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The effects of gypsum and açai as amendments on bauxite residue as a growth medium: chemical properties, mobility of toxic trace elements and vegetation experiment

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ABSTRACT

As the third most common element in the earth's crust, aluminum possesses functional qualities for a variety of industrial and household applications. The extraction of primary aluminum from bauxite ore accelerated in response to higher demand, resulting in significant increase in bauxite residue. This by-product has unique features resulting from the diverse ore compositions and additives employed in the Bayer manufacturing process. With features such as high pH, high salt content, and the presence of toxic trace elements, the environment is significantly challenged by discharges in addition to rehabilitation and exploitation of disposal areas.

In this thesis, the effect of adding gypsum and açai both individually and in combination to improve the bauxite residue into a functioning growth medium is investigated. Bauxite residue that has been treated in the field is examined for changes in pH, electrical conductivity, organic carbon content, as well as toxic trace elements (arsenic, vanadium, and aluminum) in the porewater before, during, and after vegetation experiment with ryegrass (*Lolium perenne*). Simultaneously, the uptake of toxic trace elements in the vegetation is analyzed.

The results were calculated using the mean values of triplicates for each amendment. The addition of 10% açai alone lowered the pH from ~10 to ~9, whereas the addition of gypsum alone or in combination with açai significantly lowered the pH to ~7-8, which provided a favorable environment for plant growth. The amendment with 10% açai + 10% gypsum showed the best growth measured in height. The results also showed that a combination of gypsum and açai together led to better growth than either component alone. Trace element concentrations in porewater were dominated by pH, indicating degrees of leaching from solid phase to solution. Trace elements in porewater samples with higher pH in oxidizing conditions were present in anionic form and exhibited higher concentrations. The best-growing samples did not demonstrate a higher uptake of trace elements, but they were likely bound to the DOC present in the solution.

Comparisons between the amendments revealed that açai alone was insufficient to enhance the bauxite residue conditions. The lack of plant-available nutrients and organic carbon in gypsum-only amendments also inhibited plant development, but proved that gypsum is an effective approach for forming a pH-appropriate basis. Amendments with gypsum and 10% açai required no more than 10% gypsum since the system presumably reached saturation and did not increase cation exchange between Ca and Na. For future studies, it may be advantageous to experiment with additive concentrations to obtain optimal plant development and perform geochemical modeling to determine metal speciation and mobility to substantiate the findings. In addition, a larger-scale experiment with seeding in the field and an evaluation of microbiological activity may be valuable

to assess the long-term effect.

SAMMENDRAG

Som det tredje mest forekommende stoffet som finnes i jordskorpen har aluminium allsidige egenskaper til mange bruksområder i både industri og husholdning. Ekstraksjon av primæraluminium fra bauksittmalm økte i høyt tempo etter forespørsel og har ført til store mengder med bauksittavfall. Dette biproduktet innehar spesielle egenskaper som stammer fra ulike sammensetninger av malmen samt tilsetninger i Bayer prosessen benyttet i produksjonen. Med karakteristikkene som høy pH, høyt saltinnhold og inneholder toksiske sporelementer, utfordres omgivelsen i stor grad i forbindelse med utslipp ved lagring i deponi og tiltak for rehabilitering og nyttiggjørelse av deponiområder.

I denne oppgaven undersøkes effekten av tilsats av gips og açai både hver for seg og i kombinasjon for å forbedre bauksittavfallet til et fungerende vekstmedium. Bauksittavfall som ble behandlet på forhånd i felt analyseres for endring i pH, elektrisk konduktivitet og innhold av blant annet organisk karbon, samt toksiske sporelementer (arsen, vanadium og aluminium) i porevannet før vekstforsøk med gress (*Lolium perenne*), under og etter vekst sammenlignet med ubehandlede prøver. Samtidig analyseres opptak av toksiske sporelementer i vegetasjon fra samme vekstforsøk.

Resultatene ble behandlet med gjennomsnittsverdier av triplikater fra hver behandling. Tilsats av 10% açai alene senket pH fra ~ 10 til ~ 9 , mens tilsats av gips alene og i kombinasjon med açai senket pH-verdien betraktelig til mellom $\sim 7-8$, som utgjorde et godt grunnlag for plantevekst. Behandlingen med 10% açai + 10% gips viste best vekst målt i høyde. Resultatene viste også at kombinasjon av gips og açai sammen førte til bedre vekst enn kun ved tilsats av den ene. pH-en utgjorde den dominerende faktoren for konsentrasjoner av sporelementer i porevann, som indikerte utlekking fra fast fase til løsning. I prøver med høyere pH og antatt oksiderende forhold var sporelementene tilstede i anioniske former og hadde dermed høyere konsentrasjoner i porevannsprøver. Prøver med forhold som resulterte i best vekst hadde derimot ikke høyere opptak av sporelementer, men var antatt bundet til DOC tilstede i løsningen.

Sammenligning av behandlingene viste at açai alene ikke var tilstrekkelig til å forbedre forholdene i bauksittavfallet. Mangel på plantetilgjengelige næringsstoffer og organisk karbon i behandlinger med kun gips førte heller ikke til gode vekstresultater, men bekreftet bruk av gips som en bra metode for å danne et akseptabelt grunnlag når det gjelder pH. Behandlinger med kombinasjoner av gips og 10% açai krevde ikke mer enn 10% gips da systemet antakeligvis nådde metning og økte nødvendigvis ikke kationbytte mellom Ca og Na. For videre studier kan det være verdifullt å eksperimentere med mengder av tilsatsene for å oppnå optimale vekstresultater og utføre geokjemisk modellering for å bestemme metallspesier og mobiliteten for å underbygge funnene. I tillegg utvide eksperimentet til større skala med planting i felt og evaluere mikrobiologisk aktivitet for å bestemme langtidseffekten.

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List of Abbreviations

ANC	Acid Neutralization Capacity
BR	Bauxite Residue
BRDA	Bauxite Residue Disposal Area
DOC	Dissolved Organic Carbon
DSP	Desilication Product
EC	Electrical Conductivity
ESP	Exchangable Sodium Percentage
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
TOC	Total Organic Carbon

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1 Introduction

1.1 Background

As the third largest naturally occurring element, aluminum is the most abundant metal in the earth's crust. Metallic aluminum was first produced in 1825 by Hans Christian Ørsted by heating aluminum chloride with potassium amalgam, which was then separated into aluminum and mercury via distillation. Greater quantities of aluminum were produced after 1886 when the Hall-Héroult method was invented to separate pure aluminum from aluminum oxide by electrolytic reduction (Haupin, 2003). Aluminum has unrivaled features, including its light weight, resistance to corrosion, versatility, and ability to be recycled with only 5% of the energy necessary to produce primary metal (Hydro, 2021). Bauxite is the most common material for extracting alumina in aluminum production and the illustration of the process is shown in Figure 1.1.

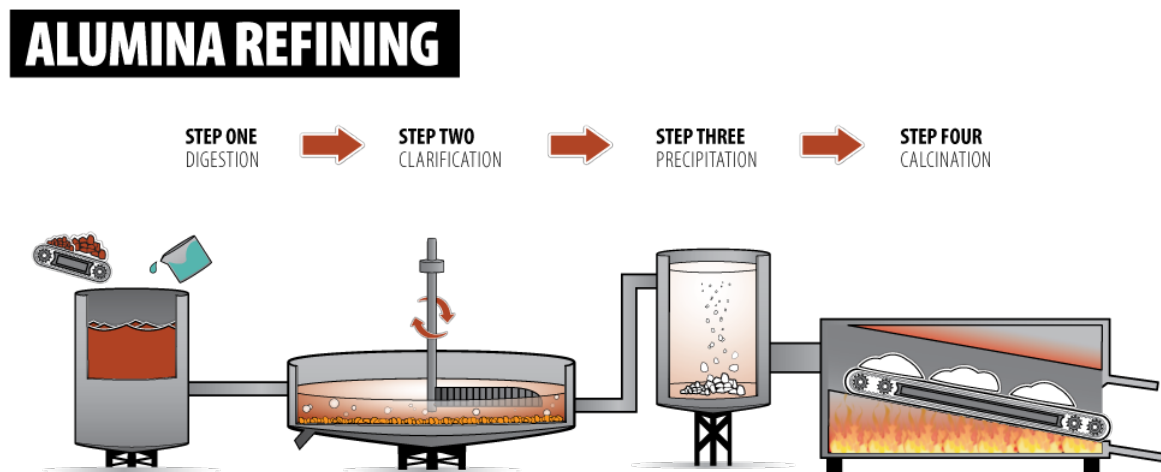


Figure 1.1: Alumina refining process (Australian Aluminium Council, 2022).

The third largest alumina refinery worldwide, Hydro Alunorte is located in Barcarena, in the state of Pará. Alunorte produced approximately 6 million tons of alumina in 2021, which corresponds to 11 million tons of bauxite residues. The residue is washed, dry-stacked, and stored in Alunorte's two DRS1 and DRS2 refinery solid residual deposits. DRS1 is nearing the end of its life, and investigations and testing have begun to determine how to best rehabilitate the landfill area. In 2014, Alunorte also invested in a new residue deposit area, DRS2, which employs an industry-leading technology for handling bauxite residue (Hydro, 2019a). Regarding closure of the area, it is planned to be restored with local plant species by direct vegetation, which is dependent on the use of amendments to enhance bauxite residue as a suitable growth medium (Okkenhaug, 2018).

Similar to other ores, bauxite includes trace levels of toxic elements, including arsenic, cadmium,

and chromium, which remain in residues after extraction. Additionally, there are challenging chemical properties, such as salinity, sodicity, and high alkalinity which are the most significant obstacles to its rehabilitation. Therefore, disposal of bauxite residue is dependent on land area, climate, geographical conditions, and management technology. Remediation with amendments such as gypsum and vegetation can lower alkalinity and hence reduce the risk of environmental damage. The addition of organic matter can also assist in growth promotion (Gräfe et al., 2011).

1.2 Objectives

The aim of this master's thesis is to gain a better understanding of how treatments of bauxite residue can contribute to improving disposal areas. Focusing on amended bauxite residue from Hydro Alunorte, the effect of amendment with gypsum, and/or organic waste on bauxite residue as a growth medium is investigated. The following objectives are identified:

- To investigate pH, electrical conductivity, and sodium development in porewater in amended bauxite residue (BR)
- To assess the mobility of toxic trace elements (aluminum Al, vanadium V and arsenic As) in amended bauxite residue
- To study the uptake of trace elements (Al, V and As) in grass vegetation

2 Study site

Several of Hydro’s operations are located in the northern Brazilian state of Pará. It is one of the warmest areas in Brazil with an average temperature of 27°C and high precipitation. As a part of the Amazon region, the annual precipitation is more than 2000 mm, and can reach as high as 3000 mm per year (INMET, 2020). With a humid tropical and subtropical climate except from partly dry areas in the north, the conditions are favorable for bauxite formation. The process is further described in the theory section (3.1).

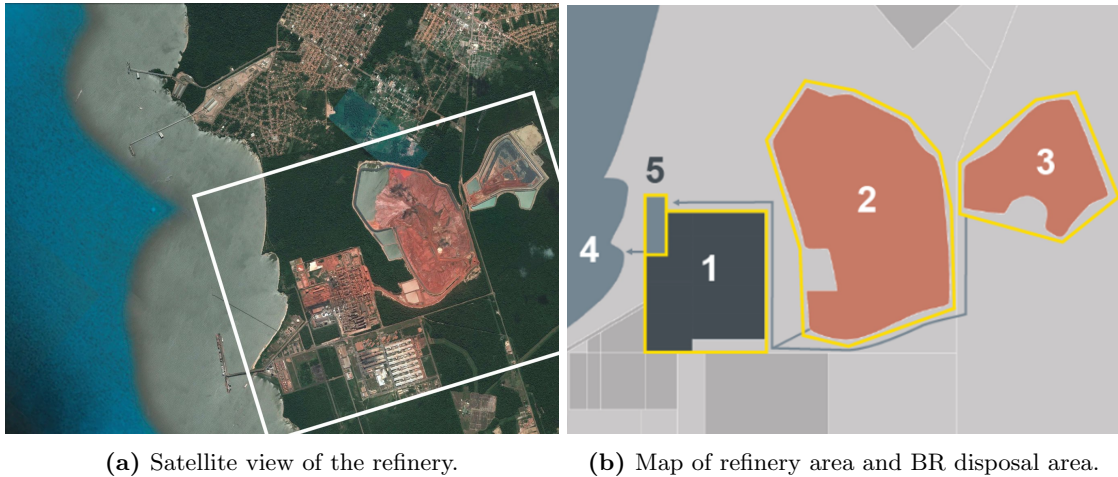


Figure 2.1: The Hydro Alunorte refinery and locations of 1) refinery area 2) DRS1 3) DRS2 4) licensed discharge to Pará river and 5) waste water treatment plant (Hydro, 2019b)

Paragominas and Trombetas are home to two significant bauxite mines that produce approximately 29 million tons of bauxite annually. From Paragominas, the bauxite is transported through a pipeline, and from Trombetas by ship through the port of “Vila do Conde”, to the refinery in Barcarena. Both mines contain primarily gibbsitic bauxite, which is preferable as it can be refined at lower digestion temperatures than the other types of alumina bearing minerals (Alves, 2012; Hydro, 2022a).

Bauxite from Paragominas is mined using strip mining technology in which an undesired layer (overburden) overlying the deposit is removed. The overburden can be used to reconstruct the mined area. The raw material is then sorted and crushed for transportation to Alunorte refinery. From the processing of bauxite to alumina, approximately 170 million tons of bauxite residue were generated in 2021 and deposited in Hydro’s bauxite residue deposit area (BRDA), DRS1 and DRS2 (Hydro, 2022b).

3 Theory

3.1 Bauxite formation

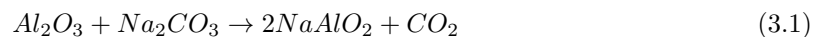
The world's bauxite reserves are estimated to be between 55 and 75 billion tons, distributed across several continents, with Guinea, Australia, Brazil, Vietnam and Jamaica accounting for more than 70% of the total (USGS, 2014).

In tropical and largely humid climate zones with alternating dry period, high temperature and precipitation, laterization (a prolonged chemical weathering process) is favored which transforms parent rock into lattice clay materials and release of laterite constituents (iron - Fe, aluminum - Al, titanium - Ti, and manganese - Mn). Leaching due to a rainy season followed by a dry period results in leaching of silica and bases, which are more mobile than Al and Fe, and enrichment of aluminum in oxides and hydroxides (Norton, 1973). With a wide variation in composition, bauxite has a relatively high aluminum content making it one of the world's main sources of aluminum. As a mineral deposit, it is rich in alumina which are aluminum oxides such as gibbsite [γ -Al(OH)₃], boehmite [γ -AlO(OH)] and diaspore [α -AlO(OH)].

Together with iron oxides, quartz, aluminosilicates, titania, small quantities of trace elements such as vanadium (V), chromium (Cr), lead (Pb) and arsenic (As) are also present. Many deposits are still developing in the tropics, and a few in the temperate regions with gibbsite as the major mineral. The climate, including physical processes such as groundwater flow, erosion, the presence of chemical components, and ecosystems with vegetation and bedrock matrix, is the most important influencing factor for the formation of bauxite (Xue et al., 2016).

3.2 The Bayer process

Bauxite is used in the chemical industry, metallurgy, and as a raw material in construction and road aggregates, as well as being the sole source of aluminum manufacture via the Bayer process. The method was invented in 1887 by Karl Josef Bayer to extract alumina. The Bayer process involves extraction of aluminum oxide by combining molten sodium carbonate with bauxite. With the addition of water, leachable sodium aluminate and carbon dioxide are produced, see Equation 3.1. In the precipitation stage, sodium aluminate is dissolved in CO₂ to produce aluminum hydroxide, which is then filtered and dried to obtain alumina (Habashi, 2005).



The Bayer process is an alkali refining of gibbsite bauxite producing more than 90% of alumina

globally (Bertilorenzi and Mioche, 2013; Xue et al., 2016). Depending on the composition, the production yields a different ratio of alumina product to bauxite residue. In general, four tons of standard bauxite generates two tons of each alumina and bauxite residue (Bertilorenzi and Mioche, 2013).

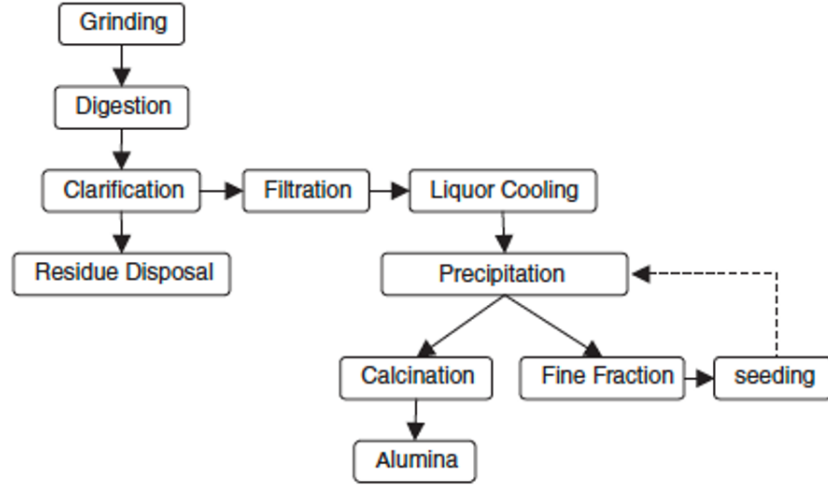
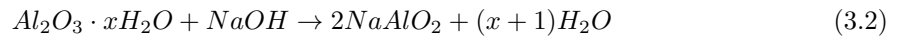


Figure 3.1: A schematic diagram of the Bayer process (Jones and Haynes, 2011).

The process can be described in four stages: digestion, clarification, precipitation and calcination, see Figure 3.1. The first process entails crushing, grinding, and heating bauxite in caustic soda (NaOH) to around 150-200°C under pressure, such that NaOH solution reacts with aluminum-containing particles in bauxite, as described in Equation 3.2 and produces slurry.



The temperature and concentration of NaOH are determined by the type of bauxite used which has varying solubility due to the strength of hydrogen bonds, and therefore different energy inputs. Gibbsite requires 3M NaOH at 100-150°C, boehmite at 200-250°C, and diaspore may require 7M NaOH with even higher temperature. Prior to being transferred to the digestion units, especially bauxite with low reactive silica content, the slurry is frequently pumped into holding tanks in order to allow the start of the pre-desilication phase.

In the next stage, a saturated solution of sodium aluminate is obtained which remains suspended and is separated in the precipitation step. Remaining bauxite residue is precipitated on the bottom, filtered and pumped to residue storage. By using heat exchangers, the desired solution is cooled and silica precipitates due to heat in the pre-desilication phase by treating with seed crystals of aluminum trihydrate ($Al_2O_3 \cdot 3H_2O$) to induce precipitation. As indicated in Equation 3.3, hydrated

alumina is extracted, washed and dried by heating to 1000-2000°C for dehydration. Alumina, Al_2O_3 , a sand-like white powder is then transported to an aluminum smelter facility (Jones and Haynes, 2011).



Since bauxite has a wide range of compositions, it contains in many cases both organic and inorganic impurities that can dissolve in aluminate solutions and cause reduced productivity. For example, undesired precipitation of oxalate which is oxidized from organic compounds with hydrates results in quality concerns. At lower temperatures, sodium silicates can be formed which react with sodium aluminates from Equation 3.2, resulting in insoluble sodium aluminosilicate also known as desilication product (DSP). Consequently, it causes a buildup of scale and thus pipe blockages and contaminating alumina as an end-product (Jamieson et al., 2017; Jones and Haynes, 2011).

3.3 Storage and disposal of bauxite residue

During the alkaline leaching, fine mud solids separated from the aluminate solution are disposed as bauxite residue (BR), also known as “red mud”. More than 120 million tons of BR is generated from the Bayer process as each ton of alumina produced also results in 0.81-1.8 tons of BR (Tang et al., 2022). With varying factors of bauxite quality, alumina extraction efficiency, and caustic losses between operations, an average ratio of 1.5 of BR to alumina produced is regarded suitable (Power et al., 2011).

