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Gypsum addition to soils contaminated by red mud: Implications for aluminium, arsenic, molybdenum and vanadium solubility.

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ABSTRACT

Red mud is highly alkaline (pH 13), saline and can contain elevated concentrations of several potentially toxic elements (e.g. Al, As, Mo and V). Release of up to 1 million m^3 of bauxite residue (red mud) suspension from the Ajka repository, western Hungary, caused large scale contamination of downstream rivers and floodplains. There is now concern about the potential leaching of toxic metal(loid)s from the red mud as some have enhanced solubility at high pH. This study investigated the impact of red mud addition to three different Hungarian soils with respect to trace element solubility and soil geochemistry. The effectiveness of gypsum amendment for the rehabilitation of red mud-contaminated soils was also examined. Red mud addition to soils caused a pH increase, proportional to red mud addition, of up to 4 pH units (e.g. pH 7 $\rightarrow$ 11). Increasing red mud addition also led to significant increases in salinity, dissolved organic carbon (DOC) and aqueous trace element concentrations. However, the response was highly soil specific and one of the soils tested buffered pH to around pH 8.5 even with the highest red mud loading tested (33% w/w); experiments using this soil also had much lower aqueous Al, As, and V concentrations. Gypsum addition to soil / red mud mixtures, even at relatively low concentrations (1% w/w) was sufficient to buffer experimental pH to 7.5-8.5. This effect was attributed to the reaction of Ca^{2+} supplied by the gypsum with OH^- and carbonate from the red mud to precipitate calcite. The lowered pH enhanced trace element sorption and largely inhibited the release of Al, As and V. Mo concentrations, however, were largely unaffected by gypsum induced pH buffering due to the greater solubility of Mo (as molybdate) at circumneutral pH. Gypsum addition also leads to significantly higher porewater salinities and column experiments demonstrated that this increase in total dissolved solids persisted even after 25 pore volume replacements. Gypsum addition could therefore provide a cheaper alternative to recovery (dig and dump) for treatment of red mud affected soils. The observed inhibition of trace metal release within red mud affected soils was relatively insensitive to either the percentage of red mud or gypsum present, making the treatment easy to apply. However, there is risk that over-application of gypsum could lead to detrimental long term increases in soil salinity.

KEYWORDS: Alkaline red mud, contaminated soils, gypsum, toxic trace elements, arsenic, vanadium, aluminium, organic matter leaching, pH reduction.

INTRODUCTION

Fine fraction bauxite residue (red mud) is a by-product of alumina refining, with up to 120 million tonnes produced worldwide each year (Grafe and Klauber 2011). Red mud typically comprises residual iron oxides, quartz, sodium aluminosilicates, titanium dioxide, calcium carbonate/aluminate and sodium hydroxide which raises the pH up to 13 (Grafe et al. 2011; Gelencser et al. 2011; Burke et al. 2012). The failure of the bauxite residue dam at the Ajkai Timfoldgyar Zrt alumina plant, western Hungary, on the 4th October 2010 resulted in the release of up to 1 million m^3 of caustic red mud suspension (Reeves et al. 2011). The waste inundated homes and land downstream causing 10 deaths and over 150 serious injuries. Approximately 40 km^2 of agricultural and urban land was affected and the red mud was transported over 120 km downstream (Mayes et al. 2011; Reeves et al. 2011). This was the largest recorded environmental release of red mud and, as such, studies on the after-effects of the spill have both improved the knowledge-base on risks associated with red mud (Gruiz et al. 2012) and informed broader management strategies for stockpiled red mud. At Ajka, Hungary, red mud samples contained elevated concentrations of potentially toxic trace elements such as Al (75000 mg kg^{-1}), As (150 mg kg^{-1}) and V (900 mg kg^{-1}) (Mayes et al. 2011; Ruyters et al. 2011). Red mud leachates are also hyperalkaline (pH 13), and can be directly toxic to aquatic life (Wilkie and Wood 1996). Equally important is the enhanced mobility of several oxyanionic forming trace elements at high pH (Langmuir 1997). Indeed, water in contact with Ajka red mud had dissolved Al concentration of 800 mg L^{-1}, and dissolved As, V, and Mo concentrations of 4 - 6 mg L^{-1} (Mayes et al. 2011).

The initial response to the accident was to dose affected rivers with weak acids and gypsum (up to 23,500 t: Rédey 2012) to neutralise the water, and (in some cases) to plough the red mud into the fields to prevent dust formation (Burke et al. 2012; Gelencser et al. 2011; Renforth et al. 2012). Longer term strategies included the building of new containment dams and the large scale recovery of red mud deposits from affected land, although thin deposits of red mud (< 5 cm) were not routinely recovered (Klebercz et al. 2012). Studies on the effect of the red mud in soils conducted in the weeks following the spill suggested that the high NaOH present inhibits plant growth (Ruyters et al. 2011), however, little is known about the longer term leaching and potential for bioaccumulation of metal(loids) into plants grown in soils affected by the Ajka red mud spill.

Acid dosing and gypsum addition to rivers were both effective in lowering pH values and metal(loid) concentrations in river waters downstream of the spill (Burke et al. 2012; Mayes et al. 2011; Renforth et al. 2012). Lack of Ca^{2+} in red mud leachate (Renforth et al. 2012) limits the natural pH reduction mechanism (Equations 1 and 2). Providing excess free Ca^{2+} is therefore the main effect of gypsum addition. The reaction, which involves CO_2 in-gassing to form calcite with net OH^- removal, can be rapid in high pH systems (Renforth et al. 2012).

$$OH^-_{(aq)} + CO_{2(aq)} \rightarrow HCO^-_{3\,(aq)} \quad (1)$$

$$2OH^-_{(aq)} + CaSO_4.2H_2O_{(s)} + 2CO_2 \leftrightarrow CaCO_{3(s)} + SO^{2-}_{4\,(aq)} + 2H_2O_{(l)} + H_2CO_{3(aq)} \quad (2)$$

