



Effectiveness of amendments on the spread and phytotoxicity of contaminants in metal–arsenic polluted soil

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ABSTRACT

A metal–arsenic polluted soil from sulphide-mine waste was treated, in all possible combinations, with two different amounts of marble sludge (98% CaCO₃), compost (41% organic carbon), and Byferrox (70% Fe). Lixivate and pore water from each treated and untreated soil were analysed, and lettuce-seed bioassays were performed. None of the treatments decreased the electrical conductivity of lixiviates or the concentrations of all pollutants found in both solutions. Marble sludge and compost increased the pH values and decreased the zinc, cadmium, copper, and lead concentrations in both solutions while increasing the arsenic concentrations in the lixiviates. Byferrox did not alter the physicochemical parameters or the concentrations of zinc, cadmium, copper, or lead in either solution but significantly decreased the arsenic concentrations in pore water. Compared with the Byferrox treatment, the mixture of marble sludge and Byferrox decreased redox potential values, increasing the arsenic concentrations in both solutions and the electrical conductivity of the pore water. All lixiviates were highly phytotoxic and seeds did not germinate. Pore-water phytotoxicity was related to electrical conductivity values and heavy-metal concentrations. The combination of marble sludge and compost was most effective at diminishing toxicity in lettuce. The soils treated with Byferrox, alone or mixed with marble sludge or compost, were the most phytotoxic.

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1. Introduction

Mining activities are associated with pollution problems in soils and aquifers [1,2]. The gradual abandonment of mines and the lack of security measures have increased the risk of pollution spreading to areas not directly affected by mining activities. Different techniques can be used to remediate polluted soil [3]. Immobilisation techniques focus on reducing the availability and activity of trace elements but not on removing the pollutant from the soil. These techniques are based on the addition of suitable amendments to accelerate natural soil processes (sorption, precipitation, and complexation reactions), with the aim of decreasing mobility and bioavailability of toxic elements [4]. Numerous amendments have been incorporated into soils polluted with metal(oids) to immobilise pollutants. These amendments include individual additions of lime [5,6], phosphate [7,8], iron oxides [9–11], organic materials [12,13], industrial residues such as red mud [14,15], and municipal biosolids [16,17]; and combinations of amendments, including organic and liming materials [18,19], compost and iron oxide [20], and iron oxides and lime [21], among others. In some cases, an

amendment may be effective at immobilising one pollutant but may increase the mobility of another [22]. In other cases, the effectiveness of adding two amendments together is reduced relative to when using each individual amendment [23].

On the other hand, many studies analyse the effectiveness of immobilisation techniques under environmental conditions by measuring the solubility and bioavailability of trace elements in the soil [24–26]. In other cases, the effectiveness of amendments is studied by the analysis of lixiviates [22,27,28]. However, very few studies have jointly analysed lixiviates and pore water [29], although the chemical compositions of both solutions are usually related. Thus, decreased concentrations of trace elements in pore water could be related not to immobilisation but to a higher extraction through lixiviation. In this case, improving soil properties involves the spread of pollutants through surface runoff and drainage into the soil and can result in pollution of both the surrounding ecosystems and groundwater.

In this paper, soil polluted by sulphide-mine waste was, individually and in binary and ternary combinations, amended with marble sludge from the cutting and polishing of marble, compost from greenhouse agriculture wastes, and iron oxides. Lixiviates and pore water were analysed to assess the effect of the amendments and their interactions on the spread of pollutants and phytotoxicity of both solutions.

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Table 1

Mean values and standard deviation of the main properties and total trace element concentrations ($n=3$) in contaminated soil (S), and organic (CM) and inorganic (MS and BF) amendment.

	Amendment							
	S		CM		MS		BF	
	Mean	sd	Mean	sd	Mean	sd	Mean	sd
CaCO ₃ (g kg ⁻¹)	nd	–	nd	–	982	5	nd	–
pH	3.1	0.1	8.7	0.2	8.5	0.1	7.6	0.1
EC (dS m ⁻¹)	34.9	1.0	7.2	0.2	2.1	0.1	1.7	0.1
OC (g kg ⁻¹)	7.8	0.4	412	13	0.79	0.08	nd	–
Sand (g kg ⁻¹)	683	6	–	–	38	4	–	–
Silt (g kg ⁻¹)	279	5	–	–	646	8	–	–
Clay (g kg ⁻¹)	38	2	–	–	323	7	–	–
Cd (mg kg ⁻¹)	6.1	0.3	0.09	0.02	0.21	0.03	nd	–
As (mg kg ⁻¹)	179	5	1.3	0.1	3.8	0.1	28	3
Zn (mg kg ⁻¹)	3127	57	71	1	7.0	0.1	499	17
Pb (mg kg ⁻¹)	3564	39	17	0.4	1.2	0.1	3.8	0.2
Cu (mg kg ⁻¹)	47	2	0.60	0.06	5.1	0.2	0.92	0.03

nd, not detected.

2. Materials and methods

Contaminated soil from the El Arteal mining district (Almeria, SE Spain) was amended with CaCO₃, organic matter, and iron oxides. The lixiviates and pore water from the soils were analysed, and the toxicities of both solutions were estimated by lettuce bioassays.

