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Applied Geochemistry

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## Mobilisation of arsenic from bauxite residue (red mud) affected soils: Effect of pH and redox conditions



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### ARTICLE INFO

#### Article history:

Available online 20 October 2014

Editorial handling by M. Kersten

### ABSTRACT

The tailings dam breach at the Ajka alumina plant, western Hungary in 2010 introduced ~1 million m<sup>3</sup> of red mud suspension into the surrounding area. Red mud (fine fraction bauxite residue) has a characteristically alkaline pH and contains several potentially toxic elements, including arsenic. Aerobic and anaerobic batch experiments were prepared using soils from near Ajka in order to investigate the effects of red mud addition on soil biogeochemistry and arsenic mobility in soil–water experiments representative of land affected by the red mud spill. XAS analysis showed that As was present in the red mud as As(V) in the form of arsenate. The remobilisation of red mud associated arsenate was highly pH dependent and the addition of phosphate to red mud suspensions greatly enhanced As release to solution. In aerobic batch experiments, where red mud was mixed with soils, As release to solution was highly dependent on pH. Carbonation of these alkaline solutions by dissolution of atmospheric CO<sub>2</sub> reduced pH, which resulted in a decrease of aqueous As concentrations over time. However, this did not result in complete removal of aqueous As in any of the experiments. Carbonation did not occur in anaerobic experiments and pH remained high. Aqueous As concentrations initially increased in all the anaerobic red mud amended experiments, and then remained relatively constant as the systems became more reducing, both XANES and HPLC–ICP–MS showed that no As reduction processes occurred and that only As(V) species were present. These experiments show that there is the potential for increased As mobility in soil–water systems affected by red mud addition under both aerobic and anaerobic conditions.

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### 1. Introduction

Bauxite residue (red mud) is the fine fraction waste remaining after Al extraction from bauxite using the Bayer Process. The composition of red mud varies depending upon the quality of the ore and processing methods (Hind et al., 1999; Liu et al., 2007; Somlai et al., 2008). Typically, it comprises residual iron oxides, quartz, sodium aluminosilicates, titanium dioxide, calcium carbonate/aluminate and sodium hydroxide (Brunori et al., 2005; Gelencser et al., 2011; Grafe et al., 2011; Hind et al., 1999). Red mud can also contain problematic concentrations of potentially toxic metals and metalloids, including As, Cr, Ni, Pb, Mo and V

(Brunori et al., 2005; Grafe et al., 2011; Klebercz et al., 2012). Water in contact with red mud is saline and highly alkaline (between 1.4 and 28.4 mS m<sup>-1</sup>, up to pH 13 (Grafe et al., 2011; Mayes et al., 2011)) due to the presence of NaOH. Under these conditions there is potential for enhanced mobility of oxyanion forming trace elements (e.g. Al, As, Cr, Mo and V) (Cornelis et al., 2008; Langmuir, 1997; Smedley and Kinniburgh, 2002) due to their reduced adsorption to surfaces at high pH. These issues aside, the abundance of red mud as a waste product (up to 120 million tonnes are produced annually (Power et al., 2011)) has led to much research into possible uses. These include: recovery of Al, Fe, trace and rare earth metals (Hammond et al., 2013; Hind et al., 1999); a low cost sorbent for water decontamination (Altundogan et al., 2002; Bhatnagar et al., 2011; Liu et al., 2011); in CO<sub>2</sub> sequestration (Yadav et al., 2010); as an additive to ceramics and building materials (Liu and Zhang, 2011; Somlai et al., 2008) or as a soil amendment (Feigl et al., 2012; Friesl et al., 2004; Gray et al., 2006; Lombi et al., 2002).

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On 4 October 2010 the tailings dam of Cell X at the Ajkai Timfoldgyar Zrt alumina plant was breached, releasing  $\sim 1$  million  $\text{m}^3$  of red mud suspension (Adam et al., 2011; Reeves et al., 2011). The surge of red mud down the Torna and upper Marcal valleys inundated homes and land, killing 10 people and injuring over 150 (Adam et al., 2011; Enserink, 2010). An estimated 40  $\text{km}^2$  of low-lying agricultural land and riparian wetlands were affected (Mayes et al., 2011; Reeves et al., 2011) and red mud was transported 120 km downstream by rivers, eventually reaching the Danube (Adam et al., 2011; Enserink, 2010; Reeves et al., 2011). The immediate emergency environmental response sought to neutralise the pH of affected rivers and streams by the addition of acid and/or gypsum (Adam et al., 2011; Renforth et al., 2012). Further remediation efforts removed red mud from the affected land (Adam et al., 2011) but at some locations thin red mud deposits (<5 cm) were ploughed into soils to prevent dust formation and further dispersal (Adam et al., 2011; Anton et al., 2012; Gelencser et al., 2011). It was not possible to recover red mud deposited in low lying riparian wetlands.

This addition of red mud to soils introduced several potential contaminant trace elements (Mayes et al., 2011; Ruyters et al., 2011), including the highly toxic and redox sensitive metalloid arsenic. Ajka red mud contains  $\sim 200 \text{ mg kg}^{-1}$  As, primarily as inorganic arsenate phases (Burke et al., 2012a). Adsorption of As to red mud is known to be enhanced at circumneutral pH (as opposed to very high > 11.5, and low < 4.5 pH) (Altundogan et al., 2000; Genc-Fuhrman et al., 2004) and previous tests have found As leaching from Ajka red mud/soil mixtures (up to 16% red mud w/w) does not occur readily under aerobic conditions (Ruyters et al., 2011). These and similar findings have led researchers to conclude that fears of toxic metalloid leaching from red mud to soils have been overstated and that the main short-term issues from red mud addition to soils relate to increased pH and salinity (Anton et al., 2012; Gelencser et al., 2011; Gruiz et al., 2012; Klebercz et al., 2012; Ruyters et al., 2011).

Redox conditions in natural soils and sediments are prone to seasonal variations, particularly with fluctuations in groundwater levels. This can have a profound influence on the transport of As in the environment. Soils containing only modest As concentrations (<7  $\text{mg kg}^{-1}$ ) can produce unacceptably high concentrations of aqueous As in soil pore-waters under reducing conditions (Charlet and Polya, 2006; Hery et al., 2010). One of the key mechanisms responsible for high As concentrations is the reduction of arsenate to more soluble arsenite species during microbially mediated processes and the mobilisation of further As during the reductive dissolution of arsenate-bearing Fe(III) oxides (Islam et al., 2004; Lloyd and Oremland, 2006). Thus, if red mud deposits that have been mixed with soils in floodplain settings become exposed to anaerobic conditions, there is an increased possibility

of microbial processes leading to As release, and very high pore-water As concentrations might be expected (O'Day et al., 2004; Smedley and Kinniburgh, 2002).

The specific objectives of this study were: (1) To use aerobic and anaerobic batch experiments to investigate the potential for arsenic mobilisation from Ajka red muds and representative soil–red mud mixtures. (2) To use a combination of X-ray absorption spectroscopy and high performance liquid chromatography–ion coupled plasma–mass spectroscopy to determine changes in solid or aqueous phase As speciation induced by long term anaerobic incubation. (3) To determine the effects of red mud addition on biogeochemical processes in soil–water systems and relate soil geochemistry to mechanisms controlling As solubilisation in red mud amended soils.

