Environ Sci Pollut Res (2016) 23:6046–6054
DOI 10.1007/s11356-015-4287-z

CONTAMINATION RELATED TO ANTHROPIC ACTIVITIES. CHARACTERIZATION AND REMEDIATION

Chemical and plant tests to assess the viability of amendments to reduce metal availability in mine soils and tailings

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Received: 2 December 2014 / Accepted: 26 February 2015 / Published online: 15 March 2015

Abstract The goal of this research was to assess the potential of several industrial wastes to immobilise metals in two polluted soils deriving from an old Pb/Zn mine. Two different approaches were used to assess the performance of different amendments: a chemical one, using extraction by ethylenediaminetetraacetic acid (EDTA), and a biological one, using *Lupinus albus* as a bio-indicator. Four amendments were used: inorganic sugar production waste (named 'sugar foam', SF), sludge from a drinking water treatment sludge (DWS), organic waste from olive mill waste (OMW) and paper mill sludge (PMS). Amendment to soil ratios ranged from 0.1 to 0.3 (*w*/*w*). All the amendments were capable of significantly decreasing ($p<0.05$) EDTA-extractable Pb, Zn and Cu concentrations in the two soils used, with decreases in ranges 21–100, 25–100 and 2–100 % for Pb, Zn and Cu, respectively. The amendments tested were also effective in reducing the bioavailability of Pb and Zn for *L. albus*, which gave rise to a decrease in shoot metal accumulation by the lupine plants compared to that found in the control soil. That decrease reached up to 5.6 and 2.8 times for Pb and Zn, respectively, being statistically significant in most cases. Moreover, application of the OMW, DWS and SF amendments led to higher average values of plant biomass (up to 71 %) than those obtained in the control soil. The results obtained showed the technology put forward to be a viable means of remediating mine soils as it led to a decrease in the availability and toxicity of metals and, thus, facilitated the growth of a vegetation layer.

Keywords Soil pollution · Metals · Immobilisation · Amendments · Metal availability

Introduction

Metal mining activities significantly affect the environment due to the large amount of abandoned spoils, tailings and ponds created without there being, in most cases, any environmental regulations to control these. The aforementioned types of waste includes pollution by metals of soils, groundwaters and surface waters in the mines and surrounding areas (González and González-Chávez 2006; Fu and Wei 2013; Zhang et al. 2012; Šajn et al. 2013). This issue should be tackled in forthcoming years by European governments. In fact, Directive 2006/21/EC of the European Union 'on the management of waste from extractive industries' establishes that: 'Member States must develop technologies for the rehabilitation of closed waste facilities using appropriate risk assessment procedures and remedial actions having regard to the variation of geological, hydrogeological and climatological characteristics across Europe'.

In Spain, there are several areas matching the abovementioned scenario. More specifically, the soils used in this study were taken from 'San Quintín' an old Pb/Zn mine, located in the southern central part of the Iberian Peninsula. It belonged to one of the most important mining districts for lead and zinc production during the late nineteenth and early twentieth century, i.e. Alcudia Valley (Palero-Fernández and Martín-Izard

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Responsible editor: Zhihong Xu

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2005). The total surface area covered by the dumps and sediments deriving from the mining activities of the San Quintín mine is about 600,000 m^2. Recently, we have emphasised the environmental risk caused by the spread of pollution to the surrounding pasture and arable lands (Rodríguez et al. 2009).

Several organic and inorganic materials were studied for use as amendments to reduce the bioavailability of metals in soils (see reviews by Gadepalle et al. (2007) and Bolan et al. (2014)). Organic amendments included manures, biosolids, sawdust, wood ash, compost derived from different source materials, sewage sludge, bark chips and woodchips. As for inorganic amendments, we can mention phosphate-derived products (KH_2PO_4, hydroxyapatite, phosphate rock and phosphogypsum), liming materials (lime, $Ca(OH)_2$, natural and synthetic zeolites, 'red mud', a by-product produced on refining bauxite to alumina, and 'sugar foam', an alkaline waste generated from sugar production from sugar beet), alkaline sludge from drinking water facilities and, more recently, biochar. All the above materials can be added to soil to immobilise the metals in it by different mechanisms (metal precipitation, adsorption, complexation and redox reactions), thus reducing the environmental risk of this type of pollution (Brown et al. 2005). That technology avoids the high costs of soil removal and transport; moreover, it often promotes microorganism and plant growth leading to the creation of vegetation covers capable of stabilising the soils (phytostabilisation) and minimising erosion and dissemination of the contaminants. Additionally, taking into account that most of the materials listed are industrial by-products and wastes, the use of amendments for metal immobilisation has been proposed as a potentially cost-effective and environmentally friendly strategy to remediate mining-contaminated sites (Mendez and Maier 2008; Pardo et al. 2014).

