Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-024-35650-3

RESEARCH ARTICLE

Promoting the recovery of soil health in As and Sb-polluted soils: new evidence from the biochar-compost option

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Received: 30 July 2024 / Accepted: 22 November 2024

Abstract

The role of compost and biochar in the recovery of As and Sb-polluted soils is poorly investigated, as well as the influence of their application rates on soil health and quality. In this study, we therefore investigated the effectiveness over time (2, 4, and 6 months, M) of a municipal solid waste compost (MSWC) and a biochar (BC), applied at 10 and 30% rates, and of selected mixtures (MIX; applied at 10 and 30% total rates, 1:1 ratio of MSWC and BC), on labile As and Sb in a polluted soil from an abandoned Sb mine (Djebel Hamimat, Algeria). At the same timepoints, the amendment impact on soil chemistry was also monitored, while the activity and diversity of the resident microbial communities were investigated at 6 M. After 6 months, MSWC, BC, and MIX applied at the higher rate significantly increased soil pH (from 7.5 up to 8.2), while MSWC and MIX increased soil EC to worrying values. The soil dissolved organic carbon content was also greatly increased by MSWC and MIX at the higher rates (up to 50-fold), while BC showed a negligible impact. All the amendments reduced the concentration of labile Sb in soil, with BC 10% being the most effective treatment (i.e., reducing labile Sb from ~ 60 to 20 mg kg^{-1} soil). On the contrary, only BC and MIX applied at 10% significantly reduced labile As (e.g., from ~ 12 to 4 mg kg^{-1} soil in the case of BC). MSWC and MIX at both rates increased up to 2000-fold soil dehydrogenase activity, while BC showed a null impact. The Biolog community level physiological profile and sequencing of the partial 16S rRNA gene showed a reduction of catabolic activity and α-diversity and a change of the community composition of bacterial populations in treated soils. Overall, MIX treatment, especially at 10%, was the most promising option for the chemical and biological recovery of As and Sb-polluted soils.

Keywords Organic amendments · Metalloids · Gentle remediation · Bacterial diversity · Enzyme activity

Responsible Editor: Kitae Baek

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Published online: 18 December 2024

Introduction

Human activities such as mining and smelting of mineral ores are the main causes of environmental pollution due to the spread of potentially toxic elements (PTE). In Algeria, mining dates back to the fifteenth century (Wadjiny 1998) and for a long time has been one of the main activities supporting the national economy. An example is the old antimony mine in the Djebel Hammimat region (Northeast Algeria; Oum El Bouaghi province), lying in a semi-arid region approximately 90 km from Constantine, where senarmontite (Sb_2O_3) was the main Sb ore extracted. Although mining was stopped in 1952 (Rached-Mosbah and Gardou 1988), very large quantities of spoil still present at the mine site contain high levels of antimony (Sb) and arsenic (As), up to 81,000 and 3,080 mg kg^{-1}, respectively (Benhamdi et al. 2014). Such levels represent a substantial environmental risk (USEPA 1998).

Antimony and arsenic were identified as priority pollutants by the United States Environmental Protection Agency, the European Union, and the World Health Organization (USEPA 2014; Toth et al. 2016). Accordingly, the need for the recovery of Sb and As-polluted soils is urgent and shared globally. In this context, the interest for in situ remediation strategies, characterized by sustainable costs, limited environmental impact, and high public acceptability, has been constantly growing in the last decades (Garau et al. 2021). Among these strategies, the use of organic or inorganic amendments (e.g., compost, biochar, zeolite, red mud, and ashes) seems particularly promising to reduce the PTE mobility and/or bioavailability in soil (Garau et al. 2021).

In particular, municipal solid waste compost (MSWC) can act as an effective PTE-immobilizing agent alleviating the stress for plants and (micro)organisms living in polluted soils (El Rasafi et al. 2023). However, several instances of increased solubility and extractability of PTE in polluted soils treated with compost have been reported (e.g., Alvarenga et al. 2008; Pardo et al. 2011). This is particularly true in the case of soils contaminated by anionic pollutants, such as Sb(V) and As(V), for which the effectiveness of compost as PTE-immobilizing agent is debated (e.g., Manzano et al. 2016; Guo et al. 2023). The reason is the presence of a relevant negative charge in compost, due to carboxylic and phenolic functional groups of humic substances, which restricts the interaction with $Sb(OH)_6^-$ and $H_2AsO_4^-/HAsO_4^{2-}$ anions, i.e., the most abundant As and Sb species in aerated soils (Diquattro et al. 2018; Wenzel et al. 2001). Moreover, soluble organic and inorganic anions within compost (e.g., fulvic acids, sulfate, and phosphate ions) may be actively involved in anion exchange reactions leading to mobilization into the soil solution of Sb(V) and As(V) adsorbed onto soil colloids (Wang and Mulligan 2009). Nevertheless, a positive role of compost at reducing As and Sb soluble fractions in soil, the most critical in terms of biological impact, has been highlighted in several studies (e.g., Garau et al. 2019a, b; Diquattro et al. 2021; Caporale et al. 2023). It also emerged from these studies a correlation between the amounts of compost added and the reduction of labile As and Sb in soil (i.e., the easily soluble and exchangeable fractions), while the opposite was shown in other studies (e.g., Hassan et al. 2023).

Biochar (BC) is another organic-based amendment that can be employed for the recovery of PTE-polluted soils (Abou Jaoude et al. 2019, 2022; Bolan et al. 2024). Biochar capacity to immobilize PTE is mostly due to its microporous structure, large surface area, and the presence of functional groups that may retain positively and negatively charged pollutants (Pinna et al. 2022). Specifically, oxygenated functional groups (e.g., carboxyl, hydroxyl, and phenolic groups) can be involved in outer and inner-sphere complexation of metal cations, while the increase of soil pH (most biochars are highly alkaline) may promote their precipitation (Fang et al. 2016). The BC effectiveness at immobilizing anionic contaminants, such as As(V) and Sb(V), was previously reported, even if few studies addressed this issue (Fang et al. 2016; Pinna et al. 2022). Inner-sphere complexation of the metalloids by ligand exchange reactions with surficial -OH and/or -OH_2 groups, particularly of Fe/Al oxides within biochar, can be responsible for As(V) and Sb(V) immobilization, along with their intraparticle diffusion and/or precipitation with cations released by biochar (e.g., Ca^{2+}) (Fang et al. 2016; Pinna et al. 2022). However, as mentioned for compost, a mobilizing activity of biochar towards Sb and As was also reported (e.g., Beesley et al. 2014; Hua et al. 2019; Hassan et al. 2023), while the combination of both amendments seems important in terms of reduced metalloid mobility, soil fertility, and functionality (Abou Jaoude et al. 2019; Qian et al. 2023; Garau et al. 2024). The latter aspect, i.e., the combined use of biochar and compost for the recovery of PTE and specifically As and Sb-contaminated soils, is at present poorly investigated, as well as the influence of the respective application rates on soil health (Hassan et al. 2023; Song and Zhang 2023; Garau et al. 2024). For instance, adding 25% biochar to green waste compost increased the photosynthetic pigment content and biomass of *Centaurea cyanus* (Song and Zhang 2023), while mixing 20% compost with 6% biochar revealed ideal for improving plant growth and land reclamation in an As and Pb co-polluted soil (Hassan et al. 2023). Adding up to 80% compost mixed with biochar (in a 19:1 ratio, respectively) decreased the phytoavailable concentration of Al, Co, Cu, Fe, and Ni and increased *Brassica juncea* growth in a mine soil (Rodríguez-Vila et al. 2016).

Finally, adding a 10% mixture of compost and biochar (in a 1:1 ratio) to a PTE-polluted soil decreased Cd and Zn availability by ~ 86% but increased that of As by ~ 370% (Tang et al. 2020).

Overall, the effectiveness of compost, biochar, or their mixture to reduce labile As and Sb and improve the functionality of polluted soils is not fully understood and needs to be assessed on a case-by-case basis. At the same time, the impact of these amendments on the activity and diversity of the microbial community inhabiting the As and Sb-polluted soils is poorly investigated. This is a key point when selecting options for soil remediation, as microbial activity is crucial for soil organic matter turnover, biogeochemical nutrient cycling, and plant growth (e.g., Wu et al. 2023; Daunoras et al. 2024).

In this context, our study focused on the Sb and As-polluted Djebel Hammimat mining area (Algeria) with the aim to evaluate the impact of MSWC, BC, and their combination on different aspects (i.e., chemical and biological) of soil health. In particular, the As and Sb mobility, as well as different soil chemical, biochemical, and microbiological characteristics, were investigated in mesocosm study for a more complete evaluation of the amendment effectiveness in view of its potential use for in situ remediation. To the best of our knowledge, this is the first study investigating the role of gentle remediation using compost and biochar for the recovery of an As and Sb-polluted soil from Algeria.

Materials and method

Origin of soil and amendments and mesocosm setup

The soil studied was taken from the area of the abandoned Djebel Hammimat antimony mine located in the North-Eastern Algeria (35° 58′ 37″ N – 7° 11′ 22″ E). The area is characterized by a semi-arid Mediterranean climate, with an average annual temperature of around 15 °C and 44 mm annual precipitation (Zekri et al. 2019). The soil had a sandy clay loam texture with 23% clay, 16% silt, and 61% sand (Meghnous et al. 2019; USDA classification, 1975). Soil samples ($n = 120$; ~ 2.5 kg each) were taken at random (between 5 and 20 cm depth) from the largest mine spoil (~ 1 ha) in the most Sb-contaminated area of Djebel Hammimat (Benhamdi et al. 2014). The samples were then pooled and blended in the laboratory to obtain a composite soil.

The MSWC used in the study was made at the École Nationale Supérieure de Biotechnologie (ENSB) in Constantine (Algeria) by mixing municipal waste, green waste, and sheep manure. The BC was produced from tree and shrub waste with a pyrolysis temperature of 500 °C. Both MSWC and BC were ground and sieved to < 2 mm and then added to mesocosms. The main chemical characteristics of the MSWV and BC are shown in Table 1.

