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Short-term experiment for the in situ stabilization of a polluted soil using mining and biomass waste



Diego Baragaño^{*}, José Luis R. Gallego, Rubén Forján

INDUROT and Environmental Biogeochemistry and Raw Materials Group, Campus de Mieres, Universidad de Oviedo, Mieres, Asturias, Spain

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ABSTRACT

Mining and biomass waste were used to remediate a brownfield affected by As, Cd, Cu, Pb and Zn pollution in a pilot scale experiment, and a plant used for phytoremediation purposes was used as an indicator of possible toxicological effects. To carry out the experiments, plots in field conditions were treated with magnesite (mining waste), magnesite-sludge compost, and magnesite-biochar respectively, while untreated soil was used as a control. The plots were then irrigated and left for one week, after which seeds of the ryegrass Lolium perenne L. were sown. Soil properties such as metal(loid) availability, pH, phosphorus availability, total nitrogen, organic carbon, and nutrients were monitored for two months. Finally, the ryegrass was harvested and pollutant concentrations were analyzed in the aerial parts. Magnesite proved to be an excellent amendment for metal(loid) immobilization, although the notable increase in soil pH and Mg content inhibited plant growth. However, the application of magnesite in combination with the sludge compost (rich in N and P) favored plant growth and also immobilized metals, although As availability increased. In contrast, the analysis of plants in this treatment revealed lower As and metal concentrations than those grown in the untreated soil. In turn, the application of magnesite and biochar was also effective in reducing metal(loid) availability; however, the plants did not grow under these conditions, probably due to the low N and P content of biochar. In this regard, the combined application of mining waste and sludge compost emerges as a useful nature-based solution for soil remediation in the context of the circular economy.

1. Introduction

The process of industrial change across Europe has led to the phenomenon of 'brownfields', particularly in urban and industrialized areas. Brownfields may be defined as urban or periurban former industrial sites affected by abandonment and soil contamination exceeding soil screening levels. These sites are derelict and underused, they may have real or perceived contamination problems, and they require intervention to bring them back to beneficial use (Oliver et al., 2005). The need to recover brownfields can be linked to the European Commission's Zero Wastes Policy (European Commission, 2014), that is, to restore or recondition these areas by applying amendments made with by-products or green elements. In turn, the Zero Wastes Policy is coherent with the new trend of pursuing nature-based solutions (NBSs) for environmental remediation. The European Commission defines NBBs as "Solutions that are inspired and supported by nature, which are cost-effective, simultaneously provide environmental, social and economic benefits and help build resilience, bringing more, and more diverse, nature and natural features and processes, through locally adapted, resource-efficient and systemic interventions" (European Comission, 2017). In this regard, NBSs offer great potential in the remediation of polluted soil and brownfield redevelopment (Kisser et al., 2020). These technologies include bioremediation (Staicu et al., 2020), and mainly stabilization in situ and phytoremediation (Chiang and Gu, 2015; Song et al., 2019).

The application of low-cost natural materials, by-products or waste for soil stabilization in brownfield sites is consistent with the principles underlying NBSs and the Zero Wastes Policy. In this context, magnesite is usually obtained after mining as a waste/by-product of the production of magnesium oxide, and it has been used as an amendment to improve soil properties (Slukovskaya et al., 2019; Xu et al., 2018; Zhang et al., 2018). Comprising mainly magnesium carbonate with impurities of Fe, Mn, Ca, Co or Ni, magnesite is classified as a carbonate mineral (Schroll, 2002). The application of this mineral-based material to soil can decrease the concentrations of available metals, thus preventing their uptake by plants (Robinson et al., 1999). Also, materials containing

* Corresponding author. E-mail address: diegobcoto@uniovi.es (D. Baragaño).

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Received 13 April 2021; Received in revised form 16 June 2021; Accepted 26 June 2021 Available online 12 July 2021 0301-4797/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). magnesite as the main component have proven effective in removing Co (II), Cu(II), Ni(II), Pb(II) and Zn(II) ions from an aqueous solution (Masindi and Gitari, 2016). However, other authors observed that magnesite can impair the development of plants such as *Pinus sylvestris*, *Larix sukaczewii*, and *Betula pendula* (Zavyalov et al., 2018). Magnesite is characterized by high levels of magnesium (Mg) and also calcium (Ca), which confer it with a highly alkaline pH (Slukovskaya et al., 2019; Zavyalov et al., 2018). Furthermore, the Mg and Ca contribution to soil may cause an imbalance of other key nutrients such as P (Huang et al., 2014). In this regard, we hypothesize that the potential negative impact of magnesite can be mitigated by combining it with organic amendments such as compost or biochar.