In spite of the research developed in this area, Bolan et al. (2014) have recently concluded that more studies are necessary in order to demonstrate how effective immobilisation is. The overall objective of our research was to assess the feasibility of soil restoration for the San Quintín mining area by means of using amendments based on industrial by-products and wastes. In this paper, we have used two different and complementary approaches to assess the effectiveness of amendments for metal immobilisation in mine soils: a chemical one, based on analysing the changes in EDTA-extractable metal concentrations, and a biological one, using phytoextraction by *Lupinus albus* (white lupine) as an indicator of metal availability. EDTA allows the quantity of mobilisable metals to be estimated and may in general correlate well with the quantity of Cd, Cu, Ni, Pb and Zn in the plants (Vidal et al. 1999; Sahuquillo et al. 2003; Ruiz et al. 2009). White lupine was selected because it is atypical crop found in Spain and more specifically can be located in the area being researched, and moreover, it grows better in acidic soils (Lopez-Bellido and Fuente 1986).

Materials and methods

Soil and amendments characterisation

Soil samples were taken in the surroundings of the San Quintín Pb-Zn mine, located approximately 250 km south of Madrid, Spain. This mine was an important Pb–Zn producer during the late nineteenth and early twentieth century with galena (PbS) and sphalerite (ZnS) being the main extracted ore minerals. In a previous paper, we gave a detailed geochemical characterisation of metal pollution in the soils around the mine (Rodríguez et al. 2009). Full recovery of the affected area needs to encompass both mine tailings and arable land soils, so we selected two soil samples with different features to carry out this study: one corresponding to arable land (the SQ1 sample) close to the San Quintín mine (0388997, 4297590 UTM) and the other to mine tailings (the SQ2 sample) from a former sedimentation pond (0389462, 4297663 UTM). These two samples were selected based on our previous characterisation results (Rodríguez et al. 2009), and they were representative of the two land uses (mine tailings and agriculture) that can be found in the San Quintín mining area. Soil was sampled at a depth of 0–25 cm, air-dried at room temperature for 72 h, disaggregated and, finally, sieved to <2 mm and <63 μm. One sample of each soil type (both corresponding to just one sampling point) was used for all the experiments. The <2-mm fraction was used for the experiments and for measuring the physicochemical properties of the soil. The 63-μm fraction was only used to analyse its total metal content, as well as for the concentration of EDTA-extractable metals in the incubation experiments. The main physical-chemical properties of these two soils are shown in Table 1.

The soil pH was measured in a 1:5 soil/water (*w*/*v*) mixture, total organic carbon (TOC) and inorganic carbon were determined using a TOC analyser (Shimadzu TOC-VCSH, Columbia, USA), particle-size distribution (clay, silt and sand content) was determined using laser diffractometry (Beckman Coulter LS, Fullerton, USA), and cation exchange capacity (CEC) was measured by the ammonium acetate saturation method. To determine the total concentration of Cu, Pb, and Zn (<63-μm fraction) in the soil samples and amendments, 0.5 g of sample was digested with a mixture of acids (9 mL of concentrated HNO_3 + 3 mL of concentrated HCl) in a microwave unit (CEM MARS 5, Matthews, USA), according to the EPA 3051A method.

Four amendments were used in this study: sugar foam (SF), paper mill sludge (PMS), drinking water treatment sludge (DWS) and olive mill waste (OMW). Sugar foam is a calcium carbonate-rich waste generated when beet juice is purified by flocculation of colloidal matter with a lime solution followed by treatment with carbon dioxide; it has been used in the past to reduce soil acidity (Garrido et al. 2003) and metal mobility

Table 1 Basic physico-chemical properties of mine soils and amendments

	Mine soil SQ1	Mine soil SQ2	SF	PMS	DWS	OMW
pH	6.3	4.1	12.7	8.2	7.5	5.4
CEC (cmol kg^{-1})	0.49	0.14	0.2	2.5	2.0	1.6
TOC (%)	1.29	0.11	0.3	16.1	49.0	45.1
IC (%)	n.d.	n.d.	8.2	3.9	n.d.	n.d.
Clay (%)	12.8	9.8	–	–	–	–
Silt (%)	47.8	45.7	–	–	–	–
Sand (%)	39.4	44.5	–	–	–	–
Water-Holding Capacity (%)	44.0	23.0	50.7	330.8	84.9	65.8
Total Pb (mg kg^{-1})	1017	9166	5.0	42.0	37.3	17.7
EDTA-Pb (mg kg^{-1})[a]	690 (68)	7049 (77)	n.d.	9.38 (22)	0.68 (1.8)	1.08 (6.1)
Total Cd (mg kg^{-1})	1.3	7.8	n.d.	n.d.	0.4	n.d.
EDTA-Cd (mg kg^{-1})[a]	0.59 (45)	1.01 (13)	n.d.	n.d.	n.d.	n.d.
Total Zn (mg kg^{-1})	227	2070	6.52	201	52.5	18.7
EDTA-Zn (mg kg^{-1})[a]	73.6 (32)	295 (14)	0.71 (11)	66.1 (33)	23.9 (46)	14.8 (79)
Total Cu (mg kg^{-1})	19.8	471	3.0	65.2	2.4	17.0
EDTA-Cu (mg kg^{-1})[a]	6.45 (33)	8.68 (1.8)	n.d.	18.4 (28)	0.78 (33)	13.4 (79)