Table 1 Chemical characteristics of the amendments used

	Biochar	*Compost*
pHH_2O	8.32 ± 0.02	8.50 ± 0.10
EC ($dS·m^{-1}$)	0.28 ± 0.01	9.13 ± 1.70
C org (%)	97.1 ± 0.22	37.9 ± 0.06
DOC ($g·kg^{-1}$)	0.06 ± 0.00	4.7 ± 0.00
Total N (%)	0.50 ± 0.00	2.77 ± 0.05
P-Olsen ($mg·Kg^{-1}$)	87.5 ± 0.00	354 ± 0.00
CEC ($cmol(+)·Kg^{-1}$)	20.3 ± 0.00	78.6 ± 0.00
As ($mg·Kg^{-1}$)	n.d	n.d
Sb ($mg·Kg^{-1}$)	n.d	n.d

The composite soil was used to set up 21 mesocosms (5 kg each) including the following seven treatments, each replicated three times: untreated mining soil (Control); 10% (w/w) and 30% (w/w) municipal solid waste compost (MSWC 10% and MSWC 30%); 10% (w/w) and 30% (w/w) biochar (BC 10% and BC 30%); 5% (w/w) compost + 5% (w/w) biochar (MIX 10%); and 15% (w/w) compost + 15% (w/w) biochar (MIX 30%). Mesocosms were incubated for a total 6 months during which they were kept at room temperature (25 °C) and constant humidity (15%). The choice of the amendment rates (i.e., higher than those usually reported in literature) was made to deepen our understanding on the role of MSWC and BC in the recovery of metalloid-polluted soils (as mentioned this point is currently debated). It was also made to assess in particular whether such rates could have beneficial or negative effects on soil quality in terms of chemical, biochemical, and microbiological characteristics.

Soil chemical analyses

After 2, 4, and 6 months (M2, M4, and M6), duplicate soil aliquots were collected from each mesocosm and subject to chemical characterization. Briefly, soil pH (ISO 2021) and electric conductivity (EC) (ISO 1996) were determined in 1:5 soil to water suspensions. Potential cation exchange capacity (CEC) was determined using the $BaCl_2$-triethanolamine method (ISO 2018), while organic C and total N were quantified by a CHN analyzer (Leco CHN 628) with LCRM no. 502–697 and CRM no. 502–814 as calibration samples for soils and amendments, respectively. Dissolved organic carbon (DOC) was estimated in 1:10 w/v soil to water suspensions as previously described (Manzano et al. 2020). The pseudo-total concentration of As (As_{tot}) and Sb (Sb_{tot}) was quantified after microwave soil digestion (Milestone ultraWAVE 2 SRC Technology) with reverse aqua regia (HNO_3 and HCl 3:1 ratio), using a PerkinElmer ICP-OES (Avio220 Max). The NIST-SRM 2711A standard reference material was included for quality control. The concentration of labile (i.e., water-soluble and readily exchangeable) As and Sb was determined by treating 1 g of soil with 25 mL of an $(NH_4)_2SO_4$ solution for 4 h at 20 °C (Wenzel et al. 2001) and quantifying As and Sb in the extracted solutions as previously reported.

Analysis of soil biochemical characteristics and community-level physiological profile

Selected soil enzyme activities, such as dehydrogenase (DHG), β-glucosidase (GLU), and urease (URE), were determined according to Alef and Nannipieri (1995) in duplicate soil samples collected from each mesocosm at M6. Briefly, DHG activity was quantified (as triphenyl formazan released; TPF) after incubation of soil aliquots with a triphenyltetrazolium chloride solution for 24 h at 30 °C. GLU activity was measured (as *p*-nitrophenol released; PNP) after incubation of soil aliquots with *p*-nitrophenyl glucoside for 1 h at 37 °C, while URE activity was quantified (as ammonia released) after incubation of soil aliquots with urea for 2 h at 37 °C.

The community-level physiological profile (CLPP) of soil microbial communities inhabiting the different soils was determined at M6 by means of Biolog EcoPlates™ (Biolog Inc., Hayward, CA, USA). Briefly, soil aliquots (10 g) from each mesocosm were mixed with a sterile sodium pyrophosphate solution (2 g L^{-1}), and the soil suspensions were shaken for 30 min at 120 rpm and 25 °C. Tenfold dilutions were then obtained using a sterile saline solution (0.89% NaCl) which was centrifuged (250 g, 2 min), filtered (Whatman grade 40), and used to inoculate the Biolog Ecoplate wells (120 μL each). The Biolog EcoPlate is a 96-well microtiter plate containing 31 different carbon sources (Insam 1997) and a control well without any C sources (all replicated 3 times). A redox dye (i.e., tetrazolium violet) was incorporated in each well to reveal C source consumption. To quantify this latter, the inoculated plates were incubated in the dark at 25 °C for 96 h, and during this time, the optical density at 590 nm (OD_{590}) of each well was determined every 24 h by means of a Biolog MicroStation microplate reader (Biolog, Hayward, CA, USA) (Diquattro et al. 2021).

The raw OD_{590} values were used to determine the following indexes as described by Garau et al. (2023): the average well color development (AWCD), i.e., a measure of the potential metabolic activity of the microbial community (Eq. 1);

$$\text{AWCD} = \sum_{i=1}^{31} (Ri - C)/31 \tag{1}$$

where *Ri* is the absorbance value (OD_{590}) in each well, *C* is the OD_{590} of the control well, and 31 is the number of C substrates in the plate; the Shannon–Weaver index (*H*), i.e., a measure of the catabolic diversity of the microbial community (it takes into account the diversity and evenness of C source consumption) (Eq. 2);

$$H\prime = -\sum (pi(\text{Log } pi)) \tag{2}$$

where *pi* is the OD_{590} ratio of each of the 31 C substrates to the total absorbance value of the plate; the richness (*S*), i.e., the number of C substrates used ($OD_{590} > 0.15$) by the microbial community.

Standardized OD_{590} values (i.e., OD_{590}/ AWCD) were used for principal component analysis (PCA), for which the variance/covariance matrix was employed (Garau et al. 2023), to further explore possible differences between soil microbial communities. The CLPP data presented refer to the 72-h incubation time since this timepoint provided the best discrimination between treatments.

Molecular analysis of soil bacterial communities, bioinformatics, and biostatistics

Soil DNA extracts of each mesocosm collected at M6 using the DNeasy PowerSoil Pro Kit (Qiagen, Milan) were provided to the Novogene sequencing center (Cambridge, UK) for the performance of amplicon sequencing according to their Illumina MiSeq 2 × 300 bp in-house protocol for amplicons obtained with the V4 515F(5′-GTGCCA GCMGCCGCGGTAA-3′)/806R(5′-GGACTACHVGGG TWTCTAAT-3′) primer pair (Caporaso et al. 2012).

Quality assessment and control (QC) was performed on the resulting sequence reads with the dada2 v1.28.0 (Callahan et al. 2016) package of the R software v4.1.3 (R Core Team, 2023) prior generating the amplicon sequence variant (ASV) composition matrices of the samples as described here. Quality control included the sequence trimming at the first instance of very low bases (Phred Q values of 2) starting from the sequence 3′ end. Other read filtering-out cutoffs were those of the minimum allowed estimated error per read of 2 and minimum post-trimming length of 150 bp. Moreover, we removed read-pairs where the reconstruction of the amplicon of origin via merging without mismatches was impossible. A final quality control step before obtaining the matrix with the high quality ASVs was that of the removal of off target taxon ASVs (non-prokaryotic, unclassified, mitochondrial, or chloroplast). ASV taxonomic classification was performed with the dada2 module of the Bayesian Classifier (Wang et al. 2007) using the Silva v138 reference database for a bootstrap cutoff value of 80% (Yilmaz et al. 2014).

We performed a series of α-diversity indices using the Vegan v2.6–4 (Dixon 2003) and the entropart v1.6–13 (Marcon and Hérault 2015) R packages. We counted the observed richness (representative of all community), we calculated Shannon's index (representative of low in dominance ASVs) and the Reciprocal Simpson index (representative of intermediate in dominance ASVs), and we calculated Fisher's α index (representative of highly dominant ASVs) and the sample coverage with the Good's coverage estimate (Good 1953). We further used the agricolae v1.3.7 (de Mendiburu 2021) R package for performing analysis of variance (ANOVA) using the Tukey's post hoc test to compare the α-diversity indices. The non-parametric Kruskal–Wallis and the Wilcoxon rank sum analysis were used respectively in the cases where the ANOVA conditions were not met. Differential abundance tests for identifying treatment associated taxa were performed with the Kruskal–Wallis (k test-factor levels, with $k > 2$) and the Wilcoxon rank sum (pairwise) analysis.

β-diversity analysis was based on non-metric multidimensional scatterplots (descriptive analysis), while permutational multivariate analysis of variance (PERMANOVA) and canonical analysis were performed as hypothesis testing approaches. These tests were done with the vegan v2.6.4 package (Oksanen et al. 2020) of R. Finally, modeling and classification-based hypothesis testing was further performed with random forests as implemented by the randomForest v4.7–1.1 (Liaw and Wiener 2002) package in R. The raw sequence reads were submitted at the Sequence Read Archive of the National Center for Biotechnology Information and are publicly available under the BioProject number PRJNA1133654.

Data analysis

Soil chemical, biochemical, and microbiological data (presented as mean values ± standard errors) were analyzed by one-way ANOVA ($P < 0.05$) followed by post-hoc Fisher's least significant difference (LSD) test to investigate possible significant differences between treatments ($P < 0.05$). Canonical correlation analysis was used to check for significant relationships ($P < 0.05$) between chemical parameters or between these latter and biochemical ones. Data analysis was carried out using the NCSS 2007 software (v 7.1.21).

Results and discussion

Influence of MSWC and BC on soil chemical parameters

Two selected amendments, i.e., a MSWC and a BC, were used alone or mixed for the recovery of a mining soil (pH ~ 7.5) contaminated by Sb and As. The amendment influence on the main soil chemical characteristics was monitored at different timepoints, i.e., M2, M4, and M6, showing a substantial evolution of the soil chemistry during time (Figs. S1-S4).

While at M2, all the treatments significantly increased soil pH, at M6 only MSWC and BC added at 30%, and both MIX treatments showed higher pH values than control soil (Table 2, Fig. S1A). This was mainly due to the high pH of both MSWC and BC (8.5 and 8.3 respectively; Table 1), to the amounts of MSWC and BC added (e.g., a steady reduction of the pH occurred during time in soils treated with 10% MSWC and 10% BC; Fig. S1B) and/or to their interaction when mixed (Ho et al. 2022; Bolan et al. 2023).

