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Cation exchange capacity, and amendment effect of gypsum and organic matter on chemical properties and aggregate stability of bauxite residue

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Abstract

Bauxite residue (BR) is the waste product in alumina extraction from bauxite. Behind every tonne alumina, 1-2 tonnes BR is generated, and the world's largest alumina refinery is Hydro Alunorte, Brazil. Bauxite residue is highly alkaline (pH 11-13), saline and sodic, and it contains high amounts of iron and aluminium and trace elements. The aim of this thesis was to investigate knowledge gaps around how to improve BR as a plant-growth medium, as ecosystem restoration has been pointed out to be the most promising strategy for remediating BR disposal areas.

The thesis focused on three specific challenges: 1. Assessment of cation exchange capacity (CEC) in BR, by comparing the common method; ammonium acetate (NH4OAc) extractable cations and another method which includes a second step where potassium chloride (KCl) replaces adsorbed ammonium (NH4+) from the NH4OAc. 2. Amendment effect on plant performance in a column study. Here, BR was amended with 0, 5, and 10 % gypsum and 0 and 5% locally derived organic matter: Waste from Açai berry production and food waste. Water was added to the columns in a leachate series to reduce pH, electrical conductivity, and sodicity, before seeds of rye grass (*Lolium perenne)* were planted. The growth was observed for five weeks. 3. Aggregate stability on amended and unamended BR with both samples from the columns and field-samples from Hydro Alunorte.

The determined CEC by NH4OAc extraction was about 250 meq/100g, while it was about 35 meq/100g by the KCl exchangeable method. The latter was considered to better represent the true CEC in BR, while NH4OAc highly overestimated it. The leaching experiment resulted in a reduction of the EC<4 dS/m and a pH of 8.9 with 10% gypsum and 7.5 with 10% gypsum and 5% food waste. 10% gypsum was also most effective in reducing sodicity, and grass performed best in this treatment, followed by 10% gypsum and 5% Açai waste. Gypsum application resulted in significantly improved aggregate stability compared to unamended BR, and it was no significant difference between 5%, 10% or 15% gypsum added. Gypsum with Açai waste resulted in slightly better stability then when only gypsum was applied.

Based on the findings in this study and the availability of Açai in this region of Brazil, Gypsum + Açai waste could be a promising amendment, especially if the Açai waste was composted to a certain degree before augmenting, to provide more easily available carbon and nutrient sources, which could lead to richer soil fauna and greater pH-reducing effect. The effect of Açai + gypsum should therefore be further investigated, as well as its long-term effect in the field

Samandrag

Bauksittavfall (BR) er overskotsprodukt frå ekstrahering av alumina frå bauksittmalm. Bak kvart tonn alumina produserast det 1-2 tonn bauksittavfall, og verdas største aluminaraffineri er Hydro Alunorte, som ligg ved byen Belém, i nordaustlege Brasil. Bauksittavfall er svært alkalisk (pH 11-13), salint og sodisk, og det inneheld høge verdiar av jern, aluminium og sporelement. Målet med denne oppgåva var å undersøke kunnskapshol rundt korleis betre BR som eit medium for plantevekst, då økosystem-restaurering er føreslått som den beste løysinga for å forbetre bauksittavfallsdeponi.

Denne oppgåva fokuserte på tre spesifikke utfordringar: 1. Vurdering av kationbyttekapasitet (CEC) i BR, gjennom samanlikning av ein mykje brukt metode kor ammoniumacetat (NH4OAc) ekstraherer kation i BR, og ein metode som belagar seg på at kaliumklorid (KCl) bytar ut adsorbert ammonium (NH4+) etterfølgt av NH4OAc-tilsettinga. 2. Forbetringseffekt på plantevekst i eit kolonneforsøk. Bauksittavfall blei tilsett gips og lokalt organisk materiale: Avfallsproduktet frå Açai -produksjon og matavfall. Vatn blei tilført kolonnene i ei utlekkingserie for å redusere pH, elektrisk leiingsevne og saltinnhald, før tilsetning av raigrasfrø (*Lolium perenne)*. Deretter følgde eit vekstforsøk over fem veker. 3. Aggregatstabilitet av BR med dei ulike jordbetringsmidla, i laboratoriekolonner og i feltprøver frå Hydro Alunorte.

Kationbyttekapasiteten blei frå NH4OAc-ekstrahering blei bestemt til om lag 250 meq/100g, medan den var om lag 35 meq/100g med den KCl-utbyttbare metoden. Sistnemnde vart betrakta som den beste representasjonen av den sanne CEC, medan NH4OAc overestimerte den. Utlekkingsforsøket førte EC <4 dS/m og pH blei redusert til 11.9 med 10% gips og 7.5 med 10% gips + 5% matavfall. 10% gips var også mest effektiv i å redusere saltinnhald, med ein SAR = 6.1, og gras viste best vekst i denne behandlinga. Frå feltprøvene førte gips også til signifikant forbetra aggregatstabilitet samanlikna med ubehandla BR, og det var inga signifikant forskjell mellom 5, 10 og 15% gips. Gips med Açai gav litt betre stabilitet enn når berre gips var tilsett.

Basert på funna i denne masteroppgåva og tilgjengelegheita av Açai i denne regionen av Brasil, kan gips + Açai vere ein lovande kombinasjon, spesielt dersom avfall frå Açai blei behandla i forkant av tilsetning, for å auke tilgjengelegheita av karbon for mikroorganismar, som ville ført til ein rikare jordfauna og større pH-senking. Açai+ gips bør derfor bli ytterlegerare utforska, i tillegg til langtidsverknaden i felt.

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Ås, 2022

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INTRODUCTION

Aluminium is a metal found in almost everything that surrounds us. It is an important element in all industries from construction and transportation to household good and beverage containers. When used in alloys, it is a good alternative to steel, because of its high strength to weight ratio, malleable properties, and corrosion resistance. If our age should be named after a metal, it could be aluminium (Pedersen, 2021).

Aluminium is the third most abundant element in the Earth's crust (8%), after oxygen (46%) and silicon (28%) (Schlesinger & Bernhardt, 2013), but has a relatively short history as human's tool. Elemental aluminium was first produced in 1825 but only taken up commercially in the late 1800's (Geller, 2007). It is not as accessible as iron, as metallic aluminium never occurs in nature, but rather as oxides and hydroxides, or as aluminosilicates in igneous rocks and clay minerals. Secondary minerals are formed with time during weathering of old rock and soil, while hot and humid conditions speed up reactions and yield higher concentrations of the aluminium-bearing minerals. The principal ore of aluminium is the highly weathered bauxite, a rock composed of a mixture of hydrous aluminium oxides, iron oxides and trace elements. In 2018, 4-5 tonnes bauxite was mined for every tonne aluminium produced, to a total of 325 million tonnes (mt) bauxite (T J Brown et al., 2019). The largest production of bauxite takes place in Australia, China and Brazil, with 95, 62 and 32 mt produced in 2018, respectively. (T J Brown et al., 2019).

The common practice for producing aluminium (Al) can be divided into two steps: First alumina refining from bauxite through the so-called Bayer process, followed by primary Al production through the Hall-Héroult process. In the Bayer process, alumina, the common name for aluminium oxide (Al_2O_3), is extracted from bauxite. In brief, the bauxite is crushed, before it is digested in hot caustic soda (NaOH). This increases pH drastically, which significantly increases solubility of Al oxides. The NaOH solution then goes through several filtration and clarifying steps, before it is calcinated to remove water, eventually resulting in the white powder called alumina. To produce pure Al, the alumina is smelted in the Hall-Héroult electrolytic process.

The separated, residual bauxite is called red mud. The colour is due to the iron oxides and it has a high moisture content (50-70%). Common treatment processes of red mud prior to disposal include filtration to recover soda and reduce water content. Press filter technology can reduce moisture content to around 20%, which allows higher compaction of the residual waste, thus less unit area and runoff risk, when compared to wet disposal (Castro et al., 2016). At this low moisture content, the press filter material is often referred to as bauxite residue (BR).

The world's largest alumina refinery is Norsk Hydro Alunorte (AlCircle, 2018), (Norsk Hydro, consulted 02.06). It is located close to the city of Belém in North-eastern Brazil, around 100 km inland from the Atlantic Ocean along the Pará River. In 2021, around six million tonnes alumina was produced at Alunorte, which corresponded to around 11 million tonnes BR (Norsk Hydro, 2022). When produced, Al is cheap to recycle with only 5% of primary energy demand (EAA, 2006), and around 75% of all aluminium produced is still in use (International Aluminium Institute, 2018). Bauxite residue, however, represents a large environmental impact. Due to the boiling in NaOH it has a very high pH (10-13), and it contains high amounts Al and iron (Fe) oxides, as well as potentially toxic metalloids (Anton et al., 2014), and the crushing of bauxite creates a very fine-particle mass. In total, this poses a risk of wind and water erosion and pollution of groundwater, streams, and soils.

To mitigate these problems by 2030, Hydro aims to utilise 10% of bauxite residue they generate and to eliminate the need for new permanent bauxite residue storage by 2050 (Norsk Hydro, 2022). Examples of utilisation are extraction of metals and metal oxides and the application of BR as a binder in cement industries and use in concrete (Verma et al., 2017). However, many of the current large BR disposals will remain, and these cannot be left unamended. One study found that 20 year old, untreated BR maintains many of the same properties as freshly deposited BR (Bray et al., 2018). When utilisation is not possible, a promising solution for minimising environmental risks is in situ revegetation of the BR disposal areas (BRDA's) (Okkenhaug, 2018; Xue et al., 2016), which could help facilitate a more stable surface against wind and water erosion.

There are many challenges with establishing vegetation on BR. Low porosity follows BR's high density and clay-sized particles. In addition, the highly alkaline and saline environment is intolerable to most plants and organisms. Furthermore, the high Al, Fe and Na content can lead to toxicities and nutrient imbalances in plants. The BR contains little organic carbon (OC) and plant-available nutrients such as nitrogen (N), phosphorous (P), and potassium (K) (Xue et al., 2016). High Na levels can also be problematic for soil structure, as they can cause deterioration of aggregates, thereby reducing aeration and plant-available water further by clogging pores. In combination with the fine particles of BR, this creates poor water infiltration and unfavourable conditions for plants and microorganisms.

Researchers have investigated different amendments to reduce these negative properties, and gypsum and organic matter addition is often pointed to as effective ameliorations (R. G. Courtney et al., 2009), (Lehoux et al., 2013) (Gräfe et al., 2011). Gypsum can contribute to a pH reduction as well as reduce sodicity, while organic matter can loosen up the soil and reduce density, in addition to supplying BR with nutrients and microorganisms. However, there are important knowledge gaps associated with rehabilitation strategies (Okkenhaug, 2018), and the goal of this thesis is to address three main challenges: 1. -Sodicity, 2. -Aggregate stability and 3. -Establishing a vegetation cover.

The challenge of sodicity is mainly related to elevated exchangeable Na. This is the plant-available fraction, which is also important for aggregate deterioration. In BR, the determination of exchangeable Na is complicated by secondary meta-stable sodium aluminosilicates formed during the Bayer process. Gradually, they will dissolve, thus releasing Na^+ and thus increasing sodicity. As normal soils do not contain such products, common soil-analytical methods might not be suited to address Na-challenges in BR. This thesis will investigate this issue and compare two common analytic methods to compare the exchangeable sodium and the sodium from mineral-dissolution. This will be further explained in the theory chapter.

One important property of a soil that relates to sodicity is the cation exchange capacity (CEC). The CEC is the sum of negative surface charges, generally associated with clay minerals, oxides and organic matter. In general, a high CEC is favourable, because it implies that cationic nutrients are well retained in soils, and thereby available to plants. However, if Na makes out a large part of the exchangeable cations, the soil can deteriorate. This will be explained in some more detail in the theory section. BR contains meta-stable minerals, and when these dissolve during CEC analysis, they will contribute to overestimation of the CEC. These minerals are not exchangeable, rather soluble when extractants are added. This thesis therefore seeks to estimate sodicity and the actual CEC in BR from Alunorte.

The challenge of aggregate stability in BR is strongly affected by the exchangeable Na content (Xue et al., 2016). In addition to lowering the pH, gypsum ($CaSO_4$) can lead to better aggregation by replacing Na on BR surfaces. Sodium has properties that force clay particles apart, while the Ca^{2+} in gypsum can act as a bridge between them. Thus, gypsum is expected have a positive effect on aggregation, and thereby porosity and plant growth (Tian et al., 2021), (R. Courtney et al., 2013). Increased aggregate stability by augmentation of organic matter (OM) has also been investigated (Zhu et al., 2017), but the effectiveness will likely depend on type of OM. In this thesis, aggregate stability will be measured and compared with the amount gypsum added to BR, in addition to investigating if local, easily available organic matter has an effect.

The challenge of establishing a vegetation cover on BR deposits is due to the mentioned high alkalinity, sodicity and low porosity. There are very little nutrients found in BR and establishing plant life is dependent on improvements. This thesis seeks to evaluate the effect of addition of different amounts gypsum and in combination with local organic matter has on the growth of rye grass (*Lolium perenne)*. The organic amendments used is the waste from the Açai berry (*Euterpe oleracea*) production, an abundant fruit in this part of Brazil, and would therefore be practical to use to remediate BR. Also, food waste from local sources was used, as this probably is source of more plant-available nutrients. A comparison of aggregate stability before and after plant growth will also be conducted, thus testing if the vegetation has an effect on aggregate formation.

2. THEORY

2.1 Bauxite

Bauxite is a rock, or mixture of fine grained minerals, including gibbsite, diaspore and boehmite (Retallack, 2010). It is formed under prolonged weathering of aluminosilicate rocks under tropical conditions (Mondillo et al., 2021). Bauxite is characterised as sedimentary, unconsolidated and weathered material by the Food and Agriculture Organization (Jahn et al., 2006). Bauxite is the Al-rich representative of laterites,

High temperature and at times intense rainfall, can cause silica and soluble nutrient elements to leach out and lead to a relative enrichment in insoluble iron and titanium oxides and aluminium hydroxides such as gibbsite, boehmite and diaspore. The Al-rich gibbsite is the most common and can occur in microcrystalline form (amorphous bauxite) and fine grained crystals (Silva HM., 2008). Prolonged wet, tropical conditions encourage weathering which is why the characteristic red colour is often observed in tropical soils, due to the oxidised iron that is left behind when other elements are leached.

Bauxite ore is mostly found in 2-20 m thick layers, with a production weighted average of 5 m, with an average overburden (topsoil) of 2m that must be removed prior to extraction of bauxite ore (Wagner, 2016). It is strip-mined and pre-treated with water to wash away as much excess material as possible. Thereafter, it is transported to an alumina refinery.

2.2 Bayer process

The Bayer process in combination with the Hall-Héroult process is the only viable process for production of aluminium (Power et al., 2011). After the bauxite has been crushed, it is then treated with lime to remove as much silica as possible. Thereafter, it is digested with caustic soda (NaOH) at ~150 °C and ~4 bar, however the exact conditions vary with bauxite source. At this pH of >12 and temperature, gibbsite and boehmite are dissolved to produce aluminate $Al(OH_4)^-$ (Power et al., 2011). After digestion, the slurry goes through a clarification step, where solids and liquids are separated. This leaves an aqueous alumina phase $NaAl(OH)_{4\,(aq)}$ and an iron-rich residue (BR) (Araújo & Brito, 2018). The BR is then and washed to recover soda and alumina. During the washing, flocculants and lime (CaO) are added, to remove carbonate ions by precipitation of calcium carbonate ($CaCO_3$):

(1) $CaO + CO_3^{2-} + H_2O \rightarrow CaCO_{3(s)} + 2OH^-$

This reaction produces pH buffers in the system (Power et al., 2011), which will be important in the remediation process of BR. . The alumina phase goes through various filtration and precipitation steps, and the slurry leaving the precipitator is sent for calcination. Here, the alumina hydrate is washed and dried, before it is heated to 1000-1200 °C, to remove water (Power et al., 2011):

(2) $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

This leaves Al_2O_3, the white powder termed alumina. The alumina is now ready for the Hall-Héroult process, where the strong Al-O bonds are broken, and Al metal is produced.

2.3 Mineralogy of bauxite residue

Gräfe et al reported that BR typically contains about 70% crystalline phases and 30% amorphous materials, with minerals carried over from original bauxite and minerals formed under the Bayer process. (Gräfe et al., 2011). The minerals native in bauxite are iron and aluminium oxides (gibbsite, goethite, hematite, boehmite and titanium oxide), whereas Na, and Ca- aluminosilicates are often formed in extraction process (Bray et al., 2018)

Prior to and during digestion, phyllosilicate (clay) minerals such as kaolinite dissolve, which gives aluminate and silicate ions in solution (Power et al., 2011). The presence of Na^+ ions from the digestion process react with aluminate and silicates to form sodium alumino-silicates, most notable sodalite ($3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot Na_2SO_2$) and cancrinite ($Na_6(Al_6Si_6O_{24}) \cdot 2CaCO_3$). These silicates are referred to as desilication products (DSPs) (Wehr et al., 2006). The formation of DSP's thus removes silica, sodium, and hydroxide from solution by precipitating, but are only stable in alkaline solution. With a decrease in pH, these will turn unstable and create additional alkalinity upon dissolving (Na^+, OH^-, aluminate and silicates into solution) (Jones & Haynes, 2011), (Wong & Ho, 1995).

2.4 pH and alkalinity

pH in soil is often referred to as a master variable, as it strongly influences geochemical reactions (Gräfe et al., 2011), for example availability of nutrients for plants and adsorption/desorption reactions of trace metals. The pH in natural mineral soils is usually in the range of 4.5 to 8.5. A soil is termed acidic when pH is lower than 5.5 and alkaline above 7.5 (Krogstad, 1992). By contrast, BR is highly alkaline with a typical pH of around 12-13, caused by the digestion in NaOH (Kirwan et al., 2013). The Ca from the CaO makes the BR rich in $CaCO_3$, which creates a pH buffer that keeps the pH high. The presence of DSP can release Na^+ and OH^- which give the residue lasting alkalinity problems (Wong & Ho, 1995).

2.5 Surface charge

Natural soils consist of minerals and organic matter which surfaces have positive or negative electric charge, depending on pH and mineralogy. This charge determines the attraction or repulsion of ions in the water surrounding the soil (soil solution), thus if an element is either retained in or leached down the soil profile. A low pH means that the concentration of protons (H^+) is high in the soil solution and can thus be adsorbed to soil surface. As H^+ is positively charged, it provides a surplus of positive charges that gives the soil surface net positive charge. At high pH, the opposite is observed, as little free H^+ exist to occupy binding seats on the soil surface, instead being occupied by OH^-, giving it net negative charge. A negative charge on mineral surfaces or organic matter will attract positively charged ions (cations) in solution while a positive charge will attract negatively charged ions (anions), thus pH controls mobility and availability of elements in soil. Clay consists of permanently negative charged minerals, meaning it will stay negative despite pH-changes. Organic matter is positively charged at extremely low pH, weakly negatively charged at pH 5, with more and more negative charge as pH increases (Krogstad, 2020). Oxides are usually positively charged at low pH, but negative above pH 5, with more and more negative charge with higher pH (Krogstad, 1992). The high pH of BR makes it attract cations, and its large surface area due to its claylike texture provides many binding sites.

2.6 Cation Exchange Capacity

The amount of exchangeable cations adsorbed to clay, organic matter and oxide surfaces is an important property of soils, because it in part determines the amount cations that can be retained in the soil, and thereby the nutrient stock available for plants and pollution retention. It is expressed through the cation exchange capacity (CEC), which is a term within soil chemistry that describes the total number of negative exchange sites in a certain amount of soil (Weil & Brady, 2017). Since clay and soil organic matter (SOM) particles are usually negatively charged, larger amounts are associated with increased CEC. The attracted cations include base cations such as Ca^{2+}, Mg^{2+}, and K^+.

The CEC cannot be measured directly. The common method to determine CEC is to extract adsorbed cations by an extractant and thereafter measure their concentration. The extractant is a well-buffered solution, normally pH 7 or 8.1. A fixed pH is important, as it allows comparison of CEC between different soils. A common extractant is 1M ammonium acetate buffered at pH 7 (NH4OAc) (Krogstad, 1992). This can saturate the soil with ammonium (NH_4^+), which forces out and replace adsorbed cations. Then the solution is measured for cations displaced by the NH_4^+.

A common second step is adding potassium chloride (KCl) to the soil after excess NH4+ is washed with water or alcohol, so that all that is left is the adsorbed amount of NH4+. The K^+

in KCl will replace adsorbed NH_4^+ which will now go into solution. The NH4+ in the KCl extract can be measured and equals the CEC.

Determining CEC in BR offers a new challenge, however: Because of the high pH, the NH4OAc might not lower the pH to circumneutral, where CEC in soil is normally measured (Weil & Brady, 2017). In addition, the presence of meta-stable DSP minerals such as sodalite and cancrinite can lead to an overestimation, as they dissolve in NH4OAc and provide additional cations in the solution. Thus, not all extracted Na^+ and Ca^{2+} are actually exchangeable, but rather extractable. By using the two-step method mentioned above for determining CEC, the comparison between sum of NH4OAc-extractable base cations and KCl extractable NH_4^+ can give information about the analysed soil. If the former is much higher than the latter, it means that NH4OAc extracts more than the sum of the electrostatically bound cations (which equals the CEC).

