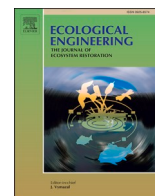


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Enhancing chemical and physical properties of bauxite residue: A one-year assessment using Açai Waste and Gypsum in in-situ rehabilitation

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ABSTRACT

Bauxite residue (BR) from alumina production poses significant environmental challenges, including establishment of a vegetation cover, due to its high alkalinity, salinity, and trace element content. The practice of using topsoil as a cover in bauxite residue storage facilities (BRSF) is unsustainable due to mounting demands on natural topsoil reserves. As an alternative, blending BR with gypsum and organic waste may offer a cost-effective method to improve its chemical and physical properties important to foster better conditions for plant growth. Contrary to previous investigations, which have focused primarily on weathered BR, this study was done on fresh, filter-pressed BR, resulting from more modern, and now commonly used, technologies in alumina production. Here, we assess the in-situ impact of a mixture of gypsum and açai berry waste one-year after its application to a BRSF of non-weathered, filter-pressed BR, in the tropical climate of Northern Brazil. The site has an average annual precipitation of 2085 mm, and the study tested the effect of additions of various mixtures of gypsum (0 %, 5 %, 8 %, and 13 % by weight) and açai waste (0 % and 8 % by weight). Results showed that the treatments with gypsum and açai waste successfully reduced pH levels from 12.0 to 7.7–8.1. Also, Electrical conductivity (EC) reduced significantly and achieved the rehabilitation goal (4mS/cm) after month 4 of the experiment. The exchangeable sodium percentage (ESP) values decreased from 98.8 % in fresh BR to 18.0 % in BR with 8 % gypsum, and to 8.4 % in treatment with 8 % gypsum and 8 % açai waste. Gypsum treatment also decreased the fraction of unstable aggregates of BR from ~70 % to ~40 %. Despite precipitation playing an important role in lowering pH, EC and alkalinity, we found that the combined use of gypsum and açai waste was the most effective in enhancing BR properties by reducing pH and ESP and increasing aggregate stability. As expected, organic material like açai seed waste adds both organic matter and major plant nutrients to BR, thus playing a key role in enhancing soil quality, and in establishing a vegetation cover. This study offers insights into the initial transformations in amended BR and provides a solid foundation for developing closure strategies using gypsum and available and low-cost organic wastes as soil enhancers.

1. Introduction

Mine tailings and mineral processing residues, particularly bauxite residues (BR) from the production of alumina, have emerged as major environmental concerns for the global mining industry. The alumina sector produces about 150 million tons of BR annually, with Brazil being the world's third-largest producer, accounting for 9 % of total

production (Courtney and Xue, 2019). Given the growing demand for aluminum (Al), it is predicted that the global inventory of stored BR could reach 10 billion tons by 2050. Despite continuous attempts to develop BR applications, its reuse is limited to approximately 3 % worldwide (Ujaczki et al., 2018; Xue et al., 2016). Bauxite Residue has been stored in Bauxite Residue Storage Facilities (BRSFs), typically containing BR dewatered with drum filter technology, also known as red

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mud, with less than 65 % solid content. In recent years, however, the industry has shifted to filter press technology, resulting in a higher solid content (>70 %) and dry storage, effectively addressing environmental challenges and concerns of geotechnical stability (Reddy et al., 2021; Kinnarinen et al., 2015). Though some countries classify BR as non-hazardous, others deem it hazardous due to its high alkalinity and high trace metal concentrations (Xue et al., 2016).

Bauxite residue is the by-product of alumina production from bauxite ore through the Bayer Process, and it is a highly alkaline, saline, sodic, and low fertility material (E Di Carlo et al., 2019; Dramou et al., 2023). The alkalinity of BR is primarily related to soluble alkalis (e.g., NaOH, Na₂CO₃, NaAl(OH)₄, Na₂SiO₃) resulting from the Bayer process and is found in pore water and secondary minerals, representing approximately 20 %–25 % of the existing alkalis in the BR (Lyu et al., 2021). In addition, desilication products (DSPs) like sodalite (Na₄Al₃Si₃O₁₂Cl) and cancrinite (Na₄Al₃Si₃O₁₂Cl, Na₆ – 7Ca1–2[Al₆Si₆O₂₄](CO₃,SO₄,Cl₂) 1–2), both formed during the Bayer Process, are present in bauxite residues and are important contributors to long-term alkalinity (Gräfe et al., 2011). At high pH in BR, Al become soluble, as negatively charged aluminate ion forms, together with elevated level of soluble iron (Fe). Trace elements may also be present in BR such as Vanadium (V), Arsenic (As), and Chromium (Cr), but this depends on bauxite age, iron content and mineralogy (Yoho et al., 2019). Untreated BR typically exhibits elevated sodicity, which has a strong negative influence on plant growth (Tian et al., 2020), high bulk density, weak aggregate structures, and low organic carbon content (Guo et al., 2022; Xue et al., 2022).

Rehabilitation of BRSFs is the most used closure method in the industry (Di Carlo et al., 2020a). However, due to the undesirable properties of BR and the large size of the storage facilities closure is challenging. The rehabilitation of some BRSF has relied on topsoil as a cover layer (cap and store) to provide a medium for plant growth. In addition, cap-and-store limits interactions of vegetation with underlying BR as well as the leaching process (Santini et al., 2015). However, sourcing topsoil to cover large areas on BRSF is not sustainable due to higher exploitation pressure in natural areas. Recently, research has increasingly focused on the development of a soil-like medium from BR rather than establishing vegetation on fresh BR (Courtney and Xue, 2019; Dillon and Courtney, 2024; Phillips and Courtney, 2022). Where topsoil is hardly available, BR is often used as a growth medium by mixing with amendments (in situ remediation) such as gypsum (CaSO₄·2H₂O) and several types of organic wastes (Bray et al., 2018; E Di Carlo et al., 2019; Zhang et al., 2023).