At M6, soil EC was significantly increased in all treated soils, particularly in those treated with compost (alone or mixed with biochar; Table 2). This was somehow expected given the high soluble ion content of the compost used (Table 1). The EC variation during the 6 months equilibration time was limited except for BC (alone), whose EC values slowly decreased during equilibration (Figs. S2A and B). Values recorded at M6 in 30% MSWC and 30% MIX were approx. 7.3 and 5.0 dS m^{-1}, respectively, posing potential

Table 2 Chemical characteristics of the different soils at time M6. Different letters in a column denote statistically significant differences according to Fisher's LSD test ($P < 0.05$)

Soil	pH	EC (dS·m^{-1})	Organic C (%)	DOC (g kg^{-1})	Total N (%)	CEC (cmol(+) kg^{-1})	As tot (mg kg^{-1})	Sb tot (mg kg^{-1})
Control	7.47 ± 0.04^{c}	2.41 ± 0.01^{f}	3.97 ± 0.05^{f}	0.02 ± 0.00^{e}	0.08 ± 0.00^{f}	13.1 ± 1.27^{f}	175 ± 20	21,552 ± 2540
MSWC 10%	7.31 ± 0.10^{d}	3.92 ± 0.02^{c}	6.93 ± 0.17^{e}	0.38 ± 0.00^{c}	0.43 ± 0.00^{c}	22.5 ± 0.69^{c}	167 ± 14	21,324 ± 2700
BC 10%	7.22 ± 0.05^{d}	2.50 ± 0.04^{e}	13.8 ± 0.51^{c}	0.02 ± 0.00^{e}	0.15 ± 0.00^{e}	14.8 ± 0.21^{ef}	114 ± 6	19,967 ± 3100
MIX 10%	7.64 ± 0.07^{b}	2.99 ± 0.01^{d}	11.6 ± 0.24^{d}	0.16 ± 0.00^{d}	0.26 ± 0.01^{d}	15.4 ± 0.29^{de}	122 ± 18	19,926 ± 660
MSWC 30%	8.01 ± 0.04^{a}	7.30 ± 0.01^{a}	15.6 ± 0.37^{c}	1.11 ± 0.03^{a}	1.09 ± 0.02^{a}	36.9 ± 1.36^{a}	96 ± 9	14,211 ± 840
BC 30%	8.16 ± 0.02^{a}	2.55 ± 0.02^{e}	33.1 ± 1.94^{a}	0.04 ± 0.00^{e}	0.23 ± 0.04^{d}	17.1 ± 0.34^{d}	96 ± 6	15,225 ± 4290
MIX 30	8.11 ± 0.00^{a}	4.71 ± 0.02^{b}	23.7 ± 1.05^{b}	0.56 ± 0.01^{b}	0.62 ± 0.01^{b}	29.3 ± 0.55^{b}	128 ± 1	14,145 ± 290

constraints to the growth of salt sensitive plants (e.g., glycophites reduce their yield by ~ 50–80% in the 4–8 dS m^{-1} range; Navarro-Torre et al. 2023). This could be a problem if 30% MSWC or 30% MIX are considered for assisted phytoremediation programs, since only salt tolerant halophytes could be grown in the soil considered.

Organic C and total N showed a similar trend at all timepoints (not shown), mainly reflecting the C and N content of the MSWC and BC used (Table 1). Accordingly, BC 30% and MSWC 30% showed the highest content of organic C and total N, respectively at 6 M (Table 2). Such organic carbon increase can have a relevant impact, e.g., in several instances, this was positively correlated with soil biodiversity and plant resilience to pathogens (Chen et al. 2020).

The DOC content in soil increased proportionally to the amount of compost added, reaching values up to ~ 1 g kg^{-1} soil in the 30% MSWC treatment at 6 M (Table 2). As opposed, BC had a negligible impact on such parameter. This was due to the high DOC content of MSWC which was ~ 70-fold higher than BC (Table 1). Such DOC increase occurring in a polluted or degraded soil can be regarded as beneficial, as this parameter is positively correlated with microbial growth and activity, which play an important role in the recovery of soil health and functionality (Garau et al. 2021; McBride et al. 2023). The substantial DOC reduction during the equilibration time in MSWC-treated soils likely indicated an active consumption of C sources (within DOC) by the relative microbial communities, and this could suggest an increase of the microbial population in such soils (Fig. S3A and B).

A significant increase of CEC was recorded in treated soils vs control at all timepoints (Fig. S4A), with MSWC (~ 79 $cmol_{(+)}$ kg CEC; Table 1) showing an expected greater impact than BC (~ 20 $cmol_{(+)}$ kg CEC; Table 1), probably due to the higher presence of negatively charged carboxylic and phenolic groups in the compost. At M6, 30% MSWC and 30% BC increased the soil CEC by approx. 3- and 1.3-fold, respectively (Table 2). A certain reduction of CEC was also recorded in BC-treated soils during the equilibration time (Fig. S4A and B). This could be due to some BC micro and/or mesopores clogging by colloidal soil particles during time which prevented the access to a few cation exchange sites (Tang et al. 2021). Given the low CEC of the polluted soil (i.e., 13 $cmol_{(+)}$ kg), BC and MSWC appeared as useful treatments to enhance its fertility and promote its functional recovery. However, while such increased CEC in the amended soils can be relevant to immobilize PTE in cationic forms (Li et al. 2017; Silvetti et al. 2017), its impact on anionic PTE such as As and Sb is essentially unclear (Garau et al. 2019a, b; Silvetti et al. 2017) .

Influence of MSWC and BC on labile As and Sb in soil

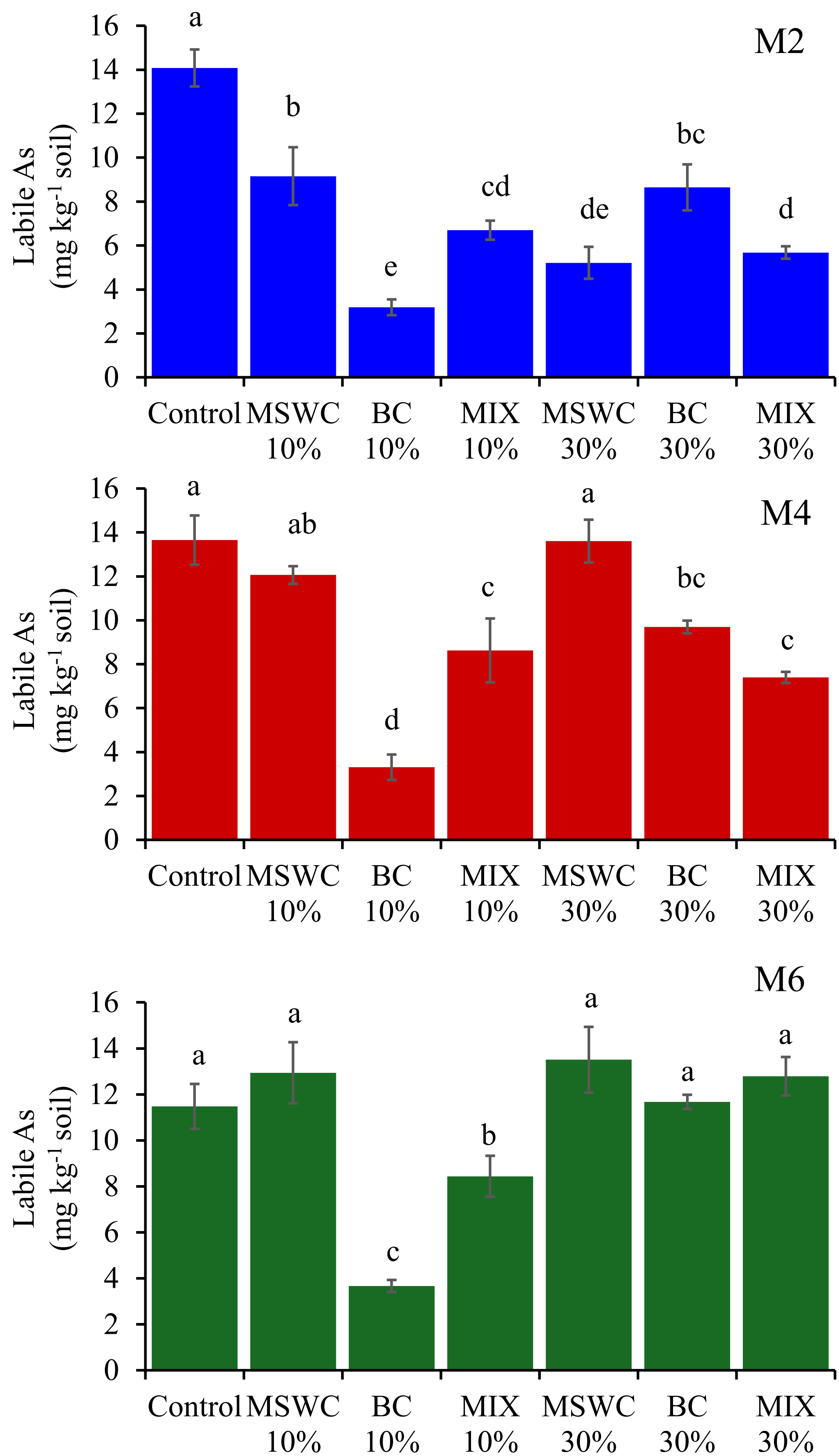
The pseudo-total concentrations of As and Sb in the mining soil investigated were very high, i.e., ~ 175 and 21,550 mg kg^{-1}, respectively (Table 2), and largely exceeded the threshold and the higher guideline values for metal(loid) s in soil established by the Finnish legislation (Ministry of the Environment—MEF, 2007). The Finnish threshold (5 and 2 mg kg^{-1} for As and Sb, respectively) and guideline values (100 and 50 mg kg^{-1} respectively) were chosen as a reference since they are very close to the mean values of different national systems in Europe and India (Toth et al. 2016). According to this reference system, the As and Sb pollution in the studied soil presents relevant ecological and health risks (Toth et al. 2016).

To evaluate the MSWC and BC effectiveness in the recovery of such polluted soil, the labile fractions of As and Sb were investigated at different timepoints, i.e., M2, M4, and M6. Such labile fractions, including both water-soluble and easily exchangeable As and Sb, are those most mobile and relevant from an ecotoxicology viewpoint since they can easily come in contact with soil (micro)organisms as well as reach surface and groundwater (Garau et al. 2021).