Compost was one of the first amendments made of waste material to be used for soil remediation (Forján et al., 2018). The amendment of soil with this material has many advantages, most of which are related to an increase in organic matter. This enhancement alters soil properties, often bringing about positive effects such as improved conditions for plant growth, increased nutrient availability, and reduced mobility of inorganic pollutants. However, the use of certain types of compost can raise serious concerns about the environmental impact of this practice whenever high concentrations of potentially toxic elements are found (Paradelo et al., 2018). Thus, it would therefore be pertinent to combine compost amendments with additives that are highly effective at reducing metal(loid) leaching. Biochar is the solid product derived from the pyrolysis of waste biomass residue. Most of the carbon in biochar typically has an aromatic structure that is highly recalcitrant in the environment (Hou et al., 2020; Matoso et al., 2020). Biochar also has a high pH and cation exchange capacity and can enhance plant productivity (Zhang et al., 2013). Biochar has a liming effect and a microporous structure, resulting in a high specific surface area and active functional groups on its surface. O-containing functional groups in particular, such as hydroxyl and carboxylic, can adsorb metals via electrostatic attraction and surface complexation (Beesley et al., 2011; Lu et al., 2012; Xu et al., 2018). Given these properties, biochar is a low-cost and eco-friendly sorbent.

Finally, phytoremediation is usually combined with the application of amendments for soil recovery. Phytostabilization in particular is widely used to remediate large areas such as brownfields and mine soils (Bozdogan Sert et al., 2019, Pandey et al., 2019). Indeed, various studies report on the use of ryegrass as a phytoremediator to complement distinct soil amendments (Clemente et al., 2010; Karczewska et al.,

2013; Li et al., 2018).

In this context, here we examined in situ soil stabilization in a brownfield site affected by different sources of pollution. The treatments involved the application of magnesite alone and a novel combination with organic amendments, namely biochar and sludge compost, to examine their capacity to immobilize As and metals and improve soil properties. Also, vegetation (ryegrass) was grown, to evaluate possible harmful effects on plant parameters relevant for revegetation, or even for potential phytostabilization treatments.

2. Materials and methods

2.1. Description of brownfield and characterization of polluted soil

A polluted soil from a brownfield located in the northwest of Spain was remediated in situ (Fig. 1). This brownfield, known as Nitrastur, was one of the main fertilizer plants in Spain until its closure in 1997 (Gallego et al., 2016). During its operation, the plant generated large amounts of waste, mainly pyrite ash, which was used as a filler over an area of 20 ha. The As and metals in this waste mixed with natural soil, promoted the dispersion of the pollutants and affected to the soil and groundwater (Baragaño et al., 2020a). Several pilot-scale remediation approaches have been carried out on the site, including phytoremediation (Navazas et al., 2019, 2021), microbial-assisted phytoextraction (Mesa et al., 2017), soil washing (Fedje et al., 2017; Sierra et al., 2010), and nanoremediation (Castaño et al., 2021). However, the application of amendments for in situ soil stabilization has not been attempted to date.

The soil (S) subjected to remediation (Table 1) was obtained from a pit dug in a selected area (Fig. 1) affected by high concentrations of As, Cd, Cu, Pb and Zn, all exceeding the regional Soil Screening Levels from Asturias.

2.2. Amendment production and characterization

The three amendments tested were magnesite, sludge compost, and biochar. The magnesite (M) used is a commercial product named INERTIMAG, provided by Magnesitas de Navarra, S.A. (Navarra, Spain). This inorganic material is generated as a waste during mineral processing, and according to X-ray fluorescence it comprises 37% MgO and 4.5% CaO as major contents (a detailed characterization is shown in



Fig. 1. Location of Nitrastur brownfield in Asturias, Spain (A); study area limits (B) and experimental site construction (C).

Table 1

Characteristics and pollutant concentrations of polluted soil (S), compost (C), magnesite (M), and biochar (B).

