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Biochar-nanoparticle combinations enhance the biogeochemical recovery of a post-mining soil

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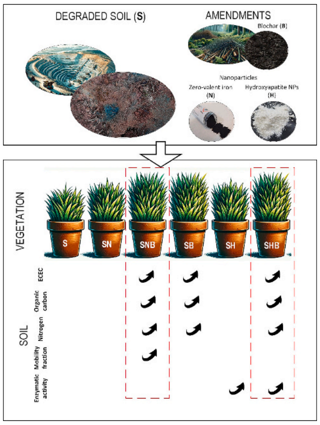
HIGHLIGHTS

- Post-mining soil treated with biochar-nanoparticle blends and phytoremediation
- Biochar facilitated significant increases in ECEC, organic C and N in soil.
- Hydroxyapatite nanoparticles (nH) revealed a better impact than nZVI in soil health.
- nH and nZVI held low availability of metal(loid)s in soil and reduced plant intake.
- Main enzymatic activities in soil boosted by the mixture of biochar and nH

GRAPHICAL ABSTRACT



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ABSTRACT

Here we addressed the capacity of distinct amendments to reduce arsenic (As), copper (Cu), selenium (Se) and zinc (Zn) associated risks and improve the biogeochemical functions of post-mining soil. To this, we examined nanoparticles (NPs) and/or biochar effects, combined with phytostabilization using *Lolium perenne* L. Soil samples were taken in a former metal mine surroundings. Ryegrass seeds were sown in pots containing different combinations of NPs (zero-valent iron (nZVI) or hydroxyapatite (nH)) (0 and 2 %), and biochar (0, 3 and 5 %). Plants were grown for 45 days and the plant yield and element accumulation were evaluated, also soil properties (element distribution within the soil fractions, fertility, and enzymatic activities associated with microbiota functionality and nutrient cycling) were determined. Results showed biochar-treated soil had a higher pH, and much higher organic carbon (C) content than control soil and NP-treated soils, and it revealed increased labile C,

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total N, and available P concentrations. Soil treatment with NP-biochar combinations increased exchangeable non-acid cation concentrations and reduced exchangeable Na%, improved soil fertility, reduced sodicity risk, and increased ryegrass biomass. Enzymatic activities, particularly dehydrogenase and glucosidase, increased upon the addition of biochar, and this effect was fostered by NPs. Most treatments led to a significant reduction of metal(loid)s contents in biomass, mitigating contamination risks. The two different NPs had similar effects in many parameters, nH outperformed nZVI in terms of increased nutrients, C content, and enzymatic activities. On the basis of our results, combined biochar-NP amendments use, specially nH, emerges as a potential post-mining soil restoration strategy.

1. Introduction

Mining is a key activity for societal development and it is expanding worldwide (Alessia et al., 2021; Horn et al., 2021). Post-mining soil (herein referred to as mine soil or soil) is often degraded and can be a source of metal(loid) dispersion via leaching and erosion (Puga et al., 2015; Santos et al., 2015; Zhou et al., 2015). The UN General Assembly has declared the period 2021–2030 to be the decade of soil reclamation (FAO, 2020). In this sense, mine soil must be recovered whenever possible to minimize the environmental impact and economic costs post-closure, and sustainable remediation strategies are preferred.

Nanotechnology has found wide applications in addressing environmental issues, particularly for site remediation using nanoparticles (NPs). Initially, the use of such nanomaterial was limited to the remediation of water affected by metal(loid) pollution (Ponder et al., 2000; Wang and Zhang, 1997). In this regard, NPs have been applied directly to soil contaminated with various potentially toxic elements (PTEs) to minimize their availability (Baragaño et al., 2020a; Gil-Díaz et al., 2019; González-Feijoo et al., 2023). Quite a few types of NPs have been used for soil remediation, the most common being zero-valent iron (nZVI) NPs (Gil-Díaz et al., 2017; Vítková et al., 2018), although other iron-based NPs and even C-based ones such as graphene oxide have been tested (Baragaño et al., 2020a; Baragaño et al., 2020b; Sebastian et al., 2019). Several authors have demonstrated that the combined application of NPs with different organic amendments leads to a reduction in PTE availability (Baragaño et al., 2020c; Martínez-Fernández et al., 2015) and can even enhance other soil characteristics (e.g., structure and water-holding capacity). However, many researchers are skeptical about applying NPs to soil due to the possible impact of this material on soil microbiology (Crane and Scott, 2012; Klaine et al., 2008; Xie et al., 2017). Thus, the assessment of soil quality should include a combined analysis of a range of physicochemical characteristics, as well as biological and biochemical parameters (Arán et al., 2022; Santos et al., 2017). In this regard, soil enzymes play a key role in soil processes and functions, including organic matter mineralization, nutrient availability, and biological N fixation, among others (Caldwell, 2005; Carpa, 2009; Dick and Tabatabai, 1993). Moreover, enzyme activity provides information on the activity of soil microorganisms, and it can serve as early biological indicators of changes in soil quality, irrespective of the amendments used (Hinojosa et al., 2008; Arán et al., 2022; Santos et al., 2014; Santos et al., 2015).

In this context, the use of biochar as an amendment for contaminated soil usually leads to a decrease in PTE availability (Ahmad et al., 2014; Forján et al., 2016). This effect is attributed its high surface area and chemical characteristics, such as its functional groups (Głąb et al., 2021). Biochar can also improve other physicochemical characteristics of contaminated soils (Bolan et al., 2014), and furthermore, it can enhance the positive effects of NPs on contaminated soil (Su et al., 2016; Yang et al., 2016). In this regard, amendments involving iron-based NPs combined with biochar have been used to recover soil contaminated with PTEs (Baragaño et al., 2020c; Su et al., 2016; Wang et al., 2019); nevertheless, the effect of the combined application of biochar and hydroxyapatite NPs (nH) has not been addressed to date. Hydroxyapatite is a naturally mineralized calcium apatite that can be applied to soils to reduce the availability of several metal(loid)s (As, Cd, Cu, Pb, Sb and Zn) (Rodríguez-Seijo et al., 2020), it can also serve as a nanofertilizer as it is biocompatible with soil, and it is readily available and inexpensive (Jiang et al., 2012a; Lago-Vila et al., 2019; Maghsoodi et al., 2020; Thirugnanasambandan, 2021).

Expanding upon previous considerations, the objective of this study was to enhance the biogeochemical properties of a mining soil by utilizing two varieties of nanoparticles (nH and nZVI), either independently or in conjunction with biochar, along with phytostabilization involving *Lolium perenne* L. Significantly, our investigation pioneers the novel application of nH nanoparticles in contaminated soil remediation. Moreover, in addition to assessing shifts in metal(loid) mobility within a typical mining soil, we placed particular emphasis on evaluating the impact of nanoparticles on the soil-plant system and soil microbial activity, as evidenced by alterations in key enzymatic activities.

