ULRR

Availability and transfer of non#essential elements in a rehabilitated bauxite residue grassland system

Item Type	Article
Authors	Dillon, Leah;Courtney, Ronan
Citation	Plant Soil
Publisher	Springer Nature
Download date	2026-01-18 04:58:33
Item License	https://creativecommons.org/licenses/by-nc-sa/4.0/
Link to Item	https://doi.org/10.34961/researchrepository-ul.24004707

Plant Soil
https://doi.org/10.1007/s11104-023-06213-1

RESEARCH ARTICLE

Availability and transfer of non-essential elements in a rehabilitated bauxite residue grassland system

L. Dillon · R. Courtney

Received: 16 June 2023 / Accepted: 1 August 2023
© The Author(s) 2023

Abstract
Aims This study investigated a 7 yr old rehabilitated grassland established on a bauxite residue storage areas(RSA) in order to assess the availability and ecosystem transfer of both nutrient and trace elements, and to determine if defined rehabilitation criteria were sustained.
Methods Rehabilitated residue/soil was sampled over depth (0–10 and 10-20 cm) and season (Spring/Summer and Autumn/Winter) and plant growth stage (green vs. senescent) to determine both essential and non-essential element (Ca, Mg, Na, Al and V) content. Invertebrates samples from both decomposer and predator specimens were assessed to determine if foodchain transfer occurred.
Results Residue-soil results showed sustained rehabilitation with pH, EC and ESP all within recommended criteria levels. Further, bioavailable fractions of Al and V remained low. Vegetation analysis revealed seasonal variation for both essential and non-essential elements and highlights the need for wider monitoring parameters. Elemental content in invertebrate samples did not indicate foodchain transfer and results were comparable to a reference site.
Conclusion Results show sustained rehabilitation with low bioavailability of non-essential elements and foodchain transfer.

Keywords Sustainable ecosystem · Insitu remediation · Invertebrates

Responsible Editor: Songlin Wu.

L. Dillon · R. Courtney (✉)
Department of Biological Science, Faculty of Science & Engineering, Bernal Institute, University of Limerick, Limerick, Ireland
e-mail: ronan.courtney@ul.ie

Introduction

Some 150 million tonnes of bauxite residue (BR) are produced annually as a by-product of the Bayer Process (Di Carlo et al. 2019; Jiang et al. 2023). Although several approaches have been investigated for bauxite residue reuse and valorization, the bulk of residue produced is stockpiled in bauxite residue storage areas (RSAs), some of which occupy footprints of hundreds of hectares (Xue et al. 2016; Phillips and Courtney 2022).

Where unamended, bauxite residue is characterized by high alkalinity and Na content, along with elevated levels of potentially bioavailable trace elements which present a potential environmental risk (Di Carlo et al. 2020a, b; Mišík et al. 2014; Olszewska et al. 2016; Ren et al. 2018). Therefore, establishing vegetation cover (rehabilitation) on (RDAs) is deemed as 'best practice' (Directive 2006/21/EC;Xue, et al. 2016; Jiang et al. 2023).

Rehabilitation strategies using an inert capping layer and soil material are employed at some RDAs, but the degree of success is variable, with some

Published online: 16 August 2023

studies reporting plant failure due to alkaline and saline contamination from capillary rise (Di Carlo et al. 2019; Wehr et al. 2006). Alternatively, gypsum amendment can be applied to the residue to decrease alkalinity and sodicity, along with organic and fertilizer sources, followed by seeding has been widely reported (Courtney and Xue 2019; Di Carlo et al. 2019; Phillips and Courtney 2022). Application of gypsum to residue can effectively decrease the high pH from > 11 to < 9, and lower the exchangeable sodium percentage (ESP) from 40–90% to rehabilitation target values of 9.5- 20% (Di Carlo et al. 2019; Jones et al. 2012). As well as improving conditions in the residue/ soil matrix, gypsum amended residue also displays improved plant performance and decreased uptake of Na and trace elements (Courtney and Harrington 2012; Di Carlo et al. 2020a, b). However, much of the published literature on bauxite residue rehabilitation strategies have been largely laboratory level or short-term field assessment (Guo et al. 2022; Tian et al. 2020; Xue et al. 2016; Zhu et al. 2017). Further long-term field trials are required to determine if rehabilitation criteria (Gräfe and Klauber 2011; Di Carlo et al. 2019) achieved with rehabilitation strategies can be sustained in the longer term. Further, in keeping with the wider mine tailings rehabilitation literature, a focus on plant and ecosystem function are required to assess bauxite residue rehabilitation success over time.

While Bray et al. (2018) investigated rehabilitated bauxite residue > 10 years after initial rehabilitation, the focus was on soil physico-chemical properties of the BR over time and depth and did not include vegetation data. Phillips and Courtney (2022), investigated rehabilitated areas of 1, 5, 8 and 10-years post rehabilitation. Plant nutrient content was assessed; however, the data was collected from a rehabilitated process residue sand ecosystem rather than rehabilitated BR ecosystem. Additionally, the vegetation samples were collected on a one-off basis. For rehabilitation to be successful in the longer-term, it is imperative that the elemental status of the vegetation growing on the surface is analysed over time to monitor the potential for the bioaccumulation of certain elements and nutrient deficiencies which could cause sward failure.

The wider literature on rehabilitation of metalliferous mine tailings has identified seasonal variation in vegetation uptake dynamics, with potential implication for herbivores and food chain transfer (Andrews et al. 1989a, b; Crilly et al. 1998; Milton et al. 2002; Ke et al. 2023). Following earthworm toxicity and biomarker stress in residue exposed earthworms, Di Carlo et al. (2020a, b) recommended that trace element uptake risk to the food chain should be investigated. Andrews et al. (1989a) reported variation in Pb content between fresh plant tissue and leaf litter (dead or decaying plant matter). Detritivorous organisms such as isopods are suitable taxa for providing reliable information on environmental quality in terrestrial habitats due to their food source and microhabitat in the upper soil layer, where elements may accumulate (Nannoni et al. 2015). Thus, assessment of trace element content in grassland invertebrates has been used to assess potential ecotoxicological risk in rehabilitated tailings (Milton et al. 2002, 2004; Milton and Johnson 1999), but has not been reported for rehabilitated bauxite residue.

The novel Tea-Bag Index (TBI) method (Keuskamp et al. 2013) has been implemented to investigate ecosystem functions across a diverse range of ecosystems including Pb/Zn tailings (Álvarez-Rogel et al. 2021, 2022) but has not been reported for rehabilitated bauxite residue sites. The method was employed in the rehabilitated grassland to investigate the rate of decomposition occurring in the engineered ecosystem.

This study investigated a 7 year old rehabilitated bauxite residue grassland system in order to assess the availability and ecosystem transfer of nutrient elements (Ca, Mg, K, Mn) and trace elements (Na, Al, V). Seasonal sampling (Spring/Summer and Autumn/ Winter) was conducted on residue/ soil at two depths (0–10, 10-20 cm) and vegetation. Samples of plant material were divided into fresh new growth (Green) and older decaying growth (senescent). Invertebrate samples were divided into detritivores and predators to assess food chain transfer with decomposition rates using the TeaBag Index (TBI) determined and compared to a reference site.