CEC cation exchange capacity, *TOC* total organic carbon, *IC* inorganic carbon, *SF* sugar foam waste, *PMS* paper mill sludge, *DWS* drinking water treatment sludge, *OMW* olive mill waste

[a] In brackets, percentage of the total metal

in soils (Campbell et al. 2006; Garrido et al. 2006). Paper mill sludge is a material removed from the wastewater stream during the pulp and paper-making process; it has been used for immobilising metals in soils due to its organic matter, silicate and carbonate content (Battaglia et al. 2007; Calace et al. 2005). The drinking water treatment sludge came from a drinking water treatment plant which used aluminium sulphate as a reactive in the coagulation-flocculation process; this material contains variable amounts of colloidal organic matter and Al oxyhydroxides, both of which are useful for decreasing metal availability in soils (Garau et al. 2014; Wang et al. 2012). Lastly, the so-called ‘olive mill waste’ is a wet solid lignocellulosic by-product, known in Spain as ‘alperujo’, generated in massive quantities by the olive-oil extraction industry; it has also been tested as an amendment in metal polluted soils (Alburquerque et al. 2011; de la Fuente et al. 2011; Fornes et al. 2009). All of these amendments, whose basic physical-chemical characteristics are shown in Table 1, were obtained from local or national companies.

Incubation experiments

Chemical assessment of metal immobilisation was made by means of an incubation test. Homogenised soil samples were thoroughly mixed with amendments in different proportions as described in previous literature (Gadepalle et al. 2007): with 10 % (*w*/*w*, i.e. amendment weight/ soil weight ratio) sugar foam soil mixtures, 15 % (*w*/*w*) soil mixtures for drinking water sludge and olive mill waste and a 30 % (*w*/*w*) soil mixture for paper mill sludge. Amended soils were placed in 150-mL plastic containers and kept in the dark at room temperature (25 °C±3) for 45 days. The mixtures were initially moisturised up to a point of 70 % of their water-holding capacity; this was determined by a standard method based on making a water-saturated slurry (MAPA 1994). Throughout the experiment, deionised water was added weekly to make up for losses caused by evaporation. Three replicates were used for treatment; additionally, samples of initial soils without amendments were incubated as controls. Samples of the mixtures were taken on days 0 and 45 and analysed for EDTA-extractable metals and pH. EDTA-extractable metals were determined by means of extraction with an aqueous solution of 0.01 M EDTA after 16 h of agitation and using a soil/ extractant ratio of 1:10 (*w*/*v*). All sample extractions were carried out in triplicate, and reagent blanks were included in every batch. All the results are shown on a dry weight basis.

Plant uptake experiments

Biological assessment of metal immobilisation by the selected amendments was carried out by means of a pot experiment using white lupine (*L. albus*) as an indicator. Plastic pots were filled with approximately 225 g of a mixture made up of the air-dried soils (sieved to <2 mm), the selected amendments and perlite. Perlite was used in order to improve pot drainage to some extent. In the soil, amendment ratios used were the same as those in the incubation experiments, while the (soil + amendment)/perlite ratio was 2:1 (*v*/*v*). Soil-perlite mixtures of the two soils tested were used as controls.

Lupine seeds were pregerminated on filter paper moisturised with a 0.5 mM calcium sulphate solution; pregermination was carried out in a germination chamber for 3 days at 28 °C in the dark. Next, five lupine seedlings were sown per pot using three replicates per amendment (and controls). The growth substrate was adjusted to approximately 60 % of its water-holding capacity, and water loss was made up for daily by adding deionised water. Plants were grown for 8 weeks under controlled conditions in a growth chamber. Twelve-hour light and 12-h dark cycles were used with 28 °C/80 % humidity and 12 °C/50 % humidity for day and night, respectively. On harvesting, shoots and roots were separated, thoroughly washed with de-ionised water, weighed, air-dried, finely ground to fine powder with a ball mill (Retsch MM200, Haan, Germany) and sealed in plastic bags for subsequent heavy metal analysis. The dry plants were digested in the aforementioned microwave unit using a mixture of HNO_3/HCl/H_2O_2, according to the 3052 EPA method.

