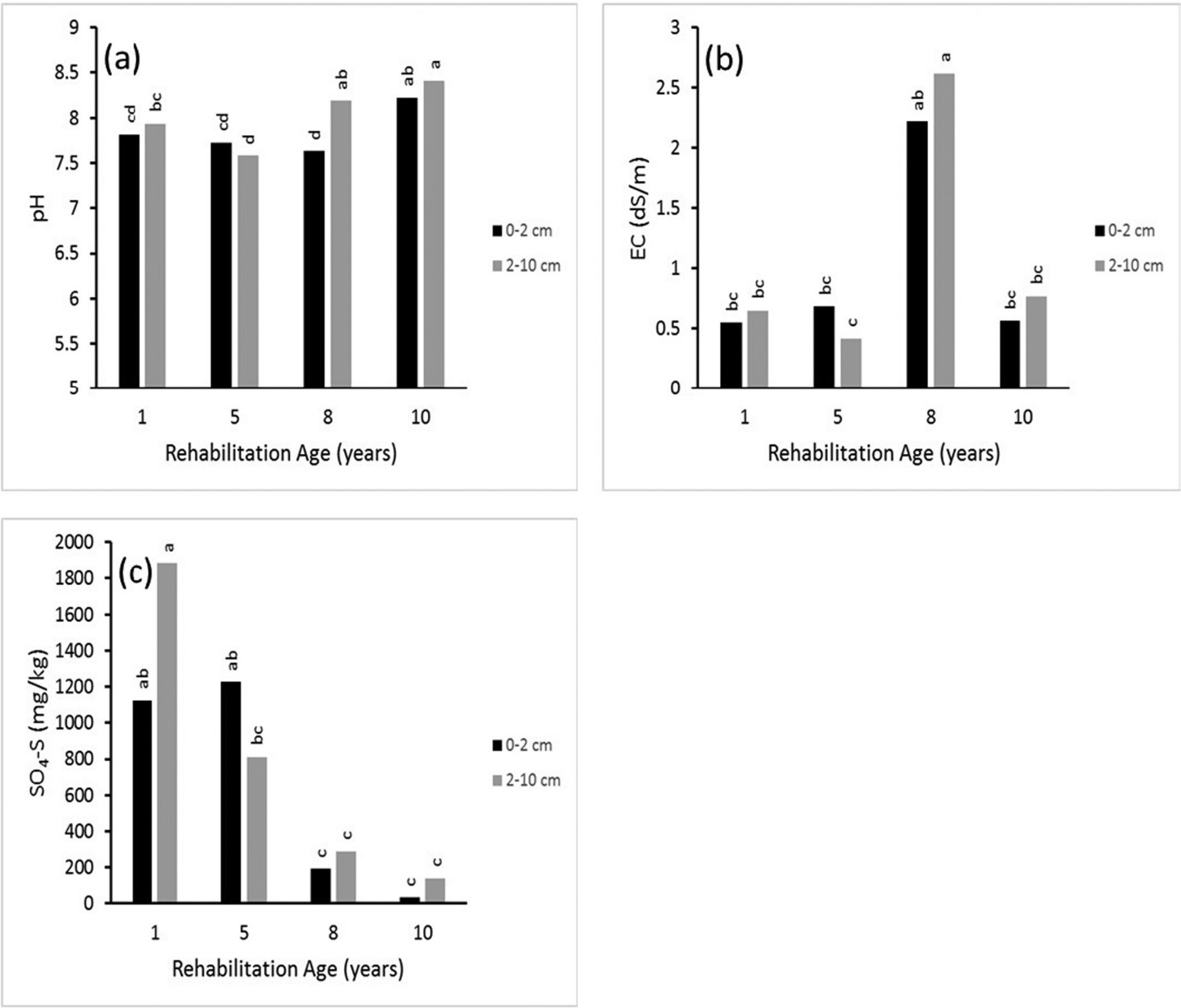

Fig. 2. Effect of age of rehabilitation on (a) pH, (b) EC and (c) SO_4-S concentrations in residue sand. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

were higher in residue sand but often the differences between sites were not significant ($p < 0.05$).

Exchangeable cation concentrations were relatively similar between the analogue and residue rehabilitation sites. Generally, micro-nutrient concentrations in the analogue and residue sites were not significantly ($p < 0.05$; Table 3) different. Nutrient concentrations were consistently higher, albeit non-significantly, in the 0–2 cm depth.

3.2.2. Leaf material

3.2.2.1. Nutrient content. The concentrations of nutrients in leaf material from the five selected plant species for each rehabilitation age is presented in Fig. 5. Leaf C was relatively similar across all rehabilitation ages but was marginally lower (≈43%; $p < 0.05$) in the two acacia species compared to the other species (≈47%).

Leaf N tended to be higher in the leguminous species (mean = 2.2%N for *A. cochlearis*, *A. rostellifera* and *H. comptoniana*) compared to non-legumes (mean = 1.3%N for *G. crithmifolia* and *S. globulosum*) (Fig. 5). Leaf P concentrations tended to increase with age of rehabilitation, although differences between species and age were often not significant ($p < 0.05$; Fig. 5). The mean leaf P content of the legume species (mean = 0.14%) was higher than that for the non-legumes (mean = 0.11%). Leaf Cl was typically <1% in all species irrespective of age (Fig. 5). The only exception was *A. cochlearis* which contained ≈2% Cl in 1-year old rehabilitation.

Leaf macro-nutrient concentrations typically followed the order: Ca > > K > Na ≈ Mg (Fig. 6) and this reflected the dominance of Ca in the residue sand (Tables 1 and 3). Interestingly, the acacia species contained relatively higher Ca and lower K than the other three species. Leaf Al generally was in the range of 100–200 mg/kg and displayed no significant difference between species irrespective of age (Fig. 6).

Leaf micro-nutrients (Cu, Zn, Mo, Mn, B and Fe) tended to show slight but often non-significant increases with rehabilitation age (Fig. 7). Concentrations generally followed the order: Fe > Mn ≈ Zn ≈ B > Cu ≈ Mo, and this reflected the availability of these nutrients in residue sand. The main exception was B which exhibited concentrations of <0.2 mg/kg in residue sand, but leaf concentrations between 15 and 30 mg/kg, depending on individual species.

When leaf N:P ratios are plotted against leaf N and leaf P (Fig. 8), leaf N is positively, and leaf P negatively, correlated with N:P. Since N:P mass ratios declined with rehabilitation age, it follows that N uptake declines and/or P uptake increases with age, and variation in N:P ratios among each of the selected species therefore may be driven by each species physiological ability to both extract and utilize the available nutrients. For example, the legumes species *A. cochlearis*, *A. rostellifera*, and *H. comptoniana* tended to have higher N:P ratios than non-legumes *G. crithmifolia*, and *S. globulosum*. In terms of other macro-nutrients, the N:P ratio displayed a negative correlation with leaf K (Fig. 8). If this pattern is consistent with that of leaf P, then any potential decline in N uptake may be a consequence of increased K availability.

