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1 **Highlights**

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3 *Some of amendments increased the pH of leachates to values around neutrality*

4 *Metal leaching was reduced by the amendments reaching overall decreases of 36-100%*

5 *The effects on leachate pH and metal release was kept throughout a 1 year period*

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**PERFORMANCE OF WASTE-BASED AMENDMENTS TO REDUCE METAL
RELEASE FROM MINE TAILINGS: ONE-YEAR LEACHING BEHAVIOUR**

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2 **ABSTRACT**
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7 4 A one-year leaching experiment has been conducted in order to assess the effectiveness
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9 5 of several amendments on metal immobilization in mine tailings from an old Pb/Zn
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11 6 mining area of Central Spain (San Quintín mine). Demineralized water was used as
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13 7 leaching solution, selecting doses equivalent to the annual rainfall conditions of the
14
15 8 studied area. Columns with mine tailings without any amendment and others treated
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17 9 with 10% of sugar foam (SF), 15% of drinking water treatment sludge (DWS), 30% of
18
19 10 paper mill sludge (PMS) and 15% of olive mill waste (OMW) were used. SF, DWS and
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21 11 PMS amendments increased the pH of leachates from values of approximately 4 to
22
23 12 around neutrality. Additionally, the release of sulfate ions from the oxidation of pyritic
24
25 13 residues was decreased in some extent by SF and DWS amendments. Metal leaching
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27 14 was effectively reduced by the amendments reaching overall decreases with respect to
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29 15 the unamended columns of 79-96% for Pb, 36-100% for Zn, 50-99% for Cu and 44-
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31 16 100% for Cd. The effect of the amendments in leachate pH, sulfate concentration and
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33 17 metal release from mine tailings was kept throughout the whole experimental period.
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35 18 Our results showed that the application of different organic and inorganic amendments
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37 19 based on by-products and waste materials may be a feasible alternative for the
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39 20 restoration of soils around abandoned metal mines.
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55 24 **Keywords:** soil pollution, metals, immobilization, amendments, metal leaching
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1 **1. INTRODUCTION**

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5 3 One of the most important metal mining areas of Spain in the late 19th and early
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7 4 20th century was the Alcludian district (Palero-Fernández and Martín-Izard 2005). It is
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10 5 located in the southern central part of the Iberian Peninsula, located approximately 250
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12 6 km south of Madrid, and includes an area of approximately 2500 km². Among the
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14 7 hundreds of mines exploited for obtaining lead, zinc and silver, the San Quintín mine
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16 8 was the most important in terms of metal production and surface covered. The mining
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18 9 activities were abandoned more than thirty years ago but, currently, a huge amount of
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20 10 mine tailings remains exposed, and without any treatment, covering an area of around
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22 11 600,000 m². The severe landscape impact caused by the tailings and the spreading of
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24 12 metal pollution (mainly due to aeolian transport and acidic mine drainage generation) to
25
26 13 the soils of the adjacent agricultural and pasture lands have been reported elsewhere
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28 14 (Rodríguez et al. 2009; Higuera et al. 2012; Martín-Crespo et al. 2015). Those previous
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30 15 works have emphasized the need to take urgent action to reduce the environmental risks
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32 16 for ecosystems and humans in the surrounding areas.
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43 18 The restoration of abandoned metal mining sites by means of *in situ* adding of soil
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45 19 amendments has been proposed as a simple and sustainable technology to reduce the
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47 20 environmental hazards derived from these type of affected sites, which usually involve
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49 21 large areas (Pardo et al. 2014; Brown and Chaney 2016). The purpose of these
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51 22 amendments is to reduce the availability of metals in soils and, therefore, its migration
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53 23 to other environmental compartments such as ground-water, surface waters and plants.
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55 24 There have been numerous organic and inorganic materials which have been studied,
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57 25 both in greenhouse and field trials, as amendments for polluted soils (see reviews by
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1 Gadepalle et al. (2007) and Bolan et al. (2014)) but, among them, those based on wastes
2 or by-products are specially interesting because their low cost and their positive
3 contribution to circular economy. In the context of mine restoration, organic
4 amendments including animal manures, municipal biosolids, composts and pulp sludge
5 have been extensively studied mainly due to their high organic content, which aids to
6 support sustainable vegetal covers in the disturbed soils. Inorganic wastes such as flying
7 ashes, aluminium-processing residuals, sludge from drinking water facilities and sugar
8 beet lime may be also cited as efficient materials to balance the low pH of the mining
9 tailings with high contents of pyrite susceptible to generate acidic mine drainage
10 (AMD) (Brown and Chaney 2016). However, it is not only relevant to assess the
11 effectiveness of amendments on metal immobilization but also to prove the duration of
12 the treatment. In other words, it is needed to know whether metals remain stable in
13 unavailable fractions after immobilization treatment or, conversely, they can be
14 remobilized with time by natural weathering processes. A few studies assessing the
15 long-term efficiency of immobilization by organic and liming amendments have been
16 conducted (Kumpiene et al. 2007; Pérez-López et al. 2007; Ruttens et al. 2010;
17 Rodríguez-Jordá et al. 2012; Kumpiene et al. 2013; Santos et al. 2014) but, as it was
18 concluded in the abovementioned review by Bolan et al. (2014), additional research is
19 necessary to more clearly state if remediation by immobilization is a technique that
20 requires, or not, repeated additions of amendments.

21
22 In a previous paper (Rodríguez et al. 2016), we reported the effectiveness of sugar
23 foam (sugar beet lime), olive mill waste, drinking water treatment sludge and paper mill
24 sludge to decrease Pb and Zn availability in both agricultural soils and mine tailings
25 from San Quintín mine area. That conclusion was supported by the reduction of the

1 EDTA-extractable concentration of metals in soil after a 45-days incubation experiment
2 and the decrease on metal uptake by lupine plants grown during 8 weeks in the amended
3 soils. In this paper, we have assessed the long-term effectiveness of the abovementioned
4 amendments for metal availability reduction in mine tailings from the San Quintín mine
5 by means of a 1-year leaching experiment. For this purpose, we have simulated the
6 exposition of both amended and unamended tailings to the rainfall conditions of the San
7 Quintín mine area recording AMD generation and metal leaching over a period of one
8 year.

10 **2. MATERIALS AND METHODS**

12 ***2.1. Material characterization***

14 The mine tailings sample used in this experiment was taken from a former
15 sedimentation pond (0389462, 4297663 UTM) of the San Quintín Pb-Zn mine. We used
16 a composite sample coming from four sampling points located in the vertices of a
17 square of 3 m edge. Mine tailings were sampled at a depth of 0-25 cm, air-dried at room
18 temperature for 7 days and, finally, sieved to <2 mm and <63 µm. The 2-mm fraction
19 was used in the leaching experiments and for the measurement of the physicochemical
20 properties of the soil, while the 63-µm fraction was used to analyse the total and EDTA-
21 extractable metal concentrations.

