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Use of municipal solid wastes for chemical and microbiological recovery of soils contaminated with metal(loid)s

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ABSTRACT

Iron-rich water treatment residues (Fe-WTRs) and municipal solid waste compost (MSWC) were added together at two different total rates (i.e. 0.5% Fe-WTRs+0.5% MSWC and 1% Fe-WTRs+1% MSWC) to a degraded sub-alkaline soil (pH 8.0) contaminated with Sb (~110 mg kg^{-1} soil), Pb (~1200 mg kg^{-1}), Cd (~23 mg kg^{-1}), and Zn (~5400 mg kg^{-1}). A large number of chemical and biological endpoints were evaluated to assess the efficacy of the treatments after five months of incubation. Both treatments significantly reduced the labile fractions of the metal(loid)s in soil, especially Sb, while increasing the abundance of culturable heterotrophic bacteria, actinomycetes and fungi (i.e. up to 6.3-, 1.6- and 4.1-fold higher than control respectively). Soil enzyme activities, i.e. dehydrogenase, β-glucosidase and urease, were also significantly enhanced in the treated soils (i.e. up to ~12-, 3- and 2-fold higher than control respectively). The amendment addition affected the structure of the soil microbial community as highlighted by the higher metabolic potential and catabolic versatility of treated soils (Biolog CLPP) and by the significantly higher α-diversity values based on high throughput partial 16S rRNA gene sequencing. Moreover, analysis of the dominant operational taxonomic units (OTUs) showed differences in the microbial communities of untreated and treated soils. Plant growth (*Helichrysum italicum*) in the treated soils was greatly stimulated while metal(loid)s uptake was significantly reduced. Overall, the results indicated that the applied treatment could be ideal for the chemical and (micro)biological recovery of sub-alkaline soils contaminated with Sb and co-occurring metals, and *H. italicum* appears to be a promising plant species for aided phytostabilisation of such soils.

1. Introduction

Antimony (Sb) is a non-essential plant element which occurs naturally in soil, with its main source being the weathering of soil parent materials containing minerals such as stibnite (Sb_2S_3) and valentinite (Sb_2O_3) (Kabata-Pendias, 2011). While natural background concentrations of Sb in soils range from 0.25 to 1.4 mg kg^{-1} (Kabata-Pendias, 2011), much higher concentrations can be found in the proximity of mining sites, mineral processing facilities and/or shooting ranges (due to human activities). In recent years, heavily Sb-polluted sites have been identified all around Europe, e.g. in Italy (~15,000 mg kg^{-1} soil), Germany (~500 mg kg^{-1} soil), Switzerland (~17,000 mg kg^{-1} soil), France (~5700 mg kg^{-1} soil) (Tschan et al., 2009) as well as worldwide (Wang et al., 2010; Sanderson et al., 2014). These sites, often characterised by critical concentrations of co-occurring metal(loid)s (Wang et al., 2010, 2011; Okkenhaug et al., 2013; Sanderson et al., 2014), can be of particular environmental concern since they represent hazardous multi-element contamination sources for neighbouring soils and water bodies and constitute a threat for soil functionality and fertility.

Bioavailable Sb and co-occurring metal(loid)s can severely compromise soil functionality by affecting the size, composition and activity of the resident microbial communities (Garau et al., 2011, 2014; Wang et al., 2011; Garau et al., 2014; Wei et al., 2015) as well as plant growth (Castaldi et al., 2009; Kabata-Pendias, 2011; Pan et al., 2011). For instance, previous studies have reported reduced growth and biomass of both grasses and legumes under Sb

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and/or heavy metal(loid)s stress (Castaldi et al., 2009; Pan et al., 2011; Garau et al., 2014) as well as decreased abundance of culturable soil microbial populations and reduced soil enzyme activities (Garau et al., 2007; Wang et al., 2011; Garau et al., 2014). Moreover, it was recently shown that elevated Sb reduced the diversity of arbuscular mycorrhizal fungi (Wei et al., 2015) and increased the distribution, diversity and abundance in soil bacterial populations of selected genes involved in Sb detoxification (Luo et al., 2014).

Although the co-occurrence of critical concentrations of Sb and additional metal(loid)s represents a substantial threat for soil and ecosystem functioning, effective and reliable approaches for the remediation of these polluted sites are currently lacking. In particular, the different speciation, mobility and bioavailability of Sb with respect to selected co-occurring metal(loid)s (e.g. trace metal cations) makes the identification of suitable amendments a very challenging task.

Antimony is commonly present in the environment in the trivalent (III) and pentavalent (V) states with the inorganic antimonite [$Sb(OH)_3$] and antimonate [$Sb(OH)_6^-$] being the dominant species in aqueous systems across a wide pH range (i.e. pH 4–10) (Okkenhaug et al., 2013). In aerated soils, the anionic species $Sb(OH)_6^-$ is prevalent (if not exclusive) (Johnson et al., 2005; Filella et al., 2009) and displays a high affinity to amorphous and crystalline Fe-(hydr)oxides with which it can form stable bidentate inner-sphere complexes (Guo et al., 2014). In the pH range of the majority of soils (i.e. pH 5–9), such interactions are particularly favoured by the high point of zero charge of amorphous and crystalline Fe-(hydr)oxides (e.g. pH_{PZC} 7.5–9.0 for goethite, 8.5 for hematite, 7.0–9.0 for ferrihydrite, 9.5–10 for akaganeite (Strawn et al., 2015)). However, in the same pH range (i.e. pH 5–9), heavy metals such as Pb, Cd and Zn behave quite differently, being commonly present in the soil solution as divalent and/or monovalent (hydroxylated) cations at acidic and circumneutral pH or as soluble SOM-metal(II) complexes at higher pH values (Kabata-Pendias, 2011). Moreover, at neutral and/or alkaline pH substantial amounts of heavy metals are immobilised as Me-hydroxides, -carbonates and/or -hydroxycarbonates. Due to their cationic nature, and in contrast to Sb(V), soluble heavy metals show a limited affinity for positively charged soil surfaces but interact more strongly with negatively charged components (e.g. soil organic matter and clay minerals).

