



Research article

Contrasting mobility of arsenic and copper in a mining soil: A comparative column leaching and pot testing approach

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ARTICLE INFO

Keywords:

Copper
Arsenic
Mining soil
Biochar
Vermicompost

ABSTRACT

The remediation of legacy metal(loid) contaminated soils *in-situ* relies on the addition of [organic] amendments to reduce the mobility and bioavailability of metal(loid)s, improve soil geochemical parameters and restore vegetation growth. Two vermicomposts of food and animal manure waste origin (V_1 and V_2) were amended to an arsenic (As) and copper (Cu) contaminated mine soil ($\leq 1500 \text{ mg kg}^{-1}$). Leaching columns and pot experiments evaluated copper and arsenic in soil pore waters, as well as pH, dissolved organic carbon (DOC) and phosphate (PO_4^{3-}) concentrations. The uptake of As and Cu to ryegrass was also measured via the pot experiment, whilst recovered biochars from the column leaching test were measured for metal sorption at the termination of leaching. Vermicompost amendment to soil facilitated ryegrass growth which was entirely absent from the untreated soil in the pot test. All amendment combinations raised pore water pH by ~ 4 units. Copper concentrations in pore waters from columns and pots showed steep reductions ($\sim 1 \text{ mg L}^{-1}$), as a result of V_1 & V_2 compared to untreated soil ($\sim 500 \text{ mg L}^{-1}$). Combined with an increase in DOC and PO_4^{3-} , As was mobilised an order of magnitude by V_1 . Biochar furthest reduced Cu in pore waters from the columns to $< 0.1 \text{ mg L}^{-1}$, as a result of surface sorption.

The results of this study indicate that biochar can restrict the mobility of Cu from a contaminated mine soil after other amendment interventions have been used to promote revegetation. However, the case of As, biochar cannot counter the profound impact of vermicompost on arsenic mobility.

1. Introduction

Legacy anthropogenic activities, such as mining and smelting, application of pesticides and chemical fertilizers, and sludge and manures application to soils are sources of increased metal(loid) input to soils (Liu et al., 2021; Xu et al., 2021; Wang et al., 2020). The environmental risk that soils with high concentrations of extant metal(loid)s pose depends on the geochemical behaviour of metal(loid)s in specific soils, influencing their leachability, bioavailability and toxicity (Helsers et al., 2022; Rehman et al., 2021; Baragaño et al., 2020a; Lebrun et al., 2019). Unlike organic contaminants, metal(loid)s are not biodegradable, and therefore persist in the soils (Babu et al., 2021). To avoid wholesale removal of soils and costly and impractical washing

procedures, *in-situ* methods to reduce metal(loid) mobility are favoured (Ha et al., 2019). Remediation involving plants, for instance, can stabilise metal(loid)s in contaminated soils after plant roots bind soils and reduce erosion (Cárdenas-Aguilar et al., 2020). Heavily contaminated sites may be characterized by a complete lack of vegetative growth (phytotoxicity) (Beesley et al., 2014) and, as a first principle, it may be necessary to apply organic amendments to soils to improve geochemical and/or physical parameters to allow vegetation to grow (Singh et al., 2022; Chen et al., 2022; Teodoro et al., 2020) in the interests of restarting natural processes.

Amongst many available organic soil amendments that have been previously studied in this context are (vermi) composts, sewage sludges, digestates, and biochars (Wang et al., 2021; Alam et al., 2020;

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Duwiejuah et al., 2020; Liu et al., 2019; Egene et al., 2018; Abbaspour and Golchin, 2011). Vermicomposts, depending on their source material and production method, have a relatively high proportion of humified organic matter and are therefore rich in available nutrients. Like other composts, an abundance of humic substances offers binding sites for metals (Alam et al., 2020; Abbaspour and Golchin, 2011), though the high PO_4^{3-} content in vermicompost may also result in the displacement of similarly charged elements, such as arsenic, when added to mine soils polluted by metals and metal(loid)s (Karami et al., 2011).

Unlike vermicomposts, biochars are produced by thermal decomposition of organic waste material under a limited supply of oxygen (O_2), at relatively low temperatures ($<700^\circ\text{C}$) (Mohanty and Kumar, 2021; Lee et al., 2019). The end-product has a carbon matrix structure with a vast surface area, often with a favourable cation-exchange-capacity (CEC) compared to composted materials (Duwiejuah et al., 2020; Beesley et al., 2011; Chen et al., 2011). The longevity (carbon half-life) of biochars in the environment is said to be 10^2 – 10^7 years (Zimmerman, 2010), meaning that their metal(loid) binding properties should remain intact long enough to ensure the restarting of natural vegetation growth and nutrient cycling. For that reason, much literature has been produced and reviewed widely recommending biochars as idealised materials for soil remediation (Sizmur et al., 2016). Recently the combination of composts with biochar has also been applied to soils, to take advantage of the advantageous properties of both composted and pyrolyzed materials simultaneously (Teodoro et al., 2020).

The broad aim of this work was to test the extent to which the combination of vermicomposts with biochar could enhance vegetation growth and reduce metal(loid) mobility in a contaminated mine soil. The specific objectives were to: a) measure the influence of two vermicomposts on plant growth (biomass), As and Cu mobility (leaching) and plant uptake; b) determine the additional value of biochar addition in combination with vermicomposts, and; c) discuss the scientific value of the findings in the context of key geochemical factors influenced by the combined vermicompost and biochar additions.

2. Material and methods

2.1. Soil and amendments preparation

Soil for this experiment was sourced from a metalliferous mining site in Northern Spain. The site/soil was selected because metal(loid) concentrations exceeded the threshold for agricultural, livestock or forestry uses, which are >40 and $>55\text{ mg kg}^{-1}$ for As and Cu concentrations, respectively (BOPA, 2014).

Vermicomposts (V_1 and V_2) were both composed of raw food wastes. For vermicompost 1 (V_1) consisting of fruit, vegetables, pistachio and eggshells in a home-made mixture, and; five hundred California Red earthworms (*Eisenia fetida*) (multiHuerto ecología S.L., Alicante, Spain) were added to the vermicomposter containing 200 g of raw food waste which was covered with cardboard (7 cm thick approximately.) as the worms are photophobic. In order to obtain suitable development of the earthworms, the optimal conditions of temperature (18 – 25°C) and moisture (70 – 80%) were maintained during the vermicomposting process (3 months approx.). The raw organic food waste was structured and mixed with dry remains (paper, cardboard, dry leaves, etc.) to facilitate their decomposition and compensate for excess moisture. This assured aeration of the mixture and the maintenance of a ratio of carbon and nitrogen suitable for earthworms. Finally, the extracted vermicompost was left to mature in darkness for one month. Vermicompost 2 (V_2) was a commercially available SIRO trademark mixture of chicken and horse manure mixed with fine sand and was utilised as purchased.