The Ca^{2+} provided by gypsum addition can also displace Na^+ from exchange complexes and potentially reduces salt stress to vegetation (Grafe and Klauber 2011; Grafe et al. 2011). Although gypsum addition has also been shown to be very effective in the rehabilitation of stock-piled red mud (Courtney and Kirwan 2012; Courtney and Timpson 2004, 2005), studies have focussed primarily on soil sodicity and availability of major ions (e.g. Al, Na, Ca: Courtney and Kirwan 2012; Courtney and Harrington 2012; Courtney et al. 2009) and less on the mobility of potentially toxic trace elements (e.g. As, Mo and V). At Ajka, gypsum addition to affected soils was not attempted, but it is therefore possible that gypsum addition may have been a useful tool for soil stabilisation and negated the need for such extensive recovery of marginally-contaminated soils. Indeed, this was highlighted as a more appropriate and cost-effective alternative approach for dealing with red mud-contaminated floodplain areas in official reviews of the disaster response (Adam et al. 2011).

The primary objective of this study was to investigate the potential geochemical effects of red mud mixing with several different soils collected from the Torna and upper Marcal catchments.

Batch experiments were used to determine the evolution of chemical properties (e.g. pH, salinity) when soil was mixed with red mud. The solubility of several potentially problematic elements (Al, As, Mo and V) was investigated as a function of red mud loading and the resultant perturbation in soil pH. Finally, gypsum was added to soil / red mixtures in batch and column tests to determine the effectiveness of gypsum addition for treatment of red mud-contaminated soils. As such, the study provides information not only on potential remedial strategies for environmental release of red mud but also provides analogue data on the soil and leachate quality that would be anticipated in amended red mud in bauxite residue disposal areas (BDRAs).

MATERIALS AND METHODS

Sample Collection. Samples were collected in May 2011. Red mud was collected from inside the breached Ajka repository (Lat. 47°4'58"N, Long.17°29'34"E) and three soil samples (that did not receive red mud during the 2010 spill) were collected from sites representative of the varying land uses and landforms in the affected Torna and Upper Marcal catchment, western Hungary. Soil H1 was an agricultural topsoil (Lat. 47°6'38"N, Long. 17°23'43"). Soil H2 was a non-agricultural topsoil sampled from below the rootlet layer at 10-50 cm (Lat. 47° 5'46"N, 17° 15'1"E). Soil H3 was a wetland soil from within a reed bed area (Lat. 47°5'56"N, Long. 17°13'41"E). The Hungarian soils were used in the batch experiments described below. The column experiments (also described below) required significantly greater amount of soil than was originally sampled. Therefore, a well characterised sandy silt loam (soil E1), collected from north western England in May 2009, was used in column experiments. All red mud and soils were stored at 4°C ±2°C in polypropylene containers until used. Soil H3 was stored anaerobically using Anaerogen™ sachets.

Sample Characterization. The red mud and soil samples (after oven drying (105 ^{o}C) and grinding in a mortar and pestle) were characterised by X-ray powder diffraction using a Bruker D8 Advance XRD, X-ray fluorescence using a PANalytical Axios Advanced XRF spectrometer (data corrected for loss on ignition; % weight loss after furnace treatment at 1050 ^{o}C), total organic carbon analysis using a Carlo Erba NA 2500 Elemental Analyser. The pH was determined (using homogenised field moist soils) after 10 g : 10 mL suspension in deionised water [ASTM method D4972-01]. The BET surface area was determined (on oven dried samples) after degassing with N_2 on a Micromeritics FlowPrep 060 sample degas system prior to analysis with a Micromeritics Gemini V BET surface area analyser. Principal Component Analysis (PCA) of the red mud and soil samples was under-taken on standardized elemental concentration data and compared against other published samples from the red mud contaminated catchment (Mayes et al. 2011).

Batch Experiments. All soils and the red mud were homogenised by hand before establishing experiments, but otherwise were used as collected. Batch experiments were established by mixing soils H1, H2 and H3 with red mud to achieve final concentrations of 0, 1, 5, 9, 20, and 33% red mud on a dry weight basis. (After the Ajka spill, red mud deposits in fields varied from <1cm to, at most, ~20cm; and all deposits >5cm were routinely recovered (Klebercz et al. 2012). If red mud was ploughed into soils to a typical depth of ~40-50 cm, an approximate 5:50 mixing ratio (~9%), would therefore, be an important condition for study. Larger additions, up to 33% red mud, were only considered as worst case scenario.) The soil / red mud mixtures where suspended at 200 g L^{-1}, in deionised water in 15 ml polypropylene centrifuge tubes, and continuously shaken on an orbital shaker (100 rpm) for 30 days. In order to maintain an aerobic headspace, each tube was opened daily (5 days per week). Additional batch experiments were established with the same red mud conditions as above but with 4% (w/w) addition of gypsum ($CaSO_4{\cdot}2H_2O$). Finally a set of batch experiments was established which contained 9% (w/w) red mud, with varying quantities of gypsum to achieve 0, 1, 4, 8, 12, and 15% gypsum additions on a dry weight basis. After 30 days equilibration, all tubes were centrifuged (6000 g) for 5 minutes to separate aqueous and solid phases. All aqueous samples were then membrane filtered (0.2 µm). Duplicate experiments were performed at two key conditions (9% red mud, and, 9% red mud +4% gypsum) in all three soil types as a check on data reproducibility (duplicate data is reported in Appendix A, TableA1).

Column Experiments. 500 g of Soil E1 (< 2 mm fraction) was homogenised and mixed with red mud (8% w/w) with and without gypsum addition (also 8% w/w). The amended soils were hand packed into glass Omnifit™ columns (400 mm length, 50 mm diameter) with Teflon end pieces and 50 µm filters at both the influent and effluent ends. Columns were saturated with deionised water and left to equilibrate overnight. Thereafter, deionised water was pumped vertically upwards through the columns using an isocratic pump at (0.06 mL/min; 86.4 mL/day), with influent at the column bottom and effluent at the top. This rate of pumping equated to approximately 1 pore volume per day (determined as the weight difference of dry and saturated columns). Pumping was continued until approximately 25 pore volumes had passed through each column. At each sampling point, the volume of effluent was recorded and water samples were collected and filtered (0.2 µm).