Materials and methods

Site description

Samples of amended and rehabilitated bauxite residue-soil, vegetation and surface-dwelling invertebrates were collected from; a) a Bauxite Residue

Disposal Area (RDA) located in a European Union member state with a temperate oceanic climate (average annual rainfall ~1m). Bauxite residue was rehabilitated 7 years previously, known as BR7 and the area has remained under vegetative cover since rehabilitation and supports a semi-natural grassland system. The rehabilitation approach involved application of gypsum (90 t/ha rotavated-in to a depth 30 cm), process sand (10% w/w rotavated-in to a depth of 30 cm), spent mushroom compost (80t Ha^{-1} rotavated-in to a depth of 20 cm), and seeded with a grassland mix (*Agrostis stolonifera, Holcus lanatus, Lolium perenne, Trifolium repens,* and *Trifolium pratense*; 80 kg/ha) b) an area of semi-natural grassland to the north-west of the RDA sampled. This site was identified as a suitable 'Reference site' as it is not under any agricultural land usage and the grassland does not receive any nutrient inputs. Additionally, the site is located close to the rehabilitated site (BR7) and is passively managed to encourage botanical diversity.

Sampling followed a similar protocol to works carried out by Andrews et al. (1989a, b)), where soil, vegetation and invertebrates were sampled from a grassland ecosystem established on fluorspar tailings. To investigate seasonal elemental composition, samples were collected in Autumn/Winter (AW) 2020 and Spring/Summer (SS) 2021 from BR7. Samples were collected from the Reference site in SS 2021.

Soil sampling

Soil samples (n = 6) were collected at two depths (0-10cm and 10-20cm) in both the rehabilitated bauxite residue grassland (BR7) and the reference site. The samples were air-dried and sieved (< 2mm) prior to analysis. pH and electrical conductivity (EC) were measured using a ratio of 1:2.5 soil to water. Soil soluble elements were determined using deionized water. Cation (Ca, Mg, K, Na) content was determined using 1 M ammonium acetate. Plant available Mn was determined using the DTPA extraction method outlined by Lindsay and Norvell (1978). Potentially bioavailable pools of Al and V were extracted using 0.1 M Na_2HPO_4 (Bray et al. 2018).

Vegetation sampling

Amenity grass *Dactylis glomerata* was identified within BR7 and above ground samples were collected by cropping the vegetation at 2cm above ground. For the rehabilitated site, fresh green growth (Green) and older senescent growth (Senescent) vegetation samples were collected in AW and SS. In the 'reference' site only new green vegetation was collected in SS. Vegetation was oven dried at 70°C, wet digested in acid before being analysed for macro/micronutrients and trace elements (Al, Ca, K, Mg, Mn, Na, V).

Certified reference materials: NIST 1640a, NIST 1643f, NIST 1568b, NIST 1845a, NIST 1573a, and LUTS-1) were also prepared using above methods. Recovery rates were 91–100% for the elements determined. Elemental content was determined using ICPMS (7700 ICPMS Agilent).

Invertebrate sampling

Surface dwelling invertebrates were collected from both sites in SS and AW using pitfall traps (8cm diameter) over a three-week period. Specimens were recovered and oven dried at 60ºC. Samples were divided into Coleoptera and Arachnida (predators) and Isopoda and millipedes (detritivores). Samples were than pooled to 10 mg weight, milled and acid digested prior to element determination and analysed for trace elements (Al, Ca, K, Mg, Mn, Na, V).

Litter decomposition

Litter decomposition rate (*k*) and stabilization factor (S) were assessed using the Tea-Bag Index (TBI) method (Keuskamp et al. 2013). For both summer (SS) and autumn winter (AW) at both rehabilitated bauxite residue and reference site 6 pairs (6 green tea teabags and 6 rooibus teabags) of teabags were buried for 90 days before recovery. The teabags were dried, weighed, and (*k*) and (*S*) were calculated. A spreadsheet supplied by TBI (http://www.teatime4science.org/researchers/) was used to calculate k and S factors.

Statistical analysis

SPSS IBM (version 28.01.1) was used to compare the means of the treatment (T-test). Where data was not normally distributed a Mann–Whitney test was performed to compare the means. ANOVA was carried out to compare invertebrate element content within the study sites. Where significant, differences between individual means were tested using Tukey HSD tests at the 0.05 significance level. Graphs were created using GraphPad Prism (version 9.5.0).

Results

Soil

The pH values for BR7 at 0–10 cm ranged from pH 8 to 8.7, and pH 7.8 to 9 for 10–20 cm, respectively for both seasons. There was no significant difference ($p > 0.05$) between depths but there was a significant difference ($p < 0.05$) between seasons sampled. With AW having higher pH values for both depths (0–10, 10–20 cm). Although, the pH values for BR7 were above the mean values for the reference site (Fig. 1a), all samples were below the suggested rehabilitation success target value of pH 9 (Fig. 1a).

The EC values for 0–10 cm in BR7 ranged from 192 to 244 µS/cm and from 270 to 416 µS/cm at 10–20 cm (Fig. 1b). There was no significant difference ($p > 0.05$) for EC in BR7 for either depth or season. Additionally, all EC results from BR7 were below the rehabilitation target value of 4000 µs/cm (Gräfe and Klauber 2011).

There was no significant difference ($p > 0.05$) between the two depths for BR7 in either season for $Mn_{\text{-DTPA}}$. The values for 0–10 cm ranged from 0.7 to 1.5 mg/kg, and 0.6 to 1.3 mg/kg for 10–20 cm. Values in the reference site (ca. 9 mg kg^{-1})were much greater than for BR7 over both seasons (Fig. 1c).

Highest values for exchangeable Ca were recorded in SS at 10–20 cm, with values ranging from 28.8 — 37.8 cmol/kg. There was a significant difference ($p < 0.05$) for both season and depth for exchangeable Ca. Except for values at 10–20 cm, where there was no significant difference ($p > 0.05$) between values for AW and SS. Reference site values for Ca were within the range recorded in BR7, with a mean of 33.2 cmol/kg and 32.9 cmol/kg for 0–10 cm and 10–20 cm, respectively (Fig. 2a).

Exchangeable Mg values were lowest at a depth of 10–20 cm for BR7, with a range of 0.2–0.33 cmol/kg. The values at 0–10 cm depth ranged from 0.2 — 0.6 cmol/kg (Fig. 2b). There was a significant difference ($p < 0.05$) for both season and depth, except when comparing AW and SS at 0–10 cm. The reference site averages followed a similar pattern to BR7, with greater values at 0–10 cm. The mean for the reference was 0.9 and 0.6 cmol/kg at 0–10 cm and 10–20 cm, respectively.

Similarly, exchangeable K values were highest at 0–10 cm compared to 10–20 cm for BR7 (Fig. 2c). Maximum value for 0–10 cm was 0.5 cmol/kg compared to a maximum of 0.3 cmol/kg for 10–20 cm. There was a significant difference ($p < 0.5$) for both season and depth sampled. Additionally, SS had higher values than AW at both depths (0–10 cm, 10–20 cm). Average values from the reference site were 0.2 and 0.1 cmol/kg for 0–10 cm and 10–20 cm, respectively.