			S	С	М	В
Physico-chemical properties	pН	$(\mu S.cm^{-1})$	$7.76\pm0.08c$	$\textbf{7.28} \pm \textbf{0.01d}$	$9.74\pm0.00a$	$8.06\pm0.00b$
	EC		$271 \pm 61c$	3067±2b	3966±3a	92±1d
	TC	(g.kg ⁻¹)	106±1c	266±7b	$64.8\pm0.6d$	743±4a
	TOC		$100\pm 2c$	$\textbf{256.8} \pm \textbf{6.46b}$	$\textbf{36.9} \pm \textbf{1.6d}$	743±4a
	TN		$\textbf{2.07} \pm \textbf{0.86b}$	$25.5\pm0.3a$	<dl< td=""><td>$0.95\pm0.26c$</td></dl<>	$0.95\pm0.26c$
	Р	(mg.kg ⁻¹)	$\textbf{7.40} \pm \textbf{0.50c}$	$406 \pm 18a$	$5.90\pm2.40c$	$30.1 \pm 1.3 \text{b}$
Total concentrations	As	(mg.kg ⁻¹)	$80.6 \pm \mathbf{5.8a}$	$13.6 \pm 1.2b$	$14.7\pm0.6b$	$1.66 \pm 1.52 c$
	Cd		$15.8\pm0.8a$	$0.93\pm0.05b$	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Cu		$3546 \pm 120a$	172±1b	12±0c	41±3c
	Pb		2186±6a	$132\pm 8b$	20±1c	7±0d
	Zn		$5373\pm80a$	$685\pm23b$	18±0c	18±1c
Available concentrations	As	(mg.kg ⁻¹)	<dl< td=""><td>$0.77\pm0.02a$</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	$0.77\pm0.02a$	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Cd		$1.71\pm0.16a$	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Cu		$100.5\pm9.9a$	$3.3\pm0.1b$	<dl< td=""><td>$0.3\pm0.1b$</td></dl<>	$0.3\pm0.1b$
	Pb		$16.8\pm1.6\text{a}$	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Zn		$430.8\pm22.0a$	$10.4\pm1.0b$	<dl< td=""><td>$\textbf{2.10} \pm \textbf{0.10b}$</td></dl<>	$\textbf{2.10} \pm \textbf{0.10b}$
Nutrient contents	Ca	(mg.kg ⁻¹)	$1925\pm179c$	$13{,}701\pm249a$	$6644\pm368b$	$795\pm73d$
	K		145±4d	$3215\pm118 a$	$1627\pm79b$	$660\pm103c$
	Na		26±4c	$999 \pm 39a$	$352\pm18b$	32±6c
	Mg		$44\pm 2c$	$1264\pm 33b$	$9688 \pm 489a$	57±5c
Exchange cations	Ca ²⁺	$(\text{cmol}_{(+)}\text{kg}^{-1})$	$32.0 \pm 2.9c$	$228.3 \pm 4.2 a$	$110.7\pm6.1b$	$13.2\pm1.2\text{d}$
	K^+		$1.24\pm0.03\text{d}$	$\textbf{27.4} \pm \textbf{1.01a}$	$13.9\pm0.67b$	$5.64 \pm 0.87 c$
	Na ⁺		$0.75\pm0.11c$	$28.9 \pm 1.13 \mathrm{a}$	$10.1\pm0.51b$	$0.92\pm0.16c$
	Mg^{2+}		$1.22\pm0.05c$	$35.1\pm0.91b$	$269.1\pm13.5a$	$1.58\pm0.14c$
	Al^{3+}		$2.35\pm0.41a$	$2.15\pm0.37a$	$1.60\pm0.23a$	$1.64 \pm 0.24 a$
	CEC		$\textbf{37.6} \pm \textbf{3.4c}$	322±6b	$405\pm12a$	$23.0\pm1.9\text{d}$

For each row, different letters in different samples mean significant differences (n = 3, ANOVA; P < 0.05). <DL: below detection limit; EC: electrical conductivity; TC: total carbon; TOC: total organic carbon; TN: total nitrogen; P: available phosphorus (Mehlich); CEC: Cation Exchange Capacity. These results were obtained using the same methodologies described in Section 2.4.

Table 1). The use of this amendment in polluted soil was previously tested in a pot experiment, which revealed excellent results for metal immobilization, although plant growth was inhibited (Baragaño et al., 2021).