Geochemical Analysis. Sample pH was measured using a Microprocessor pH meter with electrodes calibrated at pH 7 and 10 using standard buffer solutions; Total Dissolved Solids (TDS) was determined using a Myron Ultrameter calibrated with a KCl solution. Solution colour was determined by measuring the absorbance at 254 nm using an Uvikon XL spectrophotometer and a quartz cell. Dissolved organic carbon (DOC) was measured on a multi N/C® 2100 using thermocatalytic oxidation, MC-NDIR detection analysis. In these experiments, absorbance at 254 nm and DOC concentrations were found to be significantly correlated (Pearson's correlation: r = 0.93, P = <0.001, n = 27), therefore, absorbance at 254 nm was used routinely to estimate sample DOC concentration (DOC analysis was performed on 40% of the samples). As, V and Mo concentrations were determined in aqueous samples (after acidification with 2% HNO_3) on a Perkin–Elmer Elan DRCII inductively coupled plasma-mass spectrometer (ICP-MS) (LoD = 0.49, 0.25, and 0.86 µg L^{-1} respectively). Aluminium concentrations were determined by using Flame Atomic Absorption Spectroscopy (FAAS) on an Analytic Jena ContrAA 700 (after acidification with 2% HCl; LoD = 200 µg L^{-1})

RESULTS

Sample Characterization. The red mud mineral content is dominated by hematite, calcite, magnetite, cancrinite and hydrogarnet (with some residual boehmite and gibbsite), which is very similar to other red mud analysed from the Ajka spill (Burke et al. 2012; Gelencser et al. 2011). Sample characterisation data for the red mud, the three Hungarian soils (H1-3) and soil E1 are summarised in Table 1. Principal Component Analysis compared the elemental composition of the red mud sample and the three Hungarian soil samples (shown in Table 2) to other surface and fluvial samples from the affected region (Mayes et al. 2011). Results (Figure 1) show that the soil sample compositions were consistent with other unaffected reference samples from the area and the red mud composition was consistent with other source term red mud samples from the Ajka repository.

Red Mud Addition to Soils. The addition of alkaline red mud caused an increase in experimental pH that increased with red mud loadings (Figure 2a). At low red mud additions (< 10%) pH increases were limited to 1-1.5 pH units for all three soils. At the highest red mud loadings (33%) pH increases of 3-4 pH units from pH 7-8 to around pH 11 occurred in experiments using soil H1 and H3, however, soil H2 buffered pH more effectively and pH increases were limited to 2 pH units (pH 6.5 to 8.5). TDS increased modestly in all experiments with increasing red mud addition (Figure 2b) with TDS increasing by around 500 mg L^{-1} to ~1500 mg L^{-1} in experiments receiving the highest red mud loading. DOC concentrations also increased with increasing red mud addition (Figure 2c) but the response was soil specific; experiments containing soil H3 had relatively lower aqueous DOC concentrations at higher red mud loadings. Concentrations of Al, As, V, and Mo in experiments also increase with increasing red mud addition (Figure 3a-d). Experiments containing soil H2 had relatively lower aqueous concentrations of Al, As and V compared to soil H1 or H3, but Mo concentrations were comparable in all three soils.

Gypsum Addition to Red Mud / Soil Mixtures. When 4% gypsum was added to experiments the observed pH increases were much lower compared to experiments without gypsum (Figure 2d). There was a smaller increase of pH (up to 1 pH unit) observed with increasing red mud loadings and no experiments had pH values above 8.5 even with 33% red mud addition. TDS, however, was much higher in gypsum containing experiments (Figure 2e). Also the gradient of TDS increases with increasing red mud addition was greater, with TDS increasing by nearly 2000 mg L^{-1} to around 4000 mg L^{-1} as red mud addition increased from 0 to 33%. Aqueous DOC concentrations in gypsum amended experiments were significantly lower compared to experiments without gypsum (Figure 2f) and there was no observed change in DOC concentrations with increasing red mud addition. Aqueous Al, As and V concentrations in gypsum amended experiments (Figure 3e-g) were also much lower than in unamended experiments. Aqueous Mo concentrations, however, were only slightly lower in gypsum amended experiments (Figure 3h).

In experiments where the amount of gypsum added was varied (from 0 to 15%) and red mud addition was constant (9%), it was discovered that the soils tested were relatively insensitive to increasing gypsum addition (Figure 4). Approximately equal reductions in pH and aqueous DOC, Al, As and V values were observed with 1 to 15% gypsum addition. The observed TDS increase (Figure 4b) was about 1000 mg L^{-1} between 0 and 1% addition and further increased to about 2800-3000 mg L^{-1} with 4% gypsum present. No further increase in TDS was observed for gypsum addition above 4%. Aqueous Mo concentrations do not show any reduction at any level of gypsum addition (Figure 4g)

Column Experiments. The pumped column experiments compared the changes with column volume in effluent pH and TDS, DOC and Al concentrations (Figure 5), in tests containing soil /red mud mixtures (8%), both with and without the presence of gypsum (at 8%). Addition of gypsum induces a reduction in effluent pH of about 1 pH unit compared to the unamended column. Both DOC and Al concentrations are lower in effluent from the gypsum amended column. Over the course of the experiment the difference in DOC and Al concentrations in amended and unamended columns decreases, however, the overall export of aqueous DOC and Al in particular is attenuated. TDS spiked at over 40 g L^{-1} in the first sample collected from the gypsum amended column, but reduced quickly to around 2-3 g L^{-1}, which was maintained until the end of the test. Total TDS export in the unamended column was much lower.

