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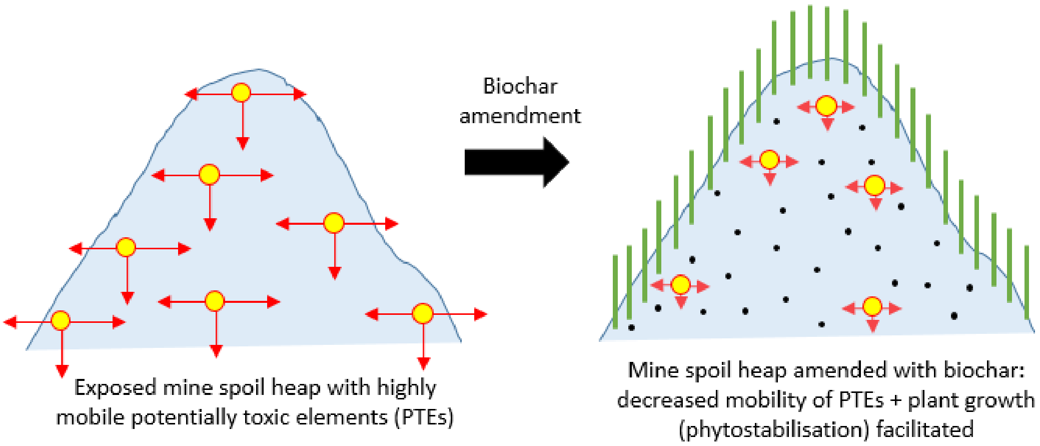
Mine spoil remediation via biochar addition to immobilise potentially toxic elements and promote plant growth for phytostabilisation

Maysaa A. M. Alhar[1], David F. Thompson[2] and Ian W. Oliver[1]*

1 School of Geography, Geology and the Environment, Keele University, Keele, UK, ST5 5BG
2 School of Chemical and Physical Sciences, Keele University, Keele, UK, ST5 5BG2

* Corresponding author i.oliver@keele.ac.uk

Graphical Abstract



Abstract

There are thousands of disused and abandoned mining sites around the world with substantial accumulations of exposed mine spoil materials that pose a direct threat to their surrounding environment. Management of such sites, and neutralisation of the environmental threats they pose, is therefore extremely important and is an issue of global significance. Low cost management and remediation strategies need to be developed because many abandoned mine sites are in remote and/or economically challenged areas. One promising option is the incorporation of biochar into spoil materials, which has the potential to immobilise leachable toxic constituents and facilitate revegetation and thereby stabilisation of spoil heaps. This study investigated the capacity of readily available biochar materials made from wheat and rice waste products to immobilise and retain key metallic contaminants Pb and Zn from solution, and also investigated the utility of biochar application for remediating mine spoil heaps from different mine types in terms of facilitating establishment of vegetation coverage and minimising porewater element mobility within spoil heaps. The results demonstrated the high sorption capacity of the biochars (typically >97% of Pb or Zn in solution) and their ability to retain the metals despite an active desorption procedure (>93% of sorbed Pb retained and >75% of sorbed Zn). The remediation trial revealed that biochar application increased plant yield and decreased plant assimilation of many potentially toxic elements and also decreased spoil porewater concentrations of Al, Cd, Pb and Zn in most cases. In some spoil types investigated biochar addition also significantly decreased porewater concentrations of As (e.g. from ~30 mg/L to ~5 mg/L), demonstrating its potential utility for low cost environmental remediation across a range of mine spoil types.

Keywords: Mine spoil; Remediation; Biochar; Phytostabilisation; Porewater; PTE

1. Introduction

There is ample evidence from across multiple continents that metal ore extraction and smelting date back to antiquity (Bromehead 1940), hence it is clear that the history of human civilisation and the ways in which modern societies function today are inextricably linked with mining. Unfortunately, despite its economic and cultural importance and the technological developments it has enabled, the long history of mining and the fact that it is such a widespread activity has left an environmental contamination legacy at thousands of sites across the globe. Moreover, many of these sites bear substantial accumulations of mine spoil (waste) materials that pose ongoing risks. This includes sites of current mining operations, but there are much greater numbers of disused, abandoned and untended mine sites that have spoil deposits left exposed that can threaten the environment and human health via potentially toxic elements (PTEs) leaching out in drainage water and/or being dispersed in the air as dust (Raous et al. 2010; Guney et al. 2017; Martin et al. 2018). Such sites require urgent remediation measures to reduce, mitigate or resolve these risks. While a range of technologically driven remediation strategies have been developed, these remain unaffordable or unfeasible for a vast number of mining spoil impacted sites and so more affordable and less technologically challenging strategies are required to address this global issue. Strategies involving plant stabilisation (phytostabilisation) of mine spoil heaps and related wastes have been proposed, and in some places tested (e.g. Kumpiene et al. 2012; Mench et al. 2010; Fellet et al. 2014), as low cost options requiring minimal technology inputs. The strategy can be effective because, if plants can be established successfully, vegetative cover protects the spoil materials from wind and water erosion at the surface while in the subsurface layers the plant roots can act as an anchor to hold the spoil materials in place and can also assimilate porewater and the elements it contains and thus restrict leaching (Fellet et al. 2014). However, limitations to such plant-based approaches can be encountered on account of the hostile habitat presented by the spoils, i.e. in terms of substrate texture and grain size distribution, water holding capacity, nutrient status, pH, and presence of excess PTEs in porewater. The addition of biochar to spoil materials may be a low cost approach that addresses some aspects of this hostility, as biochar amendment has been shown to improve water retention, nutrient levels, pH and bulk density of contaminated substrates (Fellet et al. 2011) and biochar has also been found to have the capacity to immobilise PTEs (Beesley et al. 2011; Kosolsaksakul et al. 2018). The aim of the present study was to investigate the efficacy of selected typical, ‘off the shelf’ biochars for sorbing lead (Pb) and zinc (Zn) and to determine whether biochar could be used as a low cost remediation tool to facilitate phytostabilisation of currently unvegetated, exposed mine spoil materials from five locations across the United Kingdom. The study assessed biochar generated from i) wheat straw and ii) rice husk for their capacity to sorb these key metals and determine how well the sorption could be described by mathematical sorption isotherms. Moreover, having established their capacity to immobilise (sorb and retain) these PTEs, the biochars were applied to selected mine spoils to examine their capacity for limiting porewater mobility of PTEs and to facilitate establishment of healthy vegetation cover in the form of ryegrass (*Lolium perenne*).

2. Methods

2.1 Mine spoil materials and biochar sources

Exposed mine spoil materials, completely absent of any covering vegetation, were collected from five disused/abandoned mining areas within the UK (Figure 1) that represent some of the diversity of mineral resources previously extracted in the country. The sites were: 1)

Glendinning, a former antimony (Sb) mine ~110 km south of Edinburgh (Gal et al. 2007; Macgregor et al. 2015); 2) Leadhills area, a region in southern Scotland ~80 km southwest of Edinburgh with multiple abandoned mines primarily extracted for Pb but also Au, Ag and Zn (Mighall et al., 2014); 3) Oil-shale bings ~20 km west of Edinburgh that are the residual spoil materials from oil production via retorting mineral oil from deep-mined carboniferous shale beds (Harvie 2005); 4) North Pennines, Cumbria, northern England, a former Pb, Ag and Zn mining area; 5) Anglesey, North Wales, a former Cu mine (Cooper et al. 1989). Spoil material was collected by first scraping away the top few cm of surface material (as this had likely been exposed to wind and rain much more than the underlying materials and so may not have been representative of the bulk of the material) and then scooping out sample with a trowel. The materials were sealed inside plastic containers for transportation to the laboratory, where they were air dried completely, ground by hand using a mortar and pestle, sieved to 2 mm size and stored in sealed plastic containers pending use. The pH of the spoil materials was determined in 10:1 (liquid:solid) 0.01M $CaCl_2$ solution extracts following 2h equilibration using a Jenway 3510 pH probe and meter and were all between 6.4 and 7.0 except for Anglesey, which had a pH of 2.84. Total element concentrations are presented in the Supplementary Information.

