

Article

Reuse of Dunite Mining Waste and Subproducts for the Stabilization of Metal(oid)s in Polluted Soils

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Abstract: The circular economy seeks to minimize the use of raw materials and waste generation. In this context, here we addressed the use of dunite mining tailings and subproducts to stabilize metal(oid)s in polluted soils. We first characterized the dunite mining tailings and subproducts, and a paradigmatic polluted soil in depth to determine their chemical and mineralogical properties. Experimental trials using *Brassica juncea* L. were performed to evaluate the impact of the two materials on vegetation growth, edaphic properties and pollutant stabilization yields. To this end, the plants were grown over 75 days in 1 kg pots containing the polluted soil amended with the dunite materials. Notably, both amendments caused a dramatic decrease in the available Zn and a moderate reduction in available Cu, Cd and Pb. In contrast, the concentration of available As was not modified. The cation exchange capacity (CEC) was improved by treatment with the amendments, allowing an increase in the biomass harvested. The immobilization mechanism achieved was probably due to an increase in pH and CEC. In conclusion, the dunite tailings and subproducts could be effective amendments for stabilizing polluted soil. This work paves the way for additional studies with distinct types of soils and conditions.

Keywords: dunite; soil; stabilization; metal(oid)s; mining

1. Introduction

The massive production of waste is one of the most pressing problems faced by society today [1,2]. In this regard, human consumption and production practices are having a detrimental effect on environmental quality, social equity and long-term economic stability [3–5]. In response to this issue, governments currently focus their policies on the circular economy [6,7], which has been proposed as an effective model through which to decrease the generation of waste and minimize the use of raw material, thereby achieving sustainable development [8].

Mineral production continues to be necessary for economic development. However, mining and ore processing generate large amounts of soil and liquid materials that are classified as waste [9]. Consequently, the management of mining and mineral-processing waste also raises concerns in terms of recycling and economic strategies for the future [10]. These waste products are generally harmful for environmental compartments because they contain high concentrations of potentially toxic elements [11], thus ruling out their reuse and generating the need for appropriate management. Mine waste is characterized by null edaphological properties [12] and it can often become an environmental concern since it may leach toxic elements such as heavy metal(oid)s [13–15]. However, some

non-hazardous mine wastes can be recycled as a result of their properties. In this context, such waste can, for instance, be used to reduce the available concentrations of metals in soils, thereby closing the cycle of the circular economy with zero or almost zero waste [16,17]. Well-known examples of this approach are magnesium oxide- [18] and lime-enriched waste [19], which have been used for soil remediation purposes.

In this context, given that dunite waste and subproducts are potential positive soil amendments due to their composition (mainly magnesium oxide and lime), here we evaluated the capacity of these materials to stabilize metal(oid)s in polluted soils and thus to reduce the potential leaching of contaminants. In addition, the use of Mg amendments may improve soil properties from a plant perspective. Therefore, the objectives of this study were to (a) address the potential properties of dunite waste and subproducts in order to stabilize a metal(oid)s polluted soil, (b) to improve the soil properties, and (c) to evaluate the reduction or increase of toxicity in a plant species focusing on the biomass production.

2. Material and Methods

2.1. Polluted Soil Sampling

A bulk sample of 20 kg of a polluted soil (labeled W) from a brownfield (Spain, 43.3138854W, -5.7003794N) affected by multi-element pollution was used for the experiments. Before use, the sample was air-dried and sieved through a 2-mm mesh. Regarding the soil properties, the pH and electrical conductivity (EC) were measured in suspension using a 1:2.5 (w/v) ratio of soil and deionized water [20]. Total soil carbon (TC) and total nitrogen (TN) were determined in a LECO CN-2000 module using solid samples. Available concentrations of metals were measured by means of TCLP extraction (toxicity characteristic leaching procedure) following USEPA Method 1311 (1992). Pseudo-total metal contents were extracted with aqua regia by acid digestion in a microwave oven (Milestone ETHOS 1, Bergamo, Italy). Metal concentrations were determined by ICP-OES (Optima 4300 DV; Perkin-Elmer, Massachusetts, U.S.). Exchangeable cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , and Al^{3+}) were extracted with 0.1 M BaCl_2 [21] and element concentrations were measured by ICP-OES (Perkin-Elmer Optima 4300 DV). Effective cation exchange capacity (CEC) was determined by the sum of exchangeable cation concentrations [22]. Available phosphorus was determined by the Mehlich method [23].