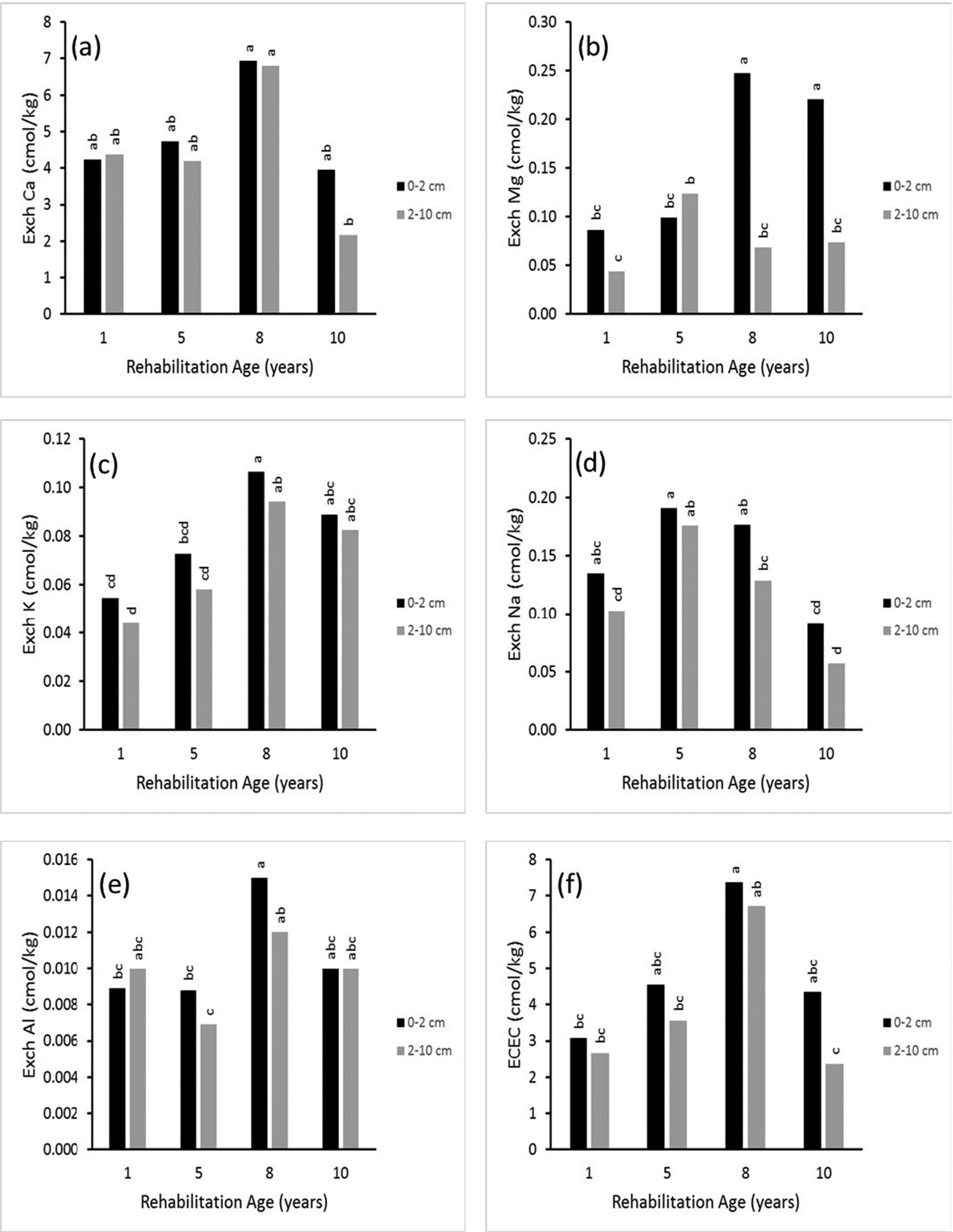

Fig. 3. Effect of age of rehabilitation on exchangeable (a) Ca, (b) Mg, (c) K, (d) Na, (e) Al concentrations, and (f) ECEC of residue sand. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

Leaf K:Ca molar ratios (Fig. 9) were significantly higher for *H. comptoniana* than the remaining species, particularly for *A. cochlearis*, *A. rostellifera* and *Grevillea crithmifolia*. Similar patterns were also observed for Na:Ca and Mg:Ca molar ratios (data not presented), suggesting an apparent preferential uptake of K, Na and Mg relative to Ca by *H. comptoniana*, or possibly this species re-distributes nutrients within the plant parts differently to the other species.

The relationship between leaf K:Ca molar ratio and leaf K and Ca contents show leaf K was positively correlated and leaf Ca negatively correlated with K:Ca (Fig. 9). This suggests increasing leaf K and

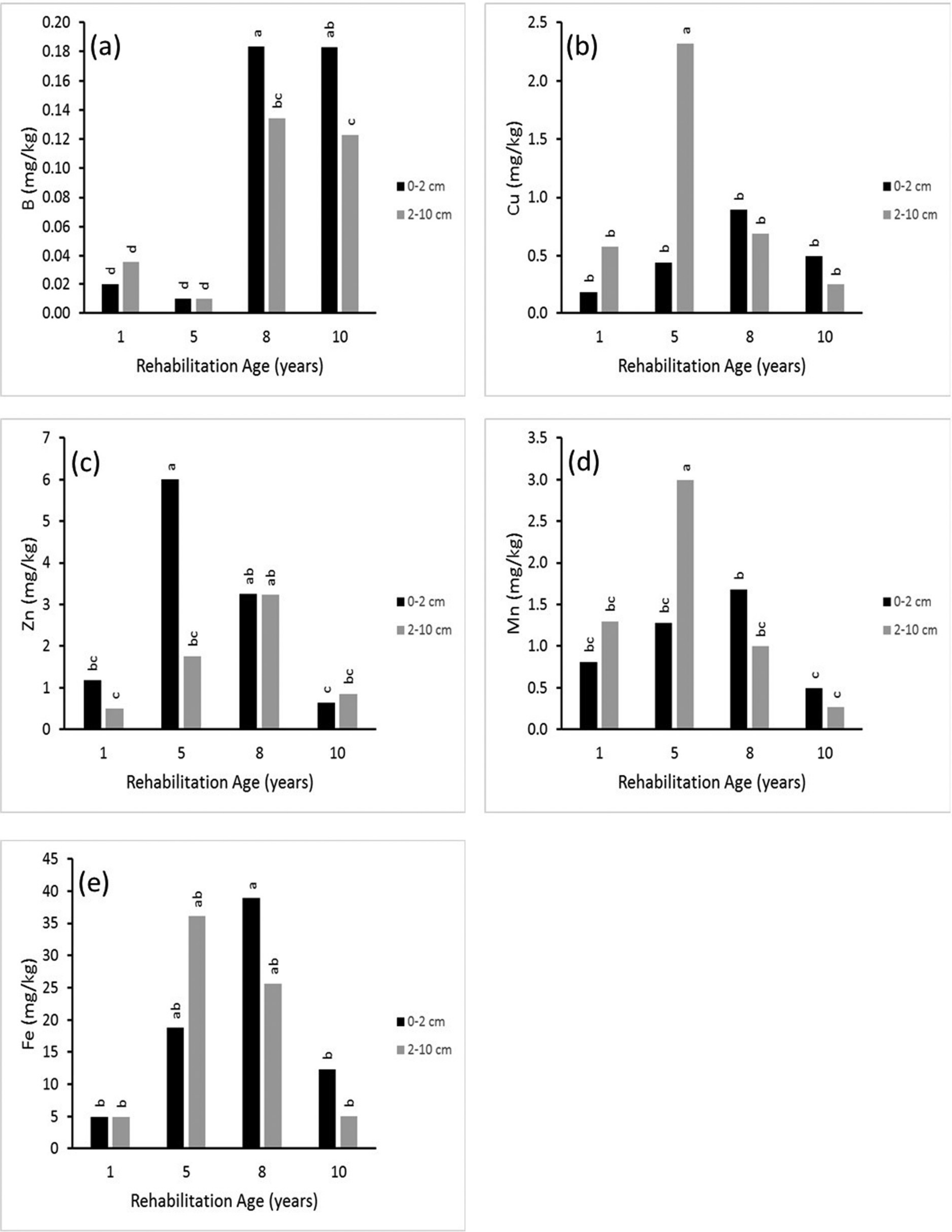

Fig. 4. Effect of age of rehabilitation on (a) B, (b) Cu, (c) Zn, (d) Mn and (e) Fe concentrations in residue sand. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

decreasing leaf Ca with rehabilitation age, a trend supported by changes in exchangeable K and Ca respectively (Fig. 3).

Leaf nutrient concentrations in 10-year old rehabilitation were very similar to those measured in the analogue site (Table 4). Leaf N and P for both the 10-year old rehabilitation and analogue species were close to the mean global values of 1.89 and 0.12%, respectively (Table 4).

Pearson correlation coefficients (Supporting Information Table S1) show leaf N was positively correlated ($p < 0.05$) with many key nutrients, such as P, K and S. Leaf P was also positively correlated with B,

Table 3
Comparison of residue sand properties under 10-year old rehabilitation and analogue sand. For each parameter, values designated by the same letter are not significantly different ($p < 0.05$).

