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Sustained Bauxite Residue Rehabilitation with Gypsum and Organic Matter 16 years after Initial Treatment

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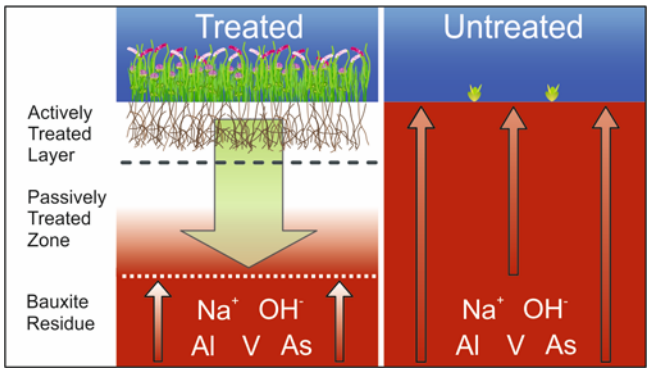
Graphical Abstract



Abstract

Bauxite residue is a high volume by-product of alumina manufacture which is commonly disposed of in purpose-built bauxite residue disposal areas (BRDAs). Natural waters interacting with bauxite residue are characteristically highly alkaline, and have elevated concentrations of Na, Al, and other trace metals. Rehabilitation of BRDAs is therefore often costly and resource/infrastructure intensive. Data is presented from three neighbouring plots of bauxite residue that was deposited twenty years ago. One plot was amended 16 years ago with process sand, organic matter, gypsum, and seeded (fully treated), another plot was amended 16 years ago with process sand, organic matter, and seeded (partially treated), and a third plot was left untreated. These surface treatments lower alkalinity and salinity, and thus produce a substrate more suitable for biological colonisation from seeding. The reduction of pH leads to much lower Al, V and As mobility in the actively treated residue and the beneficial effects of treatment extend passively 20-30 cm below the depth of the original amendment. These positive rehabilitation effects are maintained after 2 decades due to the presence of an active and resilient biological community. This treatment may provide a lower cost solution to BRDA end of use closure plans and orphaned BRDA rehabilitation.

Introduction

Globally, >100 million tonnes of alumina is produced annually.[1] Producing 1 tonne of alumina generates 1-2 tonnes of bauxite residue (known as "red mud"). The residue varies with ore type, but all are alkaline, sodic, and contain similar minerals. In the Bayer process bauxite ore is digested with NaOH at high temperature and pressure which results in recrystallization of iron oxides present. Silica is a common impurity, which is removed from solution by precipitation of a range of characteristic Na- and Ca-aluminosillicate phases (e.g. sodalite and cancrinite).[2,3] These "desilication products" reside predominantly in the fine fraction. Residual aluminium (oxy)hydroxide phases, quartz, zircon and titanium oxides (e.g. rutile and perovskite) also occur in the residues.[2,3]

Bauxite residue has few uses (cement, iron and steel production, construction materials) and most is sent to bauxite residue disposal areas (BDRAs).[4] The liquid from bauxite residue is very alkaline (pH 11-13) and contains abundant sodium.[5–7] Subsequent dissolution of desilication products such as sodalite (Eqn 1.) and cancrinite (Eqn 2), along with associated amorphous secondary phases, generates further alkalinity and releases sodium in the long term.[8–10] Trace elements in bauxite, such as V and As, become concentrated in the residue, and are often hosted in surface complexes and secondary phases.[10–14] This can be environmentally problematic as Al, V, and As form aqueous oxyanions in alkaline conditions which sorb poorly to sediments [15,16].

$$Na_6(Al_6Si_6O_{24}).2NaOH + 24H_2O \leftrightarrow 8Na^+ + 8OH^- + 6Al(OH)_3 + 6H_4SiO_4 \quad \text{(Eqn. 1)}$$

$$Na_6(Al_6Si_6O_{24}).2CaCO_3 + 26H_2O \leftrightarrow 6Na^+ + 2Ca^{+2} + 8OH^- + 2HCO_3^- + 6Al(OH)_3 + 6H_4SiO_4 \quad \text{(Eqn. 2)}$$

When left untreated, bauxite residue is infiltrated by CO_2 and the formation of aqueous and solid carbonate consumes OH^-, lowering pH.[17–19] The depth to which this

process can act within bauxite residue is controlled by the rate of in-gassing and diffusion of CO_2. These process can be enhanced by gypsum addition, providing excess Ca^{2+} for precipitation of carbonate.[20] These reactions occur rapidly at high pH and can eventually buffer the pH to 7.5-8.5.[17,21] Previous work has shown that gypsum addition can also decrease the mobility of trace metals and Al in bauxite residue effected soils.[17,21]. Other approaches to decrease bauxite residue salinity and alkalinity, such as treatment with acid[22] and seawater,[23] tend to only neutralise the aqueous, not the solid alkalinity generating phases. Ion exchange resins,[24] and bipolar-membranes electrodialysis[25] have been used to increase the longevity of treatment, yet these approaches rely on continued management and the utilisation of products by an active refinery. As such, common end-of-use practice is to cap BRDAs with an impermeable layer, cover with topsoil, and revegetate. The costs "cap and cover" approaches are high (e.g. 100k €/ha has been estimated for the BRDA in this study). However abandoning BRDAs without surface cover may lead to problems with long term water infiltration and dust formation.

