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Effect of Municipal Solid Waste Compost on Antimony Mobility, Phytotoxicity and Bioavailability in Polluted Soils

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Abstract: The effect of a municipal solid waste compost (MSWC), added at 1 and 2% rates, on the mobility, phytotoxicity, and bioavailability of antimony (Sb) was investigated in two soils (SA: acidic soil; SB: alkaline soil), spiked with two Sb concentrations (100 and 1000 mg kg^{-1}). The impact of MSWC on microbial activity and biochemical functioning within the Sb-polluted soils was also considered. MSWC addition reduced water-soluble Sb and favored an increase in residual Sb (e.g., by 1.45- and 1.14-fold in SA-100 and SA-1000 treated with 2% MSWC, respectively). Significant increases in dehydrogenase activity were recorded in both the amended soils, as well as a clear positive effect of MSWC on the metabolic activity and catabolic diversity of respective microbial communities. MSWC alleviated Sb phytotoxicity in triticale plants and decreased Sb uptake by roots. However, increased Sb translocation from roots to shoots was recorded in the amended soils, according to the compost rate. Overall, the results obtained indicated that MSWC, particularly at a 2% rate, can be used for the recovery of Sb-polluted soils. It also emerged that using MSWC in combination with triticale plants can be an option for the remediation of Sb-polluted soils, by means of assisted phytoextraction.

Keywords: potentially toxic element; gentle remediation options; organic amendments; Sb uptake; microbial activity

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1. Introduction

Antimony (Sb) is an environmentally relevant potentially toxic element (PTE), usually combined, in alloys, with metals such as lead and zinc [1]. Sb, generally detected as a trace element in the Earth's crust (0.2–0.3 g per metric ton) and water (less than 1 μg L^{-1}) [2], reached worrying levels of contamination in different world areas in the last decades [3]. This has been mainly due to anthropogenic activities, such as mining and the processing of Sb-containing ores [4]. High Sb levels in soils can also be due to vehicular traffic and recreational shooting [5–7]. Moreover, Sb is extensively used as a flame retardant in plastics, and as catalyst in the production of polyesters fibers [8]. As a consequence of its ubiquity and toxicity (Sb is recognized as carcinogenic and clastogenic agent), Sb is included in the list of high-priority pollutants by the U.S. Environmental Protection Agency and the European Union [9,10]. In most natural systems, Sb mainly occurs as reduced (trivalent Sb(III)) or oxidized (pentavalent Sb(V)) inorganic species [11]. Inorganic compounds of Sb are more toxic than its organic species, and Sb(III) compounds are predicted to be 10-fold more toxic than Sb(V) [1]. However, as emphasized by Filella et al. [12], this cannot be generalized, since toxicity depends on many factors (e.g., the target organism, the route of exposure, and the presence of other pollutants). Sb oxidation state, its reactivity, and its potential bioavailability in soil are largely dependent on the pH, redox conditions, and concentrations of co-occurring reducing and oxidizing agents [13]. Sb(V) is the prevalent form in aerobic conditions, and mainly occurs as octahedral antimonate ion, $Sb(OH)_6^-$. This latter form is considered the most stable form, compared to the thermodynamically unstable Sb(III), which mainly occurs in anoxic conditions, as $Sb(OH)_3$ [1,12,14]. On the

other hand, Sb(V) mobility is greater than Sb(III) in the 5.0–8.5 pH range, due to its negative charge (pKa $HSb(OH)_6$ = 2.55; pKa $Sb(OH)_3$ = 11.8) [1,15]. Sb in soil is mostly associated with Fe, Mn and Al (hydr)oxides and organic matter [16,17], and their occurrence and abundance in soil seems to control Sb mobility and bioavailability, e.g., [18–20].

As a PTE, Sb can affect soil microbial communities and their functionality, as well as plant growth [21,22]. Diquattro et al. [21] showed a significant Sb impact on the composition and general catabolic activity of soil microbial communities, while Yu et al. [23] recorded reduced carbon mineralization and nitrification in the presence of Sb. Moreover, in situ Sb immobilization significantly stimulated the growth of *Helichrysum italicum* [22], indirectly showing a certain impact of this PTE on plant growth, which, however, was also confirmed in other studies, e.g., [24–26].

In the search for eco-friendly materials to restore Sb-contaminated soils, and/or to limit Sb ecotoxicological impact, many organic and inorganic amendments have been studied. For instance, Garau et al. [22] observed that the addition of a municipal solid waste compost (MSWC), together with an iron(Fe)-rich water treatment residue (WTR), favored the chemical and biological recovery of a subalkaline soil that was contaminated with Sb (~110 mg kg^{-1} soil). Wang et al. [27] showed that ferrous Fe and nitrate promoted the formation of Fe plaques in rice, decreasing Sb bioavailability. Teng et al. [28] showed that Fe-modified rice husk hydrochar was effective at immobilizing Sb in soil, while the same was shown by Almas et al. [29], using Fe-rich slag in combination with $FeSO_4$.

Despite the existence of substantial literature on effective amendments that are able to immobilize Sb in soil, very limited and often conflicting information can be found on the impact of compost on Sb mobility, and its toxicity and availability for plants. Nakamaru and Peinado [30] observed an increase in Sb availability in contaminated soils that were amended with compost. Verbeeck et al. [31] observed that the complexation capacity of dissolved organic matter could increase Sb mobility under different redox conditions. Lewinska et al. [32] showed that a long incubation time with compost (i.e., 140 d) did not always lead to Sb immobilization in different shooting range soils. Finally, Clemente [33] showed that adding greenwaste compost mulch to PTE-contaminated soil increased Sb mobilization. By contrast, Abou Jaoude et al. [34] showed that compost addition to Sb-contaminated sub-alkaline soils reduced water-soluble and exchangeable Sb, and increased its residual (non-extractable) fractions. Likewise, Garau et al. [35] showed that compost reduced the concentration of labile Sb in soil. Taken together, the results from these studies highlight the need for further investigations, aimed at clarifying the impact of compost on Sb-contaminated soils, and its potential use in the remediation of polluted environments. In particular, in view of a remediation intervention, it would be useful to establish the effects of compost on soil microbial communities, enzyme activities, plant growth, and Sb uptake in Sb-contaminated soils, other than establishing its impact on Sb mobility. Accordingly, the aim of the present study was to evaluate the effect of an MSWC, added at two different rates, on Sb mobility, phytotoxicity, and bioavailability in two polluted soils, as well as its impact on soil microbial activity, catabolic diversity, and enzyme activity.

2. Materials and Methods

2.1. Soil and MSWC Origin, Characteristics and Mesocosms Set Up

Different soil samples were randomly collected (0–30 cm depth) from two soils, named SA (soil A) and SB (soil B), located in North-Western Sardinia (Italy) (soil SA: 40°56′15.7″ N 8°53′30.4″ E; soil SB: 40°43′32.77″ N 8°24′48.6″ E). These soils were selected because they had never been cultivated (they were not treated with agrochemicals), were not close to Sb-contaminated areas, did not contain Sb (i.e., Sb < 1 mg kg^{-1}), and exhibited different physical–chemical properties, which were previously reported in detail (Table S1; [21]). In the laboratory, soil samples were air dried, sieved to <2 mm and pooled together according to their origin (SA and SB). SA was a loamy coarse sand while SB was a sandy clay loam soil (USDA classification).