DISCUSION

Effect of red mud contamination on Hungarian soils. Addition of red mud to soils induced the following effects, increasing proportionally to the amount of red mud added: 1) increase in pH, 2) increase in **a**queous DOC concentrations, 3.) increase in **a**queous metal(loid)s concentrations, and 4) increase in salinity (TDS). The red mud suspension released on the 4th October 2010 was highly alkaline (pH 13), contained elevated concentrations of potentially soluble trace elements such as Al As Mo and V, and was highly saline (Klebercz et al. 2012; Milacic et al. 2012); therefore, the results observed in these experiments are to some extent expected. Soil specific behaviour, however, was observed. One of the soils tested (Soil H2) more effectively buffered the alkalinity added with the red mud, possibly due to the higher organic carbon content of this soil. This resulted in more modest increases in pH and trace element concentrations in experiments using soil H2 compared to those using soil H1 and H3. Interestingly, the higher pH buffering capacity observed for soil H2 was very similar to that of the single Hungarian soil sample used by Ruyters et al (2011) who also reported relatively small pH increases and no significant increase in trace metal concentrations in experiments using soil / red mud mixtures (up to 17% w/w red mud). In the present study significant increases in pH and trace element concentration were observed at red mud loadings less than 10% w/w using two of the three soils studied.

The pattern of increasing DOC concentrations with increasing red mud addition has not been reported previously, but can be explained by the reaction between the alkalinity present in the red mud and organic matter present in the soils. Red mud contains elevated concentrations of NaOH and Na_2CO_3, both of which have been used in alkaline extractions designed to solubilise natural organic matter (Séby et al. 1997; Macleod and Semple 2000). Furthermore, in other studies increases in DOC under analogous hyperalkaline conditions associated with a steel slag / wood shavings mix have been ascribed to alkaline hydrolysis that releases low molecular weight carboxylic acids (Karlsson et al. 2011). Therefore, red mud addition to soils produces an unintended alkaline extraction liberating organic matter to solution. Along with clay mineral dissolution (Fernandez et al. 2009; Deng et al. 2006) and sorption reactions (Konan et al. 2012), the reaction of alkalinity with natural organic matter will therefore be one of the main short term mechanisms for pH buffering in red mud / soil mixtures. Also, at higher red mud loadings, where alkalinity may be present in excess, the supply of extractable organic matter may limit DOC concentrations. The increased DOC loss from red mud affected soils in of itself has potential for wider environmental impacts in terms of degradation of soil fertility and quality, loss of carbon storage and impacts on downstream water quality.

Effectiveness of Gypsum for the Treatment of Red Mud contaminated Soils. Gypsum addition is highly effective in controlling soil pH even under high red mud loading (maximum pH observed in experiments was 8.5). Gypsum addition to red mud affected soils buffers pH by providing a source of available Ca^{2+} that can react with soluble alkalinity (both carbonate and hydroxide) to produce calcite and a pH reduction (see equation 2). The formation of calcite also provides solid alkalinity that helps buffer the system to any further changes in pH. The consumption of alkalinity prevents the alkaline extraction of natural organic matter and thus produces lower DOC concentrations in gypsum amended experiments. The Ca^{2+} produced by gypsum dissolution can displace Na^{+} from exchange complexes in the red mud (Grafe et al. 2011). It is also possible that the reduction in pH might enhance the dissolution of high pH phases, such the hydrogarnet that is present in the red mud (Hillier et al. 2007; Hind et al. 1999). These effects combined with the sulphate that is released during gypsum dissolution will all contribute to the increased amount of salinity generation observed in gypsum amended batch experiments (i.e. there is a greater relative increase in TDS observed as red mud loading is increased in experiments with gypsum present compared to experiments without gypsum). This is consistent with an observation made during the initial response to the Ajka incident that gypsum dosing of directly affected rivers resulted in an increase in sulphate concentration long distances downstream of the spill (Mayes et al. 2011).Batch experiments designed to test the effect of varying the concentration of gypsum used found no difference in TDS between 4 and 15% additions. This implies that once gypsum is added in excess an equilibrium (controlled by the solubility of gypsum) is established that limits TDS release. Interestingly the same equilibrium TDS concentration was observed in batch and column tests where gypsum was added (Figs, 4b and 5c), implying that gypsum containing soils will continue to export salinity until the gypsum is depleted. Overall the column tests also demonstrates that the positive effects of 8% gypsum addition (i.e. reduction in pH, Al and DOC concentrations) are maintained over many porewater exchanges.

In order to understand the effect of gypsum addition on trace element concentrations, aqueous Al, As, Mo and V concentrations from all the batch experiments have been plotted as a function of the measured pH (Figure 6). In experiments without gypsum present, higher red mud loadings lead to both higher additions of trace elements to the soil and higher pH. At the pH of the red mud, As, V, Al and Mo are all predicted to be present as soluble oxyanions (as arsenate, vanadate, aluminate and molybdate: Langmuir 1997; Takeno 2005). Strong adsorption of both arsenate and vanadate to mineral surfaces at circumneutral pH is widely documented (Sherman and Randall 2003; Wehrli and Stumm 1989; Genc et al. 2003; Peacock and Sherman 2004). Aluminate becomes highly insoluble below about pH 10.5 and precipitates as an amorphous oxyhydroxide phase (Burke et al. 2012; Langmuir 1997). The solubility of oxyanion-forming elements is, therefore, highly affected by pH, with sorption / precipitation reactions limiting solution concentrations at low pH (Langmuir 1997; Peacock and Sherman 2004; Ladeira et al. 2001; Genc-Fuhrman et al. 2004). In these experiments significant increases in aqueous Al, As and V concentrations are observed above approximately pH 8.5. Addition of gypsum to the soil / red mud mixtures substantially reduces pH, in many cases to below 8.5. Therefore, the pH reduction associated with gypsum addition results in both an enhancement in sorption (As and V) or precipitation (Al) that effectively inhibits metal(liod) release to solution. This pH control also explains the behaviour observed for Soil H2, where greater pH buffering leads to lower overall experimental pH and lower aqueous Al, As and V concentrations in those tests. Mo, however, only weakly interacts with soil minerals at circumneutral pH (Buekers et al. 2010; S Goldberg and Forster 1998; S. Goldberg et al. 1996), and therefore, remains highly soluble at the pH values observed in experiments where gypsum was present.