Regarding organic amendments, the compost (C), supplied by COGERSA S.A.U. (Asturias, Spain), was made from sewage sludge, which explained its notable As and Zn content (Table 1). The biochar (B), obtained from oak wood pruning (400 °C, for 4 h; see also Table 1 for main properties), was provided by Biesca Ingeniería (Asturias, Spain). Finally, the ryegrass seeds (*Lolium perenne* L.) used in this work were provided by Agricola Cueli S.L. (Asturias, Spain).

2.3. Field experiment

Four weatherproof plots were built on-site to perform pilot-scale experiments (Fig. 2). Approximately 10 m³ of soil from one of the main areas of the brownfield affected by metal(loid)s were excavated and mixed thoroughly, and 0.5 m³ (1 \times 1 \times 0.5 m) of homogenized soil (about 1 t, assuming a soil density of 2 t/m^3) was deposited onto each plot. One plot was filled only with the polluted soil (S) as a control, and the other three plots were filled with the soil treated using the different strategies; soil + magnesite (SM), soil + magnesite + compost (SMC), and soil + magnesite + biochar (SMB). All treatments (SM, SMC, SMB) had a soil/magnesite ratio of 9/1 (w/w). SMC also comprised 15% compost and SMB 7% biochar. At the beginning of the experiments, the plots were watered during a one-week incubation period to allow the amendments to exert their effects. At the end of this week, the same number of ryegrass seeds were sown in each plot. From this point, the plots were not artificially irrigated again. During the experiment, all the plots were subjected to the same environmental conditions.

To monitor the geochemical behavior of the pollutants, soil samples were taken at 3 days (T1), 30 days (T2), and 60 days (T3). At each soil collection (T1, T2 and T3), a sampling mesh was designed within each plot and random sampling was performed. The individual increases were subsequently mixed to obtain a composite sample of each treatment and the control. At the end of the experiment, the biomass of each

plot was harvested. During the 2-month experiment, there was a minimum temperature of 13.6 $^{\circ}$ C, a maximum temperature of 24.3 $^{\circ}$ C and total precipitation of 54.8 l/m^2 .

2.4. Soil analysis

Soil samples were air-dried, sieved through a 2-mm mesh, and homogenized before performing the analyses. Pseudototal metal(loid) contents were extracted with aqua regia by acid digestion in a microwave oven (Milestone ETHOS 1, Italy), and the concentrations were measured by ICP-MS (Milestone ETHOS 1, Italy). Available concentrations of metal(loid)s were determined by means of TCLP extraction (Toxicity Characteristic Leaching Procedure) following the USEPA Method 1311 (1992), and the concentrations were determined by ICP-MS. Soil pH and electrical conductivity (EC) were determined using a multi-meter METTLER TOLEDO SevenCompact in a 1:2.5 water to soil extract (Porta, 1986). Total soil carbon (TC) and total soil nitrogen (TN) were measured in a TOC-V CSH (Shimadzu) equipped with a module for solid samples. Available phosphorus (P) was determined by the Mehlich method (Mehlich, 2008). Exchangeable cations (Ca²⁺, K⁺, Mg²⁺, Na⁺, and Al³⁺) were extracted with 0.1 M BaCl₂ (Hendershot and Duquette, 1986) and concentrations were determined by ICP-MS. The effective cation exchange capacity (CEC) was calculated using the sum of exchangeable cation concentrations (Houba et al., 2000).

2.5. Plant analysis

As described in section 2.3, ryegrass seeds were sown in the control soil and the treated soils one week after filling the plots. Plants were harvested at T3 (60 days). Biomass was carefully washed with deionised water and fresh biomass was weighed immediately. Dry biomass was assessed after oven-drying for 48 h at 80 °C and cooling at room temperature. The concentration of As, Cd, Cu, Pb, and Zn was quantified by ICP-MS after acid digestion using a mixture of H_2O_2 and HNO_3 (1:2 v/v) in a microwave oven (Milestone ETHOS 1).



Fig. 2. Soil profile revealed the presence of pyrite ash (pink color) with other waste products (A), and plots at the end of the experiment: control (B), magnesite (C), magnesite + compost (D), and magnesite + biochar (E) treatments.

2.6. Statistical analysis

All analytical determinations were performed in triplicate. The data obtained were statistically treated using the SPSS program version 24.0 for Windows. Analysis of variance (ANOVA) and test of homogeneity of variance were carried out. In the case of homogeneity, a post hoc least significant difference (LSD) test was performed. When there was no homogeneity, Dunnett's T3 test was performed. A correlated bivariate analysis was also carried out by means of Pearson correlation.