The importance of organic and inorganic amendments, as well as enhanced weathering in BR rehabilitation and ecosystem development has long been demonstrated (Bray et al., 2018; Courtney et al., 2014). Gypsum is considered an essential amendment of BR, which reduces the pH through calcite (CaCO₃) formation (Lehoux et al., 2013). In addition, gypsum reduces exchangeable Na⁺ due to displacement by calcium ions (Ca²⁺) from exchange sites (Di Carlo et al., 2020b), while exchanged Na⁺ is subsequently leached together with SO₄²⁻. This Ca–Na exchange will reduce sodicity of BR and increase flocculation and aggregation (E Di Carlo et al., 2019). Furthermore, organic waste is often used as an amendment material to reduce bulk density, increase hydraulic conductivity and increase aggregate stability. Organic waste also acts as an energy source for micro-organisms, enhancing microbial respiration and CO₂ pressure in the BR deposit, resulting in an overall decline in pH. Organic waste also supplies critical nutrients to the BR like nitrogen (N), phosphorus (P), potassium (K), and magnesium (Mg)); (E Di Carlo et al., 2019; Santini et al., 2015), which may further stimulate microbial activity and plant growth (Dong et al., 2022). The provision of amendments is essential for bauxite residue remediation, whereby organic waste streams are commonly available at low cost, but their abundance may vary from country to country. Based on a laboratory column study, Miura et al. (2023) found that gypsum and açai berry waste (common berry from northern Brazil, *Euterpe oleraceae*) enhanced the properties of BR and recommended conducting field trials. Although, laboratory

studies generally indicate the benefits of organic wastes and gypsum, most of these studies were done using weathered bauxite residue while in-situ tests are often lacking. Weathered bauxite residue, which has been exposed to precipitation and carbonation over time, has undergone partial neutralization of the highly alkaline sodium hydroxide used in the Bayer process as well as leaching of Na and V. As a result, weathered bauxite residue typically has lower pH levels, lower alkalinity and aggregation of its structure reducing its reactivity and potential for leaching toxic elements. In contrast, non-weathered bauxite residue is characterized by high alkalinity (pH ranging from 10 to 13). Typically, non-weathered bauxite residue is collected right after the Bayer Process, without being affected by precipitation and carbonation. Consequently, this material can pose higher environmental risks if not managed properly, including soil and water contamination. Thus, two clear research gaps were identified: 1) a need for studies focusing on the rehabilitation of non-weathered bauxite residue and, 2) lack of empirical in-situ data on initial changes in BR properties resulting from these amendments. Addressing these gaps could offer a more comprehensive understanding of bauxite residue rehabilitation strategies.

In response to environmental, social, and safety concerns, recent international standards are increasingly advocating for the progressive revegetation of tailings. This push has led the industry to take proactive steps towards achieving closure. While prior studies confirm that amendments can enhance BR properties for vegetation growth, the depth of this knowledge is largely derived from controlled lab-scale experiments. The step from laboratory to field application has so far received little attention, as evidenced by few in-situ studies in the literature. This gap creates uncertainty about the performance of these organic and inorganic amendments in in-situ conditions. In addition, available references on field studies explored the performance of amendments in highly weathered BR. Therefore, identifying the initial changes in non-weathered BR induced by these amendments remains underexplored. The lack of such knowledge prevents the development of robust closure methodologies for BRSFs aimed at achieving sustainable vegetation cover. Here we follow up a previous laboratory test (Miura et al., 2023), where this is the first of two related studies focusing on an in-situ assessment of effects of the addition of gypsum and açai waste on the properties of non-weathered BR over a one-year monitoring period. Here, the effectiveness of each treatment on BR will be determined by comparing the observed changes in chemical and physical properties to established rehabilitation success criteria.

2. Materials and methods

2.1. Bauxite residue (BR) and amendment materials

Fresh, filter-pressed BR were sourced from the unload shed facility at the Alunorte refinery in Barcarena, Pará, Brazil. Açai (*Euterpe oleracea*) is a tropical palm tree native to the Amazon rainforest, particularly in Brazil. Its fruit, known as açai berry and widely consumed locally, contains a seed which comprises about 85–90 % of the fruit and commonly is discarded during processing. For this study the açai seed waste was collected from a açai processing plant (Ecobiomassa, Barcarena) where the pulp is extracted and the seeds are segregated to be commercialized as biomass for energy production. The açai waste was air dried and mechanically crushed (~2 mm) before being mixed with BR as an amendment. Agronomic gypsum was procured from Gesso Integral, located in Grajaú, Maranhão, Brazil.

2.2. Experimental design

The study was conducted at the Bauxite Residue Storage Facility (BRSF) of the Alunorte alumina refinery in Barcarena, Pará, Brazil (S 1°33'04", W 48°43'10"). Barcarena's climate is classified as Tropical Monsoon (Am in the Köppen climate classification) with an average annual precipitation of 2085 mm and an average annual temperature of

26.6 °C. During June and July 2021, a test area measuring 150m² with a depth of approximately 1 m (10x15x1m) was established. Contour drains were constructed to prevent surface runoff from the surroundings onto the test area. Individual plots, approximately 9m² each (3 m × 3 m), were demarcated using vertically installed, 3 m × 0.5 m high density plastic sheets, sticking out about 0.15 m above the surface. Using a random number generator, the treatments, replicated three times, were randomly allocated across these plots (Completely Randomized Design – CDR). In August 2021, gypsum and açai waste were manually mixed into the top 20 cm layer of BR at specified weight-to-weight percentages (Table 1, Fig. S11). After their establishment, composite soil samples of the upper 20 cm at each plot were collected at monthly intervals between September 2021 and February 2022, while the final two collections were done in May and August 2022. This resulted in a total of eight composite soil samples from each plot. Composite soil samples consisted of 3 subsamples per plot spaced approximately 30 cm apart. After collection, samples were stored in plastic bags, transported to the laboratory, and kept refrigerated at 4 °C pending analysis. By February 2022, the plots were planted with *Urochloa bizzanthe*. Three rows were sown roughly 3 cm deep and spaced 80 cm apart, with a density of 75 seeds per linear meter. Precipitation data were available from the Alunorte weather station, utilizing a Campbell TB4MM system.

2.3. Chemical and physical analysis

2.3.1. BR samples

Total concentrations in BR of sodium (Na), magnesium (Mg), Al, phosphorus (P), potassium (K), calcium (Ca), iron (Fe), vanadium (V), and arsenic (As) were determined following microwave digestion using HF, HCl, and HNO₃ (6,2,2). Extracts were analyzed by ICP-OES (5110 DW, Agilent) and ICP-MS (8800 Triple Q, Agilent). In açai waste, the concentrations of these elements were determined after perchloric acid digestion in a microwave digester ultraCLAVE (Milestone, Italy). Measurements for pH and EC were performed on the soil samples using a 1:10 (w/v) ratio in distilled water, after 24 h of shaking at 150 strokes per minute (spm). pH values were recorded using Thermo Scientific equipment, model Orion Star A211, while EC values were assessed using Hanna Edge EC - HI 2003.02. Chemical extraction of cations (K, Ca, Mg, and Na) was carried out using the ammonium acetate (NH₄OAc-extractable) method, buffered at pH 7, with concentrations of these elements determined using atomic absorption spectrometry (Thermo, model ICE3500). Although, extraction with NH₄OAc-extractable is usually considered to involve exchangeable cations only, this may be different for strongly alkaline BR material high in readily soluble desilication products potentially releasing significant amounts of e.g. Na and Ca. Extractable Al was determined through 1 M KCl extraction.