## 2. Materials and methods

### 2.1. Field sampling and sample handling

Samples were collected in May 2011. A red mud sample (RM) was collected from within Cell X of the Ajka impoundment (Location 47°0'18.48"N, 17°29'46.77"E). Soil was sampled from three locations in the Torna and upper Marcal floodplains that did not receive red mud during the 2010 dam breach (see Fig. 1, for sampling locations: 47°06'39.03"N, 017°23'42.77"E; 47°05'45.95"N, 017°15'00.84"E; 47°05'50.24"N, 017°13'39.94"E). The sampling locations were chosen to capture local variations in composition, total organic carbon (TOC) and initial redox conditions. Two of the soils were agricultural top soils and the third sample was collected from below the rootlet layer 50 cm below the surface of a wetland. Samples were stored at 4 °C in polythene containers, (sub-samples were stored for XAS analysis at –80 °C). The wetland soil was stored anaerobically using Anaerogen™ sachets.

### 2.2. Sample characterisation

Red mud and soil samples were characterised by X-ray powder diffraction using a Bruker D8 Advance XRD, X-ray fluorescence using a PANalytical Axios Advanced XRF spectrometer; TOC using a Carlo Erba NA 2500 Elemental Analyser; pH was determined after 1 g: 1 ml suspension in deionised water (ASTM, 2006); and 0.5 N HCl extractable Fe(II) was determined by ferrozine assay (Lovley and Phillips, 1986). Inorganic phosphate was determined using the molybdate blue method (Aspila et al., 1976). Principal Component Analysis (PCA) of red mud and the soil samples was under-taken using standardised elemental concentration data and compared against published data (Mayes et al., 2011).

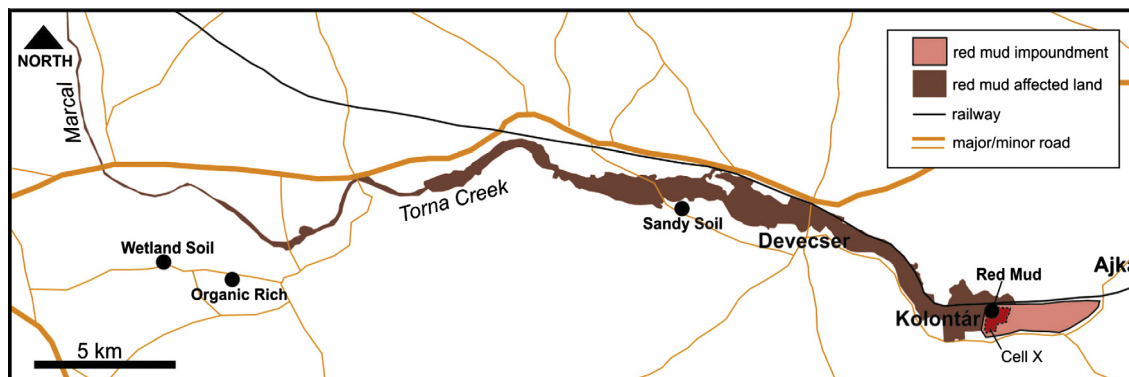


Fig. 1. Map showing the affected area and approximate sample locations.

### 2.3. Red mud batch leaching tests

Two gram aliquots of red mud were suspended in 10 mL of 0.1 M salt solutions ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{NaHPO}_4$ ) as a background electrolyte or deionised water for the 'no amendment' system. The pH values were adjusted to between 5.5 and 12.5 by addition of HCl or NaOH. After 7 days agitation on an orbital shaker (100 rpm), pH was determined and the aqueous phase was removed by filtration (0.45  $\mu\text{m}$ ) and As concentrations were determined using a Perkin–Elmer Optima 5300 DV ICP–OES.

### 2.4. Aerobic batch experiments

Triplicate aerobic microcosms for each soil type were prepared under three different conditions (all weights given as dry weight equivalents): (1) *Unamended* – 6.0 g of homogenised soil with 30 ml of deionised water in 50 mL polypropylene centrifuge tubes; (2) *9% RM addition* (representing a thin red mud deposit (~5 cm) mixed with 40–50 cm soil by ploughing) – the same as the unamended system with addition of 0.6 g RM; (3) *33% RM addition* (representing a thick red mud deposit (~15 cm) mixed with ~30 cm soil by ploughing or as a worst case scenario for wetland areas) – the same as the unamended system with addition of 3.0 g RM. Microcosms were incubated in the dark at 21 °C. The headspace was regularly exchanged with air (1 h each weekday) over a period of 100 days. During sampling microcosms were shaken and 3 mL aliquots of soil/RM slurry was extracted. Samples were centrifuged (3 min, 6000g) and the soil analysed for 0.5 N HCl extractable Fe(II). Water was analysed for pH, oxidation/reduction potential (ORP) and aliquots were filtered (0.2  $\mu\text{m}$ ) and acidified for ICP–MS analysis.

### 2.5. Anaerobic batch experiments

Triplicate anaerobic microcosms for each soil type were prepared under three different conditions, equivalent to the aerobic experiments (all weights given as dry weight equivalents): (1) *Unamended* – 20.0 g of homogenised soil with 100 ml of deionised water in 120 mL glass serum bottles; (2) *9% RM addition* – the same as the unamended system with addition of 2.0 g RM; (3) *33% RM addition* – the same as the unamended system with addition of 10.0 g RM. All bottles were purged with nitrogen before capping and crimp sealing. Triplicate anaerobic heat treated controls were also established as anaerobic experiments as, above but using autoclaved soils and red mud (120 °C, 1 h). Microcosms were incubated in the dark at 21 °C and sampled periodically. During sampling microcosms were shaken and 4.5 mL aliquots of soil/RM slurry were extracted using aseptic technique. Samples were centrifuged (3 min, 6000g) and the soil analysed for 0.5 N HCl extractable Fe(II). In these experiments the accumulation of 0.5 M HCl extractable Fe(II) in sediments is used to measure Fe(III) reduction. In sediment systems solid phase Fe(II) accumulation often precedes aqueous Fe(II) release by several weeks (Burke et al., 2006), and therefore, provides more reliable information regarding the timing of Fe(III) reduction in sediments. Water was analysed for pH, ORP and aliquots were filtered (0.2  $\mu\text{m}$ ) and acidified for ICP–MS analysis or frozen (–20 °C) for anion analysis. At the end point of each experiment 15 mL of slurry was extracted and centrifuged, the solution and the solids were frozen (–80 °C) until required for HPLC–ICP–MS analysis and XAS.

These experiments were designed primarily to investigate biogeochemical effects of red mud addition to the soils, therefore, the same inoculation of uncontaminated soil was used in all microcosms, however, the solid/liquid ratio varied by red mud loading. All experiments were initially sampled over a 100–120 day period, however, the anaerobic experiments were sampled again at

180 days as some biogeochemical reactions were still ongoing at 120 days in some tests.

(Note – from herein the experiments and controls will be referred to as 'aerobic experiments' 'anaerobic experiments' and 'heat treated controls'.)

