Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud

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Red mud was effective in immobilising heavy metals in soil.

Abstract

We evaluated the effectiveness of lime and red mud (by-product of aluminium manufacturing) to reduce metal availability to *Festuca rubra* and to allow re-vegetation on a highly contaminated brown-field site. Application of both lime and red mud (at 3 or 5%) increased soil pH and decreased metal availability. *Festuca rubra* failed to establish in the control plots, but grew to a near complete vegetative cover on the amended plots. The most effective treatment in decreasing grass metal concentrations in the first year was 5% red mud, but by year two all amendments were equally effective. In an additional pot experiment, P application in combination with red mud or lime decreased the Pb concentration, but not total uptake of Pb in *Festuca rubra* compared to red mud alone. The results show that both red mud and lime can be used to remediate a heavily contaminated acid soil to allow re-vegetation.
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1. Introduction

Heavy metal contamination of soil is a worldwide problem that affects a large number of sites. The accumulation of heavy metals in soil is an important issue because of the adverse effects they may have on food quality, soil health and the environment. In response to these negative effects, there has been ongoing development of a variety of technologies to remediate soil affected by heavy metal contamination. The traditional method of dealing with this legacy of contamination is to excavate the soil and dump it into landfills. However, this is often not considered a cost effective or environmentally sustainable remediation practice (Boisson et al., 1999). A number of alternative options have therefore been investigated which are regarded as less intrusive and more cost effective. One technology that has received a considerable amount of attention is in situ immobilisation of heavy metals in soils by the addition of various amendments. In situ immobilisation relies on the addition of an amendment to a soil to increase the proportion of the total soil metal burden within the soil solid phase, either by precipitation or increased metal sorption, thereby decreasing metal solubility (Oste et al., 2002; Basta and McGowen, 2004). The aim of immobilisation is not to remove the metal contaminant from the soil but to reduce its availability and activity.

A large number of different amendments have been proposed and tested for in situ immobilisation of heavy metals in soils. Amendments have included agricultural products such as lime (Geeblen et al., 2003), phosphate (Boisson et al., 1999; Hettiarachchi and Pierzynski, 2002; Melamed et al., 2003) and organic matter (biosolids) (Brown et al., 2003, 2004; Farfel et al., 2005), as well as various industrial products such as zeolites (Edwards et al., 1999; Oste et al., 2002; Friesl et al., 2003), steel shots (Mench et al., 1994; Geeblen et al., 2003), birnessite (Mench et al., 2000) and beringite (Vangronsveld et al., 1996; Boisson et al., 1998).

One industrial product that has been shown to have great potential to immobilise heavy metals in soils and reduce plant uptake is red mud. Red mud is a by-product of aluminium (Al) manufacturing, and is the material remaining after treatment of bauxite with sodium hydroxide during Al extraction. It is an alkaline material which is also rich in iron (Fe) (typically 25−40%) and Al oxides (15−20%). A number of studies, particularly in Western Australia, have shown that red mud applied to soils can be very effective in reducing phosphorous (P) leaching (Summers et al., 1996a), improve pasture growth (Summers et al., 1996b) and can ameliorate soil acidity (Summers et al., 1996b; Snars et al., 2004). Further, Phillips (1998) and Lombi et al. (2002a) showed that the application of red mud to heavy metal contaminated soils can also significantly increase metal sorption and decrease soluble metal concentrations, while Muller and Pluquet (1998) found that the application of red mud applied to metal contaminated harbour dredging reduced availability. Application of red mud can also lead to a reduction in heavy metal uptake by plants (Muller and Pluquet, 1998; Lombi et al., 2002b; Friesl et al., 2003). Friesl et al. (2003) showed in a pot experiment, that compared to the un-amended soil, red mud applied at a rate of 10% (w/w) significantly reduced Cd, Zn and Ni uptake in fescue and amaranthus by up to 87, 81 and 87%, respectively. In another pot experiment, Lombi et al. (2002b) showed that the application of 2% red mud (w/w) to two contaminated soils could decrease Cd, Zn, Cu and Ni uptake by oilseed rape, pea, wheat and lettuce.

Whilst laboratory and pot trial experiments have clearly demonstrated that red mud may decrease availability and plant uptake of heavy metals from contaminated soils, to date there have been no published field trials evaluating the effectiveness of red mud for immobilising heavy metals in soils. Field evaluations are essential before this in situ remediation approach can be applied to real situations. The aim of this study was therefore to determine the potential of red mud to remediate a heavy metal contaminated soil and allow its re-vegetation under field conditions. A two-year field trial was undertaken to evaluate the effect of red mud and lime on Zn, Cd, Pb, Cu, Cr and Ni availability in soil and uptake by the metal tolerant grass species *Festuca rubra* on an extremely contaminated site. In addition, a pot experiment was undertaken to determine whether heavy metal availability, principally Pb, could be further reduced by the application of phosphate in combination with red mud.

2. Materials and methods

2.1. Field experiment

A field experiment was set up adjacent to a decommissioned Zn/Pb smelter at Avonmouth in the United Kingdom. Atmospheric emissions from the smelter over a period of 80 years have resulted in contamination of soil close to the smelter with a range of heavy metals, principally Pb, Zn, Cd and Cu, and has substantially decreased the soil pH (Table 1). The field experiment was a randomised complete block split-plot design, which consisted of four main treatments and two sub-treatments. Each treatment was replicated four times, and the size of each of the main plots was 60 m^2. The main treatments were

Table 1
Total heavy metal concentrations (mg kg^{-1}) and other characteristics in the soil used in the field and pot experiment and the red mud

Soil property	Soil	Red mud
pH	4.7	10.2
Total carbon (%)	3.03	n.d.
Total nitrogen (%)	0.25	n.d.
Cd (mg kg^{-1})	79	18
Cr (mg kg^{-1})	46	1377
Cu (mg kg^{-1})	311	52
Ni (mg kg^{-1})	36	79
Pb (mg kg^{-1})	4210	84
Zn (mg kg^{-1})	3970	155
Al (%)	0.3	8.3
Fe (%)	3.6	24

n.d., not determined.