Over the last 15 years Courtney and others have examined the effect of coarse fraction bauxite residue (process sand), gypsum, and organic matter on the revegetation of bauxite residue at Aughinish Alumina Refinery BRDA, Ireland.[26–36] These studies have assessed site rehabilitation by investigating macro- and microbiology, nutrient availability, and the chemical nature of the substrate. Beneficial effects from bio-rehabilitation have also been reported elsewhere.[37,38] Yet, little is known of the longevity and reliability of such surface treatments. Lack of long term data, and poorly constrained audit trails regarding treatment and planting histories, can limit their viability in BRDA closure plans. The objective of this study was to assess the long term effects of a surface treatment to bauxite residue. Here we report the chemical and mineralogical data

sampled from depth profiles of bauxite residue nearly two decades after initial treatment, and evaluate the ability of these treatments to provide sustained rehabilitation of the substrate and associated fluid.

Methods

In September 2015 trial pits were dug to ~60 cm in a BRDA located in a European Union member state with a temperate oceanic climate (average annual rainfall ~1m). At this site bauxite residue was deposited into a 3m deep disposal cell in 1995, and subsequently treated to encourage revegetation in 1999. Therefore, sampling was undertaken 20 years after deposition and 16 years after treatment. [31] Three plots within the BRDA were investigated. The fully treated plot was amended with gypsum (3% w/w rotavated-in to a depth 30 cm), process sand (10% w/w rotavated-in to a depth of 30cm), spent mushroom compost (80t Ha^{-1} rotavated-in to a depth of 20cm), and seeded with a grassland mix (*Agrostis stolonifera, Holcus lanatus, Lolium perenne, Trifolium repens,* and *Trifolium pratense*; 100 kg/ha).[31] The partially treated plot was amended only with process sand, spent mushroom compost, and then seeded. The third plot was left untreated. Samples of bauxite residue were collected to a depth of 50 cm from the trial pits in each of three different treatment zones. Duplicate sample profiles in each plot were taken from two separate clean vertical surfaces of trial pits and stored in polypropylene tubes. The dual depth profiles were sampled to observe and account for heterogeneity in the residue.

Field moist samples were stored at 5 °C before aqueous extraction for major and trace metals. 10 gram subsamples were mixed with 10 mL of ultrapure water (18.5 MΩ) and shaken at room temperature for seven days. The solution pH was measured using a Thermo Scientific Orion ROSS Ultra electrode calibrated with 4.00, 7.00, and 10.00 buffers (Fisher Scientific). 1 gram field moist subsamples were mixed with 10 mL of a 0.1 M Na_2HPO_4 in 0.01 M NaOH and shaken at room temperature for 7 days for phosphate extraction of metal oxyanions. Supernatant solutions from both the water and phosphate

extractions were filtered through 0.2 µm disposable polyethersulfone filters (Sartorius) and acidified in 5% HNO_3 for subsequent aqueous analysis by ICP-OES (Thermo Fisher iCAP 7400 Radial ICP-OES) (see SI section S1 for further details).

Further 10 g field moist subsamples were also dried at 105 °C for 24 hours to determine residue water content and for subsequent analysis by X-ray ray diffraction (XRD; Bruker D8 Advance diffractometer, 12 min. scans, 2 to 70° 2θ), X-ray fluorescence (XRF, Olympus Innovex X-5000 XRF analyser) and total carbon analysis (TC; LECO SC-144DR carbon analyser). The crystalline phases present were determined from XRD patterns by peak fitting using EVA (version 3.0, Bruker), and semi-quantitative relative proportions were calculated by Rietveld refinement using Topas (version 4.2, Bruker). Total organic carbon (TOC) were measured after a 24 hour digestion in 10% HCl at room temperature. Total inorganic carbon (TIC) was calculated from TC and TOC measurements.

Acid soluble inorganic and organic substances (AIC and AOC) were determined in 12 samples after extraction with 2 M HCl (1 g soil in 5 mL of 2 M HCl for 3 days at 4 °C). The extractant was then separated by centrifugation at 8000 *g* for 10 min, pH neutralised by drop-wise addition of 2 M NaOH, evaporated to dryness; and finally the resulting solid dissolved in ultra-pure water at 1 $g \cdot L^{-1}$.[39] Total carbon and total inorganic carbon in the extractant was determined using a Shimadzu total organic carbon analyser 5050A (LOD 4 µg kg^{-1}).

Separate samples of bauxite residue were collected from beneath the exposed vertical surface of each trial pit using a clean spatula, and sealed in sterile polypropylene centrifuge tubes. These samples for DNA analysis were refrigerated within 4 hours and frozen within 48hrs. DNA was isolated from 0.5 g of each sample using the MPBio

FastDNA SPIN Kit for Soil. Isolated DNA mass from each sample was determined by Qubit dsDNA High Sensitivity assay on a Qubit Fluorometer (Life Technologies; further details of quantification are in SI Section S3). DNA samples were sent to the Centre for Genomic Research, University of Liverpool, where Illumina TruSeq adapters and indices were attached to DNA fragments in a two-step PCR amplification that targets the V4 hyper-variable region of the 16s rRNA gene,[40] and the result was sequenced on the MiSeq platform. Reads were processed using the UPARSE pipeline[41] within the USEARCH software package (version 10, SI Section S3).[42] Sequence reads were allocated to operationally taxonomic units (OTUs) based on a minimum sequence identity of 97% between the putative OTU members, and then classified using the SILVA Living Tree Project 16s database, version 123.[43]

Difference in average element concentration between plot treatments (untreated, fully treated, and partially treated) was tested by ANCOVA (Analysis of Co-Variance) using a general linear model to assess difference in average concentrations across the treatments, with depth of sample as a co-variate. Pairwise comparisons were tested by post-hoc Tukey test using a significance level of $p = 0.05$. Statistical significance was expressed at $p < 0.05$ and $p < 0.001$ and the degrees of freedom for all tests varied between 19 and 64.