Biochar was manufactured by Centro de Valorización Ambiental del Norte S.L. (Touro, A Coruña, Spain) in a pyrolyzer furnace (model HCV_56 CCH) designed by the Hobersal Company. Biochar was made from corn cobs (*Zea mays* L.), air-dried and pyrolyzed at 500°C for 74

min. At this temperature, 66.56% yield biomass biochar was obtained.

2.2. Soil and amendments analyses

A bulk sample of 8 kg of contaminated soil and 1 kg of each amendment were taken for chemical analysis. Soil (M) and amendments (B , V_1 and V_2) were characterized after being air-dried and sieved through a 2 mm sieve and homogenized, as follows; pH was determined using a pH electrode (Crison pH & Ion-Meter GLP 22+) in a ratio 1:2.5 soil-distilled water (Porta, 1986). The TC (Total Carbon) of the soil and the amendments were determined in LECO CNS 2000 elemental macro analyser. Pseudo-total metal(loid)s concentrations (PM) were measured by X Series Quadrupole Inductively Coupled Plasma- Mass Spectrometry (ICP-MS, Thermo Elemental) after extraction, using aqua regia by acid digestion (1:5:5 HCl– HNO_3 – H_2O_2 ratio) in a microwave oven (Milestone ETHOS 1, Italy). Exchangeable cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+}) were extracted with 0.1 M BaCl_2 (Hendershot and Duquette, 1986), and element concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES, Optima 4300 DV; PerkinElmer). CEC was calculated using the sum of exchangeable cations concentrations (Houba et al., 2008). Deionised water-extractable metal(loid)s (DWEM) concentrations were determined following the method of Dennis et al. (2020) and analysed by ICP-OES. Available P was determined by Mehlich 3 method (Mehlich, 2008) and analysed by ICP-OES.

2.3. Pot experiment

In order to determine the influence of the soil amendments when individually amended to soils a greenhouse experiment was carried out for 3 months whereby combinations of soil, vermicomposts and biochars were tested. Eighteen plastic pots, (3 per treatment) of 8 cm deep x 10 cm internal diameter were prepared. Pots containing only mine soil (CP), were compared to pots with a blend of vermicompost (10% w/w, PV_1 and PV_2), biochar (1% w/w, PB) or a mixture of both amendments (10% and 1% w/w, PBV_1 and PBV_2 ; Table 2A). After set-up, pots were left to equilibrate for 1 week at a moisture content of 60% of water holding capacity (WHC), calculated following soil saturation and weighing (field capacity). Thereafter in each pot, 1.5 g *Lolium multiflorum* (Italian ryegrass) seeds were sown, the pots were watered and weighted every two days to maintain the field capacity, with a controlled temperature of 15°C . Pore water sampling was achieved by the placement of one 5 cm long rhizon sampler into each pot at a 45° angle (Eijkkelkamp, produced by Rhizosphere; Fig. 1A). Pore waters were sampled at the fourth and tenth weeks after germination from each pot using removable syringes; two sampling periods were chosen in order to ensure sufficient total volume of sample was obtained for analysis. Immediately upon sampling of pore waters and leachates, pH was measured. Subsequently, each sample was divided in three subsamples immediately acidified with concentrated nitric acid to give a final concentration of 1% nitric acid. The metal(loid)s (As and Cu), DOC and Phosphate (PO_4^{3-}) concentrations were determined by ICP-MS, N/C 3100 multi analyser and segmented continuous flow autoanalyzer (Bran + Luebbe AA3) following the ISO standard 6878:2004 (Water quality – determination of phosphorous – Ammonium molybdate spectrometric method), respectively.

At the end of the experiment, ryegrass shoots were harvested by stainless steel scissors cutting the vegetation level with the rims of the pots. Samples were washed using deionised water and dried at 40°C for 3 days. Then the dried material was ball milled and microwave digested by Milestone ETHOS 1. After the total dry mass was determined, 0.2 g of ryegrass was weighed into Teflon containers and a ratio 1:1 hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) were added to the samples. Microwave digestion was performed at 180°C for 30 min. Once digestion was completed the samples were placed in falcon tubes and made-up with deionised water to a final volume of 50 mL. Analytical blanks

Table 1

Characteristics and metal(loid)s concentrations of contaminated mine soil (M), biochar (B) and vermicompost (V₁ and V₂).

		M	B	V ₁	V ₂
pH		3.73 ± 0.01	9.95 ± 0.03a	8.82 ± 0.01 b	7.16 ± 0.04c
TC	g kg ⁻¹	<Q.L.	3.11 ± 0.01c	15.82 ± 0.22a	8.68 ± 0.13 b
Na ⁺	cmol(+)kg ⁻¹	1.71 ± 0.38	3.56 ± 0.88c	53.21 ± 5.47a	32.32 ± 3.45 b
K ⁺		4.09 ± 0.44	378.29 ± 4.57a	206.69 ± 18.99 b	20.75 ± 1.37c
Mg ²⁺		33.29 ± 0.99	1.09 ± 0.13c	38.09 ± 4.90a	18.29 ± 0.62 b
Ca ²⁺		34.13 ± 0.79	2.12 ± 0.27 b	104.03 ± 13.73a	120.82 ± 5.44a
Al ³⁺		11.60 ± 0.14	<Q.L.	<Q.L.	<Q.L.
CEC		84.82 ± 0.56	385.08 ± 5.25a	402.02 ± 40.85a	192.18 ± 10.73 b
As	PM mg kg ⁻¹	59.48 ± 2.56	<Q.L.	1.20 ± 0.06 b	3.67 ± 0.28a
Cu		1488.26 ± 18.36	8.56 ± 0.97c	43.28 ± 1.13a	15.75 ± 0.56 b
As	DWEM	0.01 ± 0.00	0.01 ± 0.00c	0.15 ± 0.01a	0.06 ± 0.01 b
Cu		276.91 ± 17.45	0.56 ± 0.22a	0.97 ± 0.02a	0.01 ± 0.00 b
AP	Mehlich III	17.05 ± 0.76	138.62 ± 1.62c	3125.65 ± 62.59a	643.90 ± 9.32 b

In amendments characteristics (B, V₁ and V₂) for each row, different letters in different samples indicate significant differences (n = 3, ANOVA; p < 0.05). Typical deviation is represented by ±; <Q.L., below quantification limit; TC: total carbon; PM: pseudototal metal(loid)s; DWEM: deionised water extractable metal(loid)s; AP: available phosphorus (Mehlich III).

Table 2A

Composition (mass g) of materials in the pot experiment.

Treatment		CP	PV ₁	PV ₂	PB	PBV ₁	PBV ₂
Italian Ryegrass	g	1.5	1.5	1.5	1.5	1.5	1.5
Vermicompost		–	30	30	–	30	30
Soil		300	270	270	297	267	267
Biochar		–	–	–	3	3	3

CP: Contaminated mine soil control; PV₁ and PV₂: Contaminated mine soil mixed with raw food organic waste vermicompost and chicken and horse manure vermicompost, respectively; PB, PBV₁ and PBV₂: same treatments as those described with biochar added.

and reference material (IPE-952) were included in parallel, for quality control purposes. Total As and Cu concentration was analysed by ICP-MS (X Series Thermo Elemental).