Total N was determined using the Kjeldahl method (EMBRAPA, 2017), while total organic carbon (TOC) was determined by titration with potassium dichromate (K₂Cr₂O₇). Available P was analyzed by extracting the samples with 0.5 M NaHCO₃ (pH 8.5; 1:100 w/v) (Phillips and Courtney, 2022). The extracted samples were analyzed by UV-Vis spectrometer (Agilent Cary 60) at a wavelength of 600 nm (EMBRAPA, 2017).

The extractable Na percentage (ESP) was calculated by dividing extractable Na by the sum of base cations in the NH₄OAc-extractable, where all extracted metal concentrations are expressed in meq/kg:

Table 1

Treatments of the field experiment. The concentration of amendments is expressed in % (w/w).

Treatments	Gypsum 0 %	Gypsum 5 %	Gypsum 8 %	Gypsum 13 %
BR + Gypsum	Br	BrG	BrG2	BrG3
BR + Gypsum + Açai 8 %	BrA	BrGA	BrG2A	BrG3A

$$ESP(\%) = \frac{(100 * ExtractableNa)}{\sum (ExtractableCa + Mg + K + Na)} \quad (1)$$

Most studies of BR interpret ESP as the exchangeable Na percentage. However, most likely this is overestimation as the NH₄OAc-extractable metal cations in BR, in particular Na and Ca, are potentially to a significant extent derived from secondary minerals like sodalite and cancrinite. Therefore, in this study we define ESP as extractable Na percentage. Although exchangeable Na cannot be determined directly in BR, the exchangeable Na percentage (ExchSP) may be estimated based on SAR values (sodium adsorption ratio), where SAR is derived from Na, Ca and Mg concentrations in aquatic equilibrium solutions (see section 2.3.2). The applied relationship between ExchSP and SAR is in accordance with Gräfe and Klauber (2011):

$$ExchSP(\%) = 1.5 * SAR / (1 + 0.015 * SAR) \quad (2)$$

Aggregate size distribution was performed on moist material, using water as a dispersant, in a Malvern Mastersizer 3000 laser diffraction particle size analyzer. The analysis conditions included an optical model based on Mie theory, opacity between 10 and 15, stirring at 2500 rpm, and ultrasound at 25 % for 30 s before initiating the analysis.

The wet sieve method was employed to determine aggregate stability. Triplicates of air-dried soil aggregates (10 g each) were placed directly on Eijkelkamp wet sieving apparatus with 0.25 mm sieves. Aggregates of this unsorted material larger than approximately 6 mm were hand-picked and not included. The sieves were pre-wetted to moisten the soil from below, to avoid slaking. They were then placed on the apparatus and lowered into the bigger, steel cans filled with distilled water. Next, pre-weighed aluminum containers with a dispersing solution were placed on the apparatus. As dispersing solution, 2 g/L 60 % sodium hexametaphosphate (Na₆[(PO₃)₆]) was used. The apparatus was then turned on again for 10 min. The aggregates left after repeatedly immersing them in the dispersing solution were pressed carefully through the sieve, such that only particles >0.25 mm was left on the sieve. Both sets of cans (steel can with water and aluminum can with dispersing solution) and the sieves containing rest fraction >0.25 mm were placed in an oven at 105.5 °C for 24 h. The unstable aggregate fraction (water-dispersed) and stable fractions (hexametaphosphate dispersed) were determined by weighing the dry cans and subtracting the weight of empty containers, and correcting for the dry weight of the fraction >0.25 mm. The results of aggregate stability can be divided in three categories: stable, unstable and weak aggregates. In this study, we only present stable and unstable aggregates since all weak aggregates presented no significant differences between the treatments.

2.3.2. Water extractable metals and SAR

The concentration of dissolved elements (Na, Ca, K, Al, V and As) in water extracts of the different soils (Br – gypsum and açai waste mixtures) were determined by shaking the samples in a 1:10 ratio aqueous solution for 24 h at 150 (spm) using a table shaker. The concentrations were analyzed using atomic absorption spectrometry, with graphite furnace in case of As, and a flame for the other elements, using a Thermo ICE3500 model. The sodium adsorption ratio (SAR) was subsequently calculated using (Eq. (2)):

$$SAR = [Na^+] / \sqrt{([Ca^{2+}] + [Mg^{2+}]) / 2} \quad (3)$$

Where [] indicate ion concentrations of the leachate in mmol_c /L

2.4. Data analysis

Statistical analyses were executed using R Studio software. The Shapiro-Wilk normality test was first utilized to evaluate the data for normal distribution. To compare the mean values across the different treatment groups, a one-way analysis of variance (ANOVA) was

conducted, followed by post-hoc analysis using the Duncan test. To investigate potential relationships between the chemical properties of the treatments, Pearson correlation coefficients were calculated.

3. Results

3.1. Material characterization

The freshly sourced bauxite residue exhibited strong salinity and alkalinity, as evidenced by a pH of 12.3 and an EC of 3.45 dS/m, with relatively high concentration of Fe, Al, and Na (Table 2). Gypsum displayed a near-neutral pH of 7.35, EC of 2.2 dS/m, and only traces of V and As. In contrast, açai waste was mildly acidic having relatively low EC, while the concentration of total C as well as that of important macro nutrients (N, P, K) were relatively high.

3.2. Effects of amendments on chemical and physical properties of bauxite residue

We found significant differences in pH between treatments (Table 3), which all showed minor variations through the year (Supplementary material, Figure SI 2a). Only treatments involving both gypsum and açai waste achieved pH values well below 9, within a range of 7.7 to 8.1, while the pH of non-amended BR remained at about 12. Amendments with either gypsum or açai waste reached intermediate pH values (Table 3). Also, EC showed considerable differences across the treatments, exhibiting a consistent downward trend over the course of the experiment (Supplementary material, Fig. 1). After 12 months, BR treated with gypsum (a salt) had the highest EC, ranging from 2.00 to 2.89 mS cm⁻¹, whereas the lowest EC was observed in the BR treated with açai waste (BrA; Table 3).

The BrGA treatment exhibited the highest organic carbon (OC) content of all treatments (Table 3). By contrast, treatments with gypsum alone s, had OC levels as low as those in BR (~ 2 %). Similarly, TN levels in the gypsum treatments did not significantly increase. Similar to OC, TN levels increased considerably in all treatments receiving açai waste in particular if added together with gypsum. For instance, BrA recorded a total nitrogen level of 0.12 % at the experiment's end, whereas BrGA and BrG2A demonstrated significantly higher levels of 0.24 % and 0.18 %, respectively. Starting in November, TN levels decreased across all treatments, aligning with the year's driest period. Nevertheless, from January to August, during the rainy season, a rising trend in TN was noticed, particularly in treatments containing açai. It was observed that the BR, BrG, BrG2, and BrG3 treatments had an OC concentration above 1.6 % in all these treatments, although none of them received açai as amendment. This can be explained by the establishment of grasses in the adjacent plots.