Exchangeable Na values in BR7 ranged from 1.7 — 2.6 cmol/kg for 0–10 cm, and 2.1 — 3.8 cmol/kg for 10–20 cm (Fig. 2d). There was no significant

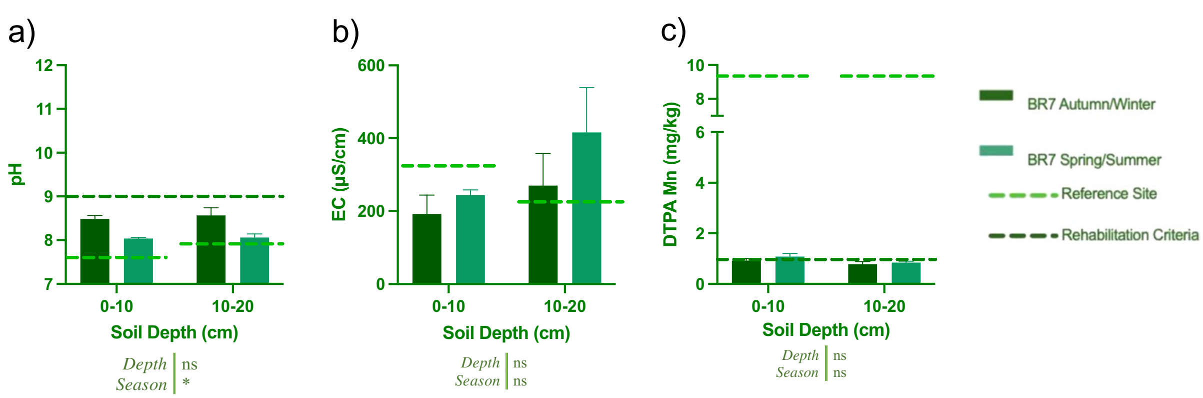

Fig. 1 Effect of seasonality and depth on rehabilitated bauxite residue (**a**) pH, (**b**) EC. The dotted line represents the rehabilitation goals defined by Gräfe and Klauber (2011)

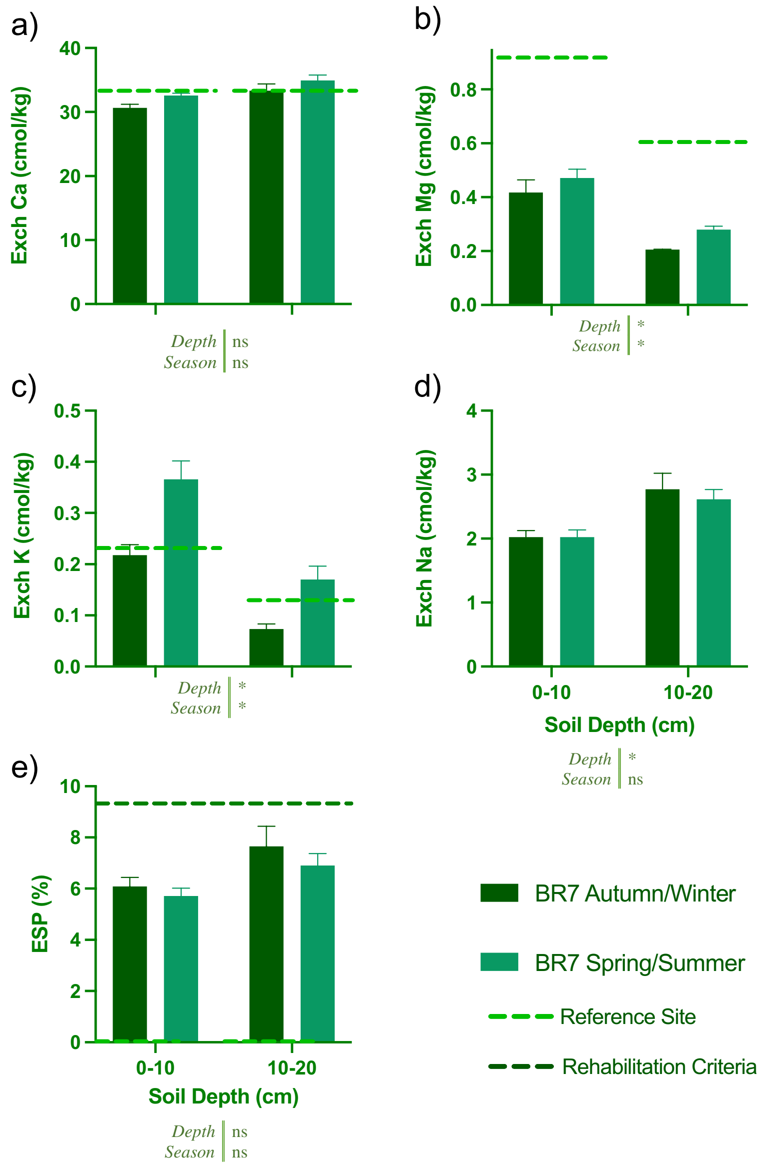

Fig. 2 Exchangeable cation content (**a**) Ca, (**b**) Mg, (**c**) K and (**d**) ESP in rehabilitated bauxite residue (BR7) over season sampling and soil depth

difference ($p > 0.05$) when comparing seasons in BR7. However, there was a significant difference ($p < 0.05$) when comparing depth, with greater values at 10–20 cm. The mean exchangeable Na value for the Reference site was < 0.01 cmol/kg for both depths sampled (0–10, 10–20 cm).

ESP values ranged from 5 to 7% and 6 to 11% for 0–10 cm and 10–20 cm, respectively (Fig. 3e). There was no significant difference ($p > 0.05$) when comparing either depth or season for BR7. All the values for BR7 were below that of the rehabilitation goal for ESP of 9.5% (Gräfe and Klauber 2011). ESP in the Reference site was < 0.5% for both depths, this is due to the negligible Na content (Fig. 2e).

Na_2HPO_4 extractable Al concentration did not differ significantly for either depth or season with values ranging from 67–77 mg/kg (Fig. 3a). Value for reference site had a mean value of 33 mg/kg at 0–10 cm and were comparable to the rehabilitated residue at 10–20 cm.

Extractable V values were 17 for 0–10 cm and 22 mg/kg for 10–20 cm in BR7. There was no significant difference ($p > 0.05$) for season, however there was a significant difference ($p < 0.05$) for depth when

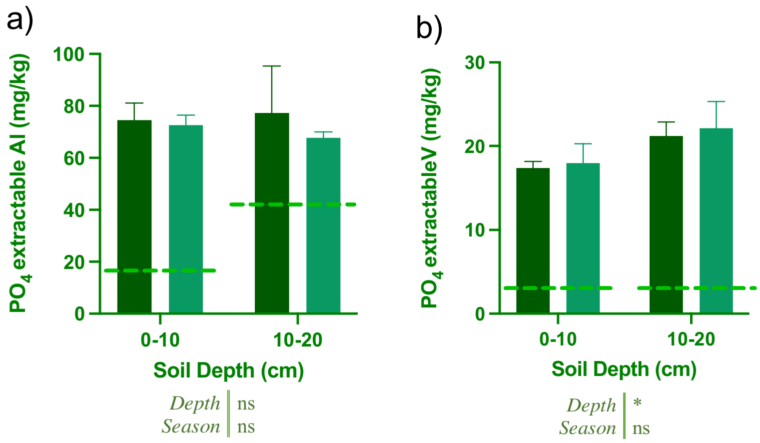

Fig. 3 Extractable (Na_2HPO_4) Al and V from rehabilitated bauxite residue and reference site at depth (0–10 and 10-20 cm) and season

comparing 0–10 cm and 10–20 cm for SS. The reference site had lower values with a mean of 3 mg/kg for 0–10 cm and 10–20 cm, respectively (line on graph) (Fig. 3b).