	Analogue		RSA		LSD
	0–2 cm	2–10 cm	0–2 cm	2–10 cm	($p < 0.05$)
Total C (%)	2.41 a	1.35 b	0.85 c	0.26 d	0.46
Total N (%)	0.111 a	0.053 b	0.038 b	0.017 c	0.035
Total P (mg/kg)	59.5 b	37.0 b	209.3 a	196.9 a	120.2
pH	6.63 b	6.51 b	8.23 a	8.42 a	0.47
EC (dS/m)	0.042 b	0.025 b	0.567 a	0.771 a	0.661
NH_4 (mg/kg)	2.55 a	0.58 c	1.51 b	0.85 c	0.54
NO_3 (mg/kg)	2.50 a	2.28 ab	2.21 a	0.93 b	1.95
Avail P (mg/kg)	3.6 b	1.5 b	16.3 ab	21.4 a	19.6
Avail S (mg/kg)	5.5 a	3 a	33.07 a	140.52 a	316.73
Exch Ca (cmol/kg)	6.90 a	5.75 ab	3.96 ab	2.17 b	4.70
Exch Mg (cmol/kg)	0.77 a	0.79 a	0.22 b	0.07 b	0.33
Exch K (cmol/kg)	0.05 a	0.03 a	0.09 a	0.08 a	0.08
Exch Na (cmol/kg)	0.13 a	0.13 a	0.09 a	0.05 a	0.15
Exch Al (cmol/kg)	0.02 b	0.05 a	0.01 c	0.01 c	0.01
ECEC (cmol/kg)	7.86 a	6.76 a	4.35 ab	2.37 b	4.39
B (mg/kg)	0.05 b	0.05 b	0.20 a	0.14 b	0.12
Cu (mg/kg)	0.05 a	0.05 a	0.52 a	0.27 a	1.52
Zn (mg/kg)	1.70 a	0.35 b	0.64 b	0.85 ab	1.27
Mn (mg/kg)	8.25 a	2.12 b	0.49 b	0.26 b	2.53
Fe (mg/kg)	19.57 a	17.63 ab	12.35 b	5.03 c	6.75

Cu, Mo and Zn. Leaf Al was negatively correlated with most nutrients. Interestingly, leaf Ca was positively correlated with leaf S but negatively ($p < 0.05$) correlated with leaf K (Supporting Information Table S2). This suggests excess Ca following gypsum dissolution may have a depressive effect on K uptake possibly due to out-competing K as a balancing cation in maintaining electro-neutrality in anion (e.g. Cl, NO_3, SO_4, H_2PO4/HPO_4) uptake from the rhizosphere. The positive correlation between Ca, Mg and S with Cl may indicate that Cl and S (as SO_4) may have been the major anions balancing cation uptake by the vegetation. Linear regression of the sum of leaf Ca and leaf K against leaf Cl + leaf S (on a "moles" basis) yielded the relationship:

$$\text{leaf } (S + Cl)\ (\text{moles}) = 1.085 \times \big(\text{leaf } (Ca + K)\ (\text{moles}) - 0.0677;\ r^2 = 0.78$$

4. Discussion

4.1. Nutrient concentrations for "fresh" residue sand, native sand (Analogue), and gypsum

Chemical composition of 'fresh' bauxite residue is consistent with the published literature (Grafe and Klauber, 2011; Grafe et al., 2011; Jones and Haynes, 2011) and presents a hostile environment for plant establishment. Application of amendments to address extreme chemical conditions and to provide a supply of plant available nutrients achieved similar results to those previously reported (e.g Snars et al., 2004; Bray et al., 2018). Gypsum is effective in addressing excess alkalinity and sodicty (Eastham and Morald, 2006; Eastham et al., 2006) with nutrient supply provided through fertiliser applications.

4.2. Effect of age on residue rehabilitation

4.2.1. Residue sand

Both pH and EC were expected to decline with age (Goloran et al., 2015a, 2015b); pH due to leaching of soluble alkalinity, calcite precipitation, atmospheric and biological carbonation, organic matter decomposition and/or plant root exudates; and EC via leaching of excess salinity. Long term monitoring demonstrated a sustained decrease in residue pH to below 9.0 as recommended by Grafe and Klauber et al. (2011) and reported for 16-years old rehabilitation (Bray et al., 2018). These findings demonstrate gypsum amendment coupled with nutrient supply can achieve the primary objectives of rehabilitation criteria. Furthermore, residue pH under legume (acacias and grevillea) species was found to be lower (pH 7.5) than under non-legumes (pH 8) (data not presented), and is consistent with the known ability of legumes to reduce soil pH (Touhami et al., 2020).

It is evident from this long term residue monitoring study that increasing organic carbon is closely linked to increased plant nutrient availability and a decline in pH. Decomposition of organic matter from plant roots, surface mulch and litter fall is a potential source of organic carbon in the presence of an active microbial community. Organic carbon can subsequently be complexed with and/or sorbed by the amorphous Fe and Al coatings on residue sand (Theng, 1980), while mineralisation can increase nutrient availability and reduce pH. Banning et al. (2010) identified the presence of arbuscular mycorrhizal fungi and ammonia-oxidizing bacteria populations in residue sand under rehabilitation, which implied functional potential in the development of plant symbioses and nutrient cycling processes, respectively. Effects of vegetation on reducing pH may be attributed to root respiration and the production of CO_2, removal of basic cations (i.e. Ca and Mg) from organic matter and sparingly soluble carbonate precipitates, and the release of H ions following dissociation from acid functional groups from plant roots (Khaitan et al., 2010; Tang and Rengel, 2003).

Various factors could be contributing to the gradual increase in total C with age, such as increasing below-ground biomass with plant root growth and architecture (Supporting Information Fig. S1), decomposition of overlying wood mulch and incorporation of decomposition products into the surface layer, washing of fine organic materials from the mulch into the surface layer via rainfall leaching, decaying litter-fall from the vegetation cover, and/or incorporation of organic materials via bioturbation (Southwell and Majer, 1982; Ossai, 2015; Courtney et al., 2018; Di Carlo et al., 2020). Furthermore, residue sand contains about 5% of amorphous Fe and Al oxides and hydroxides. The strong adsorption of organic carbon by amorphous material (Theng, 1980) would favour retention of organic C in the upper (0–2 cm) layer of the residue sand profile. Total C levels measured in the older rehabilitation (≥8 years old) were similar to levels reported by Thomoson (2012).

The primary sources of nitrogen in the older rehabilitation most likely include decomposition of surface mulch (total N ≈ 0.2–0.4%; Table 2) and plant litter fall. Litter decomposition products from legume species within the rehabilitation capable of N-fixation (e.g. *Hardenbergia comptoniana*, *Acacia cochlearis* and *A. rostellifera*) may provide significant N contributions to the underlying residue sand. The presence of mineral N in the older rehabilitation, albeit in very low concentrations, is a good indicator of the presence of a functioning microbial community in residue sand. Banning et al. (2010) found evidence of changes in microbial community structure with rehabilitation age for both arbuscular mycorrhizal fungi and ammonia-oxidizing bacteria populations, suggesting successional processes were occurring, potentially in response to the changing chemical characteristics of residue sand. Furthermore, Banning et al. (2010) reported a decline in the microbial metabolic quotient with increasing age of residue sand suggesting a potential alleviation of microbial stress with rehabilitation age.

Plant nutrient uptake is highly dependent on nutrient availability, which is dependant, among other factors, on the C:N ratio. A ratio of approximately 20:1 often distinguishes between immobilisation (high $C:N > 20$) and mineralisation (low $C:N < 20$). The C:N ratio in the 0–2 cm depth suggests N immobilisation may dominate during the early stage of rehabilitation (≤1-year old), with N mineralisation dominating in older rehabilitation. Given active microbial respiration activity has been measured in residue rehabilitation <6 months in age (Banning et al., 2010), inorganic N concentrations in the residue (as NH_4 and/or NO_3) may be low due to preferential use by the biota. Under these conditions, plant available mineral N would also be expected to be low. Whether the declining C:N ratio with age has significantly