Figure 1. Line map of the island of Great Britain showing mine spoil collection sites (see section 2.1, main text, for site definitions).

Two biochars, produced from rice husk and wheat straw feedstocks, respectively, were purchased from the UK Biochar Research Centre, Edinburgh, UK. Each had been generated by pyrolysis at 550°C. The two particular biochars were selected because they represent examples of typical or mid-range pyrolysis conditions for biochar production, and so may be considered representative of many biochars, and because the feedstocks are readily available agricultural wastes and so are the kinds of materials likely to be available at low (or no) cost for use in soil remediation efforts. The pH of the biochars, determined in spoil:deionised water slurries, were 10.06±0.62 and 9.33±0.55 for wheat and rice biochar respectively.

2.2 Biochar Pb/Zn sorption and retention study

Both Pb and Zn are commonly found in excess and potential toxic concentrations in mining impacted areas and so for biochars to be useful in remediating the spoils and soils at such locations it is important that the materials are demonstrated to have effective sorption and retention capacities for these and other metals. Here, the biochars were exposed to Pb and Zn separately in 2g:20mL batch exchange procedures in 50 mL centrifuge tubes using concentrations of 0, 10, 50, 100, 200 and 400 mg/L (all n = 2). Equilibration was achieved by shaking end-over-end for 2h (Ho et al. 2002) on a rotating shaker, after which tubes were centrifuged for 30 minutes at 6000 rpm and supernatants filtered using 0.45 µm syringe filters. The filtered solutions were acidified with high purity concentrated nitric acid and stored in the refrigerator until analysed by ICP-OES (Perkin Elmer, Optima DV 5300). Metal sorption achieved by the biochars was then calculated from the concentrations of remaining metal measured in the equilibrium solutions. Freundlich and Langmuir isotherms were plotted to determine how well they mathematically described the sorption, e.g. in the case of Freundlich by plotting $\log_{10}$ transformed sorbed masses against $\log_{10}$ transformed equilibrium concentrations and determining the line equation (see e.g. Sparks 2003).

Following a similar approach to that used elsewhere (e.g. Burton et al. 2005), potential desorption of metals sorbed by the biochars was investigated by subjecting the residual solids to a further re-suspension and equilibration with 0.001M $CaCl_2$ for 24h on an end-over-end shaker after which the samples were centrifuged, the solutions filtered and acidified, and then stored in the refrigerator pending ICP-OES analysis. Desorption concentrations were mathematically corrected for any residual entrained metals left behind in solution from the initial sorption step (i.e. any non-sorbed Pb or Zn remaining in the initial sorption solution which could not be 100% removed from around biochar solids prior to desorption); this correction was based on the volume (determined by mass) of entrained solution and the measured sorption equilibrium solution concentrations.

2.3 Mine spoil remediation trial using wheat biochar

With both biochars having demonstrated a strong and effectively equivalent binding and retention capacity for PTEs in the sorption-desorption study above (see results section), and thus providing a proof of concept for their use in remediation, a remediation pot trial was conducted using one biochar only in which the mine spoils were subjected to 0% (control), 5% or 10% (w/w) treatment with wheat biochar (100 g total mass, except in the case of Oil-shale bings samples for which the total mass was 70 g to accommodate the lower bulk density). The wheat biochar was thoroughly mixed through by hand for several minutes, with each replicate (n = 3) of each treatment having been prepared separately to ensure the correct ratio of biochar to spoil was achieved and maintained in every pot. A rhizon soil porewater sampler (Rhizon Flex, Rhizosphere Research Products, The Netherlands) was inserted at a 45° angle in selected pots; specifically, in two controls per spoil, to firmly establish the baseline, and in one 5% and one 10% biochar treatment per spoil. The solid substrate was settled around the rhizon sampler by gentle shaking. Seeds (0.5 g) of ryegrass (*Lolium perenne*) were then scattered across the surface of each pot and a small amount of perlite was added on top to prevent excessive evaporation (see supplementary information figure S1). Ryegrass was selected as the test plant because it is a common pasture species and is known to be robust and not overly sensitive to metal burdens (Gray and McLaren, 2005). The pots were wetted up with deionised water to the water holding capacity of the substrate (determined previously by saturation followed by drainage and calculation of the retained water mass). Once prepared, pots were placed in an unheated Perspex incubation chamber positioned next to a large window, with moisture maintained by watering to weight each day. The experiment was conducted under natural lighting (September, 2018, UK) for 35 days after which the aboveground plant tissues were harvested, placed in small envelopes and dried in an oven at ~50°C for two days. Plant materials were digested in high purity concentrated nitric acid (Primar Plus trace analysis) via microwave assisted digestion following EPA method 305A. After digestion, subsamples of digestion solutions were diluted to 40 mL with deionised water and analysed via ICP-MS (Agilent 7500ce) using certified standard solutions for instrument calibration. A plant material certified reference material (ryegrass ERM-CD281) was also digested as per the samples as a further quality control measure, with relevant elements all returning analysis values that were ≥80 - ≤100% of certified values. Porewater samples were extracted every 10 days via the rhizon samplers using a syringe to establish suction. Once extracted, the samples were acidified with 100 µl of high purity nitric acid and kept refrigerated pending ICP-MS analysis.

2.4 Statistical assessment

Differences between and amongst treatments and controls were assessed for statistical significance through ANOVA and t-test assessments, following checks that all underlying validity assumptions (e.g. normal distributions) were met. Relationships between measured parameters and treatments were similarly assessed using linear regression. The software packages Minitab19, SPSS 24 and Sigmaplot10 were used for these assessments.

3. Results and Discussion

3.1 Biochar Pb/Zn sorption and retention study

The sorption capacity for both Pb and Zn was very high for each of wheat straw and rice husk biochar, with sorbed concentrations approximating 4000 mg/kg at the highest initial solution concentrations imposed (Figure 2) and no indication that maximum sorption potential had been reached. Viewed in terms of the percentage of Pb or Zn ions in the initial solutions, both wheat and rice biochars sorbed ≥99% of Zn in every case, while for Pb >97% was sorbed from all initial concentrations above 10 mg/L. This compares favourably with sorption percentages reported for various biochars generated from date seeds under varying pyrolysis conditions, whose sorptions of Pb from model solutions were found to span 73-97% (Mahdi et al. 2018).

Despite similarly high sorption of the two different metals, Freundlich isotherms suitably modelled Zn sorption onto both biochar types (R^2 ≥0.9) but they did not provide a fitting description for Pb on either type (Figure 3). Langmuir isotherms were not good fits for any of the data (R^2 typically <0.2 and p values all >> 0.05, hence not displayed, also meaning that maximum sorption potential, Qm, could not be calculated from Langmuir models as is often done in sorption studies), which is in contrast with other studies reported in the literature where Langmuir isotherms did accurately describe Pb sorption onto biochars (e.g. Kwak et al. 2019; Boni et al. 2020; Zhang et al. 2020). This lack of fit observed for Langmuir isotherms in the present study may reflect the finding that sorption maxima were not approached. It is possible that adjustment to the solid:solution ratio and/or the solution concentrations employed would enable this to be quantified and also for isotherms to have closer fits.