Vegetation

Ca content (Fig. 3a) in vegetation collected from BR7 ranged from 0.2% — 0.4% for green growth and 0.3% — 0.5% for senescent growth. Ca content was not significantly different ($p > 0.05$) between seasons. All values for BR7 were below the average Ca concentration in vegetation sampled from the reference site (0.5%).

Mg concentration in BR7 was greatest at AW with average values 0.08% for both green and senescent growth. SS average values were 0.06% for green growth and 0.08% for senescent. There was no significant difference ($p > 0.05$) between either season or growth type for Mg in BR7. Similarly, the average value for the reference site was 0.08% (Fig. 3b).

The K concentration in the vegetation was higher in the green growth for both seasons sampled, with an average of 2.1% and 1.9% for AW and SS, respectively (Fig. 3c). There was a significant difference ($p < 0.05$) between green and senescent growth for both seasons sampled. Additionally, there was a significant difference ($p < 0.05$) between season for senescent values with an average value of 1.2% for AW and 0.5% for SS. The average value for the reference site was 1.4%, which was lower than the K values recorded in the green growth for both seasons of BR7.

Mn values in BR7 vegetation ranged from 7.3 — 33 mg/kg for green growth and 8.6 — 22 mg/kg for senescent growth. There was no significant difference ($p > 0.05$) between Mn values for either growth type or season for BR7. All values recorded in BR7 were below that of the average value recorded in the reference site (54 mg/kg) (Fig. 3d).

Na concentration (Fig. 3e) was highest for BR7 in the green growth for both seasons, with average values of 0.4% and 0.3% recorded for AW and SS, respectively. The average value for senescent growth was 0.2% for both seasons sampled. There was no significant difference ($p > 0.05$) between either growth type or season. Moreover, the Na content was higher than the average value recorded in the reference site (0.07%).

Al and V

Al concentration was significantly ($p < 0.05$) higher in the senescent growth than in the green growth for both seasons in BR7, with average values of 69 mg/kg and 97 mg/kg for senescent growth for AW and SS, respectively. There was no significant difference ($p > 0.05$) between seasons sampled for BR7. The reference site had an average value of 32 mg/kg, similar to average green growth values of 29 mg/kg and 41 mg/kg for AW and SS, respectively (Fig. 4f).

V concentration in green vegetation was 0.15 mg/kg and 0.04 mg/kg for AW and SS, respectively (Fig. 3g). The values in the senescent growth were significantly ($p < 0.05$) higher than in green growth samples for both seasons. Additionally, there was a significant difference ($p < 0.05$) between AW and SS when comparing green growth values. Average green growth value for AW was 0.2 mg/kg compared to 0.04 mg/kg for SS. The average value for the reference site vegetation was 0.1 mg/kg (Fig. 4).

Invertebrates

For both sites the Ca concentration was significantly higher in detritivores compared to predators (Fig. 5a). Isopoda (detritivore) had the highest concentration for both sites. Ca content for predators was significantly ($p < 0.05$) lower values for both sites with low levels for Arachnida species ranged from 0.7 – 2.9 g/kg and Coleoptera content was below level of detection (<LOD). There was no significant difference ($p > 0.05$) between the sites.

The Mg (Fig. 5b) concentration was highest in the Millipede and Isopoda species (Detritivores) for both sites. The average Mg concentration in the Isopoda species was 4.9 mg/kg and 4.5 mg/kg for the reference site and BR7, respectively. There was a significant difference ($p < 0.05$) between all species within the reference site with the results as follows; Coleoptera < Arachnida < Millipede < Isopoda. In BR7, Isopoda and Millipede had significantly ($p < 0.05$) higher values than Coleoptera and Arachnida species. The only significant difference ($p < 0.05$) between sites was found between the Coleoptera species. BR7 had significantly higher Mg concentrations then the reference site, with a mean of 1.02 mg/kg and 1.5 mg/kg for the reference and BR7, respectfully,

K concentration in the invertebrate samples followed the same pattern for both sites, Millipede < Isopoda < Coleoptera < Arachnida (Fig. 5c). The Arachnida group had a significantly ($p < 0.05$) higher concentration in both sites compared to the other invertebrate groups sampled. The concentration of K in the Arachnida species ranged from 10–11 mg/kg and 10–12 mg/kg for the reference and BR7, respectively. In the reference site, the detritivores (Isopoda and Millipede) had significantly ($p < 0.05$) lower values than the predator species. Similarly, Millipede in BR7 had significantly ($p < 0.05$) lower concentration of K than the other invertebrate species. There was no significant difference ($p > 0.05$) between species for the rehabilitated residue and reference site.

The concentration of Na (Fig. 5e) was greatest in the Arachnida group in the reference site, with values ranging from 8.3 – 16 mg/kg. However, in BR7 the Isopoda species had significantly ($p < 0.05$) greater values of Na compared to the other invertebrate groups collected from BR7, with values that ranged from 7.5 – 9.8 mg/kg. Coleoptera and Millipede species had the lowest Na concentration for both sites with a mean value of 4.7 mg/kg and 3.5 mg/kg for Coleoptera and Millipede in the reference site, respectively. Similarly, in BR7 the mean value for Coleoptera was 5.9 mg/kg and was 3.3 mg/kg for the Millipede group. There was no significant ($p > 0.05$) between the two sites, when comparing species.

Mn concentration in the reference site was significantly ($p < 0.05$) greater in the Arachnida invertebrate group (Fig. 5d), with values ranging from 45 -97 mg/kg in the reference. The Mn in Arachnida collected in BR7 ranged from 27 – 29 mg/kg, however there was no significant difference ($p > 0.05$) between the reference and BR7 Arachnida. In BR7, the predator species (Coleoptera and Arachnida) have significantly ($p < 0.05$) greater values than the detritivore species (Isopoda and Millipede). With the average values of 11 mg/kg and 12 mg/kg for isopoda and millipede, respectively. Compared to mean values of 27 mg/kg and 28 mg/kg recorded for Coleoptera and Arachnida, respectively. There was no significant difference ($p > 0.05$) found between the treatment sites.

The highest values for Al were recorded in the Isopoda group in the reference site and in rehabilitated residue. Lowest values of Al were recorded in the Coleoptera group with mean values of 53 mg/kg and 110 mg/kg for the reference site and BR7, respectively. For each invertebrate group there was no significant difference between reference and BR7. V content was higher in detritivores compared to predators, with highest content found in Isopods in BR7 (mean 4.8 mg/kg) compared to reference mean 2.6 mg/kg (Fig. 5g). Content in millipedes did not significantly differ between sites.

Plant litter decomposition

While litter decomposition rate was lower in BR7 for the summer/spring (SS) sampling, the trend was reversed in autumn/winter (AW) with higher rate recorded in the rehabilitated residue (Fig. 6). There was no significant difference for k for either site or season sampled ($p > 0.05$). S factor was slightly lower in the AW sampling with no differences between sites for either season sampling.