2.1. Contaminated soil and amendments

The top layer (20 cm) of the contaminated soil was collected, air-dried at 25 °C, sieved (2 mm), and thoroughly mixed to ensure homogeneity. The amendments used were the following: marble sludge from the cutting and polishing of marble (MS), compost from agricultural greenhouse wastes (CM), and synthetic Fe oxides (Bayferrox 920) composed mainly of goethite (BF).

The polluted soil and amendments were analysed (Table 1, three replicates). The particle-size distribution was determined using the pipette method [30]. Calcium carbonate equivalent content (CaCO₃) was estimated manometrically [31]. The pH was measured in a 1:2.5 soil:water suspension. The solution of saturation extracts was vacuum pumped, and its electrical conductivity (EC) and redox potential (Eh) were measured. The total carbon content was analysed by dry combustion in a LECO SC-144DR analyser. The organic carbon content (OC) was determined as the difference between the amounts of total carbon and inorganic carbon (CaCO₃) (see Table 2).

Polluted soil and amendments were finely ground (<0.05 mm) and digested in a 4:1 mixture of HNO₃ (65%) and HF (37%), and the total concentrations of trace elements were measured by ICP-MS (nexION 300D). The accuracy of the method was confirmed

with analyses (six replicates) of the Standard Reference Material, SRM2711. For all of the trace elements analysed, average recoveries ranged from between 94% and 101% of the certified reference values.

The application rates of the different amendments used in this study were selected based on our experience and rates frequently used by other researches [22,32–34]. Thus, polluted soil (S) was, in all possible combinations (three replicates), amended with marble sludge from the cutting and polishing of marble (MS) at 4% and 8% (w/w), compost from agricultural greenhouse wastes (CM) at 2% and 6% (w/w), and synthetic Fe oxides (BF) at 1% and 3% (w/w). One kilogram of each amended soil was prepared. The 26 possible combinations were labelled with three-digit numbers representing the supplemental amounts (% w/w) of MS (first digit), CM (second digit), and BF (third digit). Soil without amendment was labelled as 000. Because there were three replicates, in unamended soil and in each amended soil $n=3$. A total of 81 soils were grouped into eight different treatments (S, $n=3$; S-MS, $n=6$; S-CM, $n=6$; S-BF, $n=6$; S-MS-CM, $n=12$; S-MS-BF, $n=12$; S-CM-BF, $n=12$; S-MS-CM-BF, $n=24$). Each treatment includes all possible combinations of those amendments whose initials are contained in the name of treatment (e.g. S-MS-BF treatment included the amended soils 401, 403, 801, 803).

2.2. Column assay

So that the soil properties reached equilibrium, the 81 soil samples were moistened to field capacity with distilled water

Table 2

Principal-component analysis (load matrix) in lixiviates and pore water, including trace-element concentration, amount of each amendment added, pH, Eh, EC, and REI. Only ≥ 0.400 loads included.

	Lixiviates factors			Pore water factors		
	L1	L2	L3	PW1	PW2	PW3
MS (%)	-0.832			-0.772		0.402
CM (%)		0.949				-0.834
BF (%)			-0.953		0.786	
pH	-0.942			-0.965		
Eh (mV)	0.724		0.448	0.656	-0.580	
EC (dSm ⁻¹)		0.968			0.634	-0.705
Cu (mgL ⁻¹)	0.622			0.915		
Zn (mgL ⁻¹)	0.898			0.951		
As (mgL ⁻¹)	-0.536	0.690			0.733	
Cd (mgL ⁻¹)	0.861			0.951		
Pb (mgL ⁻¹)	0.964			0.948		
REI				-0.578	-0.591	
Accum. var. (%)	45	68	80	47	64	80

(200 cm³ kg⁻¹ dry soil) and allowed to dry in cycles of approximately 15 days within a 3-month period [35]. They were then placed in 16 cm-long glass columns with a 5-cm inner diameter, which narrowed towards the bottom to 0.4 cm. The bottom of the column was filled with fibreglass to keep the sample in the column. The column was hand-packed with 200 g of each soil sample, which was covered with a 2-cm layer of fibreglass to facilitate the uniform flow. Next, 120 cm³ of distilled water was added to each column, at a rate of 10 cm³/h and in the dark to avoid algal growth, and the lixivate was collected. Next, pore water was collected using Rhizon soil-moisture samplers (Rhizon Research product, Wageningen, The Netherlands). In both solutions, redox potential (Eh), electrical conductivity (EC), and pH were measured, and the solutions were immediately filtered through cellulose filters (0.45 μm pore) by vacuum suction into PyrexTM flasks previously washed with acid (HNO₃) and stored at <4 °C until analysis of trace elements by ICP-MS.