Concentrations of Cu, Pb and Zn in the soil and plant extracts were analysed by ICP-OES using a Thermo ICAP 6500 spectrometer (Thermo Electron, Cambridge, UK). The quality of these metal analyses methods was assessed by analysing standard reference materials (LGC Promochem, Barcelona, Spain).

Statistical analysis

All statistical analyses were carried out with the IBM SPSS Statistics program version 19.0. One-way ANOVA was used to assess the effect of adding an amendment to plant biomass and concentrations of metal in *L. albus* shoots. Pearson's correlation coefficient was used to measure the correlation between shoot metal concentrations and EDTA-extractable metals in soils after adding the amendment; prior to this, the normality of this data was checked by using the Shapiro-Wilk test.

Results and discussion

Characteristics of the mine soils and amendments

The main physical-chemical characteristics of the two soil samples used are shown in Table 1. The SQ1 sample corresponded to arable land close to the mine site, had a slightly acidic pH and had relatively little organic matter content. Pb concentration in the SQ1 sample was very high for agricultural soil, while its Zn content was near the upper limit of the background levels for sandy soils (Kabata-Pendias 2000). The SQ2 sample was taken from an old pond belonging to the mine, so its pH was highly acidic, its organic matter content was extremely low and the total concentrations of Pb, Zn and Cu were very high (Table 1). Pb availability was high in both soils, with EDTA extractable Pb concentrations accounting for more than 68 % of the total Pb. There was low to moderate availability of Cd, Cu and Zn in terms of EDTA-extractable concentrations (Table 1). As for their texture, although the SQ2 soil had a higher content of sand, both samples were classified as being loam soils.

The SF and PMS amendments had strongly basic pH values, whilst that of DWS was slightly basic and that of OMW was acidic (Table 1). Additionally, it must be stressed here that DWS, OMW and PMS were mainly organic amendments with consequently high TOC values, i.e. in the range of 16–49 % d.w. However, the SF amendment is an inorganic material with very low organic matter content. Total metal concentrations in the amendments were varied.

The highest metal contents were found in the paper mill sludge, i.e. 42 mg Pb kg^{-1}, 201 mg Zn kg^{-1} and 65 mg Cu kg^{-1}, and the lowest were found in sugar foam and the olive mill waste, i.e. 5–18 mg Pb kg^{-1}, 7–19 mg Zn kg^{-1} and 3–17 mg Cu kg^{-1}. The relatively high concentrations of Zn and Cu in the paper mill sludge are also noteworthy; nevertheless, these were in the same range as those previously reported for this kind of waste (Calace et al. 2005). Pb availability was low for all the amendments based on EDTA-extractable metals (0–22 % of the total Pb), while Zn and Cu were more available (11–79 % of the total Zn and 0–79 % of the total Cu, Table 1), specially for the OMW amendment; the lowest metal availability values were found for SF.

Chemical assessment of metal immobilisation

As pointed out above, chemical assessment of metal immobilisation brought about by amendments was made by means of an incubation test. Tables 2 and 3 show EDTA-extractable Pb, Zn and Cu concentrations, corresponding to the beginning and the end of the experiment, and final pH values for the SQ1 (arable land) and SQ2 (tailings) mine soils.

All the amendments caused significant decreases in ($p<0.05$) EDTA-extractable Pb, Zn and Cu concentrations, both in SQ1 and SQ2 soils (with the exception of Cu for olive mill waste in the SQ1 soil). Moreover, those decreases were greater than the weight percentage of amendment used in each case, thus proving the immobilisation capability of the amendments tested. In general, all the amendments decreased metal availability to a higher extent for mine tailings (SQ2 soil); this trend was parallel to the higher changes in soil pH for the mine tailings sample (from 3.6 to a range of 5.2–11.0, depending on the amendment) compared to those of the arable SQ1 soil (from 6.4 to 7.5–11.5, depending on the amendment) (Tables 2 and 3).

