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Using marble sludge and phytoextraction to remediate metal(loid) polluted soils

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ABSTRACT

Marble sludge, an immobilizing amendment, and *Brasica juncea* L., a plant used in phytoextraction processes, were used in combination with two different soils, an acidic metal-contaminated and a basic arsenic-contaminated. The aim of the study was to assess the effectiveness of this combination in reducing contamination spreading to surrounding areas and groundwater, while phytoextraction is taking place. In the polluted acidic soil the marble sludge significantly reduced the spread of Zn and Pb but did not prevent its uptake by the plant, especially for Pb which reached a concentration in the shoots close to those found in hyperaccumulator plants. The addition of marble sludge to polluted basic soils mainly contributed to immobilize As, which remained linked to the particles of $CaCO_3$ in non-bioavailable form, thereby minimizing its spread and uptake by plants. In both studied soils, *B. juncea* plants seem more suitable for phytostabilization purposes than for phytoextraction ones. However, the use of this combination, together with amendments promoting plant growth and improving soil structure, could provide a feasible way for long-term remediation of contaminated acid soils which currently represent a risk of contamination to surrounding areas.

1. Introduction

Immobilization techniques (using amendments) and phytoextraction (using plants) are two common approaches in soil remediation. Choosing one or another technique would depend on the objective pursued and this selection would be determined by multiple factors (e.g. initial contamination level, type of contamination, and subsequent use of the remediated soil). Although both techniques are technically feasible, the objectives of each one are different. Immobilization techniques pursue the pollutant fixation in soils in non-bioavailable form, in order to reduce its potential toxicity (Porter et al., 2004). On the contrary, phytoextraction techniques aim to remove pollutants from soils through vegetation and clean the ecosystem (Chiu et al., 2005; Barceló and Poschenrieder, 2003; Kidd et al., 2009). The use of inorganic amendments (lime, phosphates, iron oxide) is widespread in the pollutant immobilization technique (Chrysochoou et al., 2007; Castaldi et al., 2005; González et al., 2012), while chelating agents are widely used in phytoextraction in order to obtain high extraction rates (Ng et al., 2015). Organic amendments can also contribute to these two effects, on the one hand, immobilizing part on the pollutants (Alvarenga et al., 2009) and, on the other hand, facilitating pollutant mobility through low molecular weight compounds which act as chelating agents (Komárek et al., 2010).

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According to the above, an amendment that immobilizes contaminants while not limiting the uptake by plants would be a step toward the advancement of the remediation of polluted soils. This amendment would immobilize the contaminants in the soil avoiding pollution of the groundwater and the spread to surrounding areas while allowing their phytoextraction. In this way, the uptake of pollutant previously stabilized by amendments has been reported (González et al., 2013), concluding that the marble sludge was very effective to reduce the mobility of Cu, Zn, Cd, As and Pb but the plants roots were able to uptake these pollutants.

The aim of this study was to assess the effectiveness of the combination of marble sludge and Indian mustard (*Brassica juncea* L.) in remediating contaminated soil, where phytoextraction could be possible without problems associated with pollutant leaching, evaluating both phytoextraction and lixiviation rates during the process.

2. Material and methods

2.1. Contaminated soils and amendments

Two contaminated soils were selected for this study, an acidic one (A) and a basic one (B), located in the mining districts of *El Arteal* and *Rodalquilar*, respectively, both situated in Almeria (SE Spain). Marble sludge (M) from the cutting and polishing of marble was used as amendment. Soils and amendment were air dried at 25 °C, sieved through a 2-mm pore size mesh and physico-chemically characterized. The pH was measured in a 1:2.5 soil:water suspension. The saturation

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extracts of soils and amendment were prepared (USDA Soil Conservation Service, 1972), the solution was vacuum pumped and the electrical conductivity (EC) was measured. Total carbon was analyzed by dry combustion in a LECO SC-144DR analyzer and calcium carbonate equivalent ($CaCO_3$) content was estimated manometrically (Williams, 1998). The organic carbon (OC) content was determined by the difference between total carbon and inorganic carbon from $CaCO_3$. The particle size distribution was determined using the pipette method (Loveland and Whalley, 1991). Soils and amendment were finally ground (<0.05 mm) and digested in a 4:1 mixture of HNO_3 (65%) and HF (37%) and total concentration of Zn, Pb and As was measured by ICP-MS using a Hewlett Packard 4500 STA spectrometer. Standard reference material SRM2711 (six replicates) was used to confirm the accuracy of the method. Average recoveries ranged between 94 and 101% of the certified reference values. For ICP-MS calibration, all standards were prepared from ICP single element standard solutions (Merck, Darmstadt, Germany), containing all the analytes of interest at five different concentration levels. Procedural blanks for estimating the detection limits ($3 * \sigma$; $n = 6$) were <2.70 ppb for Zn, <0.22 ppb for Pb and >0.21 ppb for As. The analytical precision was better than ±5% in all cases.

The mean degree of contamination (mC) of each soil was estimated from this equation proposed by Abrahim and Parker (2008).

$$mC = (Cf_{Zn} + Cf_{Pb} + Cf_{As})/3$$

where Cf is the contamination factor of each element estimated from the ratio of the total concentration and the baseline concentrations proposed by Sierra et al. (2007) for Almería province soils (145.1 mg Zn/kg, 54.6 mg As/kg, 120.7 mg Pb/kg dry weight).