### 2.6. Geochemical methods

pH and oxidation reduction potential (ORP – as an indicator for Eh) were measured using a Thermo Scientific Orion Dualstar pH benchtop metre (calibrated daily at pH values of 4, 7 and 10 and a new factory calibrated ORP electrode was used). Acid extractable Fe(II) was determined by ferrozine assay (Lovley and Phillips, 1986). Arsenic concentrations were determined using a Perkin–Elmer Elan DRCII ICP–MS. Anion concentrations were determined by ion chromatography using a Dionex DX500 and AS9 column. Arsenic speciation in 0.2  $\mu\text{m}$  filtered end point solutions was analysed by HPLC–ICP–MS. As(V) (as arsenate) and As(III) (as arsenite) were separated using a Hamilton PRP-X100 250  $\times$  4.6 mm column at 30 °C, using an Agilent 1260 Infinity HPLC system interfaced with an Agilent 7500 ICP–MS.

### 2.7. X-ray absorption spectroscopy (XAS)

As K-edge (11,867 eV) XANES and EXAFS spectra were collected (from 0–8 and 0–14  $\text{\AA}^{-1}$  respectively) on station I18 at the Diamond Light Source, UK, in May, 2012. Approximately 100 mg of sample was prepared under anaerobic conditions for analysis as moist pastes in Perspex holders with Kapton™ windows. Spectra were collected in fluorescence mode at room temperature (~295 °K) using a 9 element solid state Ge detector. Standard spectra were collected from aqueous As(III) and As(V) solutions (as sodium arsenate ( $\text{Na}_3\text{AsO}_4$ ) and sodium arsenite ( $\text{Na}_3\text{AsO}_3$ ) respectively) at 1000  $\text{mg L}^{-1}$  [As]. As K-edge spectra from solid samples were found to be affected by beam damage presenting as an apparent change in As speciation that increased in magnitude with increased exposure to the beam. To mitigate this effect, only single As K-edge EXAFS spectra were collected (~20 min) from a spot within the sample and the sample stage automatically moved to expose an unaffected part of the sample before subsequent scans. For each sample and standard multiple XANES spectra ( $n = 4–8$ ) were averaged and normalised using Athena v0.8.061. For the red mud sample, the average of 9 arsenic K-edge EXAFS spectra were background subtracted using PySpline v1.1. EXAFS spectra were then fit in DLExcurv v1.0 (Tomice et al., 2005) over 3–14  $\text{\AA}^{-1}$  to model clusters (see SI, Section 1, for detailed methods and protocols).

## 3. Results

### 3.1. Sample characterisation

Sample characterisation of the red mud and soils has been summarised (Table 1) (see SI for XRD patterns and full XRF analysis: Figs. S1, S2 and Table S1). Briefly; XRD analysis showed that the red mud was dominated by hematite ( $\text{Fe}_2\text{O}_3$ ), calcite ( $\text{CaCO}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), cancrinite ( $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}2\text{H}_2\text{O}$ ) and hydrogarnet ( $\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$ ) with residual boehmite ( $\gamma\text{-AlOOH}$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ ) phases.

The pH value of the three soils was between pH 7 and 8. The dominant minerals in all three soil samples was quartz, feldspars and clays. The first soil was a sandy clay loam topsoil that had 4.15% organic carbon content (hereafter referred to as 'organic-rich soil'). The wetland sample was a very dark grey sandy clay loam with 1.14% organic carbon (hereafter referred to as 'wetland soil').

**Table 1**  
Red mud and soil characterisation.

Soil type	pH	% 0.5 N HCl acid extractable iron as Fe(II)	TOC (%)	As mg kg <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> mg kg <sup>-1</sup>	Major minerals present	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )
Red mud	12.2 (±0.1)	22 (±3)	0.2	200	1019	Hematite, calcite, hydrogarnet, boehmite, cancrinite	14.40 (±0.07)
Organic-rich	6.8 (±0.1)	10 (±2)	4.2	11	297	Quartz, albite, clinochlore, muscovite, illite	1.78 (±0.20)
Wetland	7.9 (±0.1)	87 (±14)	1.1	8	355	Quartz, albite, clinochlore, muscovite, illite	2.61 (±0.01)
Sandy	7.9 (±0.1)	5 (±2)	0.7	2	520	Quartz, albite, clinochlore, illite	0.94 (±0.01)

The third soil was sandy loam topsoil with 0.74% organic carbon (hereafter referred to as 'sandy soil'). Principle component analysis of red mud and the 3 soils shows that the soils have similar composition to other unaffected soils from the region and that the red mud sampled here is of a similar composition to other red mud samples from the Ajka source (Burke et al., 2012a; Gelencser et al., 2011; Mayes et al., 2011) (see SI Fig. S3 for a more detailed explanation).

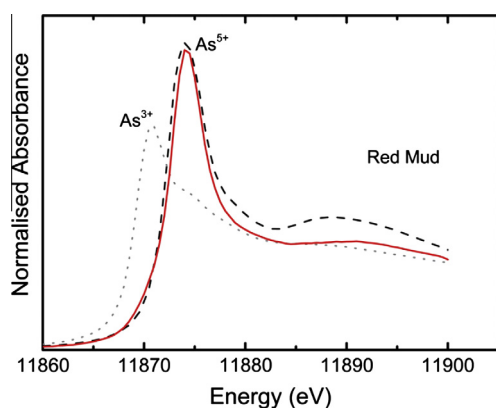
### 3.2. Arsenic in red mud

The XANES spectra collected from red mud shows that As is present as As(V) (Fig. 2). Arsenic K-edge EXAFS spectra from the same red mud sample (Fig. 3) could be fitted with a co-ordination environment of 4 oxygen backscatterers at 1.67–1.69 Å (Table 2) consistent with a tetrahedral arsenate structure. The fit of the data could not be improved by including any additional shells of Al or Fe backscatterers and there is no evidence to suggest there is any contribution from atoms at longer distances.

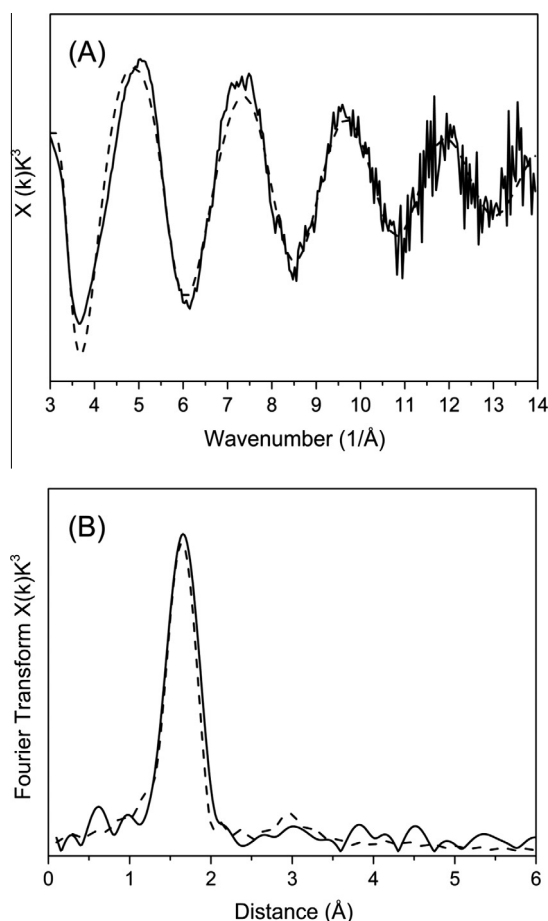
Red mud batch leaching tests (Fig. 4) show that As is mobilised from red mud at high pH. The system without a background electrolyte indicates that As is mobilised above pH 9. This effect was greatly enhanced when phosphate and, to a lesser extent carbonate were used as background electrolytes, (mobilisation started to occur at pH 8 and 8.5, respectively). When phosphate was used, there was a maximum As desorption at ~pH 10 resulting in ~6.5 mg L<sup>-1</sup> in solution representing ~15% of total As present in the red mud.