Results

Sampling observations

Both the fully treated and partially treated sites were vegetated with a variety of perennial grasses (*Holcus lanatus*), trifoliate clovers (*Trifolium pratense*), and occasional small shrubs (*Salix* spp.; Fig. S1), as has been described previously.[31] The untreated plot was largely unvegetated with one or two areas of stunted grasses (Fig. S1). The root zone of the fully treated and partially treated sites extended approximately 15 cm beneath the surface, and below 20cm the substrate had the appearance of dewatered bauxite residue with little change in appearance to 50 cm depth. The untreated profile had no root zone and at all depths had a very similar appearance to the residue in the other profiles at depths below 20 cm. The bottom of the untreated pit filled with leachate to a depth of about 10 cm after 2 hours.

Substrate characteristics

The pH of the untreated residue was 10.2 at the surface and steadily increased to 12.0 at a depth of 50 cm (Fig. 1; SI Table S2). The pH of the treated plots were notably and significantly lower ($p < 0.001$; Table S3). The fully treated residue was pH 7.6 at the surface, and increased steadily to a value of 9.6 at a depth of 50 cm. The pH value of the partially treated residue was 7.6 at the surface, increased steadily to a value of 10.8 at a depth of 50 cm, and was not significantly different from the fully treated residue ($p > 0.05$; Fig 2; Table S2-3).

The amount of sodium available to aqueous extraction of the untreated bauxite residue was ~900 mg kg^{-1} of bauxite residue, and with exception of concentrations at the surface and at 50 cm there was little variation with depth (Fig. 1, Table S2). The amount

of Na that could be extracted from the fully treated and partially treated samples demonstrated no trend with depth and were not significantly different from each other ($p > 0.05$; Table S3). Fully and partially treated residue contained concentrations approximately 10-15 % of those extracted from the untreated residue at the same depth ($p < 0.001$; Fig. 1; Table S2-3). The concentration of silicon available to aqueous extraction in the untreated bauxite residue was 5 mg kg^{-1}, and apart from the measured concentration from 50 cm there was minimal variation with depth (Fig. 1, Table S2). Si concentrations extracted from fully treated and partially treated bauxite residue were ~4 mg kg^{-1} below 5 cm, and ~ 13 mg kg^{-1} above 5cm, there was no significant difference between fully, partially, or untreated residue ($p > 0.05$; Fig. 1; Table S2-3). Calcium concentrations from the aqueous extraction of untreated bauxite residue ranged from 3 mg kg^{-1} at the surface to below the limit of detection at 50 cm (0.11 mg kg^{-1}) (Fig. 1, Table S2). In contrast Ca concentrations from fully treated and partially treated samples were significantly different to the untreated residue ($p < 0.001$; Table S3), 143 mg kg^{-1} at the surface decreasing to ~10 mg kg^{-1} at 20 cm, with further slight concentration decrease to ~2 mg kg^{-1} at 50 cm with no significant difference between treatments ($p > 0.005$; Fig. 1; Table S2-3).

The aluminium concentration available to aqueous extraction in untreated bauxite residue was ~10 mg kg^{-1} at the surface which increases steadily with depth to ~65 mg kg^{-1} at 50 cm (Fig 2. Table S2). Conversely, Al concentrations available in fully and partially treated samples were significantly different ($p < 0.001$, Table S3) and near the detection limit (0.09 mg kg^{-1}) at all depths, apart from at 30-50 cm where Al concentrations were 1-10 mg kg^{-1} (Fig 2. Table S2). There was no significant difference between treatments ($p > 0.05$, Table S3). The amount of vanadium available to aqueous

extraction from untreated bauxite residue was ~5 mg kg^{-1} and did not vary greatly with depth (Fig 2. Table S2). Aqueous extractable V in fully treated and partially treated samples were near detection limit at the surface (0.03 mg kg^{-1}) and increased gradually with depth to maximum concentrations of 3.9 mg kg^{-1} at 50 cm, significantly different from untreated residue ($p < 0.001$, Table S3) but not significantly different between fully and partially treated residue ($p > 0.05$; Fig 2; Table S2-3). Aqueous available arsenic concentrations from untreated bauxite residue were highest at the surface (0.3 mg kg^{-1}) and decrease with depth to 0.9 mg kg^{-1} at 50 cm depth (Fig 2. Table S2). With the exception of one sample, all measurements of aqueous extractable As from fully treated and partially treated bauxite residue were below detection limit (0.045 mg kg^{-1}) and significantly different from the untreated residue ($p < 0.001$; Fig 2; Table S2-3). Extraction at high pH using disodium phosphate demonstrated substantial concentrations of Al, V, and As were available in all bauxite residue treatments. Phosphate extractable Al concentrations from all treatments are generally all 25-50 mg kg^{-1} at all depths (no significant differences between treatments; $p > 0.05$; Table S2-3). V concentrations from the phosphate extraction of untreated bauxite residue range from 30-75 mg kg^{-1} at the surface to 30 mg kg^{-1} at 50 cm depth (Fig 2. Table S2). Phosphate available V from fully treated and partially treated samples was lowest at the surface (~15 mg kg^{-1}) and increases with depth to ~75 mg kg^{-1} at 50 cm, but with no significant differences between untreated, fully treated, or partially treated residue ($p > 0.05$; Fig 2. Table S2-3). Arsenic concentrations extracted from untreated bauxite residue at high pH with phosphate are ~2.5 mg kg^{-1} at the surface and decrease to < 1 mg kg^{-1} at 50 cm (Fig 2. Table S2). Phosphate extractable As from fully treated and partially treated samples increase with depth from ~1 mg kg^{-1} at the surface to ~2.5 mg kg^{-1} at 50 cm (Fig 2. Table S2). Phosphate extractable As from fully treated and partially treated residue were

229 significantly different ($p < 0.05$), though neither were significantly different from the
230 untreated residue ($p > 0.05$; Table S3).