2. Material and methods

2.1. Soil sampling

The mine soil used herein was from the surroundings of an open-pit metal mine in Asturias (northern Spain). This mine is located in an area influenced by a climate that can be described as Cfb within the Köppen-Geiger climate classification. The land in this area is currently devoted to agro-livestock activities. Mine soil samples were collected randomly in the sampling area, at a depth of 30 cm, to obtain a composite sample to be used in the pot experiment.

2.2. Amendments (NPs and biochar)

Several amendments were tested. Biochar (B), provided by PYREG Carbon Technology Solutions (Dörth, Germany), was made from wood (remains of pruning) following the PYREG® methodology (PYREG, 2023). Zero-valent iron NPs (nZVI), denominated NANOFER 25S, spherical, and with an average diameter of 60 nm, were obtained from NANO IRON s.r.o. (Zidlochovice, Czech Republic). Hydroxyapatite NPs (nH) composed of $Ca_{10}(PO_4)_6(OH)_2$) and denominated MKN-HXAP-020P, showed a filamentous morphology and 20 % of nominal size, and they were supplied by mKnano (M K Impex Corp., Ontario, Canada).

2.3. Greenhouse experiment and plant growth

A greenhouse experiment was carried out in pots (~1 kg). The soil

Table 1
Proportions (%) of amendments used in the control and treatments for soil restoration (n = 3).

Code	Polluted soil (%)	nZVI (%)	nH (%)	Biochar (%)
S	100			
SN	98	2		
SNB	93	2		3
SB	95			5
SH	98		2	
SHB	93		2	3

S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar.

was mixed with nZVI or nH, with or without biochar (B), as shown in the treatments ($n = 3$) described in Table 1. Application rates were selected according to previous studies to ensure optimal concentrations for effective treatment (Baragaño et al., 2020a; Gil-Díaz et al., 2017) while also considering cost-effective approaches to ensure the efficiency of the experiment. The amendments were added to the soil surface and mixed manually with the first ≈5 cm to simulate application in the field. After 15 days of incubation with deionized water at field capacity, ryegrass seeds (*Lolium perenne* L.), provided by Piensos Lago S.L. (Asturias, Spain), were sown (1.5 g per pot). The soils were watered to maintain field capacity throughout the experiment. Ryegrass growth was evaluated for 45 days. Afterwards, the plants were harvested, and samples were collected. Soil samples were homogenized and separated according to the type of analysis. For the physicochemical analysis, the samples were air-dried and sieved through a 2 mm mesh while for biological analysis they were only sieved (<2 mm) and kept fresh (4 °C).

2.4. Soil and biochar characterization

The initial soil, the biochar, and soil treated with NPs and/or biochar collected at the end of the experiments were characterized for the following: pH and redox potential in deionized water (1:2.5 m:V), pH KCl 0.1 M, organic C (OC) by the wet digestion method (Springer and Klee, 1954); labile organic C (LOC) (extraction with hot water and C determination by the wet digestion method); available P (Olsen method) (Olsen and Sommers, 1982); effective cation exchange capacity (ECEC); and the exchangeable non-acid cations (Peech, 1947) and total N (organic plus ammonium-N; Kjeldahl method).

The pseudototal content of metal(loid)s in the initial soil and biochar was determined by acid extraction. To this end, 0.2 g of each sample was digested with HNO_3 (69 %) and HCl (37 %) (ratio 1:3 v:v) in a microwave oven (Milestone ETHOS 1, Italy). After completion of the process, the sample was filtered and transferred to a 100-ml volumetric flask. Metal(loid)s content was then determined by Inductively Coupled Plasma Optical Emission Spectroscopy, ICP-OES (Perkin Elmer Optima 4300 DV).

A sequential chemical extraction was conducted to determine the distribution of the most abundant and hazardous meta(*oid*)s (see results; As, Cu, Zn, and Se) in the different geochemical phases of the soil—treated with NPs and/or biochar—collected at the end of the greenhouse experiment. The extraction was carried out following the procedure used by Almas et al. (2000). The reagent for the first extraction was modified (KNO_3 0.001 M instead of H_2O) based on the procedure developed by Salbu et al. (1998), which in turn, is based on that of Tessier et al. (1979). In brief, the following fractions were obtained: F1: reversible physical sorption as water-soluble metals; F2: exchangeable; F3: specifically adsorbed; F4: metal-associated, sorbed, or occluded mainly with iron and manganese oxides; F5: strongly complexed with organic matter; F6: irreversibly adsorbed; and F7: residue. After each extraction, centrifugation, and filtration, the solid phases were washed with 10 mL of distilled water, centrifuged, and filtered again. The supernatant was added to the previous extraction for further analysis by ICP-OES (Perkin Elmer Optima 4300DV) (1:10 m:V).

2.5. Plant analysis

Plant biomass was carefully washed with deionized water and weighed immediately, whereas dry mass was determined after oven-drying for 48 h at 60 °C. The dry plant tissues were ground and the contents of As, Cu, Zn, Ni, Fe, P, Ca, Mg, Mn, and K were extracted with a mixture of HNO_3 (69 %) and H_2O_2 30 % (ratio 5:1 V:V) in a microwave oven (Milestone ETHOS 1, Italy). Metal(loid) concentrations were determined by ICP-OES (Optima 4300 DV; Perkin-Elmer).

2.6. Soil fertility index

The soil fertility index (SFI) was calculated to determine possible future land use as a grassy area. This index was calculated by modifying the method proposed by Mahmoud et al. (2019). In this study, we considered OC instead of organic matter. The SFI was determined using the following equation:

$$\begin{aligned} SFI = {} & pH_{(H2O)} + OC\ (mg \cdot kg^{-1}) + \text{available P}\ (mg \cdot kg^{-1}) \\ & + \text{exchangeable K}\ (cmol_c\ kg^{-1}) + \text{exchangeable Ca}\ (cmol_c\ kg^{-1}) \\ & + \text{exchangeable Mg}\ (cmol_c\ kg^{-1}) \end{aligned} \tag{1}$$

The exchangeable Na percentage (ESP factor) is taken as a reference to control this factor. The ESP factor was determined according to the equation:

$$ESP = (\text{Exchangeable Na}/CEC) \times 100 \tag{2}$$

2.7. Soil enzymes

The samples were analyzed to determine the activity of four enzymes as (micro)biological indicators. Dehydrogenase is associated with overall microbial activity while ß-glucosidase, phosphatase, and urease are related to C, P, and N cycling, respectively. The following methods were applied for soil enzyme analysis: i) dehydrogenase determination (Tabatabai, 1994); ii) β-glucosidase (EC 3.2.1.21) (Eivazi and Tabatabai, 1988); iii) acid phosphatase (EC 3.1.3.2) (Eivazi and Tabatabai, 1977); and iv) urease (EC 3.5.1.5) (Kandeler and Gerber, 1988).

2.8. Statistical analysis

All analytical determinations were performed in triplicate. The data obtained were statistically treated using version 19.0 of the SPSS program 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.