2.3. Bioassay with lettuce seeds (*Lactuca sativa* L.)

Seed-germination and root-elongation indices (GI and REI index, respectively) were determined according to US EPA [36] procedure, OPPTS 850.4200. The *L. sativa* seeds were of the variety Villena RZ. Three replicates of 15 seeds were placed in 90-mm-diameter Petri dishes containing filter paper in the bottom for support. After the application of 5 cm³ of the different solutions (lixivate and pore water) and distilled water (control), the dishes were incubated for 120 h at 24 ± 0.1 °C. Finally, the number of germinated seeds was counted, and the lengths of the germinated seed roots were measured. The GI (proportion of germinated seeds compared to the control) and the REI (percentage of root elongation in relation to the control) were estimated. When GI and REI = 100%, there was no toxicity; when GI and/or REI < 100%, the sample was phytotoxic; and when GI and/or REI > 100%, germination and/or elongation was stimulated.

2.4. Statistical methods

Principal-component analysis (PCA) of trace-element concentrations, the amount of each amendment added, pH, Eh, EC, and REI was performed on the lixivates and pore water to reduce the number of variables and to detect structure in the relationships between them. These variables can be explained in terms of their common underlying dimensions (factors), which form a smaller group of variables, condensing the information with minimal loss [37]. PCA was carried out using the varimax orthogonal rotation option, which minimises the number of variables with a high load on each factor [38]. The data distribution in different treatments and amendments was established by calculating the mean values and standard deviations, and the differences between individual means were compared using Tukey's test ($P < 0.05$). The software package PASW Statistics 18 was used for all statistical analyses.

3. Results and discussion

3.1. Polluted soil and amendments

The soil used in this study was saline, acidic, and highly polluted (Table 1), with total concentrations of As, Cd, Zn and Pb between 3 and 29 times higher than baselines proposed for south-eastern Spain [39]. The OC was relatively low (7.8 g OC kg⁻¹ dry soil) compared to mean values for the Almería province (11 g OC kg⁻¹ dry soil, [40]) and the EC (34.9 dS m⁻¹) was very high (the soil is considered saline when EC > 4 dS m⁻¹ [41]). The MS had a very high CaCO₃ content (>98%), basic pH (8.5), low EC value (2.1 dS m⁻¹),

and low trace-element concentrations. The CM from greenhouse agriculture had a very high OC content (412 g OC kg⁻¹), high EC value (7.2 dS m⁻¹), and relatively low metal concentrations. The BF, composed of goethite with 70% Fe, showed relatively high concentrations of Zn and As (although much lower than the soil studied), a basic pH (7.6), and low EC value (1.7 dS m⁻¹).

3.2. Amended soils

3.2.1. Effects on physicochemical parameters

MS treatments (Fig. 1a), alone or in combination with other amendments (S-MS, S-MS-CM, S-MS-BF, and S-MS-CM-BF), showed the greatest increases in pH relative to untreated soil (mean pH between 6.6 and 6.8 in pore waters and between 7.1 and 7.4 in lixivates). The pH did not increase in either solution when higher amounts of MS were added (Fig. 1b). After experimentation, the CaCO₃ content of the soils was close to the amount of amendment applied, 3.56 ± 0.10% and 7.64 ± 0.11% (w/w) in soil amendments with 4% and 8% of MS, respectively, indicating that only a small part of the added CaCO₃ was weathered. The CM treatments, alone or in combination with iron oxides (S-CM and S-CM-BF), also increased the pH in lixivates and soil solutions, but to a lesser extent compared to MS treatments. The pH increased significantly when a greater amount of CM was added (Fig. 1b). Treatments with iron oxide (S-BF) only did not affect the pH, and the values were similar to those of the untreated soil (Fig. 1a and b).

CM treatments (S-CM, S-CM-BF, S-MS-CM, and S-MS-CM-BF) significantly increased the EC values of lixivates with respect to the untreated soil (Fig. 1c), and the increase was commensurate to the amount of CM added (Fig. 1d). Meanwhile, the MS and BF treatments (S-MS, S-BE, and S-MS-BF) tended to decrease the EC values (Fig. 1c), although the differences between mean values were not significant. Regardless, mean EC values in the lixivates were very high in all cases (35 ± 8 dS m⁻¹), indicating that even when the soil is amended, there is a clear risk of salinisation of the groundwater and surrounding soil. The EC values of pore water were clearly lower (5.9 ± 1.9 dS m⁻¹) than those of lixivates, and the mean values were close to those of the untreated soil. Only when the soil was amended with BF combined with CM, MS, or both were the mean EC values significantly higher (Fig. 1c); meanwhile, when the greatest amount of CM (060) and MS (800) were applied, the mean EC values significantly increased and decreased, respectively (Fig. 1d).

With respect to the untreated soil, all treatments, except S-BF, significantly decreased Eh values in the lixivates and pore water (Fig. 1e and f), which is related to both the increase in pH because both parameters are inversely related and the oxidation of Fe²⁺ present in the untreated acidic soil. Significantly lower Eh values were found when BF was combined with MS, CM, or both (Fig. 1e), indicating that when pH ≥ 6 the addition of BF promoted an increase in the e⁻ activity.