Labile As

At M2, all the amendments significantly reduced labile As, with 10% BC showing the higher effectiveness (Fig. 1 and S5). However, substantial changes occurred during the contact time, which mainly regarded the soils treated with the higher amounts of compost, i.e., labile As strikingly increased in MSWC 30% and MIX 30% (Fig. 1). At M6, only BC 10% and MIX 10% significantly reduced labile As by 70 and 27%, respectively (vs control), while all 30% treatments increased its concentration (albeit not significantly), e.g., up to ~ 20% for MSWC 30% (Fig. 1). This equals to ~ 19 kg reduction of labile As per hectare in the case of BC 10% and to ~ 6 kg increase in the case of MSWC 30% (for a 0.2 m soil depth and 1200 kg ha^{-1} density). Such overall increase of labile As in the presence of compost was previously reported (e.g., Beesley et al. 2014; Manzano et al. 2016; Silvetti et al. 2017; Hassan et al. 2023) and was likely due to competition phenomena for the same adsorption sites on soil surfaces of negatively charged molecules (organic and inorganic) released by MSWC, e.g., DOC species and/or sulfate and phosphate ions. This seems supported by the very high DOC content of the MSWC investigated (Table 1), whose role in As mobilization was previously highlighted (e.g., Bauer and Blodau 2006; Beesley et al. 2014). The reduction of DOC in compost-treated soils during time (from M2 to M6; Fig. S3), which was accompanied by a progressive increase of labile As, seems to support this view, i.e., the involvement

Fig. 1 Concentrations of labile As determined at M2, M4, and M6 in the different soils. For each timepoint, different letters on top of each bar denote statistically significant differences according to Fisher's LSD test ($P < 0.05$)



of some DOC species in anion exchange reactions at the expenses of the non-specifically adsorbed arsenate anions (note that some other DOC compounds could have been used by soil microorganisms for growth and multiplication). This was particularly evident for MSWC 30% and MIX 30% for which the correlation values between DOC and labile As were highly significant ($r = -0.79$, $P < 0.0001$ for MSWC 30%; $r = -0.90$, $P < 0.000001$ for MIX 30%). Moreover, also the formation of soluble ternary As-(Me)-DOC complexes (Wang and Mulligan 2009), as well as the pH increase recorded in soils treated with the higher amendment rates (Martiñá-Prieto et al. 2018), could be partly responsible for the observed results.

The results also highlighted a substantial As-immobilizing capacity of BC, which supported previous findings (Pinna et al. 2022). However, BC effect was greatly dependent on the amount added, i.e., 10% was effective but not 30% (Fig. 1). Given that BC As-immobilization mechanisms (outer and inner-sphere complexation, intraparticle diffusion, and/or precipitation; Li et al. 2017) are expected to be the same in the two cases, what observed could be due to the higher alkalinization of BC 30% vs BC 10% (Table 2). This also applies for the MIX treatments, where MIX 10% significantly reduced labile As but MIX 30% did not (Fig. 1). Overall, the higher As-immobilizing capacity of BC 10% compared to MSWC was likely due to the BC microporous structure within which $H_2AsO_4^-$/$HAsO_4^{2-}$ anions can diffuse, be involved in complexation reactions, and/or precipitate with divalent metal cations (e.g., Ca^{2+}, Pb^{2+}; Pinna et al. 2022).

Labile Sb

Differently from As, both amendments and their mixtures significantly reduced labile Sb at all the timepoints considered, and limited changes of its concentration occurred in the amended soils during time (Fig. S6). At M6, BC 10% was the most effective at reducing labile Sb (~65% vs control), followed by MIX 10%, BC 30% and MIX 30% (~45%), and both MSWC (~27%) (Fig. 2). This equals to ~96 and 41 kg reduction of labile Sb per hectare in the case of BC 10% and for both MSWC, respectively (for a 0.2 m soil depth and 1200 kg ha^{-1} density). Considering that labile As and Sb are co-adsorbed by BC 10% and MIX 10%, these treatments proved to be the most effective at reducing the potential bioavailability of anionic PTE. These results support earlier reports showing the capacity of BC to retain arsenate and antimonate anions (e.g., Abou Jaoude et al. 2019, 2022; Pinna et al. 2022; Khan et al. 2023; Garau et al. 2024). However, mobilization of soil Sb after BC addition was reported in some instance (e.g., Hua et al. 2019) suggesting that biochar feedstock (and pyrolysis conditions) could have a great influence on its

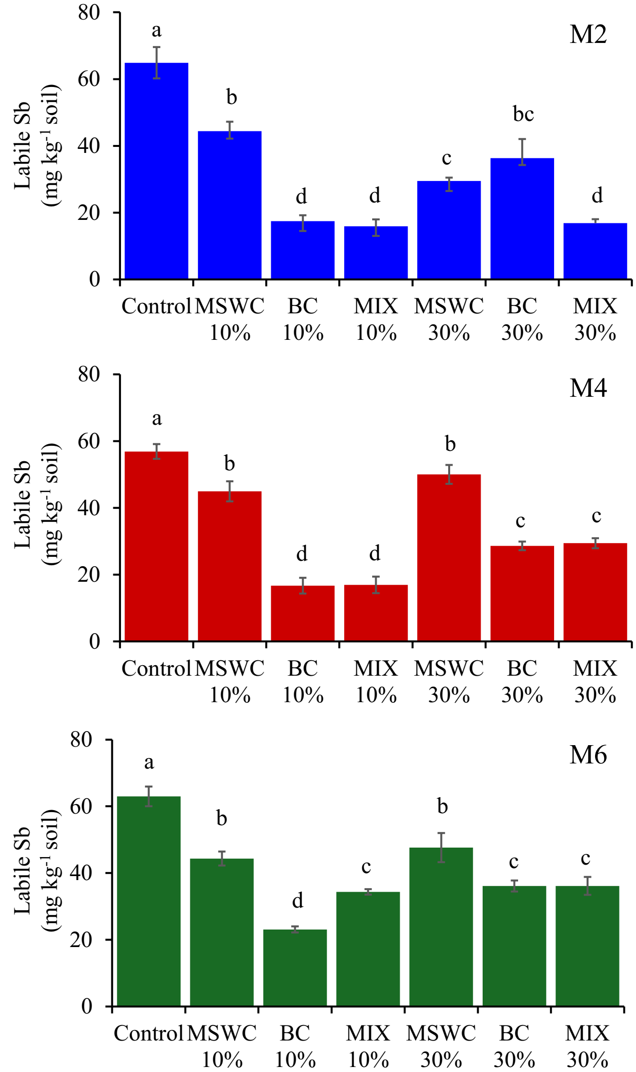


Fig. 2 Concentrations of labile Sb determined at M2, M4, and M6 in the different soils. For each timepoint, different letters on top of each bar denote statistically significant differences according to Fisher's LSD test ($P < 0.05$)

anion fixing capacity. Other than this, such inconsistent BC influence on Sb mobility can be due to the relatively short incubation times used in the majority of studies (i.e., ~1–3 months; Hua et al. 2019; Hu et al. 2024). For instance, Hu et al. (2024) recently showed that two different BCs gradually transitioned from initial mobilization, or poor immobilization, to eventual successful immobilization of As and Sb after a 2-year addition to different polluted soils. This was explained with a pH decline over time in BC-treated soils (which was also observed in our study, especially for BC 10%; Fig. S1A and S1B), with the oxidation of the soil/BC carbon fractions enhancing surface complexation of both oxyanions and cations, and with a direct metalloid adsorption by BC. Interestingly, while MSWC showed a null capacity to adsorb As (Fig. 1), it was effective at fixing Sb

(Fig. 2). This was previously observed in batch experiment (carried out at acidic pH) where it was shown the role of compost humic acids and Ca^{2+} ions in the fixation (or co-precipitation) of the $Sb(OH_6)^-$ antimonate ion (Diquattro et al. 2018). Moreover, the same study showed that the majority of Sb was bound to MSWC through stable inner-sphere complexes and/or immobilized as sparingly soluble precipitates. The abovementioned mechanisms could be also relevant to explain our results, as well as the compost Sb-immobilization capacity reported so far in a few papers (Abou Jaoude et al. 2019; Diquattro et al. 2021).

Influence of MSWC and BC on soil enzyme activities

Soil enzyme activities can be greatly affected by PTE as these latter may interact with the enzyme active sites or the enzyme–substrate complexes and/or denature the protein conformation, leading to reduced activity in contaminated soils (Aponte et al. 2020). Moreover, depressing RNA in microbial cells is another mechanism by which PTE may affect enzyme production (Kapoor et al. 2015). Given their fundamental role in the cycling of major soil nutrients (e.g., C, N, and P), enzyme activities can be considered as good indicators of soil health and/or the effectiveness of a recovery intervention (Garau et al. 2021).

Dehydrogenase (DHG) activity, which indicates the ability of selected intracellular enzymes to oxidize organic molecules, was determined in all soils after 6 months of incubation to quantify the overall oxidative activity of the respective resident microbial populations (Nannipieri et al. 2018). At M6, DHG dramatically increased up to ~3800-fold in soils treated with MSWC vs control soil, while no effect was recorded in BC soils (Fig. 3). Similarly, DHG increased by ~35- and 1400-fold in soils treated with 10% and 30% MIX, respectively (Fig. 3). These results clearly demonstrated that the MSWC investigated was able to enhance the oxidative metabolism of soil microbial communities. This was likely due to the relevant presence of easily usable C (DOC in particular; Fig. S3) and N compounds within compost (Table 1) that stimulated microbial growth and activity in the polluted soils. The relevance of DOC in feeding microbial growth and DHG activity was supported by the significant correlation between these soil parameters ($r = 0.99$; $P < 0.0000001$). Such DHG trend in the presence of compost was somehow expected as it was often recorded in polluted soils amended with MSWC (e.g., Garau et al. 2019a, b; Tang et al. 2020; Garau et al. 2024). At the same time, the significant reduction of labile Sb observed in both MSWC and MIX soils (vs control) further contributed to DHG increase, since more metabolic energy was likely devoted to microbial growth and multiplication rather than Sb detoxification processes (Aponte et al. 2020; Garau et al. 2021). It is noteworthy that BC had no effect on DHG