3. Results and discussion

3.1. Soil and biochar characterization

The general characteristics of the mine soil and biochar are shown in Table 2.

The soil had a neutral pH, while the biochar was strongly alkaline. As regards carbon, the soil had a low OC content (≈1 %), in contrast to biochar with a very high content (71.4 %). Coherently, soil LOC was low and accounted for ≈3.9 % of OC whereas, despite LOC being higher in biochar it accounted only for ≈2.1 % in this material, thereby indicating a greater percentage of recalcitrant C compared to the soil. LOC in the soil comprises simple organic compounds such as amino acids and carbohydrates, thus facilitating its transformation by microorganisms (Zou et al., 2005).

Regarding total N, the soil had a very low content (<0.1 %), while biochar showed 10-fold higher values. The C/N ratio of the soil indicated a balance with a controlled release of mineral N and soil C. On the other hand, the very high C/N ratio of biochar could lead to slow decomposition and humification of organic matter by soil microorganisms. The available P content (1.13 %) in the soil was very low compared to the total P content. In contrast, the total P content of biochar was lower than in the soil, but the available P content and percentage (63.0 %) were much higher.

The cation exchange capacities of the soil and biochar were low, with a predominance of non-acid cations in exchangeable complexes, namely Ca in the soil and K in the biochar. The low concentration of

Table 2
Soil and biochar characterization.

Parameter	Units	Mine soil (S)	Biochar (B)
$pH_{(H2O)}$	–	7.35 ± 0.04	9.65 ± 0.03
$pH_{(KCl)}$		7.04 ± 0.12	9.30 ± 0.01
OC	g kg^{-1}	10.4 ± 0.6	714 ± 1
LOC		0.41 ± 0.04	15.3 ± 1.2
N (total)		0.99 ± 0.09	9.60 ± 0.02
C/N	–	10.5 ± 0.2	74.4 ± 0.7
Available P	mg kg^{-1}	5.10 ± 0.68	102 ± 1
Ca^{2+}	cmol$_c$kg^{-1}	11.2 ± 0.7	7.52 ± 0.49
Mg^{2+}		1.90 ± 0.15	0.44 ± 0.01
Na^{+}		0.28 ± 0.11	1.40 ± 0.01
K^{+}		0.37 ± 0.03	13.51 ± 0.46
Al^{3+}		n.d.	0.33 ± 0.40
ECEC		13.7 ± 0.5	22.4 ± 0.3
ESP	%	2.04 ± 0.08	6.25 ± 0.71

Pseudototal content	Units	Mine soil (S)	Biochar (B)	T.L.A
As	mg kg^{-1}	601 ± 24	14.6 ± 0.5	40
Cu		8233 ± 281	15.7 ± 0.4	55
Zn		260 ± 12	221 ± 1	455
Se		5.10 ± 0.21	n.d.	25
P		453 ± 6	162 ± 1	–

OC: Organic carbon; LOC: Labile Organic C; ECEC: Effective Cation Exchangeable Capacity. n.d.: not detected. T.L.A: threshold levels for soils in the Principality of Asturias.

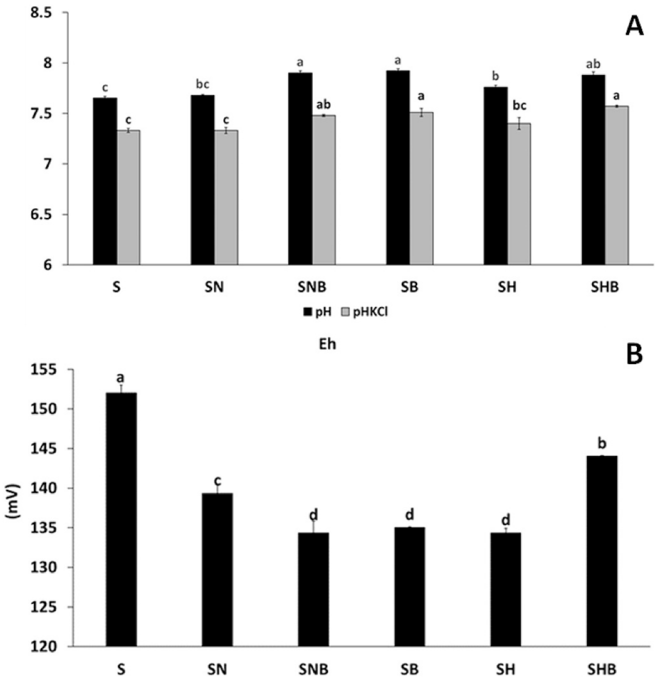

Fig. 1. (A) pH and $pH_{(KCl)}$ and (B) redox potential (Eh) in the control soil (S) and the soil treated with NPs and/or biochar. (S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar). Different letters mean significant differences ($n = 3$, ANOVA; $p < 0.05$). Data correspond to mean and error bars represent the standard deviation.

exchangeable acid cations in the soil and biochar is consistent with their pH values. The Na^{+} content of soil was low (non-sodic), as reflected by its ESP value <6. On the other hand, biochar presented an ESP value >6 (slightly sodic, i.e. ESP between 6 and 10) (Shaw et al., 1994).

Pseudototal metal(oid) contents indicated that As, Cu, Zn, and Se were the main PTEs in the soil, the pseudo-total contents of these elements are shown in Table 2. Indeed, the content of As and Cu exceeded the threshold levels for soils in the Principality of Asturias (Table 2), while Se and Zn were below the thresholds, although still high (BOPA, 2014). The pseudototal metal(oid) content in biochar was lower than that in the soil, thereby indicating no risk to its use in environmental restoration.

3.2. *Effect of the treatments on soil pH and redox potential*

The treatments involving a combination of NPs and biochar (SNB, SB, SHB) and those with biochar alone (SB) had a slightly higher pH and potential pH compared to the control soil (S) and the soil treated with NPs only (SN, SH) (Fig. 1A). This minor, although statistically significant, increase in pH can be attributed to the presence of biochar, which has an alkaline pH (Table 2) (Beesley et al., 2010; Forján et al., 2016; Jiang et al., 2012b). In fact, Dai et al. (2017) proposed that the effect of biochar in alkaline soil is less pronounced than in acidic soil. In turn, the increase in pH observed in the SNB and SHB treatments is attributed to the NPs as both nZVI and nH are also alkaline in a water suspension (Cui et al., 2013; Yang et al., 2016).