The treatments that received both gypsum and açai residues demonstrated significantly lower Na concentrations compared to those that received only gypsum (Table 4). Conversely, the treatment that used açai only displayed higher levels of extractable Na. The addition of açai positively influenced extractable Mg, with the BrA treatment exhibiting the highest Mg concentrations. As expected, treatments that included gypsum indicated elevated levels of extractable Ca, though no significant variations were noted among treatments using different rates of gypsum. In general, there were no significant differences in K across the treatments, with the exception of BrA and BrGA, which possessed the

highest concentrations. Interestingly, no substantial differences were noted in Al concentrations among the treatments. BR and treatments using only gypsum showed insignificant P concentrations, highlighting the importance of açai residue in boosting P concentrations in BR. The amendment with gypsum significantly reduced ESP (to values between 41.1 % (BrG) and 18 % (BrG2)), especially in combination with açai waste (values of 19.4 % (BrGA) and 8.4 % (BrG2A)) (Table 4 and Supplementary material, Fig. 3).

Aggregate size distributions were only carried out for three treatments (Br, BrG2, and BrG3A) at the beginning and end of the experiment (Supplementary material, Table 3). The 90 percentiles of aggregate size (D90) ranged from 53 to 403 µm. The control treatment (BR) had 90 % of its aggregates measure 83.8 µm at the start and 61.1 µm at the end of the experiment. Compared to BR, BrG showed a smaller aggregate size at the beginning of the experiment, however at the end BrG demonstrated a much larger aggregate size. The addition of açai (10 %) with gypsum (15 %) in treatment BrG3 significantly increased the aggregate size.

Unamended BR exhibited a significantly larger percentage of unstable aggregates (approximately 70 %) and a low percentage of stable aggregates (about 15 %) (Fig. 1). By contrast, BR amended with gypsum had roughly equal proportions of unstable and stable aggregates, both around 40 %. The addition of açai waste alone did not improve aggregate stability in BR, exhibiting similar levels of unstable aggregates as the unamended BR. However, when açai and gypsum were used in combination, the treatments demonstrated significantly higher percentages of stable aggregates compared to the gypsum amendment alone. All treatments presented no significant difference for "weak aggregates" therefore are not presented in Fig. 1.

3.3. Effects of amendments on water extractable elements

The data in Table 5 compares the Sodium Adsorption Ratio (SAR) and the concentrations of water-extractable elements at the end of the experiment. Values of SAR, Na and Ca over the 12 months are presented in Supplementary material, Figure SI4. The BR treatment exhibited a significantly higher SAR mean value (325.4), with a notably lower Ca concentration and a markedly higher pH and Al concentration compared to gypsum-amended treatments. Treatments with gypsum (BrG, BrG2, BrG3, BrGA, BrG2A, and BrG3A) showed significantly lower SAR and higher Ca concentrations. Regarding Al concentration, treatments BrG2A, BrG3A, and BrGA showed lower Al concentrations, whereas BrG, BrG2, and BrG3 did not show significant differences. The BrA treatment presented moderate SAR values, differing significantly from both gypsum-amended and non-amended BR. For Al and As concentrations, BrA did not show significant differences when compared to both the amended and non-amended BR. Vanadium concentration in the water-extracted samples were below the limit of detection.

4. Discussion

4.1. The effects of amendments on bauxite residue chemistry

Bauxite residue (BR) is an alkaline byproduct of the aluminum industry, characterized by its high pH value, as evident from the Table 3 where untreated BR has pH of 12.0. The addition of gypsum and açai waste reduces the alkalinity of BR. Gypsum can reduce pH values and add calcium ions which can help in the displacement of sodium ions,

Table 2

Mean pH, EC, and total elemental concentrations of used material (n = 2). * means that parameters were not determined.

Materials	pH	EC	Tot. C (%)	Tot. N (%)	C/N	Na (mg/kg)	Mg (mg/kg)	Al (mg/kg)	P (mg/kg)	K (mg/kg)	Ca (mg/kg)	V (mg/kg)	As (mg/kg)
BR	12,31	3,45	<1	<0.05	*	63,000	120	94,000	230	140	7700	490	16
Gypsum	7,35	2,2	*	*	*	70	410	1400	20	410	116,700	2,87	0,36
Açai waste	5,37	1,39	46,2	1,04	44,5	40	420	250	780	3100	600	0,44	0,05

Table 3

a Mean values and standard deviation of pH, electrical conductivity (mS/cm), organic carbon (OC, %) and total nitrogen (TN, %), ESP (%), NH₄OAc-extractable Na, Mg, Ca, K; KCl-extractable Al and NaHCO₃-extractable P (mmol/kg) at the end of the experiment. Treatments followed by the same letters do not differ significantly ($p < 0.05$; $n = 3$).

Treatments	pH	Std	EC (mS/cm)	Std	OC (%)	Std	TN (%)	Std
Br	12,0	e	0,12	1,26	b	0,11	1,90	b
BrG	11,1	d	0,34	2,22	c	0,36	1,60	b
BrG2	10,1	c	0,66	2,89	d	0,20	2,00	b
BrG3	10,8	d	0,19	2,81	c	0,11	1,69	b
BrA	9,47	b	0,17	0,51	a	0,02	3,06	ab
BrGA	8,17	a	0,12	2,00	c	0,38	4,89	a
BrG2A	7,77	a	0,25	2,34	c	0,02	3,09	ab
BrG3A	8,03	a	0,21	2,36	c	0,04	2,30	b

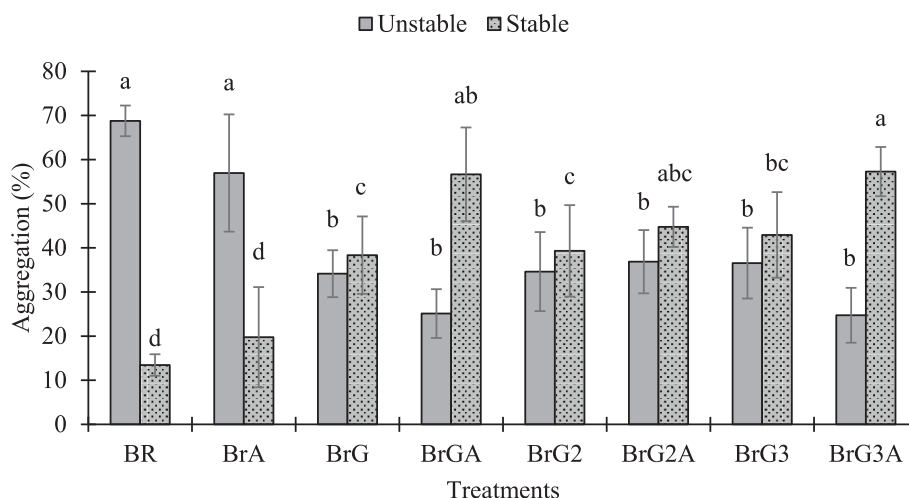


Fig. 1. Mean aggregate stability (%) by treatments ($n = 6$). Error bars represent standard deviation of the mean. Treatments followed by the same letters do not statistically differ at $p < 0.05$.