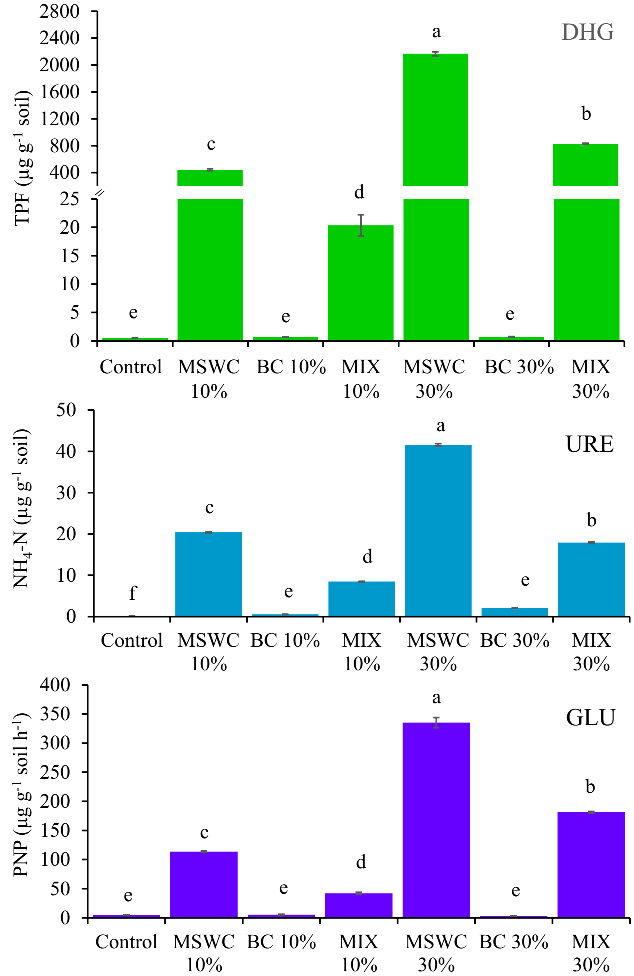


Fig. 3 Dehydrogenase (DHG), urease (URE), and β-glucosidase (GLU) activities determined at M6 in the different soils. For each enzyme activity, different letters on top of each bar denote statistically significant differences according to Fisher's LSD test ($P < 0.05$)

despite it showed the higher effectiveness (when added at 10% rate) at immobilizing both As and Sb (Figs. 1 and 2). This was previously observed (e.g., Diquattro et al. 2024; Tang et al. 2020) and could be due to the high presence of recalcitrant C in BC, to its low N and DOC content, and to its adsorption capacities towards important nutrients in soil, e.g., N, K (Manzano et al. 2020).

URE and GLU activities, catalyzing the hydrolysis of urea to release NH_4^+ ions, and the cleavage of cellobiose to release glucose molecules, respectively, followed essentially the same trend observed for DHG (Fig. 3). Similarly to DHG, both enzyme activities were detected at very low level in the control soil confirming their sensitivity to metalloids (Aponte et al. 2020). This can have relevant environmental implications since URE and GLU are involved in selected steps of the N and C cycles in soil such as urea and cellulose degradation, respectively (Turner et al. 2002; Kumar et al. 2022). Striking increases of URE and GLU were observed in soils where compost was added (i.e., MSWC and MIX), with MSWC 30% being the most effective treatment, i.e., URE activity increased up to ~ 800-fold and GLU up to 67-fold (vs control) in this soil (Fig. 3). Such enhanced activities could be due to a structural change of soil microbial community induced by MSWC which could lead to a specific enrichment of URE and GLU producing microorganisms (Garau et al. 2019a, b; Heisey et al. 2022). Moreover, what observed could be explained (at least in part) with a more abundant microbial community in MSWC-treated soils (as supported by our DHG data) which implies more GLU and URE released. This seems supported by the correlation between DOC (which feeds microbial growth) and URE and GLU, i.e., $r = 0.96$ and 0.98, respectively ($P < 0.0000001$). In both cases, the reduction of labile Sb in the soils treated with MSWC (alone or mixed with BC) is deemed important as URE and GLU, as well as DHG, have been previously found highly negatively correlated with the concentration of labile metalloids in soil (Garau et al. 2019a, b).

Like DHG, biochar addition to the polluted soil had a negligible impact on URE activity and no impact on GLU (Fig. 3). This was previously observed and explained in different ways such as the following: a toxic effect of biochar towards soil microorganisms and biochar adsorption of enzyme co-factors, enzymes, and/or substrates (Chen et al. 2013; Tang et al. 2020; Garau et al. 2023). While biochar revealed very useful at reducing the labile concentration of As and Sb (especially when added at the lowest rate), it showed a negligible influence on the biochemical activities investigated raising important questions on its suitability for the functional recovery of metalloid-polluted soils.

Influence of MSWC and BC on the microbial community level physiological profile

The Biolog EcoPlate CLPP was employed to investigate the possible impact of MSWC and BC (alone and mixed) on the structure of soil microbial community within the contaminated soil. This latter impact was evaluated in terms of potential catabolic activity and diversity (Urbaniak et al. 2024). Such approach, which primarily assesses changes in carbon source utilization by microbial communities, revealed useful to ascertain the impact of organic amendment on soil microbial consortia (e.g., Li et al. 2017; Garau et al. 2019a, b).

The CLPP analysis carried out at M6 showed a reduction of the potential catabolic activity and diversity of the microbial communities of amended soils (Fig. 4). Specifically, lower carbon source utilization values (AWCD) were recorded in all treated soil vs control (though not always statistically significant), with reductions ranging

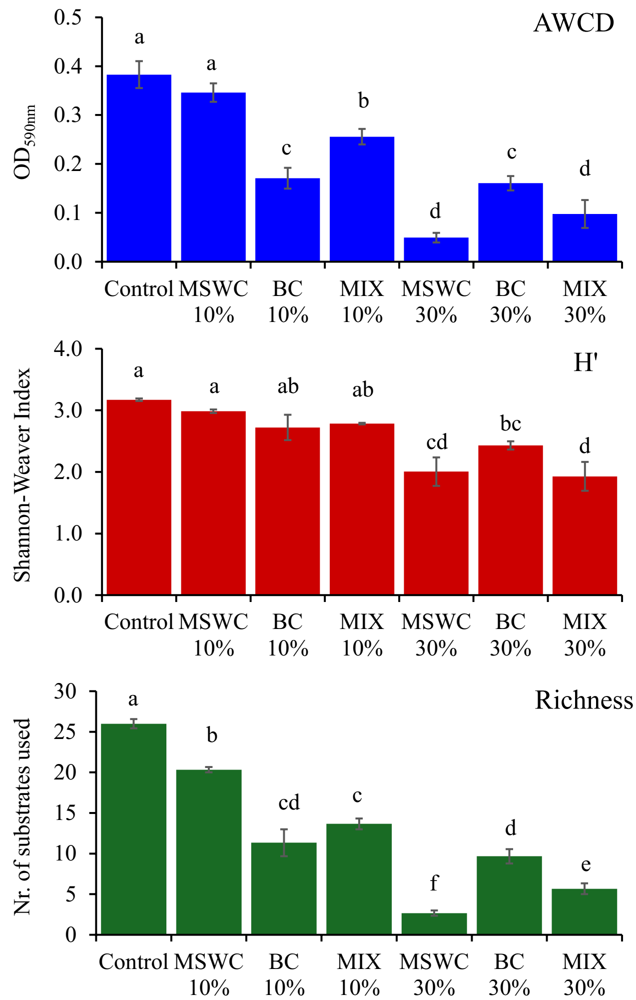


Fig. 4 Average carbon source utilization (AWCD), Shannon–Weaver index (H'), and richness values of microbial communities extracted from the different soils at M6. For each parameter, different letters on top of each bar denote statistically significant differences according to Fisher's LSD test ($P < 0.05$)

from ~ 8% for MSWC 10% to 85% for MSWC 30%. Altogether, the BC impact on the AWCD was more limited, i.e., ~ 55% less vs control, irrespective of the amendment rate (Fig. 4). Such decrease in the overall microbial activity (AWCD) was accompanied by a parallel decline of the catabolic diversity as highlighted by the Shannon–Weaver index and the richness values. The former indicated a negative influence of the higher amendment rates (30% MSWC, BC, and MIX) on the catabolic diversity of soil microbial communities, while the latter showed a clear reduction of the number of C sources utilized by the microbial communities of the amended soils (Fig. 4). These results suggest a negative influence of the tested amendments on the soil metabolic activity, although this is not necessarily the case. It has been shown previously that Biolog CLPP mainly reflects the activity of a fraction of the soil microbial community, i.e., fast-growing culturable Proteobacteria well adapted to the high substrate concentrations within the EcoPlate wells (Lladó and Baldrian 2017; Garau et al. 2007). In this sense, the results obtained in this study could be explained by the enrichment of selected microbial taxa, in MSWC and BC-treated soils, not responsive to the EcoPlate environment. This view seems supported, at least for compost-treated soils, by the high DHG, URE, and GLU data which showed (as opposed to Biolog CLPP) a significant increase of microbial activity in the amended soils. Considering all the above, the most likely interpretation of the obtained Biolog-derived indexes is a significant influence of MSWC and BC on the structure of the soil microbial community whose implications for soil functioning need to be further explored. The PCA analysis of standardized C source utilization data somehow supported this view showing a clear separation (along PC1 and PC2) of microbial communities from soils amended with 30% MSWC and 30% BC vs control, while those from the other treatments showed a certain degree of overlapping (Fig. S7). C substrates more correlated with PC1 (which explained 28% of the variance) were tween 40 ($r = 0.56$), tween 80 ($r = 0.87$), D-mannitol ($r = -0.53$), and γ-hydroxybutyric acid ($r = -0.42$), while those more correlated with PC2 (which explained 22% of the variance) were pyruvic acid methyl ester ($r = 0.80$), tween 40 ($r = 0.53$), D-cellobiose ($r = -0.77$), N-acetyl-D-glucosamine ($r = -0.50$), γ-hydroxybutyric acid ($r = -0.63$), itaconic acid ($r = 0.72$), and L-serine ($r = -0.41$).

Influence of MSWC and BC on the molecular diversity of soil bacterial communities

A total of 1,821,755 read pairs were obtained, while 832,912 high quality sequences passed the QC pipeline and were used in the subsequent analysis (Table S1).

The devoted sequencing effort was sufficient for uncovering 97.6% of the existing microbial diversity according to Good's coverage estimate (Table S2). Overall, MSWC (either alone or in mixtures) had a negative impact on all α-diversity indices tested, with the indices of Shannon and Inverse Simpson showing significant differences (Fig. 5). This can be due to the very high DOC and OM content of MSWC which likely promoted the growth of selected bacterial taxa which became dominant reducing α-diversity. Moreover, compost is not a sterile medium and its native bacterial load could have had an important role in reshaping soil microbial community (especially when it was added at the higher rate) and reducing α-diversity. Interestingly, the molecular diversity data are supported by the Biolog CLPP which highlighted a parallel reduction of the potential catabolic activity of soil microbial communities in compost-treated soils, which is compatible with a decline of the bacterial α-diversity. The microbial community compositions showed distinct patterns among treatments, particularly in the cases where MSWC was present (Fig. S8). When analyzed at as high resolution as that of the family level, multivariate hypothesis testing, performed via PERMANOVA and canonical analysis (RDA), showed significant effects of all treatments ($P = 0.001$) with the combined effects being the strongest (PERMANOVA $R^2 = 78.05\%$; Fig. 6A) and the MSWC effect being approximately equally strong (PERMANOVA $R^2 = 73.91\%$; Fig. 6B), while a significant, yet, quite lower effect was observed for BC (PERMANOVA $R^2 = 47.66\%$; Fig. 6C).

