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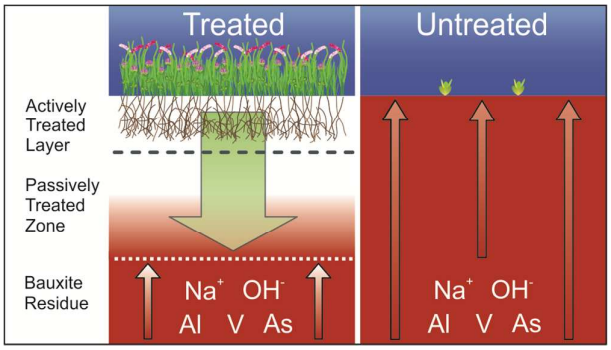
21 **Graphical Abstract**



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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

87 constrained audit trails regarding treatment and planting histories, can limit their
88 viability in BRDA closure plans. The objective of this study was to assess the long term
89 effects of a surface treatment to bauxite residue. Here we report the chemical and
90 mineralogical data sampled from depth profiles of bauxite residue nearly two decades
91 after initial treatment, and evaluate the ability of these treatments to provide sustained
92 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 significantly different ($p < 0.05$), though neither were significantly different from the untreated residue ($p > 0.05$; Table S3).

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

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

than 0.5% TOC and TIC at all depths. Acid extractable inorganic carbon (AIC) and organic carbon (AOC) was only detectable in the top 10 cm of the fully treated and untreated bauxite residue, and was below or at the limit of detection (<4 μg kg^{-1}) in all other samples (Table S2).

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

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

278 The alpha diversity indices for each sample are shown in Table S8. Here we use
279 Hill numbers[44,45] as robust bacterial diversity measures which account for the
280 distortions of rare taxa.[44–47] D_0^{α}, the operational taxonomic unit (OTU) richness, ranges
281 from ~1250 to 3850, however this diversity index is very sensitive to rare taxa, and
282 takes no account of OTU relative abundance. Indices that give a measure of the number
283 of common (D_1^{α}) and dominant OTUs (D_2^{α}; Table S8), converge across the samples,
284 demonstrating similar diversity in the OTU populations. Common OTUs represent >79
285 % of total sequence reads in each sample, and dominant OTUs accounted for 51-62 % of
286 total reads in each sample.

287

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 (≥ 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

312 to be incongruent at high pH. Cancrinite dissolution should produce equimolar
313 concentrations of Na, Si, and Al, (Eqn. 2) but the measured concentrations are far from
314 stoichiometric (Fig. S3). Aqueous extractable Na concentrations from untreated samples
315 are 100 to 400 times higher in concentration than extractable Si and 10 to 150 times the
316 Al concentration, indicating a preferential retention of Si and Al in the solid phase.

317 This preferential retention of Al and Si in the solid phase is probably controlled
318 by the precipitation of amorphous and crystalline secondary phases. At the highest pH
319 measured, Al concentrations are close to equilibrium with gibbsite ($Al(OH)_3$) (Fig S3).
320 The measured Al concentrations decrease as the pH decreases from 12 to 10, but
321 exceeds concentrations in equilibrium with gibbsite. Over this pH range, Si
322 concentrations are much lower than those expected for $SiO_{2(am)}$ equilibrium, suggesting
323 an alternative solubility limiting phase. At high pH, with high Na concentrations, Al and
324 Si can co-precipitate in amorphous cation-bridged alumino-silicate gels,[54] which may
325 explain the low concentrations observed.

326 Sustained alkalinity generation throughout untreated bauxite residue is a
327 concern because it may be associated with increased mobility of potentially toxic
328 metal(oid) oxyanions such as Al, V, and As. Both V and As are reported to be present in
329 bauxite residues primarily in the 5+ oxidation state as vanadate and arsenate species
330 [10,12], and are found as surface adsorbed species (V can also be associated with
331 neoformed hydrogarnet phases such as Katoite).[12] Conversely, Al availability is usually
332 controlled by the solubility of Al (oxy)hydroxide phases, which typically have much
333 higher solubility at high pH (see discussion above).[55] In alkaline phosphate extractions
334 both OH^- and phosphate ions compete strongly for available sorption sites and promote
335 the mobility of metal oxyanions.[14,20] The results of these extractions, therefore,

336 demonstrate that there is abundant V and As adsorbed to bauxite residue (Fig. 2). In the
337 untreated samples, where pH > 10, As and V sorb poorly to mineral surfaces,[14–16,21,56–58]
338 which is why only 10 and 15 % of the phosphate extractable As and V respectively were
339 extractable water this fraction will be mobile in residue pore waters.