231 The water content of the residue (weight of water as % of dry weight) at both the
232 fully and partially treated sites was over 50% near the surface, exhibited a minimum of
233 ~30 % at approximately 10 cm, and then increased to between 35 and 45 % at depths
234 below 20 cm (Table S2). In contrast the water content in the untreated profile was 35%
235 near to the surface, exhibited a maximum value of ~50 % at 10cm, and then decreased
236 slightly to 40 % at depths below 30 cm. Water in the untreated residue was significantly
237 different to fully treated residue ($p < 0.001$), but not significantly different from partially
238 treated residue ($p > 0.05$; Table S3)

239 The bulk mineralogy of bauxite residue from all plots were largely similar and
240 consist of 40-45% iron oxy-hydroxides, 20-30% aluminium oxy-hydroxides, 20-30%
241 titanium oxides, and 10-15% feldspathoids (Table 1, Table S4). At the untreated bauxite
242 residue plot there were no differences in the relative proportions of each phase with
243 depth. Variations in the relative proportions of phases within the residue as a function of
244 depth and treatment were within the range of uncertainty of Rietveld refinement (5 %).
245 The alkali generating feldspathoid and desilication product cancrinite was present at all
246 depths in all treatment sites (Table 1, Table S4). There was little difference in the bulk
247 elemental composition measured by XRF with either depth or treatment (Table S5). Fe,
248 Al, Ca, Si and Ti were the most abundant oxides in present each site (36 ±3, 10±2, 15 ±2,
249 5 ±1 and 4 ±1 wt. % respectively). Carbon was most concentrated in the top 10 cm of the
250 fully treated profile (Fig. 3), where TOC was approximately 2.5% and TIC was 1.5%.
251 Below 10 cm there was no discernible difference in carbon content between the fully
252 treated and untreated profiles. Samples of untreated bauxite had less than 0.5% TOC and

253 TIC at all depths. Acid extractable inorganic carbon (AIC) and organic carbon (AOC) was
254 only detectable in the top 10 cm of the fully treated and untreated bauxite residue, and
255 was below or at the limit of detection (<4 μg kg^{-1}) in all other samples (Table S2).

256 DNA mass isolated per gram of sample demonstrated a strong vertical gradient
257 and significant difference between the treated (fully treated and partially treated) and
258 untreated sites (Fig. 3, Table S6). DNA was concentrated in the top 12 cm of the fully
259 treated and partially treated sites where maximum concentrations were up to 14.3 μg g^{-1}.
260 The highest concentration of DNA in the untreated samples was 2.3 μg g^{-1} in the near
261 surface. Below 12 cm the DNA concentrations in the fully treated, partially treated and
262 untreated residue were negligible.

263 Sufficient bacterial DNA was recovered from the fully treated substrate (2 cm),
264 and partially treated substrate (2 and 5 cm) for Next Generation Sequencing (DNA
265 recovery from the untreated substrate was insufficient). Nine phyla individually
266 represented more the 1% of the population of each sample (Fig. S2, Table S7). At this
267 taxonomic level, there was little difference between bacterial communities of the fully
268 treated and partially treated substrate, with the most abundant phyla being
269 Acidobacteria (37 % of reads), Actinobacteria (19 %), Proteobacteria (18 %), and
270 Planctomycetes (14 %). The most abundant class within the Acidobacteria phylum was
271 Acidobacteria Gp6 (48 % of Acidobacteria). Actinomycetales (74 %) was the most
272 abundant order within the Actinobacteria phylum. Alphaproteobacteria (67 %) was the
273 most abundant class within the Proteobacteria. 100 % of the Planctomycetes phylum
274 mapped onto the Planctomycetaceae family.

275 The alpha diversity indices for each sample are shown in Table S8. Here we use
276 Hill numbers[44,45] as robust bacterial diversity measures which account for the distortions

277 of rare taxa.[44–47] D_0^{α}, the operational taxonomic unit (OTU) richness, ranges from ~1250
278 to 3850, however this diversity index is very sensitive to rare taxa, and takes no account
279 of OTU relative abundance. Indices that give a measure of the number of common (D_1^{α})
280 and dominant OTUs (D_2^{α}; Table S8), converge across the samples, demonstrating similar
281 diversity in the OTU populations. Common OTUs represent >79 % of total sequence reads
282 in each sample, and dominant OTUs accounted for 51-62 % of total reads in each sample.

283

Discussion

The geochemistry of 20 year old untreated bauxite residue

Fresh bauxite residue is highly alkaline (pH 10–13), highly sodic (abundant mobile Na), contains abundant solid phase alkalinity (e.g. desalination products; 2-51%) and can also can contain trace metals above threshold intervention levels. [10,12,26,27,48–52] The desilication products in fresh residue tend to have higher proportion of sodalite to cancrinite[10] however, with age sodalite can transform into cancrinite.[53] Initially the high pH and sodium contents are due to remnant NaOH from the Bayer Process. Previous work has shown that repeated replacement of pore water decreases the mass of fresh bauxite residue but does not alter final pH, Na^+, $Al(OH)_4^-$, CO_3^{2-}, or OH^- concentrations [8] due to the dissolution desilication products, and associated amorphous phases (Eqn 1, 2). When left untreated, the pH of bauxite residue is controlled by the balance between CO_2 infiltration from the atmosphere, and OH^- production through desilication product dissolution.