SA and SB soils were then spiked with Sb(V) (i.e., $KSb(OH)_6$; CAS 12208-13-8; Merck) to obtain soils with medium–low (100 mg kg^{-1}; S-100) or high (1000 mg kg^{-1}; S-1000) Sb(V) pollution level as previously reported [21]. Spiked soils were kept at 40% of their water-holding capacity (WHC) using deionized water and equilibrated for nine months at 25 °C. During this period, soils were periodically mixed once a week and maintained at constant humidity. Afterwards, triplicate mesocosms from each soil type (SA and SB) and contamination level (S-100 and S-1000) were treated as follows: T0—polluted untreated soil; T1—polluted soil amended with 1% MSWC; T2—polluted soil amended with 2% MSWC. A total of thirty-six mesocosms (each consisting of 5 kg soil; 2 soil types × 2 contamination levels × 3 amendment treatments × 3 reps) were prepared using SA (n = 18) and SB (n = 18) soils. The MSWC rates were selected based on the specific Sb-immobilizing capabilities of compost highlighted in previous studies [17,22]. The MSWC was provided by Verde Vita Srl (Sassari, Italy) and was sieved to <2 mm before addition to mesocosm soils. The main characteristics of the MSWC were previously reported [17] and resumed in Table S2. Briefly, the MSWC had sub-alkaline pH (i.e., 7.93) and 27.3% organic matter content (OM); it had high cation exchange capacity (CEC, 92.3 $cmol_{(+)}$ kg^{-1}), dissolved organic carbon (DOC, 0.82 mg kg^{-1}) and humic acids content (14.2%). After amendment with MSWC, soils were carefully mixed, brought to 40% of their WHC and equilibrated for three months at 25 °C. During this period, soils were periodically mixed once a week and maintained at constant humidity.

2.2. Soil Characterization and Sb Mobility in Treated and Untreated Soils

After the equilibration period, selected physico-chemical properties were determined in treated and untreated polluted soils (Table 1). The pH, electric conductivity (EC), total organic carbon (TOC) and nitrogen (TN) were determined for treated and untreated soils following the national standard guidelines [36]. The DOC content was estimated as previously described by Brandstetter et al. [37]. The available phosphorus was quantified following the Olsen method (P Olsen) and the CEC was determined using the $BaCl_2$ and triethanolamine method [36].

Table 1. Chemical characteristics of Sb-polluted SA and SB soils amended or not (control) with MSWC (dry matter basis). SA/SB-100 and SA/SB-1000 denote soil type and pollution level, i.e., 100 and 1000 mg Sb kg^{-1} soil. For each soil type and Sb pollution level, different letters (e.g., a, b, c) denote statistical differences (Tukey–Kramer, $p < 0.05$) between treatments.

	pH	EC (mS m^{-1})	DOC (mg g^{-1})	CEC ($cmol_{(+)} \cdot kg^{-1}$)	P Olsen (mg kg^{-1})	TOC (g kg^{-1})	TN (g kg^{-1})
SA-100 control	5.14 ± 0.59 ^{b}	77.7 ± 0.78 ^{c}	0.81 ± 0.01 ^{c}	10.6 ± 0.35 ^{b}	30.5 ± 0.33 ^{b}	13.8 ± 0.31 ^{c}	0.96 ± 0.12 ^{b}
SA-100 + 1% MSWC	6.16 ± 0.09 ^{a}	102 ± 0.78 ^{b}	1.09 ± 0.03 ^{b}	15.2 ± 0.63 ^{a}	36.2 ± 0.58 ^{a}	17.6 ± 0.03 ^{b}	1.36 ± 0.00 ^{a}
SA-100 + 2% MSWC	6.65 ± 0.26 ^{a}	116 ± 2.26 ^{a}	1.17 ± 0.02 ^{a}	16.0 ± 0.06 ^{a}	35.9 ± 0.56 ^{a}	18.8 ± 0.56 ^{a}	1.57 ± 0.14 ^{a}
SA-1000 control	5.53 ± 0.71 ^{b}	71.8 ± 5.30 ^{b}	0.82 ± 0.02 ^{c}	11.8 ± 0.01 ^{b}	30.3 ± 0.39 ^{b}	13.5 ± 0.09 ^{c}	1.12 ± 0.04 ^{b}
SA-1000 + 1% MSWC	6.46 ± 0.06 ^{a}	102 ± 1.91 ^{a}	1.00 ± 0.03 ^{b}	13.3 ± 0.52 ^{a}	34.4 ± 0.62 ^{a}	16.8 ± 0.34 ^{b}	1.24 ± 0.01 ^{a,b}
SA-1000 + 2% MSWC	6.98 ± 0.16 ^{a}	108 ± 2.83 ^{a}	1.09 ± 0.01 ^{a}	14.2 ± 0.75 ^{a}	33.4 ± 0.22 ^{a}	18.5 ± 0.52 ^{a}	1.30 ± 0.10 ^{a}
SB-100 control	7.84 ± 0.05 ^{a}	57.8 ± 1.48 ^{b}	0.29 ± 0.00 ^{c}	22.4 ± 0.86 ^{b}	10.1 ± 0.43 ^{c}	12.7 ± 0.20 ^{c}	1.06 ± 0.02 ^{c}
SB-100 + 1% MSWC	7.93 ± 0.01 ^{a}	67.7 ± 3.82 ^{b}	0.40 ± 0.01 ^{b}	24.0 ± 0.15 ^{a,b}	15.9 ± 0.46 ^{b}	15.0 ± 0.20 ^{b}	1.13 ± 0.01 ^{b}
SB-100 + 2% MSWC	7.93 ± 0.00 ^{a}	88.9 ± 2.97 ^{a}	0.69 ± 0.02 ^{a}	26.2 ± 1.05 ^{a}	19.4 ± 0.68 ^{a}	16.6 ± 0.05 ^{a}	1.19 ± 0.01 ^{a}
SB-1000 control	7.92 ± 0.04 ^{a}	63.0 ± 0.07 ^{c}	0.30 ± 0.00 ^{b}	23.2 ± 1.83 ^{b}	9.73 ± 0.43 ^{c}	13.0 ± 0.16 ^{c}	1.02 ± 0.00 ^{b}
SB-1000 + 1% MSWC	7.94 ± 0.08 ^{a}	70.7 ± 2.40 ^{b}	0.50 ± 0.01 ^{a}	25.2 ± 0.58 ^{a,b}	15.6 ± 0.59 ^{b}	15.3 ± 0.19 ^{b}	1.21 ± 0.01 ^{a}
SB-1000 + 2% MSWC	7.97 ± 0.13 ^{a}	91.3 ± 0.85 ^{a}	0.51 ± 0.01 ^{a}	27.2 ± 1.10 ^{a}	20.3 ± 0.11 ^{a}	16.9 ± 0.22 ^{a}	1.22 ± 0.03 ^{a}

Total Sb concentration was quantified in all soils after digestion with aqua regia reverse solution (HNO_3/HCl 3:1 ratio) and microwave mineralization (Milestone MLS1200), using graphite furnace atomic absorption spectroscopy (GFAAS; PerkinElmer AAnalyst 400-HGA 900, Software AA-WinLab32). A standard reference material (NIST-SRM 2711A) was included for quality assurance and quality control. The Sb mobility in polluted (amended and not) SA and SB soils, i.e., its chemical reactivity with the soil matrix, was evaluated through the sequential extraction procedure proposed by Wenzel et al. [38] with minor

modifications. Briefly, triplicate soil samples (1 g each) from each mesocosm were first treated with water (25 mL) to estimate water-soluble Sb (step 0, this was the only additional step with respect to the original procedure), then they were treated with 25 mL of a 0.05 M $(NH_4)_2SO_4$ solution to quantify the readily exchangeable Sb fraction (step 1) and 25 mL of a 0.05 M $(NH_4)H_2PO_4$ solution (step 2) to estimate surface-bound Sb, while Sb associated to amorphous and crystalline Al- and Fe-(hydr)oxides was quantified after extraction with 25 mL of a 0.2 M NH_4- oxalate solution at pH 3.25 (step 3) and with 25 mL of a 0.2 M NH_4-oxalate + 0.1 M ascorbic acid solution at pH 3.25 (step 4), respectively. After each step, soil samples were centrifuged at 3500 rpm for 10 min, filtered using Whatman filter No. 42 to separate the liquid and solid phases, and Sb concentration in the supernatant was quantified using GFAAS as previously described. A standard reference material (NIST-SRM 2711A) was included for quality assurance and quality control.