2.4. Column leaching tests

In order to determine the influence of the biochar when physically separated from the soil and vermicompost a column leaching study was performed following a modified method of Trakal et al. (2017). Plexiglass columns (20 cm length and 6 cm in internal diameter) were configured to hold soil and soil with vermicompost above a removable capsule containing biochar, so that the biochar could be removed from the columns post-leaching, without any adhered soil particles (Fig. 1B). To achieve this, the upper portion of the columns contained 300 g of air-dried soil (M) or its blend (ratio 90/10 w:w) with vermicompost (Table 2B). In the middle portion of the columns was a porous capsule containing sand, or a mixture of sand with biochar (Table 2B) acting as a filter pod allowing metal(loid) loaded leachates from the upper portion to penetrate. The lower portion of the column contained only sand to occupy the remaining volume and ensure the placement of a lower pore water sampler. Industrial sharp sand with particle size between 0.1 and

0.5 mm was used in all cases.

After column configuration, treatments were initially incubated for 7 days under moisture equal to 60% WHC, and before applying to 1.5 g of ryegrass to the soil surface at the top of each column, to ensure parity with the pot test.

Columns were gravitationally leached with deionised water (18.3 MΩ cm⁻¹) for 10 days at a constant flow rate of 0.09 mL min⁻¹, which was maintained by a peristaltic pump FB-70155. The configuration of the columns allows pore water samples to be taken from the upper portion (pre-biochar) and the lower portion (post-biochar) simultaneously (Fig. 1B). Upon germination of the ryegrass, which occurred in four of the six columns (those containing vermicompost), an additional column was affixed above the column containing soil in order that the leaching apparatus could deliver the prerequisite volume of water undisturbed throughout the duration of grass growth (Fig. 1B).

Pore water samples were sampled at 24, 48, 72, 96 and 120 h and analysed as detailed above (2.3). At the end of the experiment water flow was stopped and the columns were dismantled to remove soil and reveal the capsules, which were opened and the biochar inside separated from sand by sieving up to 0.50 mm.

2.5. Analysis of recovered biochar

A FEI Quanta 200 environmental scanning electron microscope (ESEM) equipped with an Energy Dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments X-Max EDS System) was used to characterize the morphology and the elemental composition of the removed biochar having been subject to leaching from soil and vermicompost above. The samples were fixed on an adhesive carbon tape and coated with a fine layer of gold only for morphology analysis. Secondary electron (SE) images were taken at an accelerating voltage of 10 kV. EDS spectra were collected at an accelerating voltage of 20 kV. A control biochar sample having not been inside the columns was used for comparison.

2.6. Statistical analysis

All analyses were performed in triplicate and the data obtained were statistically treated using the SPSS program (v. 24 for Windows). ANOVA analyses and test of homogeneity of variance were carried out. In the case of homogeneity, a post hoc least significant difference (LSD) test was done. If not, a Tukey's test was performed.

3. Results

3.1. Improvements to soil properties and vegetation growth by amendment (s)

The application of vermicompost to the tested mine soil was intended to counter the acidic pH (Table 1) and promote vegetation growth. Vermicomposts (V₁ and V₂) and biochar (B) had higher pH values, by ≤ 3 units, than the mine soil (Table 1), though there were some differences in the geochemical parameters specific to each vermicompost. For example, the TC content, CEC values and available phosphorus (AP) content were greatest in V₁ than other amendments (B and V₂) and soil (M). Contrastingly, V₂ had the highest concentration of Ca²⁺ and V₁ had the highest concentration of Na⁺ and Mg²⁺ of all of the measured materials.

Soil without any amendment in both the pot and column experiments (M and CP respectively) did not support any ryegrass growth, and biochar alone did not result in ryegrass growth, unless accompanied by vermicompost (Fig. 2). There were no significant differences between any of the treatments where ryegrass had grown (Fig. 2B). Where ryegrass did successfully grow, Cu uptake followed the sequence PV₁ > PBV₁ > PBV₂ > PV₂, though differences were not statistically significant in pots (Fig. 2A). Arsenic uptake by ryegrass was lower than Cu, with

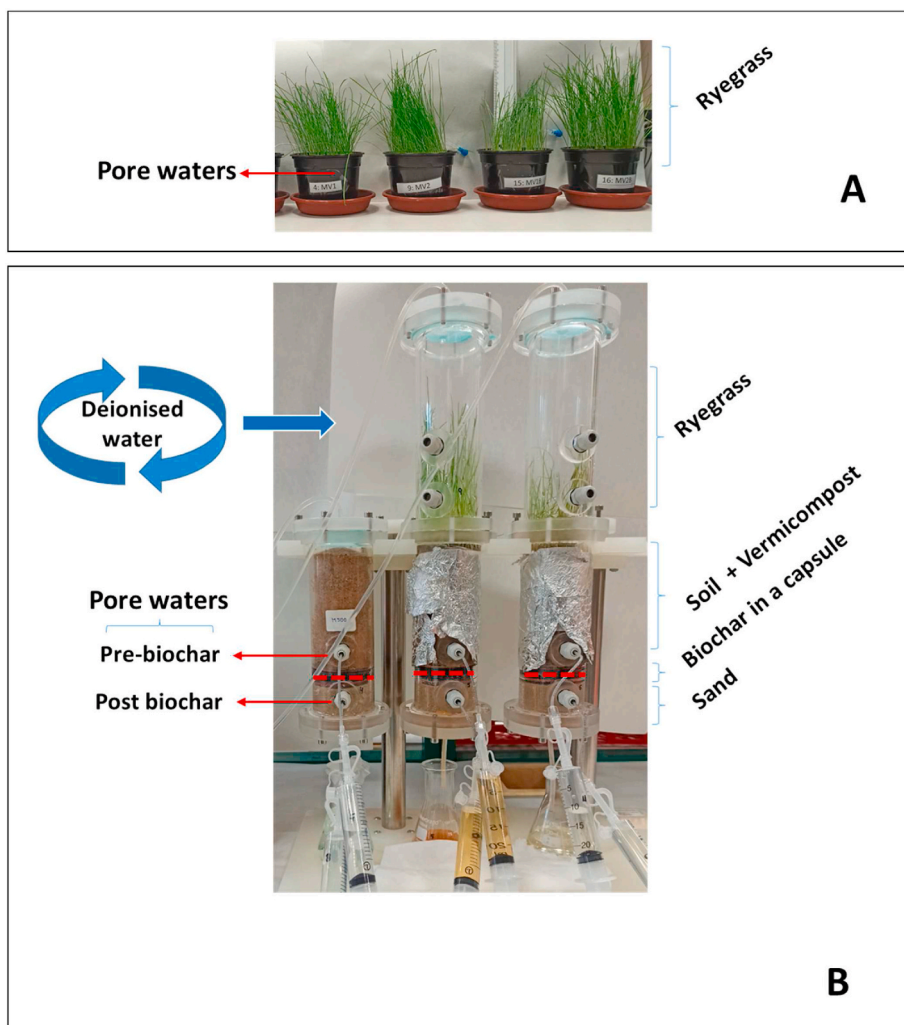


Fig. 1. Experimental design of: (A) pot experiment and (B) column leaching experiment, showing pore water sampling points and composition of the columns.