### 3.3. Aerobic incubation experiments

The pH in the unamended aerobic experiments remained relatively constant over the incubation period (Fig. 5a–c) at values close to the initial soil pH (see Table 1). Experiments with a red



**Fig. 2.** Normalised arsenic K-edge XANES spectra collected from standards and red mud (collected from within Cell X of the Ajka impoundment, May 2011). Grey dotted line = arsenite standard (As<sup>3+</sup>). Black dashed line = arsenate standards (As<sup>5+</sup>). Red line = red mud sample (RM). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** (A) Background subtracted As K-edge EXAFS spectra of a red mud sample (collected from within Cell X of the Ajka impoundment, May 2011). (B) Corresponding Fourier transforms calculated from EXAFS spectra. Dashed lines represent DLexcur V1.0 model fits using the parameters listed in Table 2.

**Table 2**

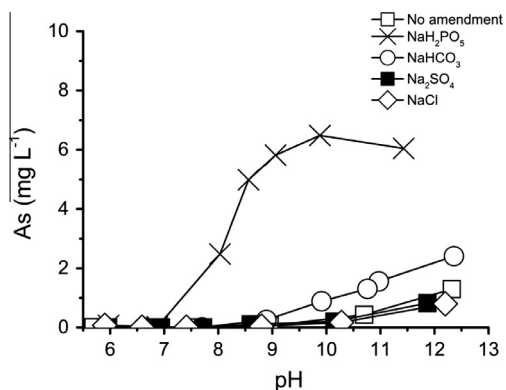
Red mud As K-edge EXAFS fits where *N* is the occupancy,<sup>b</sup> *R* is interatomic distance  $2\sigma^2$  is the Debye–Waller factor and *R* and reduced  $\chi^2$  are the least squares residual and the reduced  $\chi^2$  goodness of fit parameters, respectively.<sup>a</sup>

Shell <sup>a</sup>	<i>N</i>	<i>R</i> (Å)	$2\sigma^2$ (Å <sup>2</sup> )	Goodness of fit	
				<i>R</i> (%)	Reduced $\chi^2$
O	1 <sup>b</sup>	1.67 ± 0.02	0.010 ± 0.003	29	4.1
O	1 <sup>b</sup>	1.68 ± 0.02	0.007 ± 0.002		
O	1 <sup>b</sup>	1.68 ± 0.02	0.006 ± 0.002		
O	1 <sup>b</sup>	1.69 ± 0.02	0.007 ± 0.002		

<sup>a</sup> Four As–O bonds have been considered separately to allow for multiple scattering within the AsO<sub>4</sub> tetrahedron. *N* values were held constant during the fitting (see SI Section 1.2 for further details).

<sup>b</sup> Shell occupancy was fixed at 1 during fitting.





**Fig. 4.** Red mud leaching batch tests showing increased aqueous concentration of aqueous As with a background electrolyte of 0.1 M phosphate and carbonate when compared against a no amendment system with deionised water.

mud addition showed an increase in pH which correlated with red mud loading. The sandy soil experiments were most affected by red mud addition and initially the pH increased from pH 8 in the unamended systems to pH 10 with 9% RM addition and to pH 11.5 with 33% RM addition. The pH in the aerobic experiments with red mud addition gradually decreased over the incubation period (Fig. 5a–c) in all experiments except for the organic-rich experiment with 9% RM addition (Fig. 5a). In this experiment, there was an initial increase in pH from pH 7 to pH 8, which then remained constant.

ORP measurements in the aerobic experiments increased over the first 20 days from +50 to +150 mV to eventually reach values around +250 mV in all experiments indicating that generally oxic conditions were maintained throughout the incubation (see SI Fig. S4a–c).

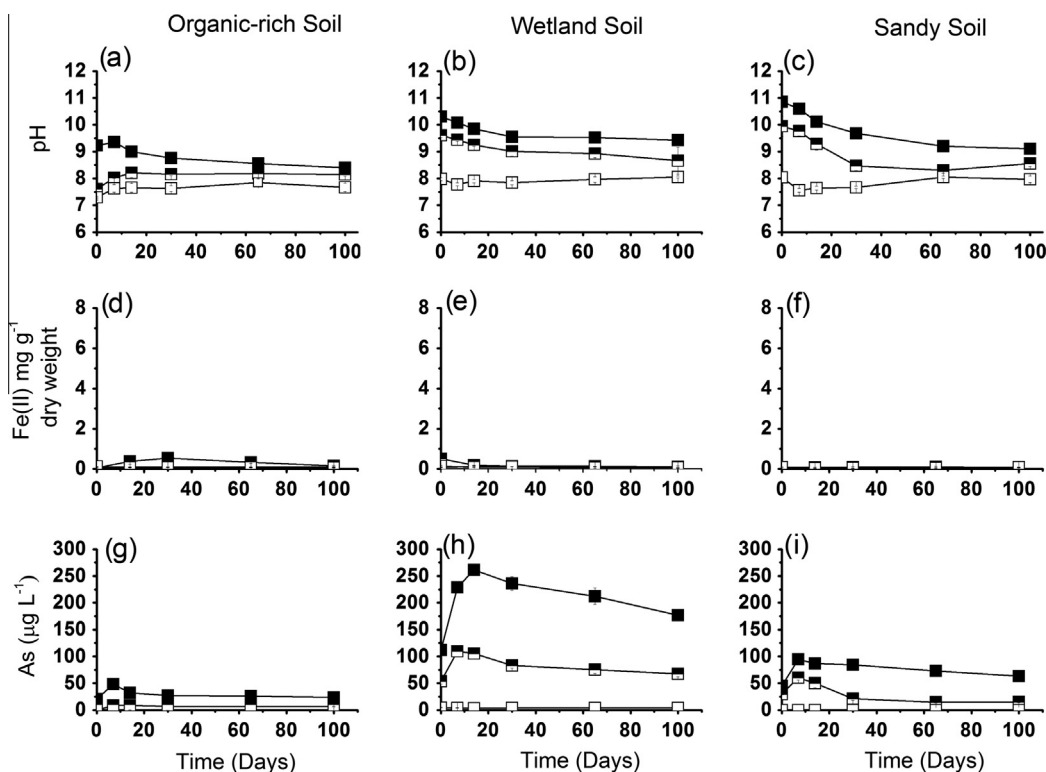
Acid extractable Fe(II) was monitored in the aerobic experiments as a check for any bioreduction processes that might affect As mobilisation (i.e. there is a strong link expected between Fe(III)-reduction and enhanced As solubility (Islam et al., 2004; Oremland and Stolz, 2005)). Concentrations in all the aerobic experiments were <1 mg g<sup>-1</sup> dry weight and, there was no significant change with time (Fig. 5d–f). Aqueous phase electron acceptors such as nitrate and sulphate were not monitored as a combination of high ORP and negligible Fe(II) accumulation was considered a sufficient negative control with respect to bioreduction processes.