2.3. Biolog Community-Level Physiological Profiles and Soil Enzyme Activities in Treated and Untreated Sb-Polluted Soils

The activity and catabolic diversity of microbial communities inhabiting the different Sb-polluted soils (amended or not) was investigated using the Biolog community-level physiological profile (CLPP) approach using Biolog EcoPlates™ (Biolog Inc., Hayward, CA, USA). In particular, triplicate soil samples (10 g) from each mesocosm were added with (90 mL) sodium pyrophosphate solution (2 g L^{-1}) and serial ten-fold dilutions were obtained using 0.89% NaCl solution. The obtained soil suspensions were centrifuged for 5 min at 500 rpm and the clear supernatant was used to inoculate the wells of the Biolog EcoPlate™ (120 µL per well). The Biolog EcoPlates™ are ready to use 96-well microtiter plates containing a different carbon source of soil/environmental relevance in each well [39]. A total of 31 different carbon sources and a control well with no carbon (all replicated three times) were present in each Biolog EcoPlate™ [40]. Inoculated plates were incubated at 28 °C for 6 days (144 h) and purple color formation in each well, due to the reduction of a tetrazolium dye and indicative of C-source catabolism, was recorded daily by measuring the absorbance at 590 nm (OD590), using an automatic Biolog MicroStation™ reader. All OD590 data were first blanked against the absorbance at time 0 and further subtracted from the respective control well (with no carbon source). Finally, they were processed to obtain a measurement of the potential catabolic activity of the microbial community, i.e., the average well color development (AWCD). The latter was calculated as follows: $AWCD = [\Sigma (R_i - C)]/31$ where C represents the absorbance value of control well, R_i is the absorbance of each response well, and 31 is the number of carbon substrates in the plate [41]. The richness value, or the number of substrates catabolized by each microbial community, was also determined as the number of wells with OD590 >0.15 [42]. Also, the Shannon–Weaver diversity index (H') was used to estimate the catabolic diversity of microbial communities and calculated as follows:

$H = -\sum(P_i \times \ln P_i)$, where P_i is the ratio between the absorbance value in the blank subtracted ith well (1 to 31) and the total absorbance values of all wells [43].

All Biolog-derived parameters (AWCD, richness and H') refer to the 120 h incubation time as this time point provided the best discrimination between treatments.

Enzymatic activities, such as dehydrogenase (DHG), β-glucosidase (GLU) and urease (URE), were determined colorimetrically in triplicate soil samples collected from each mesocosm as described by Alef and Nannipieri [44]. Briefly, the DHG activity was spectrophotometrically quantified (OD480 nm) after incubation of soil samples (10 g) with a triphenyltetrazolium chloride solution and expressed as triphenyl formazan (TPF) formed per g soil (dry weight basis). GLU activity was determined spectrophotometrically (OD400 nm) after incubation of soil samples (1 g) with p-nitrophenyl glucoside and expressed as p-nitrophenol released per g soil (dry weight basis). Finally, URE activity was determined spectrophotometrically (OD690 nm) after incubation of soil samples (5 g) with urea and expressed as ammonia released per g soil (dry weight basis).

2.4. Sb Phytotoxicity and Bioavailability in Treated and Untreated Sb-Polluted Soils

The influence of MSWC on Sb phytotoxicity was determined using triticale plants (× *Triticosecale* Wittm. cv. Universal) grown in treated and untreated Sb-polluted soils. This plant species was selected since in previous studies its growth was significantly affected by the presence of PTE in the growing medium [45–48]. A total of thirty-six pots each containing 1.5 kg of soil deriving from the different mesocosms were set up, i.e., 3 replicated pots × 3 amendment treatments (T0, T1, T2) × 2 Sb contamination levels (100 and 1000 mg kg^{-1}) × 1 plant species × 2 soil types (SA and SB). Seven triticale plants were planted in each pot after their germination in the dark at 25 °C. Planted pots were arranged in a completely randomized design and plants were grown over 8 weeks in a naturally lit greenhouse under controlled conditions (20–25 °C temperature, 60–70% relative humidity). At harvest, shoots were separated from roots, carefully washed with deionized water and dried at 55 °C for 72 h. Plant growth, i.e., root and shoot dry weight values, was used to estimate soil Sb phytotoxicity.

Sb bioavailability, i.e., the Sb uptaken by triticale plants, was determined after mineralization of roots and shoots with 2 mL suprapure H_2O_2 and 9 mL of HNO_3 and ultrapure H_2O (ratio 1:1), using a Microwave Milestone MLS 1200. The total Sb concentration in the mineralization solutions was determined using GFAAS as previously reported. Peach leaves were used as standard reference material (NIST-SRM 1515). The Sb translocation factor (TF_{Sb}) was calculated as the ratio between Sb concentration in shoots and that present in roots.

2.5. Statistical Analysis

All chemical analyses were performed in triplicate soil samples collected from each mesocosm and mean values ± standard errors were reported in tables and figures. For each soil type (SA or SB) and contamination level (100 or 1000 mg·kg^{-1}), the MSWC influence (T0, T1, T2) on Sb mobility, soil enzyme activities, Biolog-derived parameters, plant growth, and Sb uptake data was ascertained by one-way analysis of variance followed by a post hoc Tukey–Kramer test ($p < 0.05$). Moreover, differences between the above-mentioned parameters in SA-100 and SB-100, and SA-1000 and SB-1000, were assessed by a Student t-test ($p < 0.05$). Pearson correlation between the most labile Sb fraction (i.e., that extracted in step 0 of SEP) and biochemical, root dry weight, root length and Sb uptake (by roots) data was also determined. In this regard, the entire dataset from S-100 soils was considered since SA and SB soils showed comparable concentrations of labile Sb, while data from SA-1000 and SB-1000 were separately analyzed since labile Sb concentration in these two soils was very different (Figure 1). In all tests, differences were considered statistically significant at $p < 0.05$. All statistical analyses were carried out using the NCSS software (released 1 June 2011).

