



Municipal solid waste compost as a novel sorbent for antimony(V): adsorption and release trials at acidic pH

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Abstract

The ability of two municipal solid waste composts (MSW-Cs) to sorb antimony(V) in acidic conditions (pH 4.5) was investigated. Sorption isotherms and kinetics showed that both MSW-Cs could sorb antimony(V), even if in different amounts (~0.18 and 0.24 mmol g⁻¹ of Sb(V) by MSW-C1 and MSW-C2, respectively). These differences were ascribed to the chemical composition of composts, as well as to the total acidity of their humic substances. The Sb(V) sorption by both MSW-Cs followed a pseudo-second-order kinetic model, while the sorption isotherms data fitted the Freundlich model better than the Langmuir one. The humic acids extracted from composts contributed to 4.26 and 8.24% of Sb(V) sorption by MSW-C1 and MSW-C2 respectively. SEM-EDX spectra of the MSW-C+Sb(V) systems showed a certain association of Ca(II) with Sb(V), while sequential extraction procedures indicated that more than 80% of the Sb(V) sorbed was strongly retained by MSW-Cs. On the other hand, treatment with oxalic acid at pH 4.5 favored the release of more than 98 and 65% of the Sb(V) sorbed by MSW-C1 and MSW-C2 respectively, supporting a possible role of calcium in Sb(V) retention. The results from this study suggest that MSW-Cs could be used as amendments for the in-situ immobilization of Sb(V) in acidic-polluted soils.

Keywords Antimony(V) · Municipal solid waste compost · Humic acids · Sorption isotherms · Sb(V) release

Introduction

Antimony (Sb) and its compounds are considered as priority pollutants by the international environmental protection agencies (CEC 1998; USEPA 2009), because of their high toxicity and no known biological role (Filella et al. 2002a, 2002b; Tella and Pokrovsky 2009; Dousova et al. 2015). The Environmental Protection Agency of the United States (USEPA) established 6 µg l⁻¹ as the maximum contaminant level (MCL) for Sb in drinking water (USEPA 2009), while the European Union fixed a maximum admissible concentration of 5 µg l⁻¹ (CEC 1998). On the other hand, mean

background Sb levels in soils range from 0.25 to 1.04 mg kg⁻¹ (Kabata-Pendias 2010). However, the metalloid can be found in much higher concentrations where Sb-rich ores are present in the pedogenic material and/or as a consequence of anthropogenic activities (Tella and Pokrovsky 2009; Wilson et al. 2010; Martínez-Lladó et al. 2011; Tella and Pokrovsky 2012). In particular, antimony can mainly occur as stibnite (Sb₂S₃), the primary Sb ore, and valentinite (Sb₂O₃), which is an oxidation product of stibnite (Filella et al. 2002b; Kabata-Pendias 2010; Wilson et al. 2010). Anthropogenic sources of antimony include mining activity and industrial emissions; however, plastic waste, road traffic, and shooting ranges have become the dominant Sb sources in the last decades (Dousova et al. 2015; Ceriotti and Amarasinghwardena 2009). As a result, heavily Sb-polluted sites have been recently found in Europe (e.g., in Italy, Germany, and Switzerland with up to ~100, ~500 and ~17,000 mg kg⁻¹) (Tschan et al. 2009; Garau et al. 2017) as well as worldwide (e.g., in Iran, Canada, and China with up to ~640, ~1000 and ~7300 mg kg⁻¹) (Rafiei et al. 2010; Wang et al. 2010; Fawcett et al. 2015).

Antimony, according to thermodynamic equilibrium estimates, can occur in most natural systems in two oxidation

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states, +3 and +5, with the inorganic antimonite $[\text{Sb}(\text{OH})_3]$ and antimonate $[\text{Sb}(\text{OH})_6^-]$ being the dominant species in aqueous systems in a wide pH range (i.e., pH 4–10) (Filella et al. 2002b; Herath et al. 2017). Pentavalent Sb species are prevailing in oxygenated natural waters and aerated soils, at most environmentally relevant pH values, but it can also be present under reducing conditions, where the trivalent Sb is the thermodynamically stable form (Filella et al. 2002b; Buschmann and Sigg 2005; Steely et al. 2007; Wilson et al. 2010; Dousova et al. 2015).