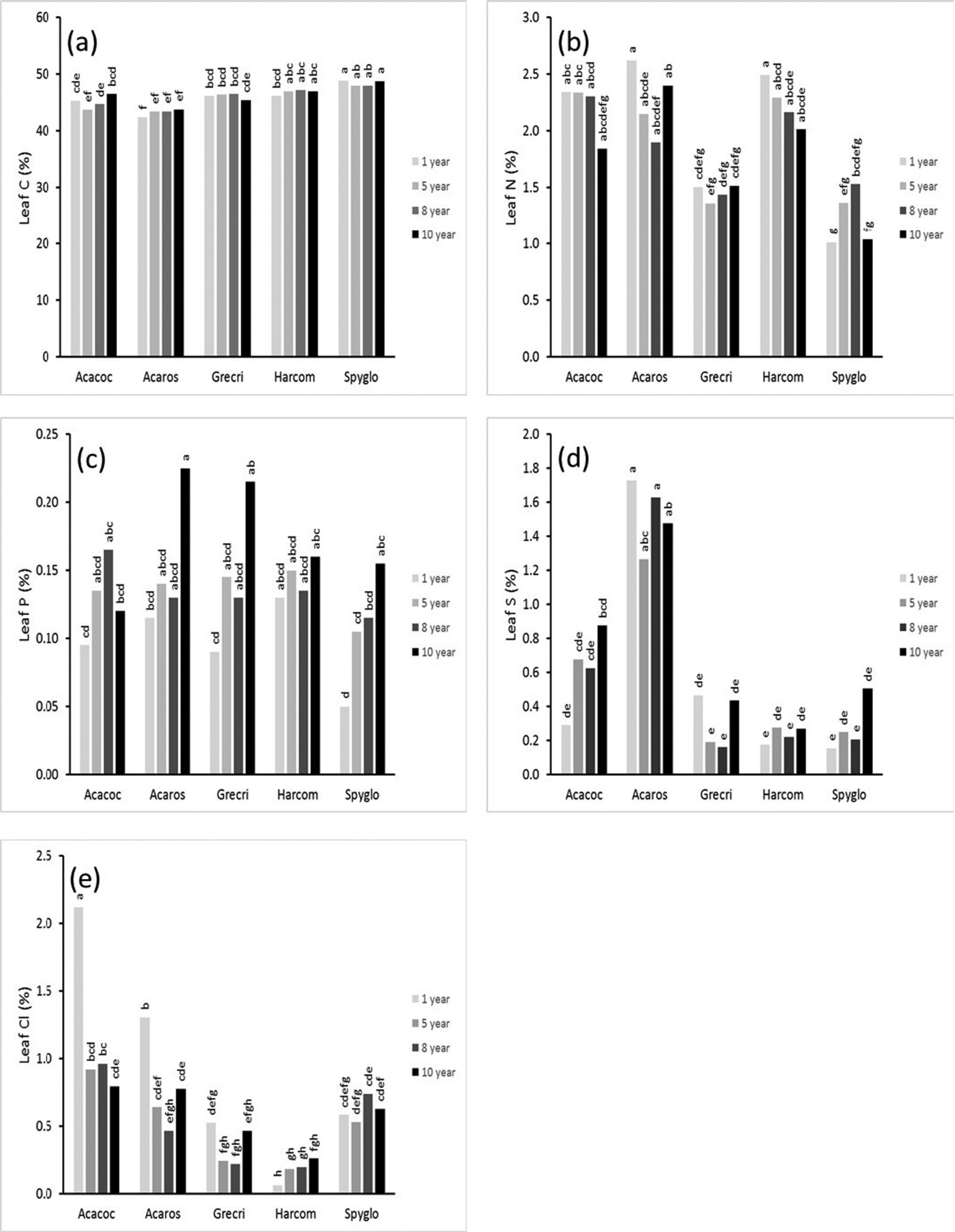

Fig. 5. Effect of age of rehabilitation on (a) C, (b) N, (c) P, (d) S and (e) Cl content in leaf material from the five selected plant species. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

influenced N (and other nutrients) availability in the plant cover was not investigated in this study.

The measured variation in total P may be linked with the initial distribution of this nutrient in the residue sand profile rather than through direct nutrient cycling. Firstly, P retention is very strong in residue sand due to the presence of hydrous Fe and Al oxides and hydroxides (Phillips and Chen, 2010) which implies higher P concentrations should be detected in the 0–2 cm depth if P levels were primarily driven by organic matter decomposition and nutrient cycling. Secondly, the primary sources of P are DAP fertiliser and gypsum (Tables 1 and 2) and these

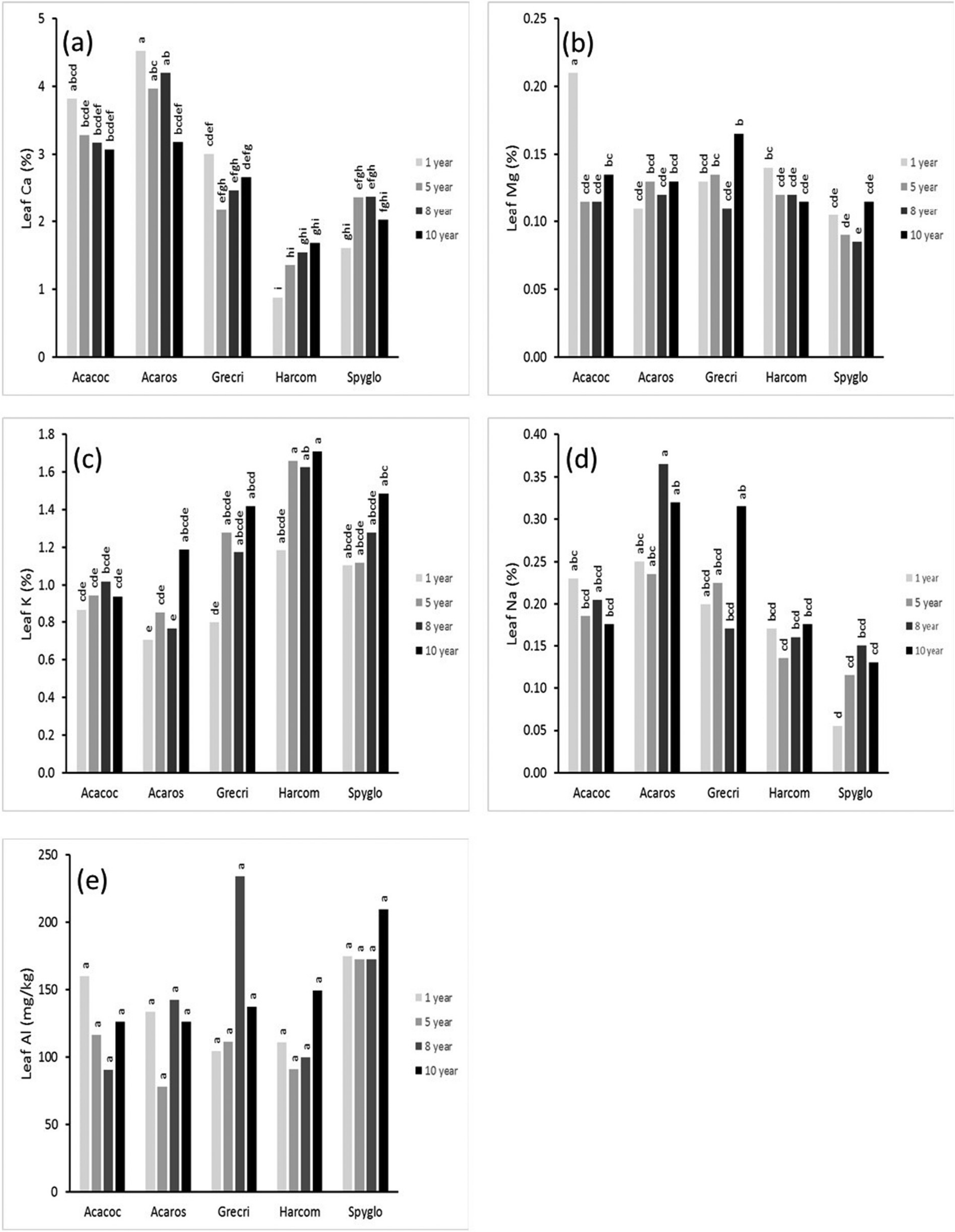

Fig. 6. Effect of age of rehabilitation on (a) Ca, (b) Mg, (c) K, (d) Na and (e) Al content in leaf material from the five selected plant species. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

materials are distributed within the 0–30 and 0–150 cm depths of the residue sand profile, respectively. Various plant species have developed sophisticated root systems capable of extracting P from "unavailable" sources such as Fe-, Al- and Ca- phosphate precipitates. Specifically, proteaceae species have developed proteoid or cluster root systems which release organic acids (e.g. carboxylates) capable of solubilising inorganic P from Fe-, Al- and Ca- phosphates (Shane et al., 2004; Lambers et al., 2012). The presence of proteaceae species in the rehabilitation such as *Hakea prostrata*, *H. lissocarpha*, *H. trifurcata*, *Grevillea crithmifolia*, and *G. thelemanniana*, along with some casuarina and