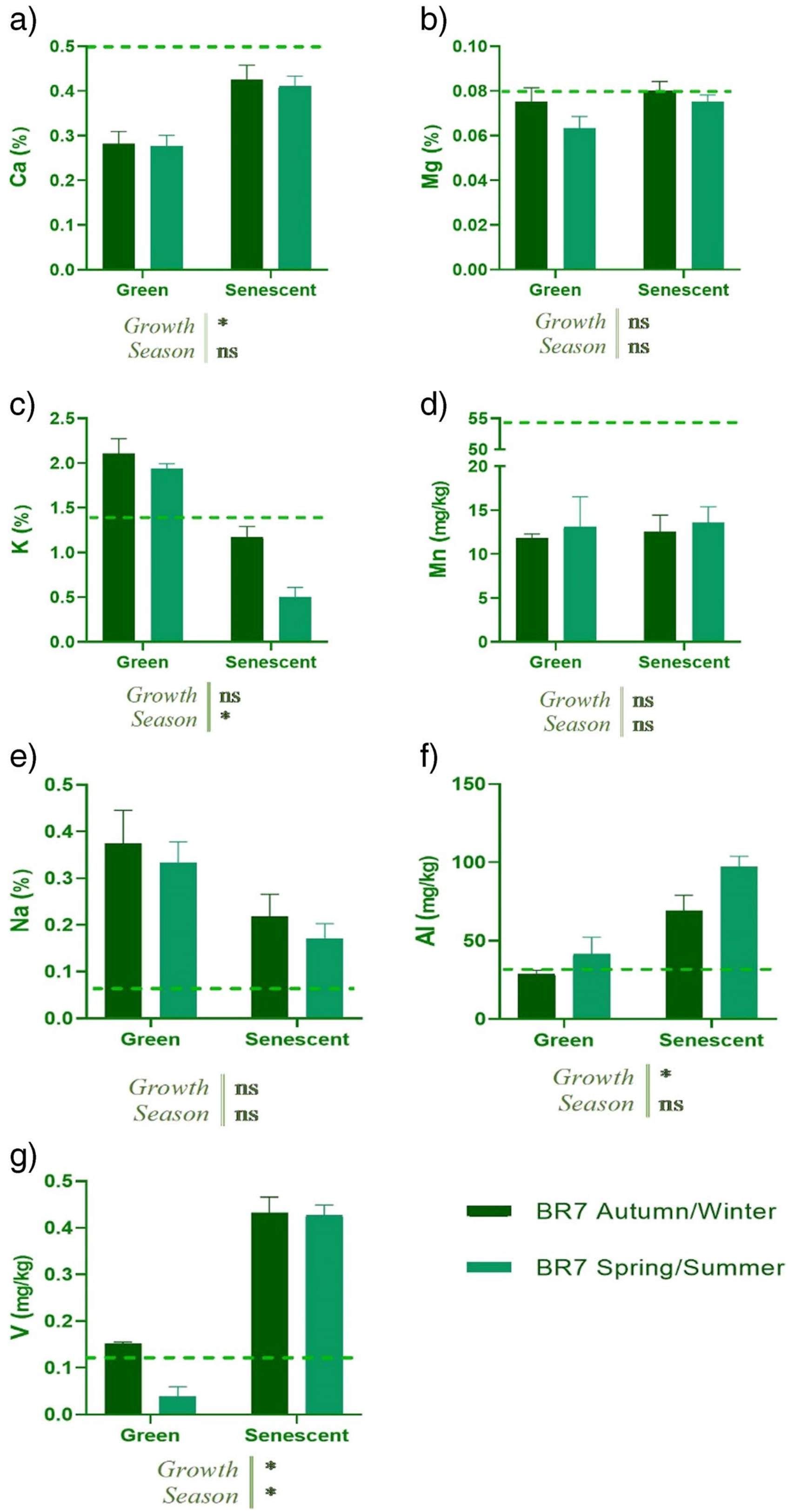

Fig. 4 Seasonal variation of **a**) Ca, **b**) K, **c**) Mg, **d**) Mn, **e**) Na, **f**) Al and **g**) V, in green and senescent plant growth in a rehabilitated grassland. The dotted line represents the mean value recorded in the Reference site

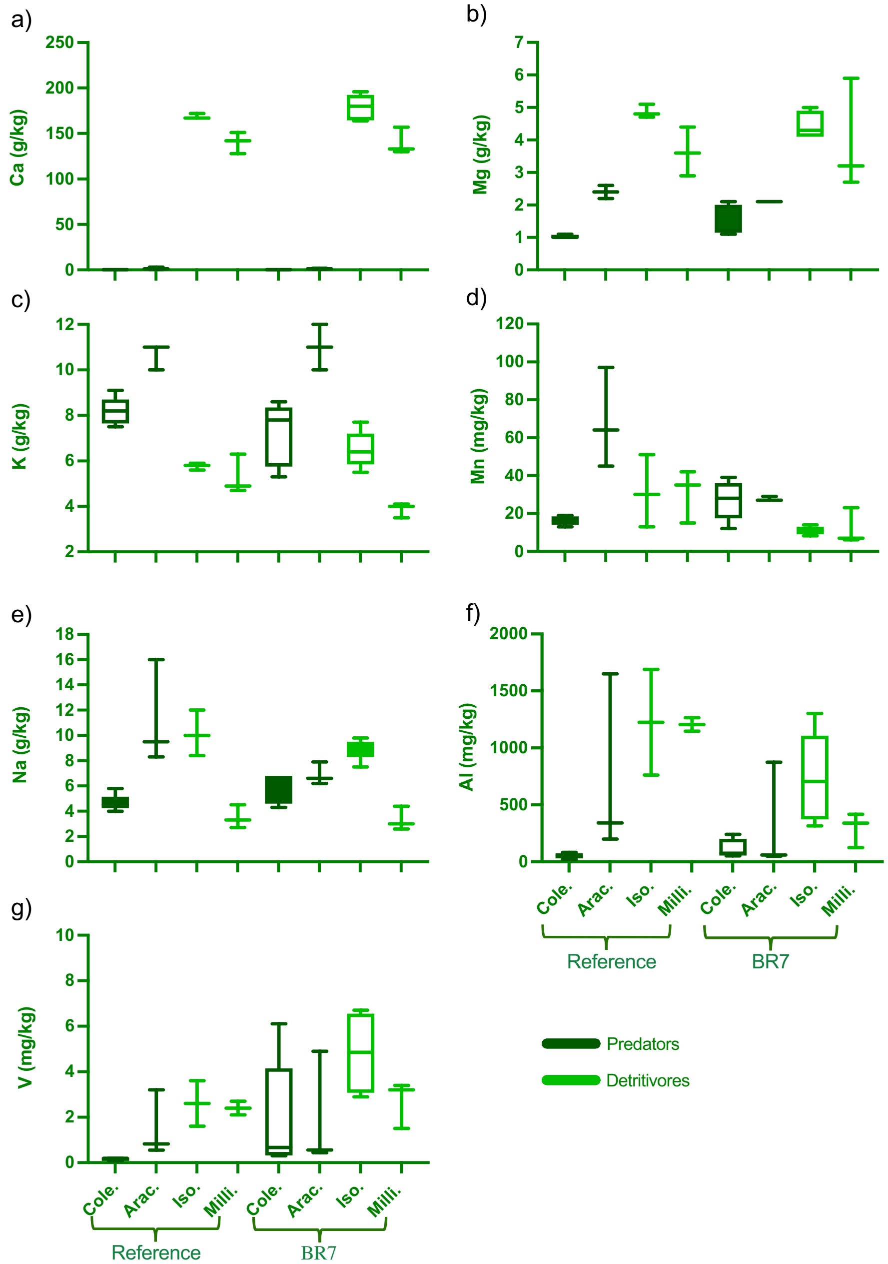

Fig. 5 Elemental composition of invertebrates collected in BR7 and a reference site. **a** Ca, **b** Mg, **c** K, **d** Mn, **e** Na, **f** Al and **g** V