Table 2B

Composition (mass g) of materials in the column experiment.

Treatment		M	MV ₁	MV ₂	MB	MBV ₁	MBV ₂
Italian Ryegrass	Top column	g	1.5	1.5	1.5	1.5	1.5
Vermicompost			–	30	30	–	30
Soil			300	270	270	300	270
Sand	Removal capsules		21	21	21	18	18
Biochar			–	–	–	3	3
Sand	Bottom column		79	79	79	79	79

M: Contaminated mine soil control; MV₁ and MV₂: Contaminated mine soil mixed with raw food organic waste vermicompost and chicken and horse manure vermicompost, respectively; MB, MBV₁ and MBV₂: same treatments as those described with biochar in the removal capsules.

values between 0.36 and 0.67 mg kg⁻¹ in PBV₂ and PBV₁ in pots, being significantly lower where V₂ was used (Fig. 2A).

3.2. Geochemical parameters of pore waters from the pot experiment

Copper concentrations in pore waters were greatest in the untreated soil (CP) and the soil treated with biochar only (PB; Fig. 3A). The addition of both vermicomposts reduced this by one (PV₁) or two (PV₂) orders of magnitude (Fig. 3A). The further inclusion of biochar had no additional impact on this parameter (PBV₁ & PBV₂; Fig. 3A). In the case of As, the inclusion of PV₁ significantly increased pore water concentrations above the untreated soil (CP; Fig. 3B). Neither the biochar alone nor combined with vermicomposts had any additional impact. Likewise,

PV₂ did not significantly impact As in pore waters above the untreated soil (Fig. 3B).

Other measured parameters, such as DOC and PO₄³⁻ responded in common with As, displaying significantly increased concentrations as a result of PV₁ or PBV₁ (Fig. 3C and D). Pore water pH responded similarly to both vermicompost amendments, increasing 2–3 units above the untreated soil with PV₁ and PV₂ (and their biochar amendment equivalents, PBV₁ and PBV₂; Fig. 3E). Biochar alone had no significant impact on these parameters (PB; Fig. 3E).

3.3. Geochemical parameters measured by column leaching

Pore waters collected at the top of the columns represent

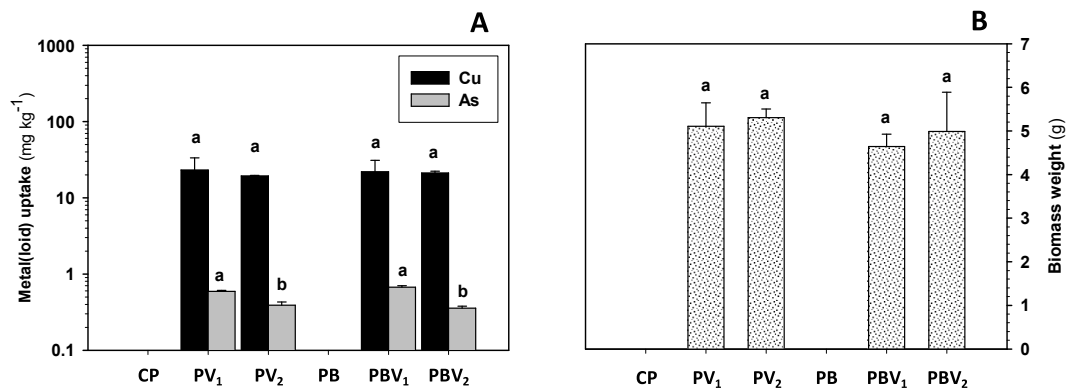


Fig. 2. Copper and Arsenic uptake (A) and dry mass (B) in ryegrass grown in the pots experiment. Statistically significant mean values (n = 6) denoted by different letter differ significantly ($p < 0.05$) according to Tukey's test.