Important families were selected using the Boruta algorithm (a random forest-based algorithm that allows the discrimination of "stochastic" vs "deterministic" features/ASVs). These were used for generating the NMDS scatter plots and performing the PERMANOVA hypothesis testing and generating random forest models (Fig. S9). According to the generated reduced dataset analysis, taxa mostly

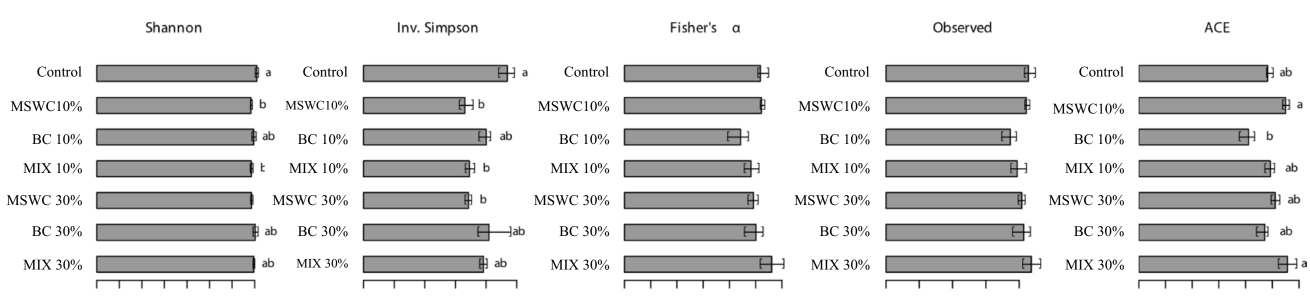


Fig. 5 Barplots (with mean values and standard deviations) showing the calculated α-diversity indices for the different soils. For each index, different letters on top of each bar denote statistically significant differences according to Tukey's post hoc analysis or the non-parametric counterparts of Kruskal–Wallis/Wilcoxon-rank-sum ($P < 0.05$)

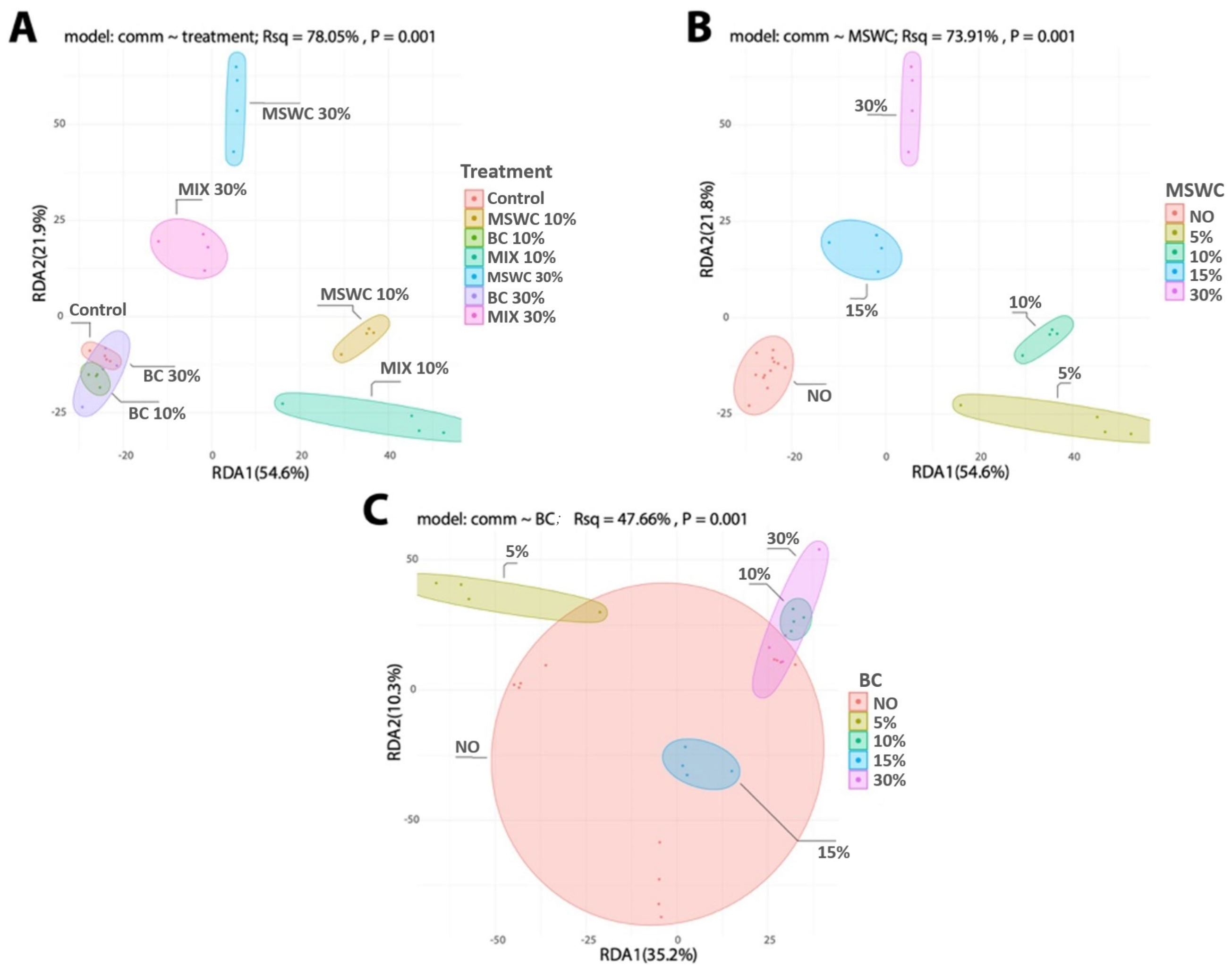


Fig. 6 Redundancy analysis scatter plots and PERMANOVA results (above each panel) for hypothesis testing according to the combined MSWC/BC effects (**A**), the MSWC effects alone (**B**), and the BC effects alone (**C**). Total explained variance is provided by the PERMANOVA R2 (Rsq) values, while the percentage of the canonical variance explained by the first two axes is also provided on the plot

associated with MSWC (when the combination of MSWC and BC were tested) were those including *Micrococcales*, *Bacillales*, *Fodinicurvataceae*, *Sphingomonadaceae*, *Rhodobacteraceae*, and *Thermomonosporaceae* (Fig. S9). The complete lists of taxa of the reduced datasets are provided in Tables S3-5 of the accompanying Excel file.

Taken together, these results showed that high rates of MSWC can have a detrimental effect on the α-diversity of soil bacterial community and a strong impact on β-diversity. Especially the former point is noteworthy since a positive effect of compost on the bacterial α-diversity is generally recognized, at least for unpolluted soils (e.g., Chen et al. 2024). In this sense, our results could be explained by both the high rates of MSWC used and/or by the significant metalloid pollution. The implications of such reduced α-diversity and change of community composition on plant growth and soil health resilience warrant further investigation.

Conclusions

After 6 months of soil-amendment contact, 10% BC or 5% BC mixed with an equal amount of MSWC (i.e., MIX 10%) revealed successful at lowering the labile concentration of both Sb and As present in a dismissed Sb mining site. The other tested treatments, i.e., MSWC and BC (alone and mixed) at higher rates, were useful to decrease labile Sb but not As. This was attributed to the high DOC content of MSWC, the alkalinity of both amendments, and the ability of compost humic acids to immobilize the antimonate $[Sb(OH_6)^-]$ ion but not the arsenate $[H_2AsO_4^-/HAsO_4^{2-}]$ ones.

Significant changes in the dynamics of labile pollutants and soil chemical properties were recorded during the soil-amendment contact time, highlighting that short contact periods could be unsuitable to evaluate the amendment impact on metalloid-polluted (or unpolluted) soils. This could explain the positive role of compost in reducing labile As, as observed in some previous studies. Six months after the amendment addition, MSWC greatly stimulated soil biochemical activity and increased EC, while BC had a negligible influence on both. On the contrary, both amendments reduced the potential catabolic activity and diversity of soil microbial communities, suggesting an impact of MSWC and BC on their structure. This was supported by the ASV data of the 16S rRNA gene V4 region, which showed a reduction of the bacterial α-diversity in soils treated with MSWC and BC, and a significant impact of both amendments on the community composition.

While BC 10% and MIX 10% revealed the best treatments for the chemical recovery of As and Sb-polluted soils, only the latter had a concurrent positive impact on soil biochemistry and could be suggested as a first choice for the recovery of metalloid-polluted soils. However, the implications for plant growth and soil health resilience of the reduced bacterial α-diversity and community structure in MSWC-amended soils need further studies. Moreover, the practical adoption of MIX 10% for the recovery of As and Sb-polluted soils could be currently limited by the high BC costs. In this regard, the effectiveness of MIX containing economically sustainable BC amounts should be explored. Overall, the study supports the emerging view that combining MSWC and BC has greater potential to improve the soil chemical and biochemical status rather than their separate use.

Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s11356-024-35650-3.

Acknowledgements The senior author was a visiting scholar to the Dipartimento di Agraria, University of Sassari (Italy) from the École Nationale Supérieure de Biotechnologie Taoufik Khaznadar (ENSB), Constantine (Algeria). The financial support from both Institutions is acknowledged.

Author contribution Conceptualization: Amina Boukhatem, Oualida Rached, Alima Bentellis; investigation: Amina Boukhatem, Sotirios Vasileiadis, Stefania Diquattro; funding acquisition: Giovanni Garau, Oualida Rached, Paola Castaldi; resources: Giovanni Garau, Oualida Rached, Paola Castaldi; formal analysis: Amina Boukhatem, Sotirios Vasileiadis, Stefania Diquattro; supervision: Giovanni Garau, Oualida Rached, Alima Bentellis, Paola Castaldi; writing—original draft: Amina Boukhatem; writing—review and editing: Oualida Rached, Alima Bentellis, Sotirios Vasileiadis, Paola Castaldi, Giovanni Garau, Stefania Diquattro.

Funding This research was supported by the Agritech National Research Center and received funding from the European Union NextGenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)—MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4—D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

Data availability Data will be made available on request.

Declarations

Ethical approval Not applicable.

Constant to participate Not applicable.