BR is used in a limited set of further processes or productions. Disposal costs are expected to account for 5% of the overall cost of alumina production. Each manufacturing country’s handling of BR is determined by available space, climate, environmental legislation as well as economic profitability. Marine disposal, lagooning (landbased slurry disposal), dry stacking, and dry cake disposal are the four major ways of handling identified in the literature. The former approach saves land area but puts the marine environment at risk of pollution. The focus has recently shifted to dry stacking and dry cake disposal, both of which have drawbacks such as additional stage of thickening and introducing impurities from the solution into the Bayer plant, which can affect the process (Power et al., 2011). BR used in this thesis originated from BRDA belonging to Hydro Alunorte, which had implemented the dry cake disposal method. An additional step of thickening was added prior to residue discharge.

In addition to thickening, a filtration step is necessary for the dry cake disposal method. Prior to disposal, water is removed from the residue to form a dry cake with a solid content of >65%wt, which

is then transported to BRDA by trucks. The amount of land required for disposal is minimized, and there is less risk of collapse because the residue may be safely stacked. Furthermore, the caustic soda can be returned to the Bayer facility for reuse, and due to low pore volume, there is less possibility of leaching. Thus, environmental risks related to open caustic lakes are minimal. Despite the advantages, there is a possibility of impurities returning to the system when the soda is recycled, as well as fine particles from the cake surface that will lead to air pollution (Power et al., 2011).

3.4 Properties of bauxite residue

3.4.1 Physical properties

As described in Section 3.2 the bauxite ore is crushed in the first step of the Bayer process resulting in mixed particle sizes between 2-2000 μm with an average diameter of 0.01 mm (Jones and Haynes, 2011; Xue et al., 2016). The particles are separated into two fractions: the fine fraction (80-90%) which is silt and clay material characterized as red mud (bauxite residue), and the remainder is the coarse fraction which is fine to medium grained sand (Cooling, 2007). The characteristic red color is due to the high content of iron oxide - 20-60% Fe_2O_3 , followed by 10-30% Al_2O_3 , 2-20% SiO_2 2-10%, Na_2O , 2-8% CaO , and 28% TiO_2 (Paramguru et al., 2004). Bulk density ranges from 1.14-1.7 g/cm^3 depending on soil texture, organic matter content and total porosity (Xue et al., 2016).

Hydraulic conductivity is a measurement of how readily water travels through a substance. It is affected by particle size and is usually low in clay soils. Fine particles, which make up the majority of bauxite residue, can consolidate and form a compact mass, which limits the number of large pores. As a result, water transport will be more difficult due to the lack of passages for water between soil particles, and thus low hydraulic conductivity (Xue et al., 2016). The capillary effect causes the water level to rise due to the upward force generated by the attraction of water molecules to a solid surface. Although the capillary effect in bauxite residue is limited due to low hydraulic conductivity, it might occur during a dry period and transport dissolved salts to the surface. This, along with low hydraulic conductivity, which also promotes water logging (poor drainage), is a restricting factor for plant growth (Torgersrud et al., 2019).

3.4.2 Chemical properties

Besides having low hydraulic conductivity, bauxite residue also has chemical properties that are challenging in regard to rehabilitation. It is characterized as highly alkaline, saline-sodic with high electrical conductivity (EC) dominated by sodium (Na^+). The pH in bauxite residue ranges from 9.7-12.8 due to alkaline anions such as OH^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, $\text{Al}(\text{OH})_4^-/\text{Al}(\text{OH})_3$ and $\text{H}_2\text{SiO}_4^{2-}$ that are dissolution products of Bayer process characteristic solids. These anions are not commonly

present in bauxite. The pH of bauxite residue remains relatively constant due to buffering by alkaline solids as demonstrated by Thornber and Binet (1999) (Jones and Haynes, 2011; Gräfe et al., 2011). Their experiment was carried out by sequentially batch leaching of bauxite residues with water, resulting in a decrease in solid weight, but not in ion concentrations or pH (Thornber and Binet, 1999). Additionally, the same experiment demonstrated that bauxite residue had the ability to neutralize acid to an extent, which was defined by acid neutralization capacity (ANC).

ANC is a measure of the total buffer capacity against pH change in a solution, such as groundwater, similar to alkalinity, which is a measure of a solubility to neutralize acids. As shown in Equation 3.4, it can be calculated as the difference between base cations and acid anions (Evans et al., 2001).

$$ANC = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] - [SO_4^{2-}] - [Cl^-] - [NO_3^-] \quad (3.4)$$

The term “saline soil” refers to soil that has a high concentration of soluble salts, as measured by electrical conductivity. The composition and concentration of dissolved salts, as well as their ability to conduct an electrical current, affect EC. High EC value implies excessive salinity, with high sodium ion concentrations being the major cause in bauxite residue (1.4-28.4 mS/cm) (Gräfe et al., 2011). The ratio of sodium to the total base cations defines sodicity which is measured by exchangeable sodium percentage (ESP) as described in Equation 3.5. ESP in bauxite residue ranges from 53-91% (Xue et al., 2016).

$$ESP(\%) = \frac{100 \cdot \text{Exchangeable Na}}{\sum (\text{Exchangeable Ca} + \text{Mg} + \text{K} + \text{Na})} \quad (3.5)$$

These chemical properties are unfortunate for plant growth as HCO_3^- predominating at pH 6-9.5 can inhibit root growth and respiration (Jones and Haynes, 2011). High levels of Na ions mainly from DSP also elevate EC of the solution above the tolerable limits ($ESP > 15$), preventing plants from water uptake and therefore growth (Gräfe et al., 2011).

3.5 Trace elements

pH has been described as the master of variable as it controls the direction of the reaction as well as stability and behavior of elemental species (Gräfe et al., 2011). As mentioned in Section 3.1, trace elements such as As and V exist in bauxite in small quantities, and correspondingly in the residue. These metals and metalloids including Al can form oxyanions in solution depending on pH and redox potential, and thus different elemental species and leaching behavior (Cornelis et al., 2008). Trace elements such as Al, As, and V present a concern for the environment since they are typically located on surface complexes and can produce aqueous oxyanions under alkaline conditions. Thus, they will adsorb poorly to the negatively charged sediments (Bray et al., 2018).

In highly alkaline soils, aluminum is reported to occur mainly in anionic aluminate form, $\text{Al}(\text{OH})_4^-$, which dominates at pH 9.2 (Figure 3.2a). Brautigan et al. verified that Al was plant accessible at $\text{pH} > 9.0$, and suggested that toxicity was governed by the species of Al rather than the concentration (Brautigan et al., 2012). High quantities of aluminate under basic conditions have also been found to be more hazardous than insoluble Al species (Gensemer and Playle, 1999). According to a pH-dependent leaching analysis conducted by Cui et al. (2019), Al followed an amphoteric leaching pattern, with leachate concentrations decreasing with increasing pH (2-7), then increasing with subsequent pH increases (Figure 3.2b).

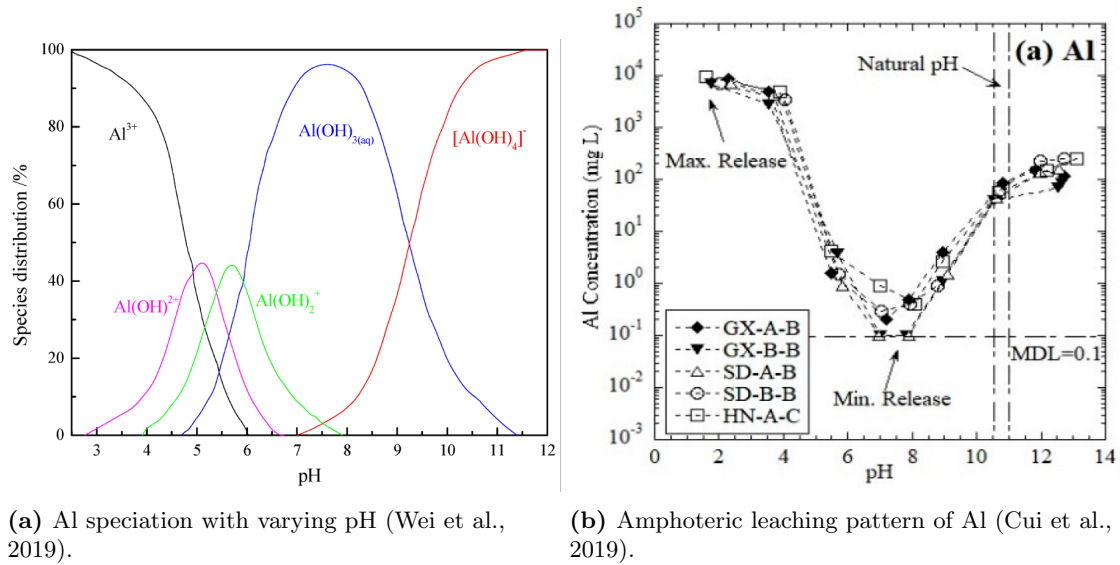
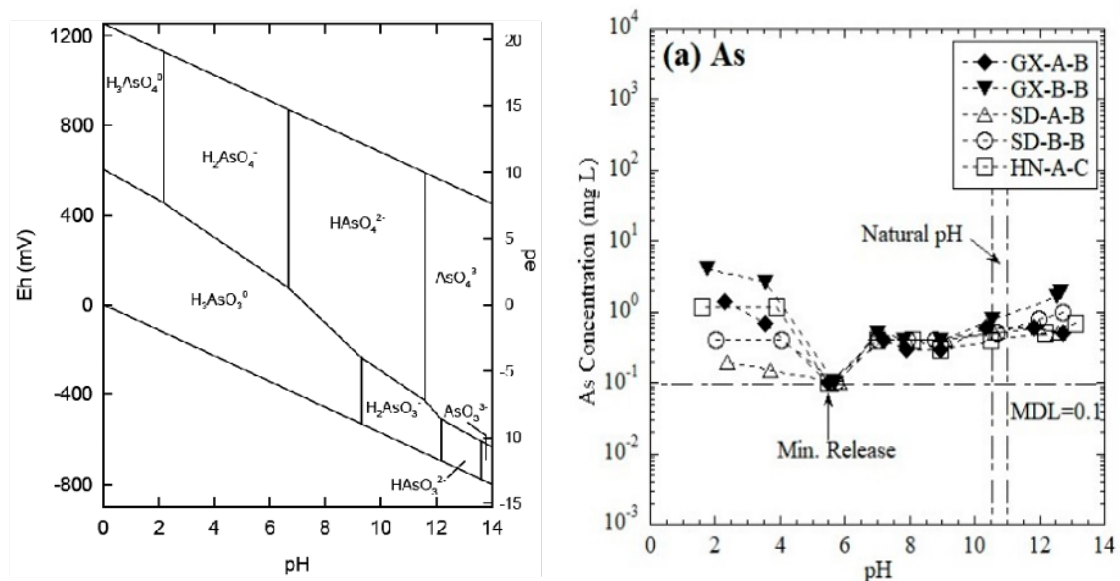


Figure 3.2: Speciation and leaching behavior of Al as a function of pH.

Under alkaline conditions such as in bauxite residue, arsenic frequently occurs as As(V) in redox state and as oxyanion arsenate (AsO_4^{3-}), see Figure 3.3a (Cornelis et al., 2008). Batch leaching tests of bauxite residue performed by Lockwood et al. (2014) and Cui et al. (2019) both demonstrates that leaching of As is pH-dependent with amphoteric pattern. Figure 3.3b illustrates the pattern which presents decreasing leachate concentration at lower pH (pH 2-6), then increasing concentration as pH further increases. A study of bauxite residue contaminated soil by Lehoux et al. (2013) also verifies this pattern by indicating that arsenate strongly adsorbs to mineral surfaces at neutral pH and aqueous As concentrations increase above pH 8.5. Additionally, the release of As is also reported to be influenced by the presence of competing ions such as phosphate and carbonate at $\text{pH} > 8$ leading to competitive desorption and release of As from solid phase to the solution (Cui et al., 2019; Lehoux et al., 2013; Lockwood et al., 2014).



(a) Eh/pH diagram for arsenic speciation (Chiban et al., 2012). (b) Leaching behavior as a function of pH with minimum leaching conc. at pH 5 (Cui et al., 2019).

Figure 3.3: Speciation and leaching behavior of As as a function of pH.

As a redox active transition metal, vanadium is predominantly present in pentavalent form (V^{5+}) and occurs as oxyanionic vanadate in alkaline waste as shown in Figure 3.4 (Cornelis et al., 2008). Similar to arsenic, the leaching behavior of V is reported to be pH-dependent with amphoteric pattern and the concentration increases at higher pH due to increased solubility, resulting in being mobile and available to the environment. The affinity of vanadate to mineral surface is however lesser compared to arsenate and aluminate (Cornelis et al., 2008).

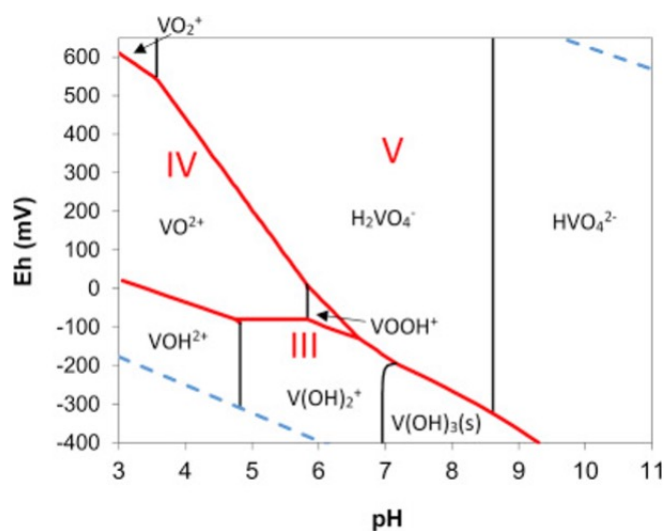


Figure 3.4: Eh/pH diagram for vanadium speciation (Gustafsson, 2019).

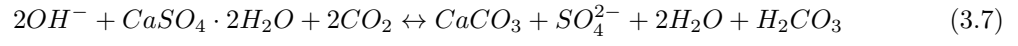
3.6 Residue amendments for closure of disposal area

Bauxite residues have challenging chemical and physical properties as they have been described so far. The most important barriers to remediation are high alkalinity and sodicity. Additionally, there are few areas of further use and applications, and they have been primarily disposed in long-term storage (Bray et al., 2018). The environment surrounded may be exposed to contamination due to weathering, erosion, and runoff. Remediation by amendment and vegetation establishment has been considered as promising strategies to stabilize the surface and initiate soil development (Courtney and Xue, 2019). In order to establish vegetation, the area must be suited for optimal plant growth. Gräfe and Klauber (2011) suggested a set of goals towards successful rehabilitation which included pH between 5.5-9, EC of <4 mS/cm, and Na, Al and trace elements below toxic threshold levels (Di Carlo et al., 2019; Gräfe and Klauber, 2011). In this thesis, samples have been amended with açai waste and gypsum.

Açai waste was chosen since it is a locally abundant plant species. Regardless of the presence of gypsum, it is a commonly used method for remediation (Jones and Haynes, 2011; Courtney and Kirwan, 2012). The use of organic matter is reported to promote BR as a growth medium. Addition of açai provides plant nutrients that otherwise are lacking in bauxite residue, including phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and naturally organic carbon. P is a well-known nutrient for plants. It is anticipated to strongly sorb to bauxite residue through ligand formation with iron oxides as reported by several studies of removal of P by using bauxite residue (Barca et al., 2021; Mendis et al., 2016; Barca et al., 2021). While Ca and Mg contributes to reduction of bulk density by acting as flocculating agents and stabilizing soil aggregates, they also assist in partially lowering the sodium content through cation exchange, along with K (Cusack et al., 2018). According to Kabata (2011), Mg can counteract excess Al in plants, which can cause Ca deficiency and lower Mg levels (Kabata-Pendias, 2011). Another effect includes being an energy source for microorganisms. Addition of organic matter can lower pH in highly alkaline conditions by hydrolysis to form humic substances and release of organic bound nutrients. The reduction of pH also leads to lower Al, V and As mobility in the actively treated residue with organic matter serving as binding agents (Bray et al., 2018; Di Carlo et al., 2019; Miura, 2022; Stubhaug, 2022).

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) contains approximately 23% calcium (Ca) which has the ability to reclaim sodic soils. Ca^{2+} ions are released when gypsum is dissolved in the solution, which react with carbonate, bicarbonate and hydroxide ions present, leading to precipitation. Equation 3.6 demonstrates the reaction between hydroxide and CO_2 which produces alkaline bicarbonate in the absence of a buffer, in contrast to when gypsum is present (Equation 3.7). Cation exchange between Ca^{2+} and Na^+ , leads to leaching of Na^+ with SO_4^{2-} or HCO_3^- (Equation 3.8). Thus, anions that

contribute to alkalinity will be removed from the system together with excess salts, resulting in a decrease in pH and EC. These anions were formed during the step of digestion in which lime (CaO) was added to eliminate impurities such as carbonates by producing calcium carbonate CaCO_3 .



Na ions contributing to high ESP values may lead to colloidal swelling and dispersion in terms of physical properties. By lowering ESP and subsequently the amount of dispersible clay, the use of gypsum can improve soil structural stability (Courtney and Xue, 2019). In contrary to treatment with acid and seawater, which only neutralize the aqueous phase, the addition of gypsum has been discovered to decrease the mobility of trace elements in solid bauxite residue. (Bray et al., 2018).

4 Materials and methods

4.1 BR samples and preparation

Bauxite residue originated from the end of the pipeline of the filter press, before transfer to the BRDA was used to establish a test field as a part of a pilot project belonging to PhD candidate Yuuki Miura (Ortiz, 2021; Stubhaug, 2022). As shown in Figure 4.1, each plot measured 9 m² and contained 2700 kg BR within a layer of 20 cm. The bauxite residue was manually mixed with combinations of açai and gypsum in random plots in the field. The waste of açai, a berry common in the Amazon region of Brazil, was collected from a processing plant where the pulp is extracted from açai seeds (Ecobiomassa near Barcarena). Gypsum used in this experiment was agronomic gypsum purchased from Gesso Integral, Grajaú (State of Maranhão), Brazil (Miura, 2022). The samples used in this thesis were collected six months after the establishment of the test field. The characteristics of raw amendment materials and fresh BR samples used in the test field are presented in Table 4.1.



Figure 4.1: A drone photography of the pilot project from which the samples were collected. Each plot measured 9 m² and contained 2700 kg of bauxite residue mixed with amendments.

Table 4.1: Characteristics of amendment and sample materials used, including pH, EC, base cations and trace elements (Miura, 2022).

Parameters	pH	EC	Tot. C	Tot. N	Na	Ca	K
			(%)	(%)	(g/kg)	(g/kg)	(g/kg)
Bauxite residue	12.31	3.45	*	*	63.0	7.70	0.14
Gypsum	7.35	2.2	*	*	0.07	116.7	0.41
Açai seed	5.365	1.39	46.22	1.04	0.04	0.60	3.10
	Mg	As	V	Al	P	Fe	
	(g/kg)	(mg/kg)	(mg/kg)	(g/kg)	(g/kg)	(g/kg)	
Bauxite residue	0.12	16.0	490	94.0	0.23	190.0	
Gypsum	0.41	0.36	2.87	1.40	0.02	0.84	
Açai seed	0.42	0.05	0.44	0.25	0.78	0.26	

The sample codes in Figure 4.2 are based on the field layout previously shown in Figure 4.1 and the explanations are presented in Table 4.2. The quantity of açai and/or gypsum added in each plot was calculated based on the weight of BR (kg). Although the percentages in the sample names in this thesis are fixed (5%, 10% and 15%), the actual percentages when recalculated from the theoretical percentages vary but considered disregarded. The complete calculation can be found in Table A.1 and Table A.2 in Appendix A. The amended samples were established in triplicates. Three of the collected samples (C4, F1, and J1) were eliminated as they were defined as control soils; instead, unamended samples (D2, D4, and E1) served as control samples. The collected BR samples were stored dark and cool at 4°C prior to the experiment, at the Norwegian University of Life Sciences (NMBU) in Ås, Norway.