(i) control, (ii) limed to give a target soil pH of 6, (iii) 3% red mud (w/w based on the mass of top 23 cm soil) + lime to achieve a target soil pH of 6, and (iv) 5% red mud (estimated to raise soil pH to 6). The subplots were amended either with or without Farm Yard Manure (FYM) applied at the equivalent of 40 t ha^{-1} fresh weight 4 months after soils had been amended with lime and/or red mud. The amendments were applied to the surface of each plot before being ploughed into the soil to a depth of 23 cm and a metal tolerant grass *Festuca rubra* cv Merlin was sown by hand onto all plots (180 g plot^{-1}).

Composite soil samples (0−23 cm) were taken from each plot prior to the application of amendments and then on four further occasions at approximately 2, 5, 14 and 25 months. Soil samples were air-dried and sieved to <2 mm before analysis. Soil pH was measured in a 1:2.5 suspension of soil and water. Soil pore water was obtained by the centrifugation method (Elkhatib et al., 1987). Soil samples were made up to 100% water holding capacity with deionised water and left to equilibrate for 7 days. Pore water was then collected by centrifugation at 3000 × g for 15 min and soluble metals concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Fisons-ARL Accuris, Ecublens, Switzerland). Dissolved organic carbon (DOC) was measured in the soil pore water using TOC 200 analyser (Analytical Sciences, Cambridge, UK). Ammonium nitrate extractable metals were determined by extracting 20 g soil with 50 mL of 1 M NH$_4$NO$_3$ at 20 °C for 2 h on a reciprocal shaker, centrifuged at 3000 × g for 10 min and filtered through Whatman 42 filter paper and metal concentrations measured by ICP-AES. Total metal concentrations in soil and red mud were determined after digestion in aqua regia as outlined by McGrath and Cunliffe (1985) and then analysed for total metal concentrations using ICP-AES. Samples were also analysed for bioaccessible Pb using a physiological based extraction test (PBET) as a surrogate for Pb availability to animals and humans (Ruby et al., 1996). Samples of 1 g of soil were shaken in 100 ml 0.4 M glycine solution buffered with HCl to pH 2.2 at 37.5 °C in a water bath for 1 h (Ruby et al., 1996). Extracts were then filtered through a 0.45 μm filter and analysed for Pb concentration using ICP-AES. Quality control was addressed by routinely analysing a certified reference material (i.e. NIST 2711) and including blanks in digestion batches. The recovery of metals was within the certified limits.

Plant samples were taken on two occasions, at 10 and 21 months after sowing. Plant sampling involved cutting grass at soil level within 10 randomly distributed 10 × 10 cm quadrats within each sub-plot. Grass samples were washed thoroughly first with tap water, then with deionised water and dried at 80 °C for at least 16 h before being ground to pass a 0.5 mm mesh using a Glen Creston hammer mill (Stanmore, UK). Subsamples were digested in hot HNO$_3$ and HClO$_4$ (Zhao et al., 1994) and then analysed for total metal concentrations using ICP-AES. A certified plant material (i.e. NIST 1570a) was used to ensure the quality of plant digestion analyses.

2.2. Pot experiment

Topsoil (0−20 cm) was sampled from the field trial site in Avonmouth, United Kingdom. Seven treatments were used in a pot experiment (i) control,

(ii) 5% (w/w) red mud, (iii) Triple Superphosphate (TSP) (1:5 molar ratio of P:Pb), (iv) Triple Superphosphate (3:5 molar ratio of P:Pb), (v) 5% (w/w) red mud + Triple Superphosphate (1:5 molar ratio of P:Pb), (vi) 5% (w/w) red mud + Triple Superphosphate (3:5 molar ratio of P:Pb), and (vii) lime (pH 7) + Triple Superphosphate (3:5 molar ratio of P:Pb). All the amendments were ground to <0.2 mm and mixed into approximately 1 kg of air-dry soil. A 3:5 P:Pb ratio was used because this corresponds to the stoichiometric P:Pb ratio for pyromorphite formation. Following incorporation of the treatments into the soil, the moisture content was raised to 60% field capacity and the soils were allowed to equilibrate in a controlled environment for 2 weeks before seeds were sown. Four replicates of each treatment were potted (1 kg soil per pot) and arranged in a completely randomised design. Seeds of *Festuca rubra* cv Merlin (0.2 g pot^{-1}) were placed just below the soil surface. Plants were grown in a glasshouse with day/night temperatures of 18/16 °C (16/8 h), and a minimum light intensity of 350 μmol m^{-2} s^{-1}. Plant shoots were harvested after 7 weeks, at which time there was sufficient plant material for analysis. Plants were rinsed in deionised water and then dried at 60 °C for 24 h, dry weights recorded, and the plants ground and digested in HNO$_3$ and HClO$_4$ and metals determined in the digest using ICP-AES. Soil solution and NH$_4$NO$_3$-extractable metal concentrations were obtained from soil samples 2 weeks after the application the different amendments.

2.3. Statistical analysis

Data were analysed using analysis of variance (ANOVA). Tukey's honestly significant difference (HSD) ($P < 0.05$) test was used for comparison between treatment means. Given that there was no significant ($P > 0.05$) difference in soil properties or plant metal concentrations for subplots amended with or without FYM (with the exception of increased grass dry matter yield with FYM in harvest 1), only means for the main treatments plots are presented. All statistical analyses were performed using Genstat 5 package (Genstat, 1993).