20 years after deposition the measured pH of the untreated bauxite residue ranges from pH 10 at the surface to pH 12 at 50 cm. XRD analysis indicates that cancrinite was the primary desilication product present (Table S4). At the surface, CO_2 in-gassing, in combination with cancrinite dissolution, and associated amorphous Fe, Al, and Si phase solubility, buffers the pore fluids to approximately pH 10. Atmospheric CO_2 in-gassing appears to extend ~20 cm from the surface (Fig. 1). Below 20 cm the bauxite residue appears to be isolated from the atmosphere and dissolution of cancrinite results in higher pH ($\geq$ 11.5; Fig. 1). Cancrinite dissolution also controls long term Na availability (Eqn. 2), and results in aqueous available Na concentrations of ~900 mg kg^{-1} in untreated bauxite residue after 20 years. However, dissolution of cancrinite appears to be incongruent at high pH. Cancrinite dissolution should produce equimolar concentrations of Na, Si, and

Al, (Eqn. 2) but the measured concentrations are far from stoichiometric (Fig. S3). Aqueous extractable Na concentrations from untreated samples are 100 to 400 times higher in concentration than extractable Si and 10 to 150 times the Al concentration, indicating a preferential retention of Si and Al in the solid phase.

This preferential retention of Al and Si in the solid phase is probably controlled by the precipitation of amorphous and crystalline secondary phases. At the highest pH measured, Al concentrations are close to equilibrium with gibbsite ($Al(OH)_3$) (Fig S2). The measured Al concentrations decrease as the pH decreases from 12 to 10, but exceeds concentrations in equilibrium with gibbsite. Over this pH range, Si concentrations are much lower than those expected for $SiO_{2(am)}$ equilibrium, suggesting an alternative solubility limiting phase. At high pH, with high Na concentrations, Al and Si can co-precipitate in amorphous cation-bridged alumino-silicate gels,[54] which may explain the low concentrations observed.

Sustained alkalinity generation throughout untreated bauxite residue is a concern because it may be associated with increased mobility of potentially toxic metal(oid) oxyanions such as Al, V, and As. Both V and As are reported to be present in bauxite residues primarily in the 5+ oxidation state as vanadate and arsenate species [10,12], and are found as surface adsorbed species (V can also be associated with neoformed hydrogarnet phases such as Katoite).[12] Conversely, Al availability is usually controlled by the solubility of Al (oxy)hydroxide phases, which typically have much higher solubility at high pH (see discussion above).[55] In alkaline phosphate extractions both OH^- and phosphate ions compete strongly for available sorption sites and promote the mobility of metal oxyanions.[14,20] The results of these extractions, therefore, demonstrate that there is abundant V and As adsorbed to bauxite residue (Fig. 2). In the untreated samples,

where pH > 10, As and V sorb poorly to mineral surfaces,[14–16,21,56–58] which is why only 10 and 15 % of the phosphate extractable As and V respectively were extractable water this fraction will be mobile in residue pore waters.

In summary, the bauxite residue from the untreated plot retains many of the characteristics of the fresh bauxite residue 20 years after deposition: high pH, a sizeable quantity of desilication products (particularly cancrinite), abundant available Na, high Al, V, and As concentrations, low organic carbon concentrations. Thus, untreated, it is an environment that is not conducive to spontaneous macro- or microorganism colonization through translocation.

Treated bauxite residue

16 years after bauxite residue treatment with process sand, organic matter and gypsum significant pH reduction (2 units) was observed over a depth that extends at least 30 cm below the actively treated surface layer (Fig. 1; Table S2). Aqueous sodium concentrations were an order of magnitude lower in the treated plots than untreated plot at all depths (Fig. 1; Table S2), and the availability of aluminium, vanadium, and arsenic were all lower in treated than untreated bauxite residue (Fig. 2; Table S2). These observations demonstrate that positive treatment effects observed in the short term are sustained, such as: improved permeability, particle aggregation, and drainage; pH neutralisation; decreased Na, Al, and Fe availability. [28,29] In natural soils, organic matter plays a key role in controlling particle aggregation,[59–61] and the application of spent mushroom compost may have improved residue structure. In highly alkaline conditions, organic matter dissolves and hydrolyses to form humic substances and lower molecular

355 weight organic anions.[62–64] This process lowers pH and releases organic bound nutrients
356 to the local environment. Other studies have reported significant reduction in pH
357 following organic matter application to bauxite residue.[28,29,65,66] Gypsum application
358 enhances pH neutralisation by CO_2 in-gassing via the precipitation of $CaCO_3$.[20,21] The net
359 reaction for this mechanism is:

360 $$CaSO_4.2H_2O + 2OH^- + CO_2 \rightleftharpoons CaCO_3 + SO_4^{2-} + 3H_2O \quad \text{(Eqn. 3)}$$

361 Increased CO_2 in-gassing and formation of dissolved carbonate species (supplementary
362 information Eqns S2-7) can buffer the pH to 7.5-8, similar to natural alkaline soils, thus
363 producing an environment less hostile to biological colonisation. At this site bauxite
364 residue treatment with gypsum (in addition to process sand and organic matter) resulted
365 in greater plant biomass in the first two years of growth,[26–28] and a more diverse and
366 developed vegetation succession after 6 years (i.e. partial replacement of clover by more
367 extensive grass cover and the establishment of small shrubs).[31] However, 16 years after
368 treatment, there is no significant chemical or microbiological difference between the fully
369 and partially treated substrate.