At the initial sampling points the unamended aerobic experiments all had no detectable aqueous As present. However, in the experiments with a red mud addition, there was detectable aqueous As in all the aerobic experiments, with the exception of organic-rich soil with a 9% RM addition. The initial aqueous As concentration was highest (~100 µg L<sup>-1</sup>) in the wetland soil with a 33% RM addition (Fig. 5g–i).

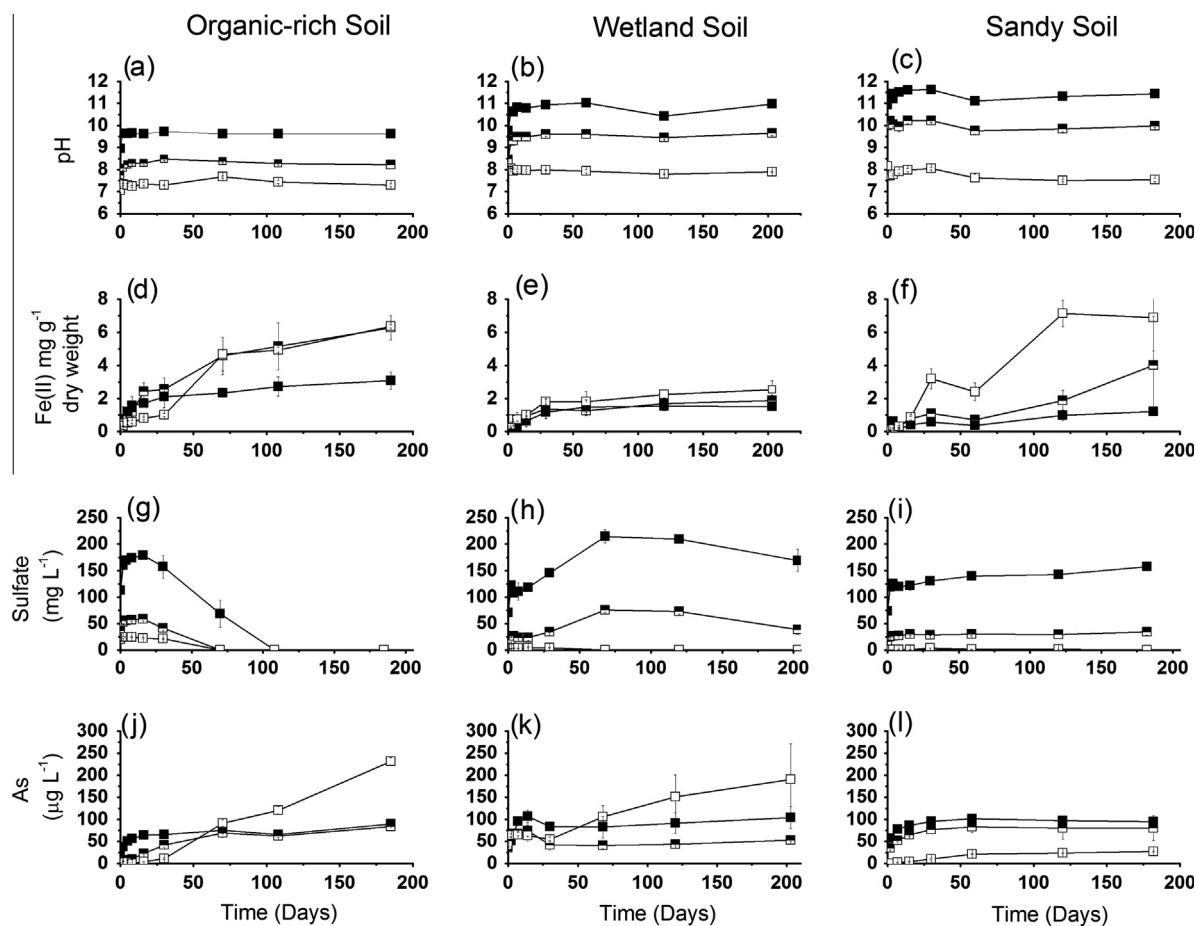
There was no increase in aqueous As concentrations in unamended aerobic experiments over the incubation period. When red mud was added to the aerobic experiments aqueous As concentrations increased in line with red mud loading to between 50 and 250 µg L<sup>-1</sup> with lowest concentrations in the organic-rich soil system and highest in the wetland soil system (Fig. 5g–h). Each aerobic experiment with red mud addition followed a similar trend of rapid release over the first 10 day followed by a long period of removal.

### 3.4. Anaerobic incubation experiments

The pH values in the anaerobic experiments (Fig. 6a–c) and in parallel heat treated controls (see SI Fig. S6a–c) varied with red mud loading and soil type. They also closely matched the initial pH values found in the corresponding aerobic experiments (Fig. 5a–c). However, the pH in the anaerobic experiments did



**Fig. 5.** Geochemical analysis time plots from aerobic experiments showing pH, Fe(II) mg g<sup>-1</sup> dry weight and total As. Empty squares = unamended, Half squares = 9% RM addition, Full squares = 33% RM addition. Error bars are 1  $\sigma$  of triplicate results (error bars are within the symbol size and, therefore are not shown). *N. b.* the scale heights for these graphs are matched with Fig. 6 to allow for comparison between data from the aerobic and the anaerobic experiments.



**Fig. 6.** Evolution of pH, acid extractable Fe(II), aqueous  $\text{SO}_4^{2-}$  and As concentrations in anaerobic red mud affected experiments and unamended controls. Empty squares = unamended, Half squares = 9% RM addition, Full squares = 33% RM addition. Error bars are 1  $\sigma$  of triplicate results (where not shown, errors are within the symbol size).

not change significantly with time. In the anaerobic microcosms ORP values show the opposite trend to aerobic tests, reducing to negative values (between 0 and  $-400$  mV) indicating progressively more reducing conditions occurred with time (see [SI Fig. S4d–f](#)).

The trend to more reducing conditions was also accompanied by changes in soluble and solid phase redox indicators. In the anaerobic experiments, there was some evidence of rapid nitrate removal occurring in the organic-rich and sandy soil experiments at the beginning of the incubation period (see [SI Fig. S5](#)).