3. Results

3.1. Field experiment

3.1.1. Soil analysis

Following the application of either lime or red mud, there was a significant ($P < 0.05$) increase in soil pH from 4.7 in the control soil to approximately 6, 5.5 and 7 in the lime, 3% and 5% red mud amended soils, respectively (Table 2). During the 2-year interval of the experiment the soil pH fluctuated slightly between sampling, but there was no significant difference ($P > 0.05$) in soil pH between 2 and 25 months.

The application of lime or red mud amendments had no significant effect ($P > 0.05$) on total Zn, Cd, Pb, Ni and Cu concentrations in soil (data not shown). The only metal that was affected by the application of an amendment was Cr in the 5% red mud treatment, which increased from 45 mg kg^{-1}

Table 2
Soil pH in soils sampled from the field trial

Sampling time (months)	Soil amendment			
	Control	Lime	3% red mud	5% red mud
0[a]	4.51a	4.79a	4.73a	4.72a
2	4.72a	5.93bc	5.48ab	6.90c
5	4.51a	5.64bc	5.18b	6.23c
14	4.89a	5.20ab	5.50ab	6.02b
25	4.81a	6.03bc	5.64b	6.49c

Means ($n = 4$) followed by the sample letter within a row are not significantly different (Tukey's HSD $P < 0.05$).

[a] Soil sampled before amendments added.

Table 3
Soil pore water heavy metal concentrations (mg L^{-1}) and dissolved organic carbon (DOC) (mg L^{-1}) from different samplings

Sampling time (months)	Soil amendment			
	Control	Lime	3% red mud	5% red mud
Zn				
2	182a	35b	55b	12c
5	249a	67b	99b	10c
25	131a	52b	71b	19c
Cd				
2	3.92a	1.30b	1.44b	0.47c
5	4.94a	1.80b	2.27b	0.51b
25	2.79a	1.32b	1.63b	0.68c
Pb				
2	1.72ab	0.46bc	0.94bc	3.18a
5	1.82a	0.42bc	0.99ac	1.35a
25	1.35a	0.33b	0.65b	0.34b
Ni				
2	0.24a	0.11b	0.07b	0.07b
5	0.31a	0.10b	0.13b	0.03c
25	0.15a	0.06b	0.09b	0.03c
Cu				
2	1.23a	0.20a	0.40a	2.48a
5	1.46a	0.18b	0.34b	0.68b
25	0.68a	0.15b	0.21b	0.23b
DOC				
5	141a	107a	187a	376b
25	111a	95a	120a	176b

Means ($n = 4$) followed by the sample letter within a row are not significantly different (Tukey's HSD $P < 0.05$).

before amendment to between 63 and 135 mg kg^{-1} because of the Cr in the red mud.

Heavy metal concentrations in soil pore water were measured in soils collected at 2, 5 and 25 months (Table 3). Whilst the application of soil amendments had little effect on total metal concentrations, all three amendments significantly ($P < 0.05$) decreased soluble metal concentrations in the soils. However, there were two notable exceptions. There was no significant ($P > 0.05$) difference in the soluble Pb concentration between the control and the 5% red mud treatment at either 2 or 5 months. In addition, there was no significant difference in soluble Cu concentrations between the amended soils at 5 months. The 5% red mud was the most effective amendment for decreasing soluble Zn, Cd and Ni concentrations compared to the control (85–96%, 75–90% and 70–90% decrease for Zn, Cd and Ni, respectively), while there was no significant ($P > 0.05$) differences between the ability of the lime or the 3% red mud amendments to reduce metal concentrations. Soluble Cr concentrations were below the detection limit of 0.02 mg L^{-1} in all of the treatments.

Dissolved organic carbon concentrations were also measured in soil pore water extracted from soils collected at 5 and 25 months (Table 3). Concentrations of DOC were significantly ($P < 0.05$) higher in the 5% red mud amended soils at both samplings, and there was a decrease (not significant) in DOC concentrations in the amended soils between 5 and 25 months.

Extractable metal concentrations were measured in soils before the application of amendments and then on four further occasions. As for soluble metal concentrations, the application of soil amendments significantly ($P < 0.05$) decreased the amount of NH_4NO_3-extractable metals in the soils (Table 4). Before the application of amendments, the soil contained on average, 34%, 39%, 9%, 4% and 5% of the soil total Zn, Cd, Pb, Cu and Ni content in extractable forms. However, the application of both lime and red mud significantly ($P < 0.05$) decreased the proportion of extractable metals. This was most noticeable in the 5% red mud amendment, which decreased the proportion of extractable Zn Cd, Cu, Pb and Ni to 9%, 20%, 0.26%, 1.6% and 2%, respectively, of the total metal content in the last soil sampling. As for soluble Cr, extractable Cr concentrations were below the detection limit in all treatments.

Bioaccessible soil Pb was determined using the PBET method, and was measured for samples collected at 14 and 25 months. Results showed that before amendment, the soil had a high proportion of bioaccessible Pb, with values on the control plots averaging 77% of the total soil Pb content (data not shown). However, unlike soluble and extractable metals concentrations, the application of soil amendments did not significantly ($P > 0.05$) affect the proportion of bioaccessible Pb, with on average 74% of the total soil Pb content across all the amended soils in bioaccessible forms.