Redox conditions and pH are the main parameters controlling Sb speciation in soils, which in turn is one of the key factors regulating Sb mobility and toxicity (Wilson et al. 2004; Scheinost et al. 2006; Clemente et al. 2008; Nakamaru and Altansuvd 2014). Sb(III) has been reported to be much more toxic (approx. 10 \times) and less stable than Sb(V) (Filella et al. 2002b; Buschmann and Sigg 2005; Steely et al. 2007; Dousova et al. 2015), but it was also recognized as less mobile and available to plants and soil microorganisms compared to Sb(V) (Nakamaru and Altansuvd 2014; Herath et al. 2017). However, this does not rule out the possibility of Sb(III) uptake by the plant (Mathews et al. 2011; Ren et al. 2014; Ji et al. 2017). The pH strongly influences the Sb sorption in soil, particularly sorption maxima for Sb(V) were reported at low pH values, i.e., below pH 6, while abrupt decreases were recorded at higher pH values (Filella and Williams 2012). This behavior can be explained considering that Sb(V) is primarily present in the soil solution as anionic $\text{Sb}(\text{OH})_6^-$ (the acidic form has a $\text{pK}_a = 2.55$) and its affinity for soil colloids gradually decreases as the net negative charges increase (Filella and Williams 2012).

Amorphous and crystalline Fe, Al, Mn-(hydr)oxides, and humic substances display a high affinity for antimony (Johnson et al. 2005; Tighe et al. 2005; Scheinost et al. 2006; Martínez-Lladó et al. 2011; Van Vleek et al. 2011; Nakamaru and Altansuvd 2014) and their occurrence in soil seems to control Sb mobility and bioavailability (Tighe et al. 2005; Clemente et al. 2008; Martínez-Lladó et al. 2011; Filella and Williams 2012; Tella and Pokrovsky 2012; Nakamaru and Altansuvd 2014).

Although substantial progress has been recently made on the comprehension of factors governing Sb mobility in soil (Wilson et al. 2010; Filella and Williams 2012; Garau et al. 2017), the remediation of Sb-polluted sites still remains a challenging task. Iron-based materials are among the most investigated and (so far) effective Sb sorbents (Tandy et al. 2017; Garau et al. 2017). However, the addition to Sb-polluted soils of sorbents containing organic matter (OM), e.g., compost, could be an alternative and more sustainable strategy for decreasing the mobility of the metalloid and improving the physico-chemical and biological properties of the soil (Dousova et al. 2015; Garau et al. 2017). There are some evidences supporting this point. It was proved that

antimony(III) can interact with both soft and hard OM ligands (e.g., thiol and COOH functional groups, respectively) (Buschmann and Sigg 2005; Tighe et al. 2005; Sh et al. 2012). Moreover, few reports suggest the Sb(V) binding to OM even if this point has not been clarified yet, and the results in literature are often controversial (Tella and Pokrovsky 2008; Filella 2011; Filella and Williams 2012; Nakamaru and Altansuvd 2014). The weak affinity of Sb(V) to soil organic matter, observed by some researchers, was explained with the anionic nature of Sb(V) in soil (i.e., $\text{Sb}(\text{OH})_6^-$), which limits the interaction with the negatively charged sites of the OM (Filella 2011; Filella and Williams 2012; Dorjee et al. 2014). Nevertheless, some researchers reported a significant Sb(V) complexation by OM and/or humic substances (Tighe et al. 2005; Steely et al. 2007; Tella and Pokrovsky 2008; Ceriotti and Amarasiriwardena 2009; Van Vleek et al. 2011; Dousova et al. 2015). Tella and Pokrovski (2008) provided a first direct evidence that poly-functional organic ligands like oxy-carboxylic acids and polyols were able to form complexes with Sb(V) in aqueous solution. Moreover, other mechanisms, such as ternary complexation in which polyvalent metal cations (e.g., Fe, Al, and Ca) act as a bridge between the negatively charged functional groups of OM and the antimony oxyacid (as demonstrated for phosphate and arsenate), could be involved in Sb(V) binding by OM (Filella and Williams 2012).