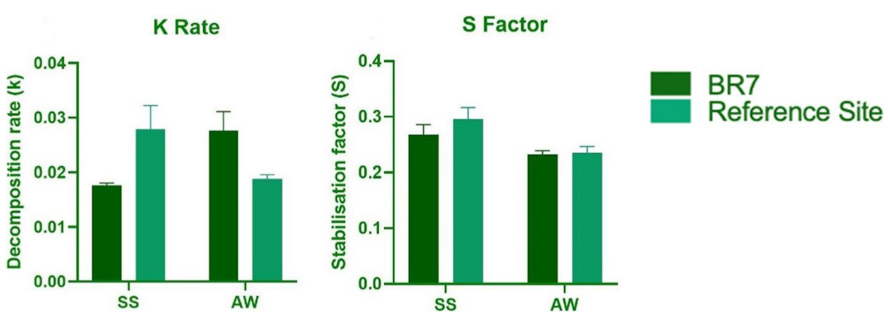

Fig.6 Effect of season on plant litter decomposition in a rehabilitated grassland using the Tea Bag Index

Discussion

Soil/residue

Freshly disposed and unamended, bauxite residue is highly alkaline (pH 10–13), saline (11–30 mS cm), and sodic (ESP 60–90%) and with elevated trace element content and low nutrients (Bray et al. 2018; Di Carlo et al. 2019) and therefore presents a hostile environment for plant establishment and ecosystem development (Phillips and Courtney 2022). The need for amendments such as gypsum, organic additions and nutrient supply to address the challenging properties is well reported (e.g.. Di Carlo et al. 2019; Tian et al. 2020; Zhu et al. 2023) but beneficial effects are often reported in the short-term.

Rehabilitated bauxite residue displayed pH < 9, salinity < 4 mS cm-1 and ESP < 10% thus achieving rehabilitation success criteria (Gräfe and Klauber 2011; Di Carlo et al. 2019). Importantly, as the rehabilitation was implemented seven years previously, the findings indicate sustained rehabilitation criteria and are in agreement with Bray et al. (2018) and Philips and Courtney (2022) who reported sustained rehabilitation after 16 yrs and 10 yrs, respectively.

Lower pH, EC and Na content at depth has been reported in both non-rehabilitated bauxite residues and in rehabilitated bauxite residue (Huang et al. 2022; Bray et al. 2018; Di Carlo et al. 2019). Lower values in the upper 0-10 cm can be attributed to vegetation induced processes such as respiration of CO_2 in rhizosphere, exudation of organic acids, and enhancement of drainage through root channels (Xue et al. 2016; Bray et al. 2018; Huang et al. 2022; Zhu et al. 2023).

Although not determined in this study, unamended bauxite residue typically has exchangeable Na content of ca. 30 cmol kg^{-1} (Phillips 1998) and laboratory column trials have demonstrated gypsum amendment can decrease levels to < 1 cmol kg with sufficient leaching (Anderson et al. 2011). Without amendment, Na reduction under field conditions is slow (Kong et al. 2017).

Findings in the current study are in agreement with Di Carlo et al. (2020a, b) who reported values of < 2 $cmol_c$ kg^{-1} exchangeable Na in 8-year-old rehabilitated bauxite residue and highlights the critical roles of amendment and leaching with rhizosphere activity achieving sustainable rehabilitation.

Higher concentrations of Mg and K in the upper 10 cm may be attributed to the greater organic content from the surface application and subsequent rotovation incorporation during rehabilitation. Exchangeable K is in the 0·16–0·33 c mol mg kg^{-1} range reported by Coppin and Bradshaw (1982) to define severe–slight deficiency in mine soils but are within the range found for the reference soil. Conversely, exchangeable Mg was well below reference soil levels. This qualification of deficiency in rehabilitated mine soils highlights the question of using agronomic methods for assessing novel soils supporting semi-natural ecosystems. Where post-closure land use is non-agronomic the interpretation of soil and vegetation data requires further elucidation (Proto and Courtney 2023).

Mn levels in residue for both seasons were at or below the threshold of critical level for Mn (1.0–5.0 mg/kg) (Sims and Johnson 1991), with no differences between depths. This finding is contrary to the observed trend for Mg and K of higher content in surface samples. Values are similar to those reported by Phillips and Courtney (2022) for rehabilitated bauxite residue after 1–10 yrs. The authors also reported a trend of decreased content by Yr10 and further investigations into assessing nutrient bioavailability in rehabilitated sites is recommended. It is worth noting that target criteria for semi-natural sites need focus as many guideline values are for agronomic use.

Gypsum addition drives pH reduction and results in an enhancement in sorption of V that effectively inhibits metal(liod) release to solution (Lehoux et al. 2013). PO_4 extractable levels of V and Al are comparable to Bray et al. (2018) who reported the elements adsorb onto sorption sites in the residue where there bioavailability is restricted. As the findings after 7 years were consistent with Bray et al. (2018) for 16 yr old residue it is likely that the effects of gypsum amendment are sustained in the long-term.

Vegetation.

While *Dactylis glomerata* is classified as a natrophile (characterised for their ability to accumulate relatively large amounts of Na in the leaf tissue)

(Chiy and Phillips 1995), concentrations were well below the 1% toxicity threshold proposed by Ruyters et al. (2011) and similar to the low values reported for a range of vegetation leaf samples in rehabilitated residue of 1–10 yrs old (Phillips and Courtney 2022). Although decreased plant Na content has previously been reported for gypsum amended bauxite residue (Courtney and Harrington 2012), findings were based on 1 yr old growth trials. Findings from the current study indicate that rehabilitation strategies using gypsum amendment are effective in the long term at mitigating plant available Na.

Ca content was similar over both winter and summer campaigns, as previously reported by Di Carlo et al. (2019), and probably reflects it being largely immobile within plants. Indeed, higher values for Ca were found in the older senescent leaves than in the green newer growth. Ca fails to move rapidly once it has been deposited in the leaf tissue which can lead to deficiencies in newer leaves (Reuter and Robinson 1997). While contents for both the newer green growth and senescent were lower than the reference site and reported values for rehabilitated residue (0.5 – 0.6%).

Conversely, K deficiency has been reported in a range of rehabilitated bauxite residue and attributed to disruption of K balance caused by excessive Na (Di Carlo et al. 2019). Sufficient levels in the green vegetation shows levels higher than the semi-natural grassland reference site. Lower levels in the senescent growth indicates it being a mobile nutrient. If K becomes limited it is redirected to the young growth and developing organs from older leaves (Reuter and Robinson 1997). Adequate K content indicates both sufficient supply in the residue soil matrix and absence of Na induced nutrient deficiencies.

Mg content for both seasons BR7 were lower than the 0.15% critical threshold reported by Reuter and Robinson (1997) but are consistent with levels report by Phillips and Courtney (2022) for vegetation in rehabilitated bauxite residue. Further, values were consistent with the reference site and findings contribute to the wider discussion on the suitability of agronomic methods for assessing semi-natural habitats in reclaimed sites.