23 Four waste-based materials were used as amendments: sugar foam (SF, a lime-rich
24 waste generated in the production of sugar from beet), drinking water treatment sludge
25 (DWS, an organic waste coming from a drinking water treatment facility which uses

1 aluminium sulfate as coagulant), olive mill waste (OMW, a lignocellulosic by-product
2 of the olive oil production) and paper mill sludge (PMS, an organic waste with silicates
3 and carbonates coming from the pulp and paper-making process). All of them were
4 selected based on the literature (Calace et al. 2005; Garrido et al. 2005; Gadepalle et al.
5 2007; Albuquerque et al. 2011; Wang et al. 2012) and had been tested for metal
6 immobilization in a previous research carried out by us (Rodríguez et al. 2016). All of
7 these amendments were obtained from local or national companies.

8
9 pH of the amendments was measured in a 1:5 soil/water (w:v) mixture; total
10 organic carbon (TOC) and inorganic carbon were analysed by means a TOC analyser
11 (Shimadzu TOC-VCSH, Columbia, USA); particle-size distribution (clay, silt and sand
12 content) was determined using laser diffractometry (Beckman Coulter LS, Fullerton,
13 USA). Major elements were determined by means of a commercial handheld XRF
14 analyser (Niton XL3t, Thermo Scientific, Tewksbury, USA) following the USEPA
15 method 6200; accuracy of the measures was assessed using the certified standards NIST
16 2710 and 2711. The EPA 3051A method was used to digest the solid samples (<63µm
17 fraction) before the analysis of total Pb, Zn, Cd an Cu concentrations; 0.5 g of sample
18 were digested with a mixture of acids (9 mL of concentrated HNO₃ + 3 mL of
19 concentrated HCl) using a microwave oven (CEM MARS 5, Matthews, USA). EDTA-
20 extractable metal concentrations in mine tailings before the leaching experiment were
21 determined by extracting the samples (<63µm fraction) with 0.01 M EDTA, using a
22 contact time of 16 h and a soil:extractant ratio of 1:10 (w:v). All digestions and
23 extractions were carried out in triplicate. Concentrations of Pb, Zn, Cd and Cu in the
24 extracts were analysed by means of ICP-AES using a Thermo ICAP 6500 spectrometer
25 (Thermo Electron, Cambridge, UK). The quality of metal analysis was checked by

1 analysing the Montana Soil 2711 certified reference material (LGC Promochem,
2 Barcelona, Spain).

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4 Qualitative mineralogical analysis of mine tailings and amendments were carried out
5 by X-ray diffraction (XRD) using semi-quantitative analysis by the Schultz's method
6 (with this method the uncertainty in the quantification can be up to 15%). Bulk
7 mineralogy was determined using the polycrystalline disoriented powder method after
8 sample grinding and homogenizing in an automatic agate mortar and sieving to <0.053
9 mm. X-ray diffractograms were carried out with a PANalytical® diffractometer, X'Pert
10 Pro model, equipped with an X'celerator detector, using CuK α radiation, a 45 Kv
11 accelerating voltage and a 40 mA current. Scanning electron microscopy (SEM) images
12 of the mine tailings, amendments and mixtures were taken using a FEI Quanta 250
13 microscope (Oregon, USA), coupled to an EDAX Apollo X EDS detector (Energy
14 Dispersive Spectroscopy) for microelemental analysis.

16 ***2.2. Leaching experiments***

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Leaching experiments were carried out using 50 mm-diameter polystyrene columns,
with a 0.45 μ m polyethersulfone filter in the bottom, coupled to 150 mL plastic flasks
where the leachate was collected. Five different series of columns were prepared, i.e.
unamended mine tailings (control) and mine tailings amended with the four waste
materials previously described. Control columns consisted of only 110 g d.w. of the
mine tailings sample. The amended mixtures were made by thoroughly mixing the mine
tailings sample with the corresponding amount of amendment to reach 110 g d.w. of

1 amended soil with the following percentages in weight: 10% for sugar foam (SF), 30%
2 for paper mill sludge (PMS) and 15% for drinking water sludge (DWS) and olive mill
3 waste (OMW). Those percentages were based on previous literature (Gadepalle et al.
4 2007) and they were the same used in our previous research (Rodríguez et al. 2016). All
5 the treatments were carried out in triplicate.

7 The columns were left in the dark at room temperature ($25^{\circ}\text{C} \pm 3$) one week to
8 equilibrate at a humidity corresponding to the water holding capacity of the soil
9 mixture. Next, 50 mL of Millipore MQ water were applied weekly to the top of the
10 columns using a pipette; this volume corresponds approximately to the annual rainfall
11 of the studied area (450 mm). In order to simulate the characteristic dry periods that
12 occur in the summers of central Spain, no water was added between days 90 and 181.
13 The leachates were collected weekly but they were only analysed in specific days: 0, 20,
14 34, 63, 90, 181, 209, 237, 265, 314 and 356. The columns were kept in the dark at room
15 temperature between successive water additions in order to inhibit algal growth.

17 pH and electrical conductivity of the leachate samples were measured immediately
18 using the corresponding electrodes. Later, a fraction of the leachate was analysed to
19 determine dissolved organic carbon (DOC) and sulfate concentrations. The rest of the
20 leachate was stabilized by adding HNO_3 Suprapur (5%) and stored at 4°C in
21 polyethylene tubes until metal analysis. DOC was measured using the abovementioned
22 TOC analyser (Shimadzu TOC-VCSH, Columbia, USA). Sulfate ion concentration was
23 analysed by ion chromatography using an 883 Basic IC Plus chromatograph equipped
24 with a Metrosep A Supp 5 column (Metrohm, Herisau, Switzerland). Concentration of

Pb, Zn, Cd and Cu in leachates was measured as described in Section 2.1 for the mine tailings and amendment extracts.

2.3. Statistical analysis

All statistical analyses were carried out with the IBM SPSS Statistics program version 22.0. Normality of the data was previously checked by using the Kolmogorov-Smirnov test. Spearman's correlation coefficient was used to measure the correlation between the different physicochemical parameters of the leachates.

3. RESULTS AND DISCUSSION

3.1. Characterization of mine tailings and amendments

TABLE 1

The main physicochemical properties of the mine tailings sample are shown in Table 1. The texture of the sample corresponded to a loamy soil. It had an acid pH of 4.1, probably due to the oxidation of the residual pyritic materials in the mine pond and the subsequent acidification. The X-ray Diffraction (XRD) analysis gave as a result a mineralogical composition of quartz, gypsum and illite as main components, with trace amounts of chlorite and beudandite. Regarding chemical composition in major elements, the high content of Si and, in a minor extent, of Al, is in agreement with the

1 presence of quartz and the aluminosilicates (illite and chlorite) detected by XRD. The
2 relatively high concentration of Ca and S is compatible with the presence of gypsum,
3 while Fe would be associated to beudandite and other pyritic phases. However, primary
4 ore materials (sphalerite and galena) and pyritic minerals were not present in
5 concentration enough to be detected by XRD; it may be attributed to the optimized
6 works carried out in the last years of mining operation (Martín-Crespo et al. 2015). As
7 expected, the organic matter content of the mine tailings sample was extremely low
8 while the total concentrations of Pb, Zn, Cd and Cu were very high, especially those
9 corresponding to the two first metals. Likewise, Pb availability was high with EDTA
10 extractable Pb concentration accounting for 77% of the total Pb. Zn and Cd showed a
11 moderate availability in terms of EDTA-extractable concentrations, while the
12 availability of Cu was low. Concentrations of metal and major elements were similar to
13 those reported by Martín-Crespo et al. (2015) for mine tailings from the San Quintín
14 mine.