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

346

347 *Treated bauxite residue*

348 16 years after bauxite residue treatment with process sand, organic matter and
349 gypsum significant pH reduction (2 units) was observed over a depth that extends at
350 least 30 cm below the actively treated surface layer (Fig. 1; Table S2). Aqueous sodium
351 concentrations were an order of magnitude lower in the treated plots than untreated
352 plot at all depths (Fig. 1; Table S2), and the availability of aluminium, vanadium, and
353 arsenic were all lower in treated than untreated bauxite residue (Fig. 2; Table S2).
354 These observations demonstrate that positive treatment effects observed in the short
355 term are sustained, such as: improved permeability, particle aggregation, and drainage;
356 pH neutralisation; decreased Na, Al, and Fe availability. [28,29] In natural soils, organic
357 matter plays a key role in controlling particle aggregation,[59–61] and the application of
358 spent mushroom compost may have improved residue structure. In highly alkaline

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

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

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

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

383 cancrinite dissolution kinetics to vary with pH in a similar manner to other
384 feldspathoids, decreasing by an order of magnitude between pH 12 and 7. This suggests
385 pH conditions established in treated bauxite residue from organic matter and gypsum
386 addition decrease the rate of OH^- and Na^+ production from the dissolution of cancrinite
387 and associated secondary phases (Fig. 1).

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

400

401 *Long term maintenance of beneficial conditions*

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

406 controlling residue neutralisation. 16 years after treatment, the original additives are
407 largely unobservable, with little chemical difference remaining from the application of
408 gypsum. This suggests that the development of resilient vegetation on bauxite residue,
409 along with associated rhizosphere microorganisms, may drive long term stability and
410 chemical safety of treated bauxite residue. The organic matter applied to the surface
411 layers is only detected in small quantities (Fig. 3) and has likely been degraded and
412 recycled into plants and microorganisms. The products of gypsum addition are minimal;
413 calcite was undetectable by XRD, and there is only a slight accumulation of Ca and TIC
414 towards the surface of both treated zones. Process sand was present in the surface layer
415 when sampling but heterogeneously distributed and undetectable mineralogically by
416 XRD and chemically by XRF.

417 The supply of H^+ ions to depth that is driving pH neutralisation in treated bauxite
418 residue may be photosynthetic in origin. This can occur via a combination of three
419 mechanisms: (a) enhanced CO_2 flux from plant roots and associated microorganism
420 respiration; (b) organic matter degradation in the biologically active surface layer,
421 producing low molecular weight organic acids; and (c) secretion of low molecular
422 weight organic acids by plant roots and rhizospheric microorganisms. The carbon flux
423 from atmosphere to rhizosphere is well documented in both the short (i.e. respiration),
424 and medium terms (organic matter production).[73] Quantification of extracted DNA from
425 both the treated plots suggests a zone of greater biological activity in the top 12 cm of
426 treated bauxite residue (Fig. 3). DNA recovery is media dependent, with particle size
427 and pH potentially affecting the efficiency of extraction. This uncertainty may over
428 emphasise the gradient of biological activity with depth, and between treated and
429 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

454 importance of maintaining a strong biologically active surface layer. Were this layer to
455 be removed or substantially disrupted, and its supply of acid neutralising molecules
456 lost, the system would likely return to a high pH steady state, with high Na, Al, V, and As
457 concentrations, similar to those observed in the untreated bauxite residue.