3. Results and discussion

3.1. pH and electrical conductivity

The pH of control soil (S) was significantly lower than that of soil treated with magnesite (SM), magnesite + compost (SMC) and magnesite + biochar (SMB) (Table 2) at 3 days (T1), 30 days (T2), and 60 days (T3). However, all plots had an alkaline pH (8–10). SM showed the highest pH value and SMB the lowest. Regarding electrical conductivity (CE), S presented significantly lower values throughout the experiment

than the treated soils (Table 2). As with the pH values, SMB had significantly lower EC values compared to SM and SMC at the three time points tested. At T60, SM had a significantly higher EC value than SCM and SMB (Table 2).

The increase in soil pH was due to the alkalinity of amendments (Table 1), which had a similar or higher pH than that of the soil, especially in the case of magnesite. Several authors showed that magnesite, compost and biochar can cause an increase in pH and EC (Alvarenga et al., 2008; Forján et al., 2017; García et al., 2004; Huang et al., 2014). Furthermore, as can be expected, the content of basic cations was higher in magnesite and compost than in biochar. Consequently, the increase in pH at the end of the experiment was greater in SM and SCM (Table 1). It has been reported that magnesium oxide (MgO) reacts with carbon dioxide and water in air and soil to become magnesium carbonate (MgCO₃) and magnesium hydroxide (Mg(OH)₂) respectively, in turn causing the soil pH to increase (Wang et al., 2015). Furthermore, the dissolution of magnesite may lead to the consumption of hydrogen ions, which maintain the pH of leachates over neutrality (Navarro and Cardellach, 2009).

Table 2

			S	SM	SMC	SMB
Time 1	pН	µs.cm ⁻¹	$\textbf{7.74} \pm \textbf{0.05d}$	$\textbf{9.62}\pm\textbf{0.01a}$	$9.36\pm0.00b$	$9.29\pm0.00c$
	EC		229±1d	1326±3a	1173±1b	594±6c
	TOC	$(g.kg^{-1})$	$93.3\pm3.1\mathrm{b}$	$87.7 \pm \mathbf{6.1b}$	$94.9\pm1.9b$	119±9a
	Ν		$1.78\pm0.19\mathrm{b}$	$1.09\pm0.03c$	$\textbf{2.90} \pm \textbf{0.13a}$	$1.39\pm0.06b$
Time 2	pH	µs.cm ⁻¹	$\textbf{7.99} \pm \textbf{0.00d}$	$9.54\pm0.01a$	$9.39\pm0.04b$	$9.19\pm0.02c$
	EC		242±7d	$1157\pm13b$	$1354\pm16a$	535±3c
	TOC	$(g.kg^{-1})$	105±1b	96±2c	107±7 ab	122±5a
	Ν		$1.43\pm0.14b$	$1.07\pm0.09c$	$3.59\pm0.08a$	$1.09\pm0.05c$
Time 3	pH	$\mu s.cm^{-1}$	$\textbf{7.76} \pm \textbf{0.01d}$	$9.67\pm0.01a$	$9.45\pm0.01b$	$9.36\pm0.00c$
	EC		603±1d	1439±7a	$1223\pm191b$	960±3c
	TOC	$(g.kg^{-1})$	102±2b	90±2c	141±3a	137±1a
	Ν		$1.34\pm0.16b$	$0.85\pm0.15c$	$5.95\pm0.32a$	$1.17\pm0.02 bc$

Monitoring of pH, electrical conductivity (EC), total organic carbon (TOC), and total nitrogen (N) of the control and treated soils during the experiment.

For each row, different letters in different samples mean significant differences (n = 3, ANOVA; P < 0.05).

3.2. Total organic carbon and total nitrogen

Table 2 also shows the evolution of total organic carbon (TOC). As could be expected, treatment with SMC and SMB caused a significant increase in TOC when compared with SM and S. According to several authors, the carbon in biochar is highly recalcitrant (Rajapaksha et al., 2016; Shen et al., 2016), and therefore, in our case, TOC values in SMB remained high and relatively stable. However, in SMC, the TOC content started lower and increased over time, possibly due to the development of the vegetation on the plot (see below, Fig. 5). At the end of the experiment, the TOC values in SMB and SMC were similar. The increase in TOC by amendment with compost has previously been reported (Anastopoulos and Kyzas, 2015; Beesley et al., 2014). This increase in TOC is relevant as organic matter can form strong bonds with metals and thus retain them in the soil (Kabata-Pendias, 2001). In the case of SBM, the increase in TOC is important because its functional groups confer capacity to complex metals (Beesley and Marmiroli, 2011; Lu et al., 2012).