	A	B	C	D	E	F	G	H	I	J
1		B1	C1	D1	E1	F1	G1	H1	I1	J1
2		B2	C2	D2	E2	F2		H2	I2	J2
3		B3						H3		J3
4		B4	C4	D4	E4		G4	H4		J4

Figure 4.2: Illustration of the test field and partitioning of randomly amended plots of bauxite residue. Gray plots are either not collected or excluded from the experiment.

Table 4.2: Sample codes and combinations of amendments with açai and gypsum in BR samples.

Sample	Amendment	Samples	Amendment
D2	no amendment	B3	15% gypsum
D4		E4	
E1		H3	
B1	10% açai	H1	5% gypsum + 10% açai
C1		H4	
G1		J4	
C2	5% gypsum	B4	10% gypsum + 10% açai
G4		E2	
J2		I2	
D1	10% gypsum	B2	15% gypsum + 10% açai
F2		H2	
J3		I1	

4.2 Experimental setup

To investigate pH, electrical conductivity (EC), and sodium development in porewater, a “pot experiment” was conducted. For each sample, a 150 ml plastic container with several holes bored into the bottom was filled with sand to approximately 1 cm with filter paper (VWR 415, 185 mm) underneath, to prevent loss of bauxite residue as well as leaching during watering sessions. Each BR sample weighing 100-150 g (depended on the amount of sample material) was placed in the container, and a rhizon sampler (5 cm female luer, Rhizosphere Research Products) connected to a 60 ml syringe (BD Plastipak) was inserted in the BR for porewater collection, see Figure 4.3.

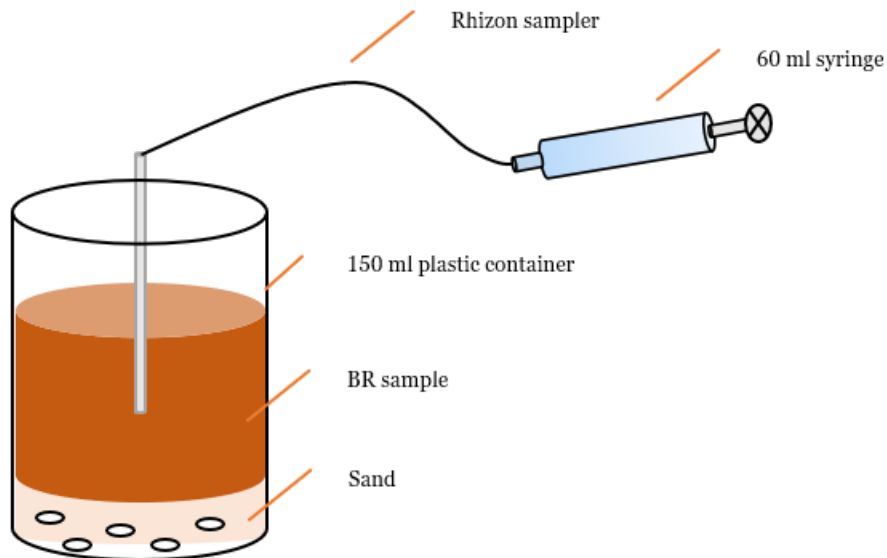


Figure 4.3: Pot experiment setup.

20 ml of deionized water was added three times per week for two weeks before seeding with ryegrass, and during vegetation growth (four additional weeks), for six weeks in total. The water added was allowed to sit in the pots for approximately an hour to reach equilibrium, before inducing vacuum in the syringes for continuous water collection. The porewater in the syringes was collected after 2, 4 and 6 weeks in the experiment, and stored in 50 ml plastic tubes at 4°C before further analysis. Figure 4.4 gives an overview of the experiment and pictures taken throughout the process.

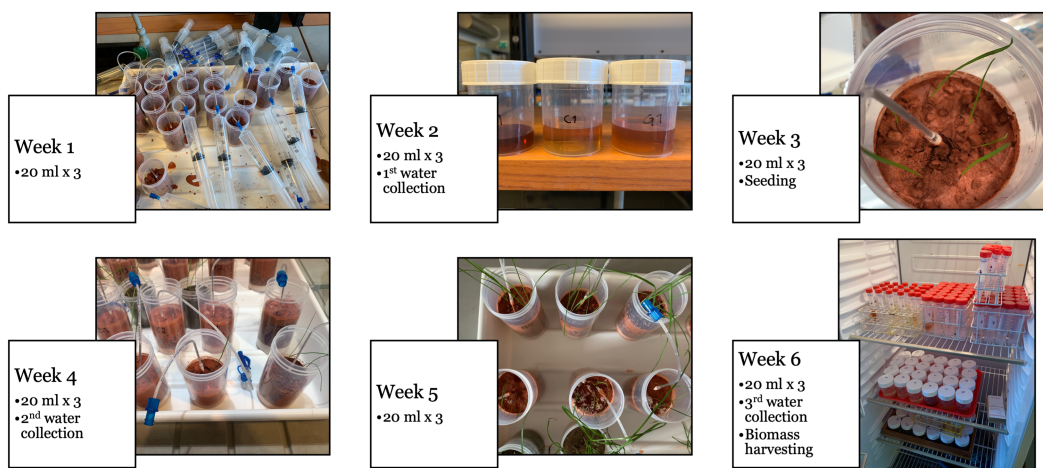


Figure 4.4: An overview of the experiment with watering sessions, seeding and harvesting, and pictures taken throughout the process.

4.3 Vegetation experiment

Six seeds of ryegrass (*Lolium perenne*) were placed approximately 1 cm beneath the surface of the BR in each container. Three additional containers were established with natural soils (pH 6.31-6.39, provided by Prof. Tore Krogstad, NMBU) for reference. The samples were stored in a climate room with constant light and temperature conditions (21°C and 16 hours of artificial light per day) at the Faculty of Environmental Sciences and Natural Resources (NMBU). The leaves were collected and their heights of the tallest grass measured after four weeks of growth. Then dried at 70°C for 72 hours and cut into small pieces. The biomass samples were weighted before and after drying, and kept in paper bags for storage at 4°C before further analysis.

4.4 Chemical analysis

4.4.1 pH, electrical conductivity and alkalinity

Approximately 5 ml of the porewater samples were used to determine EC with a conductometer (Metrohm, model 712) and pH using a PHM210 standard pH meter (Metrohm, model 914) in this order to avoid interference from the pH electrode. In addition, porewater samples were diluted for

alkalinity measurement to various factors (0.04 - 0.4x) due to limited sample volume. 0.02 M HCl was gradually added until the solutions reached pH 4.5

4.4.2 Trace elements

The remaining porewater samples were analyzed by a lab technician for concentrations of trace elements As and V using an inductively coupled plasma mass spectrometer (ICP-MS; Agilent Technologies, 8800 QQQ). Additional elements analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent Technologies, 510 dual view) included Al, Ca, Fe, K, Mg Na, P, and S (sulfur). The analysis of trace elements from the vegetation experiment was also performed by a lab technician. The biomass was decomposed with 10% v/v nitric acid (HNO₃), and analyzed for As, V, Al, Na, Mg, Ca, K, P, and Fe by ICP-MS.

4.4.3 Sulfate

Sulfate (SO₄²⁻) was analyzed by ion chromatography (IC; Thermo Scientific, Dionex ICS-6000)

4.4.4 Dissolved organic matter

Dissolved organic carbon (DOC) by TOC/DOC analyzer (Shimadzu).

5 Results

A pot experiment was conducted to study the development of pH and EC in porewater in bauxite residue, as well as concentrations of base cations (Na, Ca, K, Mg), trace elements (As, V, Al), and additional elements such as P, S, SO_4^{2-} , and DOC. Simultaneously, a vegetation experiment evaluated the uptake of base cations and trace elements by ryegrass. The average values and standard deviations for each amendment of both experiments were calculated based on the triplicates. The results of the two sub-experiments — porewater extraction and vegetation — are presented in this chapter.

It should be mentioned that the rhizon sampler in sample D1 (10% gypsum) was unable to collect enough porewater for analysis due to blockage. Additionally, neither of the triplicates of the unamended samples nor the two samples of those that had been amended with 10 % açai had any biomass.

5.1 Porewater extraction

5.1.1 pH, electrical conductivity and sodium measurements

Figure 5.1 shows the pH development in different amendments. The mean pH of unamended samples remained relatively stable (pH \sim 10) with and without vegetation. The application of açai and gypsum in varying amounts led to a significant decrease in initial pH before seeding (pH 7.0-8.5), compared to unamended samples.

Amendment with 10% açai resulted in an initial pH of 8.5, which climbed to 9.2 and 9.0 after 2 and 4 weeks of vegetative stage. Amendments with 5, 10 and 15% gypsum resulted in initial pH values at \sim 7.5, which slightly increased to pH \sim 8 after 2 and 4 weeks of vegetative stage. The addition of 10% açai to gypsum amendments decreased the initial pH values to 7-7.1; however, they increased to 7.5-7.6 at the end. As mentioned in the theory section (3.6), the threshold for pH (red line in Figure 5.1) was set to 9.0 which will be discussed in the discussion chapter.

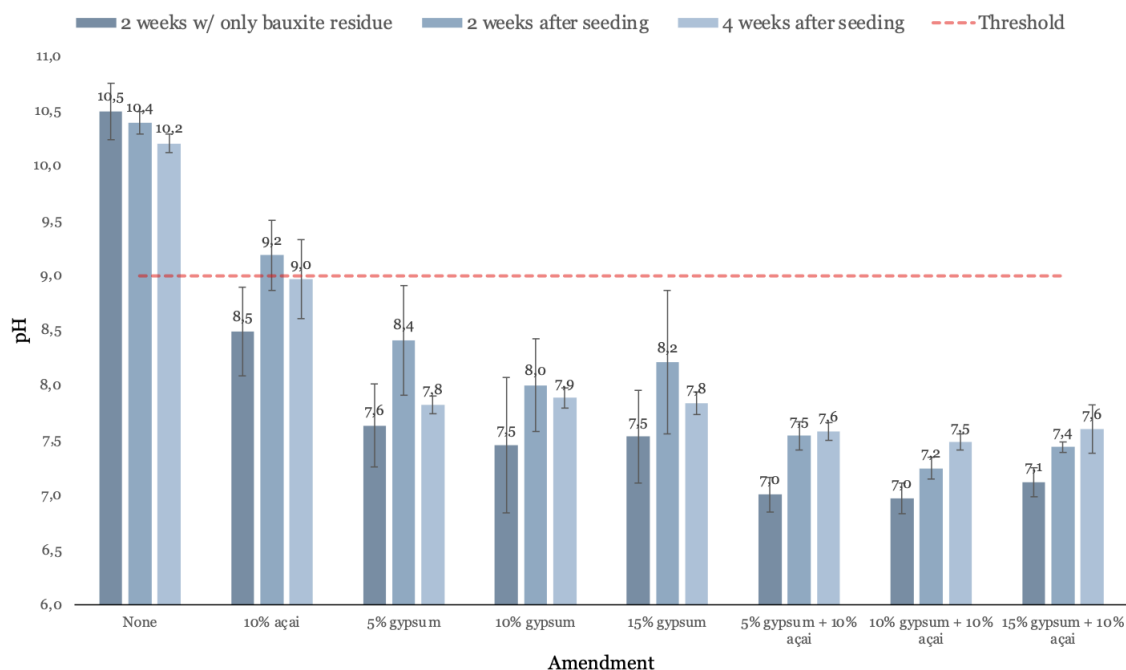


Figure 5.1: pH in porewater samples in different amendments before and after seeding (2 and 4 weeks). Each bar represents the mean value based on triplicates with corresponding standard deviation. The red line represents the pH threshold (<9) for successful remediation as suggested by Gräfe and Klauber (2011).

The mean values of the electrical conductivity measurements (mS/cm) are shown in Figure 5.2. Compared to pH, there were noticeably greater variations between the measurements, which led to larger standard deviations. In all treatments, with the exception of the 15% gypsum + 10% açai amendment, EC has been found to decrease from their initial values.

After the application of ryegrass, the EC in unamended samples decreased from 6.1 to 4.0 and 4.4 mS/cm, as did the EC of samples amended with 10% açai from 5.0 to 2.7 and 2.3 mS/cm. The amendments with 5, 10, and 15% gypsum exhibited highest initial EC values of 12.5, 11.7, and 10.8 mS/cm, respectively, which dropped over time as well. Initial EC values for samples with 10% açai added to gypsum amendments were calculated between 3.0-4.2 mS/cm, which decreased except for the sample amended with 15% gypsum and 10% açai. As mentioned in the theory section (3.6), the threshold for EC (red line in Figure 5.2) was set to 4.0 mS/cm which also will be discussed in the discussion chapter.

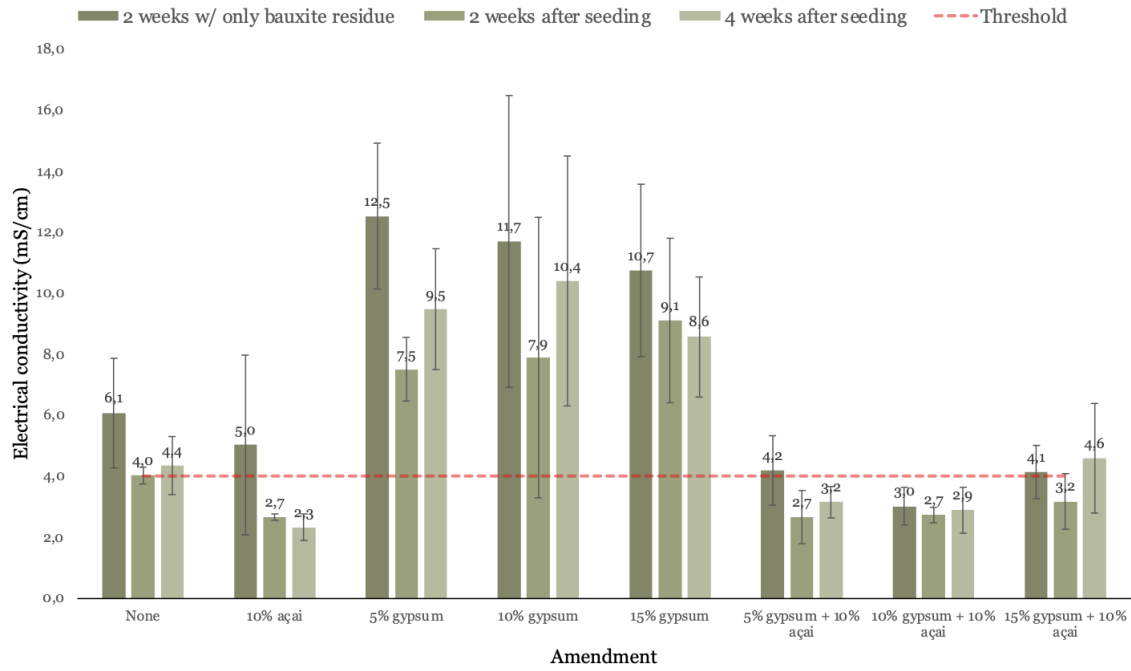


Figure 5.2: Electrical conductivity (mS/cm) in porewater samples in different amendments before and after seeding (2 and 4 weeks). Each bar represents the mean value based on triplicates with corresponding standard deviation. The red line represents the EC threshold (<4) for successful remediation as suggested by Gräfe and Klauber (2011).

5.1.2 Base cations: Na, Ca, K, Mg

Figure 5.3 shows the Na development for each amendment. Unamended samples increased in Na concentration (mg/l) after vegetating, while those amended with 10% açai showed a decreasing trend. Samples amended with varying amount of gypsum exhibited highest mean Na concentrations. There were also large variations between measurements, as indicated by the error bars. Finally, samples amended with 5% gypsum + 10% açai decreased in concentration, while the remaining samples (10% gypsum + 10% açai and 15% gypsum + 10% açai) slightly increased in Na concentration.

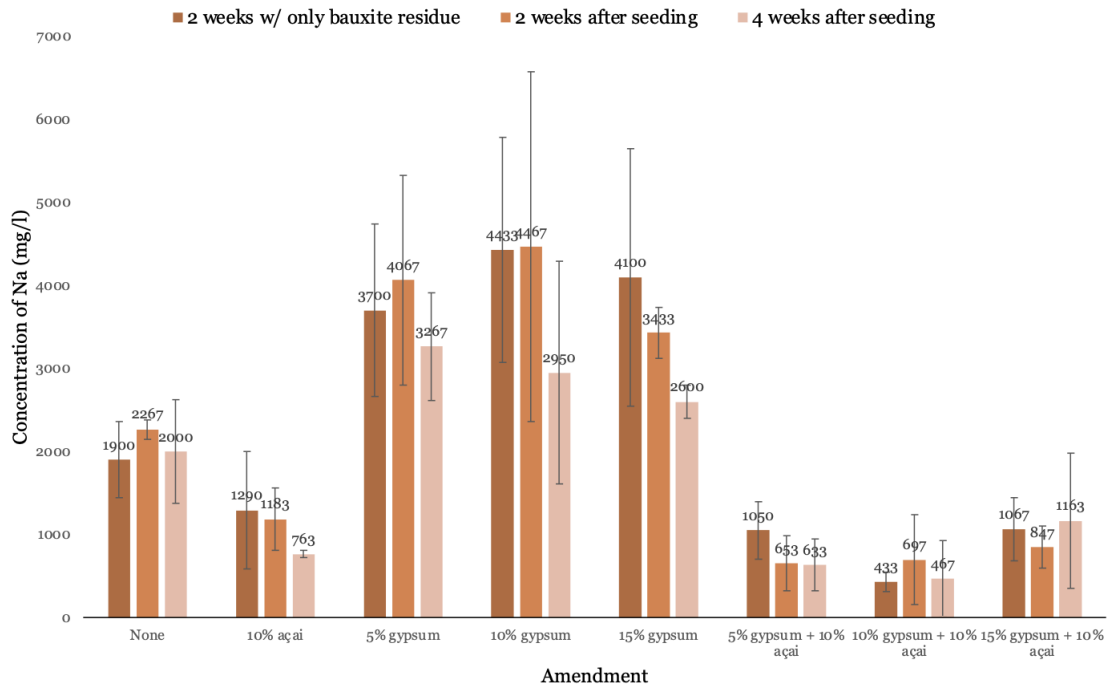


Figure 5.3: Concentrations of sodium (Na) (mg/l) in porewater samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

In addition to sodium, the concentrations of remaining base cations (Ca, K, Mg) were also measured (mg/l) as presented in Table 5.1. The concentrations were in following decreasing order for all amendments: Na > Ca > K > Mg. Comparing the additions of 5% and 10% gypsum, the Ca concentration in porewater was considerably higher when 10% gypsum was used when measured two weeks after establishment (with only bauxite residue). Samples with 10% gypsum measured 2 and 4 weeks after seeding showed higher Ca concentrations than in 5% gypsum. However, there was no significant difference in Ca concentration when 15% gypsum was added instead of 10%. The set of amendments that included açai led to substantially higher Ca concentrations.

The concentration of K in the porewater in neither of the amendments differed significantly, but the concentrations were all higher in amended samples than unamended. For Mg, multiple samples of unamended samples and those amended with only gypsum had concentrations below the detection limit (LOD = 0.000 mg/l). Samples with combinations of gypsum and açai exhibited higher concentrations before seeding with ryegrass and decreased after 2 and 4 weeks with vegetation.

Table 5.1: Concentrations of base cations Ca, K, Na, and Mg (mg/l) in porewater samples with different amendments. Values are mean and standard deviations based on triplicates.