All treatments led to a decrease in soil redox potential compared to the control soil (Fig. 1B). It is worth noting that biochar applied alone (SB) and biochar combined with nZVI nanoparticles (SNB) both resulted in a decrease in redox potential of >10 %. This effect was also observed when hydroxyapatite nanoparticles were applied alone (SH). However, the combination of biochar with hydroxyapatite nanoparticles (SHB) led to a decrease in redox potential of approximately 5 % and this indicates that its effect in reducing redox potential was lower compared to SB, SNB, or SH. It has long been known that organic matter and organic compounds (e.g., biochar), as well as some NPs (e.g., nZVI), have reducing power, that is to say, they can lower soil redox potential (Joseph et al., 2015; Kumar et al., 2014; Liu et al., 2007; Reinsch et al., 2010; Bae et al., 2018). Indeed, when nZVI are applied to soil, they rapidly oxidize to form iron oxides (Bae et al., 2018). In turn, biochar also has reducing capacity, and its oxidation is induced mainly through abiotic reactions boosted by the electron-donating properties of areas with a high density of p-electrons. Subsequently, O-containing functional groups form on the biochar surface (Joseph et al., 2015). Despite the high stability of aromatic C in biochar, this material has redox activity and functions mainly as a reducing agent, with O_2 being the most common electron-accepting species (Joseph et al., 2010). On the whole, and given the reducing power of nZVI and biochar, their combination caused changes in Eh values (Fig. 2B). This reducing behavior is commonly associated with an increase in pH caused by the consumption of H^{+} (Wang et al., 2021); however, as stated above, in this experiment, the lack of a notable change in pH can be attributed to the initial non-acidic soil pH (see Table 1). Therefore, the effect of the NP-biochar interaction on pH was not as evident as might be expected in soils with acidic pH.

As regards the Eh reduction observed when nH were added (SH and SHB), the results obtained were not concordant with those reported by Wang et al. (2022), who found that the use of hydroxyapatite increased Eh in a mine soil with a lower pH (5.1) located in a tropical humid climate (conditions notably different to ours). Other parameters that may influence soil Eh include microbial activity and the conditions of the rhizosphere system (Vítková et al., 2018; Antoniadis et al., 2017).

3.3. *Influence of treatments on organic carbon and labile carbon*

Treatments containing biochar showed the highest OC content compared to the control soil (S) and soil treated only with NPs (SN, SH) (Fig. 2A). This increase in OC is strongly associated with the substantial contribution from biochar (O'Connor et al., 2018). In fact, control soil had an OC content of 10.4 g kg^{-1}, whereas biochar had 714 g kg^{-1} (Table 2). Apart from supplying OC, biochar can adsorb soluble OC from the soil (Beesley et al., 2011). This adsorption capacity might be an additional reason why, after 45 days of the experiment, the soil treated with both biochar alone or combined with NPs had a higher OC content

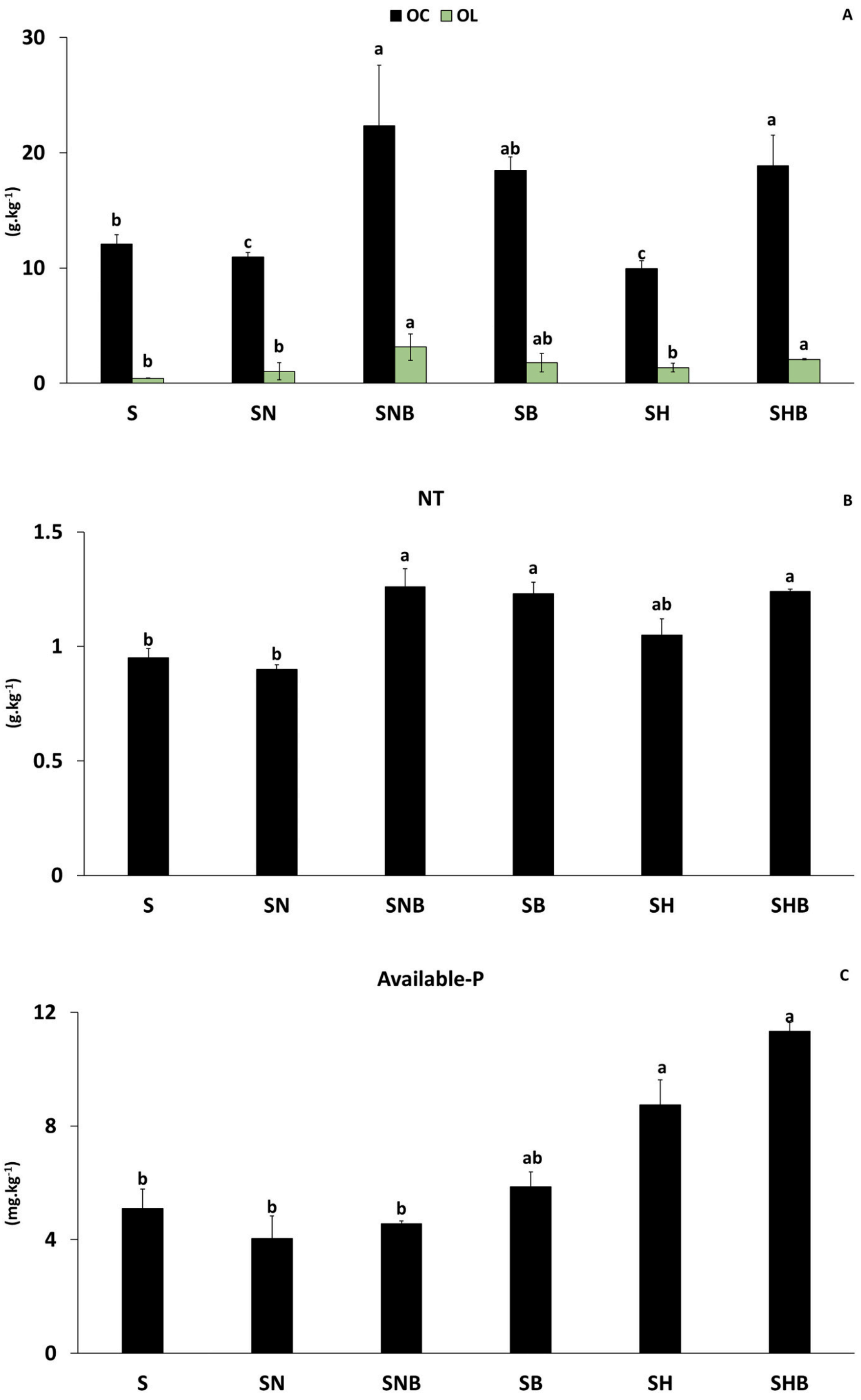

Fig. 2. A) Organic C (OC) and organic labile C (OL), (B) nitrogen (total), (C) available P in the control soil and the soil treated with NPs and/or biochar. (S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar). Different letters mean significant differences (n = 3, ANOVA; $p < 0.05$). Data correspond to mean and error bars represent the standard deviation.

than the control soil and that treated solely with NPs. nZVI and nH are inorganic and therefore their addition to the soil did not increase OC (Fig. 2A). However, in the SN and SH treatments, a significant decrease in OC was observed compared to the control soil (Fig. 2A). The decrease in organic matter following these treatments can be attributed to two mechanisms. First, humic and fulvic acids, representing essential components of organic matter, may undergo strong adsorption on the surfaces of nZVI and nH, resulting in lower OC values than anticipated (Latif et al., 2020; Tratnyek et al., 2001; Du et al., 2014; Kandori et al., 2010; Raunkjær et al., 1994; Swain and Sarkar, 2013; Xia et al., 2019). Furthermore, the adsorption of organic matter onto the nZVI surface saturates the active reaction sites of these NPs. In addition, some studies point to the degradation of organic matter by nZVI (Gueye et al., 2016; Hui et al., 2021). Regarding the reduction in OC attributed to nH, some of these studies have demonstrated that this material has a high adsorption capacity, including proteins, carbohydrates, and lipids (Du et al., 2014; Kandori et al., 2010; Raunkjær et al., 1994; Swain and Sarkar, 2013; Xia et al., 2019).