2.2. Amendments

Amendments for this study were taken from the processing plant in the only dunite mine in Spain, the David Mine, in Landoi (Galicia, 43.6981867W, -7.9268375N). The quarry of this mine is owned and operated by Pasek Minerals. Strictly speaking, the mined rock cannot be classified as dunite because it does not contain the required 90% olivine content. Its high orthopyroxene content allows it to be classified as a peridotite or more precisely harzburgite [24,25]. However, because of its high olivine content (see below) the commercial name of the product is dunite.

A variety of minerals can be identified in the rock exploited in this quarry, with some variation range due to geological changes, but the most common minerals are olivine (20%–35%), orthopyroxene (8%–16%), amphibole (14%–20%), and crisotile (0%–33%), whereas amorphous phases usually range from 5% to 30% [26]. In some areas of the quarry where weathering and hydrothermal alterations took place, minerals, such as clays, serpentine and chlorite, can also be found. The presence of these minerals is usually undesired since they accumulate in the fine fraction as a result of the blasting process. Therefore wet scalping of the feed to the primary crusher is then required, as explained below.

After blasting operations, the material with a grain size <1250 mm passes through several stages of crushing, screening and milling (Figure 1). The processing starts at the feeder, which ensures a constant feed rate to the scalper. At the scalper, the fine particles are washed out and the larger particles (>20 mm) are directed to the primary crusher. This jaw crusher is adjusted to achieve a product below 200 mm. Scalped fine particles are further processed by wet screening and hydrocycloning,

and different size fractions are recovered separately. However, the mineralogy of this fine product is not usually suitable for most current applications, so it is used as landfill, while the finest fractions (<63 microns) are stored in the tailings dam. In this context, the waste used in this study, called “dunite-tailings” (labeled DT) was taken from the hydrocyclone spigot product.

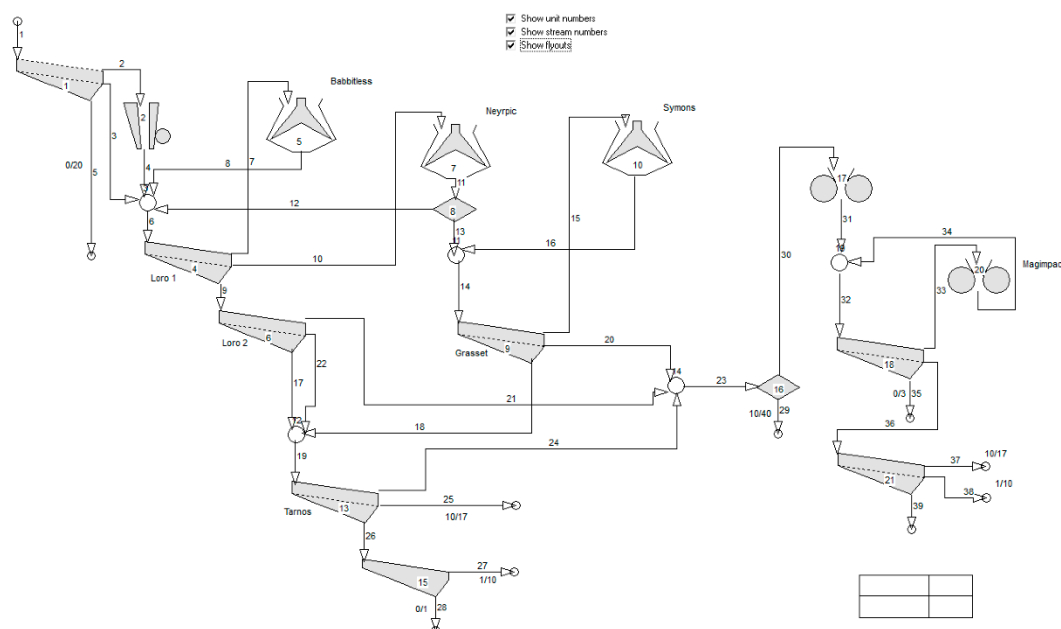


Figure 1. Flow diagram of the David Mine plant (screen capture of MODSIM 3.6).