Table 4

b Mean values and standard deviation of ESP (%), NH₄OAc-extractable Na, Mg, Ca, K; KCl-extractable Al and NaHCO₃-extractable P (mmol/kg) at the end of the experiment. Treatments followed by the same letters do not differ significantly ($p < 0.05$; $n = 3$).

Treatments	ESP (%)		mmol/kg																		
	ESP	Std	Na	Std	Mg	Std	Ca	Std	K	Std	Al	Std	P	Std							
Br	98,8	d	0,1	766	bc	136	0,11	c	0,02	85	c	18	2,19	c	0,25	0,17	a	1,72	< LD	c	0,00
BrG	41,1	c	13,7	562	ab	92	0,21	c	0,08	436	ab	244	1,35	c	0,34	0,35	a	1,59	< LD	c	0,00
BrG2	18,0	ab	12,8	588	a	80	0,16	c	0,08	768	a	394	1,59	c	0,83	0,24	a	2,81	0,10	ab	1,48
BrG3	30,5	bc	6,9	643	b	43	0,12	c	0,03	759	ab	129	1,88	c	0,11	0,16	a	1,79	< LD	c	0,00
BrA	87,4	d	1,2	428	b	53	0,83	a	0,35	141	c	7	3,70	a	0,13	0,13	a	0,32	0,23	ab	1,37
BrGA	19,4	ab	6,6	275	a	115	1,39	b	0,32	336	b	139	4,24	b	0,43	0,29	a	0,08	0,31	a	1,36
BrG2A	8,4	a	0,5	319	a	32	0,97	bc	0,46	686	ab	208	3,97	c	0,45	0,33	a	0,09	0,25	a	0,69
BrG3A	9,1	a	5,5	302	a	103	1,02	c	0,61	896	a	300	3,06	c	0,11	0,19	a	0,10	0,12	ab	0,83

Table 5

Mean values and standard deviation of SAR, and water extracted Na (mg/L), Ca (mg/L), Al (mg/L) and As (mg/L) at the end of the experiment. Treatments followed by the same letters do not statistically differ at $p < 0.05$. ($n = 3$).

Treatments	SAR		mg/L								µg/L										
	SAR	Std	Na	Std	Ca	Std	K	Std	Al	Std	As	Std	V	Std							
Br	325	c	8,80	257	b	6,96	0,0	b	0,00	0,3	b	0,25	10,6	d	1,72	7,1	b	3,15	< LOD	*	*
BrG	4,25	a	1,91	261	b	109	299	a	29,8	0,5	b	0,34	8,6	dc	1,59	0,6	a	0,20	< LOD	*	*
BrG2	1,68	a	1,21	130	ab	95	460	a	20,5	1,2	ab	0,83	5,3	dc	2,81	0,4	a	0,06	< LOD	*	*
BrG3	3,01	a	0,88	228	a	63	443	a	31,6	0,2	ab	0,11	5,8	bcd	1,79	0,5	a	0,12	< LOD	*	*
BrA	154	b	11,9	121	c	9,43	0,0	b	0,00	1,2	ab	0,13	3,0	bc	0,32	3,7	ab	0,93	< LOD	*	*
BrGA	1,26	a	0,42	72,2	c	23	269	ab	76,1	1,2	ab	0,43	0,2	a	0,08	0,6	a	0,04	< LOD	*	*
BrG2A	0,66	a	0,08	53,5	c	9,24	497	a	56,0	0,5	a	0,45	0,1	a	0,09	0,7	a	0,22	< LOD	*	*
BrG3A	0,71	a	0,46	54,7	a	36	463	a	37,3	0,2	a	0,11	0,1	a	0,10	0,6	a	0,09	< LOD	*	*

thereby potentially reducing the levels of exchangeable Na (sodicity). In addition, açai waste, an organic material, further aids in pH reduction by producing organic acids and CO₂ during its decomposition. After sixth month (Supplementary material – Figure SI2.a), following approximately 1100 mm accumulated rainfall, only amendments of gypsum combined with açai waste reached the BR rehabilitation target of pH value <9 (Santini and Banning, 2016; Taki et al., 2023). Our results also indicate that, in combination with 10 % açai waste, a gypsum dose of 5 % is sufficient, while greater gypsum doses did not result in a significantly stronger reduction in pH. Although addition of either gypsum or açai waste alone caused a significant reduction of pH, mean values remained above the target goal for BR rehabilitation after 1 year (Table 3).

The reduction of pH by gypsum alone confirms results from (Elisa Di Carlo et al., 2019a; Li et al., 2018) and is caused by the dissolution of Ca²⁺ ions, followed by the formation of Ca(OH)₂, tri-calcium aluminate (Ca₃Al₂O₆), hydrocalumite (Ca₄Al₂(OH)₁₂(CO₃).(2–3)H₂O, and CaCO₃, respectively, processes which all produce acidity (Power et al., 2011). Besides a decline in pH, divalent Ca²⁺ ions derived from gypsum also displace electrostatically bound monovalent Na⁺ ions from cation exchange sites. Subsequently, the Na⁺ ions are leached together with SO₄²⁻ ions.

The role of açai waste in decreasing the pH of BR (Table 3) has received little attention, but here we show a significant reduction in pH throughout the experiment (Supplementary material – Figure SI2.a). This is in line with a previous column test by (Miura et al., 2023). The decrease in pH in response to the addition of açai waste (BrA, BrGA, BrG2A, BrG3A) may be due to its decomposition, producing organic acids, CO₂ and thus carbonic acid (H₂CO₃) (Santini et al., 2015; Santini et al., 2015). As observed by previous studies (Banning et al., 2011; Santini and Banning, 2016), the introduction of organic waste increases microbial activity in BR. It is well established that microbial activity aids in the neutralization of alkalinity through the release of organic acid metabolites and biological carbonation due to the release of respiratory CO₂ by the microflora (Santini et al., 2015; Santini and Banning, 2016).