As the experiment progressed (T2 and T3), S had a higher TOC than SM (Table 1). This observation is attributed to the contribution of organic matter from the plants that developed on this plot. In contrast, the SM treatment did not allow plant growth (see below).

Regarding total nitrogen (TN), S had a higher content of N than SM and SMB (Table 2). This finding could be explained by several factors: first, both biochar and magnesite had a lower N content than the initial soil (Table 1) and, also, as discussed below, the plants growing in the S plot (Fig. 5) may enhance soil N, while no vegetation was present in the SM and SMB plots. The application of ryegrass as a cover crop mitigates N₂0 emissions and favours N sequestration in the soil, so that the N content is higher when this crop is present than when it is not (Boller and Nösberger, 1988; Wang et al., 2021). In addition, ryegrass crops have a higher abundance of microorganisms, bacteria and fungi which favour N fixation in the soil (Høgh-Jensen and Schjoerring., 2001).

3.3. Monitoring the pseudototal concentrations of As, Cd, Cu, Pb and Zn

Throughout the experiment, the S, SM, SMC and SMB treatments did not undergo significant changes in terms of the pseudototal concentrations of As, Cd, Cu, Pb and Zn (Table S1). These results indicate that subsequent changes in the available concentrations of these metals were not due to loss through leaching or to a dilution effect caused by the treatments themselves. It should be noted that the original soil had high pseudototal concentrations of Cu and Zn due to the presence of high amounts of pyrite ash (Baragaño et al., 2020a; Gallego et al., 2016).

3.4. Evolution of available As & P, Cd, Cu, Pb and Zn concentrations

The evolution of available As, P, Cd, Cu, P, Pb and Zn concentrations

revealed differentiated behavior between those of the metals (Cu, Cd, Pb and Zn) and those of As, a metalloid, and P (Fig. 3).

Differences in available As were notable. In S, As was not detectable (Fig. 3A). This observation is attributed to the high content of pyrite ash, formed mainly by iron oxides, which are excellent As scavengers (Baragaño et al., 2020b, c). The SM treatment also presented available concentrations of As below the detection limit (Fig. 3A) as the magnesite applied contained Mg0, Fe₂O₃ and Al₂O₃, which also have a high affinity for As. Furthermore, as shown in Table 1, SM had a significantly lower TOC and P content compared to SMC and SBM. TOC and P can mobilize anions such as As (Fitz and Wenzel, 2002). Increased TOC can enhance dissolved organic carbon (DOC), thereby causing the mobilization of As (Arco-Lázaro et al., 2016; Abou et al., 2019; Nandillon et al., 2019). The increase in TOC and P caused by the SMC and SMB treatments, especially in the case of the former, may explain the mobilization of As and is consistent with Beesley et al. (2014), who concluded that compost and biochar increased the potential for As leaching due to their effects on DOC and soluble P concentrations. At T3, when the increase in extractable As in SMC and SMB was highest, a significant positive correlation was observed between extractable As and TOC (0.68, P < 0.05) and As and P (0.96, P < 0.01). Furthermore, available As in the sludge compost can also contribute to the presence of this metalloid in the soil. In addition, as described above, the application of SMB caused an increase in pH (above 9). Therefore, the increasing mobility of As in biochar-treated soils may also result from the competition of OH⁻ with HAsO²⁻₄ for binding sites under alkaline conditions (Inyang et al., 2010; Yin and Zhu, 2016), especially in the long term, as revealed at the end of the experiment (Fig. 3A).

Regarding available P content, the SMC treatment showed the highest concentration of P, which is consistent with the abundance of this element in the compost (Table 1). Furthermore, P concentration increased over time (Fig. 3B), which is beneficial for plant development, as discussed in section 3.6, but is also in accordance with the increase in available As at the end of the experiment, suggesting competition between the two elements (Fig. 3A).

The high extractable concentrations of Cd, Cu, Pb and Zn in S are due to the mineral phases present in the pyrite ash, as detailed in Gallego et al. (2016). At the end of the experiment, the SMC treatment showed the highest decrease in the extractable concentration of Cd, Pb and Zn (Fig. 3D, E, 3F), while SM was second in effectiveness for these elements and SMB the least efficient. A minor distinct behavior was observed for Cu since the SM and SMC treatments caused similar decreases (Fig. 3C).