2.2. Greenhouse experiment

The acidic (A) and basic (B) soils were amended with marble sludge (AM and BM, respectively) at 8% (w/w) and thoroughly mixed to ensure homogeneity. In previous studies (González et al., 2013), the addition of 8% M, was found to be the most effective treatment in immobilizing trace elements. *B. juncea* was used as a plant model because of its phytoextraction potential. Contaminated and amended contaminated soils were tested in triplicate, giving a total of 12 treatments (3A, 3AM, 3B, 3BM). Before the start of the experiment, all treatments were moistened to field capacity with distilled water and allowed to dry in three cycles of 15 days to react and restore the soil microbiological communities (Martinez and Motto, 2000). Plastic pots with drainage systems for collecting lixiviates were filled with 700 g of each treatment. At the beginning of the experiment (time = 0), 300 cm^3 of distilled water was added to each pot, collecting lixiviates (L1) and pore water (PW1) using Rhizon soil-moisture samples (Rhizon Research, Wageningen, The Netherlands). Next, three seeds of *B. juncea* were sown in the pots. During the experiment, 25 cm^3 of distilled water twice per week at 50 cm^3/h was added, and 25 cm^3 of nutrient solution prepared from analytical grade reagents [4 mmol/L $Ca(NO_3)_2$, 2 mmol/L KNO_3, 2.5 mmol/L K_2HPO_4, and 2 mmol/L $MgSO_4$] was supplied once a week. The experiment was continued until establishment of the plants (time = 11 weeks from sowing). At the end of the experiment and before plants were harvested, 300 cm^3 of distilled water was added to each pot and lixiviates (L2) and pore water (PW2) were collected again. EC and pH were immediately measured in L1, L2, PW1 and PW2. After, solutions were filtered through cellulose filters (0.45 µm pore size), acidified with HNO_3 and stored at <4 °C. The As, Pb and Zn concentrations in the solutions were measured by ICP-MS.

2.3. Plant analysis

After 80 days, the *B. juncea* plants were carefully removed. The roots and shoots were divided and carefully washed with deionized water. Then oven dried at 65 °C for 72 h and weighed, obtaining the dry biomass of the roots (DBR) and shoots (DBS). The dry biomass of the plant (DBP) was estimated by the sum of the DBR and DBS. The organic material from the roots and shoots was microwave-digested in strong acid (HNO_3) and H_2O_2 (Kingston and Jassie, 1986; Sah and Miller, 1992). The As, Pb and Zn concentration in the digested organic material was measured by ICP-MS. The accuracy of the method was confirmed by analysis (six replicates) of Standard Reference Material 1572 (citrus leaves). For the three analyzed elements, average recoveries ranged between 95% and 107% of the certified reference values.

The bioconcentration factor (BF) of each element was estimated by the ratio between the total concentration in the plant (root and shoot) and in the soil in mg/kg dry weight. The translocation factor (TF) was estimated by the ratio of the concentration in shoot and root.

2.4. Statistical methods

The data distribution in the different treatments was established by calculating the mean values and standard deviation. The differences between the individual means were compared using Tukey's test ($p < 0.05$). The PASW Statistic 18 software package was used for all statistical analyses.

3. Results and discussion

3.1. Soils and amendment

The control soil was basic (Table 1), with low electrical conductivity value (EC = 0.84 dS/m), soil is considered saline when EC > 4 dS/m), loam (textural class) and concentration of trace element lower than the baselines for Almeria province proposed by Sierra et al. (2007). The soil from *El Arteal* mining district (A) was acidic, saline (EC values > 20 dS/m), loamy sand (textural class), with low organic carbon content and high trace element concentration (Table 1). The Zn, As and Pb concentrations were between 8 and 45 times higher than baseline concentrations, with mC value being extremely high (>22). The soil from *Rodalquilar* mining district (B) was basic, no saline (EC < 4 dS/m), sandy loam, with low organic carbon content and lower concentration of pollutants (mC ~ 9) but higher concentration of As than in acidic soil. The concentration of As, Zn and Pb was between 1.7 and 14 times higher than baseline concentrations. Marble sludge (M) was basic, no saline, silty clay loam, with very low trace element concentrations and very high $CaCO_3$ content.

Table 1
Mean values ± standard deviation ($n = 3$) of the main properties of contaminated acidic soil (A), contaminated basic soil (B), control soil (uncontaminated soil) and amendment (marble sludge-M).

	Arteal acidic soil (A)	Rodalquilar basic soil (B)	Control soil	Marble sludge
$CaCO_3$ (%)	nd	nd	8.73 ± 1	98.2 ± 0.5
pH	3.9 ± 0.1	8.4 ± 0.2	8.72 ± 0.02	8.5 ± 0.1
EC (dS/m)	22.8 ± 1.6	1.1 ± 0.4	0.84 ± 0.1	2.1 ± 0.1
OC (%)	0.1 ± 0.05	0.08 ± 0.05	2.81 ± 0.002	0.07 ± 0.08
Coarse sand (%)	19 ± 1	62 ± 3	11 ± 2	1 ± 1
Fine sand (%)	51 ± 2	24 ± 1	23 ± 2	2 ± 1
Silt (%)	27 ± 2	9 ± 1	43 ± 3	64 ± 8
Clay (%)	3 ± 1	5 ± 1	23 ± 2	33 ± 7
Zn (mg/kg)	2580 ± 77	243 ± 8	214 ± 14	7 ± 0.1
As (mg/kg)	377 ± 38	594 ± 21	8 ± 0.6	3.8 ± 0.1
Pb (mg/kg)	5109 ± 218	1737 ± 106	126 ± 7	1.2 ± 0.5
mC	22.3	8.9	0.95	0.04

nd = not detected, EC = electrical conductivity, OC = organic carbon, coarse sand (2–0.25 mm), fine sand (0.25–0.05 mm), silt (0.05–0.002 mm), clay (<0.002 mm), mC = mean degree of contamination.