CONCLUSIONS AND IMPLICATONS FOR REMEDIATION

Addition of red mud to soils causes an increase in pH, TDS, DOC and aqueous concentrations of oxyanion-forming trace elements. The extent of the increases observed is ultimately controlled by the amount of red mud present; however, the intrinsic ability of the soils to buffer pH is also important. Soils with low organic matter and clay content, also have lower buffering capacities, and therefore, are more at risk of suffering larger relative increases in pH, Al, As and V concentrations. In these experiments, there appeared to be threshold pH value between pH 8.5-9, above which significant increases in Al, As and V concentrations occurred. Therefore soil pH measurements could be used as a simple screening method to identify red mud affected soils where significant deleterious effects might be expected, with pH values higher than 8.5 equating to greater risk.

Gypsum addition resulted in soil pH values below 8.5 in all experiments and inhibited Al, As, V and DOC release. The immobilisation of As, V and Al is related to their enhanced adsorption at circumneutral pH. Although adsorption is reversible (e.g. at high pH; Langmuir 1997), the associated precipitation of calcite will typically buffer soil pH. However, sorbed oxyanions may be remobilised by anion exchange reactions, particularly with phosphate (and to a lesser extent carbonate), at circumneutral pH (Genc-Fuhrman et al. 2004; Altundogan et al. 2000). Mo concentrations were not affected by gypsum addition as sorption of the molybdate ion to soil minerals is low at circumneutral pH. These results indicate that gypsum addition to soils receiving red mud could be used as an emergency measure to consume the associated excess alkalinity and reduce porewater concentrations of several toxic elements, including Al, As and V. Although some long term potential for partial remobilisation may remain, the results also highlight the potential benefits that may arise in BDRAs with lower concentrations of potentially problematic trace elements where residue undergoes organic matter and gypsum amendment. The effectiveness of the treatment was found to be relatively insensitive to both the amounts of gypsum or red mud present, making this approach easy to administer. At Ajka, up to 1 million m^3 red mud slurry was released with an estimated solids content of ~8% (w/w) and density of ~1.20 g ml^{-1} (Szépvölgyi 2011) this equates to approximately 100,000 t red mud. Using the ~2:1 red mud to gypsum ratio (i.e. 9% red mud + 4% gypsum) used in many of our experiments, we calculate that around 50,000 t of gypsum would be required to treat of all the released material (cf. ~23,500 t gypsum was added to rivers following the spill; Rédey 2012). However, lower gypsum dosing ratios were also affective in our experiments (up to ~8:1 red mud: gypsum) and many thinner red mud deposits may require no treatment if the intrinsic pH buffering capacity of the soil is not exceeded. Also, much of the red mud released was transported out of the system by rivers and not deposited on land (Mayes et al. 2011); therefore, in reality much lower amounts of gypsum may actually be required (~5-10,000 t) to treat red mud / soil mixtures. There is also the potential advantage of preventing dust formation by ploughing in the gypsum during application. However, caution is also required when drawing conclusions at the field scale from laboratory experiments, as for example, the ability to achieve large scale homogenous mixing may be difficult, reducing the effectiveness of treatment.

Although addition of gypsum to soils can improve soil structure (e.g. by increasing hydraulic conductivity; Chen and Dick 2011), increased salinity (TDS) is the major disadvantage associated with gypsum addition. Indeed, for larger gypsum loadings, these salinity increases persisted for over 25 pore water exchanges (as did the beneficial effects). Increased soil salinity can cause damage to plant growth and soil microbes (Ruyters et al. 2011), therefore, gypsum addition should be carefully limited to that required to produce pH values between 8.5 and 9 in affected soils. Long terms trails of plant germination, and trace metal uptake would be a useful extension to this work to determine the effects of gypsum addition to red mud affected soils on plant growth. Alternate treatments such as soil washing and increasing dilution (of the red mud) may also significantly reduce the risk of trace metal leaching, without the associated risk of increased salinity due to gypsum addition; however, these methods are likely to be expensive and slower to administer.

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Table 1. Summary of red mud and soil characterisation data collected from the materials used in this study (* data from Law et al. 2010; Thorpe et al. 2012; Wallace et al. 2012).

	Red Mud	H1	H2	H3	E1*
pH	13.1	7.2	6.7	7.7	5.5
Dominant minerals	hematite cancrinite calcite magnetite hydrogarnet boehmite gibbsite	quartz albite microcline chlorite muscovite	quartz albite microcline chlorite muscovite	quartz albite microcline chlorite muscovite	quartz albite microcline chlorite muscovite
Corg (% w/w)	0.2	0.74	4.15	1.14	0.60
SSA_{BET} (m^2 g^{-1})	14.0 ±0.1	0.94 ±0.01	1.8 ±0.2	2.6 ±0.01	3.4 ±0.6
Munsell™ soil colour	dark red (10R 3/6)	light olive brown (2.5Y 5/6)	dark brown (7.5Y 3/2)	very dark grey (10Y 3/1)	reddish brown (2.5YR 4/8)
Texture	clay (100% clay)	sandy loam (70% sand, 30% silt and 0% clay)	clay loam (65% sand, 28% silt and 7% clay)	clay loam (69% sand, 24% silt and 7% clay)	sandy loam (52% sand, 43% silt and 5% clay)

Table 2. Concentrations of selected elements present in the red mud sample and soil samples. Soils H1, H2 and H3 were collected in Western Hungary. Soil E1 was collected in North Western England (*data from Law et al., 2010).