16 Sugar foam had a strongly basic pH as expected due to its high concentration of
17 lime, as indicated by its high content of Ca and inorganic carbon (Table 1). Paper mill
18 (PMS) and drinking water (DWS) sludge samples showed moderately basic pH values,
19 while the waste coming from olive oil production (OMW) had an acidic pH; likewise,
20 those later amendments, conversely to SF, had moderate to high concentrations of
21 organic matter, i.e. TOC values in the range 16-49 % d.w. (Table 1). Regarding major
22 elements, sugar foam had a high concentration of Ca (46.9%) according to its mineral
23 composition (determined by DRX), which mainly consisted of calcite with trace
24 amounts of portlandite. PMS had also a high content of Ca (25.8%) which can be
25 essentially attributed to carbonates and silicates (Calace et al. 2005; Battaglia et al.

1 2007); DRX analysis showed that magnesium calcite was the main mineral phase with
2 trace amounts of kaolinite and diaspore. DWS had a high concentration of Al and Fe,
3 i.e. 6.96 and 14.0% respectively, due to the coagulant used in the drinking water
4 treatment plant from which it came (aluminium sulfate) and the precipitation of iron and
5 manganese ions in the coagulation-flocculation process; however, those chemical
6 compounds would be present as amorphous compounds, since only traces of dolomite
7 were detected by X-ray diffraction. OMW was essentially an organic waste composed
8 of lignocellulosic compounds and with a high content in potassium (De la Fuente et al.
9 2011).

10
11 Total metal concentrations of the SF, OMW and DWS amendments were low with
12 values in the ranges 5.0-37.3 mg Pb kg⁻¹, 6.52-52.5 mg Zn kg⁻¹ and 2.4-17.0 mg Cu kg⁻¹;
13 Cd was only detected, in a very low concentration, for DWS. PMS had relatively high
14 concentrations of Pb, Zn and Cu but they were in the same range as those previously
15 reported for this type of waste by Calace et al. (2005). Availability of metals in the
16 amendments was, in general, moderate or low, with the exception of OMW which
17 showed high percentages of EDTA-extractable Zn and Cu (Table 1).

18 19 ***3.2. Changes in leachate pH, sulfate and DOC***

20 21 **FIGURE 1**

22
23 Seven days after the addition of the amendments, pH of the leachates from the
24 amended columns was significantly increased respect to the unamended one (Figure 1).
25 While initial pH of the leachate from the untreated mine tailings was 3.7, the initial pH

1 values of the leachates from the amended tailings corresponded approximately to those
2 of the amendments (Table 1), with SF and OMW resulting in the highest (12.0) and the
3 lowest (5.9) values, respectively. The evolution of the leachate pH after the successive
4 water additions was different for each treatment. pH of the leachate from the
5 unamended mine tailings was kept in an approximately constant value around 4.0 in the
6 first 209 days but, after that, it was gradually increased to a final value of 4.8 (Figure
7 1A). This final increase of pH coincided with a significant decrease in the leachate
8 sulfate concentrations (Figure 1B), indicating the exhaustion of the pyritic materials
9 oxidation. In spite of the high initial pH of the leachate from the sugar foam-amended
10 column, it was gradually decreased from day 20 due to the consumption of the calcium
11 carbonate and/or lime with the generated acid leachates (Santos et al. 2014). Finally, the
12 pH was stabilized near to neutral values from day 209 (coinciding with the depletion of
13 sulfide oxidation in the unamended column) until the end of the experiment (Figure
14 1A). pH of the leachate from the column amended with drinking water sludge was kept
15 approximately constant in values around the neutrality (6.3-7.5) throughout the whole
16 experiment (Figure 1A); it may be attributed to the neutralizing effect of both calcium
17 carbonate and Fe and Al hydroxides (Komarek et al. 2013; Rodríguez et al. 2016). The
18 evolution of pH in the leachates from the PMS-amended column was decreasing in the
19 first 34 days (Figure 1A), probably due to the release of organic acids from the organic
20 matter (according to the high concentrations of DOC detected in the leachate, Figure
21 1D), but after that, it was gradually increased reaching values around 7.5 until the end of
22 the experiment. Again, the buffering capacity of carbonates was probably the
23 responsible of the rise in leachate pH (Calace et al. 2005). Finally, olive mill waste was
24 not capable to neutralize the acidification of the leachates whose pH values were even
25 lower than those of the unamended mine tailings in the last 100 days of the experiment

1 (Figure 1A); it points out that the oxidation of pyritic materials was not avoided by this
2 amendment.

3
4 Sulfate concentration of the leachates coming from the unamended mine tailings
5 column had an initial value of 1633 mg L⁻¹ and it was sharply decreased in the first 34
6 days (Figure 1B). Afterwards, it increased and was kept at an approximately constant
7 value of 1250 mg L⁻¹ until day 237; finally, sulfate production decreased, reaching a
8 final value of 185 mg L⁻¹. The initial high value of sulfate concentration and its
9 subsequent decrease in leachates may be attributed to the partial solution of gypsum
10 minerals (Garrido et al. 2005); next, when the oxidation rate of the pyritic materials in
11 the experimental column reached an enough level, sulfate concentration was increased
12 and kept in a constant value until the exhaustion of the pyritic materials in the sample.
13 pH and sulfate concentration of the leachate from the unamended column was
14 negatively correlated (Spearman correlation coefficient, $r_s = -0.457$, $p < 0.05$), indicating
15 the strong relationship between the oxidation of pyritic materials and leachate pH in the
16 mine tailings sample. However, this pattern was significantly changed by the addition of
17 SF and DWS; in spite of the leachates had high sulfate concentrations at the start of the
18 experiment, they decreased reaching a steady state after 63 days, with values of sulfate
19 concentration approximately 40% lower than those of the unamended columns (Figure
20 1B). The low concentration of sulfate in the leachate from the SF-amended column
21 would be due to the precipitation of calcium sulphate (Simón et al. 2010) or,
22 alternatively, to the precipitation of Fe oxyhydroxides over pyrite grains which could
23 inhibit its oxidation (Pérez-Lopez et al. 2007). In the case of DWS amendment, the
24 reduction of SO₄²⁻ in the leachates may be attributed to its complexation onto the Al and
25 Fe oxides surface (Macris et al. 2006; Komarek et al. 2013). The pattern of sulfate

1 concentration in the leachates from the PMS-amended columns is quite similar to that of
2 the unamended ones, with the exception of the period between days 63 and 90, in which
3 the pyrite oxidation was probably balanced by the precipitation of sulfate by Ca^{2+}
4 cations from magnesium calcite (Figure 1B). Finally, the concentration of sulfate in the
5 leachates from the OMW-amended columns was higher than that of the unamended
6 columns; it may be attributed, on one hand, to the inability of that amendment to avoid
7 pyrite oxidation (as pointed out by the low pH values) and, on the other hand, by the
8 release of sulfate ions from the own amendment, as suggests the fact that sulfate
9 concentration was kept in an approximately steady value until the end of the experiment
10 (and contrary to that observed for the other treatments, including the unamended
11 columns).