Table 2 Effect of amendments on pH and EDTA-extractable metal concentrations (mg kg^{-1}) after 45 days of incubation

	pH day 45	Pb		Zn		Cu	
		Day 0	Day 45	Day 0	Day 45	Day 0	Day 45
Control	6.4	690±109a	654±75a	73.6±15.7a	76.0±13.5a	6.45±1.01a	5.79±0.50a
SF (10 %)	11.5	22.2±13.8c	n.d.	0.04±0.06c	n.d.	1.05±0.05c	0.34±0.01c
PMS (30 %)	8.0	245±33b	336±21c	41.4±1.7b	32.1±0.4c	5.56±0.20a	4.56±0.40b
DWS (15 %)	7.6	675±49a	432±21c	60.6±1.1a	15.6±0.2d	3.94±0.45b	3.23±1.25b
OMW (15 %)	7.5	539±6a	518±2b	63.0±1.3a	57.2±0.1b	7.25±0.03a	5.67±0.23a

Mine soil SQ1 (arable land). Different letters denote statistically significant differences

SF sugar foam waste, *PMS* paper mill sludge, *DWS* drinking water treatment sludge, *OMW* olive mill waste

The highest level of immobilisation overall for all the metals and soils was achieved with sugar foam, with which EDTA-extractable metal reductions from 78 to 100 % were obtained; only paper mill sludge obtained better results than SF for Zn in SQ2, but this can mainly be put down to the higher percentage of amendment used. These results are in keeping with those previously reported by other authors (Bleeker et al. 2003; Campbell et al. 2006; Garrido et al. 2006; Moraza et al. 2006). As stated above, there are important amounts of calcium carbonate in sugar foam (Garrido et al. 2003), and liming compounds are generally effective in immobilising metals in soils, mainly because the soil pH rises (Bolan et al. 2014; Moraza et al. 2006; Kumpiene et al. 2008). So, the significant rise observed in soil pH (from 6.4 to 11.5 and from 3.6 to 11 for the SQ1 and SQ2 soils, respectively, Tables 2 and 3) would have resulted in precipitation of metals and a subsequent fall in EDTA-extractable metals. It seems reasonable to expect that the aforementioned process was the main mechanism involved in metal immobilisation here. Nevertheless, other contributing factors such as metals association with the Al-hydroxy polymers, produced from hydrolysis of the Al^{3+} exchanged by Ca^{2+}, cannot be disregarded (Garrido et al. 2006).

Drinking water treatment sludge (DWS) was the organic amendment that performed best for metal immobilisation in the agricultural soil SQ1, although its effectiveness in the SQ2 soil was also high. The order of metal mobility reduction was Zn > Cu > Pb, and there were EDTA-extractable Zn decreases of 79 and 73 % for the SQ1 and SQ2 soils, respectively (Tables 2 and 3). This slightly basic amendment led to a rise in pH in both soils, especially for SQ2 soil (from 3.6 to 7.5), which can be put down to the high content of DWS in Al hydroxide (Garau et al. 2014). Several authors have shown that water treatment residuals amendments are capable of reducing Pb, Zn and Cu mobility in soils by the complexation of metals on the surface of Al oxy-hydroxides and organic matter (Garau et al. 2014; Wang et al. 2012).

The addition of paper mill sludge (PMS) to the polluted soils studied here induced a significant decrease in mobile forms of Pb, Zn and Cu, with decreases from 21 % (Cu in the SQ1 soil) to 87 % (Zn in the SQ2 soil) which can be put down to the presence of organic matter, Al silicates and carbonates (Battaglia et al. 2007; Calace et al. 2005). The PMS sample used here contained a significant amount of inorganic carbon (3.9 %, Table 1), showing that carbonates played a key role in raising the pH observed in both polluted soils (Tables 2 and 3).

Olive mill waste (OMW) caused significant decreases ($p<0.05$) in metal mobility in the two polluted soils used here, apart from Cu in the SQ1 soil (Tables 2 and 3). This latter finding may be explained by the high mobility of Cu in this amendment (Table 1); for the same reason, there was only a

Table 3 Effect of amendments on pH and EDTA-extractable metal concentrations (mg kg^{-1}) after 45 days of incubation

	pH Day 45	Pb		Zn		Cu	
		Day 0	Day 45	Day 0	Day 45	Day 0	Day 45
Control	3.6	7049±965a	6094±117a	295±46a	256±45a	8.68±3.94a	7.53±2.62a
SF (10 %)	11.0	113±41d	0.09±0.01e	90.3±0.1d	55.4±1.8d	0.17±0.02b	n.d.
PMS (30 %)	5.2	6030±117b	2783±124c	213±50b	32.3±2.1e	10.8±2.2a	3.21±0.50b
DWS (15 %)	7.5	6489±130a	4124±235b	219±3b	69.0±1.4b	7.52±0.12a	3.14±1.23b
OMW (15 %)	5.9	2315±81c	876±1d	170±15c	62.3±1.2c	7.73±1.02a	2.37±1.28b

Mine soil SQ2 (mine tailings). Different letters denote statistically significant differences

SF sugar foam waste, *PMS* paper mill sludge, *DWS* drinking water treatment sludge, *OMW* olive mill waste slight decrease in Zn mobility in the SQ1 soil. The best results were found for Pb and Zn in the mine tailings soil, where reductions of 86 and 76 % of Pb EDTA-extractable and Zn EDTA-extractable concentrations were achieved, respectively. Metals immobilisation here could be mainly explained by the complexation of metals with the OMW amendment organic matter; nevertheless, other authors have stressed the influence of higher pH on Zn solubility in soils (Fornes et al. 2009). Here, the pH of the SQ2 soil was raised from 3.6 to 5.9 after incubation for 45 days.