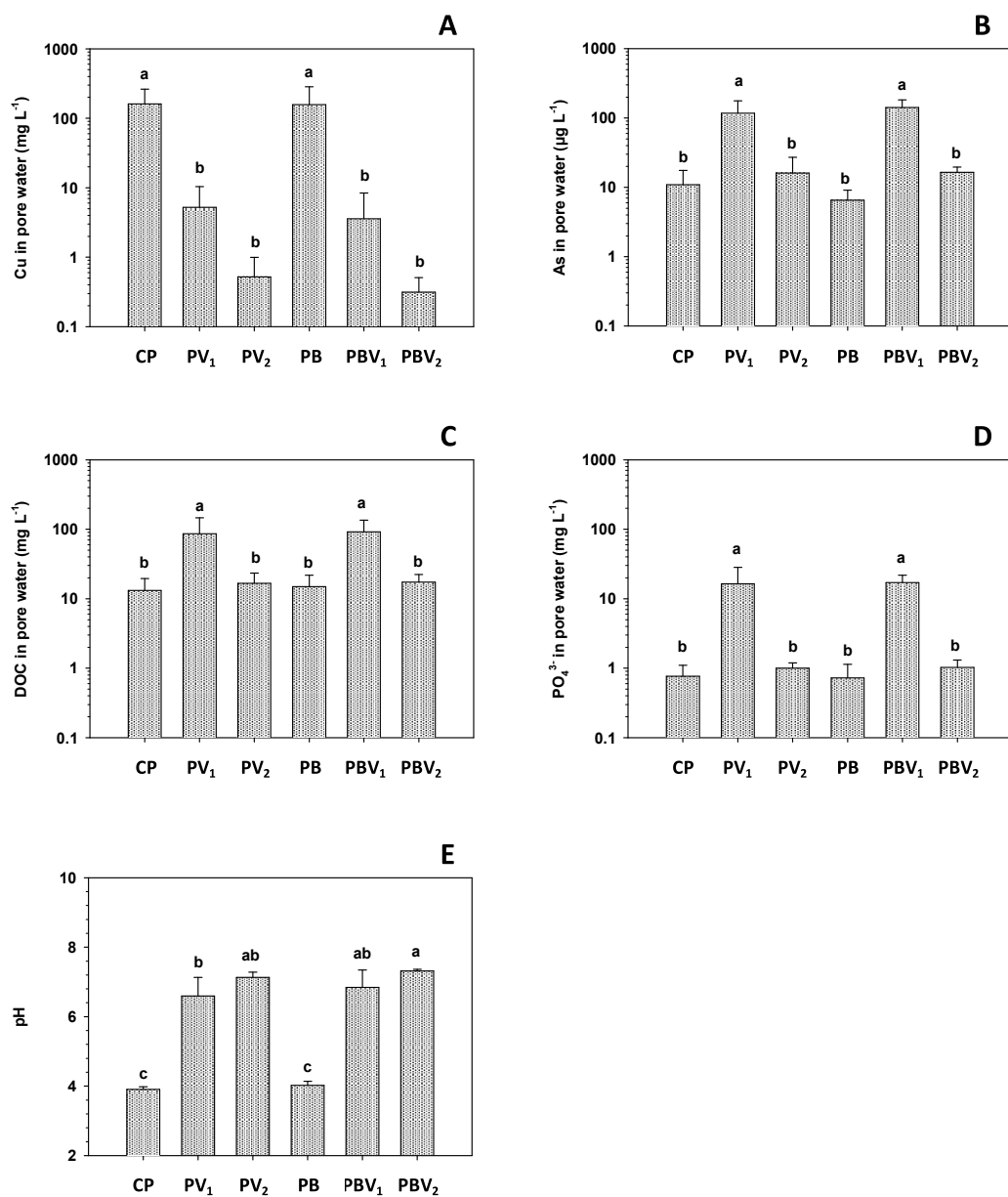


Fig. 3. (A) Copper, (B) Arsenic, (C) DOC and (D) PO₄³⁻ concentration and (E) pH value in pore water from pots experiment. Within each graph, mean values (n = 6) denoted by different letter differ significantly ($p < 0.05$) according to Tukey's test.

geochemical parameters only influenced by the soil and soil plus vermicompost mixtures; pore waters sampled here do not represent the influence of biochar. The highest Cu concentrations ($\sim 750 \text{ mg L}^{-1}$) were measured from soil alone (M) within the first 48 h of leaching, decreasing to $\sim 50\text{--}100 \text{ mg L}^{-1}$ after 72 h (Fig. 4A). In the presence of MV₁, Cu concentrations were reduced to $< 5 \text{ mg L}^{-1}$ across all sampling times, lowered further ($< 0.1 \text{ mg L}^{-1}$) by MV₂ (Fig. 4A).

Arsenic, in contrast to Cu, was weakly extractable/strongly bound to soil constituents (DWEM As $< 0.1 \text{ mg kg}^{-1}$; Table 1) with the highest pore water concentrations measurable in the presence of MV₁ ($\sim 200\text{--}750 \text{ } \mu\text{g L}^{-1}$; Fig. 4B), followed by MV₂. The lowest values were measured for soil alone (M) after 72 h leaching ($< 5 \text{ } \mu\text{g L}^{-1}$; Fig. 4B).

Other measured parameters (DOC and PO_4^{3-}) displayed their highest concentrations where MV₁ was applied, with MV₂ having little effect compared to the soil alone (M; Fig. 4 C & D). Both vermicomposts profoundly increased pore water pH throughout 96 h of the leaching test by ~ 5 units (Fig. 4E).

Pore water samples measured post-biochar (i.e. from the lower portion of the columns, below the biochar containing capsules) indicate the influence of biochar upon the geochemical parameters measured. The trends described above were largely mirrored in the case of the MV₁ and MV₂ for As, DOC, PO_4^{3-} and pH, with biochar seeming to have sporadic additional influence beyond what was measured pre-biochar (Fig. 5 B, C, D & E). The clear exception was Cu, where the addition of biochar reduced concentrations to their lowest measured values of any of the sampled pore waters ($\sim 0.02 \text{ mg L}^{-1}$) in the case of MBV₂ (Fig. 5A).

3.4. Characteristics of recovered biochar

After completing the column leaching, an EDX analysis was performed on the biochar retrieved from the capsules. The retention of Cu was quantifiable in the case of MB, MBV₁ and MBV₂ treatments (Fig. 6 B, C & D, respectively). The highest value (6.5% wt.) was measured from