12
13 Temporal variation of electrical conductivity (EC) in the leachate from the different
14 treatments is shown in Figure 1C. EC of the leachates from the unamended columns
15 remained at a steady value of around $2000 \mu\text{S cm}^{-1}$ in the first 209 days of experiment,
16 next sharply decreasing to until $200 \mu\text{S cm}^{-1}$ in the day 314. Those values were in the
17 same range as those previously reported by Pérez-López et al. (2007), but are much
18 lower than those reported by other authors (Abreu et al. 2010; Santos et al. 2014); it
19 may be due to the low amount of pyritic material in the mine tailings sample used in this
20 study. The EC pattern strongly resembled to that of the sulfate; in fact, a statistically
21 significant positive correlation between EC and sulfate was found for the leachates from
22 the control columns ($r_s = 0.600$, $p < 0.001$). Amendments did not decrease the EC of
23 leachates from treated columns, which showed values similar or higher than those of the
24 unamended columns. The decrease in sulfate anions would be balanced by the release of
25 Ca, Mg and carbonates for SF and DWS amendments (Pérez-López et al. 2007; Navarro

1 and Martínez, 2010), while the release of low molecular weight organic acids also
2 contributed to the high EC values in the leachates from PMS and OMW-amended
3 columns. The last was supported by the high DOC values found for leachates coming
4 from the columns amended with OMW and PMS in the first half of the experiment
5 (Figure 1D). Moreover, a strong positive correlation between EC and DOC was found
6 for the PMS-amended columns ($r_s = 0.719$, $p < 0.001$) but not for the columns amended
7 with OMW. Nevertheless, the leachates coming from the column treated with this last
8 amendment had a dark brown colour indicative of the presence of soluble phenolic
9 substances (Albuquerque et al. 2006), which could be in part as ionic species
10 increasing EC. In spite of the high TOC concentration of the DWS amendment (Table
11 1), leachate DOC concentrations were much lower than those of OMW and PMS,
12 indicating the stability of the organic matter in this waste material. Lastly, as it was
13 expected, the leachates from both the unamended columns and those amended with SF
14 did not practically contain organic compounds (Figure 1D).

3.3. Changes in Pb, Zn, Cu and Cd leachate concentrations

FIGURE 2

TABLE 2

22 Lead and zinc were the metals released in higher concentrations in the leachates
23 from the unamended mine tailings (Figure 2), according with the main extracted ore
24 minerals (galena and sphalerite) in the San Quintín mine. More specifically, leachate
25 concentrations ranged from 1.45 to 2.99 and from 0.56 to 50.6 mg L⁻¹ for Pb and Zn,

1 respectively, which corresponded to 0.43 and 4.27 % of the total Pb and Zn,
2 respectively, in the mine tailings columns (Table 2). Copper and cadmium were also
3 released in the leachates but their concentrations were much lower, with values ranging
4 between 0.03 and 0.51 mg L⁻¹ for Cu and from non-detectable to 0.24 mg L⁻¹ for Cd; it
5 accounted for the 0.41 and the 3.85% of the initial total Cu and Cd, respectively, in the
6 mine tailings columns. It means that Zn and Cd water leachability was higher than those
7 of Pb and Cu, which is in agreement with our previous results about metal availability
8 in this mining area (Ruiz et al. 2009); nevertheless, it can be said that, from the point of
9 view of the total amounts released, Pb and Zn are the metals with the highest
10 environmental concern in the San Quintín mine area.

12 As it can be seen in Table 2, all the amendments used were capable to greatly reduce
13 the leaching of metals in the mine tailings throughout a period of a year. The decrease
14 of total metal release, as compared with the unamended columns, were in the ranges 79-
15 96% for Pb, 36-100% for Zn, 50-99% for Cu and 44-100% for Cd, showing the
16 effectiveness of the used amendments for avoiding metal leaching. The order of
17 effectiveness on metal immobilization was PMS>OMW>SF>DWS for Pb,
18 SF>PMS>DWS>OMW for Zn, DWS>PMS>OMW>SF for Cu and
19 SF>PMS>DWS>OMW for Cd. These results are in basic agreement with those
20 previously reported by us for an incubation experiment which used EDTA extractability
21 as a method to assess the effectiveness of metal immobilization (Rodríguez et al. 2016).
22 The mechanisms of immobilization were extensively discussed in that paper; on
23 summary, metals could be immobilized by precipitating the corresponding metal
24 hydroxides and/or carbonates at neutral to alkaline pHs (sugar foam and paper mill
25 sludge), by adsorption on Al oxy-hydroxides (sugar foam and drinking water treatment

1 sludge) and by complexation with organic matter (drinking water treatment sludge,
2 paper mill sludge and olive mill waste) (Calace et al. 2005; Garrido et al. 2005 and
3 2006; Rodríguez-Jordá et al. 2012; Wang et al. 2012; Bolan et al. 2014; Garau et al.
4 2014; Rodríguez et al. 2016). DRX analysis and scanning electron microscopy images
5 (SEM), coupled to energy dispersive spectrometry (EDS) for elemental micro analysis,
6 of the amended mine tailings after the leaching experiment did not yield any new data
7 that led us to confirm the abovementioned mechanisms of metal immobilization (Figure
8 S1 in supplementary data).

10 Zn, Cu and Cd concentration in the leachates from the unamended columns
11 decreased quickly in the first 34-90 days until a steady state was reached (Figure 2B, C
12 and D). In the case of Zn and Cu, the concentrations in the steady period were very low
13 or negligible. This two-phase time-dependent pattern was also observed by others
14 authors (Pérez-López et al. 2007; Fernández-Caliani and Barba-Brioso 2010;
15 Rodríguez-Jordá et al. 2012) in studies about Zn and Cu immobilization in mining
16 wastes. Pb followed a somewhat different trend, with a nearly constant concentration in
17 the range 2.21-3.00 mg L⁻¹ during the 265 first days and a further moderate decrease for
18 the last days of the experiment (Figure 2A); it may be due to the very high
19 concentration and availability of this metal in the mine tailings sample used. Moreover,
20 it is worth pointing out another effect derived from the non-application of irrigation
21 between days 90 and 181 in order to simulate a dry period (Section 2.2). As it can be
22 seen in Figure 2, the concentrations of all metals in the leachates increased in this period
23 to a greater or lesser extent; it showed that the oxidation of mine tailings and the
24 subsequent metal release is a dynamic process that needs enough time to carry out
25 (Fosberg et al. 2008). Moreover, a significant negative correlation between pH and

1 metal concentration in the leachates was found, indicating the relationship between acid
2 mine drainage generation and metal release ($r_{s,Pb} = -0.606$, $p < 0.001$; $r_{s,Zn} = -0.702$,
3 $p < 0.001$; $r_{s,Cu} = -0.705$, $p < 0.001$; $r_{s,Cd} = -0.456$, $p < 0.05$). It also highlights the continued
4 environmental hazards posed by uncontrolled mining dumps in the studied area. This
5 problem could be circumvented by the periodic addition of amendments.