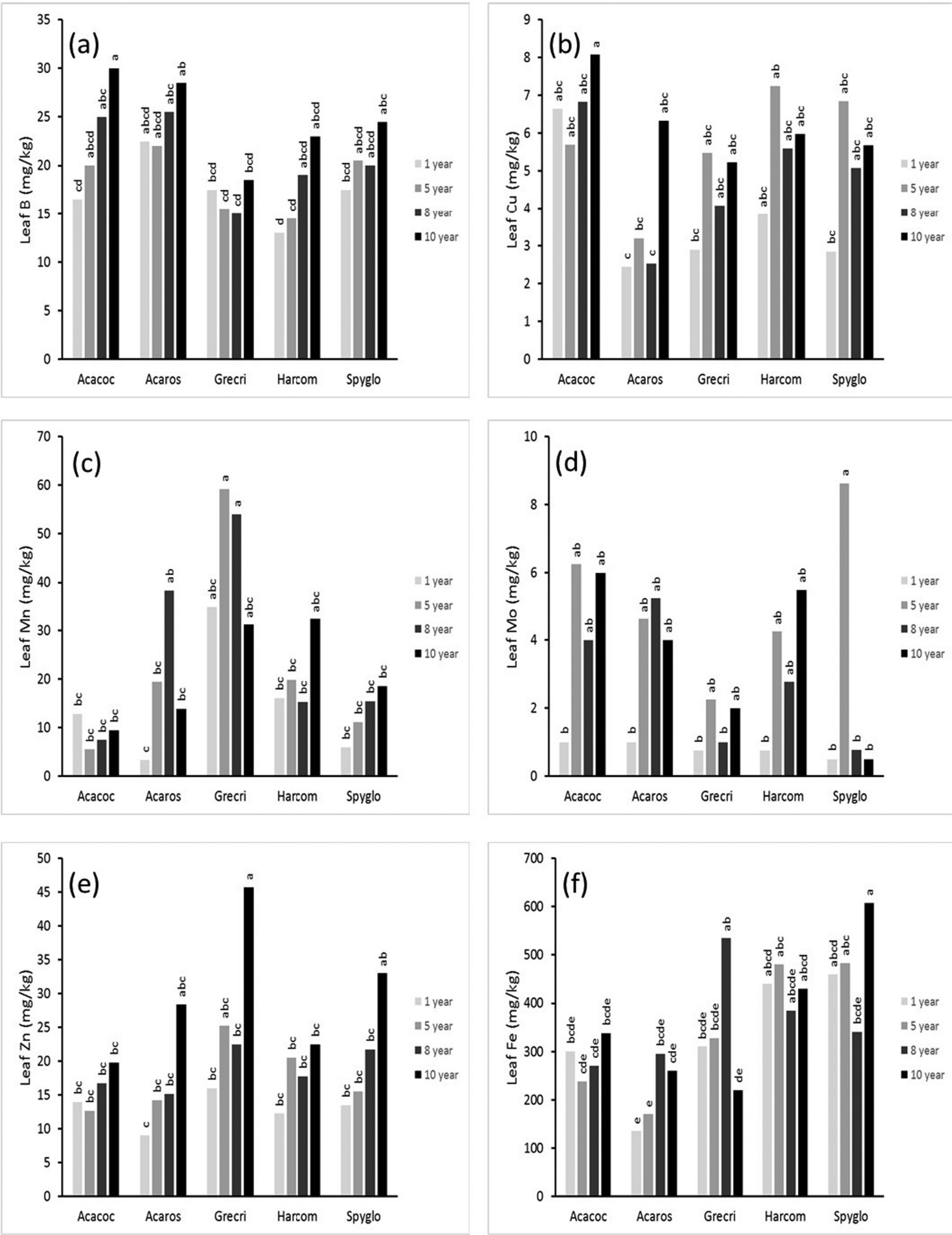

Fig. 7. Effect of age of rehabilitation on (a) B, (b) Cu, (c) Mn, (d) Mo, (e) Zn and (e) Fe content in leaf material from the five selected plant species. Bars designated by the same letter are not significantly different (LSD; $p < 0.05$).

legumes species with proteoid roots (e.g. *Kennedia prostrata*; Groom and Lamont, 2015) may be contributing to the decline in total P.

Lambers et al. (2012) observed release of sorbed P by proteaceae species, but found *Lupinus* species can also release organic acids (e.g. carboxylate) into the rhizosphere thereby mobilising sparingly soluble P sources. These workers concluded that a close relationship between the N-fixation capability of legumes and P mobilization may play an important role in remediation and rehabilitation of degraded land.

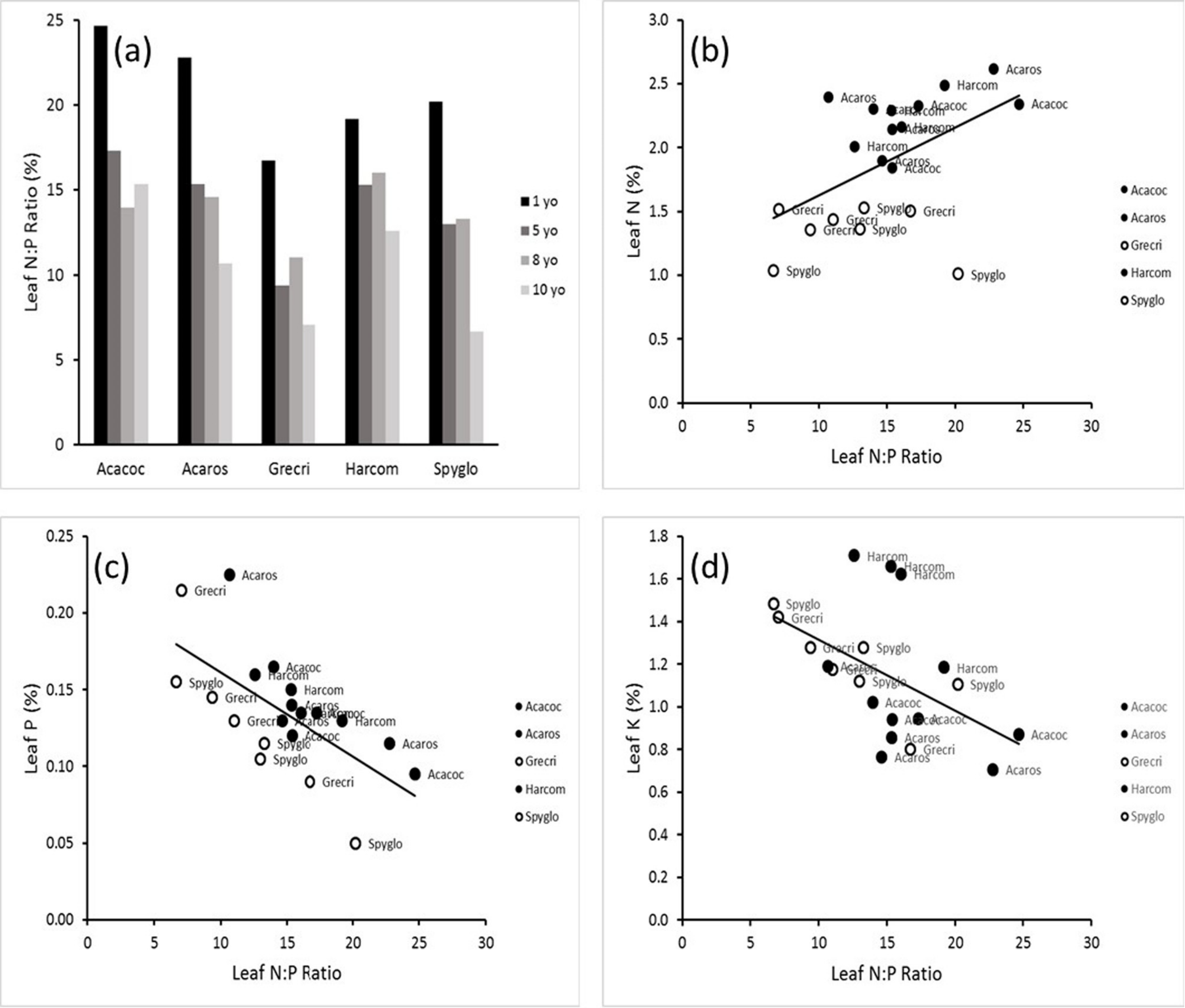

Fig. 8. (a) Effect of age on leaf N:P mass ratio for the five selected plant species; relationships between leaf N:P mass ratios and leaf (b) N, (c) P and (d) K. ● indicates legume species and ○ indicates non-legume species.