3.1.2. Plant analysis

Above ground dry matter (DM) yield measurements for *Festuca rubra* were made at 10 and 21 months after treatment (Fig. 1). At each harvest, there were significantly ($P < 0.05$) higher biomass yields on the amended plots compared to the control plots. Average yields ranged from 0.2 t ha^{-1} DM in the control plot in the first harvest, to greater than 9 t ha^{-1} DM in the red mud treated plots in the second harvest. In the first harvest, the 5% red mud treatment produced a significantly ($P < 0.05$) higher yield than the lime or 3% red mud treatments. In the second sampling, which was approximately 2 years after seeding, there were no significant ($P > 0.05$) differences in yield between the amended plots and for the most part there was virtually a full grass cover on these plots, compared to the control plots in which there was still only a very patchy grass cover (Fig. 2). There did not appear to be any volunteer plant species establishing on any of the field plots over the course of 2 years.

The application of lime or red mud significantly ($P < 0.05$) decreased the concentrations of heavy metals in *Festuca rubra* compared to the control soil (Fig. 3), except that for plant Pb concentrations at 10 months. After 10 months, plant Zn concentration was significantly ($P < 0.05$) smaller in the 5% red mud treatment than in the lime or 3% red mud treatment. However, by the time of the second harvest, there were no significant ($P < 0.05$) differences in metal concentrations in *Festuca rubra* grown on the different amended soils. This is despite the fact that generally the 5% red mud treatment had the smallest proportion of metals in soluble and extractable
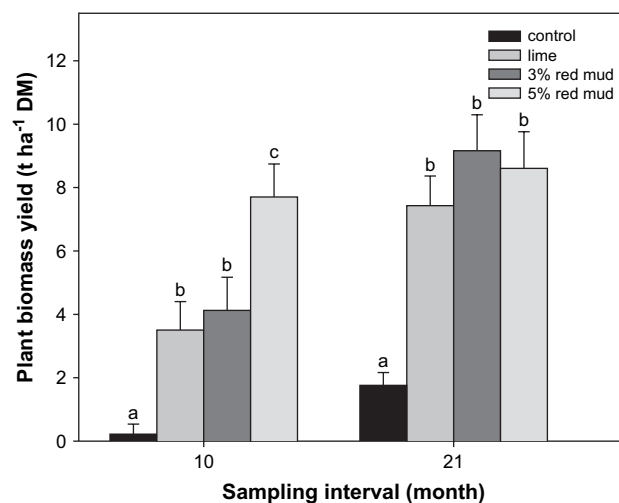
Table 4
NH_4NO_3-extractable heavy metal concentrations (mg kg^{-1}) from different samplings

Sampling interval	Soil amendment			
	Control	Lime	3% red mud	5% red mud
Zn				
0[a]	1428a	1205a	1329a	1396a
2	1930a	849b	1130b	376b
5	1536a	980b	1122b	535c
14	1434a	1044ab	868ab	490b
25	1078a	552b	772b	356c
Cd				
0	33a	28a	30a	33a
2	39a	19bc	26b	11c
5	31a	23b	27b	15c
14	32a	26a	21a	15b
25	33a	18b	25b	16b
Pb				
0	377a	334a	367a	369a
2	396a	57b	175c	52b
5	358a	136bc	238b	118bc
14	375a	179b	123b	82b
25	434a	80b	165c	67b
Ni				
0	1.73a	1.60a	1.63a	1.69a
2	2.03a	1.02b	1.22b	0.46c
5	1.79a	1.18b	1.29b	0.60c
14	2.02a	1.55a	1.23a	0.76b
25	1.88a	1.05bc	1.39b	0.73c
Cu				
0	15.7a	6.9a	12.8a	11.0a
2	18.1a	1.4b	3.5b	1.8b
5	12.8a	2.6b	5.6b	1.5b
14	10.4a	2.5b	2.3b	1.3b
25	12.6a	1.0b	2.2b	0.8b

Means ($n = 4$) followed by the same letter within a row are not significantly different (Tukey's HSD $P < 0.05$).
[a] Soil sampled before amendments added.

Fig. 1. Dry matter yield (t ha^{-1} DM) in *Festuca rubra* collected from the field experiment after 10 and 21 months. Mean ($n = 4$) and standard error followed by the same letter are not significantly different (Tukey's HSD $P < 0.05$).
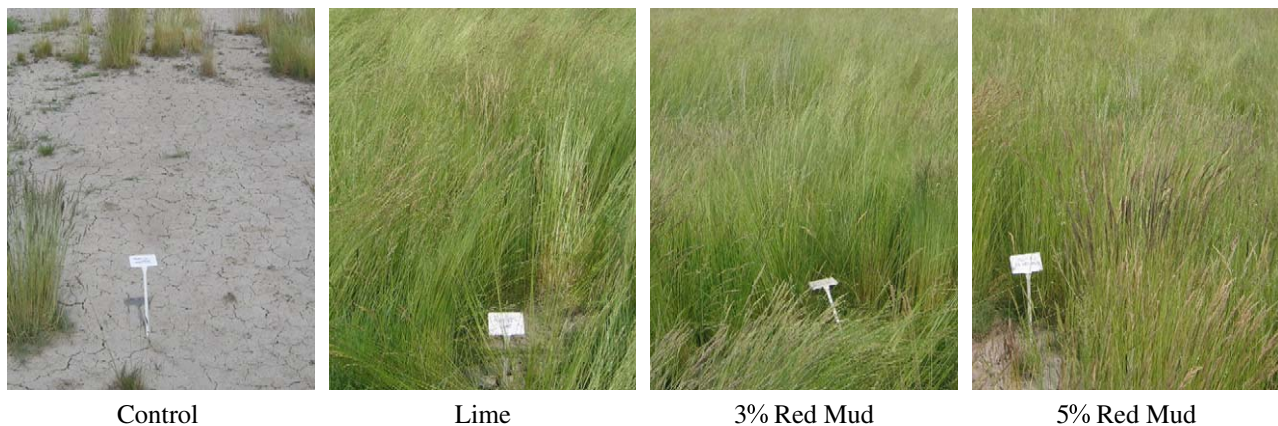
Fig. 2. Comparison of vegetative cover of *Festuca rubra* on plots before the second harvest at 21 months.

forms (Tables 3 and 4). Notably there were very high metal concentrations in plants grown on the control plots, especially Zn, Pb and Cu. In contrast, Cr concentrations in *Festuca rubra* were below limits of detection, as were Ni concentrations in the grass from the amended soils in the second harvest.