Plant test to assess metal immobilisation

For the arable soil SQ1, the addition of every amendment led to statistically significant ($p<0.001$) decreases in shoot Pb and Zn concentrations in the *L. albus* plants grown in the amended soils with respect to the control soil (Fig. 1a). Pb concentrations were decreased between 3.6 and 5.6 times, while shoot Zn concentrations were between 1.7 and 2.8 times lower than those of the control soil plants. For the mine tailings soil SQ2, all the amendments significantly decreased ($p<0.001$) shoot Zn concentrations (from 2.1 to 2.7 times, Fig. 1b) compared to those of the control soil. The great standard deviation found for shoot Pb concentration in the control soil made it difficult to obtain statistically significant differences in Pb uptake. Therefore, only the concentration of Pb in lupine shoots was significantly decreased ($p<0.05$) for the OMS amendment; nevertheless, SF and DWS amendments led to decreases of mean concentrations of Pb in shoots (Fig. 1b). The mean values of Pb in shoots decreased from 1.9 to 5.5 times. Results of plant metal uptake previously documented by other authors are varied. Battaglia et al. (2007) found that the addition of paper mill sludge caused a reduction of Pb and Zn uptake by barley. Amendment of an alkaline agricultural soil with fresh OMW did not lead to a decrease of Zn and Pb concentrations in *Beta maritima* (de la Fuente et al. 2011), but this result was achieved by using the same waste for composting (de la Fuente et al. 2011; Fornes et al. 2009). Garau et al. (2014) documented a reduction in As accumulation in wheat shoots by amendment with water treatment residuals and Al-OH-based materials. The application of an industrial sugar residue (similar to our sugar foam) to a neutral mine soil significantly decreased root and shoot concentrations of Cu, Cd and Zn in roots and shoots and Pb in *Phaseolus vulgaris* and *Holcus lanatus*. Lastly, in the review by Gadepalle et al. (2007), other results were documented both supporting and contradicting the reduction of metal uptake and accumulation by plants after soil amendment with organic-based materials. It seems clear that the effect of each amendment on metal availability and plant uptake is dependent on both the specific physical chemical properties of the soil and the plant type, so the application of amendments should be carefully assessed in each case.

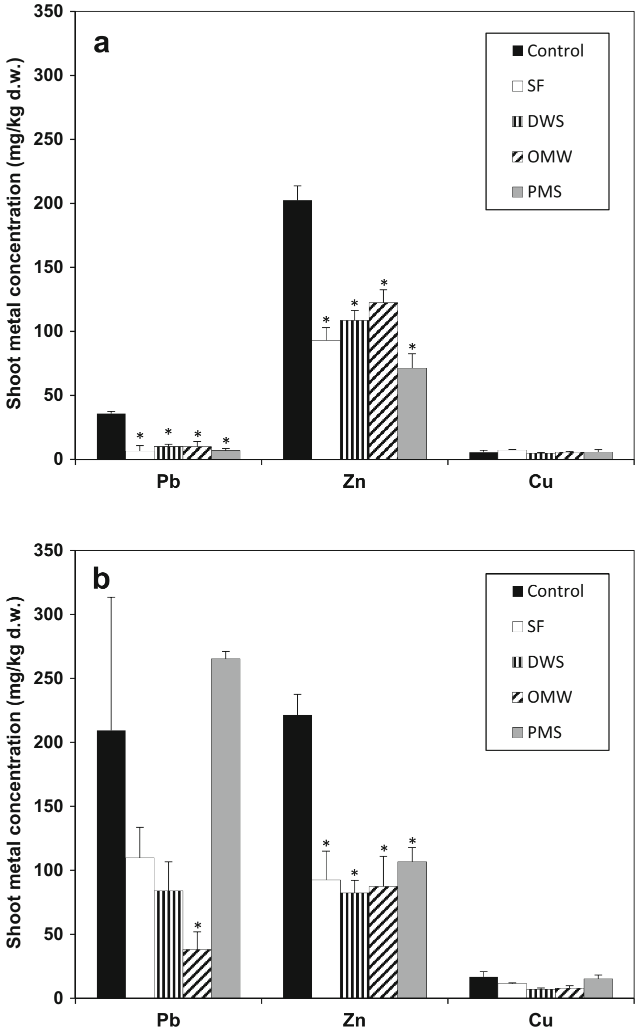

Fig. 1 Effect of amendments on plant metal uptake: shoot metal concentrations. **a** Mine soil SQ1. **b** Mine tailings SQ2. *Asterisk* denote statistically significant differences