Recently, Touhami et al. (2020) demonstrated a significant decrease in rhizosphere pH, coupled with increased release of P from moderately labile inorganic (Fe-, Al- and Ca-) and stable organic P fractions of soil. The increased availability of P and decline in pH was attributed to the release of organic acidic anions (citrate and malate) from plant roots. The combination of proteaceae and legume species may be highly beneficial to the long term sustainability of rehabilitation, and should be considered when designing a rehabilitation protocol for degraded and problematic soils and tailings (e.g. "blue lupin; Supporting Information Fig. S2).

Loss of available S may be attributed to the gradual dissolution of gypsum followed by uptake of soluble S by the plant and microbial communities, and/or leaching as Na_2SO_4 (Jones et al., 2015).

The primary long term sources of Ca are gypsum and wood mulch (Tables 1 and 2). However, wood mulch also contains relatively high levels of K, and to a lesser extent, Mg and Na. Decomposition of wood mulch should release K, Mg and Na to the soil solution, from where these cations would compete for the limited exchange sites of residue sand (<4 $cmol_+/kg$). The dominance of Ca suggests this cation may be more competitive for the limited number of exchange sites, a behaviour commonly found for soils dominated by hydrous Fe and Al oxides and hydroxides (e.g. Phillips et al., 1988a, 1988b). The relatively consistent composition of the exchange complex suggests a quasi-equilibrium between the solution and solid phases in residue sand has been achieved, with gypsum dissolution and organic matter decomposition (i.e. nutrient cycling) as potentially the main drivers.

Although quantities of micro-nutrients were initially applied with fertiliser at the time of rehabilitation establishment, the persistence of these elements with time may be via release from decomposition of the wood mulch (Table 2). Furthermore, the presence of sesquioxides and carbonates can favour retention of Cu, Zn, Mn and Fe by specific adsorption mechanisms (e.g. Kinniburgh et al., 1976; Thiyagarajan et al., 2009, 2011, 2012). Importantly, the relatively similar macro- and micro- nutrient concentrations between sites indicates 10-year old residue rehabilitation exhibits nutrient-supplying capabilities comparable with the analogue site.

4.2.2. Leaf material

4.2.2.1. Nutrient content. Differences in leaf N content between species may reflect the ability of legume species to fix atmospheric N_2. Dobrowolski et al. (2009) observed nodules on *H. comptoniana* roots growing in rehabilitated residue, providing evidence nitrogen fixation

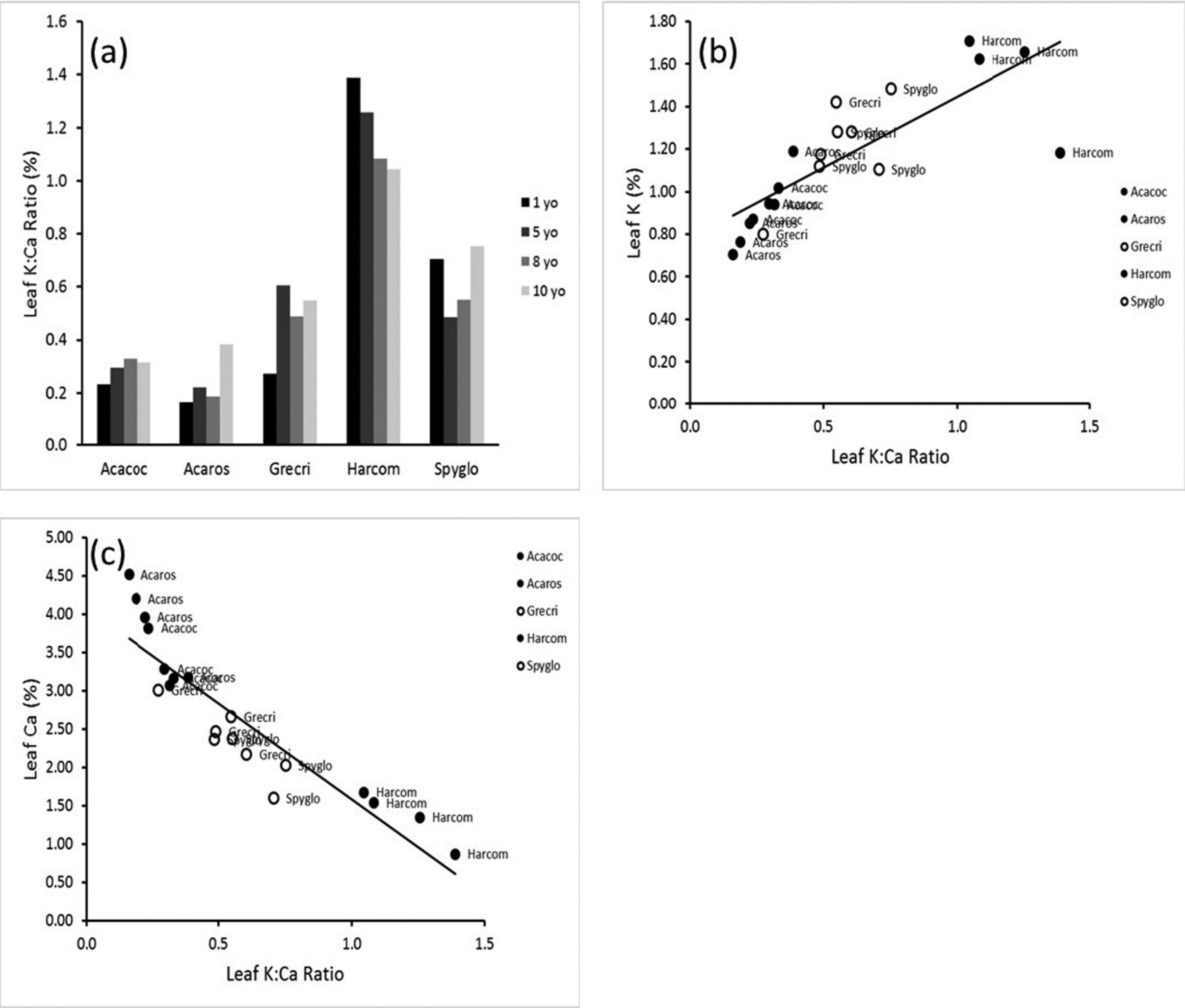

Fig. 9. (a) Effect of age on leaf K:Ca molar ratio for the five selected plant species; relationships between leaf K:Ca molar ratios and leaf (b) K and (c) Ca. ● indicates legume species and ○ indicates non-legume species.

Table 4
Comparison of leaf nutrient concentrations for plant species under 10-year old rehabilitation and analogue sand. For each parameter, values designated by the same letter are not significantly different ($p < 0.05$).

	Analogue					Residue rehabilitation					LSD
	Acacoc	Acaros	Grecri	Harcom	Spyglo	Acacoc	Acaros	Grecri	Harcom	Spyglo	($p < 0.05$)
C (%)	45.30bc	42.45d	46.15b	46.15b	48.81a	46.47ab	43.77 cd	45.46bc	46.95ab	48.75a	2.32
N (%)	2.51a	2.11ab	1.22 cd	2.51a	1.56bcd	1.85abc	2.41a	1.52bcd	2.012ab	1.04d	0.79
P (%)	0.125abc	0.095abc	0.085bc	0.102abc	0.063c	0.121abc	0.225a	0.215ab	0.168abc	0.155abc	0.138
C:N ratio	18.1a	20.1a	37.8a	18.4a	31.3a	25.2a	18.2a	30.0a	23.3a	47.1a	17.6
N:P ratio	20.0ab	22.2a	14.4c	25.1a	26.0a	15.4bc	10.7 cd	7.0d	12.6 cd	6.7d	6.9
K:Ca ratio	0.68ab	0.38bc	0.37bc	0.70ab	0.90ab	0.31 cd	0.38bc	0.55bc	1.04a	0.75ab	0.34
Cl (%)	1.315a	0.940ab	0.375def	0.155f	0.661bcde	0.795bc	0.775bcd	0.465cdef	0.261ef	0.635bcde	0.412
Al (mg/kg)	69a	80a	80a	92a	97a	126a	126a	137a	149a	209a	224
B (mg/kg)	24.1abc	37.5a	19.5c	36.4ab	23.6bc	30.5abc	28.5abc	18.5c	23.7bc	24.5abc	14.3
Ca (%)	1.57a	2.94a	2.38a	1.86a	1.48a	3.07a	3.18a	2.66a	1.68a	2.02a	1.78
Cu (mg/kg)	4.45a	4.25a	4.12a	4.85a	5.28a	8.07a	6.32a	5.22a	5.97a	5.67a	6.24
K (%)	1.05ab	1.08ab	0.85b	1.26ab	1.36ab	0.94b	1.19ab	1.42ab	1.71a	1.48ab	0.67
Mg (%)	0.26a	0.19ab	0.19ab	0.20ab	0.18ab	0.13b	0.13b	0.16b	0.11b	0.11b	0.08
Mn (mg/kg)	38.5bc	30.2cde	50.1ab	65.5a	31.5cde	9.47f	13.8ef	31.2cde	32.4bcd	18.5def	17.7
Mo (mg/kg)	0.54b	0.75b	0.51b	0.51b	0.58b	6.1a	4.5ab	2.1ab	5.5a	0.5b	4.3
Na (%)	0.155ab	0.105b	0.13b	0.225ab	0.055b	0.175ab	0.32a	0.315a	0.175ab	0.130b	0.173
S (%)	0.22b	1.05ab	0.15b	0.18b	0.17b	0.87ab	1.47a	0.43b	0.27b	0.50ab	0.99
Zn (mg/kg)	17.5a	14.0a	13.1a	35.5a	27.5a	19.8a	28.4a	45.7a	22.5a	33.0a	33.7
Fe (mg/kg)	175c	205bc	345abc	520ab	505ab	337abc	260bc	220bc	430abc	607a	319