In contrast, Mn levels were much lower compared to the reference site and confirm the low plant availability in bauxite residue due to the formation of sparingly-soluble organic and inorganic complexes or specific adsorption to hydrous oxide surfaces (Phillips and Courtney 2022).

Potential V toxicity from alkaline bauxite residue has been indicated by Mišik et al. (2014) but there have been limited field studies assessing content in rehabilitated sites. Concentrations of Al and V in current study were well below those reported Di Carlo et al. (2019) for rehabilitated bauxite residue. Higher values in the study by Di Carlo et al. (2019) may be due to the elevated pH (pH > 9) recorded in some treatments, whereas residue rehabilitation in the current study resulted in effective and sustained pH reduction. Di Carlo et al. (2019) also recorded higher content in winter compared to summer and Nordløkken et al. (2015) noted that concentrations of V and Al were up to 9 times higher in September compared to June for a range of plant species. Seasonal variation of non-essential elements (e.g. Pb) have been noted on rehabilitated tailings sites, with lower concentrations recorded in the summer months and attributed to growth dilution (Crilly et al. 1998; Milton et al. 2002). Further, higher concentrations of Pb were also found in plant litter compared to fresh growth and attributed to increase in internal metal burden and also some degree of surface contamination (Milton et al. 2002). Elevated concentrations of As was also found in plant litter on rehabilitated tailings and were, in part, attributed to the seasonal/ age accumulation and the possible affinity for non-essential elements in plant constituents that are slower to degrade (e.g. cellulose) following the decomposition of organic matter releasing mobile sugars and proteins (Milton and Johnson 1999).

Invertebrates.

Successful rehabilitation requires ecosystem functions, and both ground and soil-living invertebrates play critical roles decomposition and nutrient cycling. Establishment and functionality of soil faunal groups in rehabilitated bauxite residue has received scant attention (Di Carlo et al. 2019). Potentially hostile characteristics of bauxite residue could, through impact on invertebrate activity and element bioavailability, highlight conditions in available element content in the grassland ecosystem. For example, unamended bauxite residue was hostile to earthworm survival but toxicity indicators were mitigated when rehabilitation criteria (e.g. pH ≤ 9.1; ESP ≤ 9.2%) were achieved (Di Carlo et al. 2020a, b).

Stabilisation factor (S) and decomposition rates (k) were similar to those reported by Duddigan et al., (2020) for UK lawns, and indicate normal decomposition rates within the rehabilitated system. Findings are in agreement with Álvarez-Rogel et al. (2022) who report that acceptable soil functionality can be established in rehabilitated mine tailings with lack of organic matter and nutrients as major inhibiting factors. Soil faunal community diversity increases with age since rehabilitation, and higher plant litter decomposition rates in older rehabilitated bauxite residue sites were attributed to higher faunal densities (Finngean et al. 2018). Key decomposer organisms includes isopods, which can be absent in contaminated sites (Filzek et al. 2004) but were found in the rehabilitated site in the current study. Studies on invertebrates from grassland growing on tailings have identified risk of element uptake (e.g. Pb) and transfer (Milton et al. 2002, with no previous studies on grassland on bauxite residue. Elevated Na levels were associated with stress in residue exposed earthworms (Di Carlo et al. 2020a, b). While vegetation content in the residue site was much higher than the reference, Na content in detritivores were similar to the reference site and suggest either osmoregulation may prevent accumulation. Nutrient cations (Ca, K, Mg) were similar between rehabilitated bauxite residue and reference site and suggest that, while vegetation and bauxite residue soil were agronomically deficient, content is adequate to support ecosystem development and function.

V content in isopods (woodlice) from the rehabilitated site are slightly higher than the ca. 3 mg/kg reported by Nannoni et al. (2015) from municipal landfill sites. Higher V content in isopods (woodlice) and earthworms is attributed to their intake of soil, and values in the current study are consistent with those of Di Carlo et al. (2020a, b) where no biomarker stress was associated with the V content in earthworms. Analysis of element content in invertebrates from mine sites have shown carnivorous taxa generally have higher concentrations than species from lower trophic levels, reflecting their exposure to non-essential trace elements (Milton et al. 2004) but was not found for Al and V in the current study.

Conclusions

Analysis of rehabilitated bauxite residue showed sustained rehabilitation criteria was achieved in the rehabilitation zone (0-10 cm) and (10-20 cm) indicating soil formation processes.

Seasonal variation in plant element content highlights both the potential for nutrient deficiencies and elevated content of non-essential elements at different growth stages, with no evidence of phytotoxicity.

Decomposition processes are comparable to a reference analog site and indicate the ecosystem functions establish within rehabilitated bauxite residue.

Element content of invertebrate communities is similar to analog site with non-essential element (Al, V) not exceeding known stressful levels and no evidence of bioaccumulation.

Funding Open Access funding provided by the IReL Consortium

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Álvarez-Rogel J, Peñalver-Alcalá A, Jiménez-Cárceles FJ, Tercero MC, González-Alcaraz MN (2021) Evidence supporting the value of spontaneous vegetation for phytomanagement of soil ecosystem functions in abandoned metal (loid) mine tailings. CATENA 201:105191

Álvarez-Rogel J, Peñalver-Alcalá A, González-Alcaraz MN (2022) Spontaneous vegetation colonizing abandoned metal (loid) mine tailings consistently modulates climatic, chemical and biological soil conditions throughout seasons. Sci Total Environ 838:155945

Anderson J, Bell RW, Phillips IR (2011) Bauxite residue fines as an amendment to residue sands to enhance plant growth potential—a glasshouse study. J Soils Sediments 11:889–902

Andrews SM, Johnson MS, Cooke JA (1989a) Distribution of trace element pollutants in a contaminated grassland ecosystem established on metalliferous fluorspar tailings. 1: Lead. Environ Pollut 58(1):73–85

Andrews SM, Johnson MS, Cooke JA (1989b) Distribution of trace element pollutants in a contaminated grassland ecosystem established on metalliferous fluorspar tailings. 2: Zinc. Environ Pollut 59(3):241–252

Bray AW, Stewart DI, Courtney R, Rout SP, Humphreys PN, Mayes WM, Burke IT (2018) Sustained bauxite residue rehabilitation with gypsum and organic matter 16 years after initial treatment. Environ Sci Technol 52(1):152–161

Chiy PC, Phillips CJ (1995) Sodium in forage crops. In: Phillips CJ, Chiy PC (eds) Sodium in agriculture. Chalcombe Publications, Canterbury, pp 43–70

Coppin NJ, Bradshaw AD (1982) The establishment of vegetation in quarries and open pit non-metal mines. Mining Journal Books, London

Courtney R, Harrington T (2012) Growth and nutrition of Holcus lanatus in bauxite residue amended with combinations of spent mushroom compost and gypsum. Land Degrad Dev 23(2):144–149

Courtney R, Xue SG (2019) Rehabilitation of bauxite residue to support soil development and grassland establishment. J Cent South Univ 26(2):353–360

Crilly J, Kinsella AJ, Johnson MS, Brady E (1998) Evaluation of blood and tissue lead as estimators of exposure in sheep. Ir J Agric Food Res 37:17–28