The effectiveness of a combination of gypsum and organic amendments in reducing the pH of BR as shown in our field experiment supports previous laboratory studies (Miura et al., 2023). Earlier, in a laboratory test (Wong and Ho, 1995) observed a leachate pH of 8.5 after 1200 mL water addition (equivalent to 126 mm rainfall) in BR amended with 8 % gypsum, whereas gypsum (8 %) in combination with sewage sludge (8 %) reduced the pH to 8.4. Similarly, Jones and Haynes (2011) found, that after a leaching volume equivalent to 396 mm of rainfall, columns containing BR sand treated with gypsum (2 %) achieved a pH of 8.1, while BR treated with biosolids (~4 %) in combination with gypsum (2 %) reached a pH of 7.7. It is important to note that most of these previously published studies used weathered BR from disposal areas with lower initial pH (~10.5) than the unweathered, fresh BR samples used in our study (pH ~12.5). In contrast to weathered BR, unweathered BR has significantly more alkalinity and secondary minerals such as sodalite and cancrinite (Courtney and Kirwan, 2012).

All treatments resulted in EC values below the rehabilitation target value for salinity of EC < 4mS/cm (Power et al., 2011) at month 4 (Supplementary material – Figure SI2.b). The EC responded rapidly to precipitation, in all treatments, reaching the target value by the third month after approximately 500 mm of precipitation. Throughout the experiment, the gypsum treatments exhibited a higher EC. On the other hand, the treatment involving only açai waste resulted in the lowest EC. An increased EC in the presence of gypsum (BrG, BrG2, BrG3) is linked to the dissolution of gypsum, releasing Ca²⁺ and SO₄²⁻ into the soil solution and hence increasing the concentration of salts in solution. This finding is consistent with previous studies, such as that conducted by Jones et al., 2015, which highlighted the EC of phosphogypsum amended BR in increasing ionic strength.

As yet, there is no consensus about the sodicity threshold for the rehabilitation of BR. This is in part due to analytical challenges

associated with the determination of exchangeable Na in BR material. In soils NH₄OAc-extraction, buffered at pH 7, is commonly used and thoroughly tested as a method to determine exchangeable cations. Subsequently, exchangeable cations are used to calculate ESP (Eq. (1)). However, in BR NH₄OAc-extraction most likely overestimates exchangeable Na, due to partial dissolution of desilication products like sodalite minerals (Di Carlo et al., 2020b). Therefore, the ESP determined by this method is better defined as the NH₄OAc-extractable Na percentage, which does not involve exchangeable Na alone.

Despite the uncertainty when using NH₄OAc-extractable to determine ESP (Eq. (1)) in BR material, Di Carlo et al. (2020a) concluded that the NH₄OAc-extractable method is the most suitable method to assess Na and sodicity. In part this is because the method is simple and broadly used in studies of BR amendments, thus facilitating comparison of different amelioration approaches (Bray et al., 2018; Elisa Di Carlo et al., 2019b). A sodicity rehabilitation goal of ESP < 30 % has been suggested (Di Carlo et al., 2019). The ESP values of fresh, non-weathered BR at Barcarena are consistent with those reported in other recent studies (Di Carlo et al., 2020b; Xue et al., 2016). The ESP values (Table 3b) for the açai waste amendment (87 %) showed no significant difference compared to the unamended BR (98 %). In contrast, all treatments involving gypsum significantly reduced the ESP. By the end of the experiment in month 12 (Table 3.b), following approximately 2800 mm of rainfall, only treatments that combined gypsum with açai waste amendments successfully reached the target ESP value.

Leaching is vital in BR rehabilitation as it removes excess salts (Bray et al., 2018; Elisa Di Carlo et al., 2019b). Already in the first month after establishing the field experiment, the concentration of dissolved Na⁺ decreased significantly in BR amended with Açai waste both with or without gypsum (Supporting Information – Figure SI4b). Five months after initiating the field experiment, leaching (approximately 1000 mm of accumulated precipitation) resulted in significant decline in. This was particularly evident for treatments that were solely amended with gypsum (Supplementary material – Fig. 4.b). Even after a year-long experiment and 2800 mm of accumulated precipitation (Table 3.b), BR continued to display notable NH₄OAc-extractable Na concentrations. These concentrations were higher in unamended BR as opposed to those treatments amended with gypsum. The divalent Ca²⁺ ions displace the more weakly held monovalent Na⁺, thus making them more susceptible to leaching through the soil (Jones et al., 2015). The impact of gypsum application on reducing extractable Na can have long-term effects, as reported by (Bray et al., 2018) who showed the effectiveness of gypsum even after 16 years of BR rehabilitation. Contrary to previous assessments, the addition of açai waste alone did not enhance Na leaching compared to unamended BR (Bray et al., 2018; Dong et al., 2023; Jones and Haynes, 2011). Our results can be explained by the higher proportion of exchangeable sites occupied by the monovalent cation (Na⁺) in the absence of the divalent cation (Ca²⁺) present in açai waste (Ippolito et al., 2005; Mavi et al., 2012).

A potentially better way to estimate the exchangeable Na percentage (here defined as ExchSP) in BR material may be based on SAR (see Eq. (3)). In aquatic solutions, e.g. water extracts of BR materials, rapid equilibration between dissolved and exchangeable Na⁺ and Ca²⁺ allows the estimation of SAR and thus ExchSP (Eq. (2)). This approach to determine sodicity has many advantages as SAR only depends on solute concentrations in aquatic equilibrium solution, which can be determined with high accuracy. Elisa Di Carlo et al. (2019b) recommended a rehabilitation goal for BR at SAR < 7. A comparison of measured ESP (using NH₄OAc-extractable) and ExchSP, computed based on SAR, shows that the former exceeds the latter in nearly all cases (Fig. 2). This supports our previous assumption that Na derived from secondary minerals contributes to NH₄OAc-extractable Na, thus overestimating both exchangeable Na and ESP.

Rehabilitation goals based on SAR values were reached in 2 months in treatments involving gypsum (approximately 370 mm precipitation), while after 1 year we found SAR < 3 (Supplementary material –

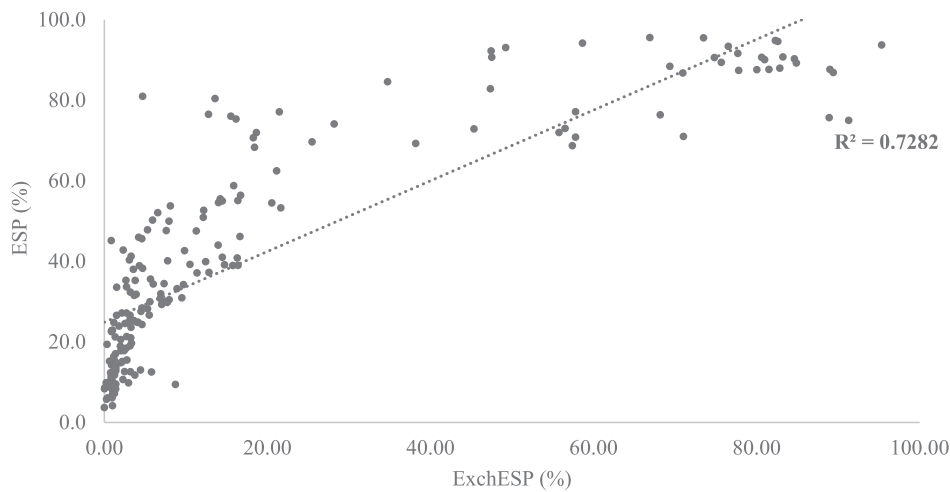


Fig. 2. Scatterplots of measured ESP (NH₄OAc-extractable) against ExchESP, as computed based on SAR (Eq. (2)) during one-year. The line indicates the 1:1 relationship.