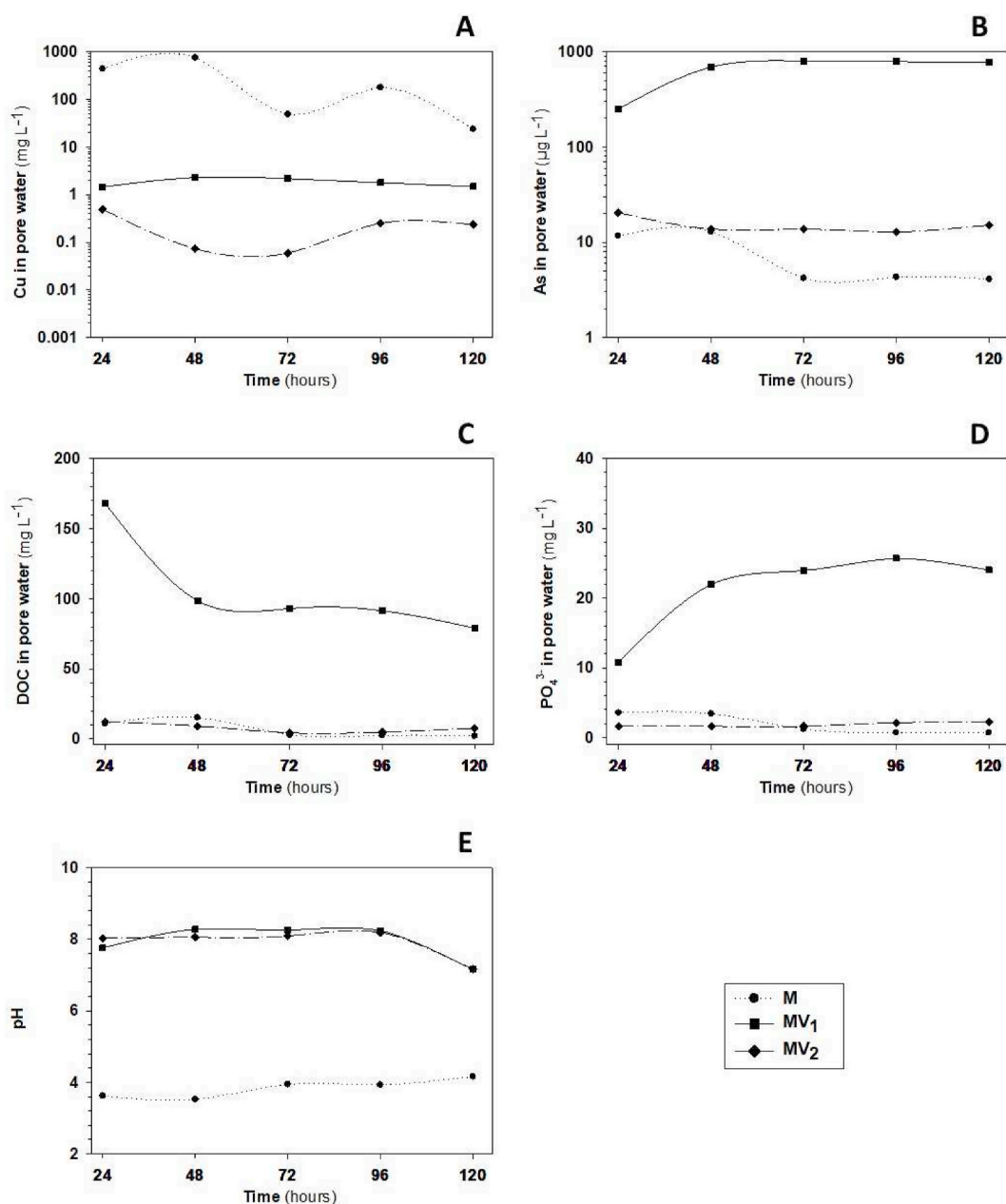


Fig. 4. (A) Copper, (B) Arsenic, (C) DOC and (D) PO_4^{3-} content and (E) pH value in pre-biochar pore water from each treatment.

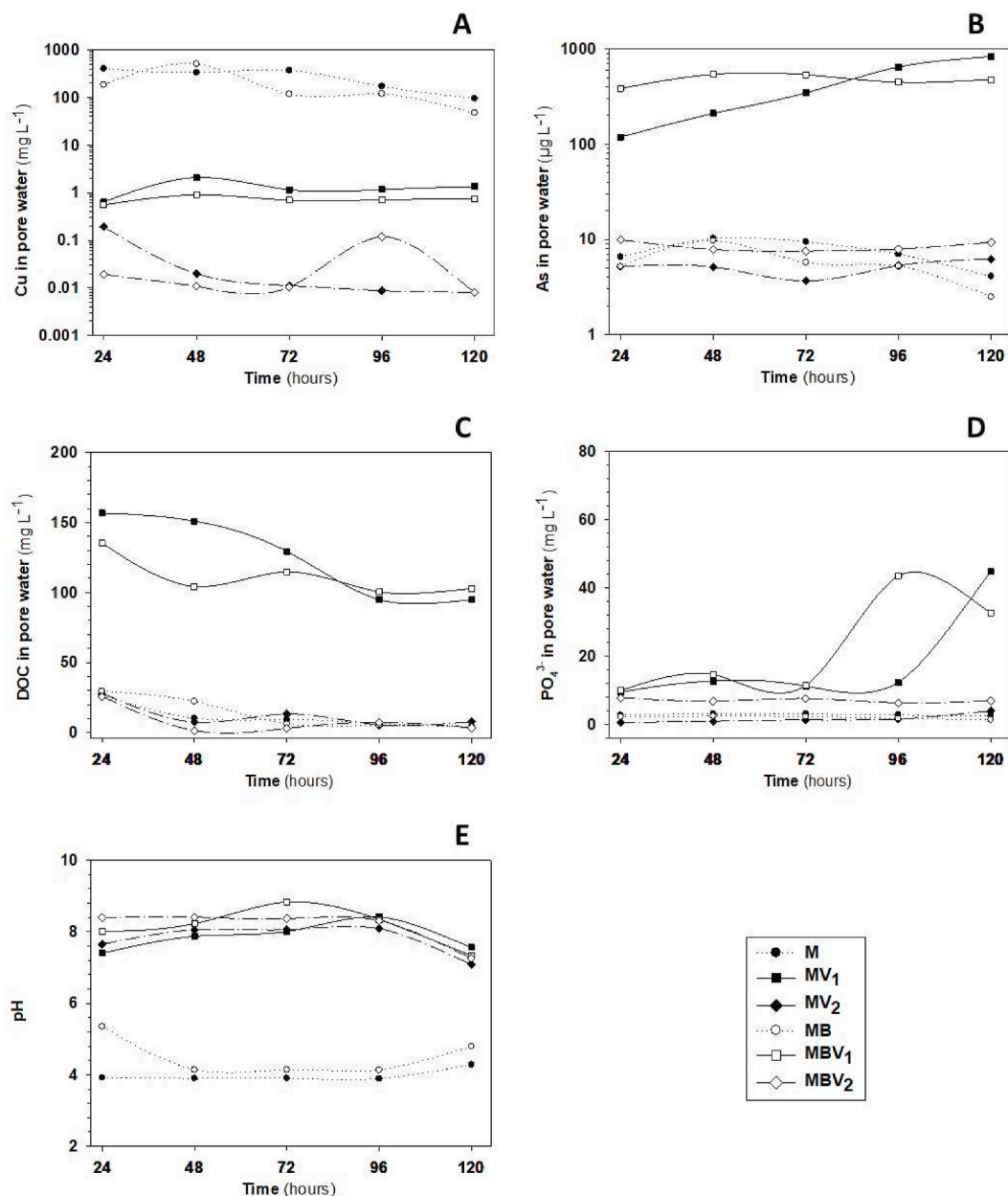


Fig. 5. (A) Copper, (B) Arsenic, (C) DOC and (D) PO_4^{3-} content and (E) pH value in post-biochar pore water from each treatment.

the column where vermicompost addition was not included (MB). In the case of MBV₁, considerable Fe (17.5% wt.) was also measured on the surface of biochar, as well as other elements at ~14% wt. (Fig. 6C).

4. Discussion

4.1. Combined impacts of vermicompost and biochar amendments on copper

The application of organic amendments to mine soils with low pH and high metal(loid) concentrations is a common practice to promote vegetation growth, and generally improve the physico-chemical parameters of degraded soils (Fangueiro et al., 2018). In this context our study clearly demonstrated that the acid pH of the tested mine soil could be neutralised by the addition of vermicomposts simply made from food and animal wastes (Fig. 3). Our study also proved that biochar addition was directly influential in the retention of Cu (Fig. 6), and that this had resulted in a reduction in Cu concentration in pore waters in the column

experiment (Fig. 5). The efficiency of biochar's sorption depends mainly on the chemical reactivity and functionality of the biochar surface and its porosity (Mohanty and Kumar, 2021). According to Xu et al. (2021), the metal stabilization efficiency of biochar is strongly influenced by its properties and reactivity, such as an alkaline pH, its feedstock type, pyrolysis conditions, composition, microporous structure, surface area, and surface functional groups. Therefore, when mixed with soil and vermicompost there would have been competing geochemical factors at play meaning that biochar did not result in any further meaningful reduction in Cu concentrations in the pore waters sampled from the pot test, when it was mixed together with the vermicompost (Fig. 3). This is likely to have been at least partially influential in the lack of ryegrass growth in soil amended only with biochar because the presence of vermicompost was required to sufficiently raise pH whilst also introducing nutrients, such as phosphate (Fig. 2) to stimulate revegetation. According to Fei et al. (2021), there is a direct relationship between organic matter and phosphorus availability. That was the case in our study, with both vermicomposts containing greater concentrations of