The decrease in the extractable concentration of Cu, Zn, Pb and Cd is due to several factors, the most important being an increase in pH. Greater alkalinity is directly related to decreased solubility of most metals. In this experiment, significant negative correlations were obtained between pH and extractable concentrations of Cu, Zn, Pb and Cd (the values were -0.92, -0.91, -0.87, -0.86; P < 0.01). These results



Fig. 3. Evolution of available As, Cd, Cu, P, Pb and Zn concentrations. Different letters in different samples indicate significant differences (n = 3, ANOVA; P < 0.05). <DL: below detection limit. Error bars represent standard deviation.

and correlations are consistent with the findings of other studies (Forján et al., 2016; Park et al., 2011; Weng et al., 2001). In turn, and as previously described, magnesite contains mainly magnesium but also iron and aluminium oxides, which contribute to increasing the metal retention capacity of contaminated soils (Bradl, 2005; Negra et al., 2005; Spathariotis and Kallianou, 2007; Vega et al., 2007). In the case of the SMC and SMB treatments, the increase in TOC also favored the decrease in extractable metal concentrations. In fact, organic matter is directly related to the decrease in extractable concentrations since it favors the formation of organometallic complexes and decreases their mobility (Adl, 2008; Uchimiya et al., 2011). Specifically, biochar has a porous microstructure that results in a high specific surface area and active functional groups on its surface, which implies a high capacity to complex metals on its surface (Beesley and Marmiroli, 2011; Lu et al., 2012). In this regard, the immobilization of Cd and Cu by biochar has been attributed mainly to surface complexation with -COOH and -OH groups (Peng et al., 2017). Finally, the observed increase in CEC (see next section) was directly related to the decrease in extractable concentrations of metals in the soil (Chandra et al., 2014), as shown by the significant correlations obtained between CEC and extractable concentrations of Cd, Cu, Pb and Zn (-0.77, -0.82, -0.80, -0.81; P < 0.80, -0.81; P < 0.80; P < 0.80, -0.81; P < 0.80; P < 0.80;0.01).

3.5. Monitoring nutrients and cation exchange capacity

The content and evolution of N and P were discussed above. However, elements such as Ca, K, Mg and Na are also important nutrients and their concentrations are shown in Table S2. In general, the SMC treatment had the highest K and Na content throughout the experiment (Table S2). These two elements, along with N and P, are the bases of most chemical fertilizers used for plant production (Hill et al., 2021). The SM treatment had the highest Ca and Mg content throughout the experiment (Table S2), which is explained by the high content of these two cations in this amendment. Generally, SMB was the treatment that contributed the least amounts of nutrients to the soil (Table S2). This finding is explained by the high capacity of biochar to retain nutrients and subsequently release them progressively (Jien, 2019; Lee et al., 2018). There are other types of biochar that have a higher content of nutrients, but they are less effective in reducing extractable concentrations of metals. For instance, biochar produced from lignocellulosic materials contains fewer nutrients than that from manure-based feed-stocks (Camps-Arbestain et al., 2015).

Fig. 4 shows the variation of CEC and cation exchange content (Ca²⁺, K^+ , Mg²⁺, Na⁺, and Al³⁺). The treatments (SM, SMC, SMB) increased CEC with respect to the control soil (S), although SM and SMC showed the highest increase in this parameter (Fig. 4).

The increase in CEC caused by the treatments is explained mainly by the Mg provided by magnesite. Indeed, a significantly positive correlation of 0.98 (P<0.01) was obtained between CEC and Mg. The increase in CEC was due to the increase in basic cations and not to the increase in Al^{3+} . The concentration of this cation decreased in SM, SMC and SMB as the experiment progressed, possibly due to the increase in pH. In the SMB treatment, the increase in CEC was lower, which could be attributable to the partial oxidation of many cations during biomass pyrolysis (Tortosa et al., 2007), causing their capacity to be exchanged to drop considerably. The increase in pH is usually closely linked to CEC and basic cations. Indeed, in the treated soils, the pH was significantly positively correlated with Mg^{2+} (0.77, P<0.01) and with CEC (0.77,



Fig. 4. Cation exchange capacity (CEC) and cations of the exchange complex for untreated soil (S) and treated soils (SM, SMC and SMB).