Figure S14.a). Gypsum treated BR maintained relatively low SAR values due to the release of Ca²⁺ from gypsum into solution, followed by its exchange with Na⁺. Subsequently, the exchanged Na⁺ is leached together with SO₄²⁻. In a column experiment, (Li et al., 2018) found that after leaching with 6 pore water volumes, the SAR of BR was 191, which was lower than values in our study (SAR = 325; Table 4). By contrast, these authors found SAR = 76 for BR treated with gypsum (1 %) and biosolids (6 %), which was significantly higher than any of our combined treatments of BR with gypsum and açai waste. Our results concur with those observed by Chaganti et al. (2015), who reported significant reductions in SAR after leaching saline-sodic soils amended with gypsum. It should be noted that these authors performed their experiment in weathered BR. When compared to unweathered BR, weathered BR show significantly lower pH, salinity and sodicity content, thus being more susceptible for amendment strategies that aim rehabilitation.

The introduction of açai waste into the BR enhanced the levels of essential nutrients (N, P, K) for plant growth (Table 3 and 3.b). Di Carlo et al. (2019), have highlighted the potentially limiting role of low available concentrations of macronutrients, Ca, Mg, K, and P, for sustainable plant growth in BR environments. Here, we report higher levels of Mg and K in treatments amended with açai. These findings support work by Jones and Haynes (2011) who documented the successful development of *Acacia saligna* shoots and roots in bauxite residue sand treated with comparable levels of Mg and K. Due to its high Fe content, BR is generally low in plant-available P (Di Carlo et al., 2019). Our field study shows that açai waste significantly increases Olsen-P and in combination with gypsum further increment on P levels was observed in BrGA and BrG2A. The fraction of stable aggregates in BrA were significantly lower than in BrG, BrG2, and BrG3. This could potentially be explained by the nature and extent of decomposition of the organic matter applied, as these factors influence soil aggregation. As an example, Harris and Rengasamy (2004) found that green manure was ineffective at binding microaggregates into larger, water-stable aggregates. Also, these authors observed that the addition of organic matter in conjunction with gypsum enhanced BR aggregation more than the sole application of gypsum.

One of the main concerns regarding the rehabilitation of BR is the presence of potentially phytotoxic elements. The concentration and type of these elements in water extracts can vary, depending on the chemical composition of the bauxite ore, the extraction and filtration process used in the refinery, and the disposal method (Reddy et al., 2021). In this study, a preliminary screening shows that only Al, As, and Na were identified at concentrations potentially toxic to plants, while other elements commonly cited BR such as Vanadium (V) were below LOD

(Table 4) (Lehoux et al., 2013; Lockwood et al., 2014; Burke et al., 2012). Similar to a previous column study, water extractable Al concentrations were significantly reduced due to the application of gypsum or açai waste compared to unamended BR (Fig. 3.a). Our results show that total dissolved Al concentrations are close to zero when the pH is below 10. High pH of unamended BR leads to elevated Al concentrations due to its dissolution (Lehoux et al., 2013; Ščančar and Milačić, 2006). At pH values of 8 and above, Al occurs mainly as the anionic species Al(OH)₄⁻ (Miura et al., 2023). Aluminum becomes increasingly insoluble below pH ~10.5, precipitating as an amorphous oxyhydroxide phase (Burke et al., 2012). Despite pH < 10, BR treatments with only organic matter showed slightly elevated Al concentrations. Ligand exchange between carboxylate groups and Al-hydroxyl groups may form stable complexes of organic compounds such as humic and fulvic acids (Perdue et al., 1976; Schlautman and Morgan, 1994). Also, Ca²⁺ may create bridging between organic matter and naturally present minerals in bauxite residue (e.g. goethite, boehmite and gibbsite), thus reducing DOC-associated Al concentrations in leachate samples (Miura et al., 2023). A decline in Al concentration and pH due to the simultaneous addition of gypsum and organic matter has been reported in previous studies. For example, in column experiments Jones and Haynes (2011) found that BR amended with poultry manure (10 %v/v) in subsurface layers caused a significant decline in Al concentration in the leachate. In another study, Lehoux et al. (2013) assessed Al concentration in the solution after batch tests with BR amended by gypsum (1 to 15 % w/w) and reported significantly lower Al concentration in the solution.

The addition of gypsum to the organic-amended BR significantly reduced As mobility throughout the experiment (Fig. 3.b). This is most likely due to the decrease in pH brought about by the addition of gypsum and açai waste, leading to an increase in the As sorption capacity of Fe (hydr)oxides that naturally occur in the BR (Dixit and Hering, 2003; Lehoux et al., 2013; Burke et al., 2012). When analyzing the treatments that received only gypsum, it was observed lower As concentrations compared to unamended Br despite presenting pH above 10. This may be explained by the increase adsorption of As(V) by clay minerals in the presence of Ca²⁺ ions due to changes in the surface charge characteristics in the gypsum-amended BR. In line with our experiment, Burke et al. (2013) reported 81 % removal of As from solution after gypsum was added to BR leachate, as a result of the association of arsenate with positively charged carbonate surfaces.