2.7 Sodicity

Commonly, the exchange sites on soil particles are dominated by Ca^{2+} and Mg^{2+} whereas little Na^+ is present. In some cases, however, where Na^+ supply is high, it can make out a major part of the exchangeable cations. The fraction of exchangeable Na^+ is called sodicity. This can lead to destruction of soil structure, which in turn may cause reduced water infiltration, resulting in waterlogging, erosion and surface runoff. The total concentrations of salts in soil water is termed the salinity of a soil, and can be measured with electrical conductivity (EC). An EC > 4 dS/m is defined as saline soil and can affect plant growth. The sodicity describes the Na^+ content in soil and can be quantified by the exchangeable sodium percentage on the exchange sites (ESP) (equation 3 and 4) and by the sodium adsorption ratio (SAR) (eq. 5).

The exchangeable sodium percentage (ESP) describes sodium's fraction of exchangeable cations (Qadir & Schubert, 2002). Soils with ESP > 15 can show deteriorated soil properties and pH> 8.5 (Weil & Brady, 2017).

(3) $$ESP = \frac{Exchangeable\ sodium, \frac{meq}{100g}}{Cation\ exchange\ capacity, \frac{meq}{100g}}\ x\ 100$$

Or:

(4) $$ESP = \frac{Exchangeable\ Na, meq/100g}{Exchangeable\ Ca+Mg+K+Na+Al, meq/100g}\ x\ 100$$

The inclusion of Al in equation 4 is for acid soils, which may contain Al^{3+} on exchange sites (Qadir & Schubert, 2002). Sodic soils are however often alkaline (pH>7.5) and exchangeable Al is negligible. Sodium adsorption ratio (SAR) is another expression to describe sodicity. It takes into account that deterioration of soil by Na is remediated by presence of Ca and Mg (Weil & Brady, 2017). SAR>13 is classified as sodic and is approximately equivalent to ESP=15.

(5) $$SAR\ (mol½/L½\ ) = \frac{[Na^{+}]}{\sqrt{(0.5[Ca^{2+}]+0.5[Mg^{2+}])}}$$

Concentrations of each cation is in mmol of charge per litre ($mmol_c/L$) in soil solution.
Saline soils have an EC>4 dS/m, but SAR<13 (ESP<15). Saline-sodic soils have EC>4 dS/m and SAR>13 (ESP>15). The latter is remediated by the presence of Ca and Mg ions. Sodic soils have EC <4 dS/m, but SAR>13 (ESP>15). This means that the exchangeable Na content is high, but soil salinity is relatively low (EC < 4 dS/m).

Sodium carbonates are much more soluble than Ca and Mg carbonates, leading to high CO_3^{2-} and HCO_3^{-} concentrations in soil solution (Weil & Brady, 2017).

2.8 Soil physics

Aggregates and aggregate stability

Soils are made up of organic matter (OM) and mineral particles in different size fractions (clay, silt and sand size particles). Clay and OM can form micro aggregates (<250 µm) and combine with silt and sand to compose macro aggregates (>250 µm). These two types of aggregates are important for soil health, as they help facilitating aeration, infiltration, permeability, structure, microbial activity etc. It is desirable that most of the clay fraction is flocculated into microaggregates which in turn is aggregated with other particles into macro aggregates (Oades, 1984).

During wetting, either from rain or irrigation, aggregates are subject to external force and can disintegrate. This disintegration of macro aggregates into micro aggregates is called slaking. With slaking the large pores are clogged by microaggregates and infiltration rate and hydraulic conductivity is reduced (Oades, 1984). The breakdown of aggregates into clay particles is referred to as dispersion (Qadir & Schubert, 2002), which creates unstable structure in soil. This dispersion is often related to sodic soils, as high concentrations of exchangeable Na^+ create wider diffuse double layers in the aqueous solution surrounding charged particles. In the diffuse double layer, the exchangeable cations exactly balance the net negative surface charge of a particle. Hydrated Na+ ions, including their associated H2O molecules, are large compared to hydrated Ca2+, Mg2+ and K+. This results in relatively wide disuse double layers in soils with Na+ as the dominant cation. Wide diffuse double layers prevent clay minerals from flocculation as they would have to overcome the force of net repulsion in the diffuse double layer.

Objectives and hypotheses

To address the introduced challenges to rehabilitate BR, this thesis will, through laboratory studies, investigate the CEC of BR from Hydro Alunorte and how gypsum and organic matter augmentation can affect aggregate stability and provide an improved medium for plant growth.

The thesis will try to address the following hypotheses:

H1: Bauxite residue contains high amount of meta-stable secondary minerals, which will lead to and overestimation of cation exchange capacity (CEC) and exchangeable Na when applying ammonium acetate for determining CEC.

H2: Adding an additional step to the ammonium acetate method, displacing exchangeable NH_4^+ by K^+ (using potassium chloride (KCl)), will allow estimation of the negatively charged sites in BR, thus giving a better estimate of the CEC.

H3: Gypsum addition to BR will lower pH in the leachate water and decrease exchangeable Na, thus significantly increasing aggregate stability and porosity.

H4: Organic matter addition will lower pH in the leachate water, and together with gypsum further increase aggregate stability and porosity significantly.

3. MATERIAL AND METHODS

3.1 Area description

Hydro’s bauxite mines and aluminium refinery are located in the state of Pará, Northern Brazil. Pará borders the Atlantic Ocean in the North and East and Amazon state in the West. The Amazon River runs through it before it reaches the sea (figure 3.1).

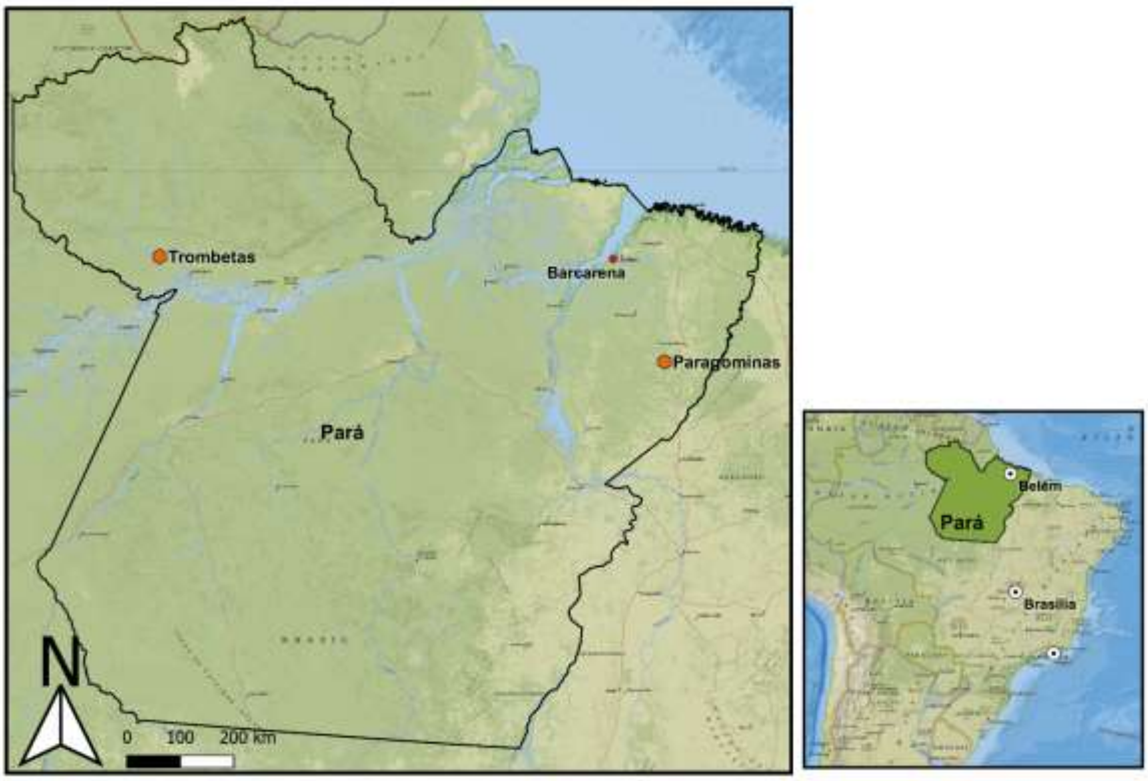


Figure 3. 1: Map of the state of Pará, Brazil. Barcarena is situated close to the city of Belem. Trombetas and Paragominas are mines from Norsk Hydro extract bauxite ore.

The Pará region is one of the warmest in Brazil, and the area around Barcarena has an average temperature of 27 °C. Pará has a tropical monsoon climate, and the average rainfall is 3384 mm annually (INMET, 2021). In Pará, the formation of bauxite and laterite, as explained in the Theory section, is particularly extensive because of the humid, warm climate. Soil layers rich in iron oxides are termed laterites/latosols and are common in this region in Brazil (figure 3.2). The term laterite is used interchangeably with latosols, and it occurs in the Paragominas and Trombetas mines. Amazonians bauxite deposits often has a thick covering of predominantly yellow clays, known as Belterra clays, which is equivalent to the region’s latosols.

Formation of laterites and bauxites are related processes, favouring bauxite formation under higher weathering intensity (leaching and solute removal) (Schellmann, 1994). When dissolved silica is leached, gibbsite stability increases.

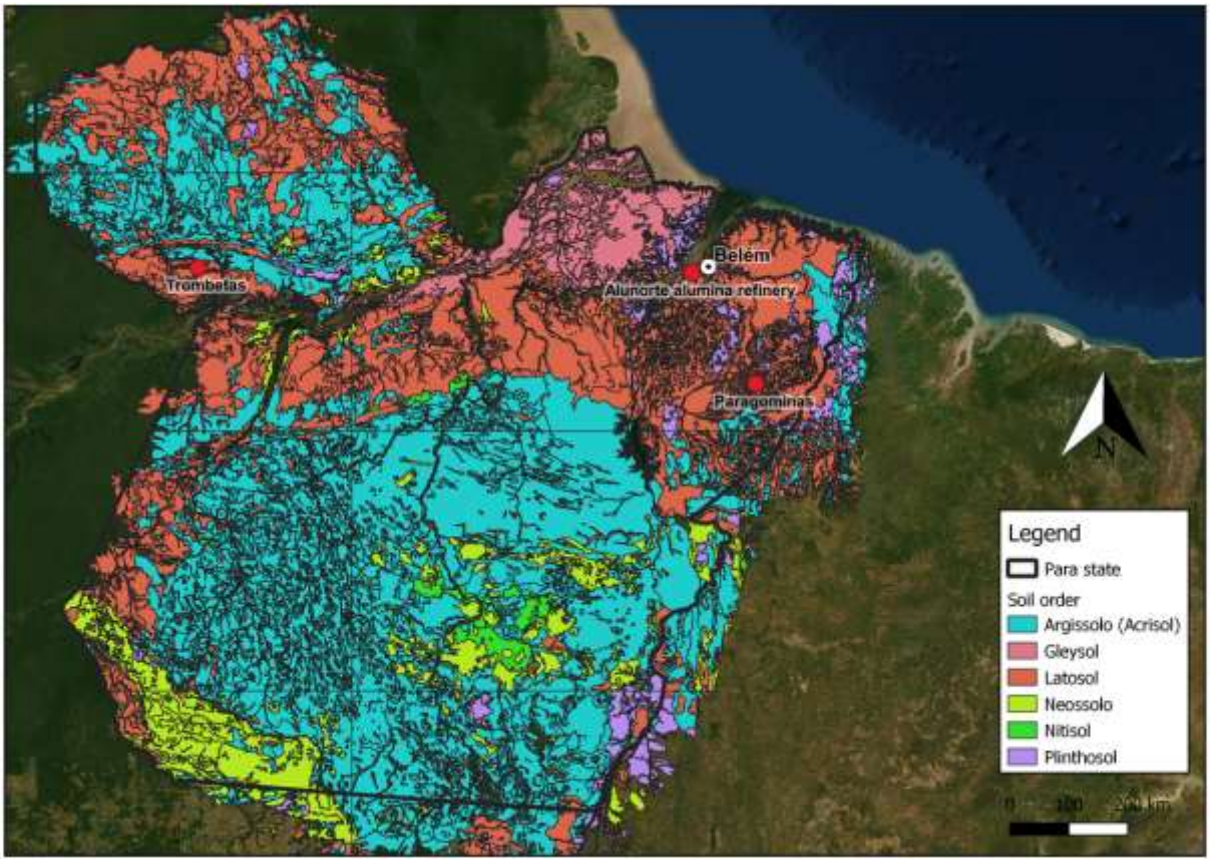


Figure 3. 2: Soil map of the state of Pará. The notable soil is the Latosol, which is seen as a belt along Amazonas. Trombetas and Paragominas is located in this belt. Soil data provided by Brazilian Agricultural Research Corporation (IGBE, 2001).

Hydro aluminium refinery

Hydro extracts bauxite from two mines, one in Paragominas, the other at Mineracao Rio de Norte (MRN) in Trombetas, western Pará state (Fig. 3.1). The majority of bauxite used comes from Paragominas, where it is strip-mined. After sorting and crushing, bauxite is transported to Alunorte at Barcarena in a 240 km long slurry pipeline (Nippon, consulted 22.04)\. From MRN the bauxite is transported by ship (Norsk Hydro, 2022).

In 2011, Hydro bought the majority of shares for the Brazilian mining company Vale's aluminium enterprise (Norsk Hydro, 2011). From before, Hydro owns the bauxite mine Paragominas and has a 5% interest in (MRN). Additionally, they have an agreement for volume offtake of bauxite from MRN corresponding to Vale’s 40 percent interest, which amounted to 5.1 million mt in 2021 (Norsk Hydro, 2022). In 2021, Hydro produced 5.384 thousand tonnes bauxite residue (on a dry basis), and the deposit increased by around 10%, in line with increased alumina production (Norsk Hydro, 2022). Hydro has two bauxite residue disposal areas (BRDA’s) at the Alunorte plant in Barcarena; DRS1 and DRS2 (Figure 3.3) Hydro also owns the primary aluminium plant Albras, together with Nippon Amazon Aluminium Co. (NAAC). Albras is Brazil’s largest primary Al producer (Norsk Hydro, consulted 10.04).

Figure 3. 3:Map of Hydro Alunorte’s alumina refinery, BRDA 1 (West) and 2 (East) and the primary aluminium plant Albras.

3.2 Samples

The bauxite residue samples used in this thesis were collected at Hydro’s plant in Barcarena in the summer of 2019. The bauxite residue samples, which had passed through the filter press, were taken before the conveyor belt transferred them to the BRDA (Wik, 2020). The samples were transported in metal containers to Oslo, Norway, where they were transferred to sealed plastic containers and stored at the Norwegian Geotechnical Institute (NGI), field moist, dark and at 4°C. (Schneider, 2020). In August 2021, BR was collected and brought to the Norwegian university of life sciences (NMBU), in Ås, Norway.

Three amendments were used in this study: Gypsum, Açai waste and food waste.
Gypsum ($CaSO_4 \cdot 2H_2O$) was used as a source of Ca^{2+}, with the goal of replacing Na^+ and improving structure in BR in addition to lowering pH. Gypsum contains 23% Ca, based on molecular weights of the components. The gypsum used was supplied by SEL-TRADE AS.
Acaí (***Euterpe oleraceae***) is a palm species native to the northern area of Brazil, with reddish-purple berries (Vasconcelos et al., 2019), and the state of Pará is the main producer of Açai berries, being responsible for 85% of the world production (Padmanabhan et al., 2016). The berry production results in a waste consisting of the seed that remains after pulp extraction process and fibres. The waste from Açai production used in this thesis was collected at a local Açai natural pellet producer (Ecobiomassa) close to Barcarena (Y. Miura, 2022a) Upon collection, the Açai waste was air dried in the laboratory. The food waste used comes from all types of food that are served at local restaurants in Barcarena. It has been mixed and dried at ~100°C before storage (Figure 3.4) (Y. S. Miura, 2022).

The pH of food waste and c waste were determined using a PHM210 standard pH meter and a combination electrode (MeterLab). Of both waste types, 10 mL dried and sieved (<2 mm mesh) material was equilibrated with 25 mL distilled water (1:2.5 volume) in 50 mL centrifuge tubes (in triplicate). They were then shaken horizontally in a table-shaker at 110 strokes per minute and left overnight at room temperature (21°C). The suspension was then shaken up again and left for some minutes to settle. The pH was read above the sediment.

Figure 3. 4:Waste of Açai (left) and food waste (right) after drying.

3.3 Characterization of BR from Hydro Alunorte

Bauxite residue (BR) is mainly dominated by iron (Fe) and aluminium (Al), present as oxides (Fe_2O_3 and Al_2O_3, respectively). Other elements are present in decreasing amounts; Si, Na, Ti and Ca (Schneider, 2020), as silicates or oxides. Schneider identified hematite, gibbsite and anatase as dominant minerals. From a grain size distribution curve, using fractions of sand, silt and clay, BR can be classified as silty clay loam (Schneider, 2020).

3.4 Cation exchange capacity (CEC) of bauxite residue

For determination of the CEC of bauxite residue, a common soil analytical method was modified. The method is and adaption of Jose Munera-Echeverri's procedure for determining CEC of biochar (Munera-Echeverri et al., 2018).

The procedure used pre-treatment of BR with hydrochloric acid (HCl) or distilled water. These different types of pre-treatments were used to test their ability to remove DSP's like sodalite and cancrinite. The pre-treatments were followed by three subsequent washings with 1M Ammonium acetate (NH4OAc). In these three washing steps all exchangeable base cations were expected to be exchanged by NH4+, although the NH4OAc extracts may also contain dissolution products of DPS if they remained after the pre-treatments. The three washings with 1 M NH4OAc were followed by three washings of either 60% ethanol or distilled water to remove excess dissolved NH4+. After these washings with ethanol or water all NH4+ remaining in the suspension was assumed to be in exchangeable form, the total amount of which exactly balanced the CEC. As the last step, the addition of 2M potassium chloride (KCl) extracted all exchangeable NH_4^+ on BR. The exchangeable NH4+ in the 2M KCl extract equals the CEC. Sodium, Ca, Mg, and K were analysed using microwave plasma atomic emission spectroscopy (MP-AES), while the extracted NH_4^+ was determined using a spectrophotometer.

3.4.1 Sample preparation

Approximately 300 grams BR was crushed with mortar and homogenized. Three samples of moist BR at about 3 grams each were weighed and added to pre-weighed ceramic crucibles and heated in an oven at 105 ˚C for 24 hours to determine the dry matter content.

To determine the concentration HCl needed to lower pH in BR solution to around 7, six BR samples of 1.0 gram moist BR were suspended in different amounts of 0.1M HCl and distilled water, to a total of 20 mL. They were shaken horizontally on a table-shaker at 110 strokes/minute for 24 hours and stored in a dark area at room temperature (21ºC) and pH was determined after 1, 3, 5, 7 and 8 days to check when it stabilized.

Nine moist BR samples were weighed to 1.00 gram and added to 50mL polypropylene centrifuge tubes. These samples were used for the pre-treatment (next section).

Additionally, a parallel set of nine moist BR samples of 1.00 gram were prepared, which followed the exact same method as described below. This will be further explained in section 3.4.4.

3.4.2 Pre-treatment

Of the nine tubes with bauxite residue, 3 replicates were suspended in 15mL 0.1M hydrochloric acid (HCl) and 5 mL deionized water, in order to obtain a HCl concentration of 0.075M. The suspensions were shaken horizontally on a table-shaker at 110 strokes/minute for 24 hours and then stored in the refrigerator or for 5 days, to reach a pH of about 7.5. Then, 3 other replicates were added 20 mL deionized water., making 3 replicates with HCl and 3 replicates with water. The suspensions in 0.075 M HCl and in water were shaken for 24 hours, before they were centrifuged at 1700g for 30 minutes. The supernatants were decanted and stored dark and cool until analysis for pH.

To both sets of three pre-treated BR samples 20 mL 2M NH4OAc was added to determine the CEC. The BR samples with HCl are denoted HCl 1, 2 and 3. The BR samples pre-treated with water are denoted H2O 1, 2 and 3. A third set of three replicates, which received no pre-treatment, also received 20 mL 2 M NH4OAc. The samples with no pre-treatment are denoted No-pre-treatment 1, 2 and 3.

3.4.3 Ammonium acetate saturation

The BR slurry left in the centrifuge tubes after extraction with dilute HCl or distilled water during pre-treatment, as well as the BR samples that received no-pre-treatment, were suspended in 20 mL 1M NH4OAc. All nine (three treatments in three replicates) NH4OAc slurries were shaken horizontally for 24 hours at 200 strokes per minute. From this step onwards they were all treated equally. The slurries suspended in NH4OAc were then centrifuged at 1700g for 30 minutes before the supernatants were removed with an automatic pipette. To ensure that the BR was saturated with NH_4^+, the BR slurries were added 20 mL NH4OAc, shaken 24 hours, centrifuged and supernatants pipetted out two more times. This means that in total three additions of 20 mL NH4OAc and three extractions of supernatants were conducted. For each pipetting of supernatants, the extracted volume and weight of centrifuge tubes were registered, to keep track of how much solution was left in the tubes, as all could not be extracted. The supernatants from these three steps were stored in the refrigerator for analysis of Ca, Mg, Na and K.