458 This is the first observation of a shallow surface layer of actively treated and
459 vegetated residue producing passive positive rehabilitation effects into deeper layers.
460 This rehabilitation is likely driven by biology activity at the surface and continues long
461 after the original treatment constitutes (gypsum, organic matter) have been depleted.
462 Rehabilitation has resulted in a physical separation between deeper zones within the
463 residue (potentially containing high alkalinity, sodium, and trace metals) and the
464 bottom of the rooted zone at around 20 cm. Rehabilitation decreases the likelihood of
465 plants being exposed to the negative characteristics of bauxite residue, and lowers the
466 possibility of trace metal transfer into foliage and the wider ecosystem. The benefits of
467 this surface treatment extend beyond the environmental; the cost of application is
468 approximately 10k €/ha, whereas the cap and cover estimate for this BDRA is 100k
469 €/ha. Gypsum application accounts for approximately 50-70 % of the total treatment
470 cost, and assessment of its value for long term rehabilitation is important. Our results
471 suggest the development of a healthy vegetation cover is key to long term stability of
472 residue rehabilitation and previous work has demonstrated the role of gypsum in
473 rapidly, and successfully establishing a resilient vegetation layer.[26–28,31,32,35] Gypsum
474 application may, therefore, offer additional security in vegetation establishment, and
475 the ultimate success and longevity of rehabilitation. However, 16 years after application
476 there are no significant chemical benefits from gypsum addition. Our study
477 demonstrates surface amendment of this nature is a viable closure option for active

478 BRDAs and a particularly good choice for rehabilitation of orphan sites where there is
479 an acute need to protect the public and environment at the lowest possible costs.

480 **Supporting Information**

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

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495

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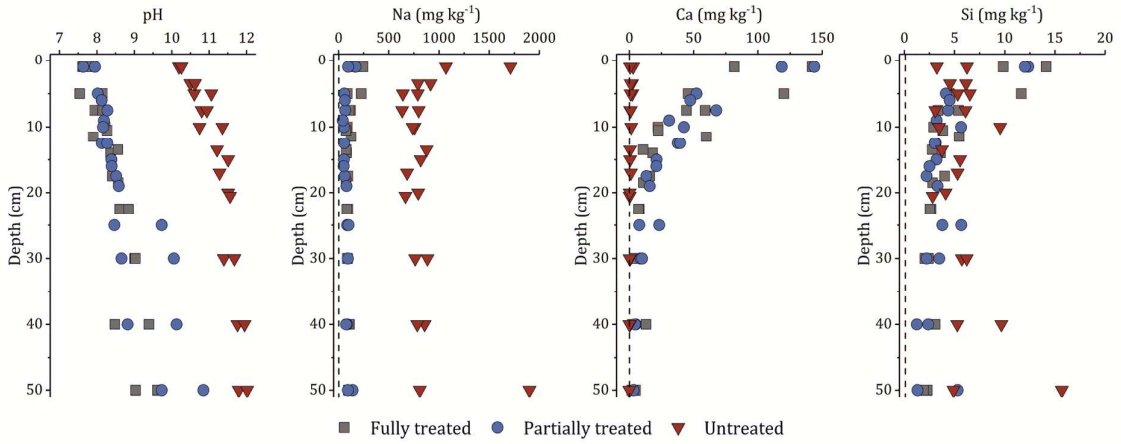
739 **Figures.**



740
741 **Figure 1**.
742 pH, Na, Si, and Ca aqueously extracted from fully treated, partially treated, and
743 untreated bauxite residue as a function of depth. The dotted line represents the limit of
744 detection for element.
745