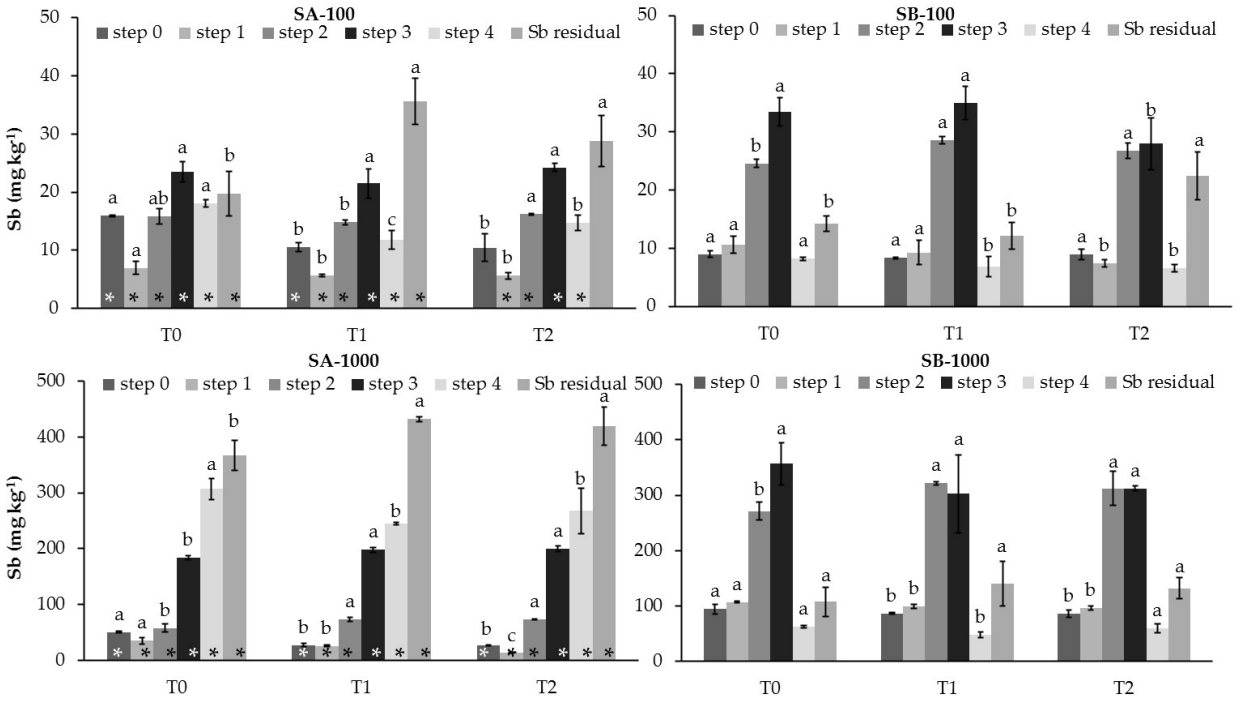

Figure 1. Sb extracted in amended and unamended Sb-polluted SA and SB soils in different SEP steps. Average values (histograms) and standard errors (bars) are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. Step 0: water-soluble Sb; step 1: exchangeable Sb; step 2: inner-sphere complexed Sb; step 3: Sb bound to amorphous Fe/Al (hydr)oxides; step 4: Sb bound to crystalline Fe/Al (hydr)oxides. For each soil and extraction step, different letters denote significant differences between treatments (Tukey–Kramer test; $p < 0.05$). For each extraction step, asterisks denote significant differences between SA-100 and SB-100, and between SA-1000 and SB-1000 (Student *t*-test; $p < 0.05$).

3. Results and Discussion

3.1. Influence of MSWC on Selected Chemical Properties and Sb Mobility in Polluted Soils

The treatment with MSWC caused a significant increase in pH in SA, and a significant increase in TOC, DOC, CEC, P Olsen, TN, and EC in both soils (Table 1). These results are in agreement with those reported by several researchers [49–52], and confirm the overall suitability of MSWC in improving different parameters related to soil fertility. This is particularly relevant in PTE-contaminated soils, which are often characterized by poor physico-chemical characteristics, and in which plant growth can be severely limited [53].

Sb mobility in soil after MSWC treatment was essentially evaluated through the sequential extraction procedure of Wenzel et al. [38], with minor modifications. In particular, an additional step (i.e., step 0) was added, to evaluate water-soluble Sb in soil. The water-soluble Sb (step 0) released from S-100-polluted soils was higher in SA than SB (~16 and 9% of total Sb, respectively), and was in accordance with previous findings [21], while an opposite trend was observed for S-1000 (Figure 1). The addition of MSWC did not change the water-soluble Sb fraction of SB-100, while a significant reduction was observed in SA-100 and in both S-1000 soils (i.e., −34, −9, and −47% in SA-100, SB-1000, and SA-1000, amended with 2% MSWC, respectively). These decreases suggested the occurrence of stable interactions between MSWC and Sb, which led to a reduction in water-soluble Sb. This is expected to have substantial positive implications from an ecotoxicological viewpoint, since water-soluble PTE represent the most biologically impacting fraction of contaminants (e.g., [34,54,55]). It is also important to underline that the concentration of water-soluble Sb in both soils was very high, even after MSWC addition (between 9.0 and 94.6 mg kg^{-1}), and it may represent a serious environmental hazard for soil organisms and other environmental compartments, e.g., surface and groundwater.

This is even more relevant considering that the Sb concentration threshold for Italian agricultural soils, which refers to total soil Sb, is 10 mg kg^{-1} [9].

A different trend was observed for Sb released with $(NH_4)_2SO_4$ (step 1, i.e., the relatively labile and exchangeable fraction), which was lower in SA than SB (e.g., ~3.5 and 9.6% of total Sb in SA-1000 and SB-1000, respectively). A limited, yet significant, reduction in Sb, extracted in step 1, was observed in all the amended soils, especially when 2% MSWC was applied (Figure 1). Overall, these findings highlighted a poor presence of a relatively labile and easily exchangeable Sb fraction in soils (note that sulphate can only exchange anions forming weak electrostatic bonds), and implied the prevalence of specific (inner-sphere) binding between Sb and soil/MSWC components. This was, in general, confirmed by the Sb concentrations extracted in step 2 (but also steps 3–4), which quantified the specifically adsorbed Sb; in this case, MSWC addition significantly increased such Sb fraction (e.g., by 15 and 28% in SB-1000 and SA-1000, amended with 2% MSWC, compared to the respective controls) (Figure 1). These results may have important environmental implications, since the specifically adsorbed Sb can be mobilized (becoming potentially bioavailable), as a result of a change in pH (e.g., due to plant and/or microbial activity) or phosphate increase [38].

Most of the soil Sb (~35 and 40% in SB and SA, respectively) was specifically associated with amorphous and crystalline Al- and/or Fe-(hydr)oxides (steps 3 and 4, respectively; Figure 1). After MSWC addition, the Sb fraction extracted with step 3 did not vary in SA-100 and SB-1000, significantly increased in SA-1000, and slightly decreased in SB-100, while the Sb fraction associated to crystalline Al- and Fe-(hydr)oxides significantly decreased in most soils (step 4; Figure 1). The Sb released in steps 3–4 is expected to have a limited impact on soil ecotoxicity, as it mainly represents the Sb involved in stable inner-sphere bonding with Fe- and/or Al-(hydr)oxides surfaces [38].

The residual Sb fraction was higher in treated and untreated SA soils (especially in SA-1000) than respective SB ones. This could be ascribed to the lower pH of untreated SA soil (i.e., 5.14–5.53), which could have promoted the formation of stable precipitates between Sb(V) and soluble Al or Fe, e.g., $FeSbO_4$ and $AlSbO_4$ [1,21,56–58]. The addition of MSWC favored an increase in such residual Sb in SB-100 (1.58-fold in 2% MSWC-amended soil), and in SA-100 and SA-1000 (1.46- and 1.14-fold, respectively, in 2% MSWC-amended soils). Overall, this is relevant, as residual Sb represents the very insoluble and/or occluded contaminant fraction, which can hardly be mobilized, and it is therefore expected to have a negligible impact on soil biota, at least in the medium term [17,22].

Taken together, these results show a substantial stabilizing/immobilizing effect of MSWC towards Sb, particularly in acidic soil (SA). This may have occurred by means of different processes, such as the formation of stable complexes between labile Sb and compost solid phases, such as ternary complexation, in which polyvalent metal cations (e.g., Fe, Al, and Ca) can act as bridges between the negatively charged functional groups of MSWC and the antimony oxyacid [18]. The precipitation of Sb, above all, with soluble Ca (abundantly present within MSWC; 6.3%, Table S2) may also have contributed to the increase in residual Sb in the treated soils. Additionally, the formation of mono- and di-ester bonds between $Sb(OH)_6^-$ and the hydroxyl functional groups of humic acids within MSWC could have also contributed to Sb immobilization in the amended soils [17].

In this context, the reduction in most labile Sb fractions in treated soils (steps 0–1) is expected to have relevant positive effects on soil microbial communities and their functionality, as well as plant growth. This has been proved for other PTE-contaminated soils (which, however, did not contain Sb) treated with MSWC [16,59].