3.2.2. Effects on soluble metals concentrations

The concentrations of zinc (Zn), cadmium (Cd), copper (Cu), and lead (Pb) in the untreated soil (Fig. 2) were much higher in lixivates than in pore water, indicating that these trace elements will tend to spread through runoff water and infiltrate the soil. These results suggest that the soils of surrounding areas and groundwater may be affected. MS treatments were the most effective in reducing the solubility of these trace elements, decreasing concentrations of Zn, Cd, and Pb in lixivates and pore water by more than 90% (Fig. 2a, c and g) and of Cu by between 50% and 60% (Fig. 2e) with respect to untreated soil. These results indicate that the solubility of Zn, Cd, Cu, and Pb are strongly pH dependent [8], decreasing sharply when pH > 6 (treatments with MS and amendment with 6% of CM). However, the addition of 4% and 8% of MS did not affect the pH (Fig. 1b) but significantly decreased the concentrations of these

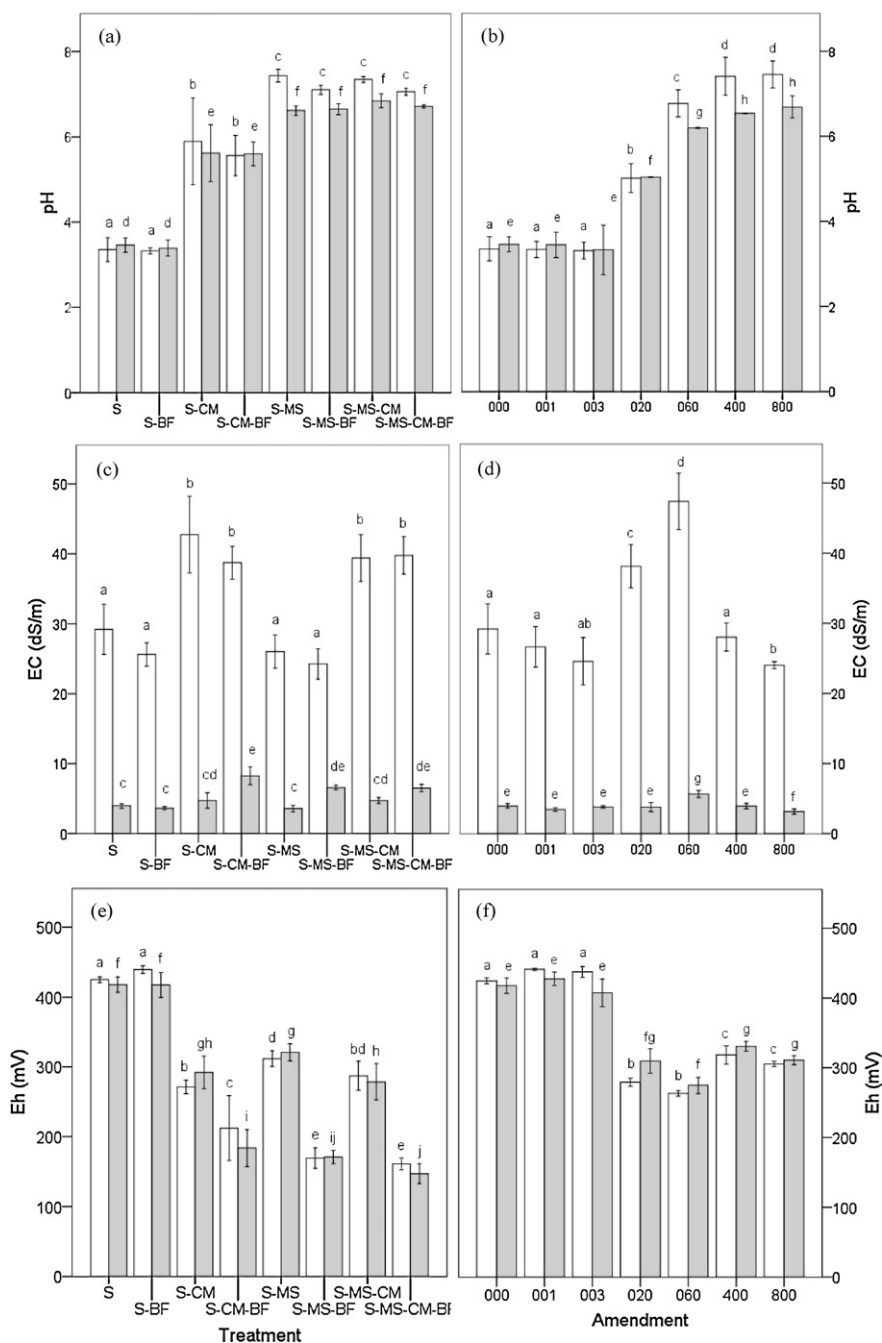


Fig. 1. Mean values and standard deviation (error bars) of pH, electrical conductivity (EC), and redox potential (Eh) in lixiviates (□) and pore water (■) from different treatments and amendments. In each solution, mean values followed by the same letter do not differ significantly (Tukey test, $P < 0.05$).

trace elements, with the exception of Pb, in the lixiviates (Fig. 2b, d and f), suggesting that the CaCO_3 played an active role in reducing the solubility of Zn, Cd, and Cu [28]. This decrease could be due to precipitation of carbonates [42–44], or more likely, sorption by iron and aluminium oxyhydroxides that precipitate on the carbonate particles at higher pH values, thereby forming coatings [45]. The enlarged surface areas of these coatings, which augment the amount of MS added, may explain the higher sorption, and therefore, the lower solubility of these trace elements. These coatings would prevent the reaction between carbonate and the soil solution, justifying that the pH of lixiviates and pore water remained constant when increasing amounts of MS were added (Fig. 1b) and that pH values were lower than the pH of water in equilibrium with CaCO_3 (≈ 8.3).