3.4.4 Ethanol washing of excess NH4OAc

To wash away NH_4^+ not adsorbed to the BR from the solution, 40 mL 60% ethanol was added after the last pipetting. The suspensions were shaken for 24 hours, centrifuged at 1700g for 40 minutes, then pipetted out with 3mL plastic pipettes. This procedure was also done three times, to ensure that all excess NH4OAc was removed. The concentration of NH4+ in in the third ethanol washing was determined with the salicylate method, where to reagents A and B are added to the sample to produce a colour corresponding to NH4+ concentration. Reagent A consist of 1.0 g of salicylic acid and 0.1 g of sodium nitroprusside in 100ml of citrate buffer (0.27M trisodium citrate dehydrate, 0.054M NaOH). Reagent B was made by dilution of 2 ml of 6% sodium hypochlorite (NaOCl) in 100 ml of water. To 3 mL sample, 0.5 mL of reagent A and 0.5 mL of reagent B were added and hand-shaken, before storing dark for three hours. A calibration curve with known concentrations of NH4+ was also prepared, by the same method as the samples. Then, the NH4+ in the ethanol extract and calibration samples were determined using a spectrophotometer (see below for details).

The parallel set with nine BR samples that followed the same procedure, were here washed with distilled water instead of ethanol, to compare effectiveness of 60% ethanol and distilled water in removing NH4+.

3.4.5 MP-AES analysis

All extracts (pre-treatments, the three NH4OAc and ethanol supernatants) were diluted 600 times, by adding 1mL (10%) HNO_3, 0.1 mL caesium chloride (CsCl) (for magnesium detection) and distilled H2O to 10 mL in 15 mL centrifuge tubes. Blank solutions were made using distilled H2O, 0.1 mL CsCl and 10% HNO_3 to match the matrix of the samples. The extracts were then measured using a microwave plasma atomic emission spectrometer (MP-AES) from Agilent Technologies (4100 spectrometer). Measurements were done at wavelengths shown in table 3.1. The accuracy was determined using 3 standards and a house standard with known concentrations.

Table 3. 1: Wavelength reading (nanometer) for determination of each element on MP-AES.

Ca	Mg	K	Na
430.253	383.829	766.491	589.592

3.4.6 Potassium Chloride (KCl) addition

To replace all NH4+ from the exchange sites of the bauxite residue, 30 mL 2M potassium chloride (KCl) was added to all tubes and shaken horizontally on a table-top shaker at 110 strokes per minute for 24 hours. This was followed by centrifugation of the suspensions at 1700 g for 40 minutes, when all particles had settled. The supernatants were then pipetted out and stored in the refrigerator. Figure 3.5 shows a schematic representation of the method used.

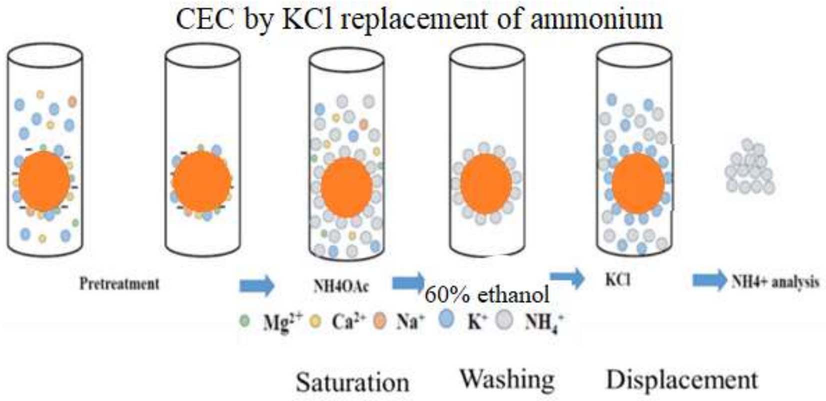


Figure 3. 5 Depiction of the method for determining CEC, based on both 1M NH4OAc (buffered at pH 7) displacement of base cations followed by NH_4^+ *displacement using 2M KCl. Schematic modified from (*Munera-Echeverri et al., 2018*).*

3.4.7 Spectrophotometer

The KCl extracts were diluted 100 times with deionized water for NH_4^+ analysis. A calibration curve was made, with 0, 100, 500, 1000, 1500, 2000, 2500 µg/L NH_4^+. All standard solutions were added 1 mL 2M KCl, to match the KCl concentrations in the extracts (1% v/v). They were then added deionized water to 100mL. A quality control sample (QC3198 certified) was also prepared (NH_4^+ concentration of 14.3±2.3 mg/L). Blank, standard solution, samples and QC were added 0.5 of a reagent A and 0.5 of a reagent B as described above and left for three hours in a dark room for colour development. They were then measured spectrophotometrically, using a Hitachi UH5300 Spectrophotometer. The absorbance was determined at 880 nm.

3.5 COLUMN EXPERIMENT

To address the challenge of aggregate stability and vegetation growth in bauxite residue, a column experiment was conducted in the laboratory at NMBU. 30 columns with five different amendments of gypsum, food- and Açai waste was made. The columns would go through a leaching series to decrease pH, alkalinity, salinity and sodicity with the intention to provide better conditions for plant growth. After repeated leachings, 15 columns were taken apart to determine aggregate stability, while the other 15 were set aside for plant growth experiments. The species of choice was rye grass (*Lolium perenne)*, due to successful germination in a preliminary vegetation test. The growth of rye grass was monitored for one month. During this time, the columns were CT-scanned three times to determine porosity and root development during germination. After vegetation, also these columns were taken apart and analysed for aggregate stability.

Aggregate stability was also determined in samples from Hydro's BRDA from the site in Barcarena, which were brought to NMBU. These included both amended and unamended (control) samples from experimental plots in the field (which had received similar amendments as the columns in the lab; (Y. Miura, 2022a). Below follows a detailed description of the column experiment.

3.5.1 Columns

15 columns were made at NGI in Oslo, which were eventually used for growth of rye grass. These are plastic, transparent, 25cm high and with inner Ø 4.5 cm. They have a rubber cap in the bottom with a small valve to lead drainage water through (Figure 3.6). Tubing was used to allow drainage into 150 mL plastic containers.

A second set of 15 columns were made, which were used for aggregate stability studies prior to plant growth. They were made of polypropylene (PP) tubes, also 25 cm high with inner Ø 4.5 cm and had a similar design, but with 3 mm holes drilled in the bottom (Figure 3.6). Drainage water was collected in 200 mL plastic containers.

All 30 columns had a bottom layer of 2 cm sand, to prevent the fine-textured bauxite to run through the drainage holes in the bottom of the columns, while still letting water pass through. The PP columns needed filter papers in the bottom to prevent sand from running out of the tubes.

Figure 3. 6: Left: NGI columns, used for plant growth studies on leached BR material. Right:PP columns used for aggregate stability study prior to plant growth.

The column study involved five different treatments, where BR was mixed with different fractions of gypsum, Açai waste and food waste (table 3.2) All fractions were added on dry weight basis. All treatments that were used for plant growth received gypsum, because unamended BR had previously been shown to be unsuccessful for the establishment of rye grass.

For each column, undried BR, gypsum, Açai waste or food waste were first added to a large bottle and shaken to thoroughly mix the components. Thereafter, they were carefully added to each column through a funnel. The first set of columns (constructed at NGI) received 236 grams in total dry weight. Because of limited supply of available bauxite residue, the second set of columns (PP) received 160 grams in total dry weight, but the same fractions as the NGI columns (as in table 3.2). After preparing the columns, one cm of glass beads (3 mm diameter) was carefully added on top, to prevent whirling up fine-textured BR upon water addition. The columns were covered with Al foil to reduce evaporation.

Table 3. 2: Overview of the different treatments used for the study of the effects on aggregate stability. Values are proportions of BR, gypsum, Açai waste and food waste in the different treatments. Experiments to study the establishment of rye grass in the leached columns did not include a treatment with 100% BR, as this material has previously been shown to be an unsuccessful growth medium (Capobianco, 2021).

Treatment	Bauxite residue (BR)	Gypsum (G)	Açaí waste (A)	Food waste (F)
BR (3)	100 %	-	-	-
G10 (6)	90 %	10 %	-	-
G10A (6)	85 %	10 %	5 %	-
G5A (6)	90 %	5 %	5 %	-
G10F (6)	85 %	10 %	-	5 %
G5F (6)	90 %	5 %	-	5 %

3.5.2 Leaching test

The leaching test was performed with sequential additions of water, over a period of 6 weeks. Distilled water was added carefully to the columns every second or third day, and leachate was collected the day after each water addition. For the NGI columns, 150 mL was added each time, while for the columns in PP this was 200 mL (the PP columns received more water each time, simply because they had more space, thus saving time). The liquid solid ratio (L/S) was recorded (based on the accumulated amount of leachate relative to the amount of solid phase in the columns), and the leaching experiment ended when 2.36 L and 1.6 L distilled water had percolated through the NGI and PP columns, respectively. Thus, 10 times more water had gone through the columns than the amount dry mass in the columns (236 gram for NGI and 160 grams for PP) and a L/S of 10 was reached.

Figure 3. 7: Polypropylene (PP) columns used for aggregate stability studies. The funnels are fastened to the cap of the bottles. The aluminium cover is to reduce water evaporation.

The leachate water was collected in 150 mL and 200 mL bottles for NGI and PP columns, respectively. From these, 50 mL were pipetted out and stored in 50 mL centrifuge tubes in the refrigerator for later analyses. Electrical conductivity (EC) and pH were measured in the leftover leachate before discarding. Infiltration rate was monitored by measuring the water head difference with time, at L/S 2.

3.5.3 pH and electric conductivity

To avoid interference from the pH electrode, EC was always measured prior to pH. For EC, a Metrohm 712 conductometer was used. The apparatus' electrode was lowered into the leachate solution, and conductance was read when it stabilised, or after 1 minute. After each reading, the electrode was washed with distilled water and carefully dried with a drying paper.

The pH was measured immediately after with a MeterLab PHM210 standard pH meter. The apparatus was calibrated before use with pH 4 and 7 buffer solutions and accuracy compared with a standard solution with pH 6.87.

3.5.4 Leachate composition of base cations

From the 50 mL centrifuge tubes, leachate was pipetted out and diluted to factors according to the element of interest. The low concentration of Mg made dilution unnecessary, while Na needed to be diluted 1500x for some samples. Samples were added to 15 mL centrifuge tubes and diluted with 1 mL HNO_3 and distilled water to a total volume of 10 mL (thus 10% HNO_3). For Mg detection, 0.1 mL CsCl was added. Lastly, the tubes were shaken thoroughly to ensure complete mixture before analysis.

Blank solutions were made by adding distilled water through a column of 2 cm layer of sand and glass beads, before addition of HNO_3 and CsCl (for Mg analysis). The blank samples were not diluted with more distilled water.

Standard solutions

Standard solutions were prepared by a lab technician for each element, diluted to required concentrations with acid concentration of 10 % (V/V) (65% w/w HNO_3).

Control standard

STD1: Ca 2, Mg 0.5, Na 2, K 0.5 (mg/L)

STD2: Ca 20, Mg 5, Na, 20, K 5 (mg/L)

STD3: Ca 40, Mg, 10, Na 40, K 10 (mg/L)

A house standard (1643h), also containing 10% acid, was analysed. This was to calibrate the instrument and ensure accuracy in the method.

Instrumental parameters

An Agilent 4100 MP-AES (Agilent Technologies, 2012) was used for the measurements. Though its software, wavelength was decided for each element, based on expected range and interferences from other elements. Expected concentrations in the samples determined the choice of wavelength regarding emission intensity.

3.5.5 Alkalinity

Column leachate from the first and last stages of the experiment (L/S 1 and 10) was added to a burette to a volume of 20 mL. It was transferred to a 50 mL glass beaker, and a magnet was added. The beaker was placed on a magnetic stirrer and a pH electrode was lowered into the solution. Starting pH (PH_0) was recorded before 0.02M HCl was added gradually while monitoring pH. The volume acid required to reach pH 8.3 was registered, before acid was added until the solution reached pH 4.5, compromising total alkalinity (A_T) (Allmennstandardisering, 1996). Equation 6 assesses the equivalent concentrations of hydrogen carbonate, carbonate and hydroxide concentration of water, and X marks potential other buffering substances, such as organic anions.

(6) $A_T \approx 2c(CO_3^{2-}) + c(HCO_3^-) + c(OH^-) - c(H^+) + c(X)$

(7) $A_T\ (mmol/L) = c(HCl(mol/L)) \times V_T\ (mL) \times 1000)/V_{Sample}\ (mL)$

3.5.6 Aggregate stability

At the end of the column leaching experiment, at LS 10, the PP columns were carefully taken apart, using a long knife along the inside of the column. The contents were placed on marked trays and left to dry at room-temperature for two weeks. All treatments were done in triplicate, except that 1 column was kept intact for the following treatments: 100% BR, BR +10% gypsum and 5% Açai waste (G10A), and BR +5% gypsum and 5% Açai waste (G5A). Two different methods were used for aggregate stability tests: The wet sieving method and rain simulator method.

Wet sieving method

The method is in accordance with Eijkelkamp's manual for the wet sieving apparatus (figure 3.8) (Ejikelkamp, 2018). Of the air-dried aggregates in the 1-2 mm fraction 4 g was added to a small container with 0.25 mm mesh sieves in the bottom. The sieves were pre-wetted to moisten the soil from below, to avoid slaking (Grønsten & Børresen, 2009). They were then placed on the apparatus and lowered into the bigger, steel cans filled with distilled water. The machine was then turned on, and the small containers were raised and lowered continuously in the outer steel containers for 3 minutes, at a rate of 30 rounds per minute (rpm). The sieve holder was then raised, and remaining water was able to leak out.

Figure 3. 8 Left: the bottom aluminium container contains 1-2 mm aggregates. Middle and right: The Eijkelkamp's wet sieving apparatus, with 0.5mm sieves in the top tray and steel containers in the bottom tray.

Next, pre-weighed containers with a dispersing solution were placed on the apparatus. As dispersing solution, 2 g/L 60% sodium hexametaphosphate (Na6[(PO3)6]) was used, because the pH was >7. For soils with pH<7, it is advised to use 2 g NaOH/L as dispersing solution (Ejikelkamp, 2018). The apparatus was then turned on again for 10 minutes. The aggregates left after repeatedly immersing them in the dispersing solution were pressed carefully with a spoon through the sieve, such that only particles >0.25 mm were left in the sieve. These outer containers with the dispersing solution now contained the material from the aggregates that were stable in water. Particles > 0.25 mm, which did not disperse (including Fe concretions and other larger mineral fragments, remained on the sieve. Both sets of cans (steel can with water and aluminium can with dispersing solution) and the sieves containing rest fraction >0.25 mm were placed in an oven at 105.5 °C for 24 hours.

Unstable fraction (water-dispersed) and stable fractions (hexametaphosphate dispersed) were determined by weighing the dry cans and subtracting the weight of empty containers, and correcting for the dry weight of fractions >0.25 mm.

Since pre-drying of the material (left at room temperature for two weeks), prior to the aggregate stability tests as described above, may have resulted in unrealistically large fractions of stable aggregates, a set of moist samples from the wet columns were also tested for aggregate stability. Then 10 grams of moist BR, BR+10% gypsum and 5% Açai waste and BR+ 5% gypsum and 5% Açai waste were used in triplicates and tested following the same method as above.

A third run of the wet sieving method was conducted, using BR with and without amendments from current field experiments at Hydro Alunorte (Y. Miura, 2022a, 2022b). In total 27 field moist samples of approximately 150 grams were collected at the BRDA and stored in plastic bags. Approximately 10 grams from each of the 27 samples were tested in duplicate. In this series, no pre-sieving was done, because of difficulty of sieving moist material and to save time. Aggregates of this unsorted material larger than approximately 6 mm were hand-picked and not included. Next, the moist samples were immersed in water for 6 minutes at a rate of 30 immersions per minute. Subsequently, the material remaining on the sieves was immersed in the dispersing solution for 10 minutes (30 immersions per minute). After dispersion, a third set of containers, containing distilled water, was placed beneath the sieves, and the remaining (very stable) material was carefully pressed through the sieve. Then fractions > 0.25 mm were left in the sieves. By this method, there was therefore one more fraction than in the previous method: The water-unstable material, the dispersed material, the very stable material that was not disintegrated by dispersion solution, and the rest fraction > 0.25 mm that could not be crushed. Lastly, all containers and sieves (containing material larger than 0.25 mm) were placed on a tray and dried for 24 hours along with the other containers.

Rainfall simulator

Rainfall simulator method applies kinetic energy from simulated raindrop-impact, and is the common method to determine aggregate stability at NMBU (Grønsten & Børresen, 2009). Here, two fractions obtained from the column leaching studies in the laboratory were used: 0.5-2 mm and 2-6 mm aggregates (note that this method was not used for samples collected in the field experiments at the BRDA, in Barcarena. Because this method requires significant amounts of each fraction (20 g) and because of the limited supply of these fractions from each column, duplicates were not possible.

Firstly, VWR Qualitative filter paper (VWR 415, 185 mm) were weighed and marked, before being wetted and placed in funnels. Then 20 g of each aggregate fraction was placed on wetted 0.5 mm mesh sieves with 15 cm diameter. The sieves were placed on a rotating disk inside the cabinet (Figure 3.9). The cabinet has 4 nozzles (Tee-jet 8005E) placed 32 cm above the disk. The water was switched on for 3 minutes (tap water, pH 7.5 and total hardness 2.9-dH (Grønsten & Børresen, 2009)), reaching the nozzles with a consistent pressure of 1.5 bar. Unstable aggregates disintegrated and the resulting suspensions were collected below the sieves.

Figure 3. 9 Left: rainfall simulator cabinet with the rotating disk in the middle. Right: 2-6 mm and 0.5-2mm aggregates placed on 0.5 mm sieves, before they were placed in the cabinet of the rainfall simulator.

The aggregate fractions remaining on the 0.5 mm sieve were transferred to porcelain bowls (figure 3.10). The bowls were then poured into the funnels, using a water dispenser to ensure that none of the material is left in the bowl. Water would then percolate and the stable fraction of 0.5-2 and 2-6 mm remained on the filter paper. These were left to air-dry for 5 days before weighing. The samples were then sieved one last time through a 0.5 mm sieve, to adjust for weight of particles >0.5mm. The weight of the filter papers was used for correction.

*(8) Unstable 1-2 mm aggregates = (Dry weight 1-2 mm aggregates before test – weight of fraction>0.5mm) – (Net weight dry material after test - weight of fraction>0.5mm) * 100 (%)*

*(9) Unstable 2-6 mm aggregates = (Dry weight 2-6 mm aggregates before test – weight of fraction>0.5mm) – (Net weight dry material after test - weight of fraction>0.5mm) * 100 (%)*

Figure 3. 10 Left: stable aggregates poured over to funnels with VWR 415 filter paper. Right: air dry material, before weighing.

3.5.7 Rye grass germination

The set of columns not used for aggregate stability tests were kept dark and cool for two weeks. They were brought to NGI in Oslo for CT scanning, and subsequently for seeding with rye grass. Glass beads were removed, before stirring up the top 0.5 cm of “soil”, before 30 seeds of rye grass were mixed in carefully. The seeded columns were then transported back NMBU and placed in the climate room at the Faculty of Environmental Sciences and Natural Resource Management. This room is temperature controlled at 21 °C and it has 16 hours of artificial light per day in the ceiling (Gavita Pro 315 (Gavita, 2022)).

The average annual rainfall in Barcarena is 3308 mm (INMET, 2021), which corresponds to 276 L/m^2/month. The surface area in the columns were 15.9 cm^2 (4.5 cm inner diameter). Thus, 438 mL was added for one month to simulate local precipitation.

Distilled water was used for watering the rye grass. In the beginning, water was sprayed carefully to prevent saturation of the "soil", while ensuring that the seeds did not dry out. After about four-five days rye grass germinated in some columns, and subsequently 14 mL of distilled water was added to each column every day with a dispenser, with 7 mL in the morning and 7 mL in the afternoon. Based on weight-loss, approximately 5 mL evaporated from the columns overnight. To keep the same treatment throughout the study, the same amount water was added to every column, independent on growth performance.

The growth rate was quantified measuring tallest and shortest grass leaf two times a week. At the end of the experiment (5 weeks) above ground biomass was harvested, dried at room temperature (approximately 20^{o}C) and weighed.

3.5.8 CT-scan of columns

The columns were transported from NMBU to NGI three times during the experiment with rye grass growth. The first scan was done prior to seeding. The second scan was done after two weeks and the final scan after 1 month of growing. Here, I only report selected images of the scans of the various columns. Later, the CT-scans will be subjected to image processing to determine root mass of the rye grass and porosity in the amended BR.