3.2. Pot experiment

3.2.1. Soil analysis
The addition of either lime or red mud to soil significantly increased ($P < 0.05$) the pH from 4.6 in the control soil to between 6.9 and 7.2 in the amended soils (Table 5). In contrast, the addition of TSP alone did not affect the soil pH. The amendment of soils with red mud either with or without TSP or lime significantly ($P < 0.05$) decreased Pb, Zn, Cd, Cu and Ni concentrations in soil pore water relative to the control soil (Table 5). However, the addition of TSP with red mud did not result in any further reduction in soluble metal concentration. Although in the two TSP amended soils, increasing the P:Pb molar ratio from 1:5 to 3:5 decreased pore water metal concentrations, these decreases were relatively small and only statistically significant ($P < 0.05$) for Pb and Cd. Similar results were found for NH_4NO_3-extractable metals where again the application of red mud either with or without TSP and lime resulted in a significant reduction in Cd, Zn, Pb, Ni and Cu concentrations relative to the control soil (data not shown).

3.2.2. Plant analysis
Dry matter yields of *Festuca rubra* in the pot experiment are given in Table 6. Notably, no plants (i.e. biomass) could be grown on the control or either of the two TSP amended soils. Seeds germinated, but plants were stunted and necrotic and died after approximately 3 weeks. This may have been due to Zn toxicity, as soil solution concentrations ranged between 225 and 250 mg L^{-1} on these treatments (Table 5), in combination with the low pH of the soil, which was approximately 4.7. In contrast, plants could grow on the other four amended soils and there was no significant ($P < 0.05$) difference in yield.

Heavy metal concentrations in *Festuca rubra* varied between amendments (Table 6). For Pb, significantly ($P < 0.05$) lower concentrations were found in plants grown on the red mud or lime amended soils which had TSP added, compared to the red mud treatment alone. The addition of TSP in combination with red mud was also effective in significantly ($P < 0.05$) decreasing plant concentrations of other metals including Cd, Ni and Cu compared to red mud alone, while plant Zn concentrations were only decreased in the red mud treatment with a 3:5 molar ratio of TSP.

4. Discussion

The application of amendments to soils that can immobilise heavy metals in situ may provide a cost effective and sustainable solution for remediation of contaminants in soils (Mench et al., 2000; Oste et al., 2002; Farfel et al., 2005). In this study we compared the ability of lime and different amounts of red mud to reduce heavy metal availability in a heavily contaminated soil and allow re-vegetation of an otherwise bare brownfield site.

In the field experiment, the application of amendments to soil had no effect on total heavy metal concentrations, with the exception of Cr in the 5% red mud treatment. The increase in Cr was because red mud contained on average 30 times more Cr than the soil Cr concentration (Table 1), and in fact the increase was close to the theoretical calculated concentration of 112 mg kg^{-1}, based on the addition rate and concentration of Cr in red mud. Nonetheless, despite Cr concentrations of up to 135 mg kg^{-1}, this value is still well below the soil guideline value of 200 mg Cr kg^{-1} for residential land use without plant uptake and 5000 mg Cr kg^{-1} for commercial and industrial land use according to the Contaminated Land Exposure Assessment (CLEA) model, indicating potentially significant risk to human health and a requirement for further investigation and/or remediation (Department of Environment, Food and Rural Affairs and Environment Agency, 2002). Furthermore, soluble and extractable Cr concentrations were found to be below detection limits, as was Cr uptake in *Festuca rubra*, indicating that Cr in the soil and red mud was present in non-bioavailable forms.
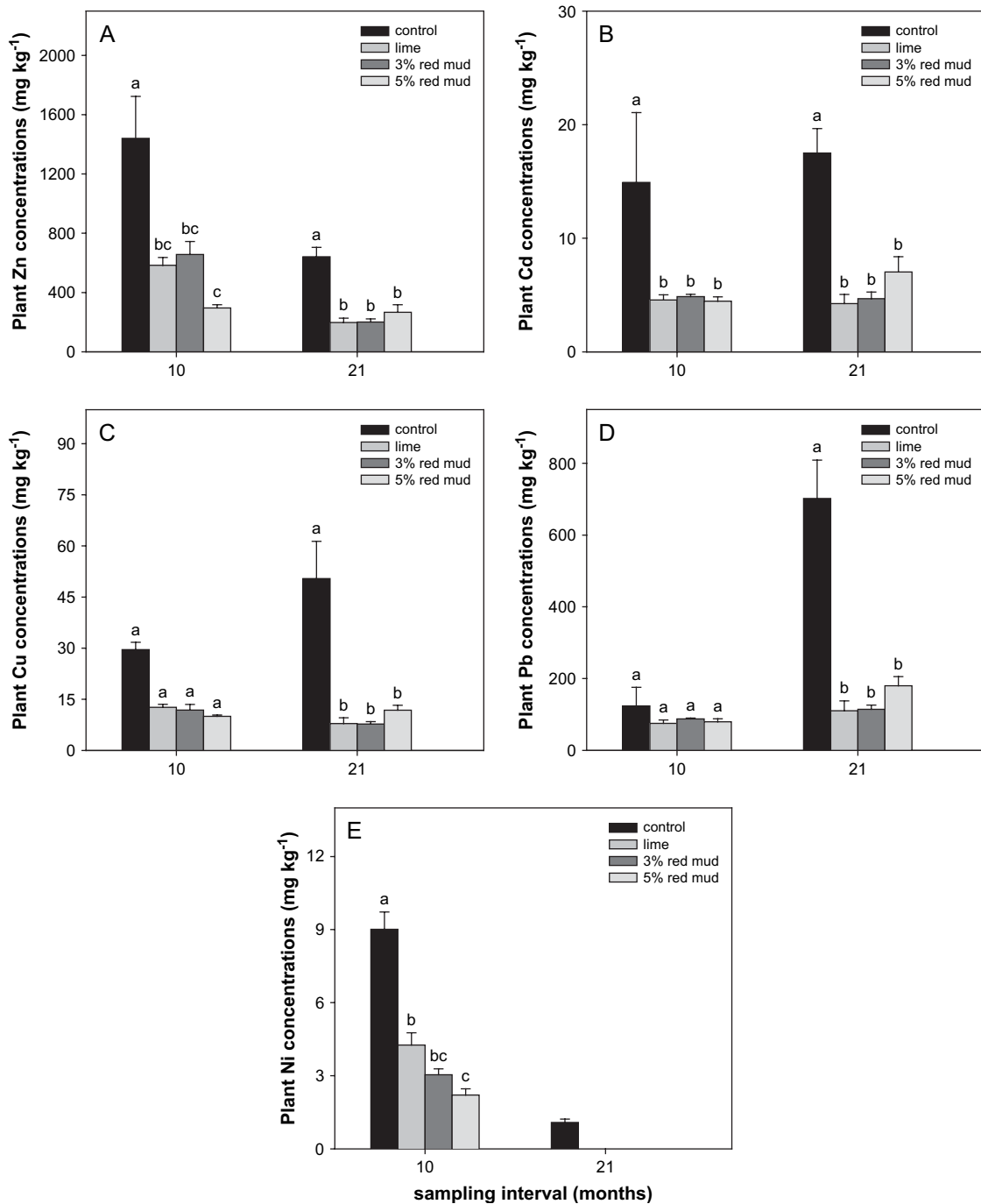
Fig. 3. Heavy metal concentrations (mg kg^{-1}) (A) Zn, (B) Cd, (C) Cu, (D) Pb and (E) Ni in *Festuca rubra* collected from the field trial at two samplings. Mean ($n = 4$) and standard error followed by the same letter are not significantly different (Tukey's HSD $P < 0.05$). Note that plant Ni concentrations were below the detection limit in some treatments.