6
7 The concentration of all metals in the leachates from the amended columns was kept
8 below the corresponding concentrations of the leachates from the unamended columns
9 throughout the whole experiment (Figure 2). It agrees with the results reported by other
10 authors for similar studies using different amendments (Calace et al. 2005; Pérez-López
11 et al. 2007; Rodríguez-Jordá et al. 2012). In general, sharp decreases in leachate metal
12 concentrations were already seen in the first water additions and they kept in low values
13 until the end of the experiment; it can be seen for SF and PMS amendments. However,
14 metal concentrations in the leachates from the DWS and OMW amended columns
15 exhibited some increases at different times throughout the experiment, e.g. Pb for DWS
16 and all metals for OMW. Although the concentrations of metals in leachates are difficult
17 to predict due to the complexity of solid-phase chemistry, the interaction with aqueous
18 solutions and the various physicochemical conditions (Santos et al. 2014), those
19 variations respect to the general pattern could be due, at least in part, to the
20 complexation of metals with dissolved organic acids, whose release from the organic
21 matter of amendments could create point increases in the metal concentrations of
22 leachates (Calace et al. 2005; Fosberg et al. 2008; Bolan et al. 2014; Santos et al. 2014).
23 The positive correlations found between Pb and DOC concentration for DWS
24 amendment ($r_s = -0.608$, $p < 0.001$) and between Pb and Cu concentrations and DOC ($r_{s,Pb}$
25 $= -0.687$, $p < 0.001$; $r_{s,Cu} = -0.898$, $p < 0.001$) seemed to support that hypothesis.

1 Nevertheless, some specific increases between days 90 and 181, e.g. Pb for DWS, Cu
2 and Cd for OMW, may be attributed to the replenishment of potentially soluble metals
3 during the dry period, as it was commented for the unamended columns.

4. CONCLUSIONS

7 Environmental hazard derived from uncontrolled mining dumps in abandoned mining
8 areas is an important problem that requires of cost-effective technologies to be
9 adequately driven. Metal immobilization through amendments based on waste materials
10 and agricultural or industrial by-products can be a viable alternative. One of the decisive
11 points in the application of this type of technologies is to know how much time metal
12 immobilization is effective after amendment addition. A one-year leaching experiment
13 was carried out in order to study the effectiveness of several amendments to reduce
14 metal release from mine tailings from an old Pb/Zn mining area in Central Spain. SF,
15 DWS and PMS amendments succeeded in increasing the pH of leachates from
16 approximately 4 to around neutrality and maintaining this effect during a full year. This
17 increase was accompanied by a lower release of sulfates coming from the oxidation of
18 pyritic materials for amendments SF and DWS. The amendments used here greatly
19 reduced the total leaching of metals as compared with the unamended mine tailings,
20 reaching decreases of 79-96%, 36-100%, 50-99% and 44-100% for Pb, Zn, Cu and Cd,
21 respectively. Moreover, that reduction in metal release was maintained for at least a
22 period of one year. Nevertheless, it must be taken into account that acid mine drainage
23 generation in pyritic mine tailings and the subsequent metal release is a uninterrupted
24 process that takes place as long as pyritic residual materials remain in the dumps. On
25 the overall, our results have demonstrated that sugar foam, drinking water treatment

1 sludge, paper mill sludge and olive mill waste are effective materials to immobilize
2 metals in mine tailings avoiding the leaching of metals to the environment in the long-
3 term. So, these low cost materials could be considered, perhaps in combination with a
4 self-sustaining vegetal cover, to restore large areas polluted by mining activities in a
5 cost-effective manner.

7 **Acknowledgements**

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FIGURE CAPTIONS

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Figure 1. Temporal evolution of pH (A), sulfate concentration (mg L^{-1} , B), electrical conductivity ($\mu\text{S cm}^{-1}$, C) and dissolved organic carbon concentration (mg L^{-1} , D) in the leachates from the unamended mine tailings columns (Control) and those amended with sugar foam waste (SF), drinking water treatment sludge (DWS), olive mill waste (OMW) and paper mill sludge (PMS). Values shown are the mean of three replicates and error bars represent the STD.

Figure 2. Temporal evolution of Pb (A), Zn (B), Cu (C) and Cd (D) concentration (mg L^{-1}) in the leachates coming from the unamended mine tailings columns (Control) and those amended with sugar foam waste (SF), drinking water treatment sludge (DWS), olive mill waste (OMW) and paper mill sludge (PMS). Values shown are the mean of three replicates and error bars represent the STD.

Figure 1 (A, B)