Treatments with BF only (S–BF) did not affect the concentrations of these trace elements in pore water, but Cd and Pb concentrations significantly decreased in the lixiviates by between 55% and 70% and 7% and 27%, respectively [46]. Only in the case of Cu (Fig. 2f) did the addition of 1% BF increase its concentration in lixiviates but decrease it in pore water. However, when BF was added with MS, the concentrations of Zn, Cd, and Cu tended to increase in the lixiviates in relation to the soil amended with MS alone (amendments 803 and 800, Fig. 2b, d and f), probably due to more reducing conditions (lower Eh values, Fig. 1) and lower sorption by oxyhydroxide coatings. Hartley et al. [22] found that the addition of Fe plus lime significantly increased heavy-metal solubility.

Treatments with CM only (S–CM) significantly reduced the concentrations of Cd, Cu, and Pb in lixiviates and pore water (Fig. 2).

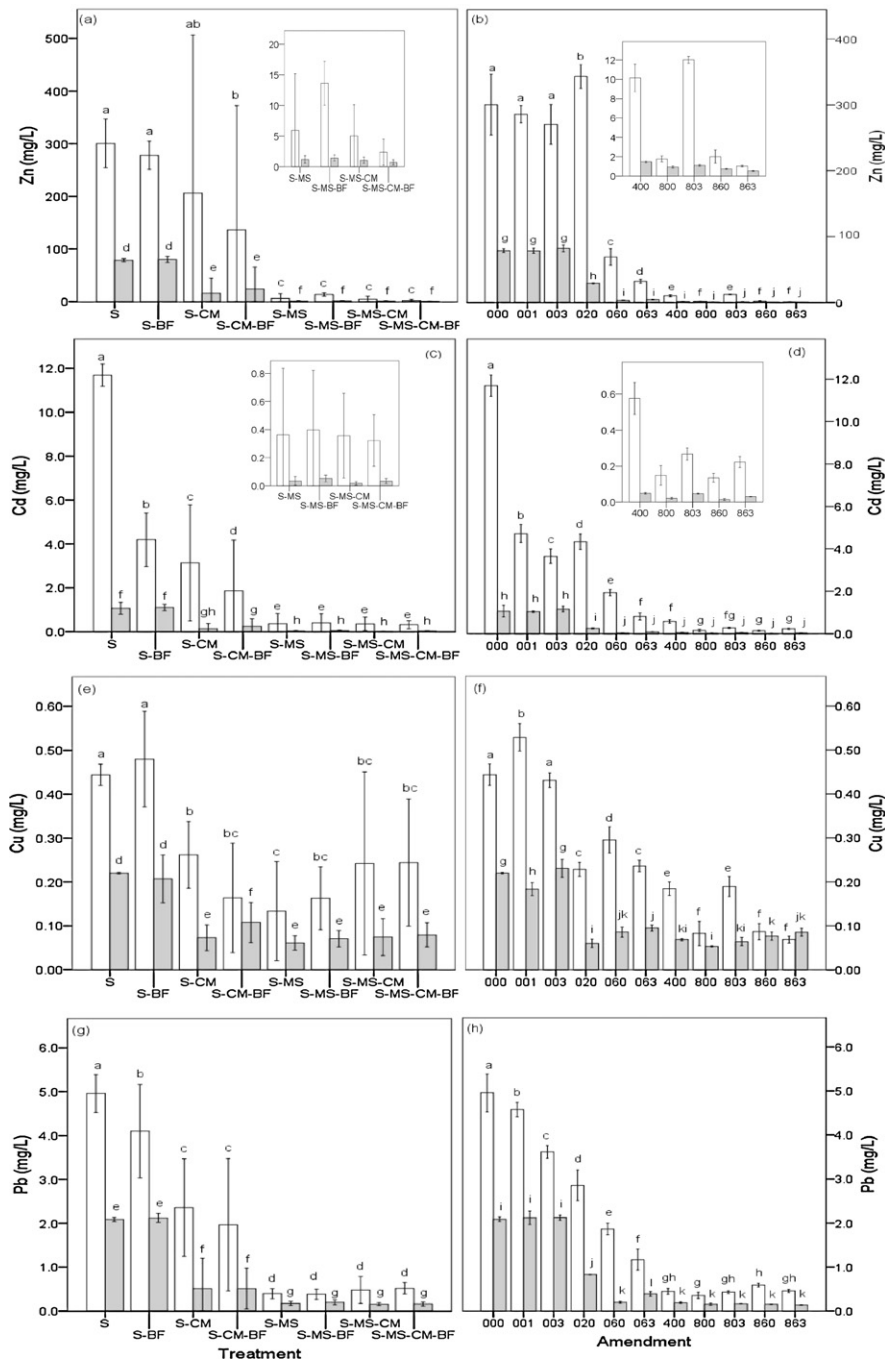


Fig. 2. Mean values and standard deviation (error bars) of Zn, Cd, Cu, and Pb concentration in lixiviates (□) and pore water (■) from different treatments and amendments. In each solution, mean values followed by the same letter do not differ significantly (Tukey test, $P < 0.05$).

