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Heavy metal retention in copper mine soil treated with mussel shells: Batch and column experiments

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HIGHLIGHTS

- Mussel shell amendment on mine soil raises pH proportionally to the shell dose used.
- Shell amendment clearly increased Cu, Cd, Ni and Zn retention in soil/shell mixtures.
- Retention decreases when increasing amounts of metal are added to un-amended soil.
- Shell amendment would favour remediation and restoration of contaminated acid soils.

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ABSTRACT

Batch and column experiments are used to study the effects of ground mussel shell amendment on the retention of heavy metals in acidic mine soil. The soil pH increases proportionally with the mussel shell concentration employed. Mussel shell amendment increases Cu, Cd, Ni and Zn retention in mine soil when compared with unamended soil. In fact, Cu retention was 6480 μmol kg^{-1} (43% of the total added) when the maximum metal concentration (1570 μM) was added to the unamended soil, whereas retention reached 15,039 μmol kg^{-1} (99.9% of the total Cu added) when soil was amended with 24 g kg^{-1} mussel shell; in the case of Cd, adsorption increases from 3257 μmol kg^{-1} (15% of the total added) for the unamended soil, to 13,200 μmol kg^{-1} (87% of the total added) for the shell-amended soil; Ni retention increased from 3767 μmol kg^{-1} (25% of the total added) corresponding to unamended soil, to 11,854 μmol kg^{-1} (77% of the total added) for the shell-amended soil; and finally, Zn retention increased from 4684 μmol kg^{-1} (31% of the total added), for unamended soil, to 14,952 μmol kg^{-1} (98% of the total added) for shell-amended soil. The results of the constant flow transport experiments show that the addition of the 24 g kg^{-1} mussel shells can retain Cu, Cd, Ni and Zn within the first few centimetres of the column length, indicating the usefulness of ground mussel shells to drastically decrease the mobility and availability of these pollutants and to facilitate soil remediation.

1. Introduction

Mine dumps and their spoils pose environmental risks worldwide. A mine dump of an old, inactive Cu mine located in Touro (A Coruña province, Spain) is composed of spoils with high concentrations of metal sulphides, such as pyrite, pyrrhotite and chalcopyrite, which cause acidification of the surrounding environment when oxidised [1–3]. The authors indicate that re-vegetation of mine dumps is the most effective method for restoring these areas; however, there are several factors that strongly limit plant establishment, including extreme pH conditions and high concentrations of heavy metals. Further, acid mine drainage is another matter of concern posing risks of environmental pollution, mainly related to exportation of substances such as arsenic [4]. In the case of the Touro, the use of dump spoils in road-making has been shown to present risks to both soil and water because the Cu leaches into the environment [5]. Alonso Vega et al. [6] studied Touro mine soil samples consisting of Cd, Cr, Cu, Ni, Pb, and Zn and found that the presence of organic matter, Fe and Mn oxides and cation exchange capacity influences heavy metal sorption and retention. They also found that most sorption and desorption experimental curves were irregular as a result of the competition for the binding sites; heavy metals were weakly binding to the soil, thus desorbing in large quantities and resulting in severe pollution risks.

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Untreated mussel shells are a waste material and are generated in large quantities in Galicia, which is ranked second in the world for mussel (*Mytilus galloprovincialis*) production [7]. Most mussel shell wastes are treated in factories to produce valuable high-end materials using processes that include washing, grinding, calcination and sieving or only washing, grinding and sieving, which results in lower energy consumption. Calcined mussel shells have proved to be efficient in phosphate removal from wastewaters, primarily because of their higher calcite content [8], and in Hg (II) removal due to their Fe and Al oxide content [7]. Ground, uncalcined mussel shell is less efficient in phosphate removal than calcined shell but could be useful in the retention of other divalent cation contaminants, such as Cd (II), Pb (II) and Zn (II) [9,10]. Ground, uncalcined shell has also been shown to be agronomically useful [11,12].

Ground (not calcined) mussel shell is produced in Galicia (Spain) at industrial scale since 1989, mainly due to the activities of Abonomar S.L. (Galicia, Spain) [13]. Calcined shell is also generated in Galicia at industrial scale since 2004, in this case mainly due to the activities of Calizamar S.L. [14]. Both enterprises have the potential of treating more than 80,000 tons raw mussel shell by year.

Mitigation treatments, such as mussel shell addition, have been used in some areas of the mine dump at the Touro opencast mine since 2000 [3]. In this way, Vega et al. [15] investigated the effects of an amendment (performed 2 years prior to when the samples were taken) consisting of sewage sludge, barley straw and mussel shells on the sorption and retention of Cu, Pb and Cd in soil developed over steep spoil heaps at the Touro opencast mine. These authors found that the amendment's increased capacity for the sorption and retention of Pb, Cu and Cd in the soil was associated with an increase in pH; most heavy metal sorptions occur through the displacement of the predominant cation through the exchange complex (Al^{3+} in unamended soils, and Ca^{2+} in amended soils). The greater total sorption from multi-metal solutions also involves the displacement of other exchangeable cations.

However, until now, and as long as we know, there were no published studies using simultaneously batch type and laboratory column experiments to investigate heavy metal retention and mobility in Cu mine soils using various concentrations of ground mussel shell as an amendment.