Regarding the primary crushed product (0–200 mm particle size), this material is treated in the following stages of the processing plant, generating several products, which are commercialized by the company. The other sample used in this study, called “dunite-comminuted” (labeled DC) corresponds to a product with a particle size of 0–1 mm.

The properties of DT and DC were determined following the same methodology used for the characterization of the polluted soil described above. Additionally, the mineralogical composition of DT was determined on the basis of powder X-ray diffraction (PXRD) patterns, measured on a Philips X’Pert Pro X-ray diffractometer with Cu $\kappa\alpha_1$ radiation (1.540598 Å). After determining the position of Bragg peaks over the range of $2\theta = 5\text{--}90^\circ$, the minerals were identified using databases of the International Centre for Diffraction Data. In addition, chemical composition was determined using a Philips PW 2404 X-ray fluorescence (XRF) apparatus.

The DC had the same composition as the dunite studied by [26], and this was checked by XRF.

2.3. Greenhouse Experiment

The experiment, which involved the use of plant pots, was carried out in a greenhouse for 75 days (Figure 2). The greenhouse was maintained at an average temperature of $13 \pm 4^\circ\text{C}$ and a humidity of $75 \pm 3\%$, replicating usual weather conditions of a brownfield site. The conditions for the experiments were as indicated in Table 1.

The total weight of each pot was 1 kg. Initially, the dunite amendments were thoroughly mixed with the soil in the pots. Pots were watered 3 days per week with drop water up to holding water capacity. Pots containing the polluted soil not treated with the amendments were used as controls (W), (Table 1). The pots containing treated soil were initially incubated for 7 days. Later, *Brassica juncea* L. seeds were pre-germinated in seedbeds until 2 fully expanded leaves had grown. The plants were then transferred to the pots. The plants were harvested at the same stage of maturity (pre-flowering state) to facilitate comparison of development.



Figure 2. Pot design with the *Brassica juncea* L. plants.

Table 1. Proportions of soil and amendments used in the treatments. W, untreated soil; WDT, soil treated with dunite-tailings; WDC, soil treated with dunite comminuted.

Code	Polluted Soil	Dunite-Tailings	Dunite-Comminuted	<i>Brassica juncea</i> L.
W	100%			yes
WDT	80%	20%		yes
WDC	80%		20%	yes

W: untreated soil; WDT: soil treated with dunite-tailings; WDC: soil treated with dunite comminuted.

After the experiment, the soil samples were air dried, sieved through a 2-mm mesh, and homogenized for the analytical procedures. The same analysis as that done during characterization of the polluted soil was performed (see Section 2.1). Regarding *Brassica juncea* L., they were carefully washed with deionized water. Fresh biomass was immediately weighed, and dry mass was assessed after oven-drying for 48 h at 80 °C and then cooling at room temperature.

2.4. Statistical Analysis

All analytical determinations were performed in triplicate. The data obtained were treated using the SPSS program, version 19.0 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 carried out. If there was no homogeneity, Dunnett's T3 test was performed. A correlated bivariate analysis was also performed by means of Pearson correlation.

3. Results

3.1. Properties of the Soil and Amendments

The characterization of the polluted soil (W) and the two amendments, dunite-tailings (DT) and dunite-comminuted (DC), is summarized in Table 2.

The data revealed high pseudo-total concentrations of the metal(oid)s of interest, although the main pollutant with a high available concentration was Zn. With respect to edaphic characteristics, the soil was found to be alkaline and to contain a very low nutrient content.

The DC composition revealed a high MgO and SiO₂ content due to the presence of forsterite, olivine and serpentine [26]. However, the amendment also contained Al₂O₃, CaO and Fe₂O₃ (Table 3). In contrast, the dunite-tailings (DT) presented a higher concentration of SiO₂ and lower concentration of MgO. However, a notable difference with respect to DC was the slight increase in CaO concentration, which could be a relevant parameter for remediation. From the point of view of mineralogy, the diffraction pattern (Figure 3) showed that DT was composed mainly of minerals from the serpentine group (lizardite) and chlorite group (clinocllore and kammererite). Hornblende and ankerite may have been present in low concentrations. The mineral composition of the two amendments was consistent with the chemical data obtained by XRF.