The concentrations of Cd and Pb decreased when greater amounts of CM were added, while that Cu increased. In the case of Zn, only the addition of 6% of CM significantly decreased the concentrations in both solutions, while the addition of 2% increased the concentrations in the lixiviates and decreased them in the pore water in a similar proportion (Fig. 2b), accounting for the large standard deviations in lixiviates from CM treatments (Fig. 2a). Many researchers have reported the fixation of these trace elements by organic matter [47,48], but because the addition of CM also increased the pH in our study, it was very difficult to separate the two effects. However, the fact that the Cu concentration increased in lixiviates and pore water as greater amounts of CM were added, suggests the formation of complexes with soluble organic compounds [49].

3.2.3. Effect on soluble arsenic concentration

Unlike the other trace elements, As concentration in untreated soil was higher in pore water than in lixiviates (Fig. 3a). The BF treatment (S-BF) did not alter the concentration of As in the lixiviates but significantly decreased it in pore water and was the only treatment that significantly decreased the total amount of soluble As estimated from the sum of the concentrations in lixivate and pore water (Fig. 3c). These results confirm the effectiveness of iron compounds in reducing the mobility of As [50–53]. However, when BF was mixed with MS and/or CM, total soluble As was not significantly changed in comparison to untreated soil (Fig. 3c), but the concentration of As increased significantly in the lixiviates and decreased in pore water (Fig. 3a). These results reveal that the

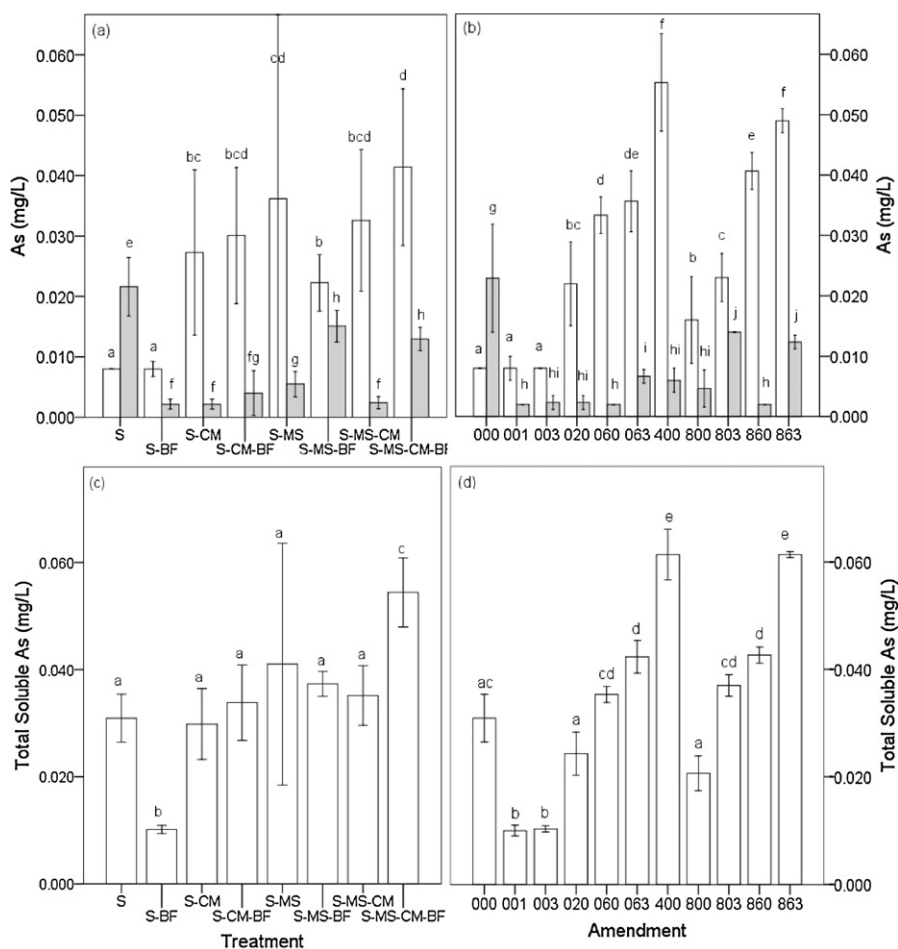


Fig. 3. Mean values and standard deviation (error bars) of As concentration in lixiviates (□) and pore water (▒) and total soluble As (sum of lixiviates and pore water) from different treatments and amendments. In each solution, mean values followed by the same letter do not differ significantly (Tukey test, $P < 0.05$).

addition of iron oxides along with amendments that increase the pH in acidic soils leads to a reduction in the effectiveness of iron in the sorption of As and promotes its removal through lixiviates. This behaviour could be attributed to the dominance of more negatively charged arsenate species under basic conditions (HAsO_4^{2-}) and the stronger rejection of negatively charged surfaces (pore walls), which increases their concentration towards the centre of the pore where they are less retained and more easily extracted by lixiviates.