Soil solution heavy metal concentrations are generally considered to be the most readily available for plant uptake (McLaughlin et al., 2000), hence decreasing the soluble pool of heavy metals in soils is likely to have the most immediate impact on metal bioavailability. Whilst the application of either lime or red mud could both reduce soluble heavy metal concentrations in soils, the 5% red mud treatment was the most effective for Zn, Cd and Ni. For example, by the last sampling the application of 5% red mud had decreased soluble Zn and Cd concentrations

from 131 and 2.79 mg L^{-1} to 19 and 0.68 mg L^{-1}, respectively. However, the application of 5% red mud to soil did initially result in a significant increase in soluble Cu and Pb concentrations. This may have been a result of the significantly higher concentrations of DOC found in soils amended with 5% red mud compared to the other treatments (Table 3). Dissolved organic carbon compounds have been shown to decrease the sorption of Cu and Pb onto soil surfaces by competing for free metals and forming soluble organo-complexes or being preferentially

Table 5
Soil pH and pore water metal concentrations (mg L^{-1}) extracted from soils in the pot experiment

Treatment	Soil pH	Pb (mg L^{-1})	Zn (mg L^{-1})	Cd (mg L^{-1})	Cu (mg L^{-1})	Ni (mg L^{-1})
Control	4.6a	4.58a	250a	6.11a	2.58a	0.30a
5% red mud	7.2c	0.71d	2.32c	0.30d	1.63d	0.01b
TSP 1:5 P:Pb molar ratio	4.7a	3.45b	233b	5.48b	2.27b	0.27a
TSP 3:5 P:Pb molar ratio	4.8a	2.54c	225b	4.90c	2.19b	0.26a
5% red mud + TSP 1:5 P:Pb molar ratio	7.2c	0.76d	2.44c	0.26d	2.00b	0.03b
5% red mud + TSP 3:5 P:Pb molar ratio	7.2c	0.84d	2.38c	0.24d	2.61a	0.04b
Lime (pH 7.0) + TSP 3:5 P:Pb molar ratio	6.9b	0.90d	4.05c	0.32d	2.15b	0.03b

Means ($n = 4$) followed by the same letter within a column are not significantly different (Tukey's HSD $P < 0.05$).

sorbed onto surfaces instead of the metals for which they are competing (Giusquiani et al., 1998). However, it appears that this effect is likely only transitory, because the increase in soluble Cu and Pb was only observed in the first few months after amendment and was not noted in the last sampling. A similar finding was made by Lombi et al. (2002a) who showed that the application of 2% (w/w) red mud to two contaminated soils resulted in an increase in DOC and soluble Cu concentrations up to 400 days after application. Increased DOC may be a result from increased pH and/or salt (Na) concentration in the red mud amended soil.

The application of amendments also significantly decreased NH_4NO_3-extractable metal concentrations, which represent heavy metals that are sorbed onto the soil solid phase and able to be desorbed into solution to replenish the soluble metal pool (McLaughlin et al., 2000). Several laboratory studies have similarly shown decreases in extractable metal concentrations in contaminated soils after the application of amendments such as lime and red mud (Muller and Pluquet, 1998; Phillips, 1998; Friesl et al., 2004). Friesl et al. (2004) showed that the application of 5% red mud significantly reduced Cd, Ni, Zn and Pb extracted by 1 M NH_4NO_3 by up to 91, 81, 94 and 83%, respectively, in several polluted soils, whilst Lombi et al. (2002a) showed that 2% red mud, and also with lime and beringite, significantly decreased exchangeable Cd, Cu, Ni, Pb and Zn.