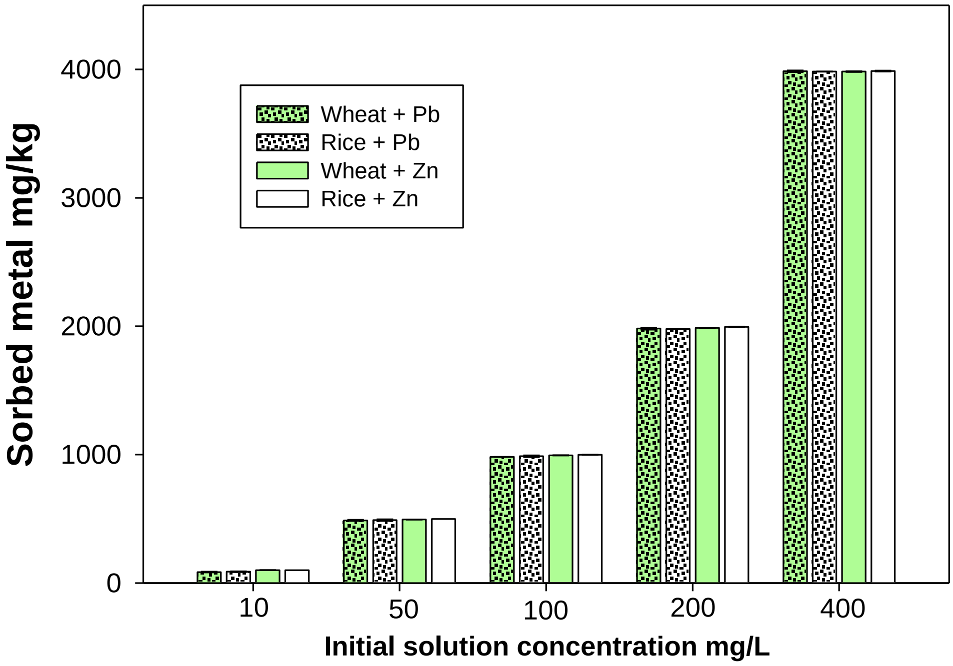


Figure 2. Mean sorption of lead (Pb) and zinc (Zn) separately onto biochar produced from wheat straw and rice husk feedstock. Error bars (where visible) indicate 2x standard error.

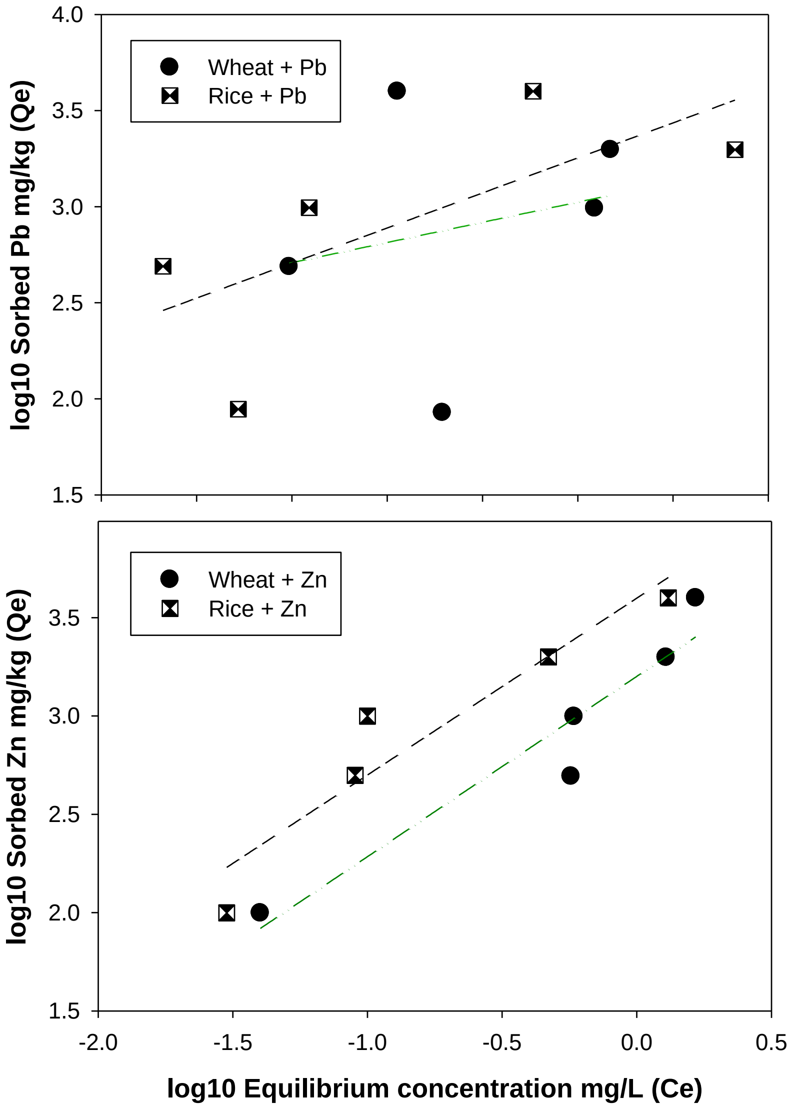


Figure 3. Freundlich isotherms of log10 sorbed metal concentration (Qe) vs log10 equilibrium solution concentration (Ce) for Pb (upper panel) on wheat ($y = 2.101x + 2.498$, R^2 0.055, p 0.705) and rice ($y = 3.648x + 2.342$, R^2 0.501, p 0.181) biochars and for Zn (lower panel) on wheat ($y = 0.917x + 3.201$, R^2 0.917, p 0.011) and rice ($y = 0.899x + 3.599$, R^2 0.897, p 0.016) biochars.

Corrected for entrained metal, the concentrations of Pb in $CaCl_2$ desorption solutions never exceeded 3 mg/L for either biochar type (Figure 4); this was even the case in treatments with initial exposure concentrations of 400 mg/L Pb, which had achieved sorption levels approaching 4000 mg/kg in the previous sorption step. Indeed, for treatments with initial exposure concentrations of 50 mg/L and above, >93% of sorbed Pb was retained during the desorption procedure (Table 1). This is consistent with a previous study that similarly found, when testing different biochars, that the Pb sorbed onto biochar was retained at high percentages (~90%) even when put through a batch desorption process with calcium chloride solution (Mahdi et al. 2018). Retention was less robust for Zn, with corrected desorption solution concentrations ranging up to ~13 mg/L for wheat biochar and up to 29 mg/L for rice (Figure 4). This equated to ~21% of the Zn sorbed by wheat biochar in the 50 mg/L initial treatment having been desorbed, and ~11% for the corresponding treatment for rice biochar (Table 1). The results indicate that, while substantial amounts of both Pb and Zn were retained, the sorption of Zn by these biochars is reversible to a greater degree via desorption with a neutral salt solution. This may have implications, both positive and negative, for field applications of these biochars in terms of contaminant immobilisation potential and metal recovery and biochar regeneration. For example, if deployed in a contaminated soil or mine spoil remediation scenario, this strong retention by biochar of non-essential and potentially toxic Pb observed here would be very positive from a plant and invertebrate health perspective (i.e. immobilising a toxicant). In contrast to that, if deployed in a water treatment or filtration scenario it might be viewed as economically advantageous if the Pb could be recovered from the biochar more easily via simple desorption with neutral salt solutions (i.e. recovering the Pb and regenerating the biochar for repeated use), rather than having to resort to large volume extractions with acidic solutions as has been documented elsewhere (e.g. Poonam et al. 2018). In relation to the essential plant nutrient Zn, it may be viewed as positive that some of the sorbed metal is held reversibly when in a land remediation and restoration scenario. That is, plants having access to an amount of Zn that is sorbed to the solid matrix but which is slowly released over time could be considered as beneficial in terms of nutrient provision and fertility. Indeed, biochars as a slow release fertiliser has become a very active area of research and even patent development, indicating the perceived potential of the material (El Sharkawi et al. 2018; Li et al. 2020).