may be occurring in the vegetation cover. Goloran et al. (2015a, 2015b) also reported higher leaf N in legume species relative to non-legumes growing in rehabilitated residue. The mean leaf N content of *A. rostellifera* and *H. comptoniana* was 1.80 and 2.73%, respectively, compared to 0.88% for *Eucalyptus gomphocephala* (Fig. 5).

The benefits of N derived from atmospheric N_2 on soil N availability and concomitant plant uptake is well-documented for acacia and other legumes (e.g. Brockwell et al., 2005). Nutrient cycling through N uptake and subsequent litterfall has also been reported to be beneficial for companion non-legumes and grasses co-exiting with legumes (e.g. Cramer et al., 2018; Paula et al., 2018). The presence of legume species in rehabilitation appears highly beneficial as a potential long term N source not only as a mechanism for enhancing nutrient availability in residue substrate, but also for supplying N and other key nutrients for microbial communities and other non-legumes contributing to the plant species mix and are regularly included in seed mixes for the rehabilitation of metalliferous mine wastes (Tordoff et al., 2000).

The mean leaf P content averaged across all species and rehabilitation age was 0.13%, being very similar to the mean global value of 0.12% (Tian et al., 2018). Although concentrations of P (total and available forms) in the residue sand appear adequate for supplying plant P requirements within the vegetation cover, the legume species may be more efficient at extracting this nutrient. Leaf P contents do not appear to be limiting plant productivity, possibly due to (a) ready-access of the plant roots to P from past DAP and gypsum application, (b) mineralisation of organic matter and subsequent release of organic-P, and/or (c) plants being capable of extracting P bound with Ca, Fe and/or Al in the residue sand (Shane et al., 2004; Lambers et al., 2012).

Ecological stoichiometry such as leaf N:P ratios has been used as a tool to characterise N and P limitations to plant growth and productivity (Sterner and Elser, 2002; Tessier and Raynal, 2003; Goloran et al., 2015a, 2015b). The N:P mass ratio for *A. cochlearis*, *A. rostellifera*, *G. crithmifolia*, *H. comptoniana* and *S. globulosum* tended to decline with rehabilitation age (Fig. 8). These findings are consistent with the study by Goloran et al. (2015a) for grass (*L. rigidium*) grown in residue sand but contrasts a corollary study for selected native (*A. rostellifera*, *H. comptoniana* and *E. gomphocephala*) species (Goloran et al., 2015b). It has been suggested leaf N:P ratios in the range of 14–16 indicate N and P co-limitation, while values below and above this range indicate N limitation and P limitation, respectively (Gusewell, 2004; Goloran et al., 2015a, 2015b). During the early stages of rehabilitation (<5 years of age) the vegetation may be P limited while in older rehabilitation N limitation may be manifesting, more so for the non-legume species. The transition from P to N limitation may reflect the enhanced ability of the vegetation to extract P from the residue sand rhizosphere, particularly as root architecture of the dominant species improves (Dobrowolski et al., 2009), and nutrient replenishment via sustained surface organic matter mineralisation (Fig. 10).

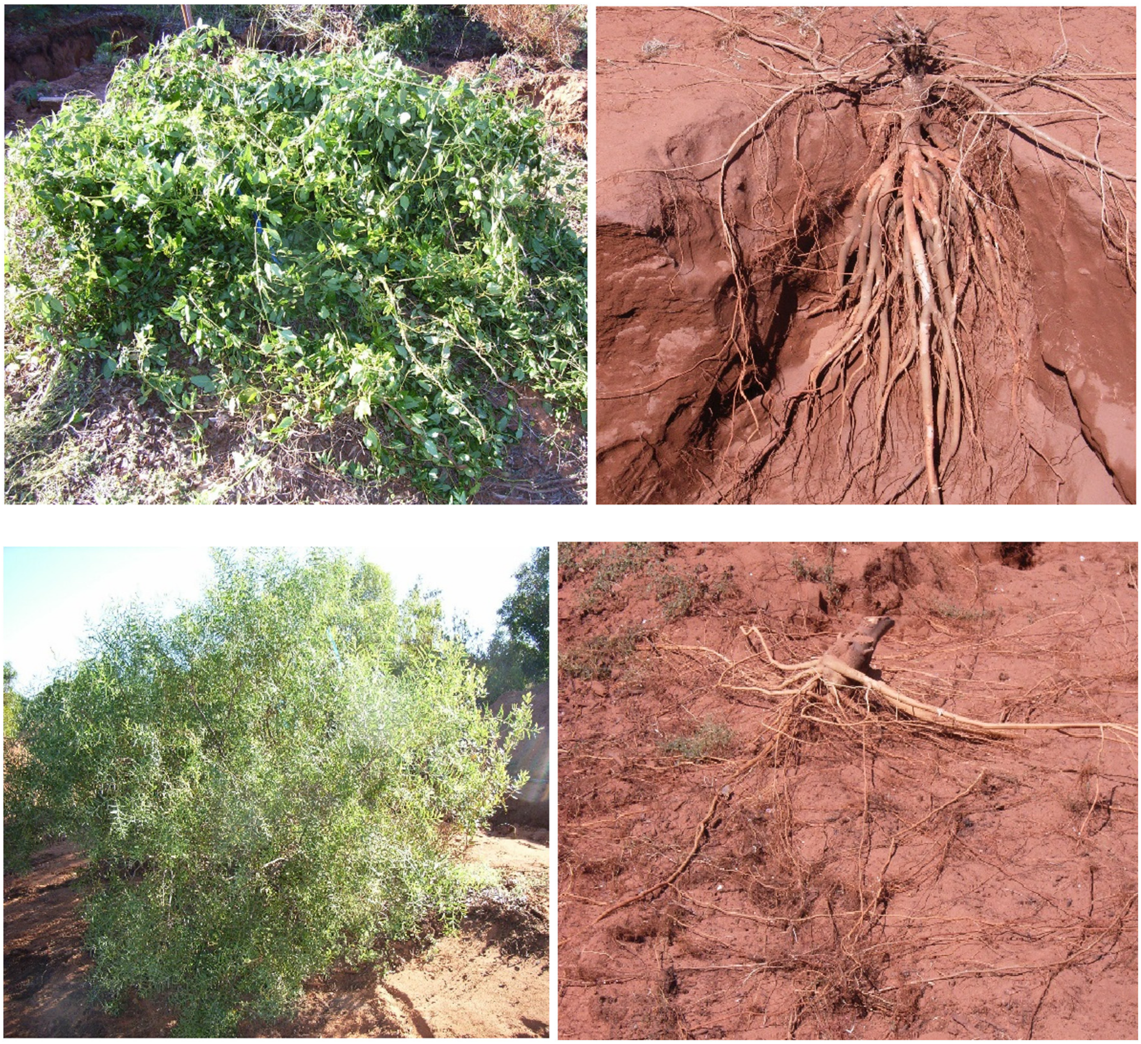

Fig. 10. Root architecture of 5-year old (a) *H. comptoniana* (0–1 m depth) and (b) *A. cochlearis* (surface distribution).