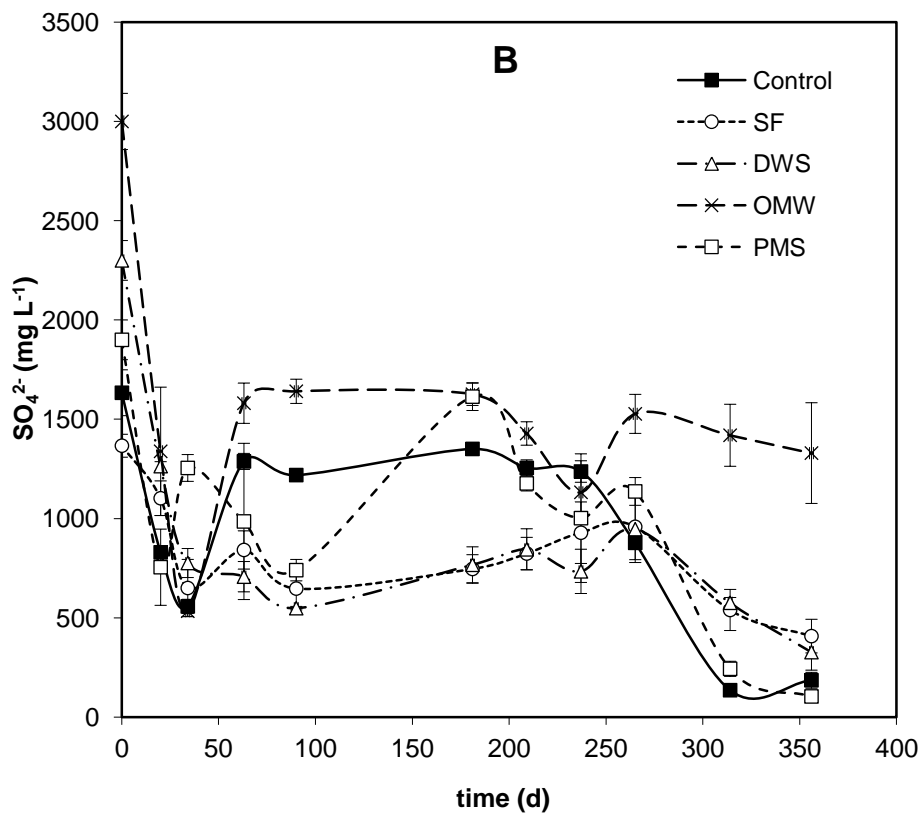
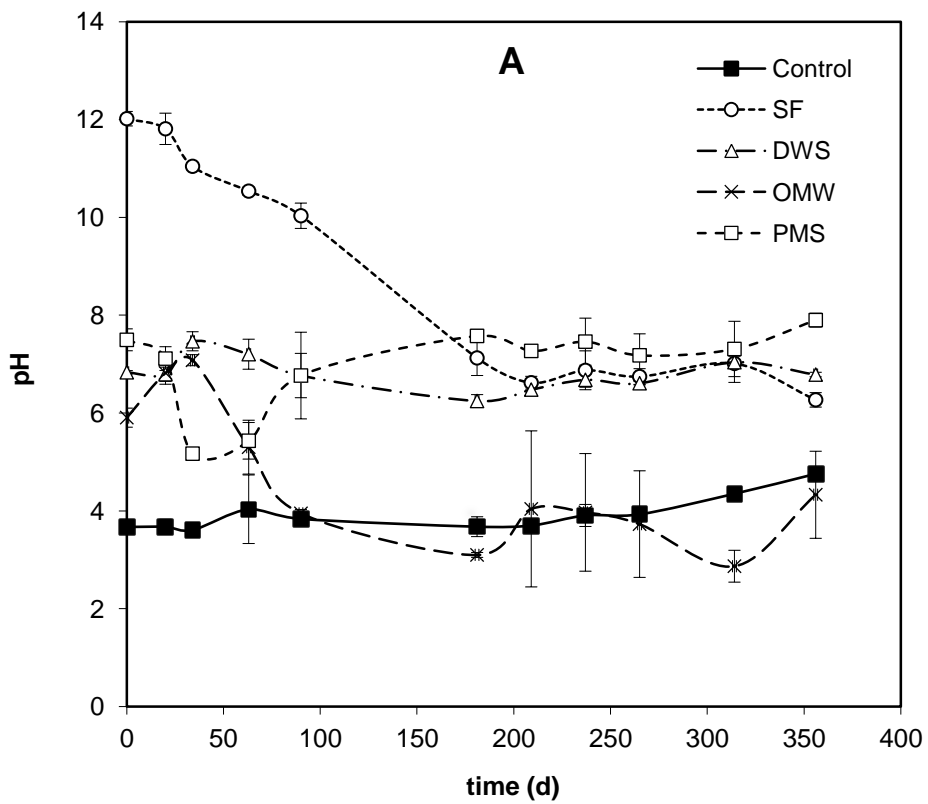


Figure 1 (C, D)

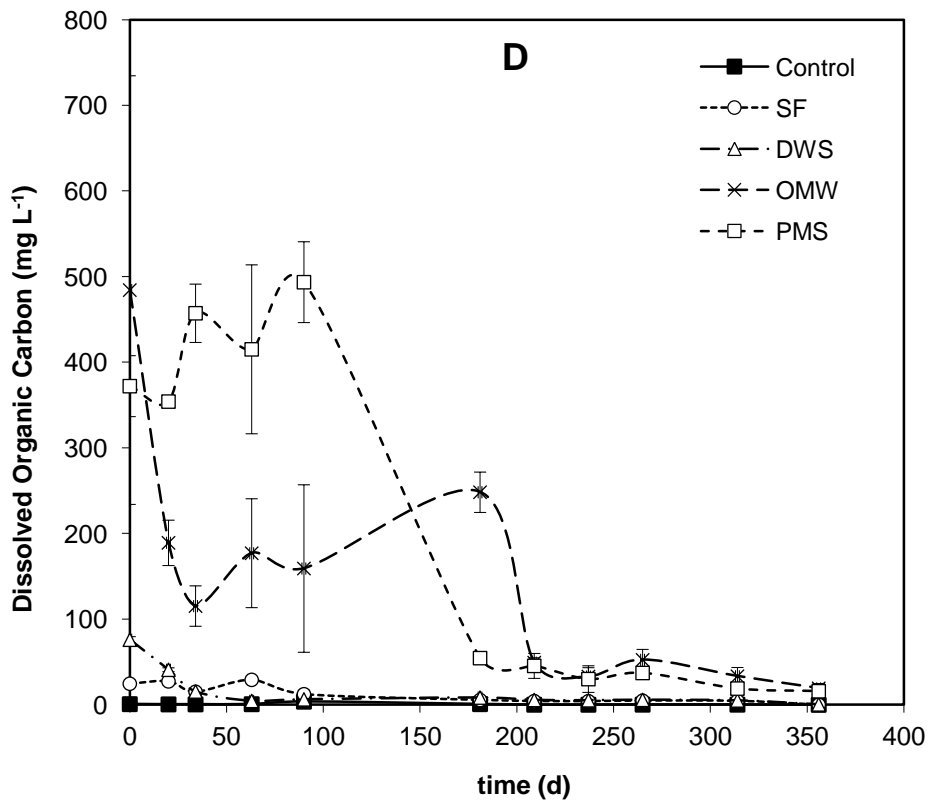
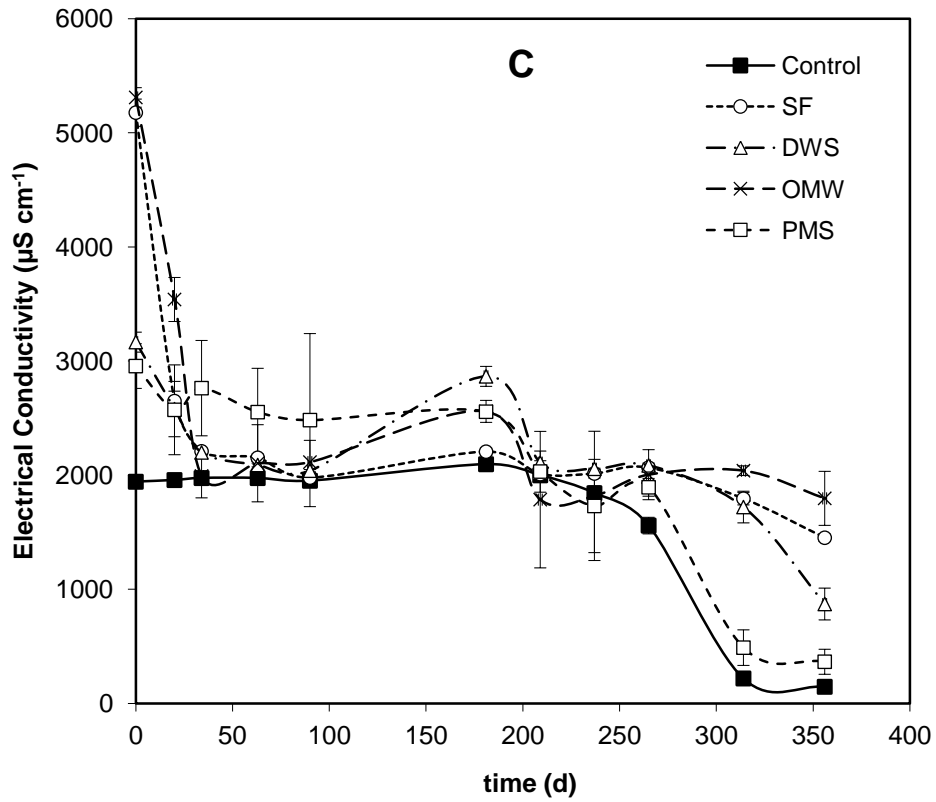