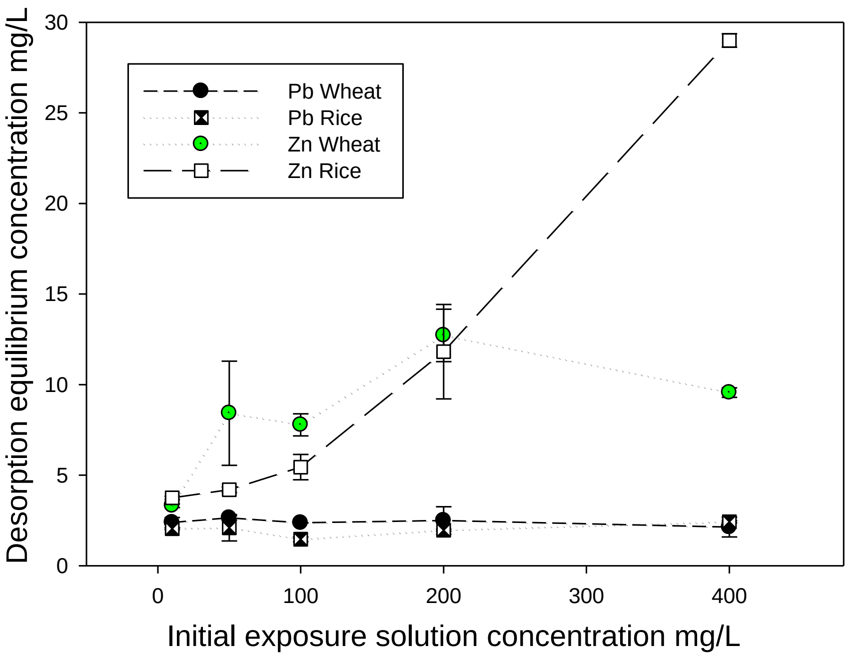


Figure 4. Concentration of metals in final desorption equilibrium solution (y-axis, corrected for entrained metals in residual solution from the sorption step) vs initial solution concentration imposed on each treatment (x-axis). Error bars indicate standard errors about means.

Table 1. Desorption amounts (mg/kg and % of initially sorbed metal, mean±SE) of Pb and Zn from wheat straw and rice husk derived biochar

Initial sorption solution mg/L	Pb desorbed from wheat biochar (mg/kg)	Pb desorbed from wheat biochar (% initially sorbed)	Pb desorbed from rice biochar (mg/kg)	Pb desorbed from rice biochar (% initially sorbed)
10	29.01±3.55	34.10±3.58	26.23±0.66	29.77±1.29
50	31.91±1.32	6.54±0.24	27.01±9.71	5.51±1.95
100	28.88±0.09	2.94±0.01	19.01±1.93	1.93±0.20
200	30.49±9.52	1.54±0.48	25.16±0.54	1.27±0.03
400	25.91±6.66	0.65±0.17	31.56±0.84	0.79±0.02
Initial sorption solution mg/L	Zn desorbed from wheat biochar (mg/kg)	Zn desorbed from wheat biochar (% initially sorbed)	Zn desorbed from rice biochar (mg/kg)	Zn desorbed from rice biochar (% initially sorbed)
10	40.62±1.41	40.78±1.50	47.31±0.94	47.46±0.94
50	102.48±34.89	20.73±7.07	53.48±2.01	10.72±0.40
100	96.31±8.52	9.69±0.86	68.97±9.18	6.90±0.92
200	155.53±17.80	7.83±0.90	152.18±32.77	7.63±1.64
400	117.20±3.98	2.94±0.10	360.16±8.45	9.03±0.21

3.2 Mine spoil remediation trial using wheat biochar

Addition of wheat biochar to mine spoils increased mean plant mass yield, although statistically significant differences were not consistently identified via ANOVA (Figure 5). This was likely impacted by the generally low amounts of growth and the variability in some control treatments (e.g. two controls in the Oil-shale bings spoils effectively achieved zero plant growth). However, the overall trend of increasing growth with addition of biochar was evident, as supported by regression analysis (growth yield vs biochar amendment %) that revealed a statistically significant relationship (p value <0.0001) when all data across all spoils and treatments were combined and also for Glendinning (p 0.003), Oil-shale bings (p 0.030) and Anglesey (p 0.015) spoils assessed individually.

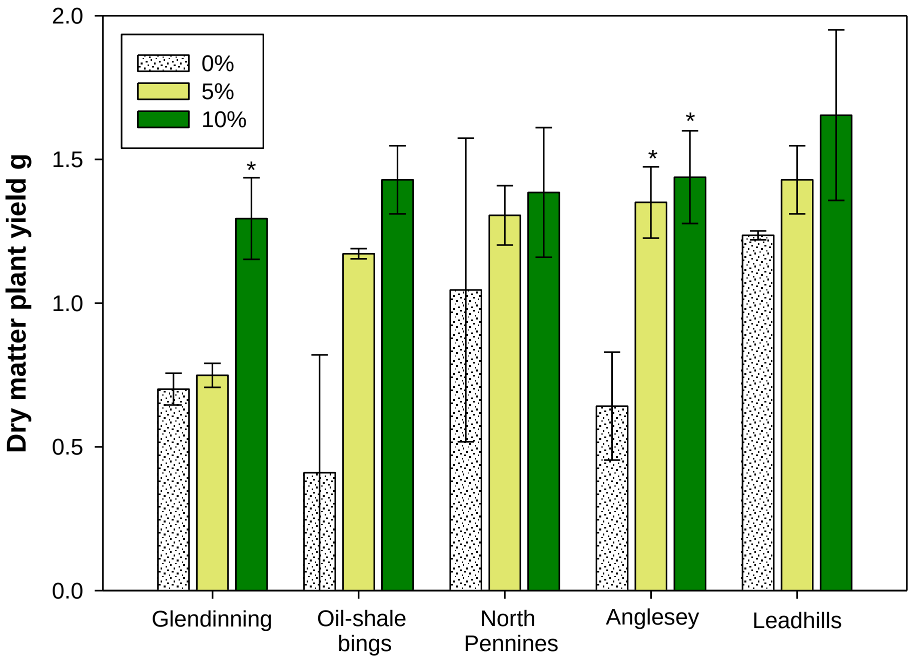


Figure 5. Mean aboveground ryegrass yield (error bars indicate standard error) in mine spoils amended with 0%, 5% or 10% (w/w) wheat straw biochar. Significant differences (ANOVA, p<0.05) from 0% treatments indicated by symbol (*).