P<0.01). The increase in CEC improves the ability of the soil to decrease the mobility of metals and also causes reduced migration of nutrients, thus allowing plants to use them more effectively (Beesley and Marmiroli, 2011).

3.6. Plant biomass and As, Cd, Cu, Pb and Zn concentrations

Although magnesite application reduced the concentration of available metal(loid)s, except As in the SMC and SMB treatments, ryegrass grew only in the control plot (S) and in the SMC treatment (Fig. 5), as observed in Fig. 2. In fact, the SM treatment was the second most effective in reducing the concentration of available metal(loid)s and it also increased soil nutrients. However, plant growth was not achieved in this treatment (Fig. 5).

To better understand the effects of the amendments on plant development, several coefficients and limit values applied for plant production based on the models of soil fertility capability classification (SFCC) proposed by Buol et al. (1975) and Hazelton and Murphy (2007) were examined. According to those authors, a soil is deficient in N when this element falls below 0.15%, which occurred in the SM and SMB treatment, although the control soil was also close to this limit. A ratio between Ca and Mg below 0.5 indicates decompensation, and we detected this decompensation whenever magnesite was added. The treatments also increased soil pH to above 9, which can hinder the development of vegetation as the availability of N, Ca and Mg for plants is reduced (Hazelton and Murphy, 2007). Furthermore, the SMC treatment had an excessive extractable P content due to its high pH, which can affect the proportions of this element within different anions in the soil and hinder plant development.

Therefore, the differences in plant growth observed could be explained by two factors. Firstly, control soil can support the development of vegetation in spite of the presence of pollutants, thus allowing the phytoremediation plant to grow. Secondly, the SMC treatment maintained stable vegetation since the compost provided a higher amount of N higher than the untreated soil and the other treatments (Table 2). However, less fresh biomass was obtained from the SMC treatment than from the control soil. This may explain why SMC presented more deficits for plant production.

As regards to pollutant concentrations in the aerial part of the ryegrass, although fresh biomass was higher in the control plot (Fig. 5D), the vegetation in magnesite-treated soil (SM) presented lower As, Cd, Cu, Pb, and Zn concentrations, which indicates the effectiveness of the treatment in reducing available metal(loid) concentrations (Fig. 5A, B, 5C). These results are in accordance with soil extractions performed to monitor metal(loid) availability (Fig. 3), except for As. For this metal-loid, the concentration decreased in plants from the SMC treatment with respect to those grown in control soil (Fig. 5A). This can be attributed to the P increase observed in SMC (Fig. 3B) that is overlapping the previously noted increase of As availability (Fig. 3A).

Finally, it is remarkable that the cost of this combination of amendments (around 7.5 \in per tonne of soi) is non-expensive and thus promotes a sustainable management of mining and biomass waste.

4. Conclusions

Following a circular economy approach, here we tested in situ the capacity of a novel mixture of amendments comprising a mining waste and two organic amendments, namely sludge compost and biochar, to restore a polluted soil affected by As, Cd, Cu, Pb and Zn. Our results reveal magnesite as a promising additive for metal(loid) immobilization, although it causes a notable increase in Mg and soil pH and thus impaired plant production. We attempted to address this drawback by combining magnesite with organic amendments. In fact, magnesite combined with sludge compost proved successful as, the increase in N and P improved ryegrass growth, thus avoiding the negative impact of Mg addition. Furthermore, in spite of the increase in As availability caused by compost addition, the concentration of pollutants in plants grown in the soil amended with magnesite and compost was lower than in those grown in the control soil. In contrast, soil amendment with biochar in combination with magnesite led to a slight decrease in pollutant availability in the soil but impeded plant growth. On the basis of our observations, we conclude the combination of magnesite and sludge compost is a promising nature-based solution for pollutant immobilization and soil restoration.



Fig. 5. As, Cd, Cu, Pb and Zn concentrations in the aerial part and fresh biomass of ryegrass plants grown in control (S) and soil treatments that showed plant growth (SMC). Different letters in different samples indicate significant differences (n = 3, ANOVA; P < 0.05). Error bars represent standard deviation.

Credit author statement

Diego Baragaño: Conceptualization, Methodology, Writing – original draft preparation. José Luis R. Gallego: Conceptualization, Supervision, Writing- Reviewing and Editing. Rubén Forján: Conceptualization, Methodology, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.113179.

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