The decrease in soluble and extractable metal concentrations in the amended soils can be attributed in part to a significant increase in soil pH after amendment with lime and red mud (Table 2). This increase in soil pH has been shown in other studies where lime and red mud has been used as a soil amendment (Lombi et al., 2002a; Friesl et al., 2004; Snars et al., 2004) and was a result of the alkaline nature of both amendments, especially the red mud which has a pH of greater than 10 (Table 1).

The large decrease in soluble and extractable metal concentrations, along with the increase in soil pH following the application of amendments, likely contributed to the observed decrease in heavy metal concentrations in *Festuca rubra*. For example, by 21 months, the application of amendments had reduced Zn and Cu concentrations in *Festuca rubra* from 1500 and 50 mg kg^{-1} to concentrations below typical toxicity thresholds of 500 and 20 mg Cu kg^{-1}, respectively (Kabata-Pendias and Pendias, 1992). Similar large decreases were observed for Cd, Ni and Pb. At 21 months, there were no significant differences in metal concentrations in ryegrass between the amendment treatments (Fig. 3). This was despite the 5% red mud treatment having the lowest soil solution Zn, Cd and Ni concentrations, and Zn having the lowest extractable concentration compared to the other amendments (Tables 3 and 4). It would appear that, while soil factors clearly have an important effect on plant availability of heavy metals, plant physiology also plays a large role in regulating metal uptake and translocation.

The application of red mud and lime was also very effective in allowing the re-vegetation of an otherwise bare contaminated site. After nearly 21 months growth, *Festuca rubra* was growing well and there was virtually a full vegetation cover on all

Table 6
Plant biomass yield (g DM pot^{-1}) and metal concentration (mg kg^{-1}) in *Festuca rubra* grown in the pot experiment

Treatment	Biomass (g DM pot^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Ni (mg kg^{-1})	Cu (mg kg^{-1})
Control	0.0a	n.d.	n.d.	n.d.	n.d.	n.d.
5% red mud	0.385b	105a	922a	108a	3.05a	29a
TSP 1:5 P:Pb molar ratio	0.0a	n.d.	n.d.	n.d.	n.d.	n.d.
TSP 3:5 P:Pb molar ratio	0.0a	n.d.	n.d.	n.d.	n.d.	n.d.
5% red mud + TSP 1:5 P:Pb molar ratio	0.564b	85b	651a	99b	1.81b	24b
5% red mud + TSP 3:5 P:Pb molar ratio	0.669b	58c	470b	78b	2.32a	22c
Lime (pH 7.0) + TSP 3:5 P:Pb molar ratio	0.553b	66c	981a	68b	3.68a	24b

Means ($n = 4$) followed by the sample letter within a column are not significantly different (Tukey's HSD $P < 0.05$). n.d., not determined.

the amended plots (Fig. 2). Vangronsveld et al. (1995) also showed in a field experiment that *Festuca rubra* mixed with *Agrostis capillaris* successfully developed on a metal contaminated soil that was amended with beringite. Re-vegetation is important because it lessens the potential risk of contaminated soil being transported off site by wind or water erosion. This is especially important for metals such as Pb where the critical exposure pathway to human is inhalation and/or ingestion of soil particles (McLaughlin et al., 2000). Decreasing this movement by re-vegetation of the soil used in the field trial was particularly important given that both the red mud and the lime amendments did not significantly decrease bioaccessible Pb measured using PBET.

A range of different mechanisms have been suggested to explain the decrease in metal mobility in soils caused by amendment with different materials. The immobilisation of heavy metals using red mud is thought to be a combination of two processes. Firstly, it is a result of an increase in soil pH caused by the application of this alkaline product. An increase in soil pH results in a corresponding increase in the net negative charge of variably charged colloids in soils such as clays, organic matter and Fe and Al oxides. This can result in an increase in heavy metal sorption and a decrease in desorption and hence reduction in soluble metal concentrations in soils (Gray et al., 1998). Secondly, the large content of Fe and Al oxides in red mud introduces new sorptive surfaces which may immobilise heavy metals in soils, through specific or chemisorption. For example, several studies (Lombi et al., 2002a; Friesl et al., 2003) have used chemical sequential fractionation to show that amending contaminated soils with red mud results in a redistribution of heavy metals from soluble and exchangeable pools to the Fe, Al and Mn oxide fractions. Once heavy metals are specifically sorbed onto these oxide surfaces, potentially they may become irreversibly fixed as a result of several mechanisms, including migration of metal into micropores on the surface of the oxides (Fischer et al., 1996), solid state diffusion of ions into the crystal lattice of the oxides (Barrow, 1987), or perhaps occlusion of metals.

There is also evidence that specific sorption of metals by Fe and Al oxides in red mud is more stable than simple pH moderated sorption (Hamon et al., 2002; Lombi et al., 2002a, 2003). For example, several studies have demonstrated that if there is subsequent re-acidification of the soil after the application of an alkaline amendment such as lime, this may result in re-mobilisation of metals. Hamon et al. (2002) showed that the application of KH_2PO_4 to a contaminated soil caused fixation of Cd and Zn through the formation of metal phosphates, and that these were stable across a wide range of pH values. In contrast, the re-acidification of the limed treatment resulted in an increase in the labile metal pool to a value even larger, at equal pH, than in the untreated soil. It was suggested the metals in the limed soil were precipitated as carbonates or hydroxides and acidification simply dissolved the precipitates. Lombi et al. (2003) similarly showed that when two metal contaminated soils amended with lime, beringite or red mud were re-acidified, the labile pool of metals increased, and for lime and beringite, the lability of metals was similar, at equal pH,

to the un-amended soil. In contrast, lability of metals in the red mud treated soil was always smaller than that in the untreated soils. Lombi et al. (2003) indicated that the mechanisms of fixation in red mud could be a combination of both precipitation of metal carbonate and hydroxides (pH-reversible) and solid-phase diffusion into the lattice of oxide materials or diffusion into micropores on these materials. Clearly the latter processes are considered more stable than soil pH moderated sorption of heavy metals in soils.