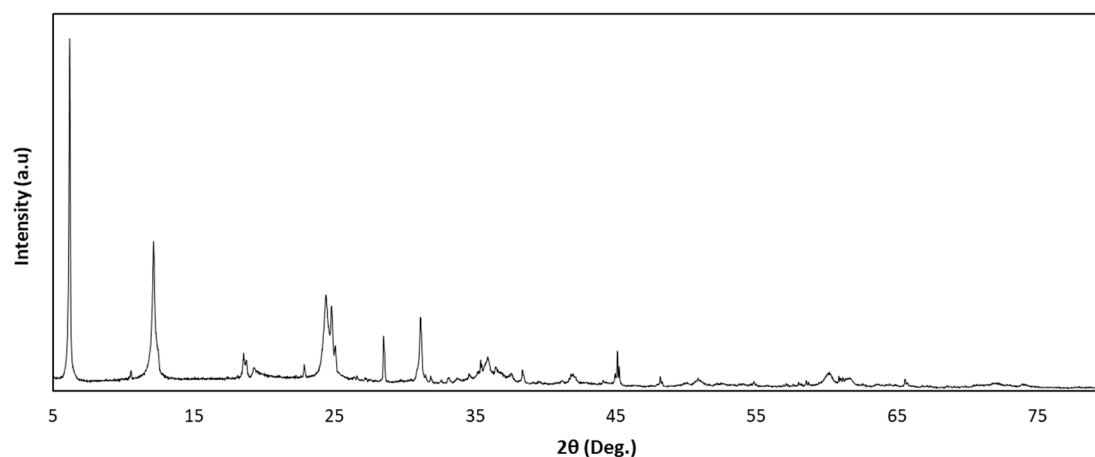
Table 2. Characteristics and metal concentrations of polluted soil (W), dunite-comminuted (DC) and dunite-tailings (DT).

Parameters	Units	Samples			
		W	DT	DC	
Edaphic	pH	7.99	9.23	9.16	
	TC	23.10	5.31	2.20	
	TN	<DL	<DL	<DL	
	P	mg·kg ⁻¹	3.14	2.21	<2.00
	K		25.75	78.60	42.55
	Mg		27.17	577.70	672.50
	Ca		466.70	120.10	143.90
	Na		3.09	20.99	24.70
	CEC	cmol ₍₊₎ ·kg ⁻¹	5.30	11.30	13.00
Pseudo-total concentration	Cu	mg·kg ⁻¹	1707.80	28.78	33.84
	Zn		3739.50	37.63	261.6
	Cd		24.61	0.89	2.53
	As		632.40	15.94	4.04
	Pb		5112.20	17.71	47.98
Available concentration	Cu	mg·kg ⁻¹	4.70	<DL	0.15
	Zn		176.54	<DL	47.41
	Cd		0.67	<DL	1.03
	As		0.32	<DL	0.09
	Pb		24.63	0.06	2.09

Values (n = 3). <DL: below detection limit; TN: total nitrogen; TC: total carbon; P: available phosphorus (Mehlich).

Table 3. X-ray fluorescence (XRF) composition of the two amendments.

Amendment	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	Others	L.O.I
DT	57.11	3.17	4.97	20.60	2.68	0.23	0.25	9.91
DC	39.86	3.00	7.62	35.34	1.73	0.07	0.35	11.91

**Figure 3.** Diffraction (DRX) pattern of dunite-tailings.

3.2. Effects of the Amendments on the Physico-Chemical Properties of the Soil

At the end of experiment, the WDT (brownfield-soil + dunite-tailings) and WDC (brownfield-soil + comminuted-dunite) treatments had significantly higher pH and conductivity values than untreated brownfield-soil (W) ($p < 0.05$). Although W had the highest values of TC (Table 3), the treatments did not show significant differences regarding this parameter ($p < 0.05$, Table 4). In addition, TN was not detectable in the W or in the WDT and WDC pots, while available P did not vary significantly. Remarkably, the cation exchange capacity (CEC) was significantly lower in W than in WDT and WDC pots ($p < 0.05$, Table 4).