The dominance of Ca in residue sand due to gypsum addition can negatively impact N (as NH_4) and P availability through cation competition for the limited exchange sites (NH_4 —Ca exchange equilibria) and/or P precipitation as Ca—P, respectively. Whereas mineral N can subsequently be lost via leaching, Ca—P should remain plant-available within the rhizosphere.

Given that major K inputs are primarily at the rehabilitation establishment phase, and cation leaching may be high in the low CEC, coarse-textured residue sand, declining K concentrations in the rhizosphere may be expected with time. However, the contributions of K from decomposing surface organic matter may offset K limitations, particularly for species with a high concentration of roots close to the residue/wood mulch/litterfall interface (Dobrowolski et al., 2009). Whether this translates to an impact on plant productivity with increasing age of rehabilitation is unknown.

The strong relationship between plant nutrient uptake and nutrient availability in the rhizosphere is well-known. For example, Cu, Mn and Zn can be found at elevated concentrations in soil but due to the formation of sparingly-soluble organic and inorganic complexes or specific adsorption to hydrous oxide surfaces, plant availability is low (Thiyagarajan et al., 2009, 2011, 2012; Rengel, 2015). Thiyagarajan et al. (2009) found native species in Alcoa's rehabilitation had markedly different leaf Mn levels, with *A. cyclops* showing Mn-deficiency symptoms in conjunction with low leaf Mn concentrations, while *H. comptoniana* and *G. crithmifolia* exhibited vigorous growth and healthy green leaves with no deficiency symptoms and containing higher Mn concentrations. The lack of Mn deficiency in *H. comptoniana* and *G. crithmifolia* suggests these two species were highly efficient in extracting residue-bound Mn. In the current study, *G. crithmifolia* in particular contained very high leaf Mn concentrations and is consistent with Thiyagarajan et al. (2009). This plant characteristic may be attributed to proteaceous species producing proteoid roots capable of mobilising nutrients such as Mn in the root-zone by organic acid secretion (Shane et al., 2004). By contrast, acacia species (e.g. *A. cyclops* and *A. saligna*) have been found less-efficient than *G. crithmifolia* in Mn uptake (Thiyagarajan et al., 2009; Anderson et al., 2011). This finding is consistent with the relatively low leaf Mn detected in *A. cochlearis* and *A. rostellifera* (Fig. 7).

The alkaline pH of residue sand may have favoured formation of B (and other nutrients) as oxyanions (e.g. MoO_4^{2-} and $B(OH)_4^-$) thereby increasing plant availability in predominantly negatively charged residue sand (Goldberg, 1997; Goldberg et al., 1996; Goldberg and Forster, 1998). Borate and molybdate concentrations in the pore water (hence availability) can increase in the presence of other competing anions such as P (Vistoso et al., 2012). Therefore, conditions which increase solution P concentrations may concomitantly also increase B and Mo availability, such as release of H from roots to maintain cation/anion balance and/or a higher rhizosphere acidity under legumes.

Under alkaline conditions, residue Al exists primarily as the aluminate anion ($Al(OH)_4$) (e.g. Grafe et al., 2011) which resides primarily in the soil solution phase where it is available for plant uptake. The continued presence of Al in plant material despite very low exchangeable Al concentrations in residue sand (≈0.01 cmol/kg) suggests soluble forms of this ion may be the primary source for plant uptake. Further, plant uptake of Al, hence availability in the residue rhizosphere, may be decreasing with time. This agrees with findings of Courtney and Kirwan (2012) who reported the same trend over 5 years for grass and legume species in rehabilitated residue.

4.3. Comparing 10 year old rehabilitation with analogue site

Demonstrating nutrient deficiencies were not rapidly developing with increasing rehabilitation age confirms the importance of undertaking long term monitoring as a guide for critically evaluating rehabilitation performance (Cortina et al., 2011; Spain et al., 2015). The finding that most nutrient concentrations in 10-year old rehabilitation were similar to those in the analogue site contrasts with previous studies which suggested nutrient deficiencies may manifest in residue rehabilitation with increasing age (e.g. Courtney and Timpson, 2005; Thiyagarajan et al., 2009). Previous studies were however restricted by either short monitoring timeframes, extrapolating laboratory or greenhouse studies to field conditions, and/or lacked an analogue site for comparing nutrient concentrations hence rehabilitation performance.

N:P mass ratios suggested vegetation in the analogue may be experiencing P limitations (N:P ratio > 16) and the residue rehabilitation experiencing N limitations (N:P ratio < 14). Many Australian native species are tolerant of P-deficient soil such as found in Bassendean Dune System and as such low plant available P may not be indicative of a nutrient limitation. In contrast, the higher P content of residue sand could reduce leaf N:P ratios due to increased plant uptake, particularly in the absence of a concomitant proportional increase in leaf N. Therefore, the lower N:P ratio does not provide conclusive evidence of a trending N deficiency in residue rehabilitation. This conclusion is consistent with findings by Goloran et al. (2015a, 2015b) which found older rehabilitated residue sand embankments displayed sand and plant indices (Ca, Na, pH, EC, ESP and leaf N:P ratios) closely aligned with those of the natural ecosystem.

4.4. General discussion

The initial plant- and microbe- hostile characteristics of “fresh” residue sand was positively transformed by incorporating amendments (gypsum) and fertilizers (di-ammonium phosphate) to produce a more favourable environment for establishing a sustainable vegetation cover. Gypsum reduced sodicity and alkalinity, and acted as slow release fertiliser, while di-ammonium phosphate fertiliser provided essential macro- and micro- nutrients for the establishing rehabilitation. With increasing age of the rehabilitation, organic matter accumulation began to play an increasingly important role in nutrient supply and cycling, and in developing a diverse and functional microbial community. The extended period of monitoring reported in this study shows that in contrast to previous short term studies, nutrient deficiencies have not manifested in well-established residue rehabilitation, and that long term monitoring programs are critical for demonstrating true rehabilitation performance.

Establishing a diverse mix of plant species with characteristics capable of extracting and supplementing key nutrient inputs such as N and P should be considered a-priori to designing a rehabilitation protocol. Native species with proteoid roots appeared to mobilise nutrients such as P, Mo and Mn in the root-zone by organic acid secretion, while the inclusion of perennial legumes, coupled with recruitment of annual legumes can increase N uptake. This diversity in plant physiology and nutrient acquisition behaviour is regarded as highly beneficial to long term sustainability of residue rehabilitation.

Finding that 10-year old rehabilitation exhibited relatively similar nutrient contents to that of an analogue site provided strong evidence rehabilitation was on a positive trajectory in terms of developing into a sustainable ecosystem. Past short term and/or laboratory studies suggested deficiencies in key plant nutrients may have been developing due to the low supplying capacity of residue sand. The current study however demonstrates rehabilitation performance may in fact be improving with age, particularly for key macro- (N, P, S) and micro- (Mo and B) nutrients. Many of the other nutrients did not exhibit significant declines in leaf concentration with age primarily due to decomposition of organic materials and nutrient cycling. Whether deficiencies develop in the future will require further long term monitoring and whether nutrient outputs from the ecosystem are balanced by nutrients inputs.

5. Conclusions

Nutrient analysis of residue sand and plant leaf material from rehabilitated residue sand embankments of varying age (1 to 10 years old) found improved residue sand characteristics developed with time, primarily due to gypsum incorporation to depth, and leaching of soluble alkalinity sand salinity. The depth of gypsum incorporation to 1.5 m provided an unrestricted effective rooting depth which allowed the vegetation to develop an extensive root network for water and nutrient uptake. This uptake was favoured by plant species capable of solubilising nutrients from plant-unavailable forms, and by the ability of legumes to fix atmospheric N_2 and subsequently release this N for future uptake by the vegetation cover and the developing microbial community.

The importance of organic carbon additions to the residue sand was highlighted particularly in terms of providing a substrate for nutrient cycling. Whether the continued inputs of organic matter from litterfall coupled with declining input from the wood mulch will maintain nutrient levels in the rehabilitation is currently unknown and warrants further attention. This study has demonstrated nutrient deficiencies were not rapidly developing with increasing rehabilitation age and confirms the importance of undertaking long term monitoring as a guide for critically evaluating rehabilitation performance.

CRediT authorship contribution statement

I.R. Phillips: Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **R. Courtney:** Conceptualization, Methodology, Data curation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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