3.2. Influence of MSWC on Soil Enzyme Activities in Sb-Polluted Soils

It has been shown that Sb can adversely affect microbial growth and inhibit the activity of soil enzymes, such as dehydrogenase, urease, arylsulfatase, and β-glucosidase [21,23]. Therefore, monitoring soil enzyme activities can be helpful in the assessment of the ability of MSWC to alleviate Sb microbial ecotoxicity, and to restore the biological activity and functionality of polluted soils [22]. DHG activity can provide a good estimate of the overall oxidative capacity of a soil and, at the same time, it has often been used as an indicator

of soil microbial abundance and/or activity [59–62]. Overall, DHG activity was higher in SB soils, and in soils contaminated with the lower Sb rate (i.e., 100 mg kg^{-1}) (Figure 2). This likely reflected the different size (and possibly also the different community structure) of microbial communities inhabiting SA and SB soils, which were characterized by very different chemical properties (Table 1). For instance, the higher pH in SB soils (Table 1) is likely responsible for the larger bacterial populations and higher DHG values (compared to SA), as previously reported [21]. Moreover, the lower DHG values in both Sb-1000 soils (compared to the respective Sb-100 ones) clearly show a higher negative impact of Sb on soil microbial abundance and/or activity in these soils. Compost addition significantly increased DHG activity in the contaminated soils, and this increase was proportional to the rate of MSWC added (e.g., 3.50- and 4.26-fold higher in SB-1000 amended with MSWC at 1 and 2%, respectively, compared to the unamended control) (Figure 2). This could be due to the lower amount of labile Sb in the amended soils (i.e., Sb extracted in steps 0–1), and to the consequently reduced environmental pressure on soil microbial communities, as previously shown with other PTEs [63,64]. The negative and significant correlation between the most labile Sb (i.e., the water-soluble one) and soil DHG supports this view (Table 2). On the other hand, the improved physico-chemical properties of the soils after compost addition could have contributed to the higher DHG values in the amended soils, as pointed out in previous studies [53].

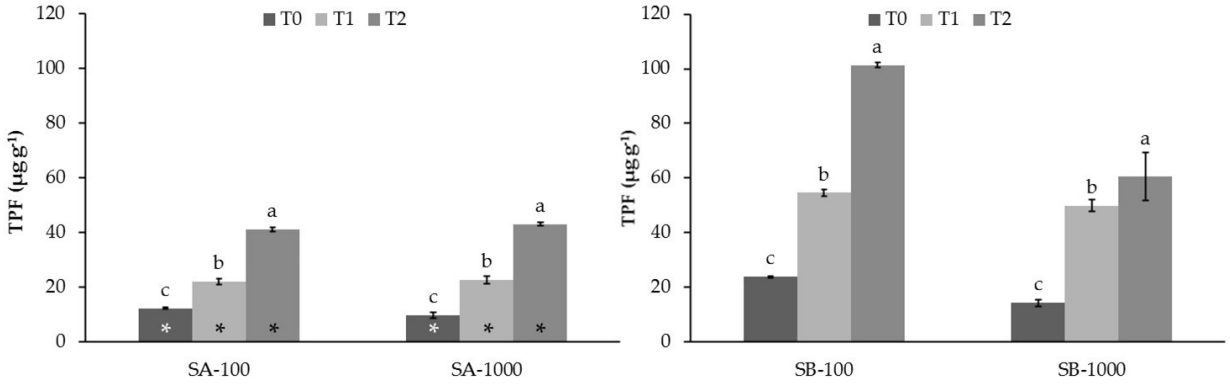

Figure 2. Dehydrogenase activity in amended and unamended Sb-polluted SA and SB soils. Average values (histograms) and standard errors (bars) are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For each soil (SA and SB) and Sb concentration level, different letters denote significant differences between treatments (Tukey–Kramer test; $p < 0.05$). Asterisks denote significant differences between SA-100 and SB-100, and between SA-1000 and SB-1000 (Student *t*-test; $p < 0.05$).

Table 2. Pearson correlations between the most labile Sb fraction (i.e., Sb extracted in step 0 of SEP), soil biochemical parameters, root dry weight, root length and Sb uptake by the roots of triticale plants.

	Root Dry Weight	Root Length	Sb Uptake$_{root}$	DHG	URE	GLU	AWCD	H′	Richness
S-100	−0.62 **	−0.72 ***	0.94 ***	−0.55 *	−0.61 **	−0.76 ***	−0.85 ***	−0.92 ***	−0.80 ***
S1-1000	−0.85 **	−0.79 *	0.72 *	−0.85 **	−0.6 ^{NS}	−0.43 ^{NS}	−0.67 *	−0.88 **	−0.78 *
S2-1000	−0.74 *	−0.67 *	−0.92 ***	−0.80 **	−0.69 *	−0.98 ***	−0.73 *	−0.91 ***	−0.90 ***

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; NS: not significant ($p > 0.05$).

A different trend was observed for URE activity, which can provide useful information on the rate of urea hydrolysis in soil (i.e., a specific step of N cycling), and was often used as a proxy of environmental stressing conditions [65–67]. URE activity increased in both soils treated with 1% MSWC, compared to the other treatments (e.g., URE was 1.9- and 2.9-fold higher in SB-100 amended with 1% MSWC, compared with the control and 2% MSWC, respectively; Figure 3) and, as for DHG, the activity decreased at higher concentrations of added Sb.

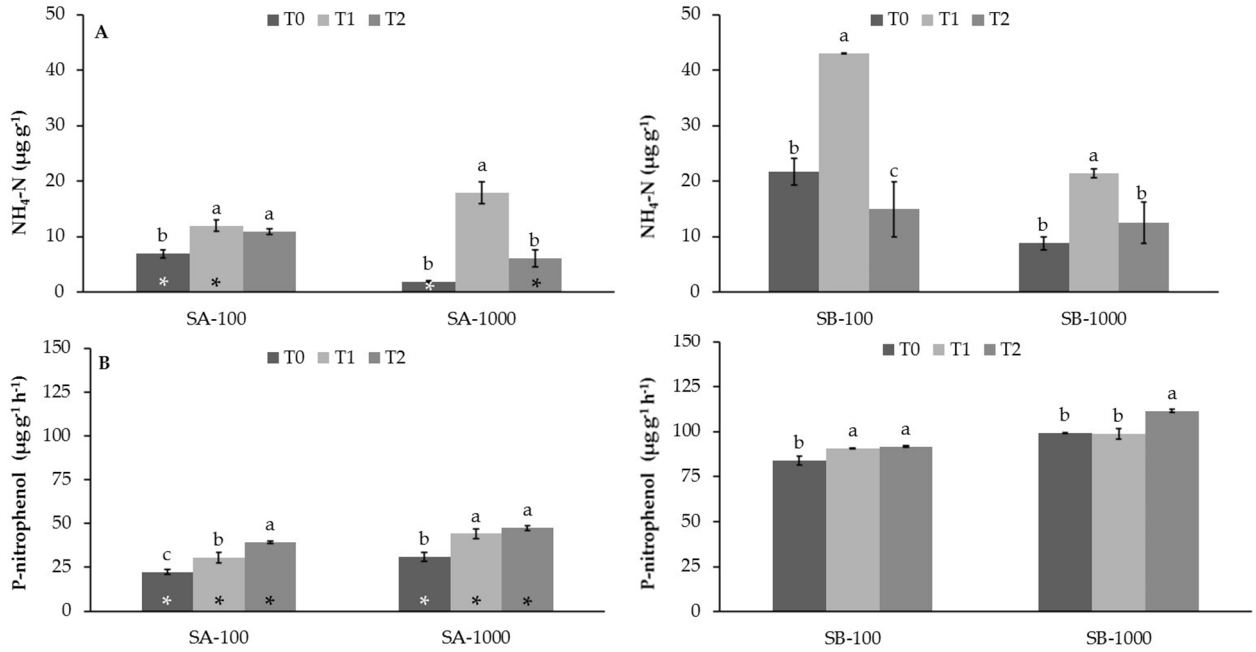

Figure 3. Urease (**A**) and β-glucosidase (**B**) activity in amended and unamended Sb-polluted SA and SB soils. Average values (histograms) and standard errors (bars) are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For each soil (SA and SB) and Sb concentration level, different letters denote significant differences between treatments (Tukey–Kramer test; $p < 0.05$). For each enzyme activity, asterisks denote significant differences between SA-100 and SB-100, and between SA-1000 and SB-1000 (Student *t*-test; $p < 0.05$).