Table 4. Physico-chemical properties of the untreated and treated brownfield soil after 75 days.

Parameters	Units	W	WDT	WDC
pH		7.99 ± 0.11b	8.21 ± 0.07ab	8.37 ± 0.14a
TC	mg·kg ⁻¹	22.6 ± 2.05a	18.5 ± 1.17b	18.6 ± 1.94b
TN		<DL	<DL	<DL
CEC	cmol(+) kg ⁻¹	4.99 ± 0.15b	8.68 ± 0.82a	8.52 ± 0.80a
Ca		447.9 ± 13.0a	392.29 ± 29.5ab	348.8 ± 29.9b
K	mg·kg ⁻¹	22.50 ± 1.38a	43.76 ± 5.22b	40.14 ± 12.7b
Mg		13.76 ± 0.09b	264.9 ± 31.4a	281.3 ± 28.8a
Na		14.75 ± 1.79a	14.11 ± 0.77a	15.25 ± 2.95a
P		3.13 ± 0.75a	2.00 ± 0.52a	2.06 ± 0.09a

For each row, different letters in different samples means significant difference (n = 3, ANOVA; $p < 0.05$). <DL: below detection level. Typical deviation is represented by ±.

Regarding cations, moderately significant changes were observed for Ca and K, whereas no variation was observed for Na. On the other hand, the abovementioned notable increase of CEC for the WDT and WDC pots was consistent with the marked increase in Mg observed ($p < 0.05$, Table 4).

3.3. Effects of the Amendments on Pollutants

The pseudo-total concentrations of As, Cd, Cu, Pb and Zn decreased (dilution effect mainly) with the addition of DT (WDT) and DC (WDC) to the polluted soil (W) (Table 5); in addition, comparison of the pseudo-total concentrations of four metalloids between treatments (WDT and WDC) revealed no significant differences ($p < 0.05$, Table 5).

Table 5. Pseudo-total concentrations of As, Cd, Cu, Pb and Zn of the untreated and treated brownfield soil.

Metal(oid)s	Units	W	WDT	WDC
As		688.4 ± 19.6a	469.1 ± 4.4b	497.0 ± 34.7b
Cd		25.5 ± 0.1a	18.8 ± 0.3b	19.3 ± 1.3b
Cu	mg·kg ⁻¹	1953.5 ± 2.37a	1298.2 ± 47.3b	1343.9 ± 85.5b
Pb		5564.2 ± 38.6a	3881.3 ± 152.6b	4051.8 ± 175.6b
Zn		3763.4 ± 48.5a	2679.4 ± 43.0b	2781.6 ± 137.3b

For each row, different letters in different samples means significant difference (n = 3, ANOVA; $p < 0.05$). Typical deviation is represented by ±.

The available concentration of As showed no significant differences once the treatments were applied (Figure 4A), whereas the available concentrations of Cd, Cu, Pb and Zn decreased with respect to the polluted soil (W) ($p < 0.05$, Figure 4A–C), irrespective of the treatment used (DT or DC).