In the last decades, a variety of potential sorbent materials for the in-situ remediation of metal(loid) polluted soils have been proposed and tested (Castaldi et al., 2009; Garau et al., 2011, 2014), however Sb-contaminated (or co-contaminated) sites have been largely overlooked and neglected until recently. To date, only a few amendments, mostly based on Fe- and Al-containing materials/minerals, have been tested with variable success as Sb-immobilising agents. For instance, adding olivine and hematite to a contaminated soil was found to have no effect on porewater Sb concentration (Okkenhaug et al., 2012), while red mud (alumina industry residues high in Fe-oxides) addition reduced porewater Sb only in some cases (Sanderson et al., 2015). The addition of organic amendments (e.g. mussel shell, cow bone, chicken manure, sodium humate) have mostly been deemed ineffective at fixing Sb (Conesa et al., 2010; Ahmad et al., 2014; Shtangeeva et al., 2014), although mussel shell and cow bone, and also red muds, reduced the labile co-occurring Pb from the soil solution (Ahmad et al., 2014; Sanderson et al., 2015). Other research has shown that a 2% commercial Fe-oxyhydroxide, and very high rates of amorphous Fe- and Al-oxyhydroxides, could effectively stabilise the antimony in different polluted soils (Alvarez-Ayuso et al., 2013; Okkenhaug et al., 2013, 2016). However, the mobilisation of co-occurring metals (e.g. Pb, Cu, and Zn) was detected after the addition of Fe-based materials to Sb-contaminated soils (Okkenhaug et al., 2013). These findings, together with the limited number of studies addressing the remediation of Sb-contaminated sites, highlight the need to deepen our knowledge on the physico-chemical factors governing the mobility of Sb (and co-occurring metal(loid)s) in soil and to further select for sorbents with ideal Sb-immobilising capabilities. Such sorbents, other than reducing the mobility and phytoavailability of Sb and co-occurring metal(loid)s, should also ideally improve soil fertility as well as soil microbial abundance, diversity and functionality.

In this context, the aim of this work was to evaluate the suitability of the combined application of two low-cost and sustainable amendments for the chemical and biological recovery of a degraded alkaline soil contaminated with Sb, Pb, Cd and Zn. Iron-rich drinking-water treatment residuals (Fe-WTRs) and municipal solid waste compost (MSWC) were the selected amendments.

The presence in Fe-WTRs of an abundant mineral component rich in Fe-(hydr)oxides makes these residues potentially effective for the immobilisation of Sb in our alkaline soil (Guo et al., 2014), while earlier studies also suggest their suitability as metal-fixing agents (Castaldi et al., 2015). On the other hand, the application of MSWC together with Fe-WTRs was expected to contribute to soil recovery mainly by improving its nutritional and functional status.

The effectiveness of the combined application of Fe-WTRs and MSWC in a 1:1 ratio, at two different total rates (i.e. 1 and 2%), was assessed in this study using a comprehensive approach that spanned chemical investigation of metal(loid)-mobility, plant growth and pollutant phytoavailability, soil microbial abundance and bacterial diversity, community level physiological profiling, and soil enzyme activity.

2. Materials and methods

2.1. Soil and amendment origins, characteristics and microcosm set up

Sixty topsoil samples (0–20 cm depth; ~2 kg each) were collected from an area of approximately 1 ha located in the abandoned mining site of Argentiera (N40°44′11″, E8°8′54″) in north-western Sardinia (Italy), where Pb, Ag and Zn were extracted for about one century (1867–1963) from silver-rich galena [(Pb, Ag)S] and sphalerite (ZnS). The site is characterized by the presence of Sb-rich minerals such as boulangerite ($Pb_5Sb_4S_{11}$), tetrahedrite [$(Cu,Fe)_{12}Sb_4S_{13}$], freibergite [$(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$], bournonite ($PbCuSbS_3$) and pyrargyrite ($Ag_3SbS_3$) (Pirri, 1996). According to particle-size analysis, carried out using the pipette method (Day, 1965), the soil in the sampled area was a sandy-loam (USDA classification) with 68% coarse sand, 15% fine sand and 17% silt.

The collected soil samples were bulked together, air dried and sieved to <2 mm before being employed for the set-up of different soil microcosms, each consisting of approx. 10 kg soil. Triplicate microcosms were amended with 0.5% (w/w) Fe-WTRs + 0.5% (w/w) MSWC (1% total amendment rate) or 1% (w/w) Fe-WTRs + 1% (w/w) MSWC (2% total amendment rate) or left untreated as controls. These rates were selected based on the specific metal(loid)s immobilising capabilities of Fe-WTRs and MSWC highlighted in previous studies (Manzano et al., 2016; Garau et al., 2014). Before addition to the microcosms, Fe-WTRs (provided by the Bidighinzu plant of the Abbanoa industry, Sassari, Italy) and MSWC (provided by the Secit S.p.A. facility plant of the Consorzio ZIR, Chilivani-Ozieri, Sassari, Italy) were oven dried at 60 °C for 48 h and sieved to <2 mm.

After amendment, treated (and untreated) soils were carefully mixed, brought to 60% of their water holding capacity and equilibrated for 5 months at 20 °C. During this period, soils were mixed