370 Long term alkalinity generation and sodium release in the 20 year old bauxite
371 residue is controlled by cancrinite dissolution. Cancrinite dissolution kinetics as a
372 function of pH is unreported in the literature, but the feldspathoids leucite and nepheline
373 exhibit dissolution kinetics that decrease by an order of magnitude as pH decreases from
374 12 to 7.[67–70] The dissolution kinetics of multioxide silicates, including aluminosilicates,
375 are controlled by the solubilities of secondary phases,[71] thus it is inferred that these
376 decreases in feldspathoid dissolution rate are linked to the solubilities of secondary
377 aluminium and silicon phases. It is reasonable to expect cancrinite dissolution kinetics to
378 vary with pH in a similar manner to other feldspathoids, decreasing by an order of

magnitude between pH 12 and 7. This suggests pH conditions established in treated bauxite residue from organic matter and gypsum addition decrease the rate of OH^- and Na^+ production from the dissolution of cancrinite and associated secondary phases (Fig. 1).

Aqueous extracted aluminium concentrations from partially and fully treated bauxite residue plotted as a function of pH (Fig. S3) fall on a line parallel to, but in between, the solubility lines of gibbsite and $Al(OH)_{3\ (am)}$. This is different to the trend observed for the untreated samples at higher pH, suggesting a different solubility controlling phase. Between pH 8 and 10 formation of dawsonite ($NaAlCO_3(OH)_2$) and an amorphous precursor to boehmite have been observed in bauxite residue treatment.[12,72] and may be the solubility controlling phases at this site. The phosphate extraction shows that there is abundant extractable Al, V, and As in both the partially and fully treated bauxite residue (Fig. 2; Table S2). However the aqueous extractions showed that nearer to neutral pH Al is secured in secondary phases, and the majority of V and As is sorbed to mineral surfaces[14–16,21,56–58] making Al, V, and As, much less available to aqueous solution (Fig. 2).

Long term maintenance of beneficial conditions

Rehabilitation of bauxite residue disposal areas by vegetation using the treatments described here is a pH dependant processes with benefits extending 20-30 cm beyond the initial treatment depth. After 20 years of rainwater infiltration the alkalinity generating phases have not been exhausted, thus other processes must be controlling residue neutralisation. 16 years after treatment, the original additives are

largely unobservable, with little chemical difference remaining from the application of gypsum. This suggests that the development of resilient vegetation on bauxite residue, along with associated rhizosphere microorganisms, may drive long term stability and chemical safety of treated bauxite residue. The organic matter applied to the surface layers is only detected in small quantities (Fig. 3) and has likely been degraded and recycled into plants and microorganisms. The products of gypsum addition are minimal; calcite was undetectable by XRD, and there is only a slight accumulation of Ca and TIC towards the surface of both treated zones. Process sand was present in the surface layer when sampling but heterogeneously distributed and undetectable mineralogically by XRD and chemically by XRF.

The supply of H^+ ions to depth that is driving pH neutralisation in treated bauxite residue may be photosynthetic in origin. This can occur via a combination of three mechanisms: (a) enhanced CO_2 flux from plant roots and associated microorganism respiration; (b) organic matter degradation in the biologically active surface layer, producing low molecular weight organic acids; and (c) secretion of low molecular weight organic acids by plant roots and rhizospheric microorganisms. The carbon flux from atmosphere to rhizosphere is well documented in both the short (i.e. respiration), and medium terms (organic matter production).[73] Quantification of extracted DNA from both the treated plots suggests a zone of greater biological activity in the top 12 cm of treated bauxite residue (Fig. 3). DNA recovery is media dependent, with particle size and pH potentially affecting the efficiency of extraction. This uncertainty may over emphasise the gradient of biological activity with depth, and between treated and untreated samples. The extracted DNA concentrations from the top 12 cm of treated bauxite residue are within the range of extracted DNA concentrations from natural soils (very approximate

soil DNA concentrations range from 2.5 to 26.9 μg g^{-1}).[74] DNA recovery from this site's untreated bauxite residue was insufficient for Next-Generation Sequencing, however other workers have shown bauxite residue to contain alkali tolerant bacteria.[75] Sequenced DNA recovered from the root zone substrate of the fully and partially treated bauxite residue was dominated by the phyla Acidobacteria, Actinobacteria, Proteobacteria, and Planctomycetes. Natural soil root zone or rhizosphere bacterial communities frequently contain Actinobacteria, Bacteroidetes, Firmicutes, and Proteobacteria taxa,[76–78] which, with the exception of Firmicutes, are present in our treated bauxite residue (Figure S2, Table S7). Many taxa of Acidobacteria are known to be tolerant to high pH, and show increasing relative abundance with increasing pH from 5.5 pH.[79–82] Many Planctomycetes taxa are halotolerant,[83–87] existing in freshwater, marine, and brackish environments. The presence of these phyla suggests the microbial communities in the fully and partially treated bauxite residue are in transition between a highly alkaline and saline residue microbiome, and a plant supported subsurface microbiome.

Surface treatment with process sand, gypsum, and organic matter is a stable, reliable, and safe solution to bauxite residue rehabilitation. Bauxite residue pH is neutralised, Na^+ is less available, and metal oxyanions (Al, V, and As) are less mobile. The beneficial effects of treatment are long term and extend 20-30 cm beyond the depth of application. The formation a passively treated zone, which is $\geq 20\%$ of the total disposal cell depth, is sufficient to separate the surface environments from the potentially highly alkaline, sodium rich, and trace metal containing residue at depth. The presence of alkalinity generating phases in both treated plots highlights the importance of maintaining a strong biologically active surface layer. Were this layer to be removed or

substantially disrupted, and its supply of acid neutralising molecules lost, the system would likely return to a high pH steady state, with high Na, Al, V, and As concentrations, similar to those observed in the untreated bauxite residue.