4. RESULTS

4.1 Cation exchange capacity of bauxite residue

Effect of pre-treatment

In an initial test, it was found that 20 mL of 0.075 M HCl was required to cause a decrease in the pH of BR to a value of about 7.5 after five days of equilibration. Therefore, this HCl concentration was used in the HCl-pre-treatment. After extraction of the pre-treatment, electrical conductivity (EC) and pH in both HCl and H_2O were measured, shown in table 4.1. This means that the NH4OAc (which is buffered at pH 7) successfully reduces the pH to the intended value of 7. Pre-treatment with water resulted in an equilibrium pH close to 11, suggesting that the NH4Oac in the next step does not have enough buffering capacity to decrease the pH to 7.

Table 4. 1. Effect of pre-treatment of BR on electrical conductivity (EC) and pH. Of the first NH4Oac extraction (buffered at pH 7). Pre-treatments were with 0.075 M HCl and distilled water, respectively. In addition, one set of none-pre-treated BR samples was included. All samples were tested in triplicate. Values are averages and standard deviations.

	Pre-treatment	
	EC (dS/m)	pH
HCl (SD)	5.7 (0.05)	7.627 (0.009)
H2O (SD)	1.72 (0.025)	10.98 (0.012)

The effectiveness of the buffered NH4OAc extractant to decrease the pH to 7 is presented in table 4.2. The first NH4OAc extraction of the pre-treated and none-pre-treated BR all had pH values significantly greater than 7, indicating that the pH buffer (pH 7) of the NH4OAc extract was not strong enough (Table 4.2). This was particularly true for the water pre-treated and the none-pre-treated BR, which had pH values well above 8. The first NH4OAc extract of BR pre-treated with HCl had pH 7.5, which was reasonably close to the target pH 7.

Table 4. 2: Effect of 1M NH4OAc on pH of the first NH4OAc extraction (buffered at pH 7). Values are pH and standard deviations.

NH4OAc 1	
Treatment	pH
HCl (SD)	7.49 (0.01)
H2O (SD)	8.260 (0.08)
No pre-treatment (SD)	8.22 (0.012)

Table 4.3 shows that in the pre-treatment with HCl, significantly more base cations (except Mg) were dissolved than in the pre-treatment with water. The effectiveness of HCl to dissolve base cations is also reflected by the lower pH of the equilibrium solution than in case of the pre-

treatment with distilled water (Table 4.2, above), which resulted in high concentrations of base cations in the pre-treatment NH4OAc extracts, decreasing in the order Na>Ca>>K>>Mg. Pre-treatment with water is less effective to decrease pH (Table 4.1) and in displacing base cations, in particular Ca (Table 4.3; Fig. 4.1). Neither of the two pre-treatments showed significant mobilization of Mg.

Table 4. 3: Concentration of base cations extracted in the pre-treatment with HCl and water, respectively, followed by the sum of base cations extracted in the three consecutive washings with 1M NH4OAc. Values are averages, medians and SDs of concentrations (triplicates) in mg/kg BR (on a dry weight basis). The NH4OAc extractions were done using sample pre-treated with 0.075 M HCl and distilled water in addition to samples that were not pre-treated.

		Pre-treatment (mg/kg BR)				Sum NH4OAc extract (mg/kg BR)			
		Ca	Mg	K	Na	Ca	Mg	K	Na
HCl (3)	average	3720	<LD	180	23100	4700	92	140	22300
	median	3660	<LD	170	23110	4700	93	120	22700
	SD	98	<LD	35	58	458	2.8	41	556
H2O (3)	average	12.9	<LD	100	8200	10400	87	110	39000
	median	12.7	<LD	100	8200	10400	88	70	40000
	SD	0.44	<LD	20	24	100	3.4	59	2194
NH4ac (3)	average	-	-	-	-	10300	88	110	47300
	median	-	-	-	-	10300	89	90	47300
	SD	-	-	-	-	498	1.8	34	385

Ammonium acetate extractable base cations were dominated by Na and Ca, with only traces of K and Mg (Table 4.3). While a single extraction with dilute HCl (the HCl pre-treatment) solubilized similar amounts of Na and Ca as each of the subsequent three extractions with NH4OAc, the single pre-treatment with distilled water (the water pre-treatment) extracted significantly lower amounts of Na and Ca than each of the subsequent three NH4OAc extractions (Figure 4.1).

The amounts of Na extracted by NH4OAc decreased in the three washings (Fig. 4.1) of the water-pre-treated and the none-pre-treated BR. For the HCl-pre-treated BR the NH4OAc extractable Na remained relatively constant from the first to the third washing.

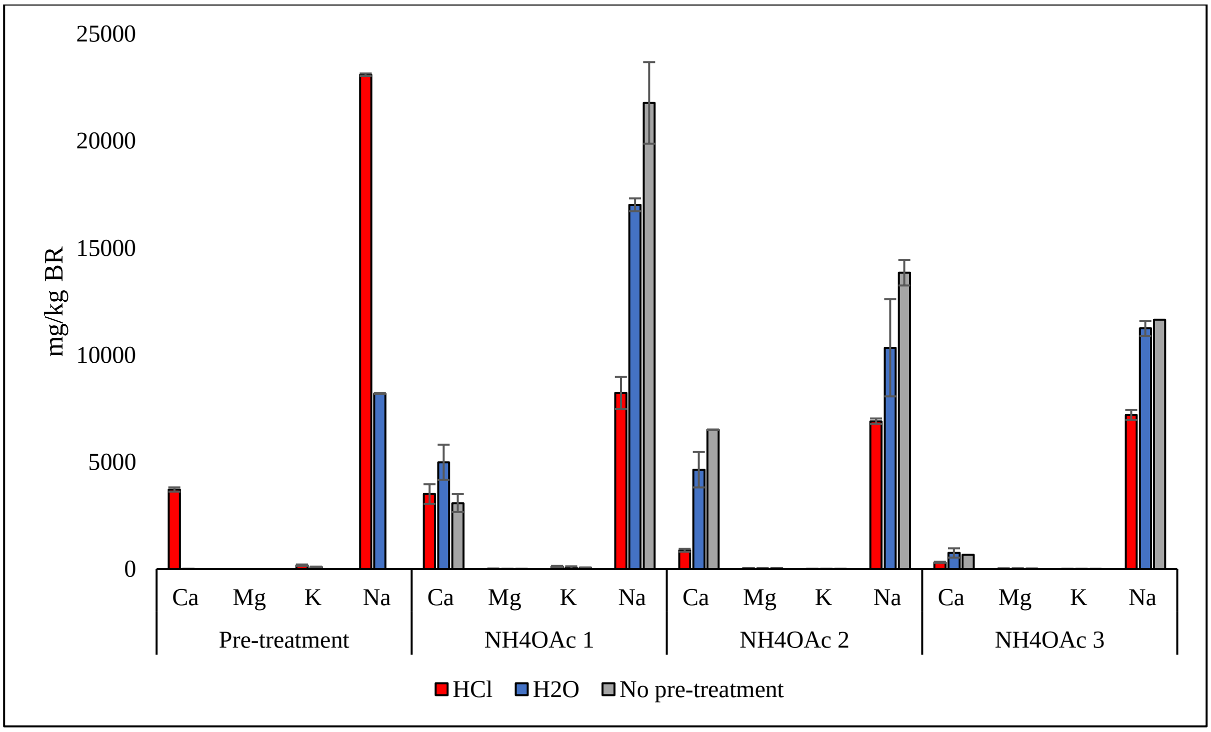


Figure 4. 1: Concentrations of NH4OAc-extracted Ca, Mg, K and Na (mg/kg BR) in the pre-treatment extraction, and the three subsequent NH4OAc-extractions. Values are means of three triplicates. Error bars indicate standard deviations.

Cation exchange capacity

The extractable amounts of Ca, Mg, K and Na are often presented in milliequivalents per 100 g BR (equal to centimoles of charge per kg), which is the common way of expressing exchangeable cations and cation exchange capacity (CEC). The total sum of cations is the sum extracted in the pre-treatments plus the sum of cations in the three subsequent NH4OAc extractions (Fig 4.2). My data indicated that the commonly used procedure to estimate the CEC, as the sum of base cations extracted using 1M NH4OAc (buffered at pH 7) added to none-pre-treated soil material, resulted in a CEC of about 250 meq/100g BR. This value was high compared to those commonly reported in the literature, ranging from about 46 to 111 meq/100g. (Jones & Haynes, 2011), (Cusack et al., 2018). The sum of NH4OAc extractable base cations in non-pre-treated BR was similar to the sum of extracted base cations in the HCl- and water extracts of the pre-treatments, plus the NH4OAc-extracted amount in the pre-treated BR (Fig. 4.2).

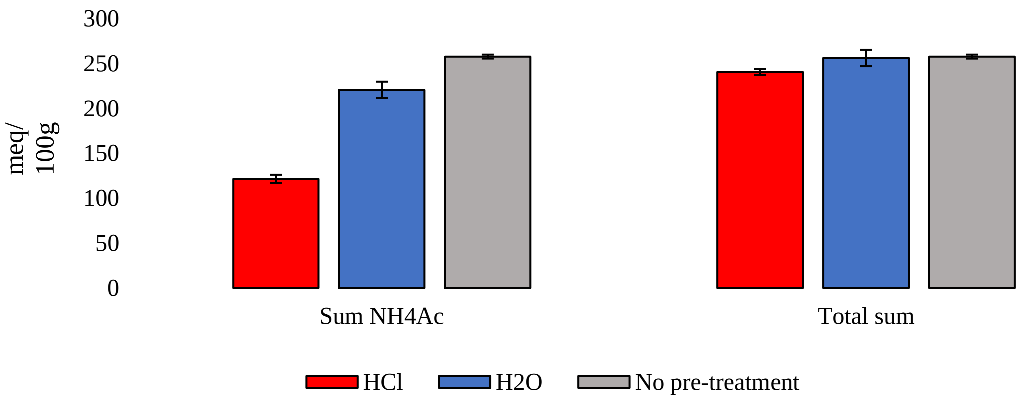


Figure 4. 2: Sum of cations (summed up for the three NH4OAc extractions) and total sum of extracted cations (pre-treatment + three NH4OAc extractions, indicated as "Total sum"). Values are in meq/100g BR.

This study uses two methods for determining CEC (explained in the Theory section): The NH4OAc-extractable and the K^+-replaceable method, which results can be found in Tables 4.4 and 4.5, respectively. In BR, the result of the NH4OAc extraction is highly dependent on pre-treatment. The calculated NH4OAc-extractable amount is 122± 4.5 meq/100g for the HCl pre-treated BR. The H_2O pre-treated samples have an extractable amount of 221± 9.2 meq/100g, while without any pre-treatment it was determined to be 258±2.2 meq/100g.

Table 4. 4: NH4OAc-extractable Ca, Mg, K and Na (meq/100g BR) in pre-treated and none-pre-treated BR. Values are based on three replicates.

Sum NH4OAc extractable (meq/100g)

Treatment		Ca	Mg	K	Na	**Sum extractable**
HCl	average	23	0.76	0.4	97	**122**
	median	24	0.77	0.3	99	**124**
	SD	2.3	0.023	0.1	2.4	**4.5**
H2O	average	51.9	0.72	0.3	168	**221**
	median	51.9	0.72	0.2	173	**226**
	SD	0.5	0.028	0.15	9.5	**9.2**
No pre-treatment	average	51	0.72	0.29	206	**258**
	median	51	0.73	0.23	206	**257**
	SD	2.5	0.015	0.09	1.7	**2.2**

The CEC, based on K^+ replacement of NH_4^+ after the BR sample had been saturated with NH4+ after three washings with NH4OAc, was about 35 meq/100g BR, irrespective of pre-treatment (Table 4.5). According to the literature this method to determine the CEC is less error-prone than the one based on the sum of extractable base cations in NH4OAc. The results of both methods, show that the CEC value of BR, based on KCl extraction of NH4+, was significantly smaller (with a factor of about 7), than the estimate of the CEC based on the NH4OAc-extractable sum of cations.

Table 4. 5: Cation exchange capacity of BR based on displacement of NH_4^+ by 2M KCl in NH4+-saturated BR. Values are based on three replicates.

KCl displacement of NH4+ (meq/100g)

Treatment		CEC
HCl	average	36.5
	median	36.1
	SD	0.81
H2O	average	33
	median	32
	SD	2.2
No pre-treatment	average	35
	median	36
	SD	3.2

The certified reference material (QC) was measured to 13.50 mg/L NH4+, which was within the concentration uncertainty range of 14.3± 2.3 mg/L. This means that the accuracy in the method for determining NH4+ in the KCl extracts is good. Ethanol washed out and removed NH4+ in solution, so that the only amount NH4 left is the electrostatically bound amount. The measured NH4+ in the last ethanol extract was between 0.6 and 2 mg/L, corresponding to about 300 mg/L measured in the KCl extract (Table A.4, Appendix A.II). Distilled water was not able to separate the solid/liquid phase properly, and results from NH4+ analysis was discarded.

4.2 Exchangeable sodium percentage and sodium adsorption ratio

Two expressions (ESP and SAR), commonly used for characterization of sodicity in soils, have been used for BR (Table 4.6). Here, I follow the literature (Li et al., 2018; Weil & Brady, 2017) and base ESP and SAR on NH4OAc extractable Na and the sum of base cations (commonly considered to represent the CEC, but here shown to cause a significant overestimation) in none-pre-treated BR.

Table 4. 6:Exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR). The ESP is based on the sum of NH4OAc extractable Na and base cations (three subsequent extractions) in none-pre-treated BR, while the SAR is based on Na, Ca and Mg (in meq/L) in the pre-treatment extract with distilled water (H2O) Values are based on three replicates.

SAR (√(mol/l))	ESP (%)
H2O pre-treatment	none-pre-treated NH4OAc extract
143 (2.5)	79.2 (0.91)

4.3 Column experiment

The NGI columns were used for plant growth and were analysed for leached concentrations of Ca, Mg, K and Na, DOC, and aggregate stability after 1 month of plant growth. The PP columns followed the same leaching steps, but were only used for aggregate stability before plant growth. Figure 4.3 shows the leachate water from the columns after the second water addition. Due to highly uneven infiltration rate within the treatments, the results were considered to be a factor of column performance and not treatment, and therefore disregarded.

Figure 4. 3: Leachate colour *after 400 mL water had percolated through the polypropylene (PP) columns (Most of the first 200 mL added was retained in the columns). From the left: 100% BR, 10% gypsum (G), 10%G, 5% Açai waste, 5%G, 5% Açai waste and 10%G, 5% food waste. The colour difference decreased as the leachate volume increased (increased L/S).*

pH and electrical conductivity

The pH of Açai- and food waste was 4.84 ±0.009 and 4.57 ±0.025, respectively. Figure 4.4 shows the pH of the leachate water from the different treatments. The unamended treatment with only BR had a consistent pH > 12 until the last leachate, which was 11.93 +/- 0.05 Addition of 10% gypsum to BR caused a significant decrease in leachate pH to about 10. Upon the addition of both gypsum (10%) and Açai waste (5%) the leachate pH decreased further to about 9 and to values between 6 and 8 for BR mixed with gypsum (10%) and food waste (5%). Addition of 5% gypsum and 5% of organic waste resulted in leachate pHs of about 9. These data suggest that only food waste with 10% gypsum (G10F) was able to significantly lower pH further than the other treatments, pointing to acidifying effect of gypsum in combination with organic acids.

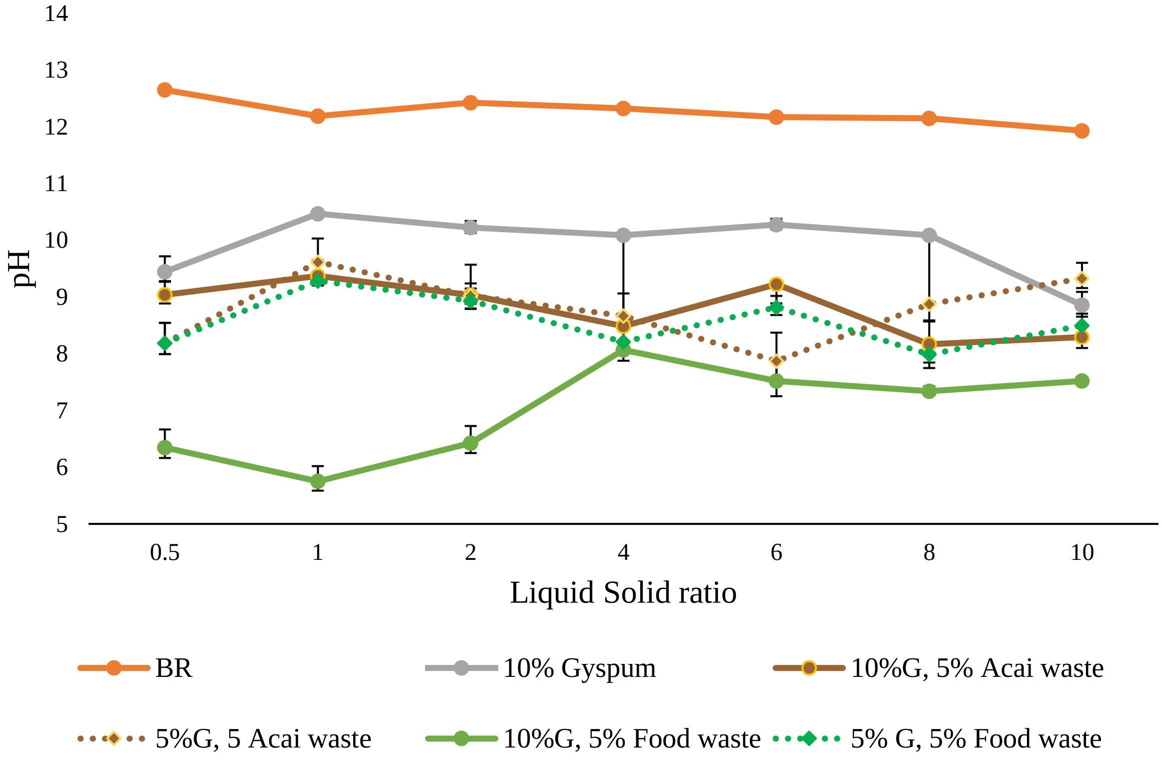


Figure 4. 4 pH in the leachate water from BR columns with and without amendments at increasing L/S ratios. G indicates the addition of gypsum. Values are means and standard deviations (error bars).

The unamended BR and BR mixed with 10% gypsum and 5% food waste (G10F) had highest electrical conductivity (EC) in the beginning of the experiment. At L/S 10 however, there was no significant difference between BR columns with or without 10% gypsum. BR with Açai and food waste (5%) and 5% gypsum had similar EC values at L/S 10, but Both G5F and G5A (5% gypsum, 5% Açai waste) has significantly lower EC than the other treatments at the two last stages of the leaching experiment. Thus, the EC is below the threshold value of 4 dS/m in all treatments.

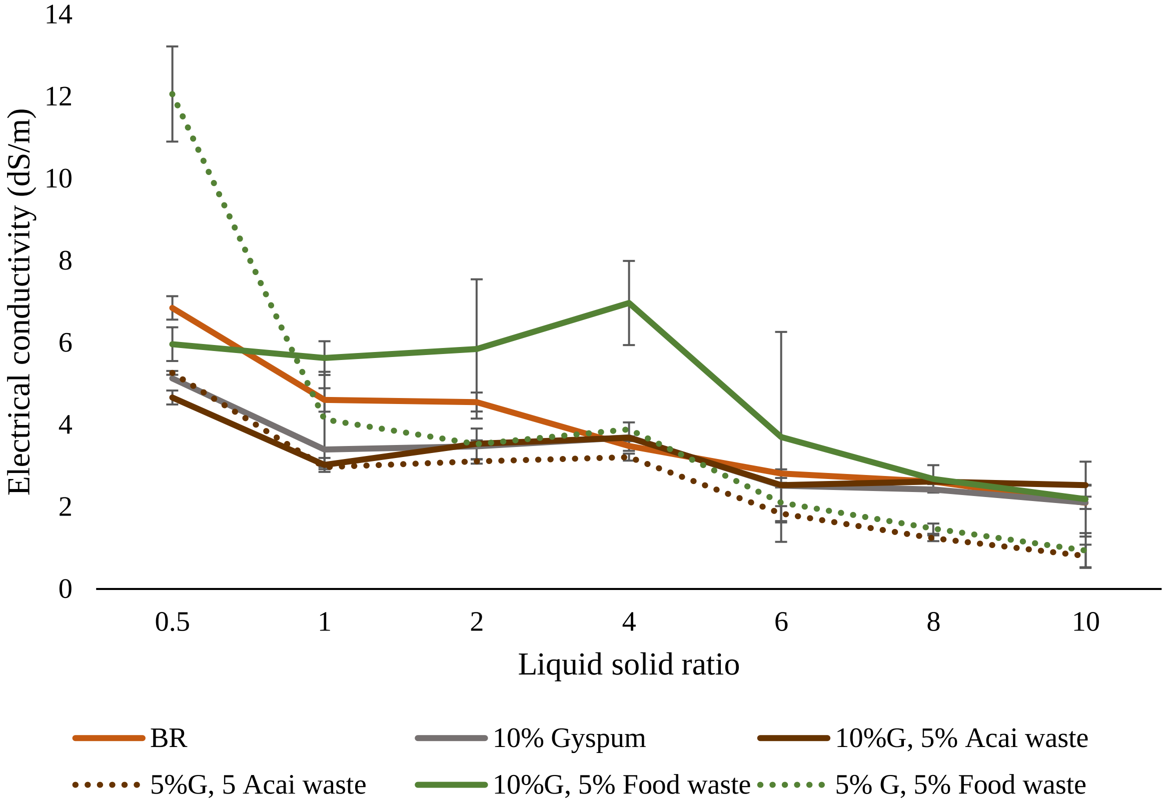


Figure 4. 5 Electrical conductivity (EC) in leachates from columns. Values are means and standard deviations (error bars). Units in dS/m.