Taken together, these data suggest that OM can have an influence on Sb(V) mobility in soil and that OM-based sorbents, such as compost, could be used as alternative and sustainable amendments for the remediation of Sb-polluted soils. However, the Sb(V)-immobilizing capabilities of composts were never investigated and should be experimentally proved.

The aims of the present study were therefore (i) to evaluate the sorption capacity of two municipal solid waste composts (MSW-Cs) for Sb(V) in aqueous solutions at pH 4.5; (ii) to estimate the role of the MSW-C humic acids in Sb(V) sorption; (iii) to quantify the different Sb(V) pools bound to the MSW-Cs through specific extraction procedures; and (iv) to evaluate the capacity of low molecular weight organic acids (LMWOAs) commonly present in soils, i.e., citric and oxalic acids, to mobilize the metalloid sorbed by the MSW-Cs.

Materials and methods

Municipal solid waste composts (MSW-Cs)

Two different municipal solid waste composts (MSW-Cs), deriving from mixed green and food waste, were investigated: the first compost (MSW-C1) came from the Secit S.p.A. facility plant of the Consorzio ZIR (Sassari, Italy), while the second (MSW-C2) came from Verde Vita S.r.l. (Sassari, Italy).

The composts were dried at 25 °C, then ground and sieved to < 2 mm for chemical analyses which were performed according to Chefetz et al. (1996) and Castaldi et al. (2008) (Table 1).

The total concentration of selected heavy metals was determined on dried (105 °C) composts using a Perkin Elmer Analyst 600 flame atomic absorption spectrometer after microwave (Milestone MLS 1200) digestion of the samples with aqua regia (HNO₃/HCl, 1:3).

For Sb(V) sorption/desorption trials, compost samples were brought to pH 4.5 with either 0.01 or 0.1 M HNO₃ solutions. The chemical characteristics of the untreated composts, and of MSW-Cs brought to pH 4.5, are reported in Table 1. Each determination was carried out on

triplicate compost samples and mean values ± standard deviations are reported.

Sorption isotherms of Sb(V) on MSW-Cs at pH 4.5

MSW-C1 and MSW-C2 samples brought at pH 4.5 were artificially polluted with solutions containing increasing concentrations of Sb(V) (pH 4.5) derived from K₂Sb(OH)₆·7H₂O. Chemicals were of analytical grade and used without further purification. At the pH selected for this trial, and at the highest metalloid concentrations tested (i.e., 6 mM), more than 99% of Sb(V) was present in solution after 48 h, thus ruling out the formation of Sb(V) precipitates. Polyethylene bottles containing 1.0 g