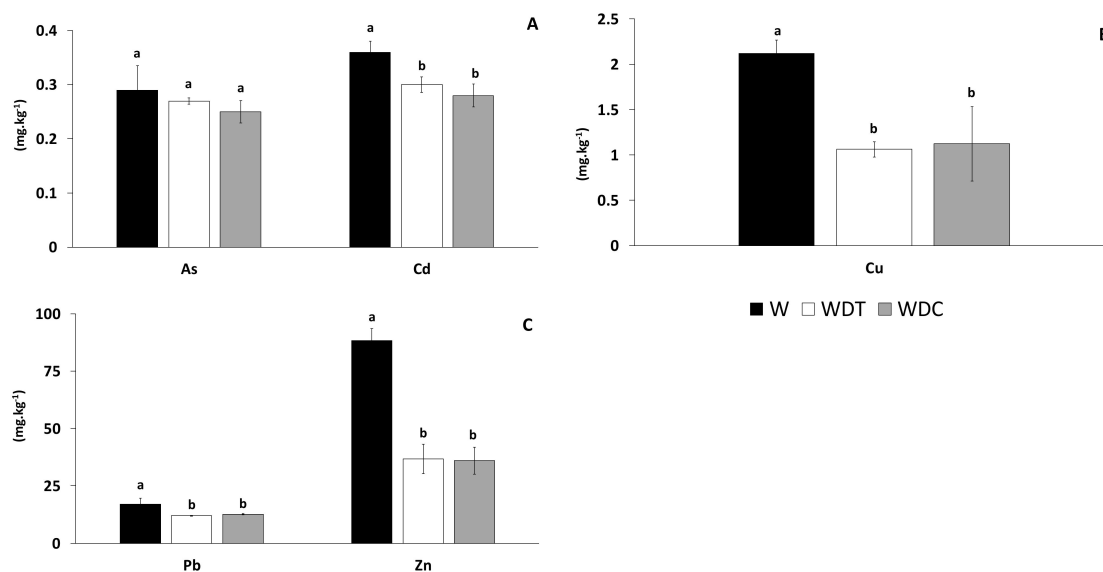


Figure 4. Influence of DC and DT on the available concentrations of As and Cd (A), Cu (B), Pb and Zn (C). For each row, different letters in different samples mean significant differences ($n = 3$, ANOVA; $p < 0.05$). Error bars represent standard deviation.

3.4. Harvested Biomass of *Brassica juncea* L.

The WDT and WDC treatments yielded a higher dry biomass of *Brassica juncea* L. than W (Figure 5; $p < 0.05$). This parameter was significantly higher in WDT than in WDC.

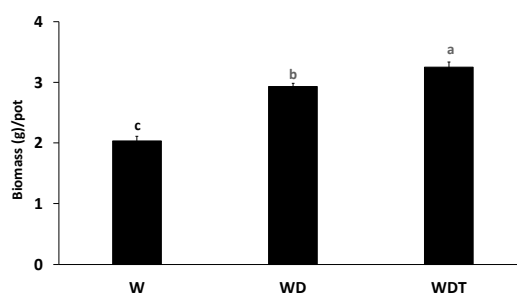


Figure 5. Harvested biomass of *Brassica juncea* L.

4. Discussion

The increase in soil pH after treatment of polluted soil with DT and DC was due to an increase in the concentration of Mg and, to a lesser extent, of K. These increases improved the CEC, which was correlated positively with the increase in pH (0.82 , $p > 0.01$). This upgrading can be explained by the high percentage of Mg in the dunite [27–29]. Mg was the element that increased most in response to treatments and it was also positively correlated with pH (0.83 , $p < 0.01$). In this context, an increase in CEC is relevant since correct soil CEC values indicate greater resistance to the chemical changes in a soil [30]. In fact, on the one hand, correct CEC values indicate good soil capacity to retain nutrients for plants [31]; on the other hand, CEC and pH are factors that play a crucial role in the availability of soil metals [32,33]. Therefore, an increase in the value of these factors will contribute to decreasing the available concentration of metals in the soil.

The decrease in TC values after the treatments is attributable to a dilution effect since DT and DC are inorganic amendments. Although significant differences in TC values were observed between the W, WDT and WDC treatments, according to [30], all three fall in a moderate category in terms of carbon content (average structural condition, average structural stability).

The addition of DT and DC to the polluted soil did not increase the concentration of available As, in spite of the high pseudo-total concentration of this compound. This is a relevant observation because elevated As levels in soil and/or irrigation water can affect the growth and development of plants and could considerably increase dietary intake through plant-based items for consumption, thereby posing an additional threat to human health [34]. Availability of As generally increases as pH increases; however, in this case, the amendments increased the pH but did not enhance the available As concentrations. The negative effect of a pH higher than 7 on the increase of available As has already been reported [35,36]. In turn, another key factor in the mobilization and immobilization of As is the phosphorus (P) concentration [37]. We found positive correlations between the concentrations of As and P (0.79, $p < 0.01$). In our case, DT and DC had a lower concentration of P than W. Therefore, the concentrations of P did not increase after application of the treatments, which would also explain the lack of an increase in As concentration.