Amendment	Ca	K	Na	Mg
2 weeks w/ only bauxite residue				
None	1 ± 0.2	3 ± 1.0	1900 ± 458.3	<LOD
10% açai	13 ± 5.5	9 ± 5.2	1290 ± 707.9	0.9 ± 0.73
5% gypsum	370 ± 0.0	9 ± 5.4	3700 ± 1039.2	<LOD
10% gypsum	557 ± 191.4	10 ± 3.1	4433 ± 1357.7	0.7 ± 0.88
15% gypsum	563 ± 50.3	9 ± 5.7	4100 ± 1552.4	0.2 ± 0.23
5% gypsum + 10% açai	557 ± 230.3	11 ± 0.6	1050 ± 350.0	7.2 ± 0.84
10% gypsum + 10% açai	673 ± 40.4	8 ± 3.3	433 ± 117.2	3.9 ± 1.50
15% gypsum + 10% açai	730 ± 121.2	9 ± 4.0	1067 ± 381.8	7.1 ± 2.23
2 weeks after seeding				
None	1 ± 0.2	4 ± 1.6	2267 ± 115.5	<LOD
10% açai	12 ± 1.7	8 ± 0.9	1183 ± 375.3	0.5 ± 0.14
5% gypsum	613 ± 80.2	9 ± 5.7	4067 ± 1266.2	<LOD
10% gypsum	533 ± 70.9	7 ± 2.0	4467 ± 2107.9	<LOD
15% gypsum	573 ± 23.1	5 ± 1.0	3433 ± 305.5	<LOD
5% gypsum + 10% açai	627 ± 41.6	5 ± 3.2	653 ± 327.2	5.5 ± 2.95
10% gypsum + 10% açai	803 ± 259.3	10 ± 7.5	697 ± 545.0	4.1 ± 2.00
15% gypsum + 10% açai	663 ± 177.9	8 ± 2.1	847 ± 255.0	5.6 ± 3.10
4 weeks after seeding				
None	2 ± 1.2	3 ± 2.3	2000 ± 624.5	<LOD
10% açai	11 ± 2.8	5 ± 1.1	763 ± 46.2	0.4 ± 0.20
5% gypsum	597 ± 195.0	6 ± 2.6	3267 ± 650.6	<LOD
10% gypsum	455 ± 21.2	4 ± 1.3	2950 ± 1343.5	<LOD
15% gypsum	433 ± 5.8	3 ± 0.6	2600 ± 200.0	0.2 ± 0.11
5% gypsum + 10% açai	650 ± 193.1	5 ± 2.6	633 ± 310.9	4.1 ± 0.95
10% gypsum + 10% açai	727 ± 125.8	6 ± 6.4	467 ± 461.9	2.9 ± 2.08
15% gypsum + 10% açai	647 ± 83.3	6 ± 5.3	1163 ± 813.7	5.1 ± 2.82

5.1.3 Alkalinity

Table 5.2 presents mean values of alkalinity measured in the triplicates (mEq/l). The alkalinity was highest in unamended samples, and samples to which 10% açai has been added. Comparing samples that received solely gypsum, there was no significant difference in alkalinity between samples for all periods. In the series where 10% açai was added in addition to gypsum, the alkalinity was slightly lower in the first measurements (2 weeks with only BR). It eventually increased, but the results were accompanied by higher uncertainties as indicated by the standard deviations.

Table 5.2: Mean alkalinity (mEq/l) and standard deviation, based on triplicates for different amendments before and during vegetating.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	65.3 ± 16.76	86.6 ± 9.59	65.7 ± 7.49
10% Açai	14.8 ± 9.09	27.6 ± 12.66	15.6 ± 6.41
5% Gypsum	1.5 ± 0.22	1.6 ± 0.25	1.2 ± 0.22
10% Gypsum	1.5 ± 0.13	1.5 ± 0.71	1.4 ± 0.06
15% Gypsum	1.2 ± 0.21	1.1 ± 0.05	1.2 ± 0.16
5% Gypsum + 10% açai	1.1 ± 0.22	1.4 ± 0.28	1.4 ± 0.38
10% Gypsum + 10% açai	0.7 ± 0.07	1.4 ± 0.19	1.2 ± 0.2
15% Gypsum + 10% açai	0.9 ± 0.3	2.2 ± 0.97	1.6 ± 0.52

5.1.4 Trace elements: As, V, Al

Figure 5.4 shows that the mean concentration of As ($\mu\text{g/l}$) in the porewater of unamended samples generally decreased with time, with large standard deviations among the triplicates. For samples amended with 10% açai, the concentration increased from 19.0 to 21.0 $\mu\text{g/l}$ after 4 weeks of vegetation growth. Amendment with 5, 10 and 15% gypsum as well as in combination with 10% açai contributed to significantly decreased concentrations compared to unamended samples.

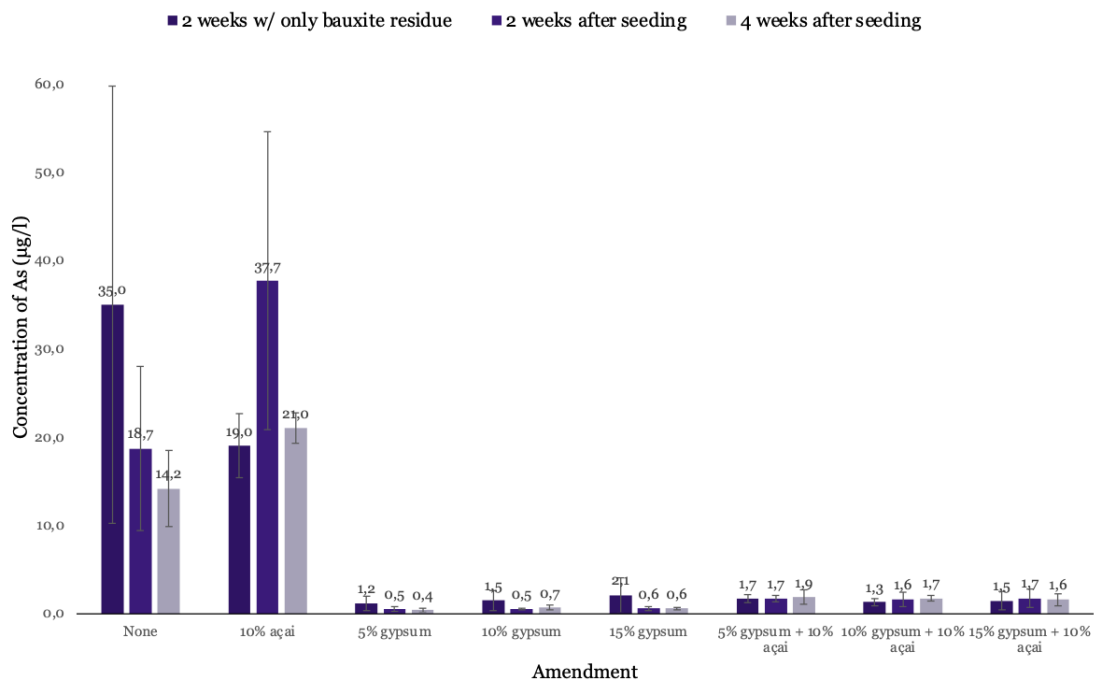


Figure 5.4: Concentrations of arsenic (As) ($\mu\text{g/l}$) in porewater samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

Although there were greater variations in samples with only gypsum with decreasing trend. Samples with both gypsum and açai exhibited more consistent concentrations between 1.3 and 1.9 $\mu\text{g As/l}$.

Similar to the results for arsenic concentrations, the mean concentration of vanadium ($\mu\text{g/l}$) in unamended samples also decreased after 2 and 4 weeks of vegetation growth, as shown in Figure 5.5. The mean concentration of the samples amended with 10% açai increased from 209 to 363 $\mu\text{g/l}$ after 2 weeks of growth, then decreased to 260 $\mu\text{g/l}$ after 2 additional weeks. Concentrations of V in further samples are considerably lower (9-50 $\mu\text{g/l}$), and generally decreased after seeding with ryegrass. The variations in samples with only gypsum and consistency when açai was combined were also seen here similar to the development in arsenic concentrations.

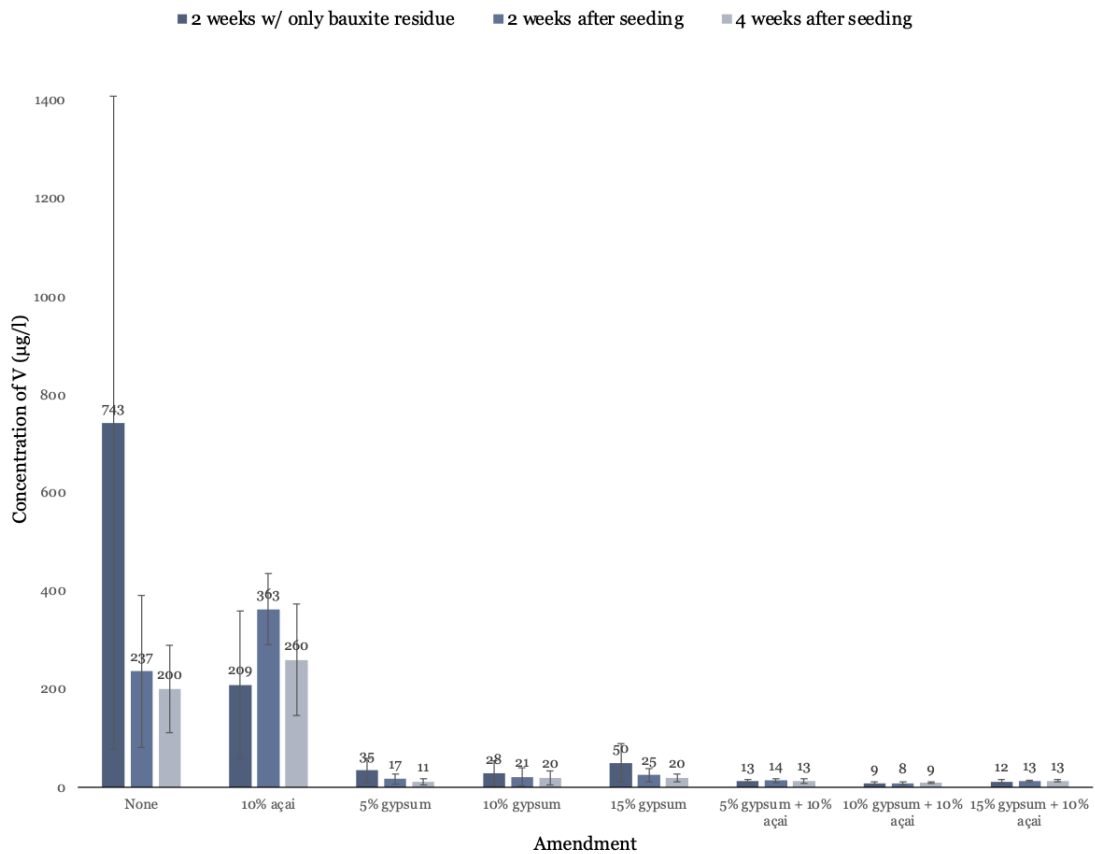


Figure 5.5: Concentrations of vanadium (V) ($\mu\text{g/l}$) in porewater samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

The mean concentration of Al (mg/l) in unamended samples showed the same trend as for As and V. The initial concentration was significantly higher than amended samples, then decreased after 2 and 4 weeks of vegetation growth. Those samples amended with 10% açai slightly increased, then decreased in mean concentration after seeding. Amendment with 5, 10, 15% gypsum resulted in increasing order of Al concentration in the porewater, all with decreasing trend after vegetation growth. For samples amended with 10% açai in addition to gypsum, the concentration of Al were

shown to be remarkably lower than the other treatments, see Figure 5.6.

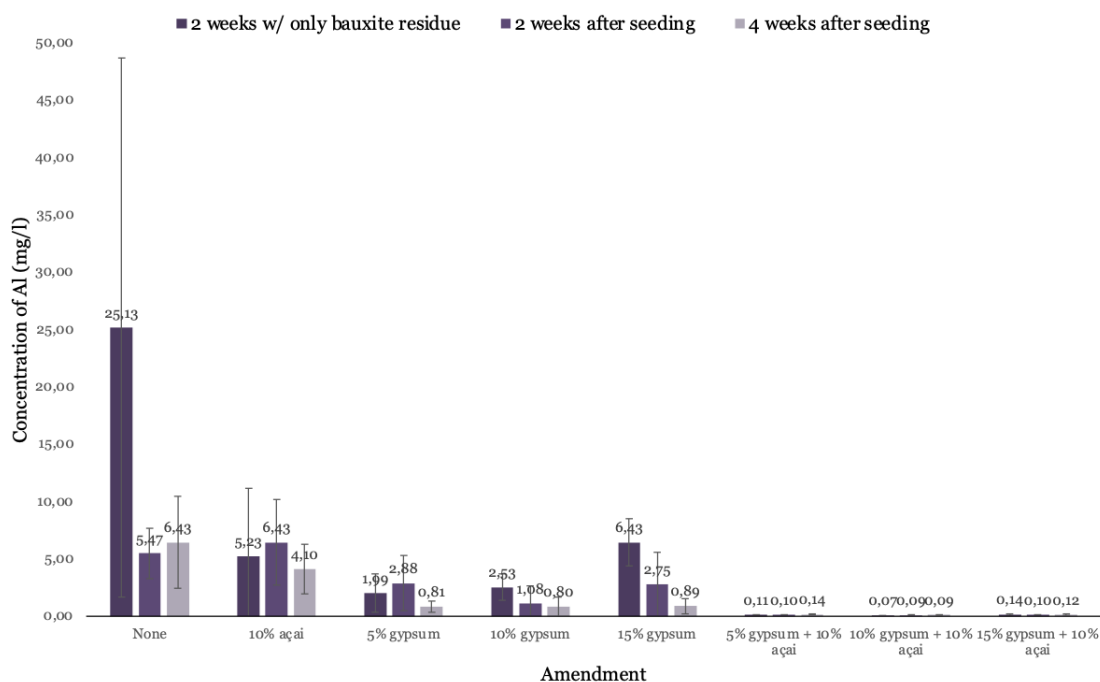


Figure 5.6: Concentrations of aluminum (Al) (mg/l) in porewater samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

5.1.5 Additional elements: P, Fe and SO₄²⁻

Iron (Fe), phosphorus (P), sulfate (SO₄²⁻) and sulfur (S) concentrations were quantified in addition to toxic trace elements. Concentrations of Fe (mg/l) are shown in Table 5.3. The analysis of Fe showed that the majority of the samples had concentrations below limit of detection (LOD = 0.0029 mg/l) or limit of quantification (LOQ = 0.0096 mg/l). Therefore, only unamended samples and 10% açai-amended samples obtained results. However, the concentration in unamended samples tended to decrease over time, while it was not possible to draw any conclusions regarding the açai amended samples due to large standard deviations. The complete calculations of Fe is shown in Table B.9. Only triplicates amended with 10% açai (0.7±0.45, 2.4±1.97, and 1.4±0.82 mg/l respectively, after 2 weeks with only BR, 2 weeks after seeding, and 4 weeks after seeding) showed results in the analysis of P. The remaining samples had concentrations below the detection limit (0.015 mg/l).

Table 5.3: Mean concentrations of Fe (mg/l) and standard deviations in porewater samples, based on triplicates for different amendments before and during vegetation.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	0.4 ± 0.31	0.1 ± 0.07	0.1 ± 0.14
10% açai	12 ± 16.62	17.2 ± 15.14	4.4 ± 4.12

Additionally, concentrations of sulfate SO_4^{2-} were measured in porewater samples. The results are shown in Figure 5.7. The highest sulfate concentrations were found in samples amended with 5, 10, and 15% gypsum. While the unamended samples showed the lowest concentrations and decreasing trend, followed by amendment with 10% açai. There was no significant difference between samples amended with 10% açai in addition to varying percentages of gypsum, with mean values between 2-3000 mg/l. The concentrations of S which would indicate sulfate concentrations are shown in the appendix.

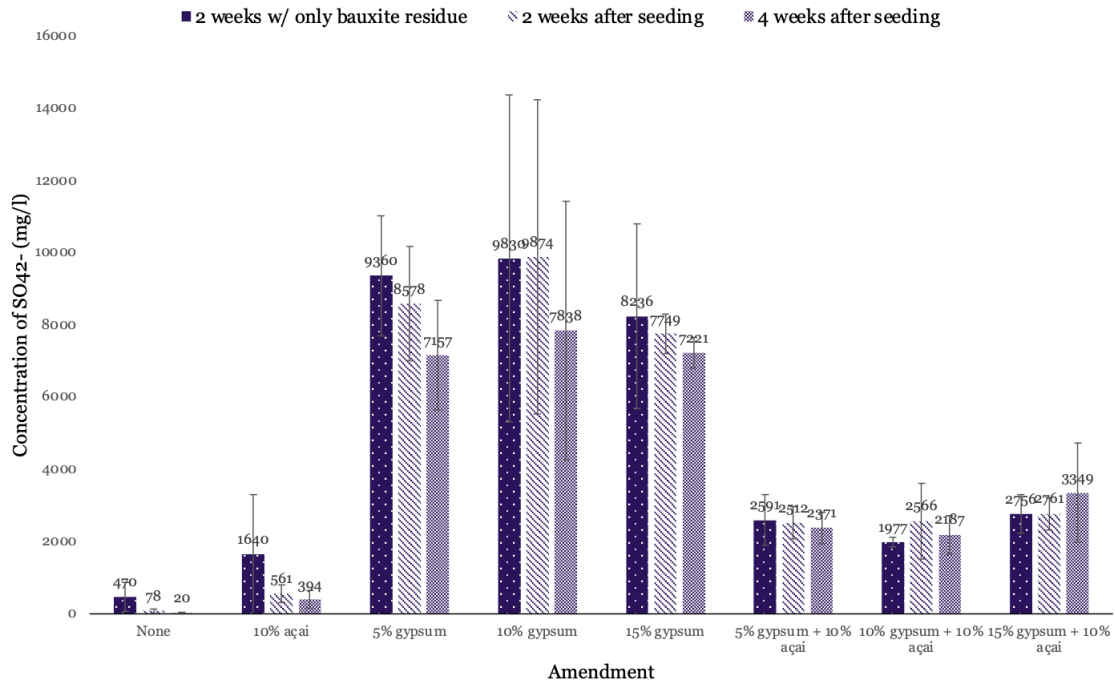


Figure 5.7: Concentrations of sulfate (SO_4^{2-}) (mg/l) in porewater samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

5.1.6 Dissolved organic carbon (DOC)

Porewater samples were diluted with deionized water and analyzed by TOC/DOC analyzer for dissolved organic carbon (DOC). Table 5.4 shows the calculated mean DOC (mg/l) concentrations and standard deviations in each amendment before and during vegetating.

Table 5.4: Mean DOC concentrations (mg/l) and standard deviation, based on triplicates for different amendments before and during vegetating.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	36 ± 8.7	23 ± 9.8	19 ± 7.4
10% açai	238 ± 131.0	197 ± 80.0	132 ± 24.3
5% gypsum	20 ± 15.1	11 ± 5.1	8 ± 3.4
10% gypsum	18 ± 6.1	12 ± 4.1	9 ± 3.1
15% gypsum	16 ± 7.5	8 ± 1.1	7 ± 0.8
5% gypsum + 10% açai	15 ± 3.1	12 ± 1.6	13 ± 4.9
10% gypsum + 10% açai	20 ± 1.9	13 ± 3.8	13 ± 4.0
15% gypsum + 10% açai	26 ± 19.5	19 ± 6.6	14 ± 6.2

The results showed highest DOC concentrations in samples amended with 10% açai, followed by unamended samples. There was no significant difference among the samples amended with 5, 10, and 15% gypsum, and the concentration tended to decrease over time. The lowest DOC concentrations were observed in samples amended with sole gypsum. Samples amended with 10% açai in addition to gypsum had slightly higher DOC concentrations than those with only gypsum, but with no significant difference between the amendments.

5.2 Vegetation experiment

5.2.1 Biomass

The heights of ryegrass leaves were measured when collected after four weeks, and weighted before and after drying. The data were calculated to mean values and corresponding standard deviations based on triplicates as shown in Table 5.5. Images of the biomass samples before harvesting are shown in Figure 5.8. In addition, the ratio between dry and wet weight (D/W) were also calculated based on the triplicates. The bars labeled “Reference” in the following diagrams in this subsection correspond to the biomass samples in natural soil.

Table 5.5: Heights (cm), weights before and after drying (g), and ratio between dry and wet weight of the biomass calculated to mean values and standard deviations based on triplicates.