Constant for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Abou Jaoude L, Castaldi P, Nassif N, Pinna MV, Garau G (2019) Biochar and compost as gentle remediation options for the recovery of trace elements-contaminated soils. Sci Total Environ 711:134511. https://doi.org/10.1016/j.apsoil.2019.06.011

Abou Jaoude L, Nassif N, Garau G, Darwish T, Castaldi P (2022) Biochar addition decreases the mobility, bioavailability, and phytotoxicity of potentially toxic elements in an agricultural contaminated soil. Commun Soil Sci Plant Anal 53:1655–1671. https://doi.org/10.1080/00103624.2022.2063313

Alef K, Nannipieri P (1995) Methods in applied soil microbiology and biochemistry no. 631.46 M592ma. Academic Press

Alvarenga P, Gonçalves AP, Fernandes RM, de Varennes A, Vallini G, Duarte E, Cunha-Queda AC (2008) Evaluation of composts and liming materials in the phytostabilization of a mine soil using perennial ryegrass. Sci Total Environ 406(1–2):43–56. https://doi.org/10.1016/j.scitotenv.2008.07.061

Aponte H, Meli P, Butler B, Paolini J, Matus F, Merino C, Cornejo P, Kuzyakov Y (2020) Meta-analysis of heavy metal effects on soil enzyme activities. Sci Total Environ 737:139744. https://doi.org/10.1016/j.scitotenv.2020.139744

Bauer M, Blodau C (2006) Mobilization of arsenic by dissolved organic matter from iron oxides soils and sediments. Sci Total Environ 354(2–3):179–190. https://doi.org/10.1016/j.scitotenv.2005.01.027

Beesley L, Inneh OS, Norton GJ, Jimenez EM, Pardo T, Clemente R, Dawson J (2014) Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. Environ Pollut 186:195–202. https://doi.org/10.1016/j.envpol.2013.11.026

Benhamdi A, Bentellis A, Rached O, Du Laing G, Mechakra A (2014) Effects of antimony and arsenic on antioxidant enzyme activities of two steppic plant species in an old antimony mining area. Biol Trace Elem Res 158:96–104. https://doi.org/10.1007/s12011-014-9917-7

Bolan N, Sarmah AK, Bordoloi S, Bolan S, Padhye LP, Van Zwieten L, Sooriyakumar P, Khan BA, Ahmad M, Solaiman ZM, Rinklebe J, Wang H, Pal Singh B, Siddique KHM (2023) Soil acidification and the liming potential of biochar. Environ Pollut 317:120632. https://doi.org/10.1016/j.envpol.2022.120632

Bolan S, Sharma S, Mukherjee S, Kumar M, Rao ChS, Nataraj KC, Singh G, Vinu A, Bhowmik A, Sharma H, El-Naggar A, Chang SX, Hou D, Rinklebe J, Wang H, Siddique KHM, Abbott LK, Kirkham MB, Bolan N (2024) Biochar modulating soil biological health: a review. Sci Total Environ 914:169585. https://doi.org/10.1016/j.scitotenv.2023.169585

Callahan BJ, McMurdie PJ, Rosen MJ, Han AW, Johnson AJA, Holmes SP (2016) DADA2: high-resolution sample inference from Illumina amplicon data. Nat Methods 13:581–583. https://doi.org/10.1038/nmeth.3869

Caporale AG, Porfido C, Roggero PP, Di Palma A, Adamo P, Pinna MV, Garau G, Spagnuolo M, Castaldi P, Diquattro S (2023) Long-term effect of municipal solid waste compost on the recovery of a potentially toxic element (PTE)-contaminated soil: PTE mobility, distribution and bioaccessibility. Environ Sci Pollut Res 30(58):122858–122874. https://doi.org/10.1007/s11356-023-30831-y

Caporaso JG, Lauber CL, Walters WA, Berg-Lyons D, Huntley J, Fierer N, Owens SM, Betley J, Fraser L, Bauer M, Gormley N, Gilbert JA, Smith G, Knight R (2012) Ultra-high-throughput microbial community analysis on the Illumina HiSeq and MiSeq platforms. ISME J 6:1621–1624

Chen J, Liu X, Zheng J, Zhang B, Lu H, Chi Z, Pan G, Li L, Zheng J, Zhang X, Wang J, Yu X (2013) Biochar soil amendment increased bacterial but decreased fungal gene abundance with shifts in community structure in a slightly acid rice paddy from Southwest China. Appl Soil Ecol 71:33–44. https://doi.org/10.1016/j.apsoil.2013.05.003

Chen XD, Dunfield KE, Fraser TD, Wakelin SA, Richardson AE, Condron LM (2020) Soil biodiversity and biogeochemical function in managed ecosystems. Soil Research 58(1):1–20. https://doi.org/10.1071/SR19067

Chen L, Zhou S, Zhang Q, Zou M, Yin Q, Qiu Y, Qin W (2024) Effect of organic material addition on active soil organic carbon and microbial diversity: a meta-analysis. Soil Tillage Res 241:106128. https://doi.org/10.1016/j.still.2024.106128

Daunoras J, Kačergius A, Gudiukaitė R (2024) Role of soil microbiota enzymes in soil health and activity changes depending on climate change and the type of soil ecosystem. Biology 13(2):85. https://doi.org/10.3390/biology13020085

de Mendiburu F (2021) Agricolae tutorial (Version 1.3–5). Universidad Nacional Agraria: La Molina, Peru

Diquattro S, Garau G, Lauro GP, Silvetti M, Deiana S, Castaldi P (2018) Municipal solid waste compost as a novel sorbent for antimony(V): adsorption and release trials at acidic pH. Environ Sci Pollut Res 25:5603–5615. https://doi.org/10.1007/s11356-017-0933-y

Diquattro S, Garau G, Garau M, Lauro GP, Pinna MV, Castaldi P (2021) Effect of municipal solid waste compost on antimony mobility, phytotoxicity and bioavailability in polluted soils. Soil Syst 5:60. https://doi.org/10.3390/soilsystems5040060

Diquattro S, Pinna MV, Garau M, Pulina A, Obinu L, Porceddu A, Roggero PP, Castaldi P, Garau G (2024) Valuable non-food crops for biochar-assisted phytoremediation of contaminated soils: the case of cardoon, rapeseed and safflower. Appl Soil Ecol 198:105349. https://doi.org/10.2139/ssrn.4344152

Dixon P (2003) VEGAN, a package of R functions for community ecology. J Veg Sci 14(6):927–930

El Rasafi T, Haouas A, Tallou A, Chakouri M, Aallam Y, El Moukhtari A, Hamamouch N, Hamdali H, Oukarroum A, Farissi M, Haddioui A (2023) Recent progress on emerging technologies for trace elements-contaminated soil remediation. Chemosphere 341:140121. https://doi.org/10.1016/j.chemosphere.2023.140121

Fang S, Tsang DCW, Zhou F, Zhang W, Qiu R (2016) Stabilization of cationic and anionic metal species in contaminated soils using sludge-derived biochar. Chemosphere 149:263–271. https://doi.org/10.3390/toxics9080184

Garau G, Castaldi P, Santona L, Deiana P, Melis P (2007) Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil. Geoderma 142(1–2):47–57. https://doi.org/10.1016/j.geoderma.2007.07.01

Garau G, Porceddu A, Sanna M, Silvetti M, Castaldi P (2019a) Municipal solid wastes as a resource for environmental recovery: impact of water treatment residuals and compost on the microbial and biochemical features of As and trace metal-polluted soils. Ecotoxicol Environ Safe 174:445–454. https://doi.org/10.1016/j.ecoenv.2019.03.007

Garau M, Garau G, Diquattro S, Roggero PP, Castaldi P (2019b) Mobility, bioaccessibility and toxicity of potentially toxic elements in a contaminated soil treated with municipal solid waste compost. Ecotoxicol Environ Safe 186:109766. https://doi.org/10.1016/j.ecoenv.2019.109766

Garau G, Roggero PP, Diquattro S, Garau M, Pinna MV, Castaldi P (2021) Innovative amendments derived from industrial and municipal wastes enhance plant growth and soil functions in potentially toxic elements-polluted environments. Ital J Agron 16(2):1777. https://doi.org/10.4081/ija.2021.1777

Garau M, Castaldi P, Pinna MV, Diquattro S, Cesarani A, Mangia NP, Vasileiadis S, Garau G (2023) Sustainable restoration of soil functionality in PTE-affected environments: biochar impact on soil chemistry, microbiology, biochemistry, and plant growth. Soil System 7:96. https://doi.org/10.3390/soilsystems7040096

Garau M, Pinna MV, Nieddu M, Garau CP, G, (2024) Mixing compost and biochar can enhance the chemical and biological recovery of soils contaminated by potentially toxic elements. Plants 13:284. https://doi.org/10.3390/plants13020284

Good IJ (1953) The population frequencies of species and the estimation of population parameters. Biometrika 40(3–4):237–264

Guo G, Zhang D, Lei M, Wan X, Yang J, Wei H, Chen S (2023) Phytoextraction of As by Pteris vittata L. assisted with municipal sewage sludge compost and associated mechanism. Sci Total Environ 893:164705. https://doi.org/10.1016/j.scitotenv.2023.164705

Hassan SH, Chafik Y, Sena-Velez M, Lebrun M, Scippa GS, Bourgerie S, Trupiano D, Morabito D (2023) Importance of application rates of compost and biochar on soil metal (loid) immobilization and plant growth. Plants 12(11):2077. https://doi.org/10.3390/plants12112077

Heisey S, Ryals R, Maaz TM, Nguyen NH (2022) A single application of compost can leave lasting impacts on soil microbial community structure and alter cross-domain interaction networks. Front Soil Sci 2:749212. https://doi.org/10.3389/fsoil.2022.749212

Ho TTK, Van Tung T, Le Hai T, Nguyen NKQ, Tran CS, Nguyen PT, Vo TDH, Thai VN, Bui XT (2022) Compost to improve sustainable soil cultivation and crop productivity. Case Stud Chem Environ Eng 6:100211. https://doi.org/10.1016/j.cscee.2022.100211

Hu Y, Wang L, Mašek O, Chen B, Xu Y, Liang P, Hou D (2024) Biochar amendment gradually immobilized soil As and Sb over 2 years. Soil Use Manage 40:e13026. https://doi.org/10.1111/sum.13026

Hua L, Zhang H, Wei T, Yang C, Guo JK (2019) Effect of biochar on fraction and species of antimony in contaminated soil. J Soil Sediment 19:2836–2849. https://doi.org/10.1007/s11368-019-02251-4

Insam HA (1997) New set of substrates proposed for community characterization in environmental samples. In: Insam H, Rangger A, (eds) Microbial communities. Springer: Berlin/Heidelberg, Germany. https://doi.org/10.1007/978-3-642-60694-6_25