Lastly, Cu uptake by *L. albus* was not influenced by adding an amendment to either soil (Figs. 1 and 2), with shoot Cu concentrations being much lower than those of Zn. In a previous paper, we documented lower Cu uptake by different crop plants from the soils of the same mining area compared to those of Zn and Pb (Ruiz et al. 2009), as firstly, there was low concentration of Cu in the soil and, secondly, the antagonistic Zn/Cu interaction could cause Cu uptake to be low when Zn soil concentrations were high, such as what occurred in our case (Bose and Bhattacharyya 2008; Bose et al. 2008; Kabata-Pendias 2000).

Bioavailability of metals under field conditions, i.e. the potential for living organisms to absorb chemicals from polluted soils, has been studied by many researchers (Bolan et al. 2014). Both chemical extractions and bioassays tests have been used to assess this parameter. A large number of chemical extractants have been used in order to estimate trace metal availability in the soil ($CaCl_2$, NH_4NO_3, NH_4OAc, DTPA, EDTA); however, the results have been diverse, and to date,

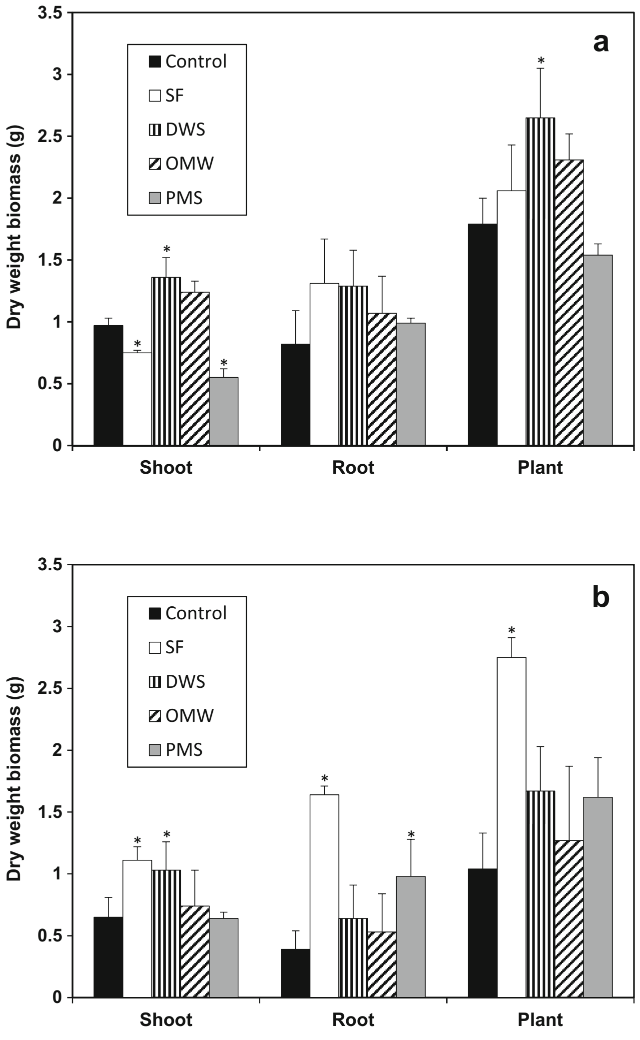

Fig. 2 Effect of amendments on dry plant biomass. **a** Mine soil SQ1. **b** Mine tailings SQ2. *Asterisk* denote statistically significant differences

there is not a general consensus about the most suitable extractant for determining metal availability in soils (Anjos et al. 2012; Lago-Vila et al. 2014). In a previous paper, we reported that both single extractions with EDTA or $CaCl_2$ and the BCR sequential extraction were useful methods to assess Pb and Zn phytoavailability in soils from the San Quintín mining area (Ruiz et al. 2009). Taking into account those results, we decided to select EDTA as the chemical extractant to be used in this study. Thus, a statistically significant correlation was found between concentrations of Pb and Zn in the *L. albus* shoots (Fig. 1) and EDTA-extractable metal concentrations in the corresponding soils (Tables 2 and 3) after the incubation experiments (Pearson's coefficient $R=0.701$ and $p<0.05$, for Pb, and Pearson's coefficient $R=0.754$ and $p<0.05$, for Zn). Therefore, it has been shown that, in the soils being researched and for *L. albus*, the decrease in EDTA-extractable metals found in the incubation tests was reflected in the amount of metal uptake by plants. This correlation between metals extracted by EDTA and plant metal contents, specifically with the plant available fractions of Cd, Cu, Ni, Pb, Mn and Zn, was previously documented by several authors (Alvarez et al. 2006; Brun et al. 2001; Quevauviller et al. 1996; Ruiz et al. 2009). Nevertheless, this is not a general conclusion in the study of the relationship between chemical and bioassay tests; because of the complexity of both metal-organism and metal-soil interactions, chemical methods can provide, at best, only an estimate of metal availability to plants and animals (Bolan et al. 2014).