Elemental analysis of plant tissues (Table 2) revealed that biochar application significantly reduced Cd assimilation into ryegrass ~2 to 4 fold in Oil-shale bings, North Pennines and Leadhills spoils. The mean concentrations of Pb also decreased following biochar addition in all spoils, but the decreases were only statistically significant for North Pennines and Anglesey spoils due to variation within treatments and controls. Arsenic and Sb were significantly decreased in ryegrass grown in treated spoils from the former Sb mine, Glendinning, showing an efficacy for the particular contaminants of concern at that site. Assimilation of Zn was significantly decreased in treated spoils from the former Pb/Zn mines of North Pennines and Leadhills, as well as treated spoils from Anglesey. In some cases, this lowered the Zn tissue concentrations from the toxic range for grass crops such as barley (*Hordeum vulgare*; toxicity thresholds variously reported across the range ~200 – 500 mg/kg tissue; Reuter et al. 1997) down to within the adequate/tolerance range. It is worth stating that the decreases in assimilation of non-essential elements such as As, Sb, Cd and Pb observed may be viewed as beneficial from the viewpoint of plant health and limiting food web contamination, but decreases in assimilation of essential elements such as Zn need closer examination because of the potential risk of deficiency developing. However, despite the substantial decreases in Zn assimilation by ryegrass observed in several of the treated spoils, all plants had tissue Zn concentrations well above deficiency thresholds for the species (i.e. 10 mg/kg; Reuter et al. 1997).

The changes in plant tissue elemental concentrations following biochar addition can therefore be seen as generally improving plant health, even without any complementary addition of other organic or inorganic fertilizer amendments, and thus biochar treatment may be a way of establishing plant growth on these bare spoils and therefore providing stabilisation and reduction in dust generation potential. However, the growth improvements achieved were modest and these may be enhanced with the further addition of manure or sewage biosolids. Such extra additions would add expense and complexity to any remediation effort, but has been found elsewhere to assist in the establishment of plant cover on mining wastes and mining impacted soils. For example, Novak et al. (2019) found that biochar applications achieved greater increases in switchgrass (*Panicum virgatum*) yield on mining impacted soils when combined with co-applications of manure and woodchip composts. In a different approach, Zhao et al. (2020) found that blending local soil with mine spoils also enhanced plant growth on the mine wastes they examined, through an increase in the proportion of fine materials in the substrate which resulted in greater water retention and thus better growth; investigations should therefore be conducted to determine whether this approach could be combined with biochar application to produce an effective and low-cost phytostabilisation strategy. Beyond establishment of vegetation cover for phytostabilisation of spoil materials and mining contaminated soils, other studies have explored phytoextraction and recovery of potentially valuable elements and also phytoremediation whereby total concentration of potentially toxic elements in solid substrates are decreased to tolerable levels through successive plant removals. However, prospects for phytoremediation and phytoextraction and recovery of elements from the spoils examined in the present study are not high if using solely the biochar employed here and ryegrass. This is because the yields were too modest and the concentrations in plant tissues too low, the latter of which is typically the case with non-hyperaccumulator species such as ryegrass (e.g. Broadhurst and Chaney 2016). Co-cropping with hyperaccumulating plants may, however, provide more potential here for achieving both spoil stabilisation and phytoremediation because it would combine the biomass, surface coverage and below-ground exudates of ryegrass with the hyperaccumulating capacity of species such as yellowtuft (*Alyssum murale*) or black nightshade (*Solanum nigrum*) (Broadhurst and Chaney 2016; Niu et al. 2015). Even so, phytoremediation is at best a very long term strategy, with some estimates for the time taken to achieve remediation success put at decades to hundreds or even thousands of years (Tschan et al. 2009; Suman et al. 2018).

In general pore water element concentrations were substantially decreased following biochar application, with statistically significant negative relationships evident between biochar application rate and concentrations of key PTEs, including Al, Cd, Pb and Zn, in the case of most spoils (Tables 3-7). For example, in the spoils from the Leadhills and North Pennines, where Zn and other metals were once mined, applications of biochar reduced porewater Zn concentrations by more than 95% in every treatment (Table 3 and Table 4). Moreover, while the porewater Zn concentrations in the untreated controls of those spoils were at or above concentrations reported to impair microbial functions in some European soils (e.g. EC10 and EC20 values of ~10 mg/L; Smolders et al. 2004), the biochar treatments reduced the Zn levels to well below this threshold and so had an ecologically meaningful positive effect. Perhaps on account of its low pH, the highest Pb concentrations were observed in the porewaters of the untreated spoil from Anglesey (>1000 µg/L; Table 5) and these were in the range associated with detectable impacts to collembolan (*Folsomia candida*) reproduction in soils (Bur et al. 2012), however biochar treatment decreased the concentrations by orders of magnitude and thus once again had an ecologically relevant positive effect on porewater toxicity. Also for that spoil from the former Cu mine at Anglesey, the 5% w/w biochar treatment decreased porewater Cu concentrations by 85-95%, while the 10% biochar treatment reduced it by ~99% (Table 5). The highest Cd concentrations were observed in the untreated spoils from the Leadhills (up to ~200 µg/L, Table 3) and were potentially within the range that exerts toxic effects in some soils (Bur et al. 2010), yet the biochar treatments decreased the concentrations to less than 10 µg/L in the 5% w/w treatment and to ~1 µg/L in the 10% w/w treatment.

The greatest porewater As concentrations, by far, were noted in the untreated spoils of Glendinning in which the values approximated 30 mg/L (30000 µg/L) at each time period (Table 7). This is in agreement with a previous study at the site which similarly determined the presence of substantial amounts of mobile As (Macgregor et al. 2015). Biochar treatment successfully reduced these concentrations to approximately 5 mg/L or below, which corresponds with the significant decrease in plant tissue As concentrations also observed in the 5% and 10% w/w biochar treatments. This decrease in As mobility brought about by biochar addition is consistent with some other studies that have also observed this effect (Rinklebe et al. 2016) but is at odds with other studies that reported biochar addition to have increased porewater As concentrations (Beesley et al. 2010; Beesley et al. 2013). The potential varied effects of biochar on As mobility in contaminated soils and mining spoils thus needs careful attention and further research.

4. Conclusions

High sorption capacities for Pb and Zn were demonstrated by both wheat straw and rice husk biochars, with Freundlich isotherms accurately describing the sorption of Zn but not of Pb. Desorption of Pb was minimal in mild neutral salt extracts whereas for Zn the sorption appeared readily reversible for a portion of the sorbed metal and this supports the idea of using biochar in the development of slow release fertiliser for micro-nutrient trace elements. Biochar incorporation into mine spoil material successfully restricted the mobility of potentially toxic elements in spoil porewater, thereby demonstrating the utility of the approach for decreasing concentrations in leachate and run-off and lowering the associated environmental risks. Biochar applications also improved plant growth and plant health, in terms of element content of tissues, indicating that biochar additions can successfully establish vegetative cover on, and thus phytostabilise, mine spoil heaps. However, co-addition of manure or compost with biochar may facilitate greater levels of vegetation growth and so this should be further explored.

Credit author statement

Alhar conducted and led project activities on a day to day basis and provided initial interpretation and write up. Thompson contributed to project development and analytical approach. Oliver conceived the project and contributed to interpretation and write up.

Declaration of competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Beesley, L., Marmiroli, M., Pagano, L., Pigoni, V., Fellet, G., Fresno, T., Vamerali, T., Bandiera, M., Marmiroli, N., 2013. Biochar addition to an arsenic contaminated soil increases arsenic concentrations in the pore water but reduces uptake to tomato plants (Solanum lycopersicum L.). Science of the Total Environment 454–455, 598-603.

Beesley, L., Moreno-Jimenez, E., Gomez-Eyles, J.L., 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environmental Pollution 158, 2282-2287.