Major Elements (Weight %)	**Red Mud**	**Soil H1**	**Soil H2**	**Soil H3**	**Soil E1***
Si	6.0	42	38	34	35
Al	4.2	1.1	1.7	2.4	5.8
Fe	13.4	0.6	0.6	1.0	3.1
K	0.04	0.4	0.5	0.7	2.7
Na	3.0	0.3	0.3	0.4	1.0
Mg	0.4	0.2	0.6	0.5	0.5
Ti	3.1	0.2	0.2	0.3	0.4
Ca	5.7	0.4	1.6	0.8	0.2
Mn	0.2	0.04	0.02	0.03	0.1
P	0.04	0.02	0.02	0.02	0.02
S	0.1	0.002	0.01	0.01	-
Ba	0.007	0.014	0.04	0.03	0.04
Loss on Ignition	*1.0*	*1.8*	*5.1*	*1.2*	*4.1*
Minor Elements (mg kg^{-1})					
As	196	2	11	8	-
Ce	607	17	47	34	-
Co	59	3	11	5	<10
Cr	864	50	68	62	30
Cu	104	2	12	6	<30
Ga	26	4	10	6	-
La	283	10	26	18	23
Mo	15	1	1	1	-
Ni	361	5	23	14	17
Pb	215	9	25	12	42
Sb	22	1	1	2	-
Sr	318	47	78	94	58
Th	98	2	6	4	-
U	21	1	3	2	-
V	1132	30	72	51	81
W	17	<1	<1	<1	-
Zn	162	21	52	26	51
Zr	1223	88	122	102	251

< denotes less than given level of detection

- denotes not determined.

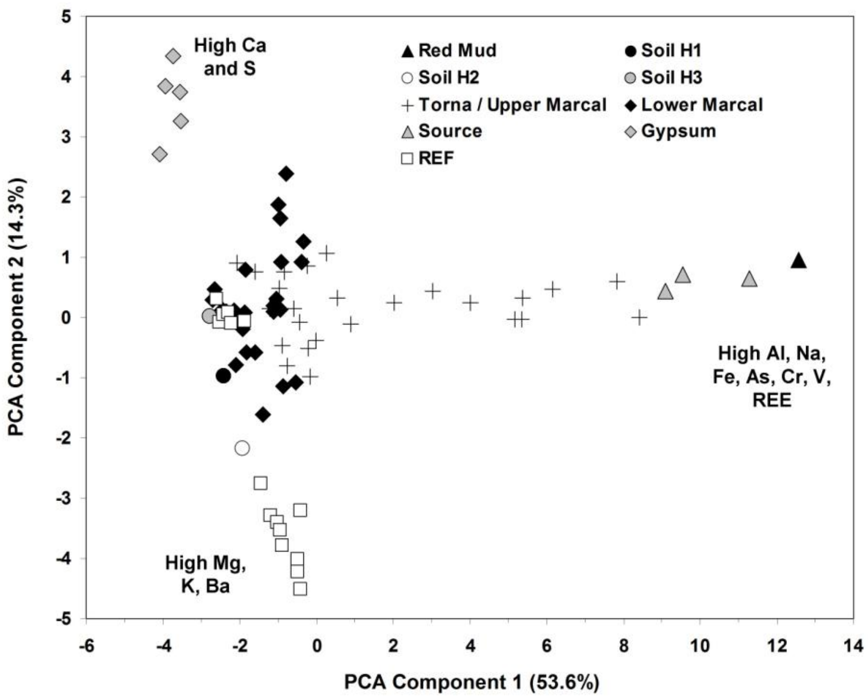

Figure 1. Principal Component Analysis based on major and minor elemental abundance in the red mud and soil samples using data from background and red mud affected sites in the Torna and Marcal catchments. Note that the red mud data ('Red Mud') plots at the extreme right hand side with other source term materials ('Source'); the soil samples used in this study all plot in a group on the left hand side with unaffected sites from the lower Marcal River and unaffected reference ('REF') samples (see text and Mayes et al. 2011, for detail). REE = rare earth elements

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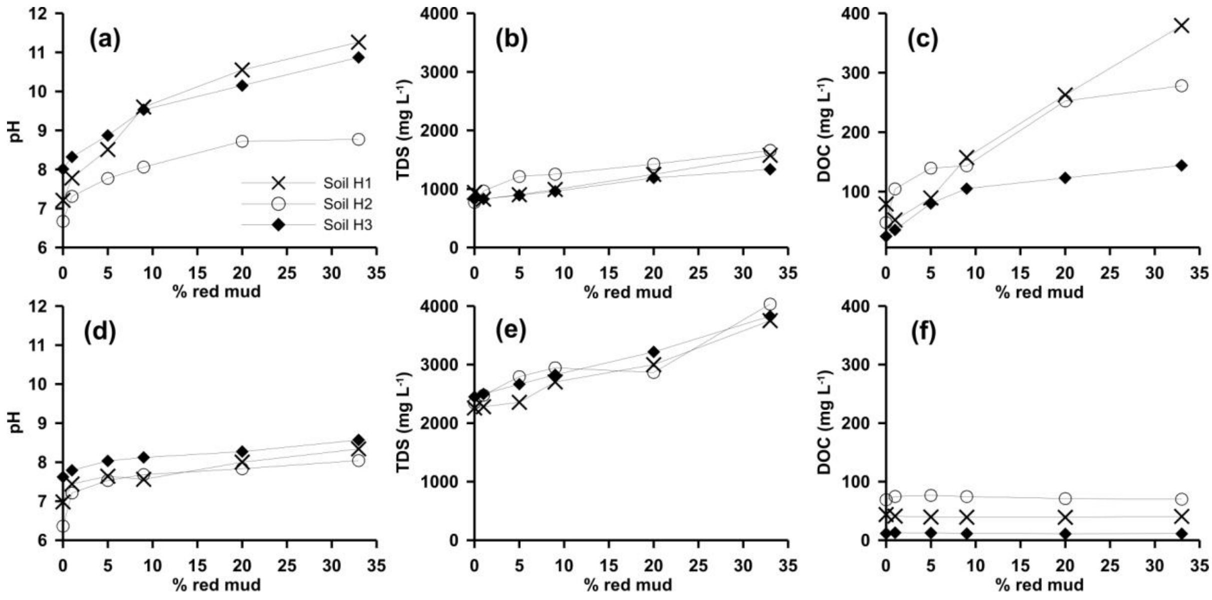

Figure 2. The effect of increasing red mud addition to three Hungarian soils on experimental pH, total dissolved solids (TDS) and dissolved organic carbon (DOC). Results are shown in both the absence (upper three panels) and presence (lower three panels) of 4% (w/w) gypsum addition.