Amendment	Height (cm)	Wet weight (g)	Dry weight (g)	D/W
None	0	0	0	0
10% açai	3 ± 2.3	0.01 ± 0.01	0.002 ± 0.0019	0.2 ± 0.15
5% gypsum	6 ± 1	0.02 ± 0.006	0.005 ± 0.0013	0.2 ± 0.04
10% gypsum	7 ± 2.6	0.02 ± 0.012	0.006 ± 0.0037	0.4 ± 0.29
15% gypsum	7 ± 0.6	0.05 ± 0.01	0.011 ± 0.0033	0.2 ± 0.03
5% gypsum + 10% açai	14 ± 1.2	0.23 ± 0.038	0.029 ± 0.0117	0.1 ± 0.04
10% gypsum + 10% açai	16 ± 4.4	0.21 ± 0.107	0.035 ± 0.0122	0.2 ± 0.08
15% gypsum + 10% açai	9 ± 4	0.08 ± 0.096	0.012 ± 0.0118	0.2 ± 0.05
Natural soil (ref.)	24 ± 2.6	0.65 ± 0.053	0.125 ± 0.03	0.2 ± 0.06

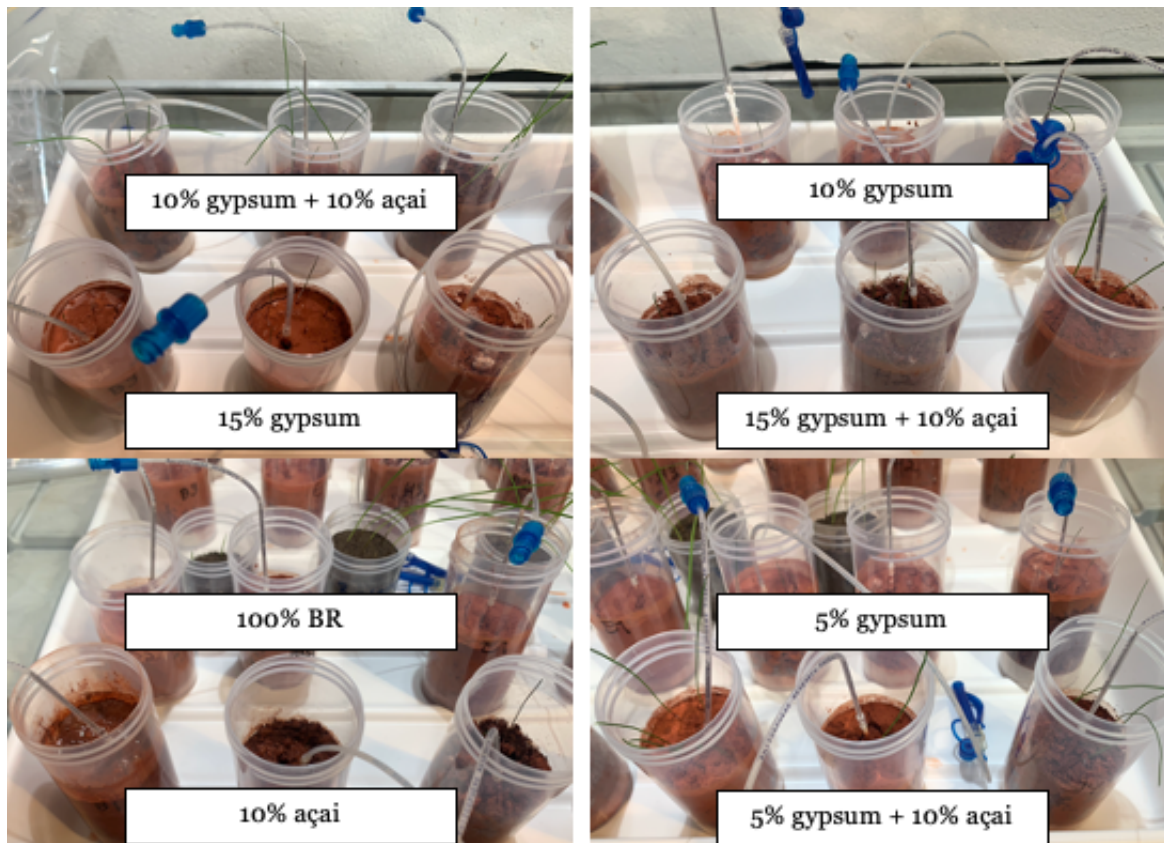


Figure 5.8: An overview of biomass samples before harvesting after four weeks of growth.

Compared to reference samples with seeds planted in natural soil, the majority of the samples exhibited poor growth. No growth was seen in unamended samples or one of the samples amended with 10% açai. Based on height measurements, the latter amendment showed minor growth overall. In samples containing 5, 10, and 15% gypsum, there were no significant differences in growth (6-7 cm on average), with the exception of one sample in the set of 10% gypsum that measured 10 cm.

Individual samples amended with gypsum and açai exhibited more varied development, with heights ranging between 5 and 21 cm. The results indicated that, subject to standard deviation, samples amended with 10% gypsum and 10% açai exhibit the best growth. Therefore, there is no significant difference between this treatment and the treatment containing 5% gypsum and 10% açai.

The ratio between dry and wet weight showed an average value of 0.2 in most samples, except 0.4 in samples amended with 10% gypsum, and 0.1 in samples amended with 5% gypsum + 10% açai.

5.2.2 Base cations in biomass

Unfortunately, there was insufficient biomass to analyze unamended samples and two individual samples amended with 10% açai. Therefore, the unamended samples were excluded from the diagrams in upcoming subsections to ensure an accurate portrayal of the concentrations, and the results for 10% açai were based on a single replicate.

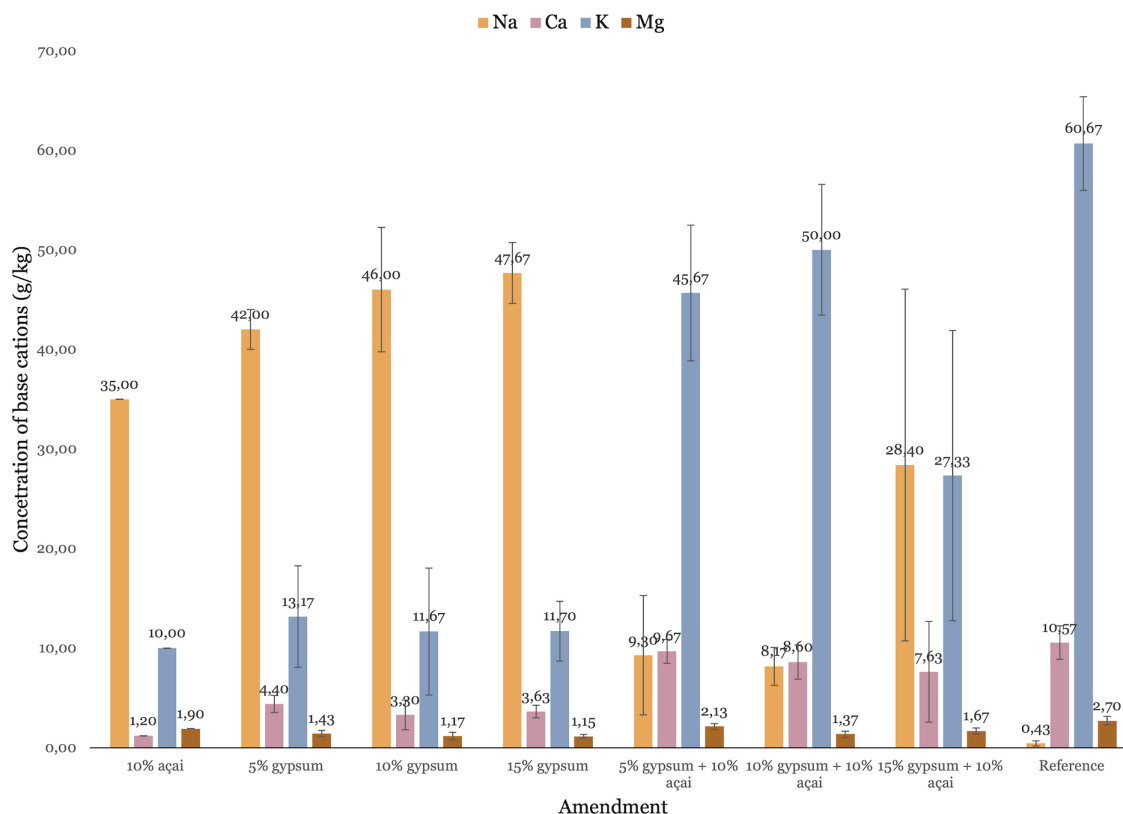


Figure 5.9: Concentrations of base cations Na, Ca, K, and Mg (g/kg) in biomass samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

Figure 5.9 demonstrates that the uptake of Na predominated in samples amended with 10% açai, 5, 10, and 15% gypsum, with no significant differences between the gypsum amended samples. In contrast, K uptake predominated in samples amended with a mixture of gypsum and açai, and similarly for the samples containing natural soil (reference). In samples containing 15% gypsum and 10% açai, Na and K uptake were nearly equivalent, but it was not possible to draw any conclusions due to large standard deviations.

5.2.3 Trace elements in biomass: As, V, Al

In addition to base cations, As (mg/kg), V (mg/kg), and Al (g/kg) were also analyzed by ICP-MS. Figure 5.10 and Figure 5.11 show the uptake of the trace elements within each amendment. The

concentrations were calculated to mean values and standard deviations based on triplicates (except for 10% açai), see Table 5.6.

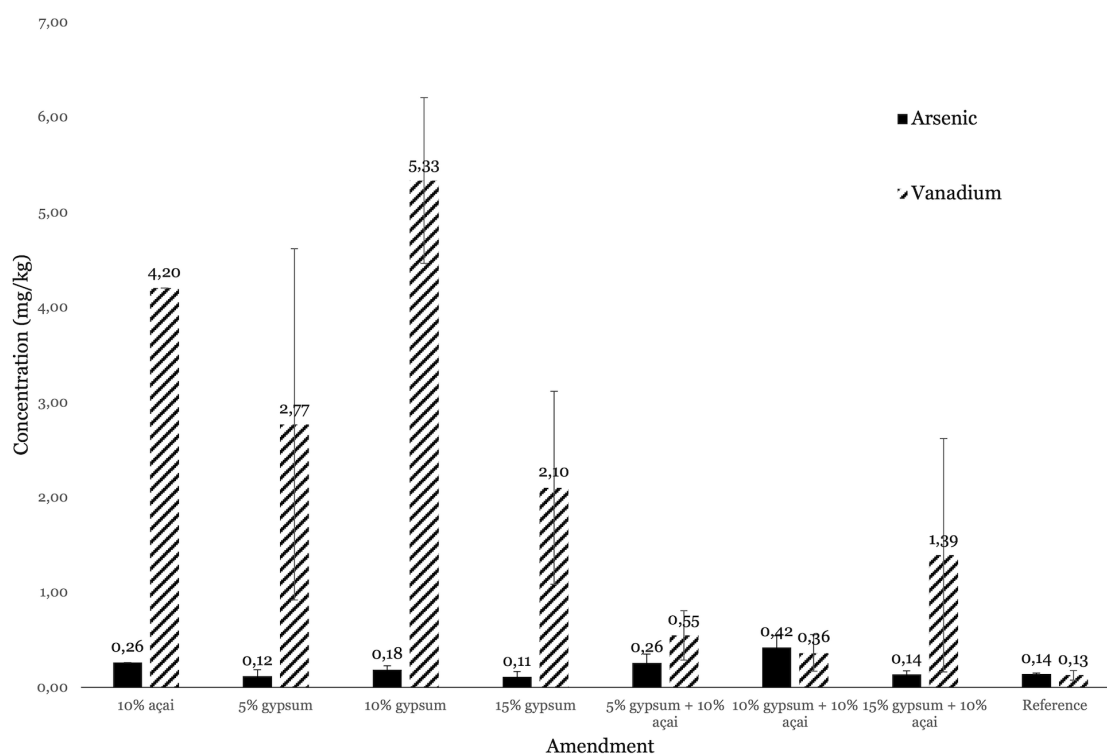


Figure 5.10: Uptake of As (mg/kg) and V (mg/kg) in biomass within each amendment. Each bar represents the mean values and corresponding standard deviation.

Vanadium uptake was higher than arsenic uptake in all amendments, as shown in Figure 5.10. This also included larger corresponding standard deviations. The concentration of V was 4.2 mg/kg in the single sample that was amended with 10% açai. The amendment with 10% gypsum had the highest concentration of vanadium (5.33 mg/kg), followed by 5% (2.77 mg/kg) and 15% (2.1 mg/kg). In the set of samples treated with both gypsum and açai, the maximum concentration was found in the sample treated with 15% gypsum and 10% açai (1.39 mg/kg).

The maximum As uptake overall (0.42 mg/kg) occurred in samples with 10% gypsum + 10% açai, while the concentration of V was lowest in this amendment. The concentration of As in general seemed to be higher when açai was added, including the single replicate with a concentration of 0.26 mg/kg, except for the amendment with 15% gypsum + 10% açai.

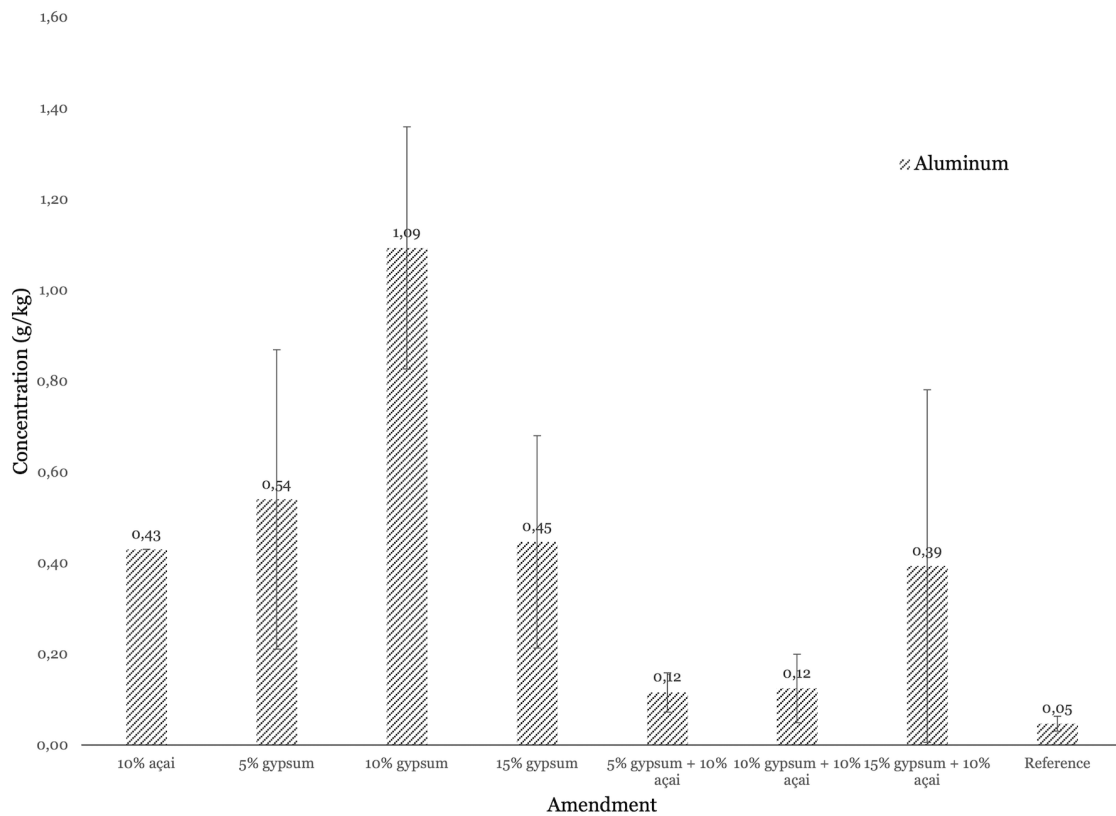


Figure 5.11: Uptake of Al (g/kg) in biomass within each amendment. Each bar represents the mean values and corresponding standard deviation.

The maximum concentration of Al was found in the amendment with 10% gypsum (1.09 g/kg), which was twice as high as both the second-highest concentration (0.54 g/kg) in samples amended with 5% gypsum, and the third-highest concentration (0.45 g/kg) with 15% gypsum. The single replicate with 10% açai obtained a slightly lower concentration of 0.43 g/kg. In addition, samples amended with gypsum and açai had approximately half the concentrations of samples with gypsum only, with the exception of those amended with 15% gypsum + 10% açai. The last amendment obtained a concentration approximately three times higher, but with a significantly larger standard deviation.

Table 5.6: Concentrations of trace elements As, V, Al, and including P and Fe in biomass samples with different amendments. The data were calculated to mean values and corresponding standard deviations based on triplicates.

Amendment	As (mg/kg)	V (mg/kg)	Al (g/kg)	P (g/kg)	Fe (g/kg)
None	0	0	0	0	0
10% açai	0.26	4.2	0.43	9.3	1.9
5% gypsum	0.12 ± 0.065	2.77 ± 1.848	0.54 ± 0.329	3.83 ± 0.85	1.39 ± 0.878
10% gypsum	0.18 ± 0.042	5.33 ± 0.874	1.09 ± 0.266	3.73 ± 0.802	2.07 ± 0.404
15% gypsum	0.11 ± 0.057	2.1 ± 1.015	0.45 ± 0.234	3.6 ± 0.361	1.06 ± 0.502
5% gypsum + 10% açai	0.26 ± 0.093	0.55 ± 0.26	0.12 ± 0.043	1.97 ± 0.115	0.31 ± 0.131
10% gypsum + 10% açai	0.42 ± 0.121	0.36 ± 0.192	0.12 ± 0.075	2.3 ± 0.557	0.19 ± 0.006
15% gypsum + 10% açai	0.14 ± 0.037	1.39 ± 1.229	0.39 ± 0.388	2.8 ± 1.058	0.66 ± 0.558
Reference	0.14 ± 0.01	0.13 ± 0.051	0.05 ± 0.017	7 ± 0.6	0.13 ± 0.006

5.2.4 Additional elements: P, Fe

Simultaneously, P and Fe in the biomass were analyzed (g/kg), and the results were incorporate into Table 5.6. Beginning with P, the single sample amended with 10% açai obtained the highest concentration of 9.3 mg/kg. There were no significant differences between the amendments with only gypsum, where 5% gypsum showed the highest uptake of P (3.83 g/kg), followed by 10% (3.73 g/kg), and 15% gypsum (3.6 g/kg). The addition of 10% açai to gypsum amendments resulted in slightly lower concentrations of P, but also with no significant difference.

In the case of Fe, the amendments containing only gypsum also resulted in the highest concentrations, with 10% gypsum presenting the maximum concentration (2.07 g/kg), followed by 5% (1.39 g/kg), and lastly, 15% gypsum (1.06 g/kg). The concentrations were considerably lower when 10% açai were added to the gypsum amendments.

6 Discussion

This thesis aimed to investigate how amendments of bauxite residue with gypsum, açai seeds, and combinations of these can improve disposal areas. A clear relationship between the amendments and plant growth was anticipated. Simultaneously, it was essential to study how the amendments interact with each other and affect the chemical and physical conditions that serve as the basis for establishing effective growth. In this section, the results will be collated and discussed to determine how various factors have contributed to the enhancement of bauxite residue.

To evaluate and compare the effects of the amendments, it is considered appropriate to use the vegetation experiment as a reference point. In addition, it is assumed that the measured heights of the biomass can indicate the quality of growth. This assumption is based on the fact that not all seeds germinated for several reasons, such as poor water uptake or drainage due to low hydraulic conductivity. Therefore, using either the wet or dry weight of the biomass will not be representative. On the other hand, the ratio between the dry and wet weight can indicate the relative water content in the biomass and if the water content in some way relates to the uptake of other elements.

Due to the varying amounts of sample materials, each sample was not weighed before use in the pot experiment. The samples would have to be dried, crushed, and rectified for the amount of water to achieve the same starting condition, which posed a possibility of material loss. Additionally, as shown in Table 4.1, selected characteristics constituting the total composition of materials used in this experiment were determined in advance. The values represent the raw materials, i.e., fresh bauxite residue, before mixing in the field, as the mixed samples were collected six months after field establishment. Therefore, comparisons of the characteristics will not be precise, but comparable trends are expected to be observed.