Boni, M.R., Chiavola, A., Marzeddu, S., 2020. Remediation of Lead-Contaminated Water by Virgin Coniferous Wood Biochar Adsorbent: Batch and Column Application. Water Air and Soil Pollution 231.

Broadhurst, C.L., Chaney, R.L., 2016. Growth and Metal Accumulation of an Alyssum murale Nickel Hyperaccumulator Ecotype Co-cropped with Alyssum montanum and Perennial Ryegrass in Serpentine Soil. Frontiers in Plant Science 7.

Bromehead, C.E.N., 1940. The Evidence for Ancient Mining. The Geographical Journal 96, 101-118.

Bur, T., Crouau, Y., Bianco, A., Gandois, L., Probst, A., 2012. Toxicity of Pb and of Pb/Cd combination on the springtail Folsomia candida in natural soils: Reproduction, growth and bioaccumulation as indicators. Science of The Total Environment 414, 187-197.

Bur, T., Probst, A., Bianco, A., Gandois, L., Crouau, Y., 2010. Determining cadmium critical concentrations in natural soils by assessing Collembola mortality, reproduction and growth. Ecotoxicology and Environmental Safety 73, 415-422.

Burton, E.D., Phillips, I.R., Hawker, D.W., Lamb, D.T., 2005. Copper behaviour in a Podosol. 1. pH-dependent sorption-desorption, sorption isotherm analysis, and aqueous speciation modelling. Australian Journal of Soil Research 43, 491-501.

Cooper, D.C., Nutt, M.J.C., Smith, I.F., Easterbrook, G.D., 1989. Base-metal and gold mineralisation in north-west Anglesey, North Wales. Mineral Reconnaissance Programme Report 99. British Geological Survey Technical Report WF/89/2.

El Sharkawi, H.M., Tojo, S., Chosa, T., Malhat, F.M., Youssef, A.M., 2018. Biochar-ammonium phosphate as an uncoated-slow release fertilizer in sandy soil. Biomass and Bioenergy 117, 154-160.

Fellet, G., Marchiol, L., Delle Vedove, G., Peressotti, A., 2011. Application of biochar on mine tailings: Effects and perspectives for land reclamation. Chemosphere 83, 1262-1267.

Fellet, G., Marmiroli, M., Marchiol, L., 2014. Elements uptake by metal accumulator species grown on mine tailings amended with three types of biochar. Science of the Total Environment 468–469, 598-608.

Gal, J., Hursthouse, A., Cuthbert, S., 2007. Bioavailability of arsenic and antimony in soils from an abandoned mining area, Glendinning (SW Scotland). Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 42, 1263-1274.

Gray, C.W., McLaren, R.G., 2005. The effect of ryegrass variety on trace metal uptake. New Zealand Journal of Agricultural Research 48, 285-292.

Guney, M., Bourges, C.M.J., Chapuis, R.P., Zagury, G.J., 2017. Lung bioaccessibility of As, Cu, Fe, Mn, Ni, Pb, and Zn in fine fraction (<20μm) from contaminated soils and mine tailings. Science of The Total Environment 579, 378-386.

Harvie, B., 2005. West Lothian Biodiversity Action Plan: Oil Shale Bings.

Ho, Y.S., Porter, J.F., McKay, G., 2002. Equilibrium Isotherm Studies for the Sorption of Divalent Metal Ions onto Peat: Copper, Nickel and Lead Single Component Systems. Water, Air, & Soil Pollution 141, 1-33.

Kosolsaksakul, P., Oliver, I.W., Graham, M.C., 2018. Evaluating cadmium bioavailability in contaminated rice paddy soils and assessing potential for contaminant immobilisation with biochar. Journal of Environmental Management 215, 49-56.

Kumpiene, J., Fitts, J.P., Mench, M., 2012. Arsenic fractionation in mine spoils 10 years after aided phytostabilization. Environmental Pollution 166, 82-88.

Kwak, J.H., Islam, M.S., Wang, S., Messele, S.A., Naeth, M.A., El-Din, M.G., Chang, S.X., 2019. Biochar properties and lead(II) adsorption capacity depend on feedstock type, pyrolysis temperature, and steam activation. Chemosphere 231, 393-404.

Li, H., Li, Y., Xu, Y., Lu, X., 2020. Biochar phosphorus fertilizer effects on soil phosphorus availability. Chemosphere 244, 125471.

Macgregor, K., MacKinnon, G., Farmer, J.G., Graham, M.C., 2015. Mobility of antimony, arsenic and lead at a former antimony mine, Glendinning, Scotland. Science of the Total Environment 529, 213-222.

Mahdi, Z., Yu, Q.M.J., El Hanandeh, A., 2018. Removal of lead(II) from aqueous solution using date seed-derived biochar: batch and column studies. Applied Water Science 8.

Martin, R., Dowling, K., Nankervis, S., Pearce, D., Florentine, S., McKnight, S., 2018. In vitro assessment of arsenic mobility in historical mine waste dust using simulated lung fluid. Environmental Geochemistry and Health 40, 1037-1049.

Mench, M., Lepp, N., Bert, V., Schwitzguébel, J.-P., Gawronski, S.W., Schröder, P., Vangronsveld, J., 2010. Successes and limitations of phytotechnologies at field scale: outcomes, assessment and outlook from COST Action 859. Journal of Soils and Sediments 10, 1039-1070.

Mighall, T., Cortizas, A.M., Sánchez, N.S., Foster, I.D., Singh, S., Bateman, M., Pickin, J., 2014. Identifying evidence for past mining and metallurgy from a record of metal contamination preserved in an ombrotrophic mire near Leadhills, SW Scotland, UK. The Holocene 24, 1719-1730.

Niu, M.F., Wei, S.H., Bai, J.Y., Wang, S.Q., Ji, D.D., 2015. Remediation and Safe Production of cd Contaminated Soil Via Multiple Cropping Hyperaccumulator Solanum nigrum L. and Low Accumulation Chinese Cabbage. International Journal of Phytoremediation 17, 657-661.

Novak, J.M., Ippolito, J.A., Watts, D.W., Sigua, G.C., Ducey, T.F., Johnson, M.G., 2019. Biochar compost blends facilitate switchgrass growth in mine soils by reducing Cd and Zn bioavailability. Biochar 1, 97-114.

Poonam, Bharti, S.K., Kumar, N., 2018. Kinetic study of lead (Pb2+) removal from battery manufacturing wastewater using bagasse biochar as biosorbent. Applied Water Science 8, 119.

Raous, S., Becquer, T., Garnier, J., Martins, E.D., Echevarria, G., Sterckeman, T., 2010. Mobility of metals in nickel mine spoil materials. Appl. Geochem. 25, 1746-1755.

Reuter, D.J., Edwards, D.G., Wilhelm, N.S., 1997. Temperate and tropical crops, in: Reuter, D.J., Robinson, J.B. (Eds.), Plant Analysis an Interpretation Manual. CSIRO Australia, Collingwood, pp. 81-284.

Rinklebe, J., Shaheen, S.M., Frohne, T., 2016. Amendment of biochar reduces the release of toxic elements under dynamic redox conditions in a contaminated floodplain soil. Chemosphere 142, 41-47.

Smolders, E., Buekers, J., Oliver, I., McLaughlin, M.J., 2004. Soil properties affecting toxicity of zinc to soil microbial properties in laboratory-spiked and field-contaminated soils. Environmental Toxicology and Chemistry 23, 2633-2640.

Sparks, D.L., 2003. Environmental Soil Chemistry, 2nd ed. Academic Press.