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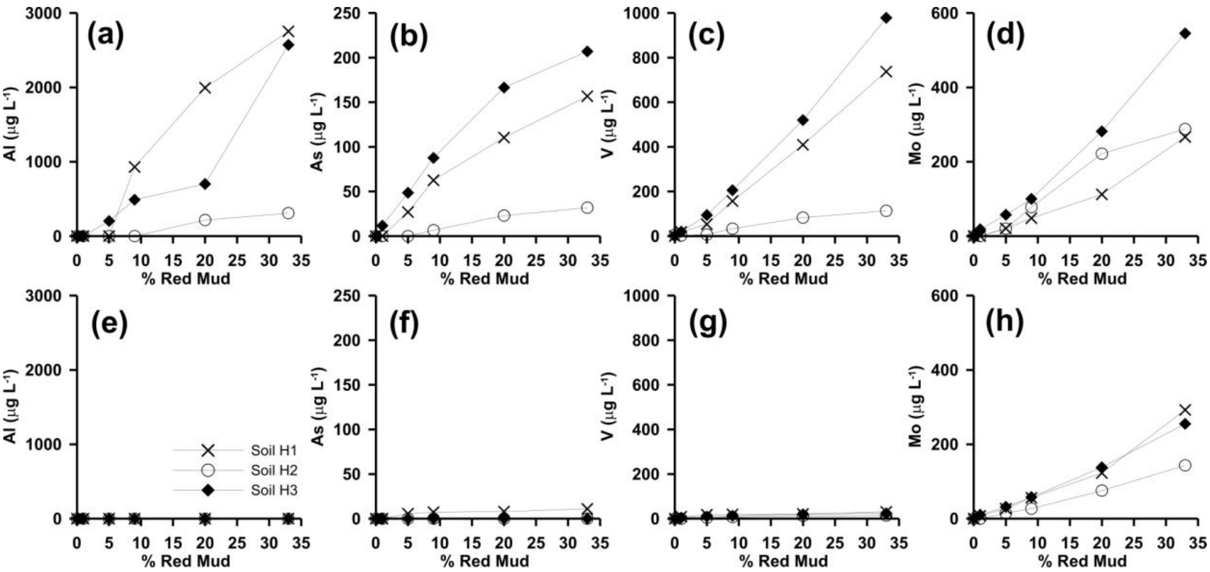

Figure 3. The effect of increasing red mud addition to three Hungarian soils on experimental trace element concentrations. Results are shown in both the absence (upper four panels) and presence (lower four panels) of 4% (w/w) gypsum addition.

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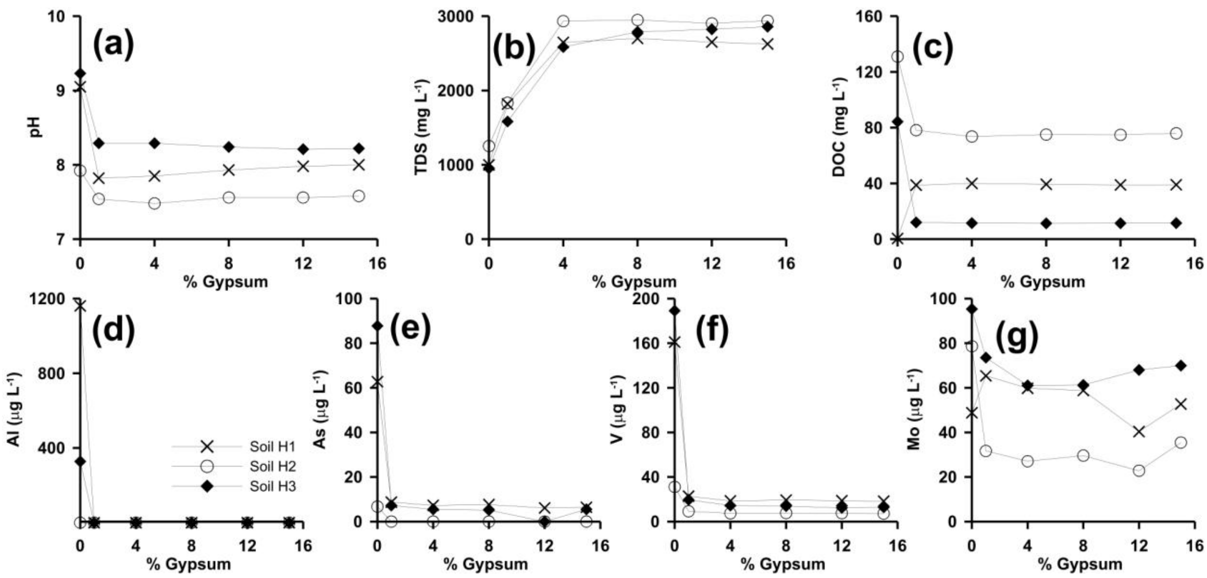

Figure 4. The effect of increasing gypsum addition to soil / red mud mixtures (9% red mud w/w) on experimental pH, total dissolved solids (TDS), dissolved organic carbon (DOC) and trace element concentrations.