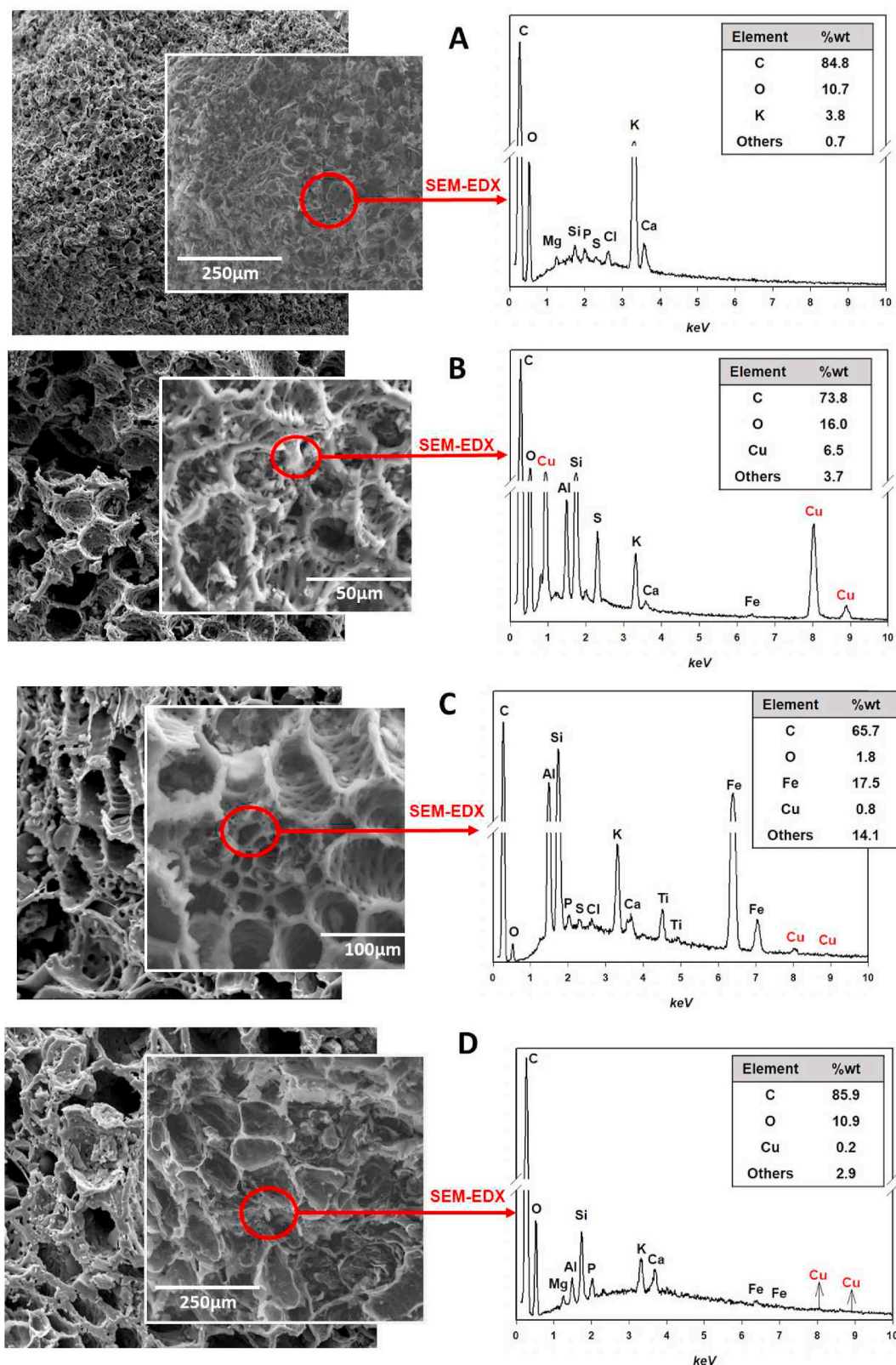


Fig. 6. SEM-EDX images. A: Original biochar; B, C and D: Biochar from treatments MB, MBV₁ and MBV₂ of the columns leaching, respectively.

Ca²⁺, Mg²⁺ and Na⁺ than biochar and soil (Table 1). Other authors have noted that carbon in more labile forms (Fulvic acid) may also stimulate or 'prime' microbial action in soils, and result in nutrient assimilation (Jing et al., 2017; Wang et al., 2016). According to Sarma et al. (2018), the vermicompost application increase labile soil organic carbon

fractions, C mineralization and soil respiration, however the biochar application stimulate stable soil organic carbon (fulvic acids, humic acids and recalcitrant carbon), increasing the degree of humification. Additionally, Canellas et al. (2015) have mentioned that humic substances are considered recalcitrant to microbial activity and introduce

beneficial microorganisms for the soil and the plants. [Shahid et al. \(2012\)](#) showed that fulvic acids were capable of forming complexes with metallic pollutants in solution.

In our study the largest generation of DOC was noted in the presence of vermicompost V₁ (made from raw food wastes; [Figs. 3C, 4C and 5C](#)) compared to V₂, supporting the notion that this amendment may have largely contributed to an increase in available nutrients in soil; and may have also contributed to formation transportable complexes (Cu-DOC), which could explain the high concentration of Cu in pore water due to the application of V₁.

[Rehman et al. \(2021\)](#), revealed that the efficiency of biochar to adsorb metals was greater at high pH compared to low pH, presumably because of the hydrolyzation of functional groups on the biochar surface, which helps to induce negative charge and increase the cation exchange capacity of carbon surface ([Rehman et al., 2021; Huang et al., 2007](#)). That means that the sharp pH increase resulting from vermicompost addition to the mine soil tested in our study (4 units; [Fig. 4E](#)) would have provided conditions further conducive to the sorption of Cu to biochar surfaces ([Egene et al., 2018; Zhang et al., 2013](#)).

In addition, Cu has high affinity to bind on the negatively charged surfaces, which are extant in vermicomposts, but more numerous in biochars ([Forján et al., 2016; Covelo et al., 2007](#)). In addition, the vermicompost may provide humic (more stable organic matter) and fulvic acids (more mobile organic matter) which also stimulate Cu immobilisation ([Halim et al., 2003](#)). Other authors ([Qiu et al., 2022; Li et al., 2022](#)) have noted that the superior surface area of biochars, compared to amorphous organic materials, increase the reactive surface for removal of metals in solution. This is particularly the case in some drought prone soils, where biochar addition can also more favourably influence soil water retention, than other organic amendments ([Mitchell et al., 2022](#)). Finally, the high PO₄³⁻ concentration of vermicompost and increased pH stimulate Cu precipitation ([Forján et al., 2018; Jadia and Fulekar, 2008; Kumpiene et al., 2008](#)) so that the vermicompost-biochar combination here appears to have been highly efficacious for Cu immobilisation.