ISO (1996) Soil quality - determination of the specific electrical conductivity. ISO 11265:1994/Cor 1:1996

ISO (2018) Soil quality - determination of effective cation exchange capacity and base saturation level using barium chloride solution. ISO 11260:2018

ISO (2021) Soil, treated biowaste and sludge-Determination of pH. ISO 10390:2021

Kapoor V, Li X, Elk M, Chandran K, Impellitteri CA, Santo Domingo JW (2015) Impact of heavy metals on transcriptional and physiological activity of nitrifying bacteria. Environ Sci Technol 49(22):13454–13462. https://doi.org/10.1021/acs.est.5b02748

Khan BA, Ahmad M, Iqbal S, Ullah F, Bolan N, Solaiman ZM, Shafique MA, Siddique KHM (2023) Adsorption and immobilization performance of pine-cone pristine and engineered biochars for antimony in aqueous solution and military shooting range soil: an integrated novel approach. Environ Pollut 317:120723. https://doi.org/10.1016/j.envpol.2022.120723

Kumar M, Bhardwaj M, Yadav P, Vashishth D, Chahal S, Dalal S, Kumar Kataria S (2022) A review on distribution, properties, genetic organization, immobilisation and applications of urease. J Appl Nat Sci 14(4):1413–1429. https://doi.org/10.31018/jans.v14i4.3668

Li H, Dong X, da Silva EB, de Oliveira LM, Chen Y, Ma LQ (2017) Mechanisms of metal sorption by biochars: biochar characteristics and modifications. Chemosphere 178:466–478. https://doi.org/10.1016/j.chemosphere.2017.03.072

Liaw A, Wiener M (2002) Classification and regression by random. Forest R News 2:18–22

Lladó S, Baldrian P (2017) Community-level physiological profiling analyses show potential to identify the copiotrophic bacteria present in soil environments. PLoS ONE 12(2):e0171638. https://doi.org/10.1371/journal.pone.0171638

Manzano R, Silvetti M, Garau G, Deiana S, Castaldi P (2016) Influence of iron-rich water treatment residues and compost on the mobility of metal (loid)s in mine soils. Geoderma 283:1–9. https://doi.org/10.1016/j.geoderma.2016.07.024

Manzano R, Diquattro S, Roggero PP, Pinna MV, Garau G, Castaldi P (2020) Addition of softwood biochar to contaminated soils decreases the mobility, leachability and bioaccesibility of potentially toxic elements. Sci Total Environ 739:139946. https://doi.org/10.1016/j.scitotenv.2020.139946

Marcon E, Hérault B (2015) entropart: an R package to measure and partition diversity. J Stat Softw 67:1–26. https://doi.org/10.18637/jss.v067.i08

Martiñá-Prieto D, Cancelo-González J, Barra MT (2018) Arsenic mobility in as-containing soils from geogenic origin: fractionation and leachability. J Chem 2018:7328203. https://doi.org/10.1155/2018/7328203

McBride SG, Osburn ED, Lucas JM, Simpson JS, Brown T, Barrett JE, Strickland MS (2023) Volatile and dissolved organic carbon sources have distinct effects on microbial activity, nitrogen content, and bacterial communities. Soil Microb Ecol 85:659–668. https://doi.org/10.1007/s00248-022-01967-0

Meghnous O, Dehimat L, Doumas P, Kassa-Laouar M, Mosbah F, Rached O (2019) Oxidative and antioxidative responses to antimony stress by endophytic fungus Aspergillus tubingensis isolated from antimony accumulator Hedysarum pallidum Desf. Biologia 74:1711–1720. https://doi.org/10.2478/s11756-019-00305-z

Ministry of the Environment, Finland (2007) Government decree on the assessment of soil contamination and remediation needs (214/2007, March 1, 2007)

Nannipieri P, Trasar-Cepeda C, Dick RP (2018) Soil enzyme activity: a brief history and biochemistry as a basis for appropriate interpretations and meta-analysis. Biol Fertil Soils 54:11–19. https://doi.org/10.1007/s00374-017-1245-6

Navarro-Torre S, Garcia-Caparrós P, Nogales A, Abreu MM, Santos E, Cortinhas AL, Delaunay Caperta A (2023) Sustainable agricultural management of saline soils in arid and semi-arid Mediterranean regions through halophytes, microbial and soil-based technologies. Environ Exp Bot 212:105397. https://doi.org/10.1016/j.envexpbot.2023.105397

Oksanen J, Blanchet GF, Friendly M, Kindt R, Legendre P, McGilinn D, Minchin PR, O'Hara RB, Simpson GL, Solymos P, Henry M, Stevens R, Szoecs E, Wagner H (2020) Vegan: community ecology package. R package version 2.6–4. 2020, from https://CRAN.R-project.org/package=vegan. Accessed 20 Nov 2024

Pardo T, Clemente R, Bernal MP (2011) Effects of compost, pig slurry and lime on trace element solubility and toxicity in two soils differently affected by mining activities. Chemosphere 84:642–650. https://doi.org/10.1016/j.chemosphere.2011.03.037

Pinna MV, Lauro GP, Diquattro S, Garau M, Senette C, Castaldi P, Garau G (2022) Softwood-derived biochar as a green material for the recovery of environmental media contaminated with potentially toxic elements. Water Air Soil Pollut 233(5):152. https://doi.org/10.1007/s11270-022-05616-7

Qian S, Zhou X, Fu Y, Song B, Yan H, Chen Z, Sun Q, Ye H, Qin L, Lai C (2023) Biochar-compost as a new option for soil improvement: application in various problem soils. Sci Total Environ 870:162024. https://doi.org/10.1016/j.scitotenv.2023.162024

Rached-Mosbah O, Gardou C (1988) Relation sols-plantes dans des zones pastorals à substrat riche en antimoine: exemple du Djebel Hamimat (Algérie). Colloque Phytosociologique XVI: Phytosociologie et pastoralisme. Paris 307–320

Rodríguez-Vila A, Forján R, Guedes RS, Covelo EF (2016) Changes on the phytoavailability of nutrients in a mine soil reclaimed with compost and biochar. Water Air Soil Pollut 227:1–12. https://doi.org/10.1007/s11270-016-3155-x

Silvetti M, Demurtas D, Garau G, Deiana S, Castaldi P (2017) Sorption of Pb, Cu, Cd, and Zn by municipal solid waste composts: metal retention and desorption mechanisms. Clean: Soil, Air, Water 45:600253. https://doi.org/10.1002/clen.201600253

Song T, Zhang L (2023) Biochar and cattle manure amendments improve the quality of green waste compost as growing substrate for Centaurea cyanus. J Mater Cycles Waste Manag 25:1359–1368. https://doi.org/10.1007/s10163-023-01613-y

Tang J, Zhang L, Zhang J, Ren L, Zhou Y, Zheng Y, Luo L, Yang Y, Huang H, Chen A (2020) Physicochemical features, metal availability and enzyme activity in heavy metal-polluted soil remediated by biochar and compost. Sci Total Environ 701:134751. https://doi.org/10.1016/j.scitotenv.2019.134751

Tang S, Liang J, Gong J, Song B, Yang Z, Fang S, Zhang P, Cao W, Li J, Luo Y (2021) The effects of biochar/compost for adsorption behaviors of sulfamethoxazole in amended wetland soil. Environ Sci Pollut Res 28:49289–49301. https://doi.org/10.1007/s11356-021-13959-7

Toth G, Hermann T, Da Silva MR, Montanarella LJEI (2016) Heavy metals in agricultural soils of the European Union with implications for food safety. Environ Int 88:299–309. https://doi.org/10.1016/j.envint.2015.12.017

Turner BL, Hopkins DW, Haygarth PM, Ostle N (2002) β-Glucosidase activity in pasture soils. Appl Soil Ecol

20(2):157–162. https://doi.org/10.1016/S0929-1393(02)00020-3

Urbaniak M, Mierzejewska-Sinner E, Bednarek A, Krauze K, Włodarczyk-Marciniak R (2024) Microbial response to nature-based solutions in urban soils: a comprehensive analysis using Biolog® EcoPlates™. Sci Total Environ 928:172360. https://doi.org/10.1016/j.scitotenv.2024.172360

USDA (United States Environmental Protection Agency) (1975) Soil taxonomy, USDA, Agric. Handb US Govern Print of Washington. DC, pp 436–446

USEPA (United States Environmental Protection Agency) (1998) Integrated risk information system (IRIS): arsenic, inorganic, Cincinnati, CASRN 7440–38–2

USEPA (United States Environmental Protection Agency) (2014). U.S. Priority Pollutant List. Retrieved from https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf. Accessed 20 Nov 2024

Wadjiny A (1998) Le plomb au Maroc: cas des districts de Touissit et de Jbel. Aouam Chronique De La Recherche Minière 531–532:9–28

Wang S, Mulligan CN (2009) Enhanced mobilization of arsenic and heavy metals from mine tailings by humic acid. Chemosphere 74:274–279. https://doi.org/10.1016/j.chemosphere.2008.09.040

Wang Q, Garrity GM, Tiedje JM, Cole JR (2007) Naive Bayesian classifier for rapid assignment of rRNA sequences into the new bacterial taxonomy. Appl Environ Microbiol 73(16):5261–5267. https://doi.org/10.1128/AEM.00062-07

Wenzel WW, Kirchbaumera N, Prohaskab T, Stingeder G, Lombi E, Adriano DC (2001) Arsenic fractionation in soils using an improved sequential extraction procedure. Anal Chim Acta 436:309–323. https://doi.org/10.1016/S0003-2670(01)00924-2

Wu H, Cui H, Fu C, Li R, Qi F, Liu Z, Yang G, Xiao K, Qiao M (2023) Unveiling the crucial role of soil microorganisms in carbon cycling: a review. Sci Total Environ 436(2):909. https://doi.org/10.1016/j.scitotenv.2023.168627

Yilmaz P, Parfrey LW, Yarza P, Gerken J, Pruesse E, Quast C, Schweer T, Peplies J, Ludwig W, Glöckner FO (2014) The SILVA and "All-species Living Tree Project (LTP)" taxonomic frameworks. Nucleic Acids Res 42(D1):D643-8. https://doi.org/10.1093/nar/gkt1209

Zekri J, Rached O, Sahli L, Yilmaz MA, Temel H, Tahar A (2019) assessment of soil contamination and plant stress tolerance in an antimony mining area: case study for Scabiosa atropurpurea L. and Santolina chamaecyparissus. Environ Ecol 37(3):747–757