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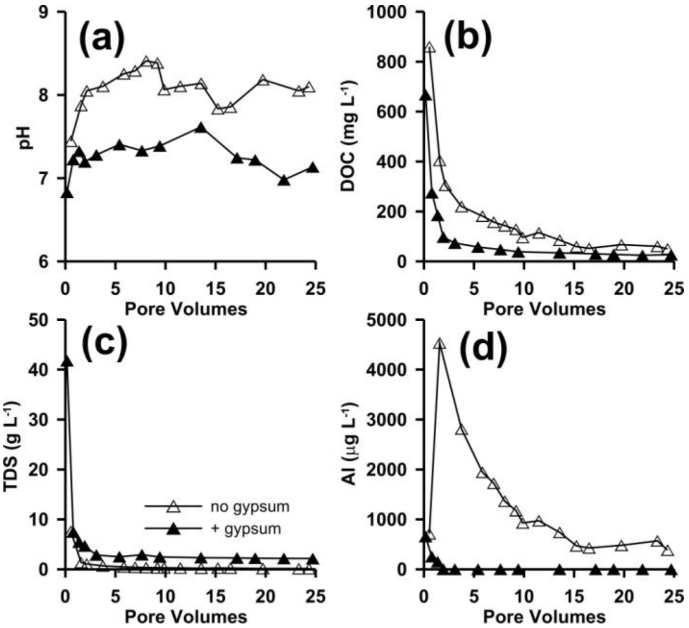

Figure 5. Evolution of effluent pH, total dissolved solids (TDS), dissolved organic carbon (DOC) and aluminium concentrations in column experiments, containing soil / red mud mixtures (8% red mud w/w) both with and without gypsum addition (also 8% w/w).

[TO BE REPRODUCED AT SINGLE COLUMN WIDTH]

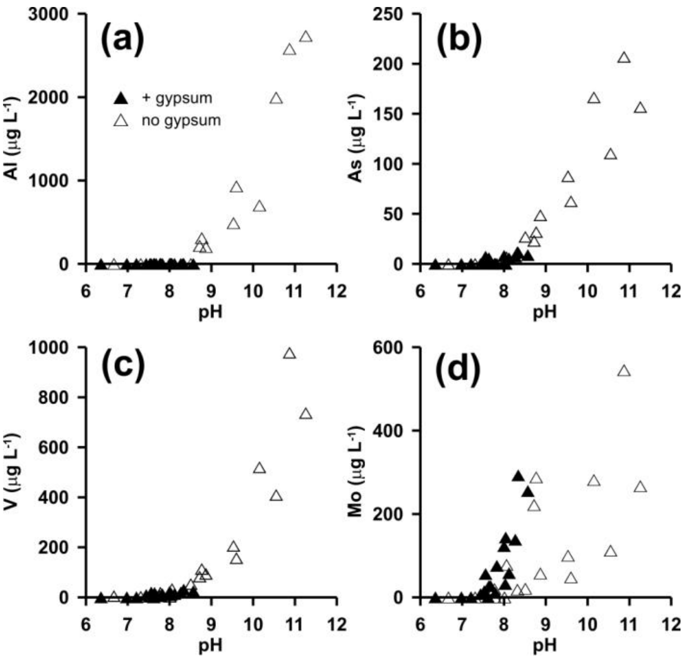

Figure 6. Plots of trace element concentrations vs final pH in batch experiments containing soil / red mud mixtures (N.B. highest pH and trace element concentrations were observed in experiments with highest red mud loadings), both with and without gypsum addition (4% w/w).

[TO BE REPRODUCED AT SINGLE COLUMN WIDTH]

APPENDIX A

Table A1. Data from duplicate batch experiments preformed using soils H1-3. The mean value and the range of duplicates are quoted in bold italics.

	pH	TDS (mg L^{-1})	DOC (mg L^{-1})	As (µg L^{-1})	V (µg L^{-1})	Mo (µg L^{-1})	Al (µg L^{-1})
9% red mud addition							
Soil H1	9.0, 9.6 ***9.3 ±0.3***	998, 991 ***994 ±4***	157, 99 ***128 ±29***	62.7, 62.6 ***62.7 ±0.1***	161, 157 ***159 ±2.0***	48.8, 48.2 ***48.5 ±0.3***	1161, 930 ***1045 ±116***
Soil H2	7.9, 8.1 ***8.0 ±0.1***	1253, 1252 ***1252 ±1***	143, 131 ***137 ±6***	6.7, 6.6 ***6.6 ±0.1***	31, 33 ***32 ±1.1***	78.6, 78.0 ***78.3 ±0.3***	<200, <200 **-**
Soil H3	9.2, 9.5 ***9.4 ±0.15***	952, 960 ***956 ±4***	157, 99 ***128 ±29***	88.0, 87.0 ***87.5 ±0.1***	189, 206 ***198 ±8.4***	95, 100 ***97.7 ±2.4***	328, 489 ***408 ±81***
9% red mud + 4% gypsum addition							
Soil H1	7.6, 7.9 ***7.8 ±0.15***	2703, 26471 ***2675 ±28***	39, 40 ***40 ±1***	7.3, 7.3 ***7.3 ±0***	19.2, 18.6 ***18.9 ±0.3***	56.0, 59.8 ***57.9 ±1.9***	<200, <200 **-**
Soil H2	7.7, 7.5 ***7.6 ±0.1***	2945, 2933 ***2939 ±6***	75, 73 ***74 ±1***	<0.5, <0.5 **-**	7.4, 7.6 ***7.5 ±0.1***	27.1, 29.6 ***28.3 ±1.3***	<200, <200 **-**
Soil H3	8.1, 8.3 ***8.2 ±0.1***	2826, 2585 ***2706 ±121***	11, 12 ***12 ±0.5***	5.5, 5.5 ***5.5 ±0***	13.2, 14.4 ***13.8 ±0.6***	57.9, 61.1 ***59.5 ±1.6***	<200, <200 **-**

< = less than given limit of detection

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