The main objective of this study is to evaluate the effects of three different concentrations of mussel shell amendment on Cu mine soil when aiming to increase the retention of Cu, Ni, Zn and Cd in the soil and thus decrease their mobility and availability for plant uptake, reducing the overall risks of soil and water pollution.

2. Materials and methods

2.1. Mine soil, mussel shells and soil/shell mixtures

Mine soil samples were taken from the Touro Cu mine dump emplacement (Touro, A Coruña province, Spain), where Cu mining ended in the early 1980s because of the decline in the ore's quality. The geological substrate is amphibolite, consisting of significant quantities of metal sulphides such as pyrite, pyrrhotite, and chalcopyrite. Previously shell-treated areas of the mine dump [3] were excluded from the sampling in this study. To ensure consistent sampling across the unamended mine dump area, 10 soil sub-samples (0–20 cm depth) were collected in a zig-zag pattern with a soil auger. The composite soil sample was air-dried and sieved through a 2 mm mesh.

Ground, non-calcined mussel shell (MS) was obtained from the largest facility of its kind in Galicia (Abonomar S.L., Illa de Arousa, Pontevedra Province, Spain), where waste shell is washed, grounded and sieved. The sampled ground mussel shell was <1 mm in size.

Table 1
General characteristics of the ground mussel shell and the mine soil.

	Mussel shell	Mine soil
pH_{water}	9.4	3.8
pH_{KCl}	9.0	3.0
C ($g\,kg^{-1}$)	114	2.6
N ($g\,kg^{-1}$)	2.1	0.4
Ca_e ($cmol_{(+)}\,kg^{-1}$)	24.75	0.36
Mg_e ($cmol_{(+)}\,kg^{-1}$)	0.72	0.29
Na_e ($cmol_{(+)}\,kg^{-1}$)	4.37	0.14
K_e ($cmol_{(+)}\,kg^{-1}$)	0.38	0.24
Al_e ($cmol_{(+)}\,kg^{-1}$)	0.03	2.87
CIC_e ($cmol_{(+)}\,kg^{-1}$)	30.25	3.89
Ca_T ($mg\,kg^{-1}$)	280,168	603
Mg_T ($mg\,kg^{-1}$)	981	8383
Na_T ($mg\,kg^{-1}$)	5173	411
K_T ($mg\,kg^{-1}$)	202	3186
Fe_T ($mg\,kg^{-1}$)	1855	135,157
Mn_T ($mg\,kg^{-1}$)	49	295
Cr_T ($mg\,kg^{-1}$)	4	99
As_T ($mg\,kg^{-1}$)	1.1	7
Cu_T ($mg\,kg^{-1}$)	8	773
Cd_T ($mg\,kg^{-1}$)	0.07	0.08
Ni_T ($mg\,kg^{-1}$)	8	5
Zn_T ($mg\,kg^{-1}$)	28	57.8
P_{olsen} ($mg\,kg^{-1}$)	54.2	8.8
Al_{ox} ($mg\,kg^{-1}$)	178	563
Fe_{ox} ($mg\,kg^{-1}$)	171	41,860

X_e: exchangeable concentration; X_T: total concentration; Al_{ox} and Fe_{ox}: Al and Fe extracted with ammonium oxalate.

To conduct the retention experiments, soil/shell mixtures were prepared at concentrations of 6, 12 and 24 g of MS per kg of soil. The mixtures were agitated for 72 h and homogenised with a riffle splitter.

The mussel shell and mine soil components were characterised using the following parameters (Table 1): the pH in water and in KCl were measured with a pH meter [16]; C and N were determined using the elemental Tru Spec CHNS auto-analyser; and the effective cationic exchange capacity (eCEC) was estimated as the sum of the base cations Na, K, Ca and Mg displaced by 1 M NH_4Cl [17] and Al displaced by 1 M KCl [18]. The concentrations of divalent base cations and Al were determined by atomic absorption spectroscopy, and the concentrations of Na and K were determined by atomic emission spectroscopy. The total concentrations of Ca, Mg, Na, K, Fe, Mn, Cr, As, Cu, Cd, Ni and Zn were determined in soil and mussel shell samples using microwave-assisted digestion (ETHOS 900 Microwave Labstation). The procedure consist in the addition of 3 mL of HNO_3 and 9 mL of HCl to 0.2 g of finely milled mine soil or mussel shell. The mixtures were digested in a microwave at 190 °C for 15 min (800 W) and the extracts were determined by ICP-MS. For quality assurance and control (QA/QC) purposes, samples of a certified reference material (ERM-CC141 loam soil) were digested and the recoveries of the Cu, Cd, Ni and Zn resulted in a deviation from certified values below 5%.

The available P was quantified using the Olsen method [19], whereas amorphous Fe and Al were quantified using ammonic oxalate extracts [20].

Furthermore, the pH of the soil/shell mixtures was measured in water and in KCl, and the crystalline composition of the shells was determined by X-ray diffraction analysis (Philips PW1710 diffractometer), following the crystalline powder technique procedure performed at the University of Santiago de Compostela (Spain).

All measurements were conducted in triplicate, and the coefficients of variation were lower than 5%.