Alkalinity

Table 4.7 presents data for alkalinity in the leachates of columns with amended and unamended BR, at the beginning and end of the experiment (LS 1 and 10, respectively). The alkalinity was highest in unamended BR and significantly lower in all other treatments. The alkalinity was significantly reduced in BR, BR with 10% gypsum (G10), and G10A. The leachates differed considerably in alkalinity even within each treatment, as the standard deviation shows. Therefore, the alkalinity result in this thesis should only be used as an indicator for alkalinity. There is no significant difference between 5% and 10% gypsum addition within each organic waste treatment neither at L/S 1, nor at L/S 10.

Table 4. 7: Measured total alkalinity in each treatment. Values in mmol/L, corresponding to how much acid required to reach pH 4.5.

Total alkalinity (mmol/L)		
Treatment	L/S 1	L/S 10
BR	16.8 ± 0.58	8 ± 1.5
10% gypsum	2.7 ± 0.20	0.41 ± 0.09
10% gypsum 5% Acai	5.0 ± 0.95	1.6 ± 0.41
5% gypsum 5% Acai	4 ± 1.9	3.3 ± 0.88
10% gypsum 5% food waste	2.3 ± 0.58	2 ± 1.3
5% gypsum 5% food waste	2.6 ± 0.18	4 ± 1.4

Dissolved organic carbon

Dissolved organic carbon (DOC) is an indicator of labile carbon in the columns, which consists of compounds that microbes can utilize for energy (Weil & Brady, 2017). The DOC from food waste is significantly higher in the early stages than towards the end of the experiment (Fig. 4.6), with initial concentrations of 2600±804 mg/L for G10F5 and 3400±804 mg/L for G5F5. There was no significant difference between these treatments. The DOC at LS 1 from G5A5 is significantly higher than G10A5, with 577±107 and 257±84 mg/L, respectively. However, the G10 treatment showed higher DOC than both Açai treatments at L/S 10, even though it had not received any organic material.

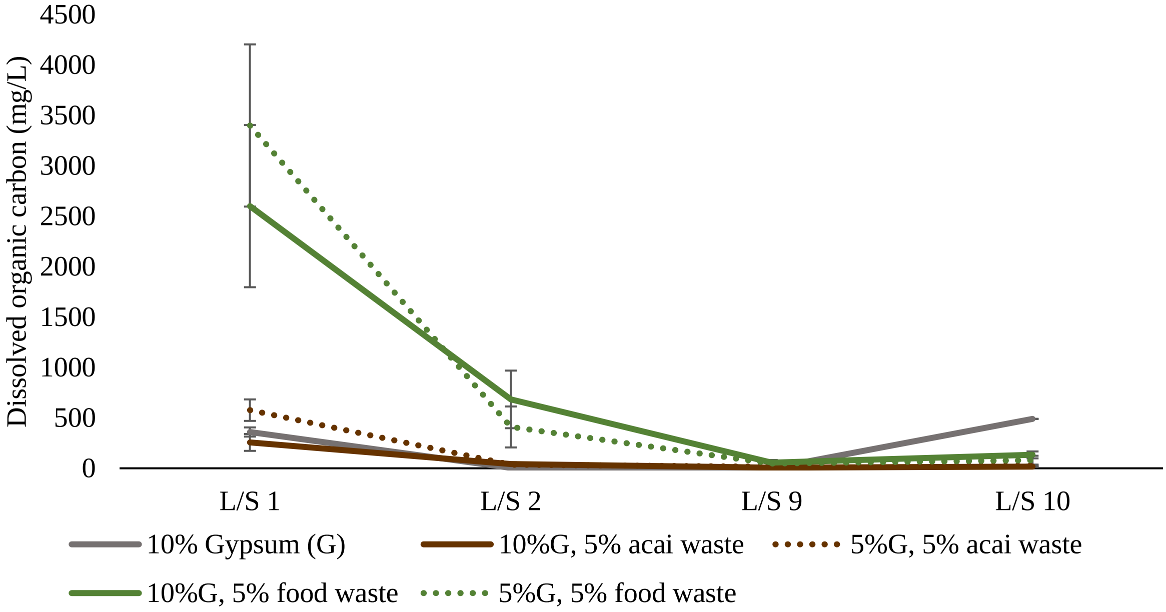


Figure 4. 6 Concentration of dissolved organic carbon (DOC) in column leachates at L/S 1,2, 9 and 10. Values are means and standard deviation, based on 3 replicates.

Base cations (Na and Ca)

A 10% addition of gypsum resulted in doubling of the amount of Ca leached if compared with a 5% gypsum addition to BR amended with Açai and food waste (Table 4.8). These data also showed that significantly more Ca was leached from G10F than G10 and G10A. When 5% gypsum was applied, there was no significant difference in leached Ca between Açai and food waste treatments. The opposite is observed for Na, for which G10, G10A and G5A leached significantly higher amounts Na than both food waste treatments.

There was no significant difference in leached Mg amounts between the treatments. With respect to Mg, many of the leachate samples were under detection limit or under quantification limit (<0.085 mg/L). There was significantly more K leached from the treatments with gypsum + organic matter than when only gypsum is applied. Also, BR amended with 10% gypsum + 5% Açai leached significantly more K than BR amended with food waste.

Table 4. 8: Total leached amount Ca, Na, Mg and K at L/S 10. Values are means and standard deviations based on three replicates. Same letters behind means indicates no statistical significance between treatments.

Leached base cations (Ca and Na in **g/kg**, Mg and K in mg/kg)

Treatment	Ca (**g/kg**)	Na (**g/kg**)	Mg (mg/kg)	K (mg/kg)
10% gypsum	6.2 (0.1) a	48 (6.3) a	0.3 (0.07) a	130 (11) a
10% gypsum 5% Acai	6.3 (0.3) a	47 (2.8) a	2 (1.0) a	380 (33) b
5% gypsum 5% Acai	2.9 (0.3) b	51 (1.9) a	0.8 (0.4) a	330 (32) b
10% gypsum 5% food waste	6.8 (0.4) a	29 (2.0) b	6 (2.3) b	235 (8.4) c
5% gypsum 5% food waste	3.1 (0.9) b	34 (1.5) b	3 (2) ba	260 (39) c

The SAR in the column leachate was also calculated, both at initial and final state of leaching (Table 4.9). At the initial leachate, the SAR is significantly higher in the 10% gypsum and gypsum + Açai treatments, the As L/S 10 was following the last water addition, this can be viewed as the SAR in the growth medium. The median shows that the SAR from the Açai treatments is skewed, and the high SD in the treatments makes the G10 treatment that reduce SAR to <13.

Table 4. 9: Measured SAR in the initial and final leachate (L/S 1 and 10, respectively). The L/S 10 is the leachate that can represent the plants growth medium, as this was the last water addition before planting rye grass.

SAR (mol/L/√mol/L)			
Treatment		L/S 1	L/S 10
10% gypsum	Mean	283.77	6.1
	Median	305.69	6.1
	SD	54.88	0.1
10% gypsum, 5% Acai	Mean	240.68	12.9
	Median	230.47	7.9
	SD	14.52	7.2
5% gypsum, 5% Acai	Mean	326.15	50.4
	Median	347.95	61.4
	SD	31.10	27.3
10% gypsum, 5% food waste	Mean	70.01	12.3
	Median	50.45	12.0
	SD	27.87	2.8
10% gypsum, 5% food waste	Mean	134.39	23.7
	Median	135.06	19.3
	SD	16.15	8.7

Mass balance of calcium

Mass balance of Ca was calculated to compare total leached amount with the amount of Ca added as gypsum, ultimately to see if the sorbed amount of Ca corresponded to calculated CEC, assuming that the sorbed Ca^{2+} now occupied the exchange sites on BR. The method is described in Appendix III (conversions). As the CEC (based on KCl) was not significantly different with or without pre-tretreatment, the average value was used (35 meq ±2.8 meq/100g). It was assumed that gypsum addition resulted in a saturation of all cation exchange sites with Ca2+, but probably this is a slight overestimation. A gypsum addition with 5 and 10% of 236 grams total solid mass, corresponded to a Ca input of 58 and 116 meq Ca/100g, respectively. The Sum of Ca leached from the columns are presented in Table 4.11.

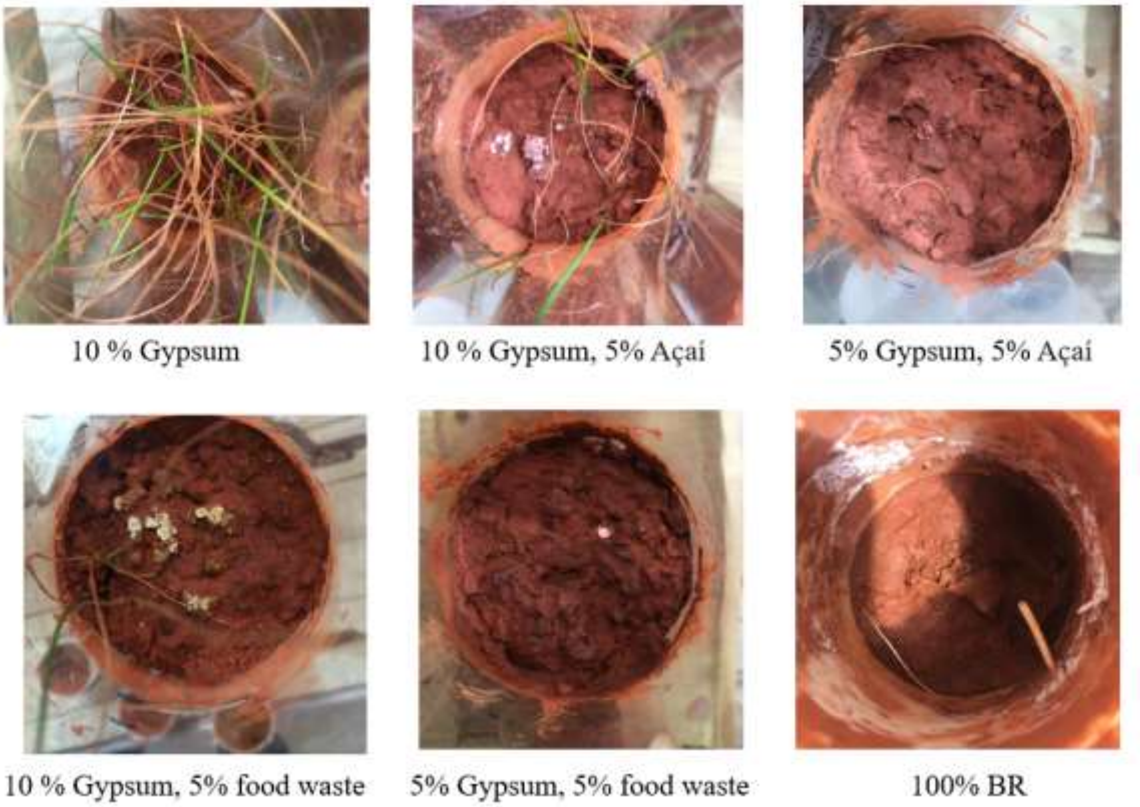
Table 4. 10: Approximate amounts Ca either leached out, potentially sorbed to cation exchange sites (CEC), or stored in BR as $CaCO_3$.

	Mass balance of Ca (meq/100g)				
Treatment	10% gypsum (G)	10% G, 5% Açai	5%G, 5% Açai	10%G, 5% food	5%G, 5% food
Amount Ca added	116	116	58	116	58
Sum leachate	32.9 ±0.30	33 ±1.64	15 ±1.46	35 ±2.4	16 ±4.6
CEC	35±2.8	35±2.8	35±2.8	35±2.8	35±2.8
Ca retained in BR	50 ±2.8	50 ±3.2	10 ±3.2	48 ±3.7	9±5.4

A 10% addition of gypsum resulted in about twice as much Ca leached than with a 5% addition. Furthermore, electrostatic binding of Ca to the CEC was of the same order of magnitude as the loss of Ca by leaching, if 10% gypsum was added, but this, of course, is only an assumption and has not been tested. Comparing the pH in figure 4.4 and the Ca stored as $CaCO_3$ in the columns indicated a significant pH-reducing effect of gypsum addition to BR mixed with food waste. Between G10F and G5F, the pH was significantly lower when 10% was used instead of 5% gypsum, at the end of the leaching series. This will be further explained in the Discussion section.

Rye grass growth in amended BR following leaching

There was generally poor performance of rye grass in the columns. The 10% gypsum treatments showed best results, based on length and number of grass leaves (Figure 4.7; Table 4.11). When mixing in Açai waste in BR, the addition of 10% gypsum resulted second best performance. In BR with 5% food waste, 10% gypsum did not result in any significant development of rye grass.


10 % Gypsum

10 % Gypsum, 5% Açai

5% Gypsum, 5% Açai

10 % Gypsum, 5% food waste

5% Gypsum, 5% food waste

100% BR

Figure 4. 7 Photographs of *the germination and development of rye grass, two weeks after seeding. From top left to bottom right. 10% gypsum, 10% gypsum + Açai waste, 5% gypsum + 5% Açai waste, 10% gypsum + 5% food waste and 5% gypsum + 5% food waste.*

Figure 4.7 also showed that there was no visual difference of rye grass growth between unamended BR and amended BR with 5% gypsum and organic matter. The photographs also reflect the length and biomass weight of the treatments in Table 4.12.

Table 4. 11: Measurements of leaf length of the rye grass leaves (weeks after germination). Values are the highest and shortest leaf, in cm, in each one of the columns (triplicates).

Treatment		**Highest/shortest leaf of rye grass (cm)**				**Biomass weight (g)**	
		1st week	2nd week	3rd week	4th week	roots	shoots
10% gypsum 1	1	8/1.8	13/3	15/5	14/7	0.164	0.115
	2	8.5/3.5	12/7.5	15/8	12/6	0.211	0.155
	3	8.5/4	12/4	13/9	13/6	0.311	0.129
10%gypsum + 5% Acai w.	1	5/1	6/1	7.5/1	7.5/2	0.05	0.013
	2	5/2	7.5/2	8/1	8.5/2	0.055	0.04
	3	-	6/2	7.5/1	8/1	0.009	0.011
5% gypsum + 5% Acai w.	1	1	3/1	4/2	4/1	-	-
	2	-	-	2/1	-	-	-
	3	1	1	1	-	-	-
10% gypsum + 5% food w.	1	-	-	-	-	-	-
	2	-	4/1	6/2	8/1	0.07	0.032
	3	-	1	-	-	-	-
5% gypsum + 5% food w.	1	-	-	-	-	-	-
	2	-	-	-	-	-	-
	3	-	1	1	-	-	-

AGGREGATE STABILITY

Wet sieving method on field samples

Aggregate stability analysis on field samples from Hydro's BRDA was conducted using the wet sieving method, presented in Figure 4.8. It is important to note that these samples were field moist, and were not air-dried according to common procedure for aggregate stability (Grønsten & Børresen, 2009), (Ejikelkamp, 2018). The field-treatments are similar to the treatments in the column experiment, with some additions: In the field plots, treatments with soil are included and larger amounts gypsum and Açai are used (see below). The treatments BR and BR+10%soil had a fraction of unstable aggregates being significantly greater than BR mixed with gypsum (5, 10 and 15%). There is no significant difference in unstable fractions between BR, BR + 10% soil, and BR + 10% Açai waste (the treatments without gypsum). Also, by visual inspection, unamended BR stands out compared to amended BR (figure 4.9).

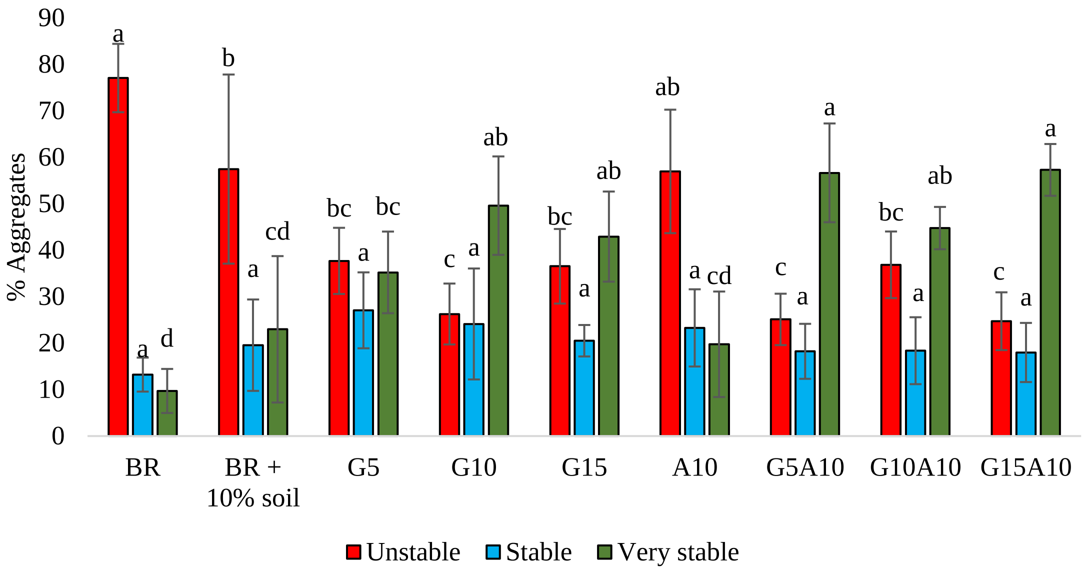


Figure 4. 8 Aggregate stability of field samples from the *BRDA, at Barcarena. The wet sieving method was used for these samples. Values are means and standard deviations based on* 6 *samples* for each treatment.

The BR amended with 10% soil (without gypsum) had one observation with high stability, which caused the SD to increase considerable.

Figure 4. 9 Field moist bauxite residue from with 10% gypsum (left) and unamended BR (right). Samples taken prior to plant growth, approximately six months *after application of gypsum* (Y. Miura, 2022a).

Wet sieving method on laboratory columns

When taking out the column material, the amended BR came out as more structured than unamended BR, judged by visual inspection (figure 4.10). Upon drying, the BR turned to a brick-like substance, and aggregates was not dispersed. Thus, air-dried samples were not appropriate for the wet sieving method, and results can be found in Appendix A.V (aggregate stability).

Figure 4. 10 Photographs taken of BR (left) and BR+10% gypsum (right) immediately after taking down the columns, three days after the last water addition.

A third analysis was made for aggregate stability by the wet sieving method, with column material after plant growth. This time, the same procedure as for the field plot was used, using undried, un-sieved material. However, to get them out of the columns as undisturbed as possible, they were left without water additions for 1 week. Based on this result, unamended BR has significantly higher stable fraction than the other treatments, and the same tendency as the wet sieving method, with hardsetting of the material, was observed. The result from wet sieving method after plant growth can be found in Appendix A.V, Figure A.2.

Rainfall simulator

The rainfall simulator for aggregate stability was conducted on the treatments prior to and after growth of rye grass. The method applies greater disruptive force to the aggregates and was thought to produce better results than by the wet sieving method. Stability was tested for aggregate fractions 0.5-2 mm and 2-6 mm, according to the method described by Grønsten and Børresen (Grønsten & Børresen, 2009). However, also by this method, the air-dried samples were not appropriate for analysis, so that aggregate stability of the columns prior to plant growth (air-dried for two weeks), was also disregarded. Figure 4.11 presents the rainfall simulator results on the columns after plant growth, which had not dried for so long, and could thereby provide more useful information.

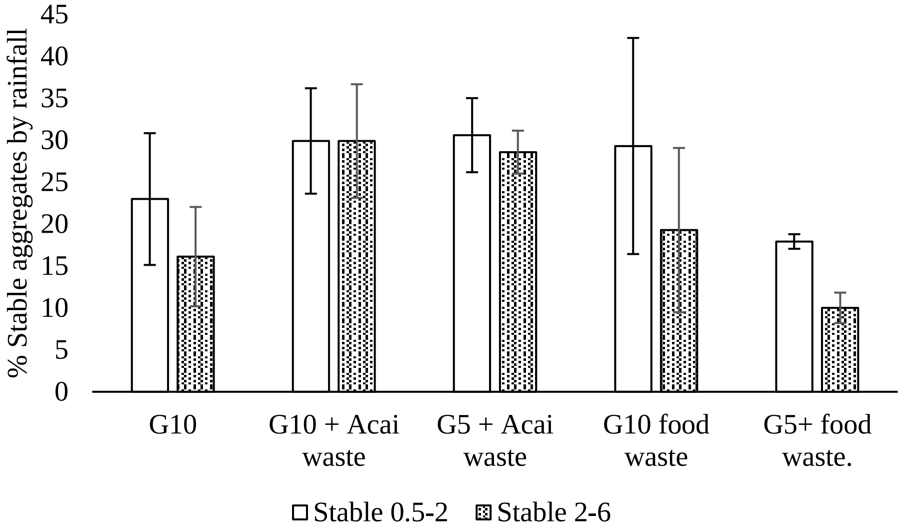


Figure 4. 11: Aggregate stability by rainfall method, where stable aggregates are shown in percentage. Values are means and standard deviations based on three observations for each treatment.