The amount of 0.5 N HCl extractable Fe(II) in the solid phase increased significantly with incubation time in most anaerobic experiments from initial values  $\leq 1$   $\text{mg g}^{-1}$  ([Fig. 6d–f](#)). For each soil type the largest increases in acid extractable Fe(II) were observed in the unamended experiments, with progressively smaller increases with a 9% and 33% RM addition (although in the unamended and 9% RM addition experiments with organic-rich soil exhibited similar overall increases). The rate of accumulation of acid extractable Fe(II) also varied with soil type. The organic-rich and wetland soil systems showed increases after only short incubation times (before 30 days), but the sandy soil experiments responded much more slowly. Heat treated controls showed no significant increases in acid extractable Fe(II) in the wetland or the sandy soil systems ([SI Fig. S6e–f](#)). Acid extractable Fe(II) does increase in heat treated organic-rich soil controls, but the increases are smaller than those observed in the equivalent anaerobic experiments.

In the unamended anaerobic experiments the aqueous  $\text{SO}_4^{2-}$  concentration was  $\sim 25$   $\text{mg L}^{-1}$  in the organic-rich soil, and negligible in the wetland and sandy soils ([Fig. 6g–i](#)). The addition

of RM caused a significant increase in  $\text{SO}_4^{2-}$  concentrations for all the soil types that was roughly proportional to the amount of RM added. The pattern of  $\text{SO}_4^{2-}$  removal was different for each soil system. In the organic-rich soil anaerobic experiments complete removal of  $\text{SO}_4^{2-}$  occurred after 100 days under all conditions (no removal occurred in corresponding heat treated controls, see [SI Fig. S6g–i](#)). The wetland soil system exhibited a rapid increase in  $\text{SO}_4^{2-}$  concentrations between 30 and 60 days in the 9% RM and 33% RM additions which was followed by a gradual removal. Again, no removal occurred in corresponding heat treated controls. In the sandy soil system the  $\text{SO}_4^{2-}$  concentrations were proportional to the amount of RM addition and remained relatively constant throughout the incubation period for both the anaerobic experiments and heat treated controls.

At the initial sampling point, the unamended anaerobic experiments containing the sandy and organic-rich soil had no detectable aqueous As present. However, the wetland soil anaerobic experiments contained  $\sim 40$   $\mu\text{g L}^{-1}$  As. The aqueous As concentrations in all three unamended anaerobic experiments increased above their initial values by day 30, and continued to rise for the remainder of the experiments. Concentrations reached  $>200$   $\mu\text{g L}^{-1}$  in the organic-rich and wetland soil microcosms, but did not exceed  $25$   $\mu\text{g L}^{-1}$  in the sandy soil experiments. HPLC–ICP–MS analysis performed on the aqueous phase sampled at experiment end points showed that  $\sim 50\%$  of aqueous As was present as As(III) in all three soil-only systems ([Table 3](#)).

When red mud was added to the anaerobic experiments there was an increase in the initial aqueous As concentrations that

**Table 3**

Percentages of As(V) (as arsenate) and As(III) (as arsenite) present in end point solutions taken from anaerobic experiments.

Soil	Red Mud (%)	Total As $\mu\text{g L}^{-1}$	% As(III)	% As(V)
Organic-rich soil	0	232 ( $\pm 9$ )	50 ( $\pm 0$ )	50 ( $\pm 0$ )
	9	84 ( $\pm 10$ )	1 ( $\pm 1$ )	99 ( $\pm 1$ )
	33	89 ( $\pm 5$ )	4 ( $\pm 4$ )	96 ( $\pm 4$ )
Wetland soil	0	190 ( $\pm 81$ )	53 ( $\pm 2$ )	47 ( $\pm 2$ )
	9	53 ( $\pm 3$ )	0 ( $\pm 1$ )	100 ( $\pm 1$ )
	33	104 ( $\pm 25$ )	0 ( $\pm 1$ )	100 ( $\pm 1$ )
Sandy soil	0	27 ( $\pm 1$ )	47 ( $\pm 9$ )	53 ( $\pm 9$ )
	9	80 ( $\pm 28$ )	1 ( $\pm 1$ )	99 ( $\pm 1$ )
	33	95 ( $\pm 8$ )	0 ( $\pm 1$ )	100 ( $\pm 1$ )

directly related to red mud loading (Fig. 6j–l). The As concentration increased over the first 30–60 days of incubation with all three soils but then remained relatively constant thereafter. The final As concentration in all the anaerobic experiments with red mud addition was between 50 and 125  $\mu\text{g L}^{-1}$ . HPLC–ICP–MS analysis performed on the aqueous phase sampled at the end of the incubation period showed that <5% of aqueous As was present as As(III) in all anaerobic experiments with a red mud addition (Table 3).

Arsenic K-edge XANES spectra (Fig. 7) collected from the Hungarian soils all have absorption edge positions and white line peaks at the same energy as the arsenate standard indicating that As in the soils is primarily present As(V). The spectra collected from the wetland soil have a shoulder on the As(V) absorption edge at the same energy as the white line peak of the arsenite standard, indicating a small contribution from As(III) to this spectra. The spectra from unamended anaerobic experiments at the incubation period end-point showed an As(III) shoulder for the wetland and sandy soils, and an increase in the shoulder for the organic-rich soil suggesting that some of the As present in the unamended anaerobic experiments was reduced to As(III) during incubation.

Sediment from the incubation end point from anaerobic experiments that contained red mud and either wetland or sandy soil have very similar As XANES spectra to the equivalent heat treated controls. The edge position and white line peaks are at the same energy as the arsenate standard, indicating that the majority of As is present as As(V). XANES spectra collected from samples taken from the organic-rich anaerobic experiments with either 9% or 33%

RM have small shoulders at the same energy as the arsenite standard. This shoulder is not apparent in samples from corresponding heat treated controls indicating that some of the As present had been reduced to As(III) in these experiments.

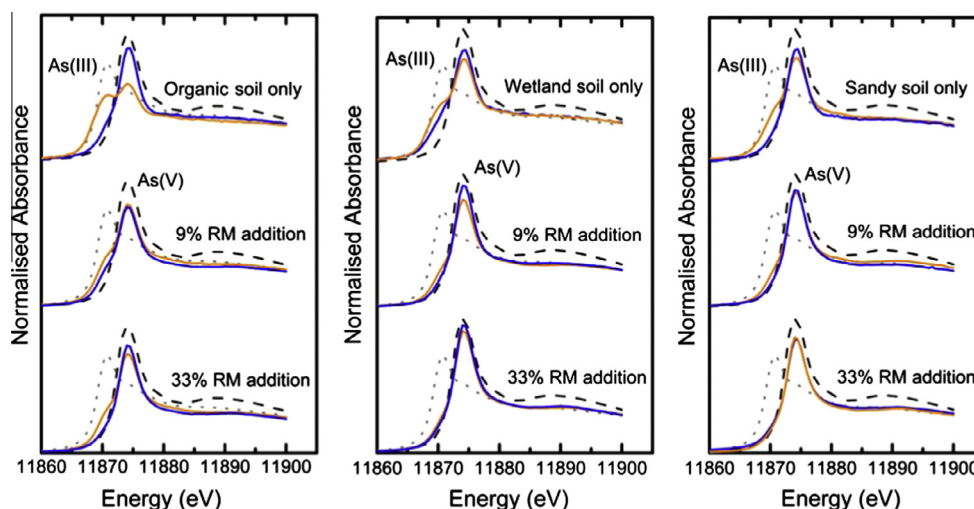
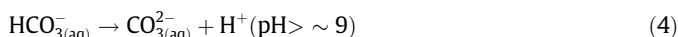
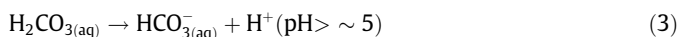
## 4. Discussion