We observed that the LOC content increased in the soil treated with biochar, particularly in the nZVI + biochar (SNB) and nH + biochar

(SHB) combinations, compared to the control (S) and treatments with NPs (Fig. 2A). Liang et al. (2012) suggested that combining certain organic and inorganic amendments can enhance this carbon fraction. Moreover, the presence of biochar may contribute to increasing the LOC content by promoting the development of microorganisms and facilitating the organic matter cycle (Kuzyakov et al., 2009; Zimmerman et al., 2011).

3.4. *Influence of treatments on nitrogen and available phosphorus*

The soils treated with biochar with or without NPs (SB, SNB, and SHB) exhibited the highest N contents (Fig. 2B). Biochar demonstrated a nitrogen content of 9.60 $g\cdot kg^{-1}$ (Table 1), and thus its incorporation into the soil, even at low application rates, led to a N enhancement in the study soil. This property of biochar may influence its capacity to host and promote the development of microorganisms influencing the N cycle (Chan et al., 2007, 2008; Major et al., 2009). Furthermore, biochar can reduce N leaching and N_2O emission (Anderson et al., 2011; Xu et al., 2016).

The soil treatments containing nH (SH, SHB) had the highest available P concentrations, followed by those involving only biochar (SB) (Fig. 2C); note that it is likely that SB would have been grouped with the SN and SNB treatments if the same percentage of biochar had been used. Several studies have shown that the P concentration of nH renders it useful as a nanofertilizer (Montalvo et al., 2015; Wei et al., 2016). Note that the soil treated with nH showed P concentrations above the desired limit, according to Hazelton and Murphy (2007). Also, biochar can mobilize P due to the negative charges on its surface and the dissolved OC that is released into the soil (Hale et al., 2013; Pandit et al., 2018). Biochar can also modify the availability of phosphorus by adsorbing chelating organic compounds like phenolic acids, amino acids, and complex proteins or carbohydrates. The adsorption of organic molecules onto biochar surfaces can directly capture cations, leading to delayed P adsorption or precipitation in the soil (Zhu et al., 2018).

Soil treatments involving nZVI (SN, SNB) and also the control soil (S) had the lowest available P concentrations (Fig. 2C). Baragaño et al. (2020c) demonstrated that nZVI, alone or combined with biochar, decreases the available concentrations of anionic species, such as phosphates, in soils. We also observed this effect of nZVI, as the application of this nanomaterial alone or in combination with biochar did not result in a significant increase in available P compared to the control soil (S) (Fig. 2C).

Table 3
Cations in the exchange complex, ECEC, and ESP factor in the untreated mine soil and the soil treated with NPs and/or biochar.

	S	SN	SNB	SB	SH	SHB
Ca^{2+}	11.79 ± 0.68c	11.63 ± 0.19d	13.88 ± 0.27a	14.07 ± 0.90a	12.88 ± 0.21b	13.97 ± 0.59a
Mg^{2+}	2.04 ± 0.07a	1.99 ± 0.06ab	1.75 ± 0.05b	1.67 ± 0.10b	2.16 ± 0.07a	1.88 ± 0.00b
Na^{+}	0.49 ± 0.34a	0.22 ± 0.15a	0.48 ± 0.09a	0.15 ± 0.03a	0.26 ± 0.07a	0.37 ± 0.60a
K^{+}	0.58 ± 0.25b	0.30 ± 0.07b	0.94 ± 0.15a	0.73 ± 0.09ab	0.41 ± 0.04b	0.80 ± 0.13a
Al^{3+}	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
ECEC	14.92 ± 1.15b	14.15 ± 0.24b	17.06 ± 0.46a	16.63 ± 1.02a	15.71 ± 0.35ab	17.02 ± 1.33a
ESP (%)	3.58 ± 1.62a	1.23 ± 0.05b	2.49 ± 0.15ab	0.91 ± 0.14bc	1.35 ± 0.16b	0.11 ± 0.01c

S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar). Different letters mean significant differences (n = 3, ANOVA; $p < 0.05$). u.d.l.: under detection limit.

3.5. *Influence of treatments on ECEC and ESP*

The low concentration of acid cations (Al) in the exchangeable complex of all the treatments is associated with the high pH of the amendments and the dominance of non-acid exchangeable cations (Table 3). Furthermore, the soil treatments containing biochar had the highest concentrations of non-acid exchangeable cations, except for Mg, thereby confirming the great capacity of biochar to retain and release these cations over time (Forján et al., 2019; Hossain et al., 2020). This property can be attributed to several biochar characteristics, including its large specific surface area and the charges distributed over this surface, which enable it to adsorb cations (Hossain et al., 2020; Karer et al., 2015). The ECEC of biochar is closely related to surface functional groups such as carboxylic and phenolic OH groups (Liu et al., 2013).

The application of the different treatments resulted in a decrease in ESP values (Table 3) due to a slight increase in the concentration of cations such as Ca (for instance in SB) described above, and not to a Na decrease (not statistically significant as shown in Table 3). At any case, ESP was also low in the control soil and thus, the values obtained indicate that no treatment caused salinity or sodicity issues. These results are consistent with those reported by Ali et al. (2017) and Saifullah et al. (2018).

3.6. *Effect of treatments on As, Cu, Zn, and Se distribution in the different geochemical phases*

The content and percentage distribution of As, Cu, Zn, and Se among the geochemical phases in the control soil and soil treated with biochar and/or NPs are shown in Table S1 and Fig. 3, respectively. The differences observed in the total sum of the different fractions (Table S1) of each element result from the heterogeneity of the soil and the biochar used. Therefore, the results are also indicated as percentages extracted from each fraction (Fig. 3).

Regardless of the treatment, the results of As fractionation suggest that the soil mineral fraction (F6) is the main component retaining most of the As, thus justifying its limited availability. Organic matter and Fe and Mn oxides also contributed to As retention in the soil, further limiting its availability. The content of As in F5 depended mainly on the presence of natural organic matter than on the increase in OC induced by the biochar. In fact, the application of the amendments did not increase As associated with F5. Although the content of As associated with Fe and Mn oxides (F4) and organic matter (F5) was slightly lower in the soil with biochar and/or NPs (except with nH) than in the control, our results revealed that As was not detected in the most available fractions of the soil, regardless of treatment with amendments (F1, F2, and F3).