There was no significant difference between application of 5% and 10% gypsum to the BR, for neither 0.5-2 nor 2-6 mm fractions. This is in line with the measured aggregate stability of the field samples.

5. DISCUSSION

5.1 Cation exchange capacity of BR from Hydro Alunorte

The CEC of BR is an important property for understanding the amount of cations that can be retained through electrostatic bonding, and thus express potential nutrient availability as well as how well aggregates are held together. As the ESP is based on CEC in soils (equation 3), it is also an important property for evaluating salinity.

A problem with estimating CEC on BR is the content of unstable minerals such as sodalite, which are formed during desilication in the Bayer process. Under ambient field or laboratory conditions they can be relatively soluble, but this depends on temperature, impurities of solution and type of DSP (Vaughan et.al., 2019). To determine the exchangeable cations, the challenge is therefore to find a way to differentiate between cations derived from unstable minerals like sodalite and actual exchangeable cations. Because bauxite is digested in caustic soda during the refining process to alumina and the high pH, Na will occupy most exchangeable binding sites on the BR surface. In sodic soils the solubilization of Na from minerals, such as sodium zeolites by extracts intended to determine the exchangeable fraction of Na only, is also a problem (Qadir & Schubert, 2002) (Wong & Ho, 1995).

The CEC is commonly determined through extraction of base cations with 1M NH4OAc (buffered at pH 7). My results suggest that a pre-treatment step to lower pH to circumneutral and remove some of the unstable minerals is important to limit overestimation of the actual CEC (Table 4.4). With pre-treatment, readily soluble Na and Ca were washed out (Table 4.2). The pH in the first NH4OAc extractions was as mentioned 7.5, 8.3 and 8.2 in HCl-, and H_2O-pre-treated and none-pre-treated samples, respectively. Figure 4.1 shows that at these pH values, the Na concentration are initially very high. Even for the pre-treated BR, this can be an effect of dissolution of remaining DSP. The NH4OAc method can therefore overestimate the CEC of bauxite residue, since it can release cations that really are found as inner sphere complexes in the DSP's.

The CEC based on replacement of NH4+ by K+ is significantly lower than the sum of base cations extracted by NH4OAc (Table 4.5). The difference between NH4OAc base cations and the KCl- extractable NH4+ means is that the NH4OAc-extractable method likely overestimates the CEC, due to contribution by Na and Ca from the dissolution of secondary minerals.

The CEC based on KCl extractable NH4+ (the second step in the method) did not depend on pre-treatment of BR, as it was about 35 meq/100g BR irrespective of pre-treatment. This is significantly lower than the CEC based on exchangeable cations in 1M NH4OAc and is in the range of clay loams or clay (Weil, 2017). KCl-extraction of NH4+ is therefore a more realistic estimation of CEC on BR, since now, base cations derived from soluble material have been removed, and only elements on the exchange sites of BR are left. The KCl extractable NH4+ is not related to "readily soluble cations" and is a much better estimate of the CEC (negative charge) in the BR. Wong & Ho reported similar results, where they first saturated red mud with Na^+, removed excess Na+ with 99% ethanol, and then displaced the adsorbed Na^+ with NH_4^+ using 1M NH4OAc, thereafter analyzing exchanged Na^+(Wong & Ho, 1995). They reported a CEC of 42±3.1 meq/100g and exchangeable Na^+ content to be 39.6±0.6 meq/100g. This means that in their study 39.6/42*100=93% of CEC is occupied by Na^+ when saturated with Na^+.

The determined CEC of about 35 meq/100g BR will represent the actual exchangeable amount, different to the value obtained from NH4OAc (Table 4.5 and 4.4, respectively). For BR, the extracted base cations should rather be denoted NH4OAc-extractable and not exchangeable base cations.

Based on this study, it is recommended to wash excess NH4OAc with 60% ethanol. There was difficulty in separating the solid and liquid phase when washing with water, resulting in possible removal of suspended BR when extracting supernatants. This assumption is based on the lower and inconsistent values for NH4+ in the KCl replacement, when measuring spectrophotometrically. Three subsequent washings with 60% ethanol removed NH4+ down to 0.5 to 2 mg/L, which corresponds to 0.2 and 0.6 % of the NH4+ measured in the KCl extract. Therefore, 60% ethanol was effective in removing excess (not adsorbed) base cations from the BR.

5.2 Sodium adsorption ratio and ESP

The value obtained for SAR in BR was 122 (Table 4.6), which was derived from the concentrations of Na Ca in the pre-treatment with water. As Mg was under detection limit, the equation was only dependent on Na/Ca. The low amounts of Mg^{2+} has also been reported in another study of NH4OAc extraction in BR (Di Carlo et al., 2020). This SAR value is in the range reported by Gräfe et al., with a SAR of 307 ±233. Soils that have SAR values >13 may be characterized by an increased dispersion of organic matter and clay particles, reduced saturated hydraulic conductivity and aeration, and a general degradation of soil structure (Weil & Brady, 2017).

The ESP of about 80% found in the NH4OAc extract without pre-treatment (Table 6 is in the same range reported by Jones and Haynes, at 60-90 % (Jones & Haynes, 2011), and is a good indicator for plant-toxicities (R. Courtney, 2022). However, as stated above, it is not exchangeable Na and should rather be referred to as extractable Na percentage.

5.3 Column experiment

The EC was reduced to well below 4 dS/m halfway through the leachate series (L/S 5) in all treatments, including unamended BR (Figure 4.5). Salinity was in other words reduced to appreciable levels.

The pH in unamend BR is lowered from 12.6 to 11.9, at L/S 10 (Figure 4.4). This reduction can be explained by the reaction of OH^- in BR with CO_2 from the atmosphere, producing HCO_3^-. The leaching experiment lasted for five weeks, which allowed the columns to react with the atmosphere. The measured alkalinity at L/S 10 was half of the measured, initial value (table 4.7) However, a large, continued reduction in alkalinity in unamended BR might not occur, as the sodalite formed under the Bayer process can dissolve and contribute to a slow release of Na+ and OH^- ions from bauxite residues over time during storage (Barrow, 1982; Wong and Ho, 1995; Menzies et al., 2009). This pool of residual alkalinity will increase pH and exchangeable Na over time. Additon of 10% gypsum lowered the pH from 11.9 to 8.9 (Figure 4.4), which can be attributed to Ca^{2+} reacting with CO_3^{2-} and precipitating $CaCO_3$, thus reducing buffer capacity, as in equation 10 (Lehoux et al., 2013), in addition to the reaction with CO_2.

$$(10) \qquad 2OH^-_{(aq)} + CaSO_4 \cdot H_2O_{(s)} + 2CO_2 \leftrightarrow CaCO_{3(s)} + SO_4^{2-}{}_{(aq)} + 2H_2O_{(l)} + H_2CO_{3(aq)}$$

This can be said to be in accordance with Lehoux's findings, where they combined red mud with soils with and without gypsum added. They found that soils with 4% gypsum added resulted in smaller pH increase. (Lehoux et al., 2013).

With incorporation of OM to BR in combination with gypsum, pH-reduction could be expected, with respiration from decomposition and release of organic acids. In these alkaline conditions, organic matter can dissolve and hydrolyse, which can form humic substances and organic anions, which again lowers pH (Bray et al., 2018). Humic substances can develop from food waste (X. Zhou et al., 2022), and as they contain a variety of functional groups such as carboxylic, phenolic and hydroxylic compounds, which can affect the soil's pH and nutrient dynamics (Y. Zhou et al., 2014). Humic acid can also form complexes with polyvalent metals such as Al (Adeleke et al., 2017).

The initial pH reduction in the food waste compared to Açai treatments points to more labile carbon in the food waste. This is supported by the higher DOC (figure 4.6) leached from food waste, from which Açai waste leached approximately the same amount as gypsum without organic amendment. DOC is often related to the amount of OM easily available to soil fauna (Weil & Brady, 2017). At the final leaching steps, the treatments with 10% gypsum were about one pH unit lower than the treatments with 5% gypsum, pointing to the combined pH reducing effect of gypsum + OM.

The pH reduction by augmenting OM to BR can be attributed by the ability of plants, bacteria and fungi to produce citric, oxalic and tartaric acid, which can dissolve and complex metals, and thus translocate them (Oades, 1984).

The alkaline hydrolysis of organic carbon can release carboxylic acids and thereby liberating organic matter to solution, in addition to reducing alkalinity in BR. Alkaline reactions with natural organic matter can therefore be one of the main short-term mechanisms for pH buffering, in addition to clay mineral dissolution and sorption reactions (Lehoux et al., 2013). At lower pH, cations should sorb better to the BR surface. Reduction in alkalinity should also reduce DOC caused by alkaline extraction of organic matter.

Interestingly, leached Na is significantly higher from the G10 and Açai treatments than from food waste (4.8). This is surprising, since food waste would be expected to contain more Na. Food waste has a finer texture than Açai and may be able to better retain Na. In theory, the gypsum addition should exchange Na for Ca on exchange sites of BR, and force Na into soil solution. Here, the opposite is observed with significant difference between G10F5 and G5F5: The 5% gypsum treatment leads to higher leached amount Na than 10%.

As stated in the CEC section above, lower pH can cause dissolution of DSP solids such as sodalite. However, there is no significant relations between lower pH and Na concentrations in the leachates. Bray et al. also found that cancrinite was the dominant specie of DSP, and that its dissolution controlled Na availability (Bray et al., 2018). But they found a surprising result: Dissolution of cancrinite should equimolar concentrations of Na, Si and Al, but the aqueous extractable Na was far higher than Si and Al, which pointed to a certain retention of the latter elements relative to Na. At the high pH in BR, Al and Si could precipitate into amorphous and crystalline secondary phases (Bray et al., 2018).

5.4 Plant growth

The grass development in the columns varied largely but were quite consistent within each treatment (Figure 4.10 and table 4.11). Grass development was not as good as expected, but it was quite consistent with within each treatment. The high concentrations of Na^+, OH^- and HCO_3^- can itself be toxic, but also the physical conditions can be a restriction. An excess of specific ions can have toxic effects on various plant physiological processes and high Na^+ levels can cause Ca^{2+} and Mg^{2+} deficiencies (Bresler et al., 1982).Even though the rye grass may be tolerant of high Na concentration, the poor soil physical conditions can still cause them to fail (Bresler et al., 1982).

The SAR value determined from the leachates at L/S 10 (Table 4.9) showed that only the treatment with 10% gypsum managed to lower it below the desired value of 13. In the other treatment, SAR was either too high (food waste treatments) or too variable (Açai, from the SD) to conclude that SAR was reduced to below 13. The SAR observation is very much in line with the grass growth, as G10 clearly showed best results. The G10A treatments showed second lowest SAR, and these columns also showed second best grass performance. Interestingly, in all the six food waste treatments, the SAR was lowest in the only column with grass development, with a value of 9 (Appendix A.IV table A.11). Another study of SAR from BR from Barcarena has been conducted, also with increasing leachate steps (Wik, 2020). There, the SAR of unamended BR was 110 at L/S 10 and decreased to 18 at L/S 50. In the present study, the SAR was considerably lower at L/S 10 (21 ±20, based on all treatments), especially with 10% gypsum addition, with a value of about 6.

The SAR value is the only explanation for why the grass performed so poorly in the columns. Electrical conductivity, pH, and leached elements are not very different from the other columns, and the most apparent difference between all treatments, aside from SAR, is the measured lower alkalinity in the G10 columns. But these measurements are as mentioned only an indicator, as the results were highly variable (Table 4.7). Also in the preliminary test conducted at NGI prior to this thesis, 10% gypsum performed best (Capobianco, 2021)

Due to poor performance of rye grass in the OM-augmented columns, it is not possible to decide effect of Açai versus food waste. Simply applying 10% gypsum gave the obvious best results, which is line with the lower SAR from the leachate water from G10. However, treatments with

Açai waste and gypsum in the field at Barcarena has proved to be adequate for growth, as vegetation has been established in research plots at the BRDA (Y. Miura, 2022a).

5.5 Aggregate stability

Laboratory samples

It appears that standard pre-treatment with drying soil in room-temperature for 7 days is not suited for BR. The BR developed very hard, brick-like properties, and around 80% were stable and no trend of treatment effect could be observed (Appendix, Table A.14). The dispersion solution was not able to disintegrate aggregates. Sodium can have a dispersive effect when wet, but strengthens when dry (Sumner, 1993). Sumner states that sodic behaviour can include hardsetting, caused by poor aggregation and clay disperses and reorientates on wetting, so that very high soil strengths are observed on drying. The high Na content can also be the reason for the ineffectiveness of the hexametaphosphate in dispersing the aggregates because it is based on Na adsorption and displacement of other cations so coagulating properties are neutralized (Krogstad, 2009). In BR however, adsorption sites are already saturated with Na, and addition of more might not help dispersion.

Field samples

Using undried samples from PhD. Candidate Yuuki S. Miura gave results that pointed to the important role of gypsum for aggregate stability (Figure 4.8). Comparing unamended BR and BR with 10% addition of soil, it was no significant difference in stability, which means that soil addition does not improve stable aggregate formation, while only a 5% addition of gypsum, does. Since there was no observable difference between 5%, 10% and 15% gypsum it means that 5% is enough for aggregation, possibly due to replacing Na^+ with Ca^{2+}. A study on gypsum and compost application on red mud found that gypsum clearly reduced clay dispersion (R. G. Courtney et al., 2009), in addition to lowering sodium percentage in solution. This seems to follow the findings in this study from aggregate stability in field samples. Also by the wet sieving method with Eijkelkamp, Courtney et al. found increased aggregate stability in gypsum and OM amended BR, and that the stability only increased with time (1 and 8 years after augmentation) (R. Courtney et al., 2013), which was attributed to higher biological activity and accumulation of recalcitrant carbon, and lower Na content.

Gypsum will as previously mentioned provide Ca^{2+} to BR, and possibly replace the monovalent Na^{+}. The large, hydrated radius of Na^{+} is a dispersive element in soils, which can be observed in simple experiments with soil, water and NaCl. This dispersion behaviour gives a soil/water mix plastic properties and it will not flocculate as easily.

As mentioned earlier, the high pH in the BR solution may cause SOM to disperse and/or dissolve, thereby actually reduce aggregate stability. Simple acids produced from respiration and degradation of organic matter can promote dispersion of clays in upper horizons and thereafter clay mobilization downwards in the profile (Oades, 1984). However, this effect might not be as obvious, as gypsum + Açai waste produced slightly better stability than gypsum without Açai waste. As root systems develop, mature, and decompose, the rhizosphere organisms can establish themselves and increase aggregate stability (Oades, 1984).

A study on micromorphology of BR and BR amended with phosphogypsum and vermicompost, found that their combination had a significant positive effect on aggregate size distribution and water-stable aggregates (Zhu et al., 2017). They suggested that vermicompost had a positive effect on formation and stabilization of water-stable aggregates, while gypsum improved silt-sized microaggregate flocculation. From the field samples from Barcarena, puddles of water could be observed in the plots with unamended BR and one plot with 5% gypsum added (Y. Miura, 2022b), which indicates the effect flocculation of aggregates has on water storage and transport. Crust formation at the surface is much more sensitive to Na than hydraulic conductivity (Sumner, 1993).

Thus, the method was modified by using undried BR from the field and undried laboratory columns, post plant growth. However, it can seem that the formation of stable aggregates is more time consuming and/or dependant on activity microorganisms, which might not be enough for this column experiment to develop significant differences.

The increased stability with time is also suggested by other authors, who showed that most of the physical evolution of soil-incorporated organic matter is established during the first year, from degradation of organic matter (Grosbellet et al., 2011). They state that aggregates are dynamic, and its stability can increase over time in relation to the incorporation of organic matter. As the Barcarena field treatments have undergone more time and exposure to its environment, their aggregate stability results could be viewed as more reliable and representative than those in the columns.

However, no significant trend of treatment effect could be observed prior to and post plant growth. This is actually not surprising, considering the poor root and shoot development in most treatments. The G10 samples did, surprisingly, not show any difference before and after, even though these showed good vegetation growth. Thus, rye grass cannot be said to improve aggregate stability in this experiment, when using dried samples.

5.6 Mass balance in relationship with CEC and aggregate stability

Based on Figure 4.8, there is no significant difference in aggregate stability between a 5%, 10% and 15% gypsum addition to BR. This may be explained by the lower CEC found in this thesis (35±2.2 meq/100g) than by NH4OAc-extractable amount, which roughly corresponds to illite clays (Tan, 1994). All gypsum additions surpass this amount (5% gypsum =73.5, 10% gypsum =146.9 and 15% gypsum =220.4 meq/100g). The rest will be leached out or possibly precipitated as $CaCO_3$, which would decrease pH (see equation 10). If Ca^{2+} from the gypsum addition would exchange the cation ion binding sites, which presumably is mostly occupied by Na^+, that Ca^{2+} would contribute to increased stability.

Even though the excess gypsum might not directly improve aggregate stability, the 10% gypsum addition lowered the pH 1 unit compared to 5% gypsum in the last stages of the leaching experiment. This is probably due to the precipitation of $CaCO_3$ and removal of OH^-. As mentioned, alkaline conditions might deter aggregate stability by hydrolysing OM, so this lowered pH effect can thus indirectly remediate dispersion.

6. CONCLUSION

This study tried to fill some of the knowledge gaps around CEC, ESP and SAR from unamended BR from Hydro Alunorte, as well as soil-physical and chemical improvements from the already established amendments: gypsum and organic waste from food and the Açai berry production.

It is important to be careful with expressing exchangeable cations or Na in BR. The exchangeable (CEC) and extractable cations was found to be ≈35 and ≈250 meq/100 g BR, respectively. This indicates that BR is a mineralogically unstable material, and DSP minerals can dissolve in extracting solutions such as 1M NH4OAc. Thus, when using sodicity and salinity expressions such as ESP and SAR, one must be careful not to include the dissolved Na-containing minerals, as this will lead to an overestimation of the actual exchangeable amount.

The lower CEC obtained using K^+ adsorption and displacement of NH_4^+, corresponds to the measured aggregate stability in the field samples. The analysis showed that 5% gypsum was enough to significantly increase stability, and 10% or 15% gypsum did not have a drastic, additional effect. The CEC and mass balance of Ca^{2+} supports that a 5% gypsum addition to BR is enough for Ca^{2+} to occupy BR's exchange sites and instead of Na^+, thereby improving aggregation. As more gypsum is added, more $CaCO_3$ can form which will lead to pH-reduction, which was also observed in the leaching experiment, where 10% gypsum lowered the pH with ≈1 unit, compared to 5%, when combined with food waste.

Especially food waste with gypsum showed the most obvious reduction in pH, presumably because it supplied a more labile form of organic carbon than Açai waste did, which is also supported by more leached DOC from food waste.

Gypsum with Açai gave good results in aggregate stability from the field, with slightly improved stability, compared to gypsum only. Also, with Açai, the gypsum demonstrated its importance for aggregation, as only Açai amelioration did not have a significant positive effect. By the amendments tested in this thesis, gypsum combined with a high labile carbon-source of organic matter would be the best amendment. The acidifying effect in addition to the significantly improved aggregate stability in the field would promote permeability and aeration, which would improve soil microorganisms and plants conditions. Açai is readily available in this region of Brazil, and if it was allowed to go through a decomposition phase before augmentation, it could provide more labile carbon than what was observed in this thesis. A 5% gypsum augmentation would That way, a 5% or 10% weight augmentation together with 5% gypsum could be a good option for rehabilitation of bauxite residue.

Further studies could be conducted on different pre-treatments of Açai waste, to enhance their effect once incorporated to BR. Also, long term performance of Açai combined with gypsum should be investigated, with respect to chemical properties and aggregation, as aggregate stability can increase further over time.

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8. APPENDIX

A.I MP- AES from NH4OAc- extraction

A.II Spectrophotometer from NH_4^+-displacement by KCl

A.III Conversions

A.IV Column leachate chemistry- pH, electrical conductivity, DOC, Ca, Mg, Na, K

A.V Aggregate stability

A.I MP- AES from NH4OAc- extraction

Table A. 1: Weights and volumes of the three treatments.