Suman, J., Uhlik, O., Viktorova, J., Macek, T., 2018. Phytoextraction of Heavy Metals: A Promising Tool for Clean-Up of Polluted Environment? Frontiers in Plant Science 9, 1476.

Tschan, M., Robinson, B.H., Schulin, R., 2009. Antimony in the soil–plant system – a review. Environmental Chemistry 6, 106 – 115.

Zhang, W.W., Du, W.H., Wang, F., Xu, H.T., Zhao, T.H., Zhang, H.J., Ding, Y., Zhu, W.Q., 2020. Comparative study on Pb2+ removal from aqueous solutions using biochars derived from cow manure and its vermicompost. Science of The Total Environment 716.

Zhao, W.T., Zhou, Y.P., Xu, H., 2020. Formula and basic geochemical research to create new technology for vegetation restoration of mine slag heap (slope). Environmental Science and Pollution Research 27, 2464-2473.

Table 2. Element concentration (mean ± SE) in above ground ryegrass tissue (mg/kg dry mass)

Spoil	Treatment	As	Cd	Cr	Cu	Pb	Sb	Zn
Glendinning	0%	46.6±3.9	0.08±0.03	0.267±0.08	9.61±0.61	1.71±0.43	11.54±2.06	47.1±5.9
	5%	27.8±2.0*	0.07±0.05	0.23±0.07	9.52±1.00	0.93±0.11	2.92±0.38*	44.6±9.6
	10%	27.3±1.6*	0.03±0.01	0.05±0.01	7.77±0.77	0.70±0.18	1.94±0.69*	42.4±1.1
Oil-shale bings	0%	1.9±0.4	0.05±0.01	0.31±0.20	12.06±2.07	2.29±0.77	0.21±0.06	54.8±1.0
	5%	1.8±0.1	0.02±0.01*	0.27±0.09	11.48±0.76	1.51±0.83	0.21±0.09	52.2±1.5
	10%	1.3±0.3	bdl*	0.18±0.08	10.90±1.77	1.25±0.29	0.05±0.01	50.3±14.1
North Pennines	0%	2.8±0.7	4.38±0.94	1.20±0.02	13.14±2.09	25.43±1.09	0.32±0.15	368.7±60.1
	5%	1.8±0.3	0.99±0.24*	0.22±0.13*	11.92±1.98	12.23±1.47*	0.24±0.04	175.6±4.5*
	10%	1.7±0.6	0.36±0.11*	0.15±0.08*	11.34±0.73	6.28±0.86*	0.11±0.05	106.0±4.8*
Anglesey	0%	1.7±0.7	0.32±0.10	0.23±0.01	14.56±1.09	8.16±0.66	0.18±0.07	81.4±6.1
	5%	1.5±0.1	0.21±0.06	0.19±0.01	13.43±1.78	3.42±1.44	0.17±0.07	68.3±2.9
	10%	1.3±0.3	0.07±0.03	0.19±0.04	11.83±1.48	1.20±0.18*	0.15±0.02	58.4±1.8*
Leadhills	0%	1.6±0.4	8.3±0.54	2.40±0.69	15.14±1.47	23.44±4.08	2.90±0.61	297.3±5.6
	5%	0.8±0.1	2.47±0.60*	0.26±0.01	14.85±0.46	20.76±4.30	0.80±0.25*	145.0±10.6*
	10%	0.6±0.1	1.95±1.00*	0.30±0.13	14.43±1.02	11.35±2.17	0.39±0.11*	94.1±6.1*

* Significantly different (ANOVA $p<0.05$) from 0% treatment control.

Table 3. Porewater element concentrations (µg/L) in untreated control and biochar treated Leadhills mine spoils + regression parameters for biochar % (w/w) vs element concentration (mean of 2 ± SE for 0% controls)

	-------------- Day10 ---------------			-------------- Day20 ---------------			-------------- Day30 ---------------			Regression	
										p value	r^2
	0% Biochar	5%	10%	0%	5%	10%	0%	5%	10%		
Al	18.67±0.11	14.32	1.67	19.03±2.25	19.82	0.12	9.36±2.25	9.36	6.18	0.019	0.5706
Cd	166.4±29.3	7.75	1.31	201.1±11.9	8.02	0.92	175.1±11.0	9.01	0.90	0.002	0.7719
Cu	20.39±3.13	13.73	15.78	15.56±0.70	13.58	7.80	12.76±0.90	9.56	5.47	0.072	0.3908
Fe	9.45±.1.08	2.92	1.18	1.57±0.22	1.23	0.51	4.65±2.10	2.07	b/d	0.038	0.4819
Mn	2298±981	36.57	7.21	1697±690	26.00	2.91	1244±696.2	12.38	3.06	0.005	0.6941
Ni	23.74±3.00	5.60	5.43	21.31±3.67	3.27	3.16	14.44±2.79	2.25	2.29	0.006	0.6787
Pb	150.5±20.5	141.2	94.09	123.6±13.25	117.10	93.23	140.9±10.2	123.30	111.25	0.006	0.6867
Zn	11566±2703	143.2	51.86	10947±2403	126.60	25.51	7199±1528	148.70	34.86	0.004	0.7162
As	268.9±31.0	15.19	7.04	304.0±202.0	13.80	4.43	305.3±101.5	13.66	5.28	0.002	0.7684
Sb	17.53±1.22	4.09	2.48	22.78±2.01	5.14	1.86	24.89±0.01	6.39	1.77	0.001	0.828

Table 4. Porewater element concentrations (µg/L) in untreated control and biochar treated North Pennines mine spoils + regression parameters for biochar % (w/w) vs element concentration (mean of 2 ± SE for 0% controls)

	-------------- Day10 ---------------			-------------- Day20 ---------------			-------------- Day30 ---------------			Regression	
										p value	r^2
	0% Biochar	5%	10%	0%	5%	10%	0%	5%	10%		
Al	12.06±5.1	7.26	4.58	7.07±3.87	1.95	b/d*	6.75±0.42	4.59	1.49	0.014	0.5989
Cd	32.02±0.65	1.67	0.88	26.80±1.05	1.53	0.82	24.67±0.53	1.5	0.85	0.004	0.7154
Cu	43.21±1.0	11.88	8.82	38.23±2.02	9.37	3.3	34.86±0.99	7.82	2.31	0.827	0.001
Fe	7.52±1.52	7.35	5.4	9.84±1.08	4.84	0.09	18.23±1.15	5.5	0.04	0.01	0.632
Mn	398.2±9.8	6.04	2.77	59.58±2.13	4.45	2.53	35.50±5.4	4.01	2.55	0.132	0.2933
Ni	12.70±0.13	7.83	3.87	9.82±1.12	6.83	2.79	7.86±0.35	4.99	2	0.001	0.8157
Pb	122.3±13.9	101.27	74.76	100.9±7.0	82.73	68.78	108.7±11.40	73.05	65.82	0.002	0.7746
Zn	6328±292	158.7	97.14	4498±399	136.4	86.13	3572±171	130.5	83.74	0.005	0.696
As	531.1±10.0	32.06	5.36	533.0±22.0	30.29	4.83	492.3±21.2	29.65	4.32	0.001	0.7859
Sb	18.99±1.9	6.22	1.54	20.08±1.98	6.26	1.29	21.00±1.00	6.58	1.27	<0.001	0.929

* b/d = Below detection

Table 5. Porewater element concentrations (µg/L) in untreated control and biochar treated Anglesey mine spoils + regression parameters for biochar % (w/w) vs element concentration (mean of 2 ± SE for 0% controls)