6.1 Unamended samples

The upper threshold for pH was set to 9.0 as suggested by Gräfe and Klauber (2011) for successful remediation, in addition to EC below 4 mS/cm (Di Carlo et al., 2019; Gräfe and Klauber, 2011). For unamended samples, there was no sign of growth as expected. pH measurements of the porewater showed pH ~ 10 , which remained stable throughout six weeks of weekly extraction. According to the literature and the pH characteristic determined in Table 4.1 by Miura (2022), the pH of fresh bauxite residue was 12. Although, in this case, the slightly lower pH may be caused by weathering and leaching during the months before sample collection from the field.

In addition, the constant pH is assumed to be related to the buffering capacity due to alkaline an-

ions such as CO_3^{2-} , HCO_3^- , and $\text{Al}(\text{OH})_4^-$ in the solution, which are dissolution products of the Bayer process. OH^- from the addition of sodium hydroxide in the digestion step might react with CO_2 in the atmosphere, producing HCO_3^- . Consequently, the measured alkalinity was also significantly higher than for amended samples. The measured electrical conductivity was slightly higher than in the fresh bauxite residue (3.45 mS/cm), which initial value decreased from 6.1 to approximately 4.0 mS/cm, indicating the presence of Na^+ from the DSP. The dominance of Na ions over other base cations (Ca, K and Mg) and anions (OH^- , CO_3^{2-} , HCO_3^- , and $\text{Al}(\text{OH})_4^-$) in concentration is therefore not surprising.

The results revealed that the concentrations of trace elements As, V and Al in the porewater were all higher in unamended samples compared to amended samples with any combinations of residue amendments. In an alkaline solution with pH 10, these trace elements are occurring as oxyanions arsenate, vanadate and aluminate. Based on the arsenic concentration from the final water collection which resulted in the smallest standard deviation, and the assumption that the concentrations in the remaining samples can adjust accordingly, the total concentrations may have been comparable to those of samples containing 10% açai (Figure 5.4). Arsenic concentration is known to be influenced by organic matter, pH, adsorption surface area, and competing anions. In unamended BR samples, Fe, Al, Si oxides, and hydroxide minerals with pH dependent surface charge (amphoteric features) make up the adsorption surface (Bissen and Frimmel, 2003; Ren et al., 2019). In alkaline and reducing condition, the metal oxides will have a negative surface charge, resulting in increasing leaching of As (Cui et al., 2019). In this case, the condition is assumed to be oxidizing still with a pH of 10 in unamended samples. Therefore, the As concentration is possibly higher in fresh bauxite residue with higher pH. Additionally, unamended samples recorded higher DOC concentrations than the remaining amended samples (except for 10% açai). It was uncertain where the DOC in unamended samples originated from, but assumed to stem from organic compounds in the liquor from the Bayer process. The DOC could assist in growth and also lead to less metal adsorption to the solid phase due to binding to DOC. The presence of trace metals together with high pH and EC, however, appeared to be more restricting.

6.2 Amendment with açai

The samples amended with 10% açai decreased in pH of approximately one unit (from pH 10 to 9), and the electrical conductivity was below the suggested threshold of $\text{EC} < 4$. However, given that the vegetation was measured at the lowest height (3 cm) compared to other amended samples, it is still not ideal for plant growth. The sodium concentration was relatively low in the porewater, but the uptake in vegetation was on the other hand predominating, compared to the reference samples with natural soil (Figure 5.9). This was yet not expected to be uncommon due to the absence of

gypsum containing Ca ions where the cation exchange might occur.

The concentrations of trace elements As, V and Al in 10% açai-amended samples in the porewater did not differ significantly from those unamended. The effect of açai alone as an amendment is therefore not considered sufficient to achieve successful growth and low trace element concentrations. Despite the substantial standard deviations of the data, the addition of açai resulted in DOC that was nearly ten times higher than the unamended. Similar to unamended samples, the higher DOC concentrations should be promoting growth, yet the other factors such as pH, EC, and the presence of trace metals were still restricting. However, the concentrations of trace metals in açai-amended samples were still not the highest and they were assumed bound to the DOC. Considering the contribution of DOC to plant growth was not sufficient, organic matter in general could however stabilize soil aggregates and improve the structure of bauxite residue to some extent to promote growth (Xue et al., 2016).

6.3 Amendment with gypsum and açai

Among the samples amended with gypsum, 10% and 15% gypsum obtained best growth (7 cm). Despite a larger standard deviation for 10%, there was no significant difference between the growth in these amendments. The ratio between dry and wet weight also indicated relatively same amount of water uptake and potential loss of biomass in the cutting and digesting process. The success is also seen in the amendment with 10% gypsum + 10% açai (16 cm), although the Na concentration in porewater is lower than in 5% gypsum + 10% açai and 15% gypsum + 10% açai.

The results for the porewater showed a clear reduction of pH from 10 to 7-8 when gypsum was added, both alone and in combination with açai. The addition of gypsum has been assessed as an effective way of lowering pH. Dissolved Ca ions can either exchange with Na ions or react with carbonates leading to precipitation and removal of alkaline anions from the system. Removal of Na from the solid phase also enhances growth due to reduction of salt stress on vegetation (Gräfe and Klauber, 2011; Lehoux et al., 2013). The elevated EC (Figure 5.2) and Na concentrations in the porewater samples for 5%, 10% and 10% gypsum (Figure 5.3) confirmed accordingly the effect of gypsum addition. The same trend was also observed for sulfate, which is the corresponding anion to Na.

Compared to the samples with only gypsum, the pH and electrical conductivity in samples amended with gypsum and açai combined were slightly lower. The Na concentrations in turn were expected to be at the same levels as samples with only gypsum due to displacement of Na ions in the same manner, but exhibited much lower concentrations (Figure 5.3). Na might probably have leached out from the BR several months before sample collection in the field and use in the pot

experiment. It remains uncertain as the samples were exposed to the same conditions as they were established in the same field. The addition of açai might also have led to suspension of displaced Na to the negatively charged surface of organic matter bound to Ca ions.

An attempt to correlate Na concentrations in the biomass as a function of height is shown in Figure 6.1. There is a negative correlation as the Na concentrations are decreasing with increasing heights. Although the concentrations in the porewater were expected to increase for the mixed samples, there is still a good correlation ($R^2 = 0.8$) between the concentrations in the biomass and growth quality overall. Finding the link between the concentration in the porewater and the biomass appears to be inadequate as the leachate is not dependent on the uptake.

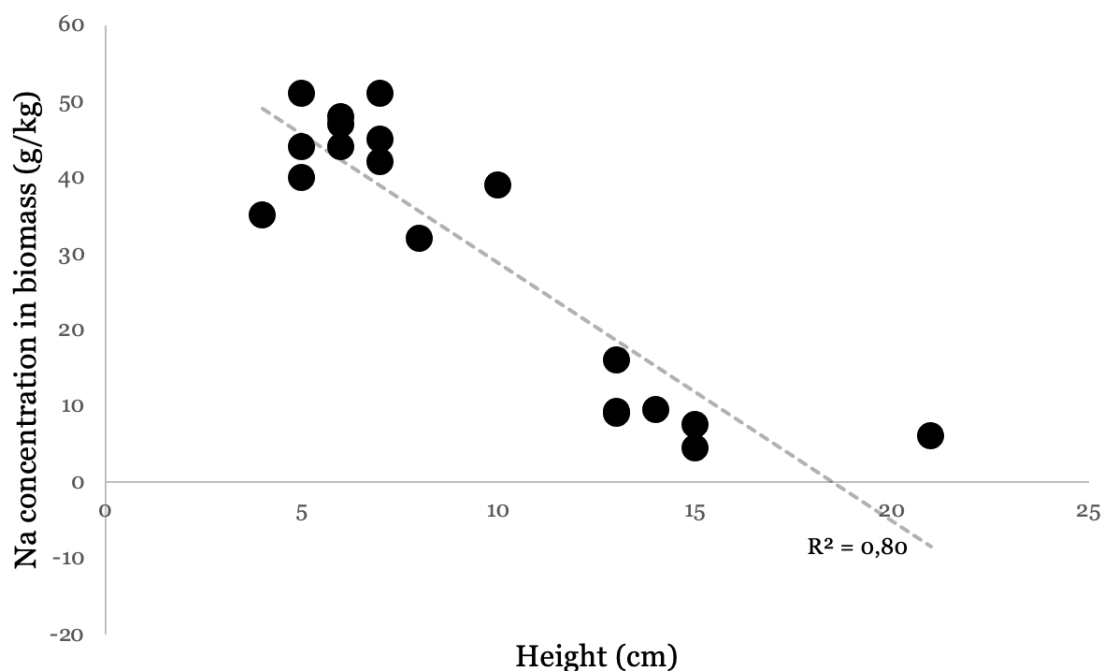


Figure 6.1: Concentrations of Na (g/kg) as a function of height.

It is challenging to evaluate whether there are significant changes due to the high standard deviations in the results for trace element uptake in plants, as there has been the case in the majority of the results. Aside from the deviations, it appeared that the samples with the best growth (amended with gypsum and açai) had higher uptake of V, but lower uptake of As and Al compared with samples containing only gypsum. The uptake of V, which is higher than As in all samples, is consistent with the distribution of the original composition. It appears that the uptake of trace elements is mostly regulated by pH associated with solubility, adsorption and precipitation, and the presence of other substances. For instance, the uptake of V is pH-dependent and is higher for vanadate than vanadyl at higher pH levels. Although both ionic forms aid in vanadium uptake by plants, a clear

relationship between soil and vegetation vanadium is not reported (Di Carlo et al., 2019; Kabata-Pendias, 2011).

The relationships between trace elements in porewater and the most influential factor are illustrated by plotting the concentrations as a function of pH. Figure 6.2 shows the leaching behavior of As in the porewater samples from all amendments for comparison. The concentration increases with increasing pH. It is difficult to distinguish between the concentrations in the pH range between 7 and 8.5, which shows that there are no significant differences below pH 8.5. Arsenate is also affected by iron oxides in terms of solubility and subsequently leaching. Oxyanionic arsenate in general adsorbs to the positive surface charge of hydrated Fe(III) oxides in aquatic environments. However, under reducing conditions, Fe(III) can be reduced to Fe(II) and already adsorbed As can be mobilized (Bissen and Frimmel, 2003). Additionally, arsenate can reduce to more soluble species, leading to a higher aqueous concentration than originally in the solid (Lockwood et al., 2014).

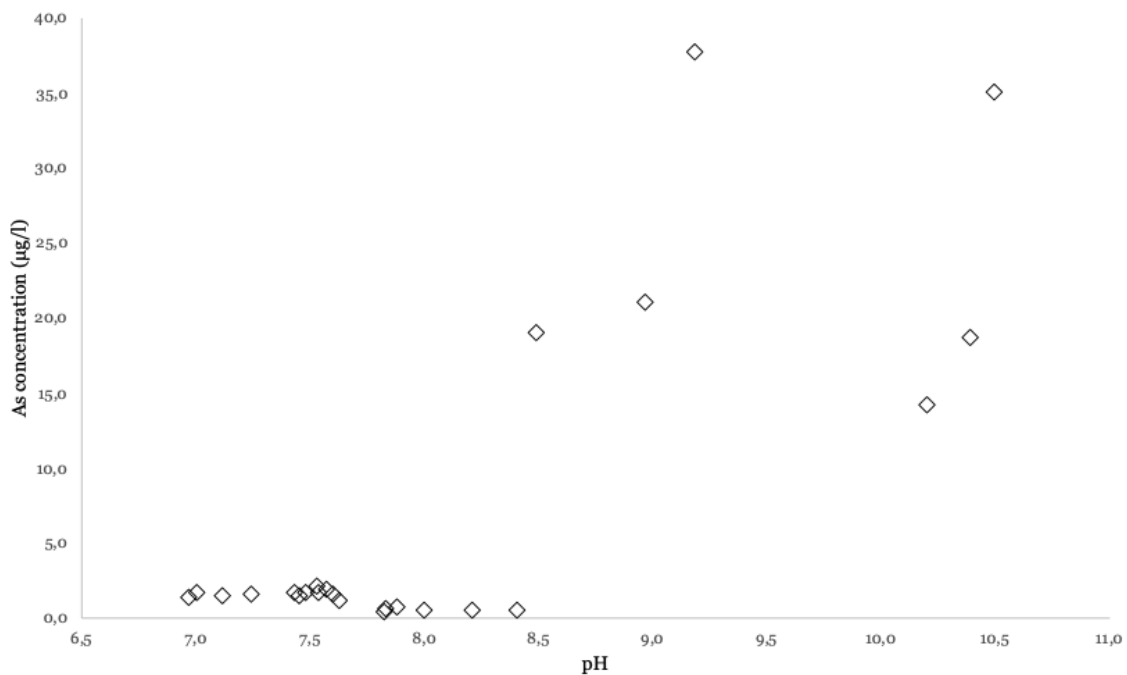


Figure 6.2: As concentrations ($\mu\text{g/l}$) in the porewater from all amendments as a function of pH.

The concentration of V as a function of pH is shown in Figure 6.3. The leaching behavior is similar to the pattern for arsenic, as are the concentration levels in the range of pH 7-8.5. It has also been reported to strongly adsorb to the mineral surface at neutral pH, although with lesser affinity than for As (Burke et al., 2012; Cornelis et al., 2008). However, the reduction of pH led to significant decrease in V concentration due to decreased solubility governed by pH.

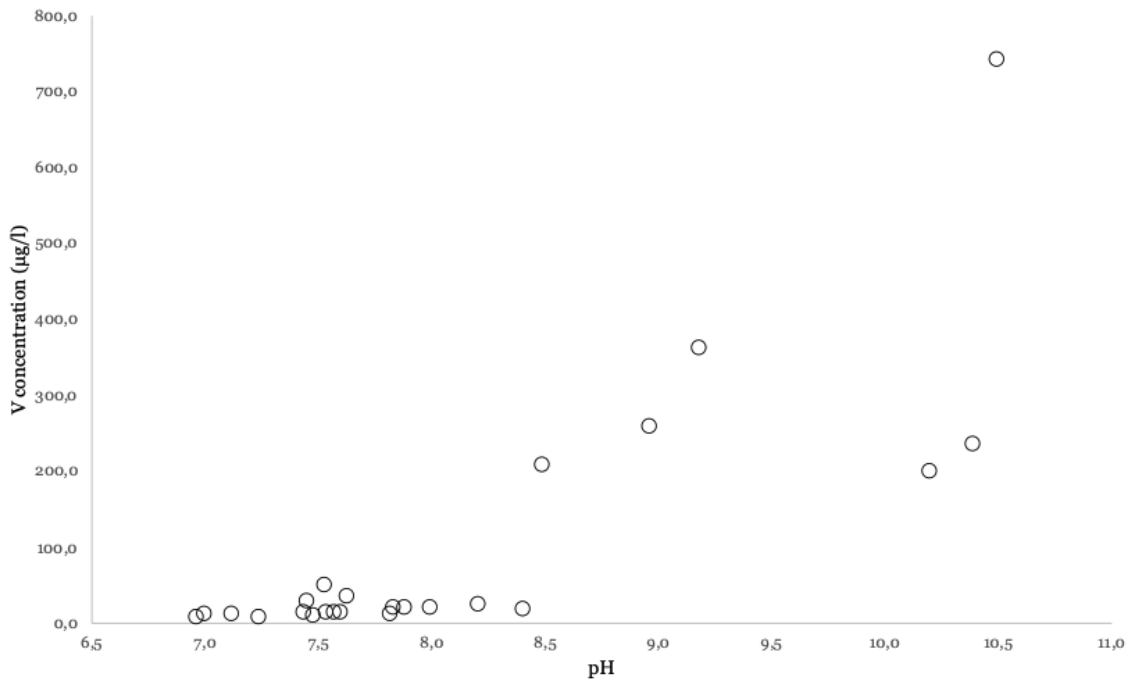


Figure 6.3: V concentrations ($\mu\text{g/l}$) in the porewater from all amendments as a function of pH.

Al concentrations in the porewater showed greater variation than As and V concentrations. Figure 6.4 shows the Al concentrations from all amendments plotted as a function of pH. At pH 10 as for unamended samples, Al is formed as anionic aluminate, and the concentrations are clearly higher than for those at neutral pH. This mechanism is confirmed by several studies that aluminate is insoluble at $\text{pH} < 10.5$ and will precipitate as amorphous oxyhydroxide phase (Brautigan et al., 2012; Lehoux et al., 2013). Al concentration at lower pH could not be observed, but it was presumed that it would have followed the amphoteric leaching pattern.

According to Kabata-Pendias (2011), excess Al in plants could also induce Ca deficiency and reduce transport, as well as significantly reduce the content of Mg. The addition of Ca and Mg to soil would therefore counteract Al and thus reduce toxicity. This was also observed in the results in which samples with high concentrations of Al (5, 10, and 15% gypsum) had fairly low concentrations of Ca and Mg (Figure 5.9).

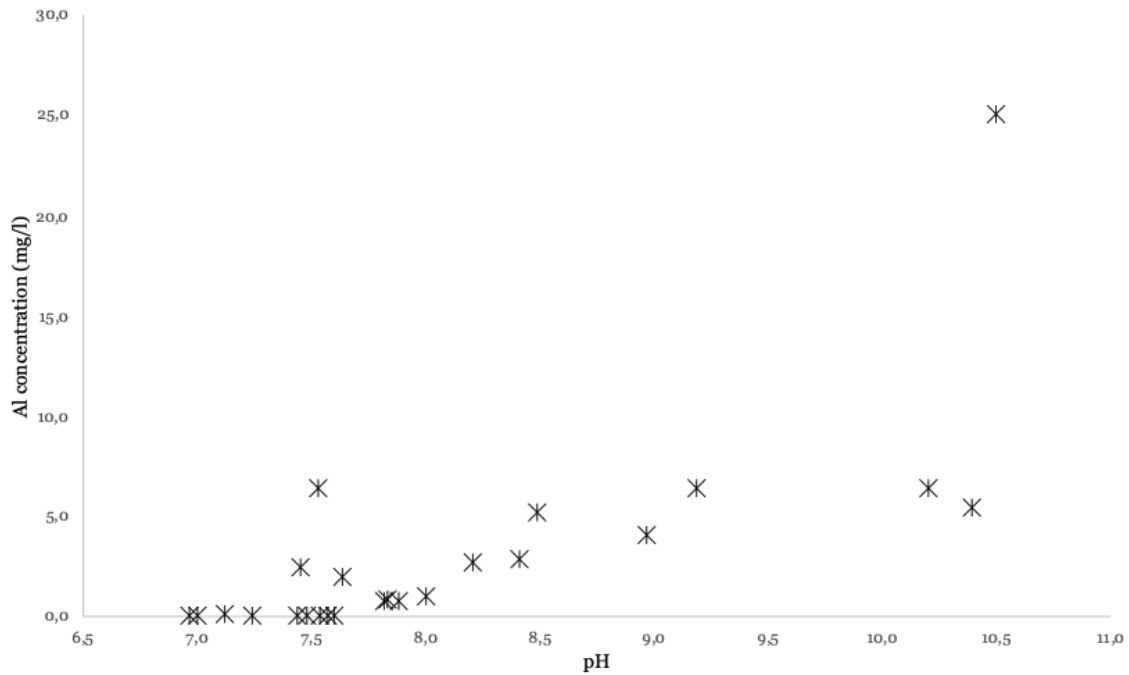


Figure 6.4: Al concentrations (mg/l) in the porewater from all amendments as a function of pH.

6.4 Comparisons between amendments

The results demonstrated that even with the addition of only 5% gypsum, the pH was significantly lowered, creating a favorable environment for plant development. The results of Na concentrations and EC in the porewater supported the impact of gypsum addition. It was also anticipated that samples containing combinations of gypsum and açai would provide similar results. Even though less Na leaching was discovered in the latter samples, these were the ones that exhibited the best growth. The heights were measured to be twice as tall as those amended with only gypsum. However, it does not appear that açai was the determining factor, as all samples with gypsum and açai included the same quantity of açai, but rather gypsum. Still, açai contributed to improve the uptake of Ca and K in the biomass when combined with gypsum, as seen in Figure 5.9.