Table 1 Chemical characteristics of the MSW-Cs investigated

Chemical parameters	MSW-C1		MSW-C2	
	Untreated	pH 4.5	Untreated	pH 4.5
pH	7.93 ± 0.06	4.5	8.60 ± 0.02	4.5
EC (mS cm ⁻¹)	3.26 ± 0.03	–	4.59 ± 0.01	–
Ashes (% d.m.)	42.05 ± 3.21	38.88 ± 2.61	46.42 ± 2.84	31.05 ± 0.49
Humidity %	9.75 ± 0.53	5.78 ± 0.44	5.02 ± 0.68	5.99 ± 0.14
Total organic carbon (TOC, % d.m.)	27.34 ± 0.61	26.98 ± 0.28	25.48 ± 0.33	24.86 ± 0.45
Dissolved organic carbon (DOC; mg kg ⁻¹ d.m.)	0.817 ± 0.04	0.573 ± 0.04	0.603 ± 0.04	0.405 ± 0.03
Cation exchange capacity (cmol ₍₊₎ kg ⁻¹)	92.30 ± 0.83	62.50 ± 0.19	77.75 ± 0.21	59.28 ± 0.13
Total phosphorus (% d.m.)	0.71 ± 0.11	0.57 ± 0.02	1.30 ± 0.10	0.78 ± 0.08
Elemental composition C (% d.m.)	27.46 ± 0.37	26.70 ± 0.28	26.38 ± 0.39	25.58 ± 0.57
Elemental composition N (% d.m.)	2.18 ± 0.04	2.60 ± 0.06	2.80 ± 0.07	3.72 ± 0.06
Elemental composition H (% d.m.)	3.17 ± 0.01	4.67 ± 0.05	3.20 ± 0.01	5.07 ± 0.05
Total extractable carbon (TEC: % d.m.)	16.35 ± 0.17	17.82 ± 0.23	13.34 ± 0.58	16.44 ± 0.15
Humic acids (HA: % d.m.)	14.24 ± 0.11	12.06 ± 0.06	11.18 ± 0.25	10.85 ± 0.04
Total Acidity (meq g ⁻¹ HA)	8.71 ± 0.24	8.48 ± 0.66	9.43 ± 0.44	9.39 ± 0.31
COOH (meq g ⁻¹ HA)	5.19 ± 0.84	5.06 ± 0.53	5.86 ± 0.53	5.94 ± 0.88
Ar-OH (meq g ⁻¹ HA)	3.52 ± 0.34	3.42 ± 0.69	3.57 ± 0.39	3.45 ± 0.55
Fulvic acids (FA: % d.m.)	1.10 ± 0.21	0.75 ± 0.05	1.01 ± 0.13	0.69 ± 0.07
Total Acidity (meq g ⁻¹ FA)	13.29 ± 1.44	12.86 ± 1.59	13.41 ± 1.53	12.68 ± 1.69
COOH (meq g ⁻¹ FA)	11.56 ± 1.59	12.24 ± 1.60	11.61 ± 1.42	12.45 ± 1.46
Ar-OH (meq g ⁻¹ FA)	1.75 ± 0.09	0.62 ± 0.02	1.81 ± 0.07	0.23 ± 0.00
Metals (mg kg ⁻¹ d.m.)				
Pb	3.72 ± 0.15	0.16 ± 0.00	n.d.	n.d.
Zn	30.52 ± 3.20	17.46 ± 1.49	26.91 ± 0.89	21.70 ± 2.07
Cd	n.d.	n.d.	n.d.	n.d.
Cu	19.24 ± 1.74	4.68 ± 0.39	n.d.	n.d.
Fe	5587 ± 88	6498 ± 65	5494 ± 66	7456 ± 54
Mn	140.5 ± 5.7	123.7 ± 4.8	147.9 ± 6.2	100.4 ± 4.9
Na	993.3 ± 24.2	369.9 ± 15.5	2534 ± 28.5	928.6 ± 18.7
K	1709 ± 21	372.3 ± 17.9	2780 ± 24	696.7 ± 19.1
Mg	5403 ± 135	1453 ± 169	4504 ± 121	1407 ± 60.8
Ca	63,444 ± 130	22,599 ± 105	80,113 ± 122	32,339 ± 245

of MSW-C1 or MSW-C2 were filled with 100 mL solutions of Sb(V) at pH 4.5. Nine different Sb(V) concentrations were used [from 0.0 to 6.0 mM]. A background electrolyte of 1.0 mM NaNO₃ was used for all batch experiments. The final mixtures were shaken for 24 h at constant temperature (20 ± 1 °C). Afterwards, the samples were centrifuged at 8000 rpm for 15 min and filtered using a 0.2-µm filter paper. Antimony(V) in the supernatant was measured by ion chromatography using an IonPac AS9-HC Analytical Column equipped with an IonPac AG9-HC Guard Column, 4 mm (Castaldi et al. 2014; Silveti et al. 2017a). Sodium bicarbonate (10 mM) was employed as the eluent at a flow rate of 1.0 mL min⁻¹. The sample loop was 10 µL. Each point of the sorption isotherms derived from Sb(V) quantification in three independent samples and mean values ± standard deviations are reported.

To investigate the role of humic acids (HA) in Sb(V) sorption, HA were extracted from composts as described by Ciavatta et al. (1990) and brought at pH 4.5. Polyethylene bottles containing 250 mg of the extracted HA were filled with 25 mL of 3.0 or 6.0 mM Sb(V) solutions (1:100 w/v ratio). The mixtures were shaken for 24 h at constant temperature (20 ± 1 °C) and then centrifuged and filtered, and Sb(V) in the supernatant was quantified as described above.