In contrast to As, the Cu content in the soil was mainly associated with the available fractions, especially with the exchangeable (F2) and specifically sorbed (F3) fractions, thereby indicating the high availability and mobility of this metal (>80 % of total Cu). The treatments with biochar and NPs did not significantly decrease the Cu content in these fractions, thereby suggesting that these amendments had a limited effect on Cu retention. Although biochar and NPs can immobilize Cu through several mechanisms (Arán et al., 2016), this capacity seems to be lower than that of the natural organic matter and oxides in the soil. In fact, Cu content strongly complexed with organic matter (F5) increased only slightly in the SN, SNB, SH, and SHB treatments. In addition, the residual fraction (F6) also increased slightly with the SNB, SB, SHB treatments, potentially due to the formation of low solubility solid phases resulting from Cu fixation on the NPs or the formation of stable organometallic compounds with biochar.

The Se content in the control soil and soil treated with NPs and/or biochar was associated with organic matter (F5), which could limit its availability in the soil, or specifically bound to cation exchange sites in the soil (F3). This profile did not show significant differences regardless of treatment. Although the F3 fraction may be available for organisms, it was less accessible than F1 and F2. Moreover, Se was not found to be

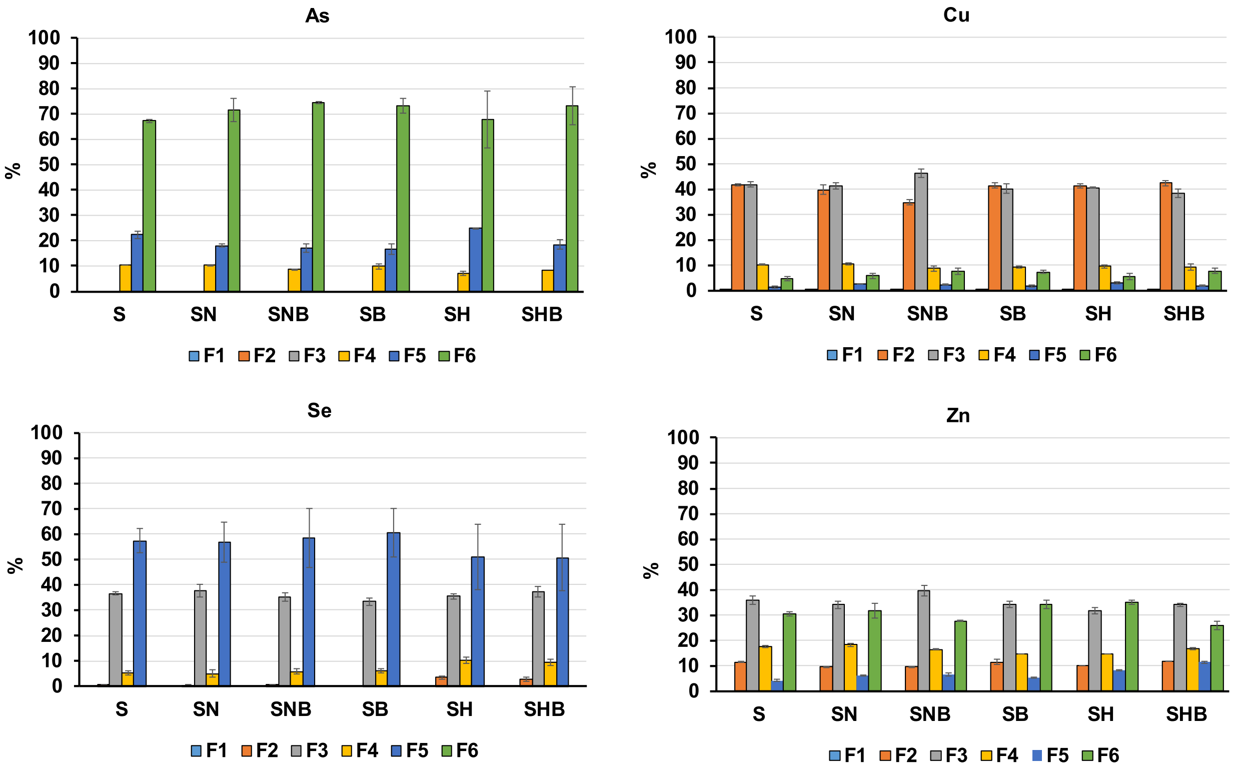

Fig. 3. Percentage of As, Cu, Se, and Zn in each fraction in the untreated mine soil and the soil with the different treatments applied. Values calculated from the data are shown in Table S1 – Supplementary material. (S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar).

associated with the residual fraction (F6) or the soluble fraction (F1), thereby suggesting that this element was not present in the soil in solid phases with low solubility nor was it easily leached and mobilized to other compartments of the ecosystem.

Zn was more evenly distributed among the different soil fractions than other elements such as As, Cu, and Se. In addition, Zn associated with the residual fraction (F6) was slightly higher in soils treated with biochar and nH (SH) and nZVI (SB), although practically no significant differences were observed in the exchangeable (F2) and specifically sorbed (F3) fractions.

3.7. *Soil fertility index*

The Soil Fertility Index (SFI) was assessed to determine soil capacity to support the growth and development of plants in relation to the amendment (biochar and/or NPs) applied (Fig. 4A). The soil containing biochar resulted in a higher increase in SFI (Fig. 4A). In addition, the biochar + nZVI (SNB) and biochar + nH (SHB) treatments had higher SFI values than those involving the amendments alone. This observation indicates synergistic effects between biochar and the two types of NPs, improving the SFI. The positive effect of biochar on SFI values is consistent with the data obtained by Mahmoud et al. (2019). Assessing soil fertility is essential in soil management because this parameter reflects the productive capacity of soil to support plant growth (Wasli et al., 2011). We observed that the treatments that most improved the SFI were those with the highest biomass at the end of the experiment (Fig. 4). Observation of the SFI and biomass data reveals that the treatments had a positive effect on these factors. Furthermore, biochar was critical to enhancing these factors (Beesley et al., 2011; Forján et al., 2018; Karer et al., 2015), bringing about the highest values of OC, LOC, TN, available nutrients, and ECEC (Fig. 2 and Table 3).

3.8. *Treatment effects on yield and metal(oid) content in ryegrass*

The amount of ryegrass biomass (wet and dry) produced in the control soil and soil treated with biochar and/or NPs and the content of As, Cu, and Zn in the plant are shown in Fig. 4 (Se was not detected in the aerial part). The changes observed in plant development and growth can be considered important biological indicators of the effect of environmental conditions and soil characteristics (Arán et al., 2022).

The plants grown in the control soil showed the highest contents of the PTEs examined, with As and Cu exceeding the limits considered phytotoxic for general plants (Kabata-Pendias, 2011) thus explaining the lowest amounts of biomass produced during the experiment (Fig. 4). The available soil fraction of these elements in the soil was not higher than for soil treated with the amendments. A comparison of the treatments (with and without amendments) revealed no clear relationship between PTE contents in plants and the available fractions. In the case of As, the available fractions in the soil (F1, F2, and F3) were always below the detection limit, thereby impeding confirmation of a decrease in its availability upon treatment. However, the content of As, Cu, and Zn in the aerial part of ryegrass decreased considerably after all the treatments compared to the control conditions.