In the present study, we cannot ascertain how much of the decrease in metal availability after the application of red mud was due to an increase in soil pH, and how much was due to specific sorption/aging. However, it would appear that depending on the mechanisms involved, changes in soil properties (i.e. pH) may have different effects on the long-term sustainability and suitability of using amendments for in situ remediation. Whilst results from the field experiment indicate that lime may currently perform as adequately as the red mud amendment, the re-acidification of the soil, which is a natural soil process, may in the future result in the liberation of bound metals. This raises the question as to whether lime as an in situ amendment meets the criteria of being environmentally sustainable for this particular contaminated site.

The pot experiment was undertaken to determine whether heavy metal availability, principally Pb, could be further reduced by the application of phosphate in combination with red mud. Results from the field trial indicated that while the application of lime and red mud were effective at immobilising metals such as Zn and Cd early on in the trial, they did not appear to be as effective at immobilising Pb. Consequently, grass Pb concentrations were still too high for animal grazing. The use of phosphorus compounds as soil amendments to immobilise metals is based on the geochemical principle that many metals, including Pb, naturally and rapidly form a range of phosphate minerals that are stable and insoluble under conditions likely to be present in soils (Berti and Cunningham, 1997; Boisson et al., 1999; Scheckel and Ryan, 2004). Numerous studies have shown that the application of rock phosphate (Chen et al., 1997; Geeblen et al., 2003) and soluble P fertilisers (Hettiarachchi and Pierzynski, 2002; Melamed et al., 2003) decreased Pb solubility and plant uptake in Pb contaminated soils.

Soil pore water data indicated that while adding phosphate without red mud can reduce Pb solubility, presumably by the formation Pb-pyromorphite minerals, the addition of phosphate and red mud resulted in a much greater decrease in soluble Pb concentration. Furthermore, compared to the red mud treatment alone, the addition of phosphate with red mud resulted in a significant decrease in Pb concentration in *Festuca rubra* (Table 6). Similar results were also found for the other metals tested. While this may have been a result of an increase in the ability of the added phosphate to form metal phosphate precipitates, which in the case of Pb is the formation of pyromorphite, this appears unlikely as there were no significant differences in soluble Pb concentrations between the red mud amended soil either with or without phosphate (Table 5). A more likely explanation is plant dilution, as the

plant yield increased with increasing phosphate treatments. In fact, when total metal uptake was calculated using metal concentrations and plant biomass, it was found that the addition of phosphate with red mud did not result in any further decrease in Pb uptake. A similar result was found for Cd and Cu where there was no difference in total metal uptake between treatments, while for Zn and Ni, total uptake was highest on the lime and phosphate treatment (data not shown).

A possible explanation for why the addition of phosphate with red mud did not result in a significant decrease in Pb uptake may be that the soluble phosphate added to the soil was being sorbed onto the red mud before it had an opportunity to complex with the soluble Pb in the soil. Red mud has been shown in several studies to be very effective in decreasing phosphate solubility in soils through sorption onto the Fe and Al oxides (Summers et al., 1996a). However, this does not explain the fact that the lime and phosphate treatment was equally as effective as the red mud and phosphate treatment in reducing soluble and plant Pb concentrations. It may be therefore that the presence of competing cations in lime such as Ca, and the other metal contaminants in the soil, i.e. Cu, Mg, Cd, Zn and Ni, which have been to shown to precipitate as metal phosphates (Cotter-Howells and Capron, 1996; Ma et al., 1994), may have decreased the amount of dissolved phosphate. Scheckel and Ryan (2004) also suggest these cation-phosphate reactions as a reason why that in some studies where P added to soils even at rates of up to 3.2% sometimes only results in only a portion of the soil Pb being converted to pyromorphite. Nonetheless, regardless of the mechanisms involved, it would appear that even at the high rate of P application used in this study, which was up to 566 kg P ha^{-1}, the rate of application was still insufficient to provide enough soluble phosphate for Pb-pyromorphite formation. Whilst a higher application of P, such as those used by Boisson et al. (1999) who applied hydroxyapatite at a rate up to 5% (w/w) may induce Pb-pyromorphite formation, introducing large amounts of P to the soil system also increases the potential risk of eutrophication of water from P leaching and surface run off.

5. Conclusions

Results from the field experiment indicate that the addition of lime and 3% or 5% red mud can increase soil pH and at the same time decrease soluble and extractable heavy metal in soil compared to the control soil. Both lime and red mud were also equally effective in reducing Zn, Pb, Ni, Cd, and Cu uptake in *Festuca rubra* and allowed a near complete re-vegetation of a previously bare soil. Further monitoring is needed to evaluate the longevity of red mud compared to lime amendments. The pot trial experiment showed that the addition of P together with red mud or lime resulted in a decrease in soluble Pb concentration compared to the control soil. However, P in combination with red mud did not result in a further decrease in Pb uptake in *Festuca rubra* compared to red mud alone. It would appear that there was not a sufficient amount of soluble phosphate for the formation of Pb-pyromorphite, and hence reduce Pb solubility. Further research should investigate the potential of the amendments to reduce heavy metal availability over a longer term. In addition, research should measure the effects of treatments on biodiversity and functions of the restored ecosystem.

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