Di Carlo E, Chen CR, Haynes RJ, Phillips IR, Courtney R (2019) Soil quality and vegetation performance indicators for sustainable rehabilitation of bauxite residue disposal areas: a review. Soil Res 57(5):419–446

Di Carlo E, Boullemant A, Poynton H, Courtney R (2020a) Exposure of earthworm (Eisenia fetida) to bauxite residue: Implications for future rehabilitation programmes. Sci Total Environ 716:137126

Di Carlo E, Boullemant A, Courtney R (2020b) Plant available Al and Na in rehabilitated bauxite residue: a field study assessment. Environ Sci Pollut Res 27:17023–17031

Duddigan S, Alexander PD, Shaw LJ, Sandén T, Collins CD (2020) The Tea Bag Index—UK: using citizen/community science to investigate organic matter decomposition rates in domestic gardens. Sustainability 12(17):6895

Filzek PD, Spurgeon DJ, Broll G, Svendsen C, Hankard PK, Parekh N, Stubberud HE, Weeks JM (2004) Metal effects on soil invertebrate feeding: measurements using the bait lamina method. Ecotoxicology 13:807–816

Finngean G, O'Grady A, Courtney R (2018) Plant assays and avoidance tests with collembola and earthworms demonstrate rehabilitation success in bauxite residue. Environ Sci Pollut Res 25:2157–2166

Gräfe M, Klauber C (2011) Bauxite residue issues: IV. Old obstacles and new pathways for in situ residue bioremediation. Hydrometallurgy 108(1–2):46–59

Guo Y, Ye Y, Zhu F, Xue R, Zhang X, Zhu M, Hartley W, Guo L, Xue S (2022) Improvements on physical conditions of bauxite residue following application of organic materials. J Environ Sci 116:198–208

Huang N, Wu H, Zhu F, Cheng Q, Xue S (2022) Natural vegetation encroachment improves nutritional conditions of bauxite residue disposal area. Bull Environ Contam Toxicol 109(1):135–141

Jiang Y, Huang S, Zhu F, Guo X, Zhang X, Zhu M, Zhang Y, Xue S (2023) Long-term weathering difference in soil-like indicators of bauxite residue mediates the multifunctionality driven by microbial communities. Sci Total Environ 890:164377

Jones BE, Haynes RJ, Phillips IR (2012) Addition of an organic amendment and/or residue mud to bauxite residue sand in order to improve its properties as a growth medium. J Environ Manage 95(1):29–38

Ke W, Li C, Zhu F, Luo X, Feng J, Li X, Jiang Y, Wu C, Hartley W, Xue S (2023) Effect of potentially toxic elements on soil multifunctionality at a lead smelting site. J Hazard Mater 454:131525

Keuskamp JA, Dingemans BJ, Lehtinen T, Sarneel JM, Hefting MM (2013) Tea Bag Index: a novel approach to collect uniform decomposition data across ecosystems. Methods Ecol Evol 4(11):1070–1075

Kong X, Guo Y, Xue S, Hartley W, Wu C, Ye Y, Cheng Q (2017) Natural evolution of alkaline characteristics in bauxite residue. J Clean Prod 143:224–230

Lehoux AP, Lockwood CL, Mayes WM, Stewart DI, Mortimer RJ, Gruiz K, Burke IT (2013) Gypsum addition to soils contaminated by red mud: implications for aluminium, arsenic, molybdenum and vanadium solubility. Environ Geochem Health 35:643–656

Lindsay WL, Norvel WA (1978) Development of a DTPA as a soil response investigation of Mn^{2+} complexation in natural and synthetic organics. Soil Sci Soc Am J 46:1137–1143

Milton A, Johnson M (1999) Arsenic in the food chains of a revegetated metalliferous mine tailings pond. Chemosphere 39(5):765–779

Milton A, Johnson MS, Cooke JA (2002) Lead within ecosystems on metalliferous mine tailings in Wales and Ireland. Sci Total Environ 299(1–3):177–190

Milton A, Cooke JA, Johnson MS (2004) A comparison of cadmium in ecosystems on metalliferous mine tailings in Wales and Ireland. Water Air Soil Pollut 153:157–172

Mišík M, Burke IT, Reismüller M, Pichler C, Rainer B, Mišíková K, Mayes WM, Knasmueller S (2014) Red mud a byproduct of aluminum production contains soluble vanadium that causes genotoxic and cytotoxic effects in higher plants. Sci Total Environ 493:883–890

Nannoni F, Mazzeo R, Protano G, Santolini R (2015) Bioaccumulation of heavy elements by Armadillidium vulgare (Crustacea, Isopoda) exposed to fallout of a municipal solid waste landfill. Ecol Ind 49:24–31

Nordløkken M, Berg T, Flaten TP, Steinnes E (2015) Essential and non-essential elements in natural vegetation in southern Norway: Contribution from different sources. Sci Total Environ 502:391–399

Olszewska JP, Meharg AA, Heal KV, Carey M, Gunn ID, Searle KR, Winfield IJ, Spears BM (2016) Assessing the legacy of red mud pollution in a shallow freshwater lake: arsenic accumulation and speciation in macrophytes. Environ Sci Technol 50(17):9044–9052

Phillips IR (1998) Use of soil amendments to reduce nitrogen, phosphorus and heavy metal availability. J Soil Contam 7(2):191–212
Phillips IR, Courtney R (2022) Long term field trials demonstrate sustainable nutrient supply and uptake in rehabilitated bauxite residue. Sci Total Environ 804:150134
Proto M, Courtney R (2023) Application of organic wastes to subsoil materials can provide sustained soil quality in engineered soil covers for mine tailings rehabilitation: A 7 years study. Ecol Eng 192:106971
Ren J, Chen J, Han L, Wang M, Yang B, Du P, Li F (2018) Spatial distribution of heavy metals, salinity and alkalinity in soils around bauxite residue disposal area. Sci Total Environ 628:1200–1208
Reuter DJ, Robinson JB (1997) Plant analysis, an interpretation manual, 2nd edn. CSIRO, Collingwood
Ruyters S, Mertens J, Vassilieva E, Dehandschutter B, Poffijn A, Smolders E (2011) The red mud accident in Ajka (Hungary): plant toxicity and trace metal bioavailability in red mud contaminated soil. Environ Sci Technol 45(4):1616–1622
Sims JT, Johnson GV (1991) Micronutrient soil tests. Micronutrients Agric 4:427–476
Tian T, Liu Z, Zhu F, Hartley W, Ye Y, Xue S (2020) Improvement of aggregate-associated organic carbon and its stability in bauxite residue by substrate amendment addition. Land Degrad Dev 31(16):2405–2416
Wehr JB, Fulton I, Menzies NW (2006) Revegetation strategies for bauxite refinery residue: a case study of Alcan Gove in Northern Territory, Australia. Environ Manage 37:297–306
Xue S, Zhu F, Kong X, Wu C, Huang L, Huang N, Hartley W (2016) A review of the characterization and revegetation of bauxite residues (Red mud). Environ Sci Pollut Res 23:1120–1132
Zhu F, Hou J, Xue S, Wu C, Wang Q, Hartley W (2017) Vermicompost and gypsum amendments improve aggregate formation in bauxite residue. Land Degrad Dev 28(7):2109–2120
Zhu F, Zhang X, Guo X, Yang X, Xue S (2023) Root architectures differentiate the composition of organic carbon in bauxite residue during natural vegetation. Sci Total Environ 883:163588

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.