Cd is particularly hazardous since it is easily taken up by plants and thus has a tendency to accumulate in food chain crops. Moreover, it is not degradable in nature and thus, once released into the environment, it will stay in circulation [38]. By increasing the pH and correcting the CEC, the amendments reduced the available Cd. This capacity is reflected by significantly negative correlations between available Cd, pH and CEC (-0.82 and -0.80 , respectively; $p < 0.01$). Other authors [39] have already shown that pH directly influences the availability of Cd in soil. Indeed, the pH value of the soil has a critical role in regulating the availability of metals. In this regard, the decrease in soil pH increases the mobility of the most labile elements in the soil, as is the case with Cd [32,33,40]. Therefore, the increase in pH caused by the amendments made a significant contribution to reducing the available Cd. Furthermore, the high concentration of Mg in the amendments promoted the retention of Cd, which is corroborated by a considerably negative correlation (-0.85 ; $p < 0.01$).

As previously commented, pH and CEC play key roles in metal solubility. In this regard, one of the metals most affected by these factors is Cu [41,42]. Significantly negative correlations between the available Cu with respect to the pH, CEC and Mg were found (-0.81 , -0.94 and -0.95 , respectively; $p < 0.01$). This observation would explain the notable performance of the treatments with respect to reducing available Cu (average approximate decrease of 50%).

W registered the highest available concentrations of Pb and Zn. Treatments with DT and DC caused an increase in pH, thereby reducing these concentrations, as occurred with Cd. These results are consistent with the predictions made in previous work [42]. In our case, a significant negative correlation between the pH and the concentrations of Pb and Zn (-0.70 and -0.79 , respectively; $p < 0.05$) was observed. The correction of the CEC was also favorable to achieve these results, since an increase in the concentration of basic cations enhances the fixation of metals. In fact, significant negative correlations were also obtained between the CEC and the available Pb and Zn (-0.78 , $p < 0.05$ and 0.95 , $p < 0.01$, respectively). A significant negative correlation was also determined between Mg vs. Zn and Pb (-0.99 and -0.79 , respectively; $p < 0.01$).

The correction of the pH and CEC values, together with the decrease in the available concentrations of Cd, Cu, Pb and Zn, caused an increase in the biomass of *Brassica juncea* L. Initially, the increase in pH and CEC in this experiment showed a significant positive correlation with the increase in biomass (-0.81 and 0.89 , respectively; $p < 0.01$) [43]. The treatment with DC was the most effective in enhancing biomass, possibly because it was the amendment that promoted the greatest increase in pH. In addition, DC was also the treatment that yielded a high increase in Mg concentration, which was positively correlated with the biomass (0.95 , $p < 0.01$). Furthermore, both amendments reduced Cd, Cu, Pb and Zn availability, thereby favoring an increase in *Brassica* biomass [44]. A significant negative correlation was observed between the biomass and the available Cd, Cu, Pb and Zn (-0.81 , -0.84 , $p < 0.01$; -0.74 , $p < 0.05$; respectively).

5. Conclusions

Here we addressed the reuse of waste and a subproduct from a dunite mine for the remediation of a soil affected by multi-element pollution. These materials had similar effects on available metal(oid) concentrations and on the edaphic properties of the soil. Irrespective of the dunite product used (tailings or comminuted), Zn was immobilized, probably due to the increase in pH and the contribution of Mg. Regarding Cd, Cu and Pb, the immobilization was moderately significant, but for As, the available concentrations were not modified. Regarding edaphic properties, the increase in Mg concentration influenced the CEC, resulting in enhanced soil properties. The amendments led to the immobilization of the metals and an increase in CEC, thereby reducing phytotoxicity and increasing harvested biomass. Given that mining activities produce a greater amount of DT than DC, the field application of the former, following the circular economy model, may offer a promising approach to promote its reuse in soil remediation strategies.

On the basis of our findings, dunite mining waste and subproducts emerge as new materials useful for stabilization of polluted soils. However, although the laboratory study has revealed good results, field-scale studies should be carried out in order to address a better understanding of the potential effectiveness of these amendments, and to identify possible difficulties that could occur (such as long-term modifications in the pollutant availability levels). Overall, future studies involving different soils, conditions, and doses are required in order to corroborate these promising results.

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