This is the first observation of a shallow surface layer of actively treated and vegetated residue producing passive positive rehabilitation effects into deeper layers. This rehabilitation is likely driven by biology activity at the surface and continues long after the original treatment constitutes (gypsum, organic matter) have been depleted. Rehabilitation has resulted in a physical separation between deeper zones within the residue (potentially containing high alkalinity, sodium, and trace metals) and the bottom of the rooted zone at around 20 cm. Rehabilitation decreases the likelihood of plants being exposed to the negative characteristics of bauxite residue, and lowers the possibility of trace metal transfer into foliage and the wider ecosystem. The benefits of this surface treatment extend beyond the environmental; the cost of application is approximately 10k €/ha, whereas the cap and cover estimate for this BDRA is 100k €/ha. Gypsum application accounts for approximately 50-70 % of the total treatment cost, and assessment of its value for long term rehabilitation is important. Our results suggest the development of a healthy vegetation cover is key to long term stability of residue rehabilitation and previous work has demonstrated the role of gypsum in rapidly, and successfully establishing a resilient vegetation layer.[26–28,31,32,35] Gypsum application may, therefore, offer additional security in vegetation establishment, and the ultimate success and longevity of rehabilitation. However, 16 years after application there are no significant chemical benefits from gypsum addition. Our study demonstrates surface amendment of this nature is a viable closure option for active BRDAs and a particularly

473 good choice for rehabilitation of orphan sites where there is an acute need to protect the
474 public and environment at the lowest possible costs.

475 **Supporting Information**

476 Detailed aqueous analysis, DNA extraction, quantification, and post sequence processing
477 methods. Stepwise reactions of gypsum promoted $CaCO_3$ precipitation and pH
478 neutralisation. On site photographs of the trial pits. Additional figures of bacterial
479 community composition and elemental ratios and solubility. Additional tables with full
480 analytical results. Sequence reads have been uploaded to the National Center for
481 Biotechnology Information (NCBI) under the Sequence Read Archive (SRA) accession
482 number TBC. Collectively, the paper and these sources provide all the relevant data for
483 this study.

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Figures.

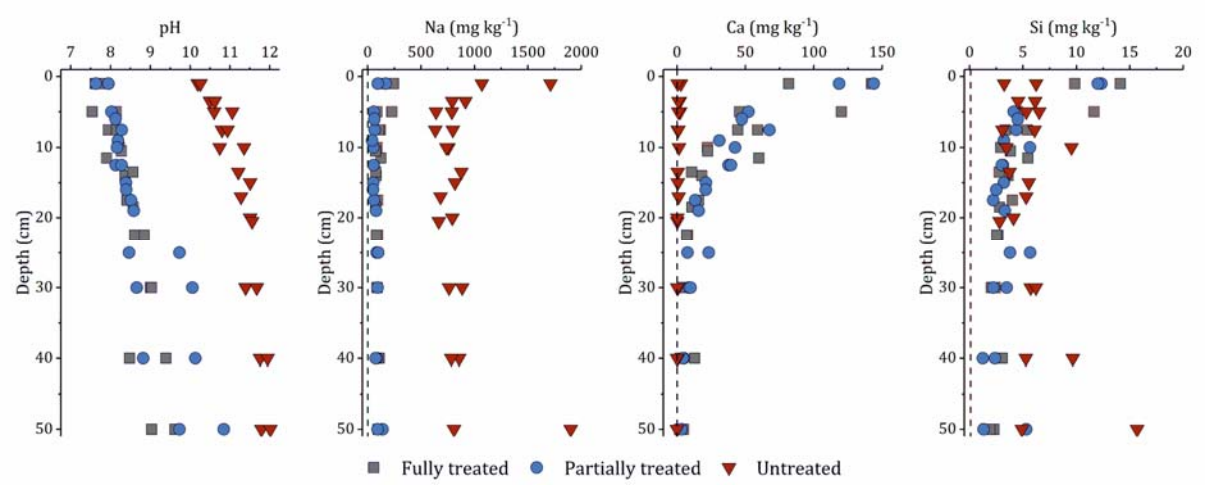
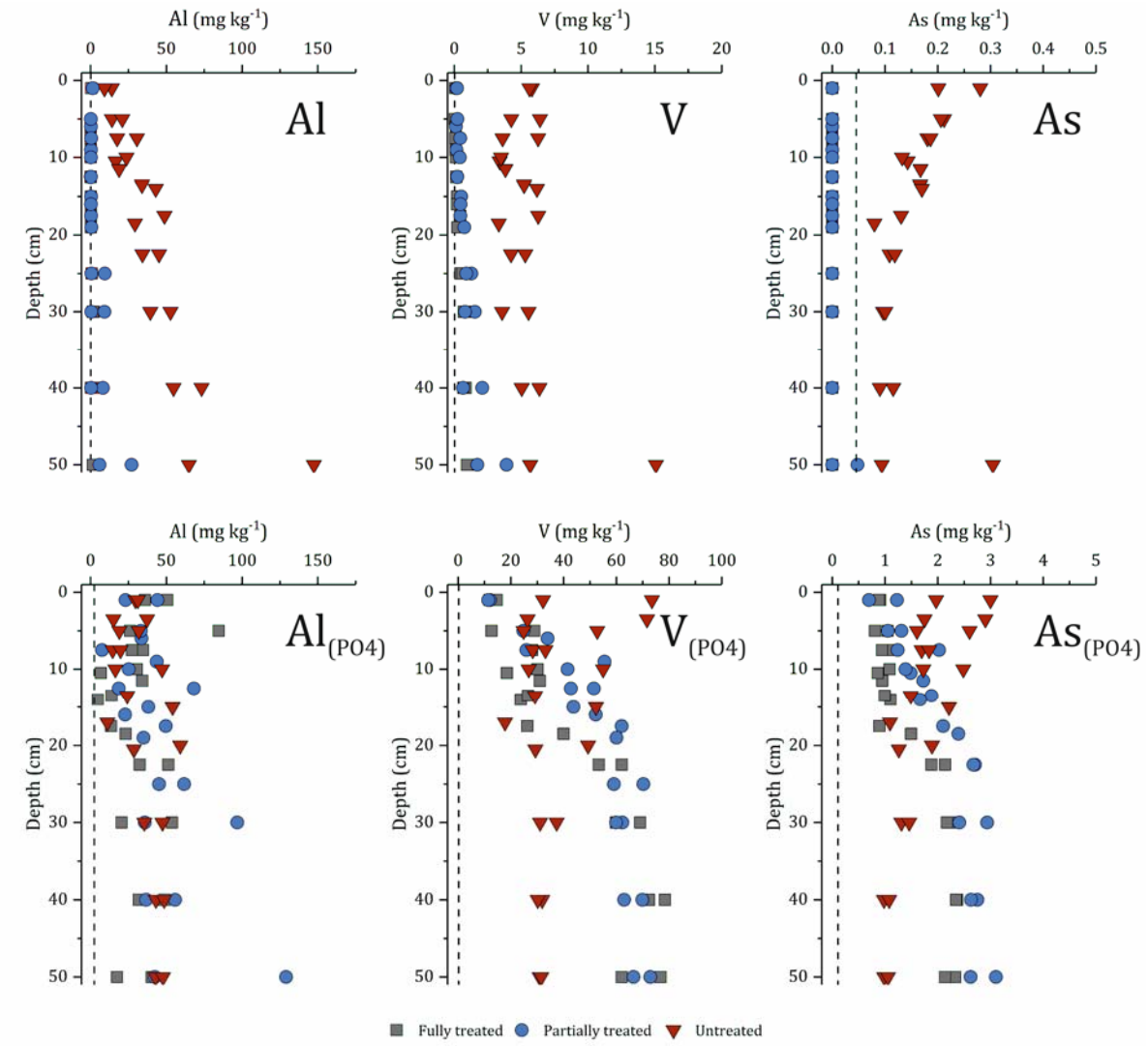