The lower URE activity recorded in soils amended with 2% MSWC (often very similar to that of respective controls) seems to be in contrast with the lower amounts of labile Sb (steps 0–1; Figure 1) recorded in such amended soils. This was reflected by the Pearson correlation values between URE and the most labile Sb fraction, which were not statistically significant for all the soils (Table 2). Previous studies showed that ureases activity can be inhibited by the binding of humic substances to the thiol group of urease [68]. This could explain the reduced URE in soils amended with the highest compost rate. Moreover, the inorganic N present in MSWC could also be involved in the inhibition of urease synthesis, which could justify the reduced URE activity in soils treated with the highest MSWC amount [69]. GLU activity, which is due to extracellular enzymes that cleave the β 1→4 bonds linking two glucose or glucose-substituted molecules, was higher in SB than SA, which is in line with what was observed for URE and DHG. The addition of MSWC (with the exception of SB-1000 amended at a 1% rate) favored a significant increase in this activity (e.g., ~1.09- and 1.77-fold higher in SB- and SA-100 amended with MSWC, respectively), and this could likely be due to an increase in the labile C pool in the amended soils [65], and/or to a decrease in labile Sb. However, as for URE, a consistent correlation between the most labile Sb and GLU was not found in all the soils (Table 2). Furthermore, it should be noted that in soils spiked with the highest Sb amount (i.e., 1000 mg kg^{-1}), GLU activities were higher, with respect to S-100 soils. This apparent stimulating effect of Sb is difficult to explain, since the relatively few studies in the literature reported that β-1,4-glucosidase activity was negatively correlated with total and bioavailable Sb [23]. Probably, as also noted by Diquattro et al. [21], the proliferation in Sb-1000 soils of Sb-resistant microbial communities, able to synthesize β-1,4-glucosidases, could explain our findings.

3.3. Influence of MSWC on Soil Microbial Activity and Catabolic Diversity in Sb-Polluted Soils

As mentioned elsewhere, ideal amendments used for environmental remediation purposes should improve soil biological and/or biochemical attributes, other than reducing the labile concentration of contaminants [53]. In this context, the role of compost

in influencing the potential metabolic activity and catabolic diversity of the microbial communities of Sb-polluted soils was investigated by means of Biolog CLPP. Such an approach, which essentially detects differences in C-source utilization (if any) by microbial communities, was revealed to be particularly useful at evaluating the impact of organic and inorganic treatments on soil microbial consortia (e.g., [34,70–73]). Our results indicated a clear impact of MSWC on the potential metabolic activity of the microbial communities of amended soils, i.e., significant increases in AWCD were recorded in both S-100- and S-1000-amended soils (Figure 4). The most striking increases were recorded in SA-100- and SA-1000-amended soils, where the AWCD was 31- and 14-fold higher compared to that of respective untreated soils. Moreover, irrespective of the treatment applied, the AWCD data supported the higher metabolic activity in SB soils (compared to SA), as also indicated by DHG activity (Figure 2); essentially the same trend was detected for the richness and H′ index values (Figure 4). Microbial communities of MSWC-amended soils were able to catabolize a significantly higher number of carbon sources (richness; up to ~14 and 5 in SB and SA soils, respectively), compared to those of untreated soils, while the catabolic diversity (Shannon–Weaver H′ values) increased up to 3- and 30-fold in SB-1000- and SA-1000-amended soils, respectively (Figure 4).

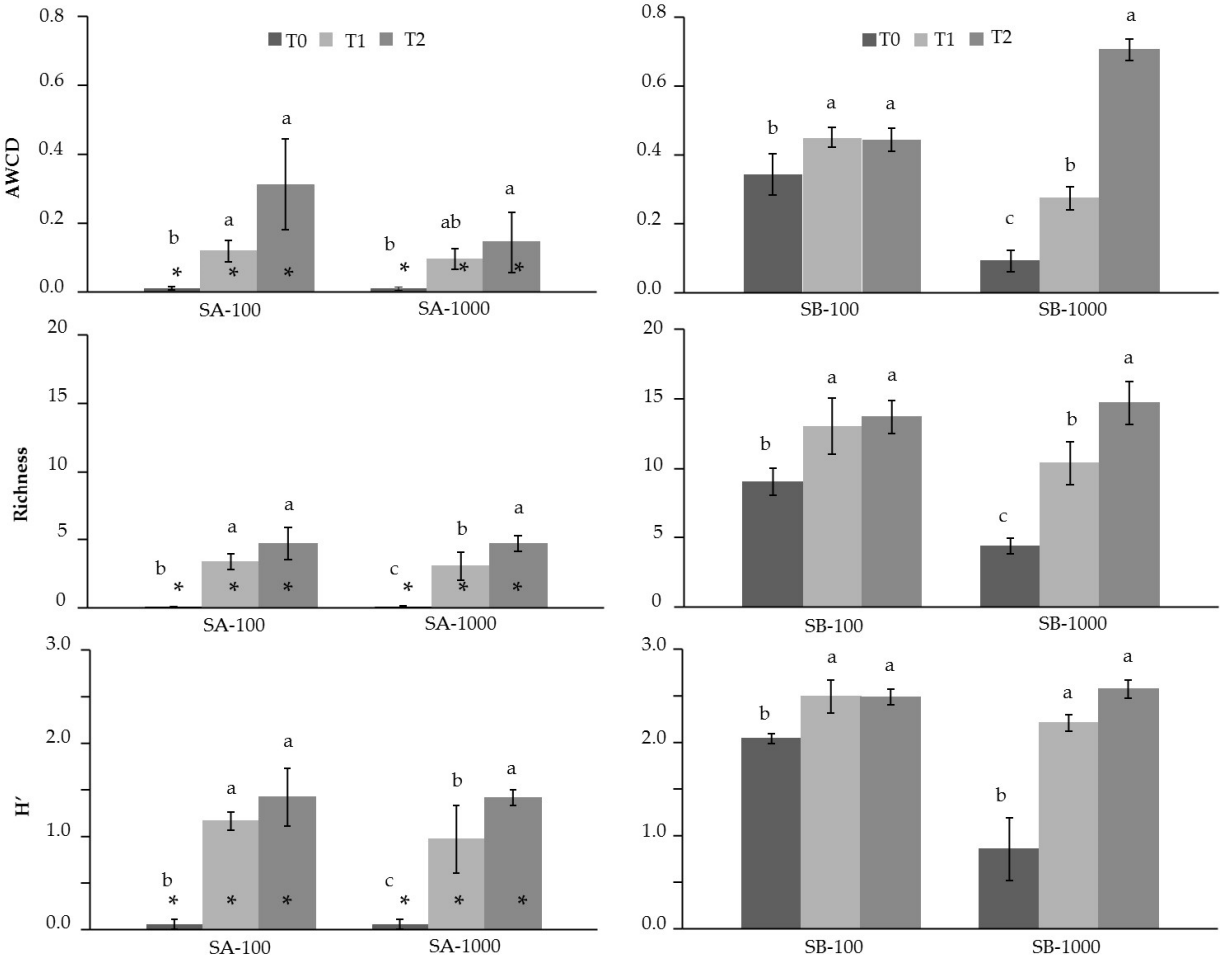

Figure 4. Biolog AWCD, richness and H′ (Shannon–Weaver) index in amended and unamended Sb-polluted SA and SB soils. Average values (histograms) and standard errors (bars) relative to the 120 h incubation time are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For each soil (SA and SB) and Sb concentration level, different letters denote significant differences between treatments (Tukey–Kramer test; $p < 0.05$). For each Biolog-derived parameter, asterisks denote significant differences between SA-100 and SB-100, and between SA-1000 and SB-1000 (Student *t*-test; $p < 0.05$).