4.2. Secondary consequences of amendments on arsenic

The contrasting behaviour of As and Cu in response to the amendment application is clear from our study, where As was generally mobilised in the presence of vermicompost and where there was no evidence that biochar provided any sorption capacity for this metal (loid); without the addition of further geochemical stimulation, As was weakly extractable in this soil (DWEM; [Table 1](#)). The behaviour of As was probably primarily the result of substantial increases in pH induced by the amendment addition, which caused a speciation change from AsO₄³⁻ to the more mobile As(V) ([Baragaño et al., 2020a](#)).

Many authors (e.g. [Mohanty and Kumar, 2021; Qambrani et al., 2017; Ahmad et al., 2014](#)) have reported that there is electrostatic attraction between positively charged molecules and biochar surfaces, which are generally negatively charged, caused by the dissociation of oxygenated hydrocarbons functional groups. For this reason, several reviews on the topic of biochar application to metal(loid) contaminated soils have highlighted the limitation of biochar in this regard, and its potential role in the mobilisation of As into solution ([Sizmur et al., 2016; Beesley et al., 2013, 2015; Hartley et al., 2009](#)). It has been reported that some soil organic matter-metal complexes can effectively bind As anions, related to the formation of a ternary complex between organic ligands and As oxyanions (As V) through iron bridging, which is of fundamental importance for As binding to OM ([Mikutta and Kretzschmar, 2011](#)).

In our study, a clear role of both raised PO₄³⁻ and pH after vermicompost addition could have contributed to this effect as especially notable in the column experiment results ([Fig. 4 D & E](#)), whereafter biochar provided no mitigation to the considerable mobilisation of As by vermicompost ([Fig. 5 C, D & E](#)). Several studies have noted that amendments containing organic matter result in the release of As into

soil pore water and accumulation of arsenic species within vegetation (e.g. rice grain; [Norton et al., 2013](#)). Phosphate and silicate compete with As for the same exchange sites in soil thus enhancing As mobility in soil via ligand exchange mechanisms ([Majumder et al., 2021](#)). According to [Ji et al. \(2019\)](#), As can be released into the soil solution after enhanced P application, whilst [Bauer and Blodau \(2006\)](#) suggested that DOM (dissolved organic matter) can contribute to the adjustment of As speciation within relatively short periods of time. Some or all of these factors could have been at play in our soil-amendment combination.

4.3. Implications to the remediation of mine soils

The application of organic amendments is an established method to significantly improve the physical-chemical and biological properties of soil whilst reducing metal(loid)s bioavailability and toxicity ([Xu et al., 2021; Alam et al., 2020](#)). This practice has been widely adopted in the remediation of mine soils ([Fangueiro et al., 2018](#)). In the present studied soil, the addition of vermicompost, or indeed some alternative amendment with a pool of labile nutrient and a liming effect, was clearly necessary to support vegetation growth. In this regard, biochar is not effective. The value of biochar here was clearly to act as a sorbent for Cu. Contrastingly As was mobilised, so utilising a higher vermicompost-soil ratio would presumably have further reduced Cu mobility, such as reported [Abbaspour and Golchin \(2011\)](#), but further increased As mobility.

A note of caveat must be mentioned here, that As concentrations in solution (pore water) were generally several orders of magnitude below those of Cu ([Figs. 3–5](#)), whilst As concentrations in ryegrass were ≤ 0.5 mg kg⁻¹, in contrast to those of Cu which were ≥ 20 mg kg⁻¹ ([Fig. 2](#)). Therefore, in this specific soil As was weakly extractable/strongly bound, thus the mobilisation of As was probably of secondary importance to the sorption of Cu; in other soils, more heavily As contaminated, consideration would need to be given to the addition of vermicompost. In this context, biochar is perhaps best applied retrospectively to leachates from soils after they have been amended with vermicompost. Such strategies have been proven highly effective at sorption of a variety of metals from waters. Modification and synthesis of biochars with Fe and Mn oxides (i.e. Nano zero-valent iron (nZVI), AMOchar, LDH (Layered Double-Hydroxide Modification)/biochar composites) may offer a method by which biochars can be made effective at simultaneously acting as an adsorbent for Cu and As in solution ([Trakal et al., 2019](#)). Further research has been done examining the potential role of including nano zero-valent iron (nZVI) in biochar manufacture, to even further enhance As sorption abilities ([Castaño et al., 2021; Baragaño et al., 2020b](#)), but such interventions may result in materials which are prohibitively costly to apply in bulk to mine and other degraded soils.

5. Conclusions

The application of organic amendments to degraded and metal(loid) contaminated mine soils is a proven method by which to favourably enhance their geochemical properties and restore vegetation growth. In this study, pot testing and column leaching methods effectively highlighted the contrasting impacts of vermicompost on As and Cu mobilisation in an amended mine soil with a low pH. Geochemical traits of vermicomposts, such as high DOC, PO₄³⁻ and alkaline pH, promoted vegetation (ryegrass) growth, where it was otherwise absent. Vermicompost substantially reduced Cu mobility and a further application of biochar was proven to sorb Cu in the leaching columns, a fact not easily elucidated from the conventional pot soil-amendment mixing experiment alone. Arsenic, whilst inherently weakly extractable in this soil, was mobilised by vermicompost whereafter biochar had no mitigation impact on this metal(loid).

In summary, the application of vermicompost can be recommended to promote revegetation and reduce Cu leaching in this mine soil, and field trials should be initiated to further validate this and gain finer-

grained detail on the longevity of this effect. The value of further biochar addition in this context is probably best served in its application to leachates retrospectively, rather than directly amended into this soil. Future research should test whether this approach is applicable to a wider range of mine and other degraded soils.

Credit author statement

Beatriz Cerqueira: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft preparation. **Emma F. Covelo:** Supervision, Conceptualization, Funding acquisition. **Sandra Rúa-Díaz:** Visualization. **Purificación Marcet:** Resources, Funding acquisition. **Rubén Forján:** Visualization, Investigation. **José Luis R. Gallego:** Visualization, Resources. **Lukas Trakal:** Conceptualization, Writing – Reviewing and Editing. **Luke Beesley:** Supervision, Conceptualization, Writing – Reviewing and Editing.

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.

Acknowledgements

D. Cerqueira would like to thank the Xunta de Galicia and the University of Vigo for the Postdoctoral grant (Ref. ED481B-2018/075). This work was partially funded by the project NANOCAREM (AEI/Spain, FEDER/EU, MCI-20-PID2019-106939 GB-I00) and by the Scottish Government Strategic Research Program (2022–2027) under project JHI-D3-1, Healthy Soils for a Green Recovery. We would like to thank the staff of department of instrumental analysis of the CACTI and more especially to Rosa Ma Lomba and Jorge Millos for support in samples analysis.

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