When the soil was treated with MS only (S–MS), total soluble As registered a large standard deviation in the lixiviates (Fig. 3c) due to a marked decline in the concentration as the amount of MS added was increased (Fig. 3b). Some authors [22,52] have suggested the formation and precipitation of As–Ca complexes under oxidising and moderate pH conditions. However, in the soil amended with MS only (400 and 800), there was an excess of CaCO_3 , while the pH and Eh values of the lixiviates were similar (Fig. 1b and f). Therefore, we believe that this mechanism alone cannot explain the sharp decline in the concentration of As. The sorption of As by oxyhydroxide coatings and the larger surface areas of these coatings with increasing amounts of added MS, may account for the sharp decline in total soluble As in the amended soil 800 relative to 400. Lower Eh values in the lixiviates and pore water when MS was combined with BF (<200 mV, Fig. 1e) result in a further reduction of Fe coatings and, presumably, in the changing of the species from As (V) to more mobile As (III) [54]. This explains the increase in As in the lixiviates and pore water in amended soils 803 and 863 relative to amended soil 800 (Fig. 3b).

When the soil was treated with CM only, the concentration of As in the lixiviates tended to increase with the addition of increasing amounts of CM (Fig. 3b), which may be attributed to higher pH values (Fig. 1c) and a greater proportion of more negatively charged arsenate species. However, it cannot be ruled out that soluble organic compounds compete with As for the adsorption site, increasing the As concentration in the lixiviates [55].

3.3. *Lactuca sativa* L. bioassay

Seeds did not germinate in the lixiviates ($\text{GI} = 0$), indicating high toxicity. Because the concentrations of trace elements in some lixiviates, mainly those from the soil amended with 8% of MS, were lower than the maximum recommended for irrigation waters (2 mg ZnL^{-1} , 0.2 mg CuL^{-1} , 0.01 mg CdL^{-1} , 1.0 mg PbL^{-1} , 0.1 mg AsL^{-1}) by the Food and Agriculture Organisation of the United Nations [56], the high toxicity must have been related to parameters other than the concentrations of potentially toxic elements, presumably high salinity ($\text{EC} = 35 \pm 8 \text{ dSm}^{-1}$). Nasri et al. [57] found that $\text{GI} \approx 40\%$ in lettuce when 150 mM NaCl were added to the solution ($\text{EC} \approx 19 \text{ dSm}^{-1}$ according to the equivalent ionic conductivity of each ion).

In pore water, almost all of the seeds germinated, and the differences between treatments and amendments were not significant (Fig. 4). Meanwhile, the root-elongation index (REI) was affected more intensely by the chemical properties of the solution, indicating that REI was the most sensitive index for estimating the phytotoxicity of the pore water. The lowest mean values of

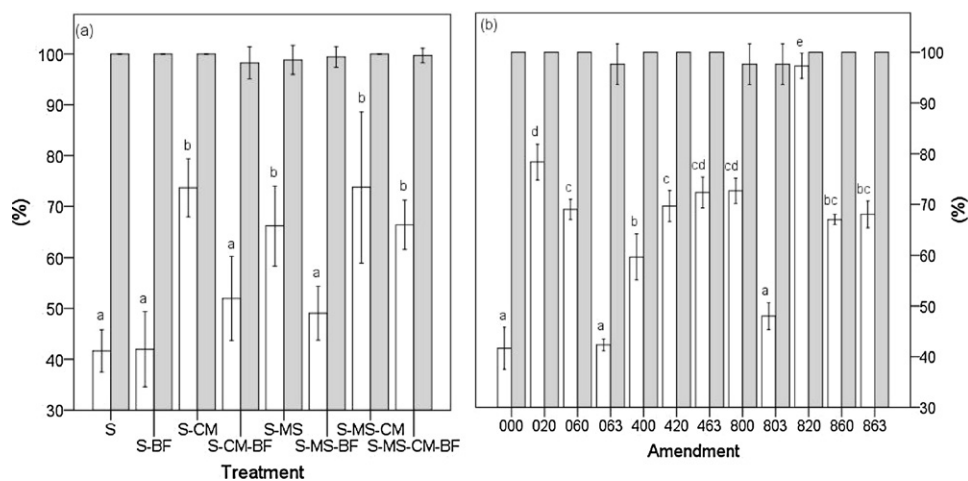


Fig. 4. Mean values and standard deviation (error bars) of germination index (■) and root-elongation index (□) in pore water from different treatments and amendments. Mean values followed by the same letter do not differ significantly (Tukey test, $P < 0.05$).