	Weight		Volume		Weight		EC	pH	Volume centrifuge tubes					Weight	Weight
	Centrifugal	BR	(mL)	Treatment	Before	After extraction	(mS/cm)			AC-1	AC-2	AC-3	OH-3	prior	post extraction
HCl 1	14.4086	1.0031	20	0.075M HCl	34.0036	16.4115	5.6	7.64	HCl-1	15	31	32	25.5	34.8092	18.0933
HCl 2	14.564	1.016	20	0.075M HCl	34.2023	16.45	5.7	7.62	HCl-2	19	32	30	28	37.3711	19.8689
HCl 3	14.4431	1.0152	20	0.075M HCl	33.0582	16.26	5.6	7.62	HCl-3	19	32	30	28	36.6248	16.8026
V 1	14.5506	1.0042	20	Distilled wate	35.5148	16.2245	1.6	10.97	V-1	14	30	30	27	43.1057	16.1836
V 2	14.5772	1.025	20	Distilled wate	35.5542	16.4665	1.6	11	V-2	19	31	30	25	37.6521	17.1333
V 3	14.5815	1.0028	20	Distilled wate	35.49	16.3492	1.6	10.98	V-3	18	27	34	33	38.2392	17.3246
BR 1	14.5756	1.0128	20	NH4OAc	-	-	-	-	BR-1	19	29	31	27	41.3329	17.9629
BR 2	14.5772	0.9911	20	NH4OAc	-	-	-	-	BR-2	15	34.5	32	32	36.6307	18.4917
BR 3	14.5815	1.0004	20	NH4OAc	-	-	-	-	BR-3	18	31	32	34	36.3998	18.3139

Table A. 2: MP-AES analysis in extracts from pre-treatment and the three subsequent additions of NH4OAc.

	Pre-treatment				NH4OAc wash 1				NH4OAc wash 2				NH4OAc wash 3			
Treatment	**Ca**	**Mg**	**K**	**Na**	**Ca**	**Mg**	**K**	**Na**	**Ca**	**Mg**	**K**	**Na**	**Ca**	**Mg**	**K**	**Na**
HCl-1	200	<0,33	12	1200	190	1.2	11	470	28	1.2	0.38	220	11	1.0	0.53	230
HCl-2	190	<0,33	7.8	1200	210	1.3	4.7	460	30	1.2	0.38	220	9.7	1.0	0.54	230
HCl-3	190	<0,33	8.6	1200	190	1.4	4.0	460	25	1.2	0.37	210	10	1.0	0.54	240
V-1	0.69	<LD	6.2	420	270	1.1	11	1200	190	1.2	0.54	390	26	1.0	0.65	360
V-2	0.67	<LD	5.5	430	290	1.1	1.8	920	140	1.2	0.54	390	16	1.0	0.54	370
V-3	0.64	<LD	3.8	420	310	1.3	1.6	910	140	1.2	0.57	260	29	0.99	0.61	340
BR-1	-	-	-	-	150	1.2	6.7	1300	210	1.1	0.54	400	21	0.97	0.55	360
BR-2	-	-	-	-	200	1.2	2.7	1200	200	1.1	0.81	460	21	0.95	0.63	380
BR-3	-	-	-	-	180	1.2	2.7	1200	200	1.2	0.61	430	21	0.92	0.59	350

A.II NH_4^+-displacement by KCl

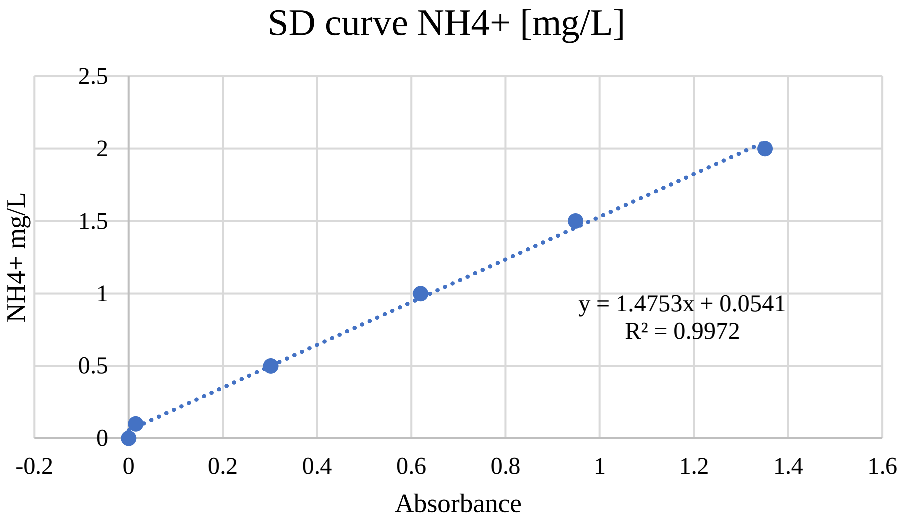

Figure A. 1: SD curve for NH_4^+ analysis with spectrophotometer. Formula y used to calculate concentrations from absorbance of treatments in table A.3.

Table A. 3: Absorbance reading for HCl, H2O and NH4OAc- pre-treatments, at 600x dilution.

	Absorbance					
	HCl	RSD	H2O	RSD	NH4OAc	RSD
1	0.34119	0.37	0.26727	0.18	0.2676	0.01
2	0.32977	0.14	0.29226	0.11	0.33109	0.02
3	0.3273	0.01	0.32042	0.02	0.32857	0.04

Table A. 4: Concentrations of NH_4^+ *in KCl-extract.*

Treat-ment	Dry weight BR	Volume KCl	[NH4+] mg/L	[NH4+] mg/g	CEC meq/100g
HCl 1	0.985	20.0	334.5	6.8	37.7
HCl 2	0.998	20.0	324.4	6.5	36.1
HCl 3	0.997	20.0	322.2	6.5	35.8
V 1	0.986	20.0	269.0	5.5	30.3
V 2	1.006	20.0	291.2	5.8	32.1
V 3	0.985	20.0	316.1	6.4	35.6
BR 1	0.994	20.0	269.3	5.4	30.0
BR 2	0.973	20.0	325.5	6.7	37.1
BR 3	0.982	20.0	323.3	6.6	36.5

Table A. 5 Certified material for NH_4^+*analysis, quality control (QC).*

	certified value (mg/L)	Measured (mg/L)
QC	14.3± 2.3	13.50

A.III Conversions

mg/L to meq/100g:

(I) $\frac{mg/L}{molweightelement(g/mol)} = mmol/L$

(II) $mmol/L * valence\ element = meq/L$

(III) meq/L * volume samples (L) / weight solid sample (g) = meq/weight sample

Convert to 100g by multiplying sample weight with factor (100g/ sample (g))

(IV) $\frac{(mg/L*volume\ of\ sample)}{weight\ solid\ [g]} = mg\ of\ element/g\ solid$

(V) $\frac{mg/g\ element}{mol\ weight\ element\ [g/mol]} * valence\ of\ element$

Table A. 6: List of mol weight (g/mol) for each element used, with valence of ion (+/-).

Ca (2+)	**Mg (2+)**	**K (+)**	**Na (+)**
40.1	24.3	39.1	23.0
NH4 (+)	**H2O (0)**	**SO4 (2-)**	**Gypsum (0)**
18.0	18.0	96.0	172.1

SAR and ESP calculation:

(VI) ESP = (100 * Exchangeable Na)/Cation Exchange Capacity

(VII) ESP = (100 * Exchangeable Na)/ Σ(Exchangeab1e Ca+ Mg + K + Na + A1)

(VIII) SAR = $[Na^{+}]/([Ca^{2+}]+[Mg^{2+}]/2^{½}$

(IX) ESP = 1.475 * SAR/(l + 0.0147 * SAR)

(X) ESP = 1.95*SAR+1.8

A.IV: Chemical properties of column leachate

Table A. 7: pH measurements of leachates at different liquid/solid ratios

pH								
L/S ratio	1	2	3	4	5	6	8	10
BR 1	12.63	12.17	12.42	12.32	12.39	12.18	12.13	11.87
BR 2	12.66	12.20	12.42	12.36	12.47	12.14	12.15	11.95
BR 3	12.66	12.20	12.43	12.30	12.36	12.19	12.17	11.98
G10 1	9.26	10.49	10.34	10.06	9.89	10.40	10.13	9.24
G10 2	9.42	10.51	10.26	10.16	10.10	10.28	10.08	8.74
G10 3	9.84	10.41	10.10	10.06	10.01	10.17	10.05	8.75
G10A 1	9.35	9.62	9.43	9.10	8.39	10.53	9.17	8.55
G10A 2	9.03	9.48	9.25	8.90	8.46	9.78	8.62	8.48
G10A 3	8.86	9.15	8.73	8.11	7.77	8.80	7.76	8.04
G5A 1	8.81	10.50	8.84	8.40	7.13	10.95	10.52	9.61
G5A 2	8.11	9.46	9.25	8.90	8.95	8.81	8.52	9.40
G5A 3	7.99	9.46	9.08	8.91	9.66	7.41	9.01	9.11
G10F 1	6.86	6.03	6.74	7.82	7.87	7.72	7.31	7.48
G10F 2	6.15	5.54	6.20	8.19	8.16	8.26	7.46	7.49
G10F 3	6.29	5.82	6.50	8.38	8.98	7.18	7.27	7.60
G5F 1	8.81	9.22	8.76	7.28	6.42	9.01	7.73	8.36
G5F 2	8.11	9.40	8.94	8.02	7.71	8.64	7.92	8.34
G5F 3	7.99	9.25	9.21	8.72	8.64	8.89	9.59	9.21

Table A. 8: Electrical conductivity measurements in leachates at different liquid/solid ratios.

L/S	1	2	4	6	8	9	10
BR 1	6.5	4.37	4.41	3.38	2.76	2.52	2.24
BR 2	6.85	4.53	4.56	3.49	2.77	2.62	2.05
BR 3	7.2	4.92	4.7	3.59	2.9	2.8	2.22
G10 1	5.3	3.5	3.5	3.75	2.51	2.43	2.1
G10 2	5.2	3.4	3.47	3.72	2.53	2.41	2.1
G10 3	4.9	3.3	3.45	3.62	2.51	2.43	2.12
G10A 1	4.7	3.1	3.61	3.65	2.52	2.37	2.27
G10A 2	4.6	2.97	3.42	3.49	2.45	2.48	2.44
G10A 3	4.7	3.0	3.59	3.93	2.62	3.0	2.88
G5A 1	4.7	3.0	3.1	3.1	1.3	0.917	0.804
G5A 2	5.7	3.1	3.13	3.2	2.15	1.74	0.81
G5A 3	5.4	2.8	3.1	3.34	2.06	1.05	0.805
G10F 1	5.5	3.3	4.51	4.4	3.88	2.13	2.03
G10F 2	6.5	7.3	7.0	6.05	3.24	1.95	2.45
G10F 3	5.9	6.28	6.04	10.46	4.0	3.97	2.09
G5F 1	12.03	4.4	3.7	4.56	2.07	2.07	0.966
G5F 2	10.66	4.4	3.6	3.66	2.27	1.15	1.2
G5F 3	13.5	3.6	3.3	3.45	1.97	1.19	0.647

Table A. 9: Dissolved organic carbon (mg/L) and acid buffer capacity of leachates (mmol/L), at early and late L/S steps.

DOC (mgL)				
Sample	**L/S 1**	**L/S 2**	**L/S 9**	**L/S 10**
G10 1	410	<2.5	<2.5	490
G10 2	300	2.9	<2.5	<2.5
G10 3	370	2.7	<2.5	<2.5
G10A 1	170	38	6.9	<2.5
G10A 2	370	64	6.4	16
G10A 3	230	20	5.9	16
G5A 1	680	62	14	19
G5A 2	430	26	12	38
G5A 3	620	22	19	22
G10F 1	3700	960	19	99
G10F 2	2300	800	82	180
G10F 3	1800	290	67	120
G5F 1	3700	190	44	140
G5F 2	2300	360	70	37
G5F 3	4200	680	27	61

Acid buffer capacity to pH 4.5 (mmol/L)		
Treatment	L/S 1	L/S 10
BR 1	16.988	7.42
BR 2	17.38	6.21
BR 3	15.992	9.87
G10 1	2.706	0.374
G10 2	2.900	0.32
G10 3	2.420	0.54
G10A 1	5.686	2.11
G10A 2	5.728	1.104
G10A 3	3.690	1.672
G5A 1	6.097	4.47
G5A 2	1.439	2.898
G5A 3	3.556	2.4
G10F 1	3.094	1.504
G10F 2	1.667	0.85
G10F 3	2.270	3.95
G5F 1	2.736	1.8
G5F 2	2.320	4.114
G5F 3	2.648	5.08

Table A. 10: Analysis of Ca, Mg, Na and K (mg/L) from column leachates, by MP-AES.

Column leachate MP-AES analysis, in mg/L									
LOD	**Ca**	**Mg**	**Na**	**K**	LOQ	**Ca**	**Mg**	**Na**	**K**
	0.90978	0.025	0.2618	0.04734		3.0326	0.085	0.8726	0.158
L/S 1-5					**L/S 6-10**				
ID	**Ca**	**Mg**	**Na**	**K**	ID	**Ca**	**Mg**	**Na**	**K**
Blank	0.12	0.011	<0,086	<0,057	Blank	0.12	0.011	<0,086	<LD
Blank	0.13	0.011	<0,086	<0,057	Blank	0.13	0.011	<0,086	<LD
1643 H	29	8.2	21	2.1	Blank	0.12	0.011	<0,086	<LD
G10 1	730	0.19	30000	94	G10 1	530	<LD	600	0.81
G10 2	770	0.29	21000	73	G10 2	520	<LD	600	0.76
G10 3	770	0.32	34000	94	G10 3	520	<LD	630	0.93
G10A 1	870	0.74	28000	240	G10A 1	550	<0,085	710	3.4
G10A 2	820	1.4	24000	270	G10A 2	540	0.12	670	3.3
G10A 3	690	0.99	22000	200	G10A 3	490	0.29	840	3.4
G5A1	680	0.34	33000	220	G5A1	350	<0,085	460	1.9
G5A2	490	0.62	28000	180	G5A2	260	<0,085	700	2.4
G5A3	800	0.59	29000	240	G5A3	350	0.12	710	2.7
G10F 1	910	1.2	12000	100	G10F 1	570	<0,085	630	3.5
G10F 2	1600	3.2	7300	88	G10F 2	530	0.39	1200	8.0
G10F 3	1500	1.2	7100	86	G10F 3	380	0.13	450	2.4
G5F 1	1300	3.9	15000	150	G5F 1	120	<0,085	530	2.9
G5F 2	540	0.96	13000	85	G5F 2	140	0.20	1000	6.0
G5F 3	1200	0.84	17000	160	G5F 3	300	<LD	590	3.2
G10 1	440	<LD	7000	11	G10 1	560	<LD	480	0.62
G10 2	460	<LD	9700	17	G10 2	560	<LD	440	0.59
G10 3	460	<LD	7700	13	G10 3	550	<LD	450	0.54
G10A 1	460	<LD	11000	59	G10A 1	570	<0,085	440	1.7
G10A 2	460	<LD	9900	61	G10A 2	540	0.14	520	2.2
G10A 3	460	0.084	10000	71	G10A 3	510	0.32	730	2.4
G5A1	420	<LD	7900	42	G5A1	4.4	<0,085	240	1.7
G5A2	340	<LD	6800	41	G5A2	84	<0,085	610	1.7
G5A3	410	<LD	9300	46	G5A3	130	<0,085	590	2.0
G10F 1	890	0.71	12000	110	G10F 1	570	<0,085	430	2.0
G10F 2	720	1.9	8100	59	G10F 2	430	0.24	750	3.0
G10F 3	750	0.62	11000	78	G10F 3	340	0.76	820	4.5
G5F 1	860	0.56	12000	93	G5F 1	56	<0,085	440	2.2
G5F 2	520	<LD	11000	84	G5F 2	53	<0,085	540	2.6
G5F 3	830	<LD	11000	84	G5F 3	160	0.31	300	1.5
G10 1	440	<LD	2400	3.3	G10 1	2400	<LD	1600	1.6
G10 2	460	<LD	2500	2.9	G10 2	2500	<LD	1500	1.3
G10 3	450	<LD	2500	2.9	G10 3	2400	<LD	1500	1.4
G10A 1	440	<LD	3400	15	G10A 1	2400	<LD	2200	6.4
G10A 2	440	<LD	2800	15	G10A 2	2300	0.034	2800	8.5
G10A 3	440	<LD	3100	15	G10A 3	2100	0.16	3900	9.2
G5A1	410	<LD	2900	11	G5A1	7.5	<LD	1200	3.3
G5A2	340	<LD	3400	13	G5A2	110	<LD	2300	5.2
G5A3	380	0.18	3300	11	G5A3	16	<LD	1300	2.7
G10F 1	590	0.28	3400	20	G10F 1	2500	<LD	1500	5.7
G10F 2	500	0.39	5200	29	G10F 2	1000	0.22	2600	12
G10F 3	470	0.13	1900	14	G10F 3	2100	0.38	2700	13
G5F 1	260	0.44	2500	13	G5F 1	220	<LD	1300	4.0
G5F 2	250	0.057	2800	15	G5F 2	97	<LD	1400	4.9
G5F 3	580	0.20	4400	25	G5F 3	53	<LD	830	4.1
G10 1	470	<LD	940	1.8	G10 1	550	<LD	510	0.74
G10 2	440	<LD	910	1.7	G10 2	530	<LD	510	0.59
G10 3	410	<LD	860	1.7	G10 3	540	<LD	520	0.61
G10A 1	520	<0,085	1100	5.6	G10A 1	530	<0,085	660	2.3
G10A 2	520	0.11	980	5.9	G10A 2	560	<0,085	660	2.3
G10A 3	490	0.24	1100	5.7	G10A 3	460	0.65	1800	5.9
G5A1	470	<0,085	940	4.8	G5A1	7.6	<LD	770	0.79
G5A2	370	<0,085	1100	3.6	G5A2	160	0.27	590	3.4
G5A3	420	0.12	950	3.8	G5A3	11	<0,085	740	2.2
G10F 1	670	0.30	1500	9.4	G10F 1	530	0.42	1000	5.1
G10F 2	610	0.84	2500	20	G10F 2	450	0.18	700	3.0
G10F 3	460	1.0	2500	17	G10F 3	270	1.0	950	4.5
G5F 1	210	0.26	1200	6.7	G5F 1	8.1	<LD	370	1.1
G5F 2	150	<0,085	1600	9.5	G5F 2	25	<LD	290	0.93
G5F 3	390	<LD	1100	6.2	G5F 3	16	<LD	280	1.1
1643 H	29	8.2	21	2.1	1643 H	28	7.9	19	2.0

Table A. 11: Sodium adsorption ratio (SAR) from column leachates at L/S 1 and L/S 10.

SAR (mol/L/√mol/L)		
Treatment	L/S 1	L/S 10
G10 1	305.7	6.0
G10 2	208.3	6.1
G10 3	337.3	6.2
G10A 1	261.2	7.9
G10A 2	230.5	7.7
G10A 3	230.4	23.1
G5A1	348.3	76.9
G5A2	348.0	12.8
G5A3	282.2	61.4
G10F 1	109.4	12.0
G10F 2	50.2	9.1
G10F 3	50.4	15.9
G5F 1	114.3	35.8
G5F 2	153.8	16.0
G5F 3	135.1	19.3

A.V Aggregate stability

Table A. 12: Aggregate stability by wet sieving method, on aggregates from field samples. Analysis was done on moist samples, stable/unstable fractions calculated on dry basis. Adjusted (a) marks that some very stable measurements were destroyed and had to be corrected with measured moisture content of these samples.