Figure 1.
pH, Na, Si, and Ca aqueously extracted from fully treated, partially treated, and untreated bauxite residue as a function of depth. The dotted line represents the limit of detection for element.



715
716 **Figure 2.**
717 Concentrations of Al, V, and As in solution following aqueous and phosphate (PO4)
718 extractions from fully treated, partially treated, and untreated bauxite residue as a
719 function of depth. Note the change in x-axis scale for aqueous and phosphate extracted V
720 and As. The dotted line represents the limit of detection for each element.
721

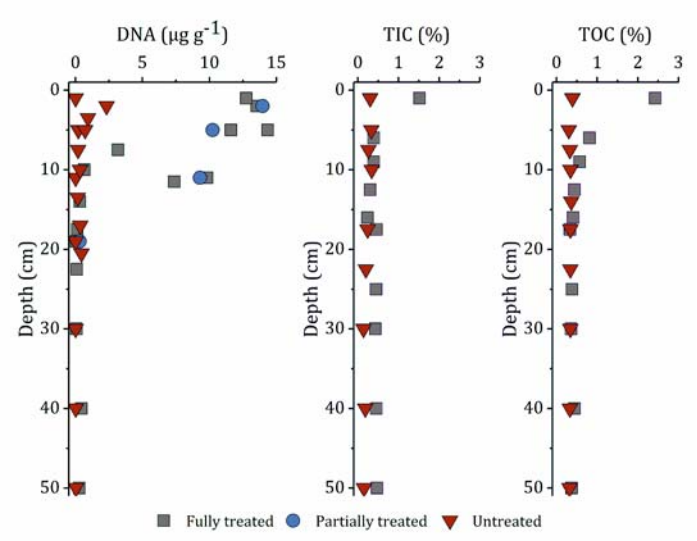


Figure 3.
DNA, total inorganic carbon (TIC), and total organic carbon (TOC) concentrations in fully treated, partially treated, and untreated bauxite residue as a function of depth.

Table 1.

Semi-quantitative percentage of crystalline phases present in bauxite residue as a function of treatment and average across depth, fitted using Rietveld refinement. Uncertainty on the Rietveld refinement is approximately 5 %. Full details are available in Table S2.

Treatment site	Fe Oxyhydroxides		Al oxyhydroxides			Desilication Products		Ti Oxides	Other minerals
	Goethite α-FeO(OH)	Hematite Fe_2O_3	Gibbsite $Al(OH)_3$	Boehmite γ-AlO(OH)	Katoite $Ca_3Al_2(OH)_{12}$	Cancrinite $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$	Sodalite $Na_8Al_6Si_6O_{24}(OH)_2$	Perovskite $CaTiO_3$	
	%	%	%	%	%	%	%	%	%
Untreated	21	16	8	10	2	14	1	20	9
Fully Treated	24	19	8	7	3	10	< 0.5	20	9
Partially Treated	19	16	11	10	10	10	< 0.5	15	8