Apart from metal uptake, the addition of amendments to the polluted soils led to changes in the amount of biomass produced by *L. albus*. Shoot, root and total plant biomass values reached by lupine plants in both amended and unamended soils are shown in Fig. 2. In a preliminary view, it can be seen that the mean values of total plant biomass were increased after adding the SF, DWS and PMS amendments; shoot and root biomass mean values also seemed to be in keeping with this general trend. However, a more detailed analysis of the results must be carried out in order to differentiate between the different amendments used.

Among the different factors influencing plant growth in our experiments, there are three of special importance, i.e. soil pH, soil organic matter content and plant metal uptake. The lower lupine biomass obtained in the extremely acidic SQ2 unamended soil with respect to that of the arable land SQ1 soil that illustrated the negative effect of an extremely low pH on plant performance, which strongly agrees with the findings reported by Castaldi et al. (2005). The lower soil metal concentrations in both unamended and amended SQ1 soils with respect to those of the SQ2 soils, and the subsequent lower uptake by plants, explain why in general plant performance was better in the former than the latter (Fig. 2).

As documented by many authors (Gadepalle et al. 2007), the addition of organic amendments should be accompanied by a performance improvement in plant biomass. In our case, the use of DWS and OMW led to a general increase in shoot, root and total plant biomass with respect to those of the control for both soils studied (Fig. 2); some of them were statistically significant ($p<0.05$), e.g. for shoot biomass in both soils and total plant yield for the SQ1 soil after adding DWS or shoot biomass for the SQ1 soil after adding OMW. This latter result contrasts with another previously documented by De la Fuente et al. (de la Fuente et al. 2011) who found that fresh solid alperujo had negative effects on the growth of *B. maritima* in amended metal polluted soils due to the high concentration of phenolic compounds in this material; in our case, that negative effect could have been offset with a lower metal uptake by the plants. Amendment with paper mill sludge increased plant growth for SQ2 but significantly decreased shoot biomass in SQ1. These findings are consistent with those found with sugar foam where there was a significant decrease in shoot biomass for the SQ1 soil but marked increases in shoot, root and total plant yields for the SQ2 soil. This can only be explained by taking into account that *L. albus* is a plant that grows better in acidic soils (Lopez-Bellido and Fuente 1986); thus, the basic pH reached after the addition of the SF and, to a lesser extent, PMS amendments to the SQ1 soil could have adverse effects on lupine growth. However, this effect had been balanced in the SQ2 soils by a fall in metal toxicity and the lower pH values reached (Castaldi et al. 2005).

Conclusions

Our results showed that the application of different organic and inorganic amendments based on by-products and waste materials is a feasible alternative for the restoration of soils around abandoned metal mines. This has been demonstrated by means of two different approaches: a chemical one, using extraction with EDTA, and a biological one, measuring metal accumulation in the shoots of white lupine plants. An incubation test showed that most of the amendments studied were capable—to a greater or lesser extent—of decreasing EDTA-extractable Pb and Zn concentrations, both in the agricultural SQ1 soil and mine tailings SQ2 soil. The impact of that decrease for mine tailings was related to the higher changes in soil pH compared to those of the arable SQ1 soil. As expected, those changes in metal availability and pH went hand in hand with lower metal accumulation in the *L. albus* shoots. Moreover, the results from chemical extraction and from plant tests were significantly correlated thereby showing the viability of EDTA extraction to simulate metal availability in polluted soils. Lastly, plant growth was, in general, enhanced by the amendments used for plant tests, apart from certain specific features of each amendment and soil type.

Sugar foam, drinking water treatment sludge, paper mill sludge and wastes coming from the olive mill industry are low-cost materials that can be used for restoring large areas polluted by mining activities in a cost-effective manner. Nevertheless, before considering a real restoration project, more research is necessary in order to assess the performance of those amendments in the long term.

Acknowledgments The financial support by the Government of Castilla-La Mancha (project PAI08-0256-7534) is greatly appreciated.

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