The tendency of the studied elements to accumulate in plants in the treatments involving amendments seems to be associated with their chemical form in solution. For As, which is in an anionic form, plants treated with only nZVI or nH, and the nH + biochar combination showed the lowest accumulation of this element, while cationic elements (Zn and Cu) were accumulated less in the nZVI-treated soil (SN) than in the other experiments (at any case all of them below accumulation in control soil); in turn, the biochar + nH treatment (SHB) favored less accumulation of Cu in the plant, while this was not observed for Zn. Therefore, there is not a single explanation for the decrease in As, Cu and Zn contents in the aerial part of ryegrass, and thus a combined response to the availability and co-existence of elements in the matrix, and possibly, antagonistic mechanisms between elements in uptake and

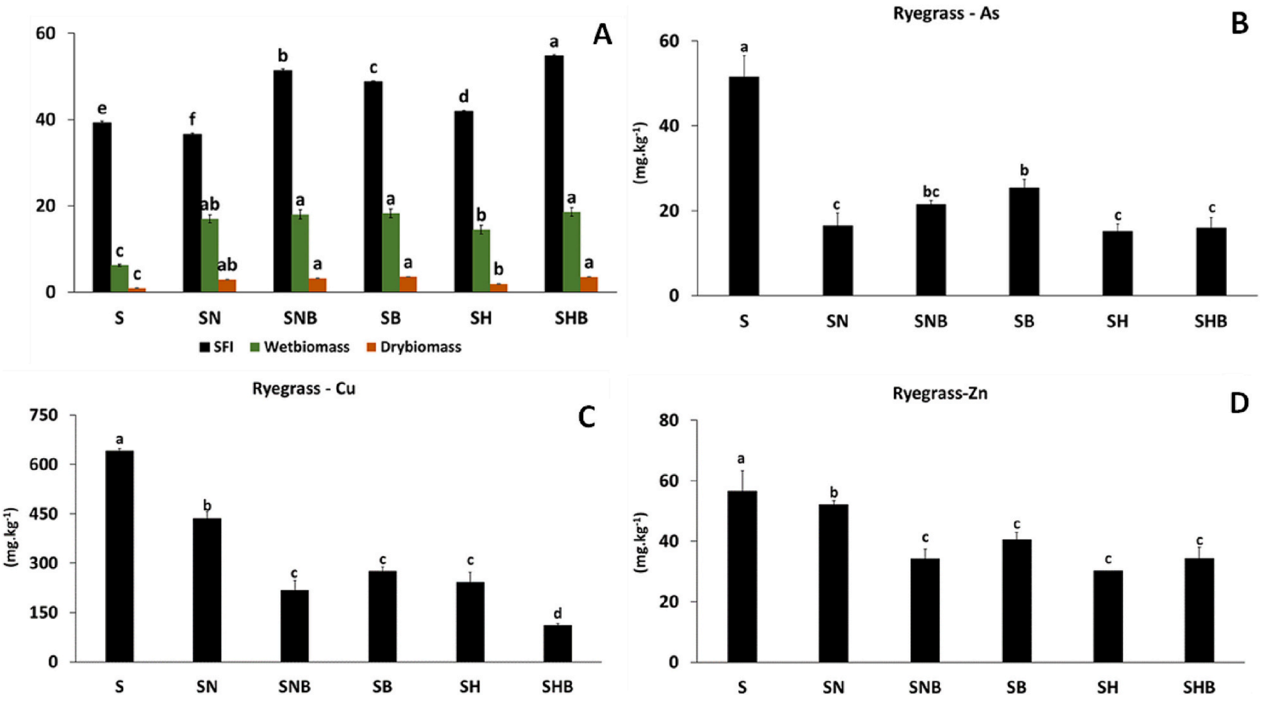

Fig. 4. (A) SFI factor, wet and dry ryegrass biomass in the mine soil treated with NPs and/or biochar. (B, C, D) Contents of As, Cu and Se found in the aerial part of ryegrass. Different letters mean significant differences (n = 3, ANOVA; $p < 0.05$). Error bars represent the standard deviation. (S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar.

translocation should be considered (Abreu et al., 2014; Kabata-Pendias, 2011).

The biomass production of ryegrass (fresh and dry weight) increased significantly in response to the amendments. In this regard, the biochar treatments resulted in the highest biomass production, while the nH treatment (SH) yielded the least (Fig. 4A). Biochar can improve the physical and chemical properties of mine soil, increasing porosity and the availability of nutrients and water, and providing favorable conditions for beneficial soil microorganisms (Zhang et al., 2021). The nH + biochar treatment (SHB) yielded the highest biomass production—this observation is consistent with the improvement in the nutrient content of the soil (Fig. 2 and Table 3) and the lowest concentrations of Cu in the aerial part of the plant.

The lowest biomass production was observed after applying the nH treatment (SH), whose Zn content was the highest observed while Cu content exceeded the phytotoxic level (Fig. 3). Finally, the low levels of biomass growth measured in control soil may be also linked to the lower concentrations of N and available P found in it (Fig. 2) compared to that treated with the amendments, as plant growth and the production of aerial biomass depends not only on the PTE load of the plant but also on the nutrient levels in the soil-plant system (Abreu et al., 2014).

3.9. *Effect of the treatments on soil enzymatic activity*

The control soil (S) and soil treated with nZVI (SN) had the lowest concentrations of all the enzymes studied (Fig. 5), including values below the detection limit for dehydrogenase and urease activity (Fig. 5A, D). Indeed, these treatments also showed the lowest contents of OC, LOC, total N, and available P (Fig. 2). On the contrary, treatments in which nH and/or biochar were applied showed, in general terms, significantly higher enzymatic activities.

Dehydrogenase is associated with the overall activity of the microbial community and the oxidation of organic matter, while glucosidase activity is involved in the degradation of complex organic matter into simpler forms that microorganisms can utilize. In both cases, organic matter, especially labile forms, acts as a food and energy source for soil microorganisms, thereby stimulating the activity of the enzymes (Demisie et al., 2014; Igalavithana et al., 2017). Variability in dehydrogenase and glucosidase activity was observed between treatments, with an increase in activity when biochar was added to the soil. Moreover, the biochar + NP combination seemed to have a synergistic effect, increasing glucosidase and dehydrogenase activity compared to the application of the NPs alone. According to several studies, dehydrogenase and glucosidase activity can favor the release of nutrients from organic matter, thereby increasing their availability (Fig. 2) (Mensah and Frimpong, 2018; Mensah et al., 2022), which would explain the subsequent enhancement of dry ryegrass biomass in the treatments involving biochar (Fig. 4). Although it is known that organic matter stimulates dehydrogenase and glucosidase activity, a significant relationship between the concentrations of OC and LOC and these enzymatic activities was not observed. Thus, the variability in the activity of these soil enzymes across the different treatments can be explained by changes in the relative abundance of recalcitrant versus easily decomposable organic C compounds (Iyyemperumal and Shi, 2008).