Looking at the consumption of different C guilds in SB soils, the addition of MSWC greatly increased the utilization of sugar and sugar derivates by soil microbial communities, while that of amino acids substantially reduced (Figure 5). On the other hand, in SA soils, the use of the different C guilds was negligible, while MSWC addition led to significant catabolic recovery, which appeared to be proportional to the rate of MSWC addition, and was in agreement with the DHG trend (Figures 2 and 6). Taken together, Biolog EcoPlate™ data indicated a clear improvement of metabolic potentials in amended soils, which can be explained by different factors, such as the observed reduction in labile Sb in these soils (steps 0–1; Figure 1). This latter reduction likely alleviated the environmental stress posed by labile Sb towards microbial communities, leading to higher microbial abundance and/or activity, as previously reported [74]. Moreover, the reduction in labile Sb in amended soils could have favored the multiplication of Sb-sensitive bacterial strains (whose presence was negligible in the polluted untreated soils), having new catabolic capabilities, as highlighted by the increased richness and H' values. Similar findings were reported by Garau et al. [59], which showed a two-fold increase in bacterial species (and a concurrent increase in Biolog AWCD and richness) in a PTE-polluted soil amended with 4% MSWC. This view was also supported by the significant negative correlations between the most labile Sb fraction in soil and Biolog-derived parameters (Table 2).

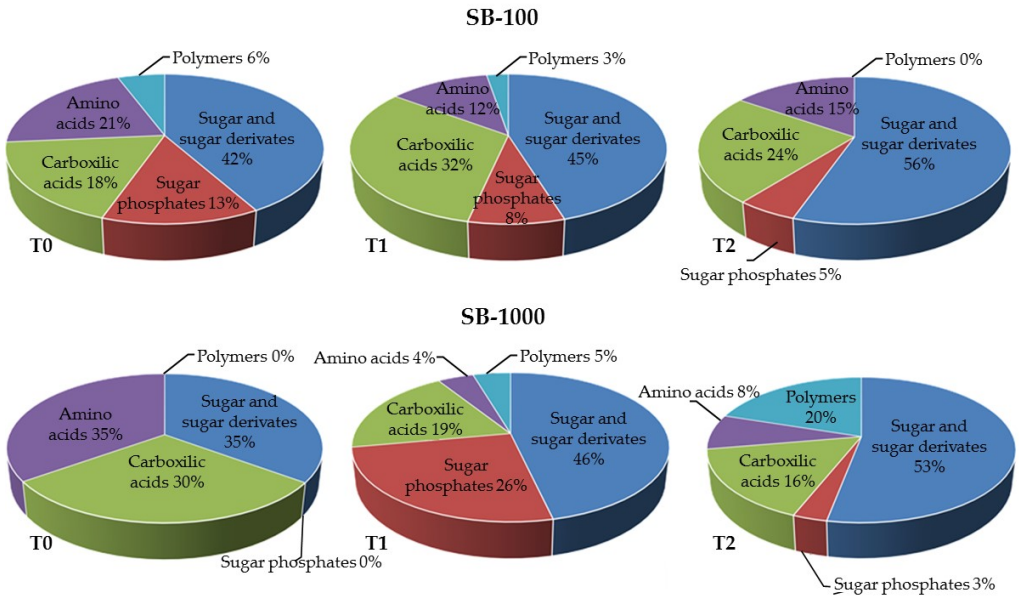

Figure 5. Use of different C-source guilds by microbial communities in amended and unamended Sb-polluted SB soils. Average percentage values relative to the 120 h incubation time are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For overall metabolic activity of the different microbial communities see Figure 4.

However, the larger availability of organic C in amended soils, which was reflected by higher DOC values (Table 1), could have reasonably contributed to the observed increase in metabolic activity and catabolic versatility, e.g., by making new and more diverse C sources available to microbial communities and/or by means of a priming effect [75]. On the other hand, links between DOC content and bacterial abundance and/or activity were also previously reported, e.g., [59,76].

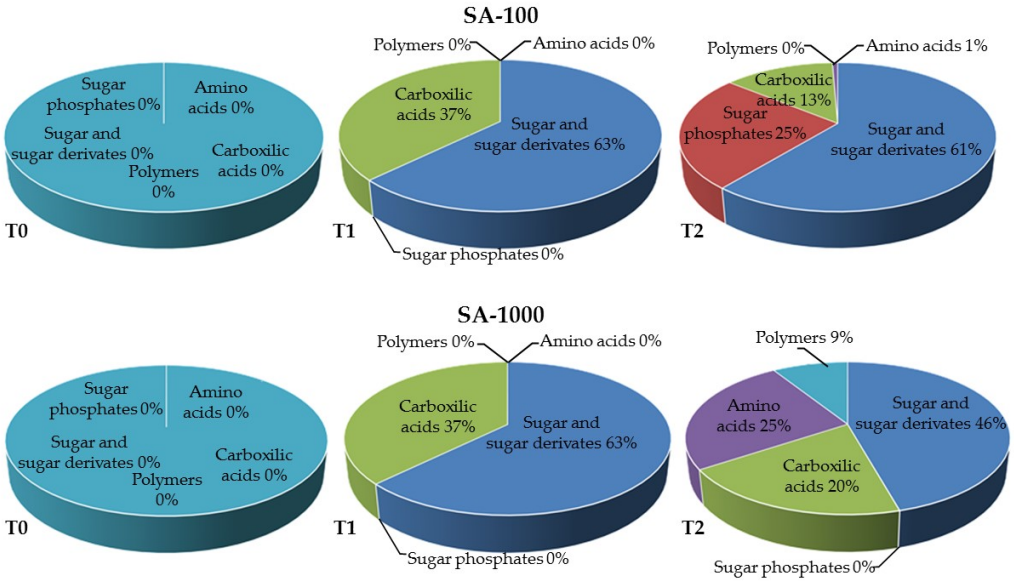

Figure 6. Use of different C-source guilds by microbial communities in amended and unamended Sb-polluted SA soils. Average percentage values relative to the 120 h incubation time are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For overall metabolic activity of the different microbial communities see Figure 4.

3.4. Influence of MSWC on Sb Phytotoxicity and Bioavailability

The growth of triticale plants was assessed in Sb-polluted SA and SB soils, to estimate the role of MSWC in the alleviation of Sb phytotoxicity. This is an important point in the evaluation of the suitability of the amendment, since plant growth in treated soils should hopefully be increased, mainly because of PTE immobilization by the amendment and/or improved soil nutritional status. Both these factors largely contribute to reduce the phytotoxicity of contaminated soils [53]. The plant growth in the Sb-1000 soils was consistently higher than that recorded in the Sb-100 ones (Figure 7). Considering that Sb was added in the form of $KSb(OH)_6$, this was likely due to the higher availability of K in the former soils; that is why a direct comparison of plant growth in Sb-100 and Sb-1000 soils can be misleading, and was therefore avoided. Overall, plant growth was significantly stimulated in the presence of MSWC, especially when the highest rate was applied (Figure 7), suggesting reduced phytotoxicity. In particular, root dry weight (rather than shoot) was greatly increased in MSWC-amended soils, e.g., up to 24% in SB-100 and -1000, and up to 14 and 47% in SA-100 and -1000, respectively (Figure 7). More limited increases were also noted for the shoot dry weight of plants grown in SA-amended soils (Figure 7). As for soil biochemical features, these results can be explained by a reduction in labile (and potentially bioavailable) Sb concentrations in amended soils (Figure 1). This view was supported by the correlation analysis, which highlighted a negative and significant correlation in all the soils, between the most labile Sb fraction and root dry weight (Table 2).