### 4.1. The occurrence of As in red mud and the effect of pH/completing ions on As release

XAS analysis has determined that As in the red mud sampled is present primarily as an inorganic arsenate phase (Fig. 2), however, in this case EXAFS analysis could not resolve the exact nature of the phases present due to a lack of evidence for second shell backscatters in the spectra. In sequential extractions, most of the As could only be extracted by HF/aqua regia (Mayes et al., 2011) suggesting that it is associated with residual phases (in Ajka red mud the residual phase consists of almost all the Fe oxides (>99%), and much of the Al, Si and Ti containing phases present (Mayes et al., 2011)). Arsenic associated with residual phases is unlikely to be easily remobilised or bioavailable. However, alkaline leaching tests indicate that a source of potentially mobile surface bound As exists in red mud. Alkaline leaching tests (Fig. 4) indicated that up to 15% of the red mud associated arsenic can be desorbed when phosphate is present as a competing ion at pH values > 8. Therefore, there is the significant potential for surface bound As to be released from red mud by competitive desorption processes involving  $\text{OH}^-$ , phosphate or carbonate ions (Ghosh et al., 2006).

### 4.2. Controls on As release during aerobic incubation

The ingress and dissolution of atmospheric  $\text{CO}_2$  in alkaline solutions results in a pH reduction as net alkalinity is consumed by the following reactions Eqs. (1)–(5):



**Fig. 7.** Normalised arsenic K-edge XANES spectra collected from standards, soil samples and solids recovered anaerobic experiments and heat treated controls. All graphs: Grey dotted line = arsenite, As(III), Black dashed line = arsenate, As(V). Top graphs: blue line = soil as sampled, orange line = soil at end point of unamended anaerobic experiments. Middle and bottom graphs: blue line = samples taken from heat treated controls at end point, orange line = samples taken from anaerobic experiments at end point. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$M^{2+}$  ions, such as  $Ca^{2+}$  and  $Mg^{2+}$ , can be exchanged from the soil by  $Na^+$  ions present in the red mud, or alternatively sourced from the dissolution of Ca aluminosilicate minerals (e.g. cancrinite/hydrogarnet (Hind et al., 1999; Rubinos and Barral, 2013)) present in red mud that are unstable below pH 12 (Castaldi et al., 2010). These  $M^{2+}$  ions, can then precipitate carbonate phases (e.g.,  $Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-} \rightarrow CaCO_{3(s)}$ ), therefore promoting the further dissolution of atmospheric  $CO_2$  as carbonate is removed from solution (Burke et al., 2013; Renforth et al., 2012).

In aerobic experiments containing red mud, there was a large variation in the concentrations of aqueous As, which varied depending upon red mud loading and soil type. However, regardless of peak As concentrations, all the aerobic experiments showed a decrease in As concentrations that was concurrent with an overall decrease in solution pH with time. This suggests that As release from the aerobic experiments is largely controlled by solution pH. In the aerobic experiments containing red mud there was a positive correlation between aqueous As concentrations and pH at the experimental end point (See SI Fig. 7a). Although the reduction in pH observed with time tended to also result in a trend towards lower As concentrations with time, the final pH was buffered in all systems to pH values (pH 8.5–9.5) where a low arsenic concentration would be expected. However, in these aerobic experiments,  $CO_2$  ingress may lead to higher aqueous carbonate concentrations (where pH buffers > 9), which would be expected to be a competing ion for available sorption sites (Arai et al., 2004), promoting As release into solution.

#### 4.3. Effects of red mud addition on biogeochemical redox processes

Unamended anaerobic experiments using the wetland and sandy soils showed increases in acid extractable Fe(II) that were not observed in either the equivalent heat treated controls or equivalent aerobic experiments, suggesting that microbially mediated Fe(III) reduction occurred during anaerobic incubation. In the case of the unamended anaerobic experiments using the organic-rich soil, an increase in acid extractable Fe(II) was observed in both the heat-treated controls and anaerobic experiments (but not in equivalent aerobic experiments). The Fe(II) increase observed in heat-treated controls may be related to recovery of microbial activity in these tests e.g. involving the survival of bacterial spores (Esty and Williams, 1924). However, the amount of acid extractable Fe(II) detected in the heat-treated controls was much lower than in the unamended anaerobic experiments (i.e. an increase of  $<1.5 \text{ mg g}^{-1}$  compared with  $>6 \text{ mg g}^{-1}$ ).

Microbial Fe(III) reduction also occurred in both red mud amended anaerobic experiments using the organic-rich soil (pH 8.5 and 9.5 respectively) and wetland (pH 9.5 and 10.5 respectively), and the sandy soil amended with 9% red mud (pH 10). Microbial Fe(III) reduction was probably inhibited in the sandy soil amended with 33% red mud due to the high pH (pH 11.5). These results are consistent with thermodynamic calculations indicating that Fe(III) reduction is not generally favoured above pH 11 (Burke et al., 2012b; Rizoulis et al., 2012). Although several groups of alkaliphilic bacteria are capable of Fe(III)-reduction at pH values up to pH 11 (Burke et al., 2012b; Pollock et al., 2007; Whittleston et al., 2011; Ye et al., 2004; Zhilina et al., 2009), these bacteria have adapted to high pH conditions by prolonged exposure. It is, therefore, unlikely that any microbes present in the sample soils have quickly adapted to life at high pH. However, these data indicate that the microbial communities present in these soils contain species capable of Fe(III)-reduction that are tolerant of the increase in pH and other challenges (e.g. increased salinity and toxic metal loadings) caused by red mud addition.

Despite the large amounts of Fe(III)-oxides present in Ajka red mud (~30–40% hematite determined previously by (Gelencser

et al., 2011)), the increases in acid extractable Fe(II) detected in the red mud amended anaerobic microcosms is equivalent to (or less than) unamended anaerobic microcosms. The iron oxides present in red mud is nanoparticulate hematite (50–200 nm) (Burke et al., 2012a; Gelencser et al., 2011; Mayes et al., 2011). Although smaller hematite nanoparticles (<10 nm in size) are potentially bioavailable (Dehner et al., 2011), hematite is much less bioavailable than poorly ordered iron oxyhydroxides (Cutting et al., 2009). Therefore, the low bioavailability of hematite can account for the lack of additional Fe(II) production observed in red mud amended experiments. The lack of reactive Fe is further evidenced from sequential extraction data indicating that all Fe in red mud was associated with residual phases (Mayes et al., 2011). Any increases in Fe(II) seen in the experiments containing red mud were, therefore, most likely the result of microbial reduction of the reactive Fe(III)-oxides already present in the soils.

Addition of red mud to microcosms increases initial sulphate concentrations compared to soil only systems. Rapid removal of  $SO_4^{2-}$  was seen in organic-rich soil anaerobic experiments amended with both 9% and 33% red mud. Slower removal of sulphate was observed in the wetland soil anaerobic experiments containing red mud but no removal of  $SO_4^{2-}$  occurred in any of the sandy soil anaerobic experiments where red mud was present. In the heat treated controls  $SO_4^{2-}$  concentrations were similar to the peak concentrations seen in the anaerobic experiments. There was no  $SO_4^{2-}$  removal observed in any of the heat treated controls. This difference in behaviour between anaerobic experiments and heat treated controls suggests that  $SO_4^{2-}$  removal was a result of microbial sulphate reduction.