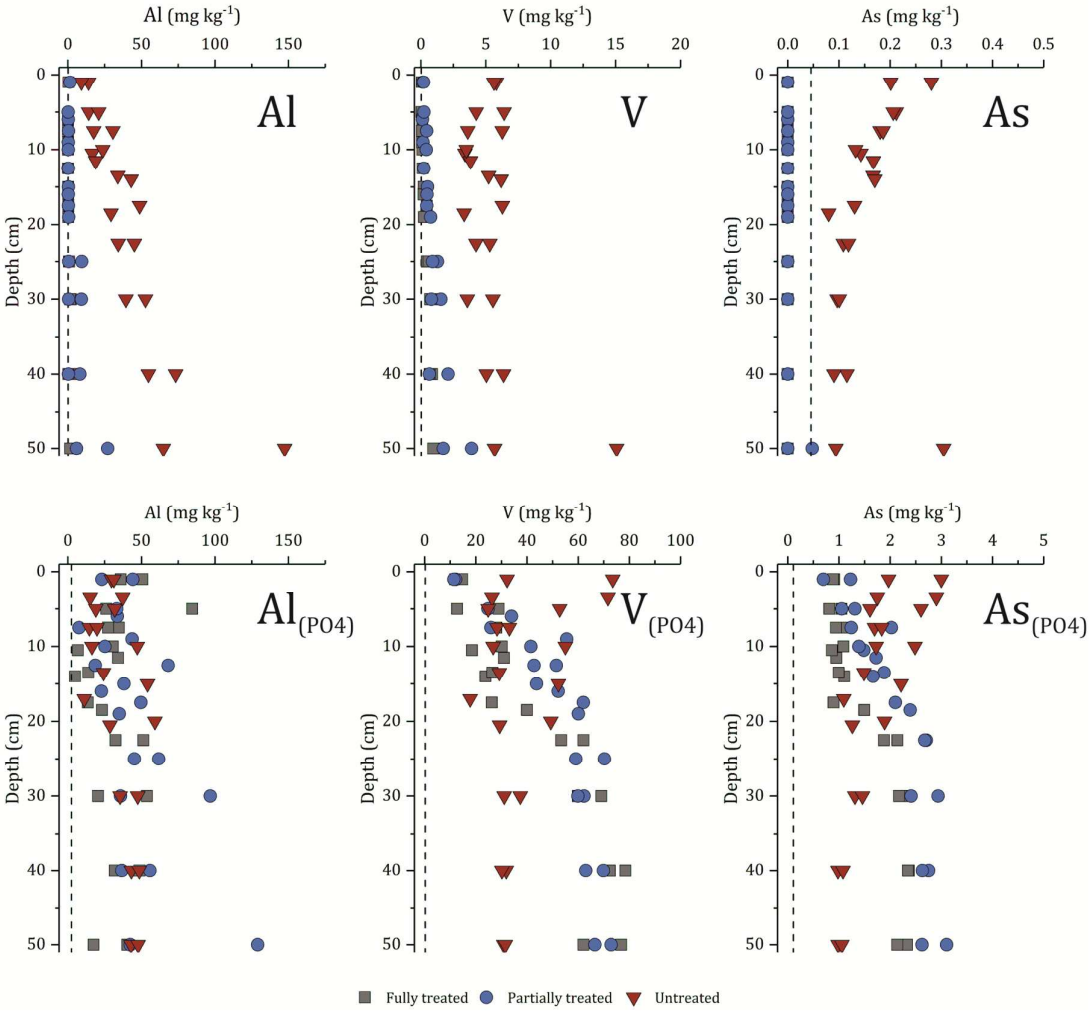


Figure 2.

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

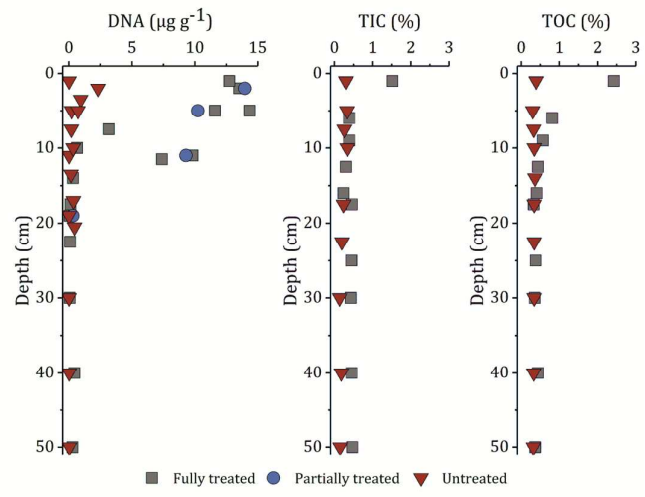


Figure 3.
DNA, total inorganic carbon (TIC), and total organic carbon (TOC) concentrations in fully treated, partially treated, and untreated bauxite residue as a function of depth.

758 **Table 1.**
759 Semi-quantitative percentage of crystalline phases present in bauxite residue as a function of treatment and average across depth, fitted
760 using Rietveld refinement. Uncertainty on the Rietveld refinement is approximately 5 %. Full details are available in Table S2.
761

Treatment site	Fe Oxyhydroxides		Al oxyhydroxides			Desilication Products		Ti Oxides	Other minerals
	Goethite	Hematite	Gibbsite	Boehmite	Katoite	Cancrinite	Sodalite	Perovskite	
	α-FeO(OH)	Fe_2O_3	$Al(OH)_3$	γ-AlO(OH)	$Ca_3Al_2(OH)_{12}$	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$	$Na_8Al_6Si_6O_{24}(OH)_2$	$CaTiO_3$	
	%	%	%	%	%	%	%	%	%
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

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