Figure 2 (A, B)

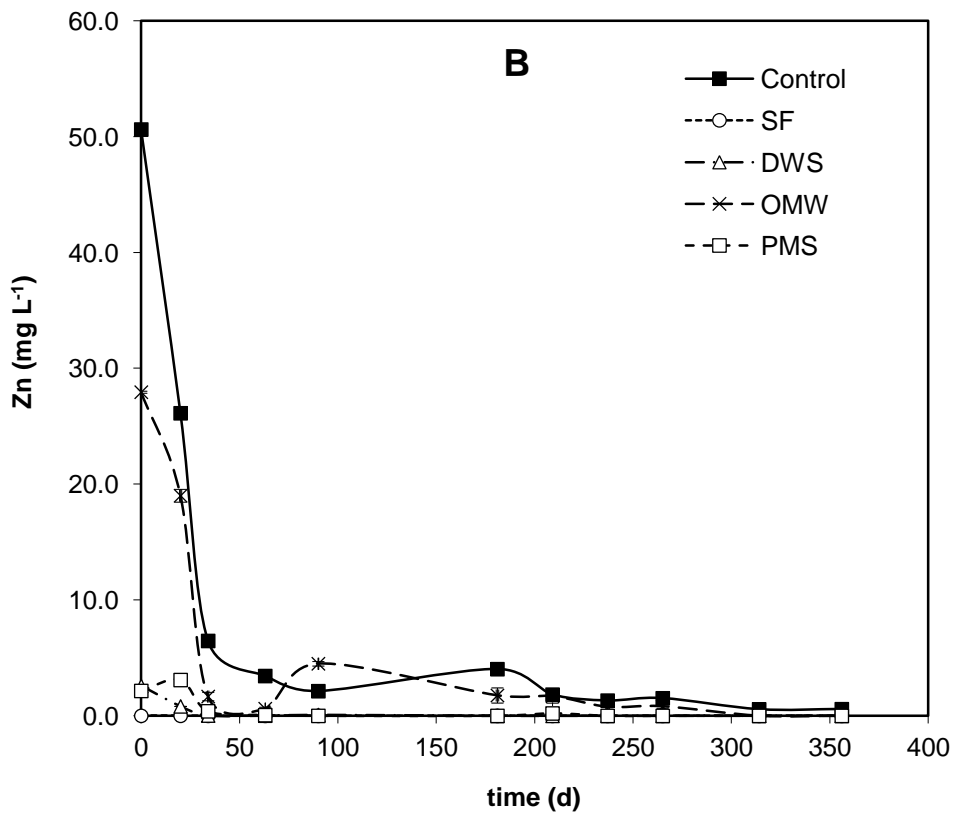
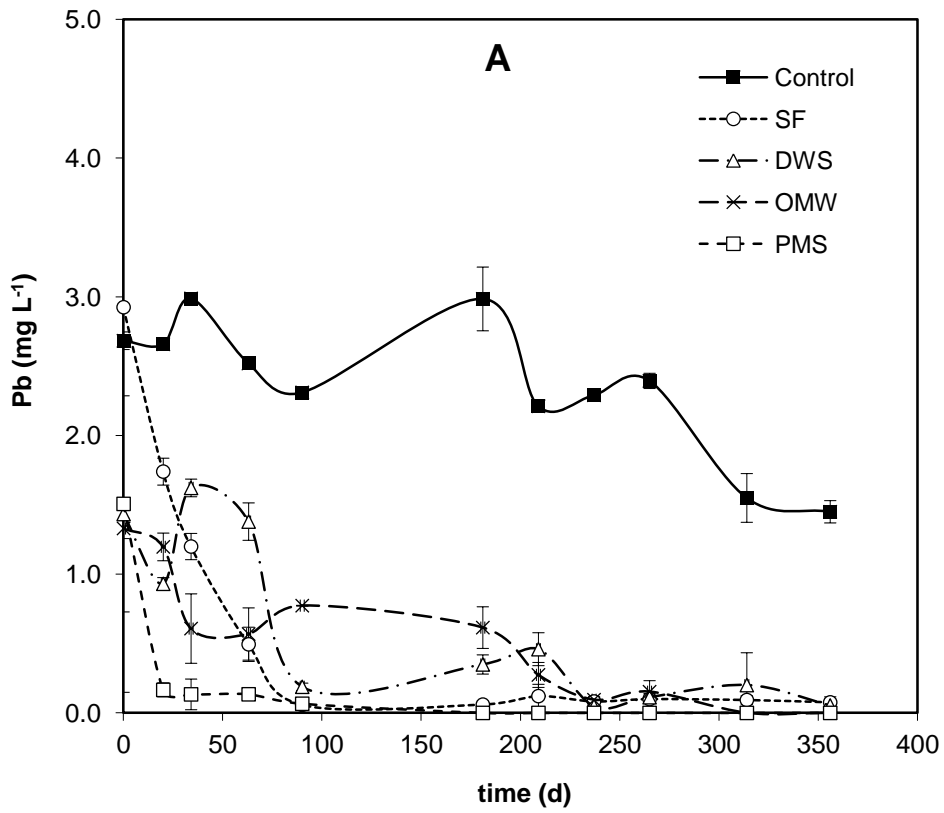
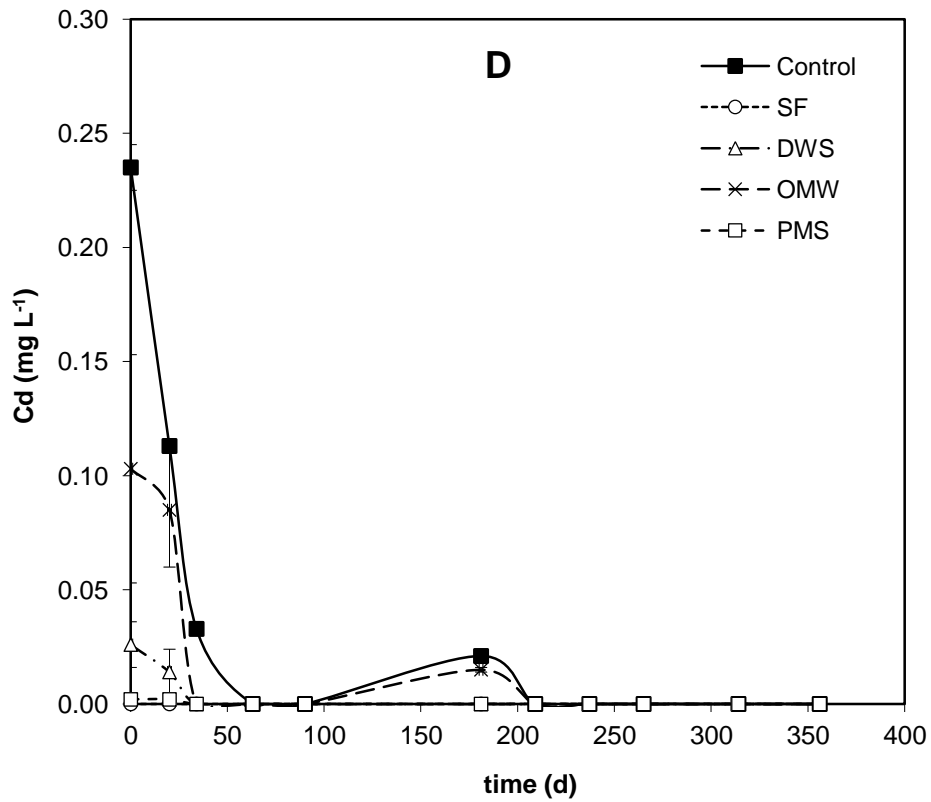
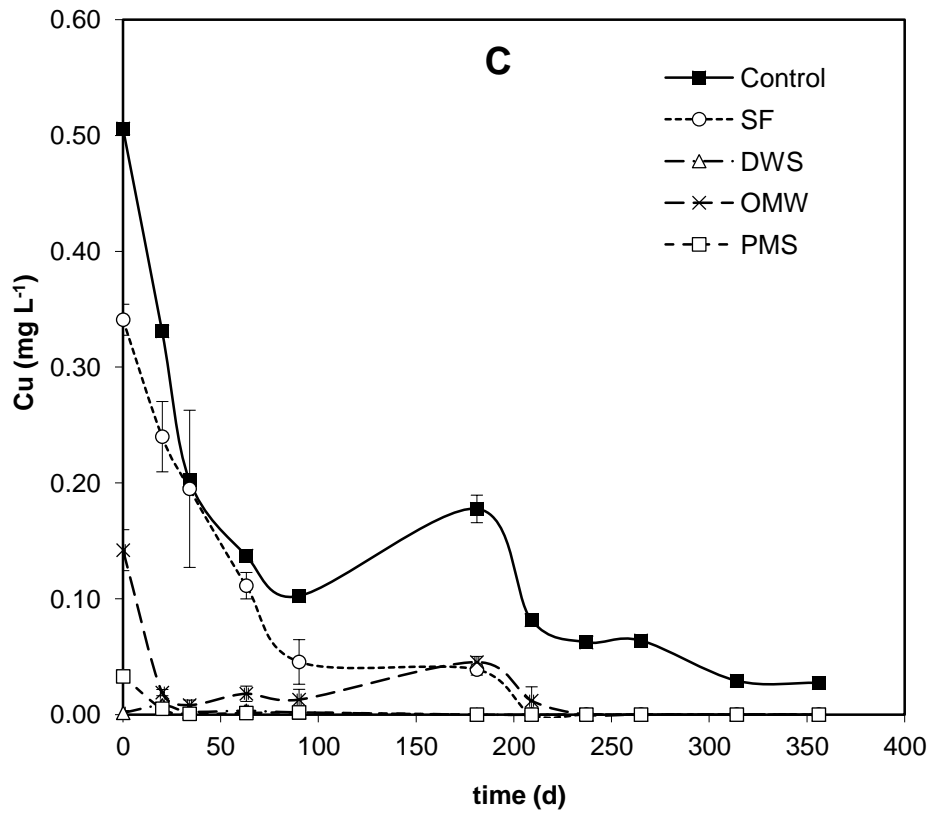