Microbial sulphate reduction is observed in some alkaline soda lakes (with an average pH up to 11) (Foti et al., 2007), but more generally sulphate reduction is not thermodynamically favoured much above pH 9 (Burke et al., 2012b; Rizoulis et al., 2012). In these experiments, three anaerobic experiments that all equilibrated between pH 9.5 and 10 had entirely different responses (i.e. organic-rich soil + 33% red mud = complete removal; wetland soil + 9% red mud addition = partial removal; and sandy soil + 9% red mud = no removal), suggesting that trends in  $SO_4^{2-}$  removal in the different systems appear to be soils specific, as they cannot be completely explained by the impact of the pH change or amount of red mud present.

#### 4.4. As release in anaerobic experiments with no red mud additions

The concentration of As in unamended anaerobic experiments were minimal at the start of incubation. However, large increases in aqueous As concentrations were seen in both the organic-rich and wetland unamended anaerobic experiments which were found to be ~50% As(III). Although increases of aqueous As were much lower in the sandy soil unamended anaerobic experiment (this is consistent with the lower native As content of this soil) aqueous As was also found to be ~50% As(III). The reduction of As(V) to As(III) in the unamended anaerobic experiments could be an indication that microbial arsenic reduction was occurring. Microbial As(V)-reduction in natural soils is well documented (Dowdle et al., 1996; Lloyd and Oremland, 2006; Oremland and Stolz, 2003) and is a key mechanism contributing to high As concentrations in naturally contaminated waters (Charlet and Poly, 2006; Islam et al., 2004; Oremland and Stolz, 2005). As(III) is generally more mobile than As(V) at circumneutral pH (Smedley and Kinniburgh, 2002; Zobrist et al., 2000), thus accounting for the increased concentrations seen in unamended anaerobic experiments. Further evidence of As reduction is present in the XANES spectra from these experiments. XANES spectra revealed that As in each of the soils was initially present primarily as As(V) but



small increases in the contribution of As(III) to XANES spectra were observed as a result of the microcosm incubation.

#### 4.5. As release in anaerobic experiments amended with red mud

XANES and HPLC–ICP–MS analysis of the anaerobic experiments containing red mud found that As was almost entirely present as As(V) with no evidence of significant As(III) accumulation in either solution or in solids. Therefore, very little As reduction occurred in any of the red mud amended systems despite the fact that microbial Fe(III)- and sulphate-reduction was supported in several of the red mud containing experiments. In addition significant microbial mediated As reduction occurred in all the unamended anaerobic experiments, demonstrating that both bioavailable As(V) and a microbial community capable of As-reduction was present in the soils used. Arsenic reduction is a common biological process in soda lakes, which are both alkaline and saline like red mud contaminated systems (Oremland et al., 2004, 2005). However, the population As reducing bacteria present in these soils were not able to tolerate the additional stresses caused by red mud addition and did not support As(V) reduction processes even when pH increases observed were relatively modest (e.g. in the experiments using the organic rich soil).

In the absence of microbial induced changes of As speciation, experimental pH should be the primary control of surface bound arsenate associated with red mud. In the anaerobic experiments, pH values were higher than equivalent aerobic experiments (as CO<sub>2</sub> ingress was prevented) but As concentrations were similar (or slightly lower) than in the aerobic experiments (see SI Fig. S7b). However, in the anaerobic experiments using the organic-rich soil with a 9% RM addition (at pH 8–8.5), As concentrations were between 5 and 10 times higher than the equivalent aerobic experiments. Fe(III)-reducing conditions developed in the anaerobic experiments (Fig. 6d). The reductive dissolution of iron oxide minerals is expected to promote the release surface bound arsenate into solution (Islam et al., 2004; Zachara et al., 2001), which might explain the increased As(V) concentrations observed in this experiment (and the overall lack of correlation between As concentration and pH observed in SI Fig. S7b).

## 5. Conclusions

Arsenic in red mud is present as As(V) as arsenate species where up to 15% is present in phosphate exchangeable surface bound complexes that have the potential to be remobilised. Arsenate release to solution from red mud is enhanced at high pH and also by the presence of competing ions such as phosphate and carbonate. In aerobic soil systems, As release is related to red mud loading and the pH value that occurs due to soil buffering reactions. Subsequent carbonation reactions reduce the pH with time resulting in a trend towards lower aqueous As concentrations under aerobic conditions. However, dissolved CO<sub>2</sub> (speciated as carbonate at pH > 9) may also provide a source of competing ions, thus increasing As concentrations. In anaerobic experiments, carbonation reactions do not occur and experimental pH is determined by red mud loading and the buffering capacity of the soils used. As(V) release is not strongly dependant on experimental pH, and some As release is observed in all experiments. Microbial reduction of As(V) to As(III) was observed in the anaerobic experiments without red mud addition, but there is no significant reduction of As(V) in anaerobic experiments containing red mud. However, Fe(III)-reduction did occur in several anaerobic experiments containing red mud, and the reductive dissolution of high surface area iron (oxy)hydroxides may have played a role in As release by reducing the overall sorption capacity present thus increasing aqueous As concentrations,

especially in experiments with a moderate pH (~pH 8.5). The inhibition of microbial As(V) reduction caused by red mud addition led to lower overall solution As concentrations in some soils with red mud addition (containing 25–74 mg kg<sup>-1</sup> As) than were observed in the soils alone (containing 8–11 mg kg<sup>-1</sup> As).

The results of this study, suggests that the pH of all the red mud affected soil systems studied (during both aerobic and anaerobic incubation) was typically sufficiently high (>pH 8.5) that release of small amounts of surface bound As from red mud occurred to some extent. Mobilisation of As from red mud affected soils may have contributed to the moderate increases in As concentrations found in river waters up to 2 years after the spill (Nagy et al., 2013). These data, therefore, vindicate the decision by Hungarian authorities to recover most of the red mud from affected land as arsenic leaching is likely to have been much greater without this intervention.

## Acknowledgements

The authors acknowledge funding from the UK Engineering and Physical Science Research Council (Doctoral training award EP/P505593/1), and the Diamond Light for access to beamline I18 (Grant SP7525) that contributed to the results presented here. We acknowledge additional support from UK Natural Environment Research Council (Grant NE/I019468/1). We thank Lesley Neve and Dr. Samuel Allshorn (University of Leeds), Bob Knight (University of Hull), Nick Marsh (University of Leicester) and Ann Mennim (University of Edinburgh) for assistance with XRD, Ion chromatography, ICP–MS, XRF and TOC analysis respectively. We also thank Tina Geraki and Prof. Fred Mosselmans (Diamond Light Source) for support during synchrotron time.

## Appendix A. Supplementary material

Detailed XAS methods, sampling map, sample characterisation data, PCA analysis, additional solution analysis data and As XANES data. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apgeochem.2014.10.009>.

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