Regarding base cations porewater samples, several samples amended with only gypsum had Mg concentrations below the detection limit, as indicated by the results. Since the samples with only açai as well as those with açai and gypsum obtained results, it was presumed that açai contributed to the Mg content. This tendency would be predicted for concentrations of K based on the original composition (Table 4.2), as açai contained higher concentration of K than BR and gypsum would have supplied. However, regardless of combination, no significant variations in K concentrations were identified across the amended samples, as observed for the results of base cations in biomass which revealed obviously higher concentrations of K when açai was included. The results for the

porewater could be explained by the fact that açai decomposed slowly, which obscured the presence of K. Nonetheless, it is unclear why the concentrations of K in porewater samples did not differ between amendments. To the benefit, this is a desirable property if a long-term effect of organic addition is required.

The sample with 10% gypsum + 10% açai exhibited the most significant growth development, followed by those with 5% gypsum + 10% açai and 15% gypsum + 10% açai. By disregarding the standard deviation, it is conceivable that the addition of more gypsum did not necessarily increase cation exchange but that the system reached Ca saturation at a lower amount of gypsum. As reported by Lehoux et al. (2013), addition of gypsum would lead to consumption of alkalinity and prevent alkaline extraction of natural organic matter, thus produce lower DOC concentration. This statement was seen in samples amended with both gypsum and açai. Although the percentage of açai was the same as those amended with only 10% açai, the DOC concentrations in solution were approximately ten times lower. This could be explained by the bridging effect between Ca ions and organic matter. Regarding the effect on trace metals, samples amended with gypsum and açai were deemed optimal since DOC could form complexes with metals and restrict their mobility concerning leaching into the solution (Lehoux et al., 2013). Amendment with gypsum and açai combined also led to increased sorption capacity for anions on iron oxides with amphoteric features as lower pH resulted in a more positive surface charge.

6.5 Sources of error

The porewater samples were collected before, during, and after the end of growth. Except for the un-amended samples, there were consistent increases in the pH measurements two weeks after seeding. An obvious difference here from the previous measurement was that organic material was introduced to the system, which could have led to a change in pH. However, the contribution from the ryegrass would have been CO₂ supply from root respiration, resulting in lower pH. From this point, the pH decreased by the last measurement for samples amended with either sole açai or gypsum but increased in those with combined amendments. The sudden increase in the middle measurement may have resulted from the timing of the measurements. Although it was uncertain if a measurement during growth should be included, the porewater was still collected. Before and after growth samples were measured simultaneously, whereas the “during” samples were measured a few weeks later and might have affected the results for all parameters. Imprecise analytical instruments may also contribute to other sources of measurement error. Although, most of the analysis was performed by lab technicians and the raw data had satisfactory levels of quality control and certified products. For pH measurement, contamination might have been the issue if the electrodes were not cleaned between readings. Nonetheless, it is improbable due to the fact that the data set from two weeks

after seeding provided consistently high values, but rather calibration error. For EC measurement, however, there is the risk of contamination or calibration error considering inconsistency in the results.

The sample preparation step could contribute to a source of error. As mentioned at the beginning of the chapter, each sample was not weighed before use in the pot experiment due to the varying amounts of sample materials. In addition, the BR samples appeared to contain varying amounts of water, and it would have been preferable to use samples with the same initial condition since it was known that the samples had been exposed to the outdoors for several months before collection, to rule out inexplicable errors. To achieve the same starting condition, the samples would have to be dried, crushed, and rectified for the amount of water which could pose a possibility of material loss. However, when the pot experiment was constructed and the first watering session was done, it was observed that certain samples were more clogged than others, resulting in water drainage without sufficient contact time.

Lastly, the percentages of amendment materials mixed into bauxite residue in the field were fixed in this thesis. As the residue was not removed to obtain a total of 100% with the same weight, the addition of differing amounts of amendments resulted in varied total weights across all plots. As additional amendment was added, the total weight increased and the actual weight of each item, including bauxite residue, decreased when recalculated. This may not be a source of error, but further research may be required to determine if the actual decrease affected the effects of the amendments.

7 Conclusion

The objectives of this thesis were to investigate how amendments with gypsum, açai, and combinations of these could enhance the properties of bauxite residue and improve disposal areas. Growth experiments were anticipated to reveal the effects, as proper growth would suggest sufficient conditions.

The set of samples with 10% gypsum + 10% açai clearly showed the best growth, where the mean height was measured to be approximately twice as high as samples to which only 10% gypsum had been added. The same performance was seen in samples added with 5% gypsum + 10% açai, with double the height as without açai. Although the addition of even 5% gypsum reduced the pH significantly, it is reasonable to conclude that the addition of açai together with gypsum contributes to significantly better growth.

The pH in the porewater was successfully lowered by the addition of either açai or gypsum, both separately and in combination. Electrical conductivity made it challenging to evaluate the effects of the amendments. However, it was still possible to identify a strong correlation between growth and the Na concentrations that predominated in the EC measurements. It may be implied that the growing circumstances were still favorable in this way.

The results showed that the trace metals As, V and Al in the porewater had similar leaching behavior, with increased concentrations at higher pH (>8.5) especially V. The concentrations also appeared to be mostly influenced by pH, due to no significant differences in concentration of other substances such as DOC, Fe or base cations. The presence of trace metals were more restrictive in enhancing growth as seen in açai-amended samples, where the concentration of DOC were almost ten times higher than in other amendments. The effect of DOC should however not be ignored, as its presence contributes to stabilization of soil aggregates, which stimulates plant growth, and preventing trace metal mobility into solution.

As discussed, high standard deviations were observed in some results, making it challenging to draw definitive conclusions. The time of sample collection in the field and the pore water samples collected for the laboratory might both have contributed to the uncertainties. However, it is reasonable to consider these sources to represent the reality in which natural influences occur. Further studies could include geochemical modeling to assess the various anion species in addition to using several replicates to substantiate the findings. Additionally, a larger-scale experiment using seeds in the field for biomass and uptake measurements, as well as an evaluation of microbiological activity, might be valuable to assess the long-term effect of the amendments.

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A Sample materials

A.1 Calculation of amendment materials

Table A.1: Calculation of amendment materials based on the initial weight of BR used in each plot (2700 kg). The total weights are sum weights of BR and relevant amendment materials applied. A = açai, G = gypsum and the numbers are percentages.

Amendment/sample	None	A10	G5	G10	G15	G5A10	G10A10	G15A10
None	2700	2700	2700	2700	2700	2700	2700	2700
A10		270				270	270	270
G5			135			135		
G10				270			270	
G15					405			405
Total weight (kg)	2700	2970	2835	2970	3105	3105	3240	3375

Table A.2: Calculation of actual percentages of BR and amendment materials based on the total weight in each plot from Table A.1. A = açai, G = gypsum and the numbers are percentages.

Amendment/sample	None	A10	G5	G10	G15	G5A10	G10A10	G15A10
None	100 %	91 %	95 %	91 %	87 %	87 %	83 %	80 %
A10		9 %				9 %	8 %	8 %
G5			5 %			4 %		
G10				9 %			8 %	
G15					13 %			12 %
Sum: 100%								

A.2 Sample numbering

Table A.3: Sample numbers with corresponding amendment and sample names.

Sample no.			Amendment	Sample name
1	25	49	None	D2
2	26	50		D4
3	27	51		E1
4	28	52	10% açai	B1
5	29	53		C1
6	30	54		G1
7	31	55	5% gypsum	C2
8	32	56		G4
9	33	57		J2
10	34	58	10% gypsum	D1
11	35	59		F2
12	36	60		J3
13	37	61	15% gypsum	B3
14	38	62		E4
15	39	63		H3
16	40	64	5% gypsum + 10% açai	H1
17	41	65		H4
18	42	66		J4
19	43	67	10% gypsum + 10% açai	B4
20	44	68		E2
21	45	69		I2
22	46	70	15% gypsum + 10% açai	B2
23	47	71		H2
24	48	72		I1

B Porewater samples

B.1 pH and electrical conductivity

Table B.1: pH and EC measurements. Sample 1-24 = 2 weeks w/only bauxite residue. Sample 25-48 = 2 weeks after seeding. Sample 49-72 = 4 weeks after seeding. A = açai, G = gypsum, and the numbers are percentages added.

Sample no.	Sample	Amendment	pH	EC	Sample no.	Sample	Amendment	pH	EC	Sample no.	Sample	Amendment	pH	EC
1	D2	None	10.8	4.9	25	D2	None	10.5	3.7	49	D2	None	10.3	3.3
2	D4		10.2	8.2	26	D4		10.3	4.2	50	D4		10.2	4.9
3	E1		10.5	5.2	27	E1		10.4	4.2	51	E1		10.1	4.9
4	B1	A10	8.9	3.7	28	B1	A10	9.5	2.8	52	B1	A10	9.4	2.1
5	C1		8.1	3.0	29	C1		8.8	2.6	53	C1		8.7	2.1
6	G1		8.4	8.4	30	G1		9.3	2.6	54	G1		8.9	2.8
7	C2	G5	7.8	10.6	31	C2	G5	8.8	8.6	55	C2	G5	7.9	8.8
8	G4		7.9	15.2	32	G4		8.5	6.6	56	G4		7.9	11.7
9	J2		7.2	11.8	33	J2		7.9	7.3	57	J2		7.7	7.9
10	D1	G10	7.3	16.2	34	D1	G10	7.6	3.9	58	D1	G10	0.0	0.0
11	F2		8.2	12.2	35	F2		8.5	12.9	59	F2		8.0	13.3
12	J3		7.0	6.7	36	J3		7.9	6.8	60	J3		7.8	7.5
13	B3	G15	7.3	10.7	37	B3	G15	7.6	8.1	61	B3	G15	7.7	8.8
14	E4		7.3	8.0	38	E4		8.1	7.0	62	E4		7.9	6.5
15	H3		8.0	13.6	39	H3		8.9	12.2	63	H3		7.9	10.4
16	H1	G5 + A10	7.0	5.0	40	H1	G5 + A10	7.6	3.1	64	H1	G5 + A10	7.5	3.2
17	H4		7.2	4.7	41	H4		7.7	3.3	65	H4		7.7	3.6
18	J4		6.8	2.9	42	J4		7.4	1.7	66	J4		7.5	2.6
19	B4	G10 + A10	7.1	3.7	43	B4	G10 + A10	7.4	2.7	67	B4	G10 + A10	7.5	2.5
20	E2		7.1	2.7	44	E2		7.2	2.5	68	E2		7.4	2.4
21	I2		6.8	2.6	45	I2		7.2	3.0	69	I2		7.5	3.8
22	B2	G15 + A10	7.3	3.7	46	B2	G15 + A10	7.4	2.2	70	B2	G15 + A10	7.4	2.8
23	H2		7.1	5.1	47	H2		7.5	3.9	71	H2		7.8	4.7
24	I1		7.0	3.6	48	I1		7.4	3.4	72	I1		7.6	6.4

Table B.2: Mean values and standard deviations for pH measurements based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	10.5 ± 0.26	10.4 ± 0.11	10.2 ± 0.09
10% açai	8.5 ± 0.40	9.2 ± 0.32	9.0 ± 0.36
5% gypsum	7.6 ± 0.38	8.4 ± 0.50	7.8 ± 0.08
10% gypsum	7.5 ± 0.62	8.0 ± 0.42	7.9 ± 0.09
15% gypsum	7.5 ± 0.42	8.2 ± 0.65	7.8 ± 0.10
5% gypsum + 10% açai	7.0 ± 0.16	7.5 ± 0.13	7.6 ± 0.08
10% gypsum + 10% açai	7.0 ± 0.14	7.2 ± 0.40	7.5 ± 0.07
15% gypsum + 10% açai	7.1 ± 0.13	7.4 ± 0.05	7.6 ± 0.22

Table B.3: Mean values and standard deviations for EC measurements of porewater samples based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	6.1 ± 1.80	4.0 ± 0.28	4.4 ± 0.95
10% açai	5.0 ± 2.94	2.7 ± 0.12	2.3 ± 0.43
5% gypsum	12.5 ± 2.40	7.5 ± 1.04	9.5 ± 1.99
10% gypsum	11.7 ± 4.78	7.9 ± 4.59	10.4 ± 4.09
15% gypsum	10.7 ± 2.83	9.1 ± 2.69	8.6 ± 1.96
5% gypsum + 10% açai	4.2 ± 1.15	2.7 ± 0.88	3.2 ± 0.51
10% gypsum + 10% açai	3.0 ± 0.61	2.7 ± 0.25	2.9 ± 0.75
15% gypsum + 10% açai	4.1 ± 0.87	3.2 ± 0.91	4.6 ± 1.81

B.2 Alkalinity

Table B.4: Alkalinity measurements. Sample 1-24 = 2 weeks w/only bauxite residue. Sample 49-72 = 2 weeks after seeding. Sample 25-48 = 4 weeks after seeding. A = açai, G = gypsum, and the numbers are percentages added.

Sample no.	Sample	Amendment	Alkalinity (mEq/l)	Sample no.	Sample	Amendment	Alkalinity (mEq/l)	Sample no.	Sample	Amendment	Alkalinity (mEq/l)
1	D2		47.92	49	D2		87.66	25	D2		71.99
2	D4	None	81.36	50	D4	None	95.56	26	D4	None	57.40
3	E1		66.57	51	E1		76.48	27	E1		67.64
4	B1		25.16	52	B1		41.04	28	B1		22.99
5	C1	A10	8.19	53	C1	A10	15.92	29	C1	A10	11.25
6	G1		11.04	54	G1		25.76	30	G1		12.64
7	C2		1.33	55	C2		1.29	31	C2		1.03
8	G4	G5	1.36	56	G4	G5	1.65	32	G4	G5	1.11
9	J2		1.72	57	J2		1.77	33	J2		1.45
10	D1		1.59	58	D1		2.22	34	D1		N/A
11	F2	G10	1.49	59	F2	G10	0.80	35	F2	G10	1.31
12	J3		1.33	60	J3		1.38	36	J3		1.39
13	B3		1.04	61	B3		1.06	37	B3		1.12
14	E4	G15	1.02	62	E4	G15	1.04	38	E4	G15	1.41
15	H3		1.39	63	H3		1.13	39	H3		1.13
16	H1		1.17	64	H1		1.16	40	H1		1.28
17	H4	G5 + A10	1.22	65	H4	G5 + A10	1.67	41	H4	G5 + A10	1.87
18	J4		0.81	66	J4		1.23	42	J4		1.17
19	B4		0.75	67	B4		1.58	43	B4		1.05
20	E2	G10 + A10	0.81	68	E2	G10 + A10	1.20	44	E2	G10 + A10	1.04
21	I2		0.67	69	I2		1.43	45	I2		1.39
22	B2		0.64	70	B2		1.30	46	B2		1.02
23	H2	G15 + A10	1.21	71	H2	G15 + A10	1.97	47	H2	G15 + A10	2.06
24	I1		0.77	72	I1		3.22	48	I1		1.63

B.3 ICP-MS and ICP-OES analysis of trace elements

Table B.5: ICP-MS and ICP-OES analysis of V, As, Al, Ca, Fe, K, Mg, Na, P and S. Sample 1-24 = 2 weeks w/only bauxite residue. Sample 49-72 = 2 weeks after seeding. Sample 25-48 = 4 weeks after seeding.

	ICP-MS	ICP-MS	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
	V	As	Al	Ca	Fe	K	Mg	Na	P	S					
	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L					
LOD	0.018431418	0.019732704	0.000	0.000	0.002886715	0.028915663	0.000	0.014634146	0.014814815	0.017106675					
LOQ	0.061438061	0.065775681	0.000	0.000	0.009622383	0.096385542	0.000	0.048780488	0.049382716	0.057022249					
1	1500	63	52	0.51	0.12	2.9	<LD	1500	<LD	190					
2	480	26	15	0.95	0.23	4.4	<LD	2400	<LD	260					
3	250	16	8.4	0.82	0.7	2.6	<LD	1800	<LD	20					
4	380	23	12	13	31	5.4	0.69	980	0.75	210					
5	150	16	1.3	8.1	0.38	6.9	0.29	790	0.21	240					
6	97	18	2.4	19	4.5	15	1.7	2100	1.1	1100					
7	50	1.1	3.7	370	<0.0096	6.5	<LD	3100	<LD	2400					
8	48	2.0	1.9	370	<LD	15	<LD	4900	<LD	3400					
9	6.3	0.35	0.36	370	<LD	5.1	0.19	3100	<LD	2400					
10	19	1.0	3.1	400	<LD	13	0.05	5700	<LD	4000					
11	57	2.8	3.3	500	<LD	8.3	<LD	4600	<LD	3400					
12	9.4	0.73	1.2	770	<LD	7.2	1.3	3000	<LD	2200					
13	24	0.92	4.2	610	<LD	9.6	0.07	4000	<LD	2900					
14	31	1.0	6.8	510	<LD	2.7	<LD	2600	<LD	2000					
15	95	4.4	8.3	570	<LD	14	0.4	5700	<LD	3800					
16	13	1.5	0.11	570	<LD	11	6.7	1300	<LD	1100					
17	16	2.2	0.11	320	0.013	12	8.2	1200	<LD	960					
18	9.0	1.4	0.12	780	<LD	11	6.8	650	<LD	750					
19	7.2	1.8	0.07	650	0.025	11	4.0	520	<LD	700					
20	11	1.0	0.08	650	<LD	4.6	2.4	300	<LD	620					
21	7.5	1.2	0.068	720	<0.0096	9.2	5.4	480	<LD	710					
22	12	0.79	0.087	800	<LD	5.1	4.6	780	<LD	900					
23	15	2.7	0.23	590	0.13	13	7.8	1500	<0.049	1200					
24	7.7	0.95	0.097	800	<LD	8.2	8.9	920	<LD	980					
25	270	18	11	2.9	0.076	6.0	<LD	2700	<LD	25					
26	230	15	4.9	0.68	0.043	2.0	<LD	1500	<LD	23					
27	100	9.5	3.4	1.1	0.3	2.1	<LD	1800	<LD	13					
28	390	22	6.5	8.2	4.1	3.3	0.22	790	0.67	97					
29	210	19	2.3	13	0.47	5.4	0.37	710	1.3	140					
30	180	22	3.5	13	8.7	4.9	0.61	790	2.3	220					
31	15	0.45	1.3	510	<LD	3.3	<LD	2600	<LD	2100					
32	15	0.59	0.8	460	<LD	8.4	<LD	3900	<LD	2900					
33	4.1	0.19	0.32	820	<LD	6.2	1.3	3300	<LD	2400					
34(blank)	<LD	<LD	<LD	0.091	<LD	<LD	<LD	<LD	<LD	<LD					
35	30	0.89	1.4	440	<LD	5.4	<LD	3900	<LD	3100					
36	9.4	0.53	0.2	470	<LD	3.5	1.0	2000	<LD	1800					

(cont.) ICP-MS and ICP-OES analysis of V, As, Al, Ca, Fe, K, Mg, Na, P and S.