Figure 2 (C, D)



1 **Table 1. Basic physicochemical properties of mine tailings and amendments (SF:**
 2 **sugar foam waste; PMS: paper mill sludge; DWS: drinking water treatment**
 3 **sludge; OMW: olive mill waste)**

	Mine tailings	SF	PMS	DWS	OMW
pH	4.1	12.7	8.2	7.5	5.4
TOC ^a (%)	0.11	0.3	16.1	49.0	45.1
IC ^b (%)	bdl ^d	8.2	3.9	bdl	bdl
Clay (%)	9.8	-	-	-	-
Silt (%)	45.7	-	-	-	-
Sand (%)	44.5	-	-	-	-
Ca (%)	1.72	46.9	25.8	1.76	1.64
S (%)	5.79	0.98	0.32	2.95	0.61
P (%)	0.18	bdl	bdl	0.29	0.42
K (%)	1.46	bdl	0.13	0.05	5.36
Al (%)	2.93	0.44	1.40	6.96	0.07
Fe (%)	5.29	0.22	0.20	14.0	0.10
Mn (%)	0.02	0.02	bdl	2.82	bdl
Si (%)	20.3	0.83	1.96	1.59	0.66
Total Pb (mg kg ⁻¹)	9166	5.0	42.0	37.3	17.7
EDTA-Pb (mg kg ⁻¹) ^c	7049 (77)	bdl	9.38 (22)	0.68 (1.8)	1.08 (6.1)
Total Zn (mg kg ⁻¹)	2070	6.52	201	52.5	18.7
EDTA-Zn (mg kg ⁻¹) ^c	295 (14)	0.71 (11)	66.1 (33)	23.9 (46)	14.8 (79)
Total Cd (mg kg ⁻¹)	7.8	bdl	bdl	0.4	bdl
EDTA-Cd (mg kg ⁻¹) ^c	1.01 (13)	bdl	bdl	bdl	bdl
Total Cu (mg kg ⁻¹)	471	3.0	65.2	2.4	17.0
EDTA-Cu (mg kg ⁻¹) ^c	8.68 (1.8)	bdl	18.4 (28)	0.78 (33)	13.4 (79)

6 ^a Total Organic Carbon; ^b Inorganic carbon; ^c in brackets, percentage of the total metal; ^d below
 7 detection limit

1 **Table 2. Cumulative metal amount (mean values in mg kg⁻¹ and, in brackets, % of**
 2 **the total metal amount) released after 356 days from unamended and amended**
 3 **mine tailings columns (SF: sugar foam waste; PMS: paper mill sludge; DWS:**
 4 **drinking water treatment sludge; OMW: olive mill waste)**

Treatment	Pb	Zn	Cu	Cd
Mine tailings (control)	39.1 (0.43)	88.4 (4.27)	1.93 (0.41)	0.300 (3.85)
SF	6.88 (0.08)	0.01 (0.00)	0.96 (0.20)	0.000 (0.00)
DWS	8.32 (0.09)	2.50 (0.12)	0.02 (0.00)	0.031 (0.40)
OMW	6.46 (0.07)	56.2 (2.72)	0.20 (0.04)	0.170 (2.17)
PMS	1.40 (0.02)	6.06 (0.29)	0.03 (0.01)	0.004 (0.05)

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Figure supplementary S1

[Click here to download Supplementary Interactive Plot Data \(CSV\): Figure S1.docx](#)