REI (without significant differences between them) were found in untreated soil and in soil treated with BF alone and combined with MS or CM. Because the pore water of untreated soil (S) and that treated with BF (S-BF) showed relatively low salinity ($EC = 3.7 \pm 0.1 \text{ dSm}^{-1}$) and relatively high redox potential ($Eh = 417 \pm 15 \text{ mV}$), the low REI values can be explained by the acidity ($pH = 3.4 \pm 0.1$) and relatively high concentrations of Zn ($80 \pm 3 \text{ mgL}^{-1}$), Cd ($1.1 \pm 0.1 \text{ mgL}^{-1}$) and Pb ($2.1 \pm 0.1 \text{ mgL}^{-1}$), which were higher than the maximum recommended for irrigation waters [56]. Meanwhile, when the soil was treated with BF and CM (S-BF-CM) or with BF and MS (S-BF-MS), the broad range of Zn ($13 \pm 18 \text{ mg}^{-1}\text{L}$) and Cd ($0.15 \pm 0.15 \text{ mg}^{-1}\text{L}$) concentrations suggest that mainly salinity ($EC = 7.4 \pm 1.7 \text{ dSm}^{-1}$) and reducing conditions ($Eh = 177 \pm 21 \text{ mV}$) accounted for the low REI values.

When the soil was treated with CM (S-CM), MS (S-MS), a combination of both (S-MS-CM), or when the three amendments were combined (S-MS-CM-BF), REI values significantly increased with respect to other treatments (Fig. 4a). This increase can be attributed mainly (Fig. 1c and e) to the lower salinity and higher redox potential (S-MS, S-CM, and S-MS-SM), or the lower concentration (Fig. 2) of dissolved trace elements (S-MS-CM-BF). These same parameters also determine the value of REI in each treatment. Thus, in the CM treatment, the decrease in REI with increasing amounts of CM added (020 compared to 060) is due to greater salinity (Figs. 1d and 4b). On the other hand, in the MS treatment, the increase in REI with increasing amounts of MS added (400 compared to 800) is associated with declines in both salinity and the concentrations of trace elements (Figs. 1d, 2 and 4b). In agreement with these results, the highest REI value was registered when the soil was amended with 8% of MS and 2% of CM (820). Only the Zn concentration in the pore water of the untreated and soil treated with BF was higher than that estimated by Lamb et al. [58] when REI decreased by 50% (16.9 mg/L). In any case, the concentrations of Cd (in all samples) and Zn (in some samples) were higher (Fig. 2b and d) than the maximums recommended for irrigation waters [56], indicating that the toxicity of pore water is conditioned by these trace elements.

3.4. Principal component analysis

Principal-component analysis (PCA) of lixivates and pore water indicated that three factors explained 80% of the variance. In the lixivates, the first factor (L1) explained 45% of the variance and included the amount of MS added, pH value, Eh value, and trace

element concentrations, which confirms that the addition of MS increases pH, decreases Eh, and promotes Cd, Cu, Pb and Zn fixation and As leaching. The second factor (L2) supports that CM addition increased EC and As leaching. The third factor (L3) confirms that BF addition tended to decrease Eh values.

In the pore water, the first factor (PW1) explained 47% of the variance and included the amount of MS added, pH value, Eh value, metals concentrations, and REI value, which confirms that MS addition promoted metals fixation (as in the lixivates), increased the REI value, and reduced toxicity. The second factor (PW2) confirms that BF addition decreased Eh and increased EC and As concentrations, decreased REI values and promoted toxicity. The third factor (PW3) supports that EC was higher after CM addition and lower after MS application.

According to these results, field application of MS and CM would decrease soluble heavy metal concentration, while As concentration in pore water would decrease and would increase in lixivates. After amendments application, toxicity would be reduced only in pore water, while lixivates would be still highly toxic and a proper handling of them would be necessary. Application of iron oxide could help to avoid As dispersion, and its field application in combination with MS and CM should be studied in more detail. In any case, to properly extrapolate these results to field conditions would be necessary further researches involving plant-amended soils interaction.

4. Conclusions

To amend soils contaminated with high concentrations of dissolved ions, it might be difficult to avoid the risk of salinisation of the water table and surrounding soils. The effectiveness of amendments may markedly differ depending on whether the analysis is performed on lixivates or pore water. None of the amendments or combinations of amendments used proved effective in reducing the soluble concentrations of all of the trace elements involved in the pollution. The amendments that raised the pH, especially marble sludge, were effective in diminishing soluble heavy-metal concentrations; however, these amendments increased As concentration in lixivates, encouraging the risk of the dispersion of this pollutant. The amendment that fixed As, iron oxide, was not effective in diminishing soluble heavy-metal concentrations. The combination of amendments did not significantly decrease the metal-arsenic soluble concentrations of each one separately. Nevertheless, the combination of 8% marble sludge with 2% compost

showed the highest root elongation index, suggesting that this combination was the most effective in reducing toxicity to lettuce. The amendments used at each contaminated site should be selected based on the physicochemical parameters of the soil and the type of contaminants present. In any case, to evaluate the effectiveness of treatments under natural conditions, new research involving successive washes and plant growth should be addressed in the future.

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