Phosphorus (P) is an essential nutrient for vegetation development (Hazelton and Murphy, 2007). The main function of phosphatase is to release inorganic phosphate from organic compounds (Clarholm, 1993; Gianfreda and Rao, 2004). The high values of this enzyme in soil treated with biochar and/or nH (Fig. 5B) are coherent with an increase in P availability in the soil (Fig. 2). Moreover, the highest phosphatase concentrations in the SH and SHB treatments indicate that this enzyme also acts in hydroxyapatite degradation, increasing P availability in the soil (Zhang et al., 2019). Thus, the use of nH with or without biochar may improve P availability for ryegrass.

The application of nH (SH) caused the greatest increase in urease activity, followed by treatments with nH + biochar (SHB) (Fig. 5D). The main function of urease is to provide soil with a source of N through the hydrolysis of urea. The enzymatic activities associated with the cycling of N could be associated with N availability (not determined in this study), which might explain the apparent incoherence between urease activities and N total contents (Fig. 2) in the SNB, SB, SH, and SHB treatments (Iyyemperumal and Shi, 2008).

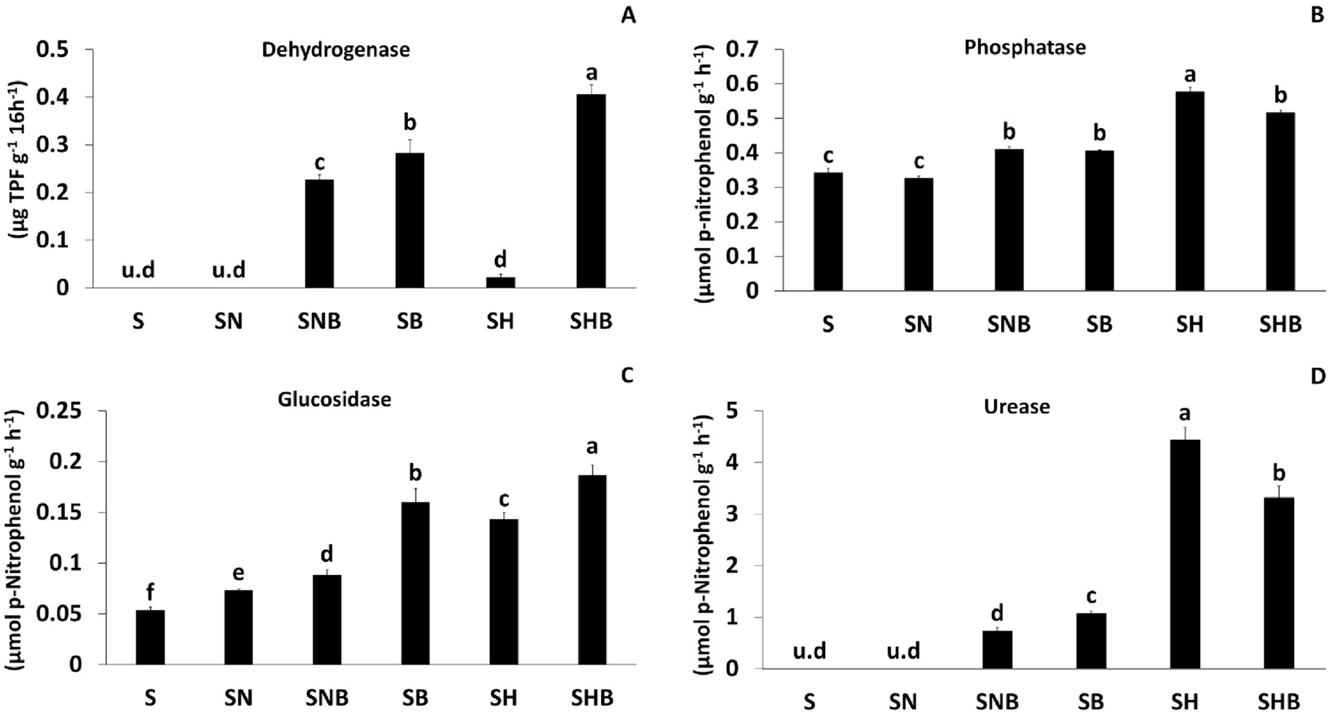

Fig. 5. Enzymatic activity of (A) dehydrogenase, (B) phosphatase, (C) glucosidase and (D) urease) in the mine soil treated with NPs and/or biochar. (S: Soil. SN: Soil + nZVI. SNB: Soil + nZVI + biochar. SB: Soil + biochar. SH: Soil + nH. SHB: Soil + nH + biochar). Different letters mean significant differences ($n = 3$, ANOVA; $p < 0.05$). Error bars represent the standard deviation.

4. Conclusions

Here we studied the effects of different amendments, namely biochar, nZVI, and nH, combined with phytostabilization using *Lolium perenne* L., in a post-mining soil that presented initial significant concentrations of As, Cu, Zn, and Se.

In terms of efficiency, no significant reduction in the availability of these pollutants nor any relevant increase was observed across treatments. However, the joint application of biochar and NPs led to increases in nutrients, fostering ryegrass growth and enhancing soil biological activity. The combined effects of biochar and NPs also showed positive correlations with pH, redox potential, and organic C, thereby indicating additional potential benefits for soil remediation. Notably, the contents of pollutants in the aerial part of ryegrass decreased considerably in all cases compared to ryegrass grown on control soil.

Regarding the two types of NPs tested, nH outperformed nZVI in crucial parameters such as P availability and the presence of labile organic carbon in the soil. In addition, nH demonstrated notable efficacy in enhancing microbial activity, as evidenced by enzymatic activity measurements. Overall, the performance of nH in specific aspects makes it a viable option for consideration in nanofertilizer combinations and as a limiting agent for metal(loid)s mobility. However, the limited bioavailability of PTEs observed in the initial soil, particularly for As, partially hindered a clear assessment of whether nH has a similar efficacy to that of nZVI for soil chemical stabilization treatments. In this specific topic, further detailed studies are required, particularly with soils with higher PTEs bioavailability from the outset, to draw more conclusive insight.

On the whole, the combination of biochar and NPs (mainly nH) emerges as a favorable approach to restore post-mining soils.

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CRediT authorship contribution statement

Rubén Forján: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Manuel Arias-Estévez:** Writing – review & editing, Supervision. **José Luis R. Gallego:** Writing – review & editing, Validation, Resources. **Erika Santos:** Writing – original draft, Investigation, Formal analysis. **Daniel Arenas-Lago:** Writing – original draft, Investigation, Formal analysis, Data curation.

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.

Data availability

Data will be made available on request.

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