Sorption kinetics of Sb(V) on MSW-Cs at pH 4.5

For kinetic studies, polyethylene bottles containing 1.0 g of each compost brought at pH 4.5 were filled with 100 mL of a solution containing 0.6 mmol of Sb(V) derived from K₂Sb(OH)₆·7H₂O. The final mixtures were shaken at constant temperature (20 ± 1 °C) for different times, i.e., 5, 10, 30, 60, 180, 360, 720, 1080, 1440 min. The samples were then centrifuged at 8000 rpm for 15 min and filtered. Supernatant aliquots were taken and Sb(V) in solution was quantified as previously described. Each point of the sorption kinetics derived from Sb(V) quantification in three independent samples and mean values ± standard deviations are reported.

Scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis

SEM-EDX analyses of untreated MSW-Cs and of MSW-Cs-Sb(V) systems at pH 4.5 [i.e., saturated with 6.0 mM K₂Sb(OH)₆·7H₂O] were carried out using an environment electron microscope ESEM-Zeiss EVO LS10 (Oberkochen-Germany). Compost samples were observed with the backscattered electron detector (BSD) and chemically analyzed with a microanalysis X-ray energy-dispersive device (EDS) INCAx-ACT (Oxford Instruments).

The whole processes occurred at low vacuum mode and a pressure of 10 Pa.

Sequential extraction of Sb(V) by the MSW-Cs-Sb(V) systems

The different Sb(V) pools bound to the MSW-Cs doped with 3.0 or 6.0 mM K₂Sb(OH)₆·7H₂O at pH 4.5 were quantified through the sequential extraction procedure (originally designed for As(V)) of Wenzel et al. (2001) with minor modifications: essentially, an additional step was added to estimate the water-soluble Sb(V), while the step designed to extract Sb(V) fractions bound to crystalline Al- and Fe-oxyhydroxides was not applied given the essentially organic and amorphous nature of composts.

MSW-C samples (1.0 g) brought at pH 4.5 and doped with 3.0 or 6.0 mM Sb(V) solutions (i.e., deriving from the sixth and the last point of the sorption isotherms) were added with 100 mL of distilled water (pH 4.5) and shaken for 2 h at 20 °C to extract the water soluble Sb(V) (step 1). Solid samples were then treated with 100 mL of 0.05 M (NH₄)₂SO₄ to extract the non-specifically sorbed Sb(V) (step 2). Solid samples were subsequently treated with 100 mL of 0.05 M NH₄H₂PO₄, to extract the specifically sorbed Sb(V) (step 3), while the Sb associated to amorphous Al- and Fe-oxyhydroxides was determined after extraction with 0.2 M NH₄-oxalate pH 3.25 (step 4). After each step of the extraction process, MSW-Cs were centrifuged at 8000 rpm for 15 min and filtered using a 0.2-µm filter paper. The concentrations of Sb(V) in solution were determined after each extraction step as previously described. Each step of the sequential extraction procedure was carried out on three independent samples and mean values ± standard deviations are reported.

Influence of organic acids on the release of Sb(V) by MSW-Cs-Sb(V) systems

Polyethylene bottles containing 1.0 g of each MSW-C+ Sb(V) brought at pH 4.5 and doped with 3.0 or 6.0 mM Sb(V) solutions were separately filled with 100 mL of 1.5 mM citric (CA) and oxalic (Ox) acids or EDTA solutions (all brought to pH 4.5). The mixtures were shaken for 24 h at constant temperature (20 ± 1 °C), centrifuged at 8000 rpm for 15 min, and filtered using the 0.2-µm filter paper. Supernatant aliquots were taken and Sb(V) quantified as described above. Each trial was carried out on three independent samples and mean values ± standard deviations are reported.

Results and discussion

The first aim of this research was to evaluate the capacity of two MSW-Cs to act as sequestering agents for Sb(V) in acidic

conditions, i.e., at pH 4.5. This pH value was selected since most of the mining soils, where trace metals and metal(loid)s are present as sulfide ores, are generally strongly acidic (pH 3.5–5.0) (Tandy et al. 2009; Manzano et al. 2016) and since preliminary trials, carried out in our laboratory, did not show any Sb-immobilizing capacity of the MSW-Cs at neutral and sub-alkaline pH.