	ICP-MS	ICP-MS	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
	V	As	Al	Ca	Fe	K	Mg	Na	P	S			
	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L			mg/L
LOD	0.018431418	0.019732704	0.000	0.000	0.002886715	0.028915663	0.000	0.014634146	0.014814815	0.017106675			
LOQ	0.061438061	0.065775681	0.000	0.000	0.009622383	0.096385542	0.000	0.048780488	0.049382716	0.057022249			
37	12	0.44	0.19	430	<LD	2.7	0.25	2400	<LD	2000			
38	19	0.62	0.97	430	<LD	2.2	0.10	2600	<LD	2200			
39	28	0.71	1.5	440	<LD	3.3	<LD	2800	<LD	2300			
40	12	1.3	0.14	820	<LD	5.0	4.7	660	<LD	910			
41	18	2.8	0.17	440	<0.0096	7.3	4.6	930	<LD	910			
42	9.4	1.5	0.10	690	<LD	2.2	3.0	310	<LD	660			
43	8.5	1.6	0.066	610	<LD	2.8	1.8	200	<LD	590			
44	11	1.5	0.094	710	0.02	1.3	1.6	200	<LD	620			
45	8.6	2.1	0.12	860	<LD	13	5.3	1000	<LD	1100			
46	14	0.88	0.056	620	<LD	0.33	1.9	290	<LD	640			
47	15	2.2	0.19	580	<0.0096	10	6.0	1300	<LD	1200			
48	11	1.7	0.11	740	<LD	9.1	7.3	1900	<LD	1700			
49	410	29	8.0	1.3	0.13	5.7	<LD	2400	<LD	49			
50	190	16	3.9	1.1	0.012	2.8	<LD	2200	<LD	56			
51	110	11	4.5	1.4	0.15	3.3	<LD	2200	<LD	16			
52	410	30	8.7	13	21	7.3	0.52	1400	0.95	260			
53	280	26	2.1	10	0.46	7.0	0.29	750	1.5	130			
54	400	57	8.5	13	30	8.6	0.54	1400	4.6	300			
55	25	0.46	4.4	620	<LD	6.7	<LD	3600	<LD	2700			
56	21	0.83	4.1	690	<LD	16	<LD	5500	<LD	3900			
57	5.9	0.27	0.14	530	0.012	5.7	0.83	3100	<LD	2400			
58	12	0.46	0.18	520	<LD	8.5	<LD	6900	<LD	5000			
59	42	0.56	2.9	470	<LD	4.7	<LD	3300	<LD	2500			
60	8.9	0.55	0.16	610	<LD	7.7	1.6	3200	<LD	2300			
61	13	0.4	0.35	560	<LD	5.1	0.15	3100	<LD	2300			
62	23	0.46	2.0	560	<LD	4.0	<LD	3500	<LD	2700			
63	39	0.87	5.9	600	<LD	5.9	<LD	3700	<LD	2700			
64	15	1.6	0.094	580	<LD	4.8	4.3	610	<LD	820			
65	17	2.1	0.14	660	<LD	8.5	8.9	1000	<LD	1100			
66	9.9	1.4	0.075	640	<LD	2.2	3.4	350	<LD	670			
67	5.1	1.4	0.12	1100	0.070	10	4.8	550	<LD	900			
68	11	0.87	0.056	690	<0.0096	3.0	1.8	240	<LD	630			
69	9.1	2.5	0.084	620	<LD	18	5.6	1300	<LD	1300			
70	13	0.84	0.094	820	<LD	5.3	3.3	590	<LD	850			
71	14	2.9	0.11	470	<LD	9.3	4.3	1100	<LD	1100			
72	12	1.5	0.10	700	0.022	8.2	9.1	850	<LD	980			
1643F	35	60	0.13	30	0.091	1.8	7.9	20	2.6	2.6			

Table B.6: Mean values and standard deviations for measurements of arsenic in porewater samples ($\mu\text{g/l}$) based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	35 \pm 24.76	18.7 \pm 9.29	14.2 \pm 4.31
10% açai	19 \pm 3.61	37.7 \pm 16.86	21 \pm 1.73
5% gypsum	1.2 \pm 0.83	0.5 \pm 0.28	0.4 \pm 0.2
10% gypsum	1.5 \pm 1.13	0.5 \pm 0.06	0.7 \pm 0.25
15% gypsum	2.1 \pm 1.99	0.6 \pm 0.26	0.6 \pm 0.14
5% gypsum + 10% açai	1.7 \pm 0.44	1.7 \pm 0.36	1.9 \pm 0.81
10% gypsum + 10% açai	1.3 \pm 0.42	1.6 \pm 0.83	1.7 \pm 0.32
15% gypsum + 10% açai	1.5 \pm 1.06	1.7 \pm 1.05	1.6 \pm 0.67

Table B.7: Mean values and standard deviations for measurements of vanadium in porewater samples ($\mu\text{g/l}$) based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	743 \pm 665.3	237 \pm 155.3	200 \pm 88.9
10% açai	209 \pm 150.4	363 \pm 72.3	260 \pm 113.6
5% gypsum	35 \pm 24.7	17 \pm 10.1	11 \pm 6.3
10% gypsum	28 \pm 25.2	21 \pm 18.3	20 \pm 14.6
15% gypsum	50 \pm 39.1	25 \pm 13.1	20 \pm 8
5% gypsum + 10% açai	13 \pm 3.5	14 \pm 3.7	13 \pm 4.4
10% gypsum + 10% açai	9 \pm 2.1	8 \pm 3	9 \pm 1.4
15% gypsum + 10% açai	12 \pm 3.7	13 \pm 1	13 \pm 2.1

Table B.8: Mean values and standard deviations for measurements of aluminum in porewater samples (mg/l) based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	25.1 \pm 23.5	5.5 \pm 2.21	6.4 \pm 4.03
10% açai	5.2 \pm 5.89	6.4 \pm 3.75	4.1 \pm 2.16
5% gypsum	2 \pm 1.67	2.9 \pm 2.38	0.8 \pm 0.49
10% gypsum	2.5 \pm 1.16	1.1 \pm 1.58	0.8 \pm 0.85
15% gypsum	6.4 \pm 2.07	2.8 \pm 2.85	0.9 \pm 0.66
5% gypsum + 10% açai	0.1 \pm 0.01	0.1 \pm 0.03	0.1 \pm 0.04
10% gypsum + 10% açai	0.1 \pm 0.01	0.1 \pm 0.03	0.1 \pm 0.03
15% gypsum + 10% açai	0.1 \pm 0.08	0.1 \pm 0.01	0.1 \pm 0.07

Table B.9: Mean values and standard deviations for measurements of iron in porewater samples (mg/l) based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	0.4 \pm 0.31	0.1 \pm 0.07	0.1 \pm 0.14
10% açai	12 \pm 16.62	17.2 \pm 15.14	4.4 \pm 4.12
5% gypsum	<LOD	<LOD	<LOD
10% gypsum	<LOD	<LOD	<LOD
15% gypsum	<LOD	<LOD	<LOD
5% gypsum + 10% açai	<LOD	<LOD	<LOD
10% gypsum + 10% açai	<LOD	<LOD	<LOD
15% gypsum + 10% açai	<LOD	<LOD	<LOD

Table B.10: Mean values and standard deviations for measurements of sulfur in porewater samples (mg/l) based on triplicates.

Amendment	2 weeks w/ only BR	2 weeks after seeding	4 weeks after seeding
None	157 ± 100.8	40 ± 17.4	20 ± 5.2
10% açai	517 ± 412.7	230 ± 72.6	152 ± 51
5% gypsum	2733 ± 471.4	3000 ± 648.1	2467 ± 330
10% gypsum	3200 ± 748.3	3267 ± 1228.4	2450 ± 650
15% gypsum	2900 ± 734.8	2567 ± 188.6	2167 ± 124.7
5% gypsum + 10% açai	937 ± 143.8	863 ± 178.2	827 ± 117.9
10% gypsum + 10% açai	677 ± 40.3	943 ± 275.2	770 ± 233.7
15% gypsum + 10% açai	1027 ± 126.8	977 ± 102.1	1180 ± 433

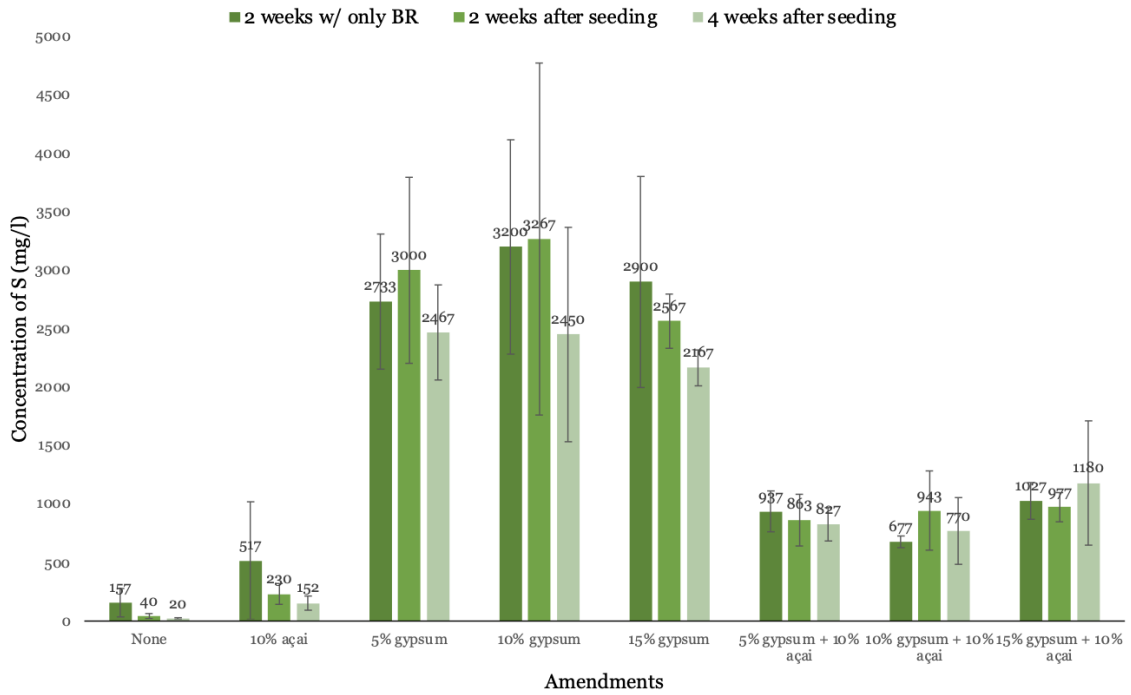


Figure B.1: Concentration of S (mg/l) in porewater samples with different amendments. Each bar represents the mean value based on triplicates with corresponding standard deviation.

B.4 IC analysis of SO₄²⁻

Table B.11: IC analysis of SO₄²⁻. Sample 1-24 = 2 weeks w/only bauxite residue. Sample 49-72 = 2 weeks after seeding. Sample 25-48 = 4 weeks after seeding. A = açai, G = gypsum, and the numbers are percentages added.

Sample no.	Sample	Amendment	SO4 (mg/l)	Sample no.	Sample	Amendment	SO4 (mg/l)	Sample no.	Sample	Amendment	SO4 (mg/l)
1	D2	None	577.14	49	D2	None	102.66	25	D2	None	22.49
2	D4		804.83	50	D4		121.77	26	D4		32.91
3	E1		27.74	51	E1		9.06	27	E1		3.71
4	B1	A10	614.46	52	B1	A10	745.59	28	B1	A10	217.37
5	C1		757.64	53	C1		283.00	29	C1		300.95
6	G1		3549.04	54	G1		653.12	30	G1		663.44
7	C2	G5	8351.85	55	C2	G5	7823.37	31	C2	G5	6691.89
8	G4		11279.08	56	G4		10398.52	32	G4		8857.06
9	J2		8448.92	57	J2		7512.05	33	J2		5920.58
10	D1	G10	14426.90	58	D1	G10	14814.92	34	D1	G10	<LOQ
11	F2		9697.12	59	F2		8190.93	35	F2		10376.66
12	J3		5365.14	60	J3		6614.69	36	J3		5300.18
13	B3	G15	7854.24	61	B3	G15	7154.48	37	B3	G15	6740.80
14	E4		5896.61	62	E4		7845.49	38	E4		7474.83
15	H3		10956.87	63	H3		8247.87	39	H3		7447.86
16	H1	G5 + A10	3108.70	64	H1	G5 + A10	2509.98	40	H1	G5 + A10	2401.19
17	H4		2875.94	65	H4		2951.33	41	H4		2796.04
18	J4		1788.93	66	J4		2073.59	42	J4		1916.87
19	B4	G10 + A10	2128.51	67	B4	G10 + A10	2051.97	43	B4	G10 + A10	1894.52
20	E2		1858.76	68	E2		1877.56	44	E2		1856.78
21	I2		1942.93	69	I2		3768.44	45	I2		2808.26
22	B2	G15 + A10	2420.05	70	B2	G15 + A10	2306.93	46	B2	G15 + A10	2015.88
23	H2		3380.97	71	H2		3178.09	47	H2		3283.32
24	I1		2468.22	72	I1		2798.35	48	I1		4747.19

B.5 Dissolved organic carbon (DOC)

Table B.12: DOC measurements. Sample 1-24 = 2 weeks w/only bauxite residue. Sample 49-72 = 2 weeks after seeding. Sample 25-48 = 4 weeks after seeding. A = açai, G = gypsum, and the numbers are percentages added.

Sample no.	Sample	Amendment	DOC (mg/l)	Sample no.	Sample	Amendment	DOC (mg/l)	Sample no.	Sample	Amendment	DOC (mg/l)
1	D2	None	37.2	49	D2	None	34	25	D2	None	26
2	D4		44	50	D4		16.4	26	D4		11.2
3	E1		26.8	51	E1		17.6	27	E1		19.6
4	B1	A10	370	52	B1	A10	276	28	B1	A10	120
5	C1		108	53	C1		116	29	C1		116
6	G1		236	54	G1		200	30	G1		160
7	C2	G5	12.8	55	C2	G5	7.6	31	C2	G5	6
8	G4		37.6	56	G4		16.4	32	G4		11.6
9	J2		10.4	57	J2		7.6	33	J2		5.6
10	D1	G10	16.8	58	D1	G10	14	34	D1	G10	blank
11	F2		12.4	59	F2		7.6	35	F2		6.8
12	J3		24.4	60	J3		15.2	36	J3		11.2
13	B3	G15	9.6	61	B3	G15	6.4	37	B3	G15	6
14	E4		14.8	62	E4		8	38	E4		6.8
15	H3		24.4	63	H3		8.4	39	H3		7.6
16	H1	G5 + A10	18	64	H1	G5 + A10	10.4	40	H1	G5 + A10	9.2
17	H4		12	65	H4		13.6	41	H4		18.8
18	J4		16.4	66	J4		11.6	42	J4		12
19	B4	G10 + A10	19.2	67	B4	G10 + A10	12	43	B4	G10 + A10	9.6
20	E2		22	68	E2		10.4	44	E2		11.2
21	I2		18.4	69	I2		17.6	45	I2		17.2
22	B2	G15 + A10	12	70	B2	G15 + A10	11.6	46	B2	G15 + A10	8.4
23	H2		48	71	H2		24.8	47	H2		20.8
24	I1		17.2	72	I1		19.2	48	I1		13.6

C Biomass samples

C.1 Height measurements

Table C.1: Height measurements of biomass samples.

Sample	Amendment	H (cm)	Wet (g)	Dry (g)
D2		0	0,00	0,000
D4	None	0	0,00	0,000
E1		0	0,00	0,000
B1		0	0,00	0,000
C1	Açai 10%	4	0,02	0,004
G1		4	0,01	0,003
C2		7	0,03	0,006
G4	Gypsum 5%	6	0,02	0,003
J2		5	0,02	0,005
D1		5	0,01	0,002
F2	Gypsum 10%	6	0,01	0,008
J3		10	0,03	0,009
B3		6	0,04	0,007
E4	Gypsum 15%	7	0,05	0,012
H3		7	0,06	0,014
H1		15	0,27	0,038
H4	Gypsum 5% + açai 10%	13	0,20	0,016
J4		15	0,21	0,034
B4		13	0,09	0,025
E2	Gypsum 10% + açai 10%	14	0,27	0,031
I2		21	0,28	0,049
B2		8	0,04	0,008
H2	Gypsum 15% + açai 10%	5	0,01	0,002
I1		13	0,19	0,025
REF1		25	0,71	0,097
REF2	Ref	26	0,63	0,156
REF3		21	0,61	0,122

C.2 ICP-MS analysis of trace elements

Table C.2: ICP-MS analysis of trace elements Na, Mg, Al, P, K, Ca, V, Fe and As in the biomass. A = açai, G = gypsum, and the numbers are percentages added.

Sample	Amendment	Na g/kg	Mg g/kg	Al g/kg	P g/kg	K g/kg	Ca g/kg	V mg/kg	Fe g/kg	As mg/kg
		ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
	LOD	0.000762	0.000574	0.00017	0.000393	0.002185	0.003198	0.001676	0.000494	0.002452
	LOQ	0.002539	0.001912	0.000566	0.00131	0.007282	0.010659	0.005586	0.001646	0.008173
D2		0	0	0	0	0	0	0	0	0
D4	None	0	0	0	0	0	0	0	0	0
E1		0	0	0	0	0	0	0	0	0
B1		0	0	0	0	0	0	0	0	0
C1	A10	0	0	0	0	0	0	0	0	0
G1		35	1.9	0.43	9.3	10	1.2	4.2	1.9	0.26
C2		42	1.1	0.43	3.0	11	5.3	1.7	0.88	0.096
G4	G5	44	1.7	0.91	4.7	19	3.6	4.9	2.4	0.19
J2		40	1.5	0.28	3.8	9.5	4.3	1.7	0.88	0.064
D1		51	1.0	0.92	3.8	8.6	2.7	5.1	2.5	0.15
F2	G10	48	0.9	1.4	4.5	7.4	2.2	4.6	2.0	0.23
J3		39	1.6	0.96	2.9	19	5.0	6.3	1.7	0.17
B3		47	1.3	0.70	3.3	15	4.0	3.2	1.6	0.17
E4	G15	51	1.2	0.40	3.5	9.1	4.0	1.9	0.96	0.10
H3		45	0.94	0.24	4.0	11	2.9	1.2	0.61	0.056
H1		7.5	2.2	0.13	1.9	48	9.3	0.56	0.32	0.32
H4	G5A10	16	2.4	0.15	1.9	38	8.7	0.80	0.43	0.15
J4		4.4	1.8	0.067	2.1	51	11	0.28	0.17	0.30
B4		9.0	1.3	0.092	2.4	51	9.5	0.27	0.18	0.55
E2	G10A10	9.5	1.1	0.070	1.7	43	9.7	0.23	0.19	0.31
I2		6.0	1.7	0.21	2.8	56	6.6	0.58	0.19	0.4
B2		32	1.6	0.84	3.2	32	12	2.8	1.3	0.17
H2	G15A10	44	1.4	0.20	3.6	11	2.1	0.82	0.36	0.14
I1		9.2	2.0	0.14	1.6	39	8.8	0.55	0.31	0.097
Ref 1		0.21	2.2	0.048	7.5	66	8.7	0.14	0.13	0.13
Ref 2	Ref	0.38	3.0	0.030	7.1	59	12	0.07	0.13	0.15
Ref 3		0.70	2.9	0.063	6.4	57	11	0.17	0.14	0.14

Table C.3: Mean values and standard deviations for trace elements Na, Mg, Al, P, K, Ca, V, Fe and As in the biomass.

Amendment	Na	Mg	Al	P
None	0 ± 0	0 ± 0	0 ± 0	0 ± 0
10% açai	35 ± 0	1.9 ± 0	0.4 ± 0	9.3 ± 0
5% gypsum	42 ± 2	1.4 ± 0.31	0.5 ± 0.33	3.8 ± 0.85
10% gypsum	46 ± 6.24	1.2 ± 0.38	1.1 ± 0.27	3.7 ± 0.8
15% gypsum	47.7 ± 3.06	1.1 ± 0.19	0.4 ± 0.23	3.6 ± 0.36
5% gypsum + 10% açai	9.3 ± 6.01	2.1 ± 0.31	0.1 ± 0.04	2 ± 0.12
10% gypsum + 10% açai	8.2 ± 1.89	1.4 ± 0.31	0.1 ± 0.08	2.3 ± 0.56
15% gypsum + 10% açai	28.4 ± 17.68	1.7 ± 0.31	0.4 ± 0.39	2.8 ± 1.06
Reference	0.4 ± 0.25	2.7 ± 0.44	0 ± 0.02	7 ± 0.56

Amendment	Ca	V	Fe	As
None	0 ± 0	0 ± 0	0 ± 0	0 ± 0
10% açai	1.2 ± 0	4.2 ± 0	1.9 ± 0	0.3 ± 0
5% gypsum	4.4 ± 0.85	2.8 ± 1.85	1.4 ± 0.88	0.1 ± 0.07
10% gypsum	3.3 ± 1.49	5.3 ± 0.87	2.1 ± 0.4	0.2 ± 0.04
15% gypsum	3.6 ± 0.64	2.1 ± 1.01	1.1 ± 0.5	0.1 ± 0.06
5% gypsum + 10% açai	9.7 ± 1.19	0.5 ± 0.26	0.3 ± 0.13	0.3 ± 0.09
10% gypsum + 10% açai	8.6 ± 1.73	0.4 ± 0.19	0.2 ± 0.01	0.4 ± 0.12
15% gypsum + 10% açai	7.6 ± 5.05	1.4 ± 1.23	0.7 ± 0.56	0.1 ± 0.04
Reference	10.6 ± 1.69	0.1 ± 0.05	0.1 ± 0.01	0.1 ± 0.01



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