4.2. The effects of amendments on soil aggregation and aggregate size

Among the treatments, the BR plots exhibited the least stable

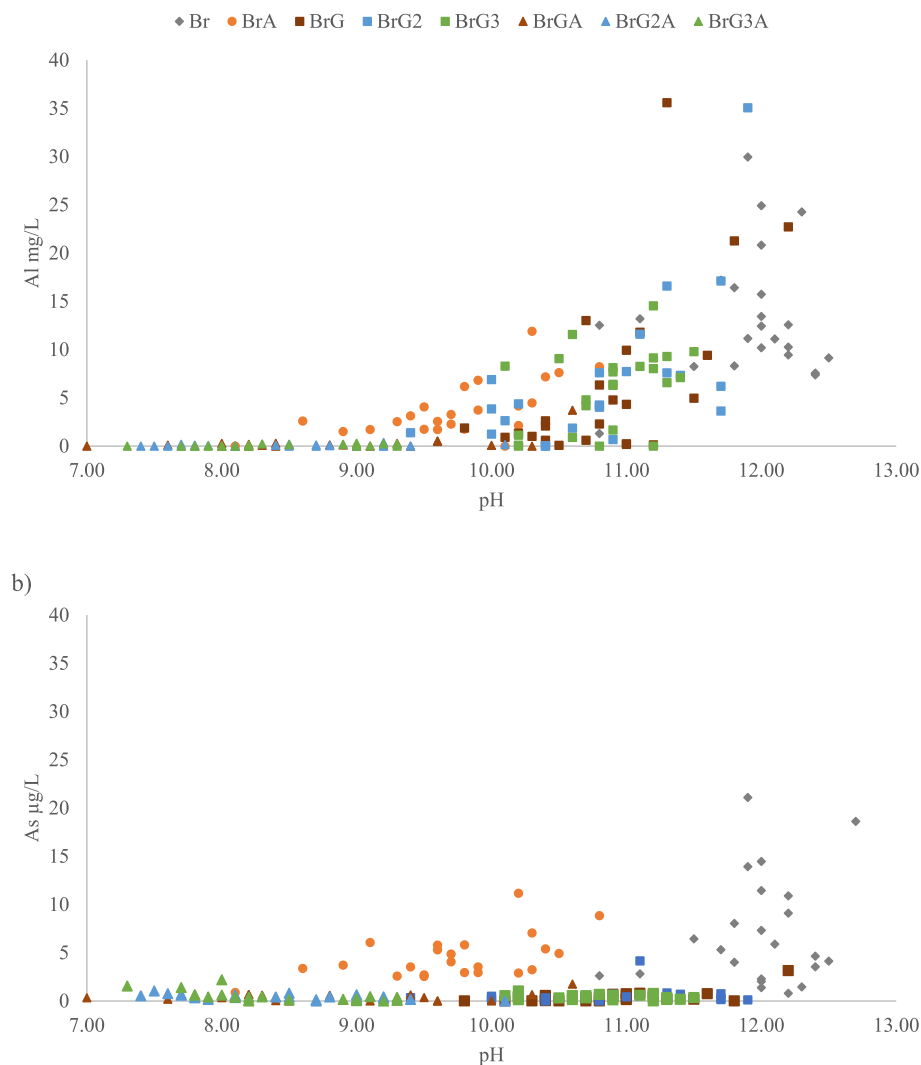


Fig. 3. Concentrations of Al (a) and As (b) in water extracts as a function of pH across treatments during the one-year experiment. Square represents treatment with gypsum only, triangle gypsum with organic matter, circle organic matter only and diamond BR only.

aggregation (Fig. 1) and smallest aggregate size (Supplementary material – Table 3). This is similar to observations in other untreated bauxite residues (Zhu et al., 2017; Haynes and Zhou 2019b). The inclusion of gypsum successfully enhanced stable aggregation and increased the diameter of the aggregates. Gypsum improved the physical properties of residues by decreasing sodicity in the soil solution. Hence, through gypsum addition, the dispersive effects of monovalent Na^+ ions is replaced by the flocculating effect of divalent Ca^{2+} , thus enhancing the stability of both microaggregates and macroaggregates (Xue et al., 2016; Zhu et al., 2017). Additionally, Ca^{2+} added by gypsum may create bridging between naturally present minerals in bauxite residue (ex: goethite, boehmite and gibbsite) with organic compounds. Tian et al. (2020), who investigated the effects of gypsum on the evolution of aggregate structure, demonstrated that aggregate size effectively increased when gypsum was added to BR. Aggregate stability of BR treated with açai waste alone did not significantly differ compared to unamended BR. However, blending gypsum with açai waste led to further enhancement of stable aggregates compared to gypsum-treated BR. Additionally, the aggregate size of BrG3A at the end of the experiment was almost twice the size compared to BrG. The enhancement of BR aggregate stability and aggregate size have been found to correlate with the application of organic matter and gypsum (Zhu et al., 2017). Organic amendments typically stimulate microbial activity when added to soils, leading to the production of complex organic compounds that

may bind soil aggregates (Santini et al., 2016). Tang et al. (2023), exploring the significant factors of physicochemical properties in shaping aggregate structure in BR, reported that citric acid tends to promote the formation of silt-clay fraction and microaggregates, while complex macromolecular organic acids are more conducive to promote the formation of large aggregates. These findings indicate the potential of amendments like gypsum and organic waste, such as açai, to transform the physical properties of BR and create conditions that are more conducive to plant growth and ecosystem restoration.

5. Conclusion and implications for rehabilitation

In this study, we performed an in-situ assessment over a year-long monitoring period to investigate the effectiveness of different amendments on BR. We sought to bridge an identified knowledge gap in the context of BR rehabilitation, specifically focusing on the early stages of changes after adding amendments to non-weathered, fresh, filter-pressed BR in a humid tropical climate. Here we show the significant potential of gypsum and açai waste as ameliorating agents in the initial stage of BR rehabilitation. Both amendments resulted in substantial reductions in pH and ESP, enhancing rehabilitation. Moreover, they improved BR physical properties by promoting aggregate stability and enhancing aggregate size, thereby making the BR more conducive to plant growth.

Additionally, the study found that the amended BR with a combination of gypsum and açai waste showed decreased mobility of potentially toxic elements such as aluminum and arsenic, thus reducing potential hazards to vegetation. While gypsum application significantly enhanced the leaching of sodium - a vital process for the removal of excess salts from BR, the application of açai waste did not appear to enhance this leaching compared to unamended BR. However açai waste does cause a decrease in toxic Al concentration in solution. The chemical composition of the amendment plays a pivotal role in the rehabilitation process. Incorporating organic matter and gypsum into BR proved beneficial in improving its aggregation and decreasing its salinity, thereby enhancing its suitability for plant growth.

This research not only contributes significantly to the understanding of initial changes in amended BR, but also provides a solid basis for developing robust closure methodologies using gypsum and açai waste. Future research should continue to optimize the effective ratios of gypsum and açai waste, aiming for the best possible outcomes optimizing costs in BR remediation and the establishment of sustainable vegetation cover.

CRedit authorship contribution statement

Yuuki Silveira Miura: Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jan Mulder:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Valentina Zivanovic:** Methodology, Formal analysis. **Ronan Courtney:** Writing – review & editing, Validation, Supervision, Conceptualization. **Adriana Souza:** Investigation, Data curation. **Hogne Stubhaug:** Formal analysis, Data curation. **Gudny Okkenhaug:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

Yuuki Silveira Miura reports financial support and equipment, drugs, or supplies were provided by Norsk Hydro ASA. Yuuki Silveira Miura reports a relationship with Norsk Hydro ASA that includes: employment.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecoleng.2024.107500>.

Data availability

Data will be made available on request.

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