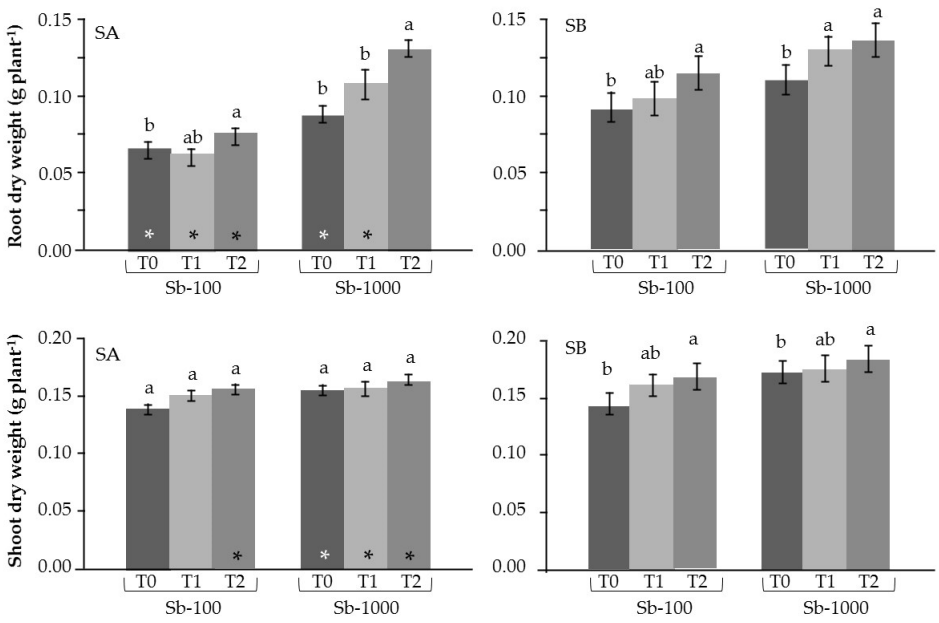

Figure 7. Root and shoot dry weight of triticale plants grown in amended and unamended Sb-polluted SA and SB soils. Average values (histograms) and standard errors (bars) are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For each soil (SA and SB) and Sb concentration level, different letters denote significant differences between treatments (Tukey–Kramer test; $p < 0.05$). For each plant part, asterisks denote significant differences between SA-100 and SB-100, and between SA-1000 and SB-1000 (Student *t*-test; $p < 0.05$).

However, the improved nutritional status of amended soils (see, for instance, the higher DOC, TOC, P Olsen, and TN content of these latter soils; Table 1) could have contributed to the better plant growth, as also highlighted in previous studies, where *H. italicum* and maize seedlings were grown in combination with MSWC and biochar, respectively [22,77]. Regarding the impact of MSWC on Sb uptake (i.e., bioavailability) by triticale, the results showed different trends according to Sb contamination level. In soils spiked with the lower Sb concentration, MSWC addition consistently decreased Sb uptake by the roots and increased that of the shoots (Table 3). In SA-1000 soils, MSWC addition increased both Sb uptake by the shoots (especially) and roots, whereas in SB-1000, these were both reduced, even if not significantly for the shoot (Table 3). Except for SA-1000 soils, a positive and significant correlation was found between the most labile Sb and its uptake by roots (Table 2), as was also reported in other studies for different PTE (e.g., [16]). This explains the reduced Sb uptake by roots in amended soils (Table 3), where a significant reduction in labile and potentially bioavailable Sb was recorded (Figure 1; steps 0–1). However, this was not the case of SA-1000 soils, for which a significant (unexpected) negative correlation between labile Sb and its uptake by roots was found (Table 2). This could be explained by higher root activity in such soils, especially in amended ones, which likely changed the relative distribution of labile Sb in amended and unamended soils. As a result, labile Sb after plant growth could have been different from that recorded before plant growth (and that was used to calculate the Pearson correlations). In particular, a higher release of phytosiderophores and organic acids, by triticale roots, in the amended SA-1000 soils (e.g., to alleviate Fe deficiency, note that SA soil contained ~65% less Fe compared to SB soil; [21]) could be responsible for the enhanced Sb mobilization, through the (partial) dissolution of Sb binding Al and/or Fe minerals [78–81]. Reasonably, this would have also occurred in SA-100 soil, where, however, this could have had a negligible effect, due to much lower Sb fractions bound to Al and/or Fe minerals (i.e., Sb extracted in steps 3–4; Figure 1). Furthermore, a progressive increase in TF_{Sb} was recorded in amended soils, according (mainly) to the compost rate (Table 3). This suggests that the enhanced

plant growth (and root activity) recorded in soils treated with MSWC (Table 3) could have possibly influenced Sb bioaccumulation by triticale, leading to a higher Sb concentration and increased translocation to shoots.

Table 3. Sb uptake, and translocation factor (TF_{Sb}), by triticale plants grown in amended and unamended Sb-polluted SA and SB soils. Average values are reported. T0, T1 and T2 refer to MSWC addition, i.e., 0, 1 and 2%, respectively. For each soil (SA and SB) and Sb concentration level, different letters (a, b and c) denote significant differences between treatments (Tukey–Kramer test; $p < 0.05$).

	SA-100			SA-1000			SB-100			SB-1000		
Sb Uptake	**T0**	**T1**	**T2**	**T0**	**T1**	**T2**	**T0**	**T1**	**T2**	**T0**	**T1**	**T2**
Shoot	1.61 ^{b}	1.42 ^{b}	2.54 ^{a}	3.36 ^{b}	5.61 ^{a}	6.31 ^{a}	0.53 ^{b}	0.92 ^{a}	0.91 ^{a}	12.38 ^{a}	10.30 ^{a}	9.66 ^{a}
Root	1.35 ^{a}	0.26 ^{b}	0.24 ^{b}	1.52 ^{b}	1.85 ^{a}	1.82 ^{a}	0.28 ^{a}	0.01 ^{b}	0.01 ^{b}	1.15 ^{a}	0.79 ^{b}	0.43 ^{c}
TF	1.2 ^{c}	5.5 ^{b}	11 ^{a}	2.2 ^{b}	3.0 ^{a,b}	3.5 ^{a}	1.9 ^{b}	92 ^{a}	91 ^{a}	11 ^{b}	13 ^{b}	22 ^{a}

Finally, it is interesting to note that triticale emerged for the first time as a phytoextracting species, with respect to Sb (i.e., $TF_{Sb} > 1$), and that MSWC could possibly be used in combination with this plant species for the remediation of Sb-polluted soils, by means of assisted phytoextraction approaches [82].

4. Conclusions

The mobility of Sb in contrasting soils, characterized by a medium–low or high pollution level, was reduced by MSWC addition and/or its residual fraction increased. Although the extent of these phenomena appeared to be dependent on the soil type and contamination level, MSWC amendment implied reduced Sb potential bioavailability, which was supported by increased soil biochemical functioning (DHG and GLU, especially) and the development of microbial communities with improved metabolic potentials and catabolic diversity. The addition of MSWC also alleviated Sb phytotoxicity towards triticale plants, and reduced, in most cases, their Sb uptake by roots. Overall, the MSWC impact on Sb-polluted soils was consistent with its use as an amendment for the recovery of such environments. The reduction in labile Sb concentration in treated soils was likely the key factor boosting soil microbial activity and diversity (and probably abundance). Reasonably, this contributed to the development of a rhizosphere environment, which favored plant growth in amended soils and stimulated Sb translocation from the roots to shoots. This is the first time that triticale has emerged as a potential species for Sb phytoextraction. In this regard, MSWC was revealed to be useful to enhance this capacity, and it appears a promising candidate, in combination with triticale, for assisted Sb (or possibly anionic PTE) phytoextraction programs. Despite a clear role of MSWC in the chemical and biochemical recovery of Sb-polluted soils, its long-lasting effect is currently unknown and should be investigated.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/soilsystems5040060/s1, Table S1: physico-chemical characteristics of SA and SB before Sb spiking; Table S2: chemical characteristics of the MSWC.

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