	-------------- Day10 ---------------			-------------- Day20 ---------------			-------------- Day30 ---------------			Regression p value	r^2
	0% Biochar	5%	10%	0%	5%	10%	0%	5%	10%		
Al	2504±386	904.6	28.01	3843±39	511.2	59.4	3434±174	388.9	6.28	0.001	0.8271
Cd	9.55±1.19	4.05	0.38	12.24±0.84	2.76	0.37	12.40±0.33	2.29	0.34	0.002	0.7513
Cu	486.3±46.7	68.58	6.54	697.0±33.1	40.97	2.08	726.6±14.2	35.85	1.55	0.002	0.7673
Fe	1094±776	5.89	4.27	1230±671	3.94	3.65	713.9±447.1	8.00	0.87	0.005	0.7028
Mn	295.9±5.0	163.2	72.67	256.9±12.0	145.25	47.5	235.1±11.0	132.35	19.3	<0.001	0.947
Ni	8.08±1.25	6.07	1.16	9.68±0.89	3.85	1.03	9.51±0.77	3.25	0.69	<0.001	0.9351
Pb	1362±196	302.6	5.05	1746±153	184.7	4.2	1860±25	170.9	2.29	0.001	0.8211
Zn	2082±259	1036	51.76	2808±204	730.4	51.68	2937±107	661	56.59	<0.001	0.9032
As	14.63±2.1	9.93	4.73	14.70±3.10	8.5	7.12	14.68±0.89	8.49	7.02	<0.001	0.9167
Sb	0.43±0.10	0.32	0.11	0.34±0.23	0.21	0.14	0.37±0.12	0.16	0.13	0.001	0.834

Table 6. Porewater element concentrations (µg/L) in untreated control and biochar treated Oil-shale bings mine spoils + regression parameters for biochar % (w/w) vs element concentration (mean of 2 ± SE for 0% controls)

	-------------- Day10 ---------------			-------------- Day20 ---------------			-------------- Day30 ---------------			Regression p value	r^2
	0% Biochar	5%	10%	0%	5%	10%	0%	5%	10%		
Al	30.66±0.70	21.73	14.54	30.79±0.10	14.08	2.47	16.57±2.10	15.5	6.52	0.007	0.6714
Cd	0.19±0.01	0.16	0.16	0.28±0.02	0.27	0.17	0.22±0.02	0.16	0.16	0.080	0.3745
Cu	2.61±0.10	2	1.92	1.56±0.09	2.02	1.29	1.16±0.20	0.97	0.53	0.343	0.1285
Fe	1.70±1.49	1.7	1.66	7.52±0.91	1.25	0.94	0.57±0.30	0.47	0.31	0.220	0.2055
Mn	1.24±0.09	0.19	0.13	0.21±0.10	0.19	0.02	0.03±0.01	0.01	b/d	0.179	0.2419
Ni	2.14±0.84	1.94	1.39	1.56±0.49	1.35	1.16	1.15±0.41	1.03	0.81	0.169	0.2514
Pb	0.12±0.01	0.08	0.01	0.15±0.01	0.08	0.02	0.03±0.01	b/d*	b/d	0.041	0.4702
Zn	27.98±3.74	22.87	22.44	31.22±2.89	29.79	10.41	40.83±13.52	24.14	17.59	0.006	0.6829
As	331.9±10.2	160	25.74	346.0±89.0	167.8	25.66	353.3±122.2	185.3	27.71	<0.001	0.9936
Sb	0.82±0.21	0.7	0.59	0.80±0.09	0.74	0.53	0.77±0.12	0.68	0.54	<0.001	0.925

* b/d = Below detection

Table 7. Porewater element concentrations (µg/L) in untreated control and biochar treated (5%, w/w*) mine spoils from Glendinning

	---------Day10----------		---------Day20----------		---------Day30----------	
	0% Biochar	5%	0%	5%	0%	5%
Al	8.95±3.41	1.99	10.16±5.39	3.92	2.82±1.92	2.53
Cd	0.55±0.06	0.4	0.43±0.01	0.27	0.32±0.03	0.21
Cu	15.99±1.05	5.14	10.19±0.45	3.88	6.73±0.24	3.62
Fe	180.8±125.8	66.22	126.5±64.9	3.14	24.52±6.1	3.7
Mn	264.2±3.3	160.4	166.9±17.6	30.12	72.60±7.8	23.66
Ni	48.34±2.43	30.9	36.69±1.75	15.3	27.09±1.2	13.85
Pb	0.38±0.18	0.57	0.25±0.05	0.22	0.09±0.6	0.12
Zn	91.37±4.6	31.2	88.64±8.8	12.5	70.59±5.9	26.67
As	26660±2080	5351	29940±11010	4125	32540±8890	4490
Sb	535.1±16.1	509.3	942±89	522.25	1095±4	611.85

* Note that porewaters from 10% w/w biochar treatments were not obtained for this spoil hence the dataset was insufficient for regression analysis.

Alhar et al. Supplementary Information

Table S.I.-1. Major compounds and elements in mine spoil materials determined using X-Ray fluorescence spectroscopy (XRF)*, percentage by mass or mg/kg units as indicated

Element/ compound	Glendinning	Leadhills	Oil-shale bings	North Pennines	Anglesey
	------------------------------ Percentage (%) w/w ------------------------------				
Na_2O	<0.01	0.508	1.607	<0.01	0.84
MgO	4.075	4.644	3.389	4.763	0.836
Al_2O_3	30.72	20.453	29.542	8.714	30.121
SiO_2	66.077	59.294	62.159	57.745	68.624
P_2O_5	0.135	<0.01	0.517	<0.01	<0.01
SO_3	1.112	1.919	2.58	2.727	3.133
K_2O	5.814	4.153	3.121	1.352	6.398
CaO	2.679	17.185	5.363	20.069	<0.01
Fe_2O_3	10.155	7.525	14.753	10.47	16.386
Pb	<0.01	3.499	0.011	1.832	0.158
Ti	0.734	0.487	0.709	0.156	0.272
	------------------------------------ mg/kg ------------------------------------				
As	13160±237.4	<1.0	<1.0	<1.0	379.1±98.4
Cd	<1.0	79.9±31.5	<1.0	120.6±50.3	<1.0
Cr	232.9±88.2	144.4±46.3	232.8±84.4	61.1±13.9	138.9±34.8
Cu	43.6±11.5	252.8±55.2	84.8±14.0	353.3±75.2	576.1±172.2
Ni	75.8±22.54	<1.0	115.6±48.23	<1.0	<1.0
Sb	459.3±111.8	58.5±10.33	<1.0	<1.0	69.8±25.32
V	215.5±90.6	130.4±52.2	302.4±96.2	36.8±9.4	45.8±10.3
Zn	851.9±154.6	19960±320	144±36.9	50880±682	243.8±89.2

* Total element concentrations were determined in powderised spoil materials via X-Ray fluorescence spectroscopy (XRF) using a PANalytical Epsilon 3 XLE (having a Silicon drift detector SD(D) with 135eV@Mn-Ka, max count rate of 1500000 counts/s at 50% dead time) according to the method of Watson (1996). Reference: Watson, J.S. (1996). Fast, Simple Method of Powder Pellet Preparation for X-ray Fluorescence Analysis. X-ray Spectrometry, 25, 173.174.

Supplementary figure S1

Supplementary Figure S1. Remediation trial setup illustrating pots equipped with rhizon soil porewater samplers (Rhizon Flex, Rhizosphere Research Products, The Netherlands) and plant growth 20 days after sowing.