Weight (gram)																	
Label	**Empty sieve, container 1, 2 and 3**				**BR**	**Dried containers**				**Treat-ment**	**Net weight**				**>0.25mm**	**Total dry**	**MC**
	Sieve	1	2	3		1	2	3	Sieve		Unstable	Stable	Very stable	Sum	**Left in sieve**	**mass**	**(%)**
H1	24.186	30.6855	2.133	2.175	10.102	32.503	3.13	6.384	25.021	G5A10	1.82	1.00	4.21	7.02	0.84	7.86	28.55
H1	24.186	30.6855	2.133	2.175	10	32.406	3.494	6.179	25.044	G5A10	1.72	1.36	4.00	7.09	0.86	7.94	25.89
H2	25.222	30.4696	2.143	2.172	10.127	31.806	3.088	6.445	26.654	G15A10	1.34	0.95	4.27	6.55	1.43	7.99	26.80
H2	25.222	30.4696	2.143	2.172	10.023	32.134	2.835	5.946	26.969	G15A10	1.66	0.69	3.77	6.13	1.75	7.88	27.24
H3	24.509	29.9847	2.172	2.16	10.112	32.371	3.148	4.891	25.662	G15	2.39	0.98	2.73	6.09	1.15	7.25	39.55
H3	24.509	29.9847	2.172	2.16	10.032	31.752	3.285	5.808	25.266	G15	1.77	1.11	3.65	6.53	0.76	7.29	37.70
H4	24.622	29.931	2.135	2.164	10.051	32.194	4.199	5.146	25.041	G5A10	2.26	2.06	2.98	7.31	0.42	7.73	30.06
H4	24.622	29.931	2.135	2.164	10.022	32.274	3.752	5.453	25.14	G5A10	2.34	1.62	3.29	7.25	0.52	7.77	29.03
J1	24.382	30.634	2.125	2.117	10.159	36.686	3.05	2.702	25.479	BR+10soil	6.05	0.93	0.59	7.56	1.10	8.66	17.32
J1	24.382	30.634	2.125	2.117	10.018	36.627	2.704	3.042	25.412	BR+10soil	5.99	0.58	0.93	7.50	1.03	8.53	17.49
J2	24.016	30.489	2.173	2.162	10.127	33.304	3.146	5.573	25.43	G5	2.82	0.97	3.41	7.20	1.41	8.61	17.58
J2	24.016	30.489	2.173	2.162	10.014	32.897	3.828	5.421	24.057	G5	2.41	1.66	3.26	7.32	0.04	7.36	36.00
J3	24.705	30.404	2.144	2.158	10.012	32.944	3.066	5.545	25.063	G10	2.54	0.92	3.39	6.85	0.36	7.21	38.92
J3	24.705	30.404	2.144	2.158	10.025	32.741	3.188	5.898	25.763	G10	2.34	1.04	3.74	7.12	1.06	8.18	22.57
J4	24.044	30.633	2.141	2.127	10.102	31.686	3.149	6.551	25.534	G5A10	1.05	1.01	4.42	6.49	1.49	7.98	26.67
J4	24.044	30.633	2.141	2.127	10.017	32.084	2.828	6.91	24.933	G5A10	1.45	0.69	4.78	6.92	0.89	7.81	28.26
B 1	24.186	2.17	2.13	2.154	10.151	4.822	4.274	3.752	24.951	A10	2.65	2.14	1.60	6.39	0.77	7.16	41.79
B 1	24.36	2.045	2.139	2.182	10.131	6.241	4.36	2.672	24.855	A10	4.20	2.22	0.49	6.91	0.50	7.40	36.87
B 2	25.222	2.142	2.127	2.161	10.093	3.08	4.04	5.502	26.525	G15A10	0.94	1.91	3.34	6.19	1.30	7.50	34.66
B 2	25.201	2.053	2.146	2.156	10.053	3.432	3.311	5.982	26.597	G15A10	1.38	1.17	3.83	6.37	1.40	7.77	29.45
B 3	24.509	2.166	2.175	2.131	10.14	4.324	3.362	5.129	26.081	G15	2.16	1.19	3.00	6.34	1.57	7.92	28.11
B 3	24.679	2.045	2.142	2.199	10.066	3.748	3.5	4.678	26.664	G15	1.70	1.36	2.48	5.54	1.99	7.53	33.77
B 4	24.622	2.163	2.167	2.133	10.136	4.477	3.494	4.45	26.025	G10A10	2.31	1.33	2.32	5.96	1.40	7.36	37.70
B 4	24.725	2.031	2.131	2.196	10.026	3.794	4.313	5.451	25.821	G10A10	1.76	2.18	3.26	7.20	1.10	8.30	20.85
C 1	24.382	2.17	2.18	2.147	10.111	5.796	2.624	3.349	25.814	A10	3.63	0.44	1.20	5.27	1.43	6.70	50.82
C 1	24.163	2.072	2.148	2.193	10.107	4.181	3.522	4.577	25.387	A10	2.11	1.37	2.38	5.87	1.22	7.09	42.53
C 2	24.016	2.146	2.132	2.137	10.108	4.948	3.949	4.451	24.946	G5	2.80	1.82	2.31	6.93	0.93	7.86	28.55
C 2	24.902	2.058	2.136	2.18	10.16	5.427	3.926	3.863	25.729	G5	3.37	1.79	1.68	6.84	0.83	7.67	32.48
C 4	24.705	2.143	2.125	2.185	10.136	6.022	3.531	4.738	25.215	BR+10soil	3.88	1.41	2.55	7.84	0.51	8.35	21.42
C 4	24.782	2.068	2.146	2.196	10.147	4.251	4.119	6.26	25.045	BR+10soil	2.18	1.97	4.06	8.22	0.26	8.48	19.62
F 1	24.044	2.168	2.139	2.173	10.178	6.165	4.937	3.169	24.855	BR+10soil	4.00	2.80	1.00	7.79	0.81	8.60	18.32
F 1	28.542	2.126	2.165	2.183	10.169		6.128	3.677	29.343	BR+10soil	4.00	3.96	1.49	9.46	0.80	10.26	-0.87
E 1	24.36	2.225	2.146	2.158	10.146	7.866	3.453	3.017	24.657	BR	5.64	1.31	0.86	7.81	0.30	8.10	25.20
E 1	24.163	2.159	2.154	2.161	10.128	7.234	3.616	3.396	24.444	BR	5.08	1.46	1.24	7.77	0.28	8.05	25.77
E 2	25.201	2.177	2.142	2.148	10.151	4.971	3.152	4.526	26.335	G10A10	2.79	1.01	2.38	6.18	1.13	7.32	38.75
E 2	24.902	2.141	2.163	2.157	10.128	5.172	2.585	5.468	25.635	G10A10	3.03	0.42	3.31	6.76	0.73	7.50	35.09
E 4	24.679	2.168	2.149	2.146	10.177	4.644	3.729	4.983	26.004	G15	2.48	1.58	2.84	6.89	1.33	8.22	23.84
E 4	24.782	2.148	2.124	2.143	10.087	5.628	3.713	3.722	25.903	G15	3.48	1.59	1.58	6.65	1.12	7.77	29.84
F 2	24.725	2.164	2.173	2.196	10.126	3.791	4.067	5.132	25.594	G10	1.63	1.89	2.94	6.46	0.87	7.33	38.22
F 2	28.542	2.137	2.126	2.167	10.135	3.668	5.228	4.198	29.46	G10	1.53	3.10	2.03	6.66	0.92	7.58	33.67
I 1	24.186	30.6855	2.154	2.169	10.126	32.694	3.345	5.166	25.731	G15A10	2.01	1.19	3.00	6.20	1.55	7.74	30.80
I1	25.222	30.4696	2.169	2.202	10.131	32.454	3.038	5.631	26.641	G15A10	1.98	0.87	3.43	6.28	1.42	7.70	31.55
I 2	24.509	29.9847	2.185	2.161	10.157	32.095	3.265	5.346	25.612	G10A10	2.11	1.08	3.19	6.38	1.10	7.48	35.82
I 2	24.622	29.931	2.187	2.165	10.154	32.073	3.306	5.07	25.926	G10A10	2.14	1.12	2.91	6.17	1.30	7.47	35.93
G1	24.382	30.634	2.139	2.138	10.102	35.303	3.644	3.063	24.864	A10	4.67	1.51	0.93	7.10	0.48	7.58	33.25
G1	24.016	30.489	2.173	2.167	10.153	35.066	3.563	2.828	24.587	A10	4.58	1.39	0.66	6.63	0.57	7.20	41.03
G4	24.705	30.404	2.154	2.163	10.108	32.369	4.972	4.948	24.959	G5	1.97	2.82	2.79	7.57	0.25	7.82	29.23
G4	24.044	30.633	2.161	2.153	10.063	33.48	4.863	3.974	24.318	G5	2.85	2.70	1.82	7.37	0.27	7.64	31.65
D1	24.785	30.631	4.199	a	8.06	31.692	5.725	a	25.128	G10	1.06	1.53	5.47	8.06	0.34	8.40	30.51
D1	28.546	30.451	2.103	a	8.084	31.608	2.862	a	28.887	G10	1.16	0.76	6.17	8.08	0.34	8.43	30.58
D2	24.703	29.945	2.168	a	8.031	34.554	2.8	a	24.868	BR	4.61	0.63	2.79	8.03	0.16	8.20	31.99
D2	24.195	29.89	4.273	a	8.032	34.731	4.789	a	24.395	BR	4.84	0.52	2.68	8.03	0.20	8.23	31.11
D4	24.687	30.567	2.159	a	8.023	34.759	2.928	a	24.847	BR	4.19	0.77	3.06	8.02	0.16	8.18	31.36
D4	25.224	30.441	2.167	a	8.02	34.768	2.671	a	25.363	BR	4.33	0.50	3.19	8.02	0.14	8.16	29.79

Table A. 13: Aggregate stability by wet sieve method prior to plant growth.

Wet sieve aggregate stability for lab samples before plant growth (dry samples)									
Treatment	Empty containers			BR	Dried containers		Net weight		
	Sieve	Cont. 1	Cont.2		Cont. 1	Cont. 2	Stable	Unstable	Sum
BR1	26.2	30.7	2.2	4.0	31.4	5.4	3.2	0.8	4.0
BR 1	25.2	30.5	2.1	4.0	30.9	2.6	0.4	0.5	0.9
BR 2	25.0	30.4	2.1	4.0	30.9	2.5	0.4	0.5	0.8
BR2	25.3	30.5	2.1	4.0	31.1	5.4	3.3	0.6	3.9
G10 1	26.1	30.0	2.1	4.0	30.7	5.4	3.3	0.8	4.0
G10 2	24.2	29.9	2.2	4.0	30.5	5.4	3.2	0.5	3.7
G10 3	26.0	30.6	2.1	4.0	31.4	5.2	3.1	0.8	3.8
G10A 1	25.2	30.5	2.1	4.0	31.2	5.0	2.9	0.7	3.6
G10A 2	25.0	30.6	2.2	4.0	31.1	2.6	0.4	0.5	0.9
G5A 1	24.5	30.4	2.1	4.0	31.3	4.8	2.7	0.9	3.5
G5A 1	24.6	30.6	2.1	4.0	31.7	4.5	2.4	1.1	3.5
G10F 1	28.8	30.7	2.2	4.0	31.4	3.0	0.8	0.8	1.6
G10F 2	24.2	30.5	2.1	4.0	30.7	2.6	0.5	0.3	0.7
G10F 3	25.1	30.0	2.2	4.0	30.2	2.5	0.4	0.2	0.6
G5F 1	24.6	29.9	2.1	4.0	30.2	2.5	0.4	0.2	0.6
G5F 2	25.0	30.6	2.1	4.0	31.3	2.8	0.6	0.6	1.3

Table A. 14: Aggregate stability by rainfall method, prior to plant growth

Aggregate stability on laboratory columns by rainfall simulator, before plant growth.

Treatment	Filter	BR	Filter	BR	Dry weight		Net		Unstable	
	paper	**0.5-2**	paper	**2-6mm**	**0.5-2**	**2-6mm**	**0.5-2**	**2-6mm**	**0.5-2**	**2-6mm**
BR 1	4.60	8.20	4.66	13.38	10.44	15.50	5.84	10.85	2.37	2.54
BR 2	2.31	9.75	2.41	10.68	8.95	11.84	6.64	9.43	3.11	1.25
G10 1	2.30	24.06	2.40	14.72	21.77	15.25	19.48	12.84	4.59	1.88
G10 2	2.35	10.12	2.41	11.75	9.33	12.70	6.98	10.29	3.14	1.46
G10 3	2.39	18.13	2.35	3.47	16.67	5.21	14.27	2.86	3.86	0.61
G10A 1	2.35	17.23	2.38	3.28	15.59	5.56	13.25	3.17	3.98	0.11
G10A 2	2.37	21.39	2.39	12.94	19.11	13.62	16.75	11.23	4.64	1.71
G5A 1	2.40	18.55	2.36	5.80	13.20	6.35	10.80	4.00	7.75	1.80
G5A 2	2.37	18.53	2.33	8.74	14.48	7.73	12.11	5.39	6.42	3.35
G10F 1	2.38	18.71	2.39	15.65	18.29	16.51	15.91	14.13	2.80	1.52
G10F 2	2.38	21.26	2.36	16.32	21.22	17.26	18.84	14.90	2.43	1.43
G10F 3	2.45	18.85	2.39	15.59	19.32	16.39	16.88	14.00	1.97	1.59
G10F 1	2.36	5.75	2.40	4.14	6.41	4.44	4.05	2.03	1.70	2.11
G10F 2	2.42	12.08	2.41	2.70	12.61	4.22	10.18	1.81	1.90	0.89

Table A. 15: Aggregate stability by wet sieving method, post plant growth

Wet sieve aggregate stability for lab samples after plant growth													
	Empty sieve and containers				Weighed	Dried, full containers and sieve				Net weight			
Treatment	Sieve	C.1	C.2	C.3	BR	C.1	C.2	C.3	Sieve	1 Net	2 Net	3 Net	SUM
G10 1	24.19	30.686	2.163	2.153	7.84	33.33	2.781	6.501	24.434	2.6405	0.618	4.348	7.6065
G10 1	25.22	30.47	2.171	2.161	7.92	33.52	3.157	5.83	25.479	3.0494	0.986	3.669	7.7044
G10 2	24.51	29.985	2.189	2.148	7.84	32.18	3.097	6.699	24.735	2.1943	0.908	4.5511	7.6534
G10 2	24.62	29.931	2.138	2.172	7.90	32.88	2.722	6.929	24.855	2.945	0.584	4.757	8.286
G10 3	24.38	30.634	2.148	2.153	8.00	33.02	2.659	6.314	24.615	2.388	0.511	4.161	7.06
G10 3	24.02	30.489	2.131	2.207	8.00	32.64	2.63	7.23	24.283	2.151	0.499	5.023	7.673
G10O5 1	24.71	30.404	2.132	2.237	8.00	32.34	2.964	6.141	25.185	1.938	0.832	3.904	6.674
G10O5 1	24.04	30.633	2.125	2.175	8.00	32.25	2.63	6.829	24.479	1.619	0.505	4.654	6.778
G10O5 2	24.36	2.143	2.196	2.098	7.92	3.265	3.237	7.539	24.782	1.122	1.041	5.441	7.604
G10O5 2	24.16	2.131	2.162	2.111	8.00	3.816	3.701	6.424	25.641	1.685	1.539	4.313	7.537
G10O5 3	25.2	2.071	2.153	2.102	7.97	2.85	2.743	8.275	25.105	0.779	0.59	6.173	7.542
G10O5 3	24.9	2.21	2.148	2.101	8.00	4.062	3.111	7.322	25.221	1.852	0.963	5.221	8.036
G5O5 1	24.68	2.165	2.151	2.133	8.00	3.23	2.548	7.328	24.709	1.065	0.397	5.195	6.657
G5O5 1	24.78	2.142	2.131	2.089	8.00	3.799	2.529	7.172	25.472	1.657	0.398	5.083	7.138
G5O5 2	24.73	2.189	2.161	2.093	8.00	2.688	2.935	8.407	25.246	0.499	0.774	6.314	7.587
G5O5 2	28.54	2.148	2.192	2.071	8.00	2.676	4.269	7.117	28.978	0.528	2.077	5.046	7.651
G5O5 3	24.19	30.672	2.208	2.175	7.92	32.96	3.229	6.377	24.635	2.292	1.021	4.202	7.515
G5O5 3	25.22	30.458	2.254	2.181	8.00	32.78	2.747	6.832	25.762	2.318	0.493	4.651	7.462
G10A5 1	24.5	29.971	2.235	2.209	8.00	31.76	2.674	7.056	24.687	1.788	0.439	4.847	7.074
G10A5 1	24.62	29.919	2.206	2.205	8.00	31.25	3.231	7.099	24.833	1.328	1.025	4.894	7.247
G10A5 2	24.38	30.607	2.201	2.177	8.00	32.41	3.05	7.008	24.625	1.801	0.849	4.831	7.481
G10A5 2	24.01	30.478	2.206	2.093	8.00	32.63	2.694	6.971	24.249	2.156	0.488	4.878	7.522
G10A5 3	24.7	30.379	2.201	4.333	8.00	32.11	2.731	8.416	24.999	1.727	0.53	4.083	6.34
G10A5 3	24.04	30.611	2.211	2.243	7.96	32.37	2.621	6.589	24.29	1.758	0.41	4.346	6.514
G5A5 1	24.36	2.189	2.119	2.148	8.00	3.215	3.242	7.916	24.615	1.026	1.123	5.768	7.917
G5A5 1	25.2	2.211	2.121	2.188	8.00	3.444	2.496	8.316	25.556	1.233	0.375	6.128	7.736
G5A5 2	24.68	2.202	2.113	2.193	8.00	2.797	2.828	8.554	24.969	0.595	0.715	6.361	7.671
G5A5 2	24.72	2.262	2.109	2.156	8.00	2.747	2.556	8.932	25.008	0.485	0.447	6.776	7.708
G5A5 3	24.16	2.222	2.161	2.227	8.00	3.149	3.2	7.999	24.412	0.927	1.039	5.772	7.738
G5A5 3	24.9	2.251	2.243	2.265	8.00	3.576	3.823	6.961	25.196	1.325	1.58	4.696	7.601
BR 3	24.78	2.205	2.161	2.235	8.00	2.81	2.741	9.035	25.077	0.605	0.58	6.8	7.985
BR 3	28.54	2.261	2.214	2.178	8.00	2.893	2.673	9.021	28.922	0.632	0.459	6.843	7.934

Table A. 16: Rainfall simulator aggregate stability, post plant growth

Aggregate stability on laboratory columns by rainfall simulator, AFTER plant growth.												
Treat-ment	Filter paper weight		BR	>0.5mm particles		Dry weight (incl. Filter)		Unstable amount		Stable amount		
	0.5-2mm	2-6mm		0.5-2mm	2-6mm	0.5-2mm	2-6mm	0.5-2mm	2-6mm	0.5-2mm	2-6mm	
G10 1	4.0	5.8	20.0	-	-	17.5	21.3	13.4	15.5	6.6	4.5	
G10 2	3.9	3.9	20.0	-	-	19.4	20.5	15.5	16.5	4.5	3.5	
G10 3	3.8	4.0	20.0	-	-	21.1	22.3	17.3	18.3	2.7	1.7	
G10O5 1	4.0	4.0	20.0	0.8	4.7	16.6	19.4	11.8	10.8	7.4	4.5	
G10O5 2	3.9	3.9	20.0	0.4	3.3	18.4	17.5	14.1	10.3	5.5	6.4	
G10O5 3	3.8	3.9	20.0	0.5	1.6	19.3	19.9	15.0	14.4	4.5	4.0	
G5O5 1	3.8	3.8	20.0	1.1	4.1	16.9	18.8	12.0	11.0	6.9	5.0	
G5O5 2	3.8	3.7	20.0	1.1	1.9	18.2	18.4	13.4	12.8	5.6	5.3	
G5O5 3	3.8	3.8	20.0	1.2	2.3	18.9	19.4	14.0	13.2	4.9	4.4	
G10A5 1	2.3	2.4	20.0	0.8	1.2	16.7	18.8	13.6	15.3	5.6	3.5	
G10A5 2	2.4	2.3	20.0	1.3	0.3	19.8	20.8	16.2	18.2	2.5	1.5	
G10A5 3	2.4	2.3	20.0	0.8	0.5	13.7	16.2	10.5	13.4	8.7	6.2	
G5A5 1	2.3	2.4	20.0	0.6	0.3	19.1	20.8	16.2	18.1	3.2	1.6	
G5A5 2	2.5	2.4	20.0	0.7	0.7	18.9	20.5	15.7	17.5	3.6	1.9	
G5A5 3	2.4	2.4	20.0	0.6	0.4	18.8	20.0	15.8	17.1	3.6	2.4	

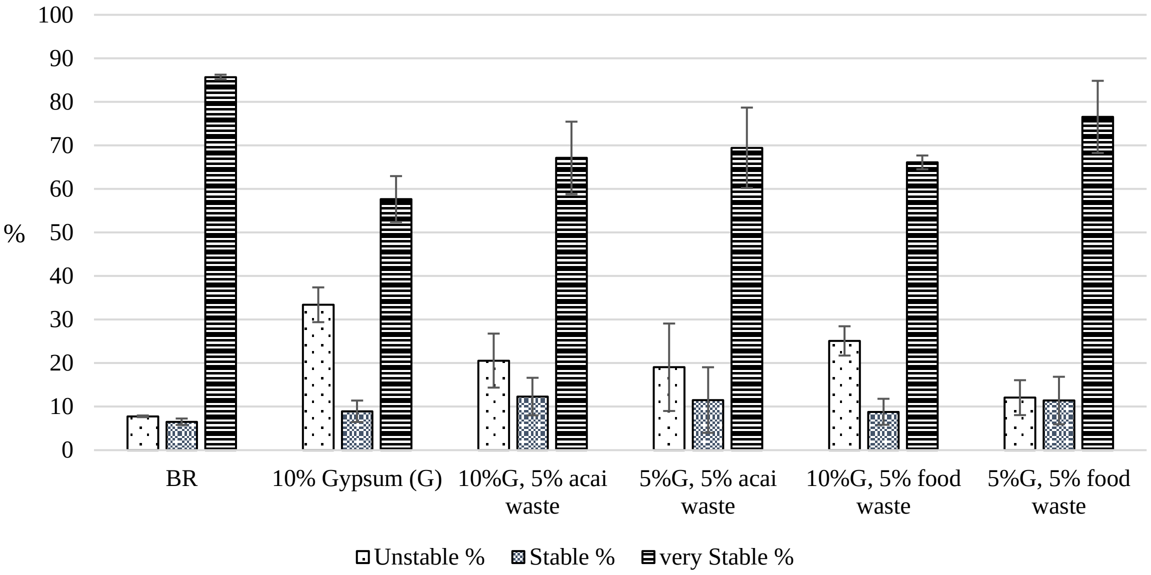

Figure A. 2: Aggregate stability of laboratory samples, which were considered overestimated.

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