Chemico-physical properties of the MSW-Cs

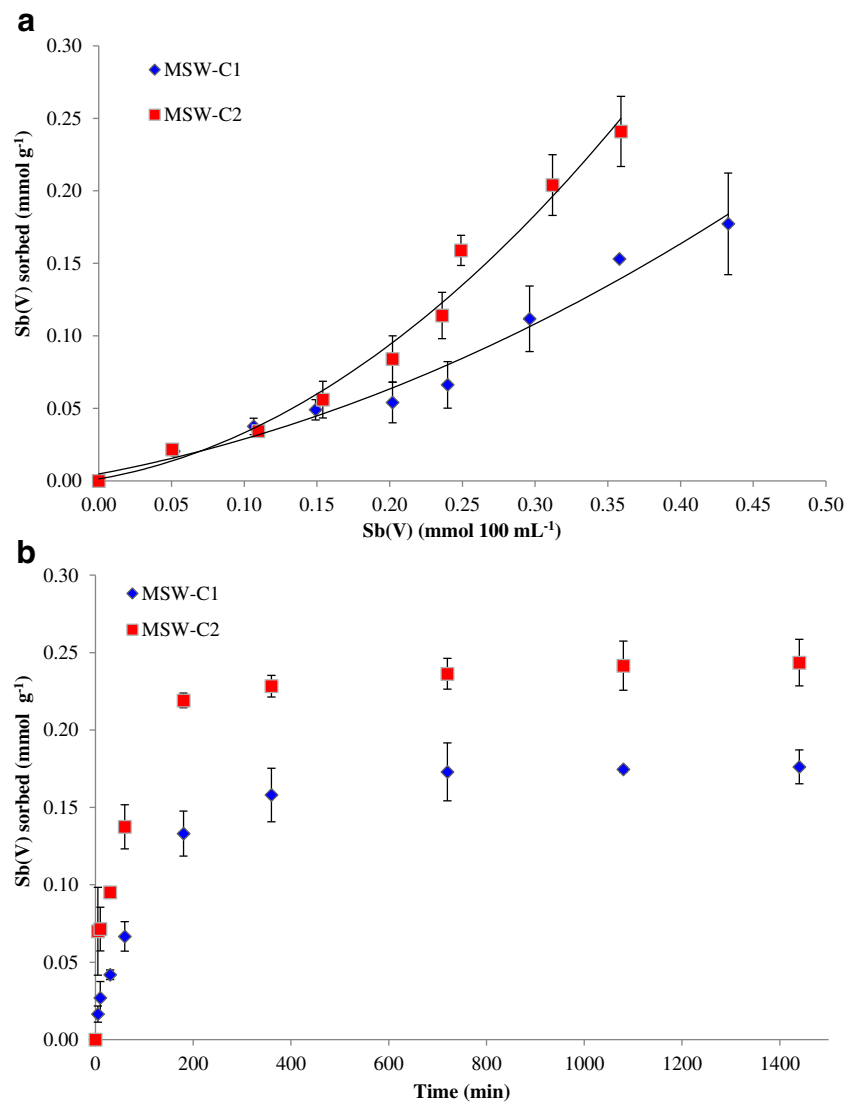
Table 1 reports the physico-chemical features of the untreated MSW-C1 and MSW-C2, and those of the same composts brought to pH 4.5. Notably, the same composts were recently investigated for their ability to bind Pb, Cu, Cd, and Zn ions from aqueous solutions at acidic pH (Silvetti et al. 2017a, 2017b). When composts were brought to pH 4.5, a decrease of DOC, CEC, total P, humic, fulvic acids and of the content

of the metals detected (with the exception of Fe) was recorded (Table 1). This was due to metal solubilization at acidic pH and to protonation processes involving the organic and inorganic phases. Fe, Mg, and, above all, Ca were the most abundant elements, with Ca and Fe being higher in MSW-C2 (Table 1). In both composts at pH 4.5, the stabilized organic matter, i.e., humic + fulvic acids (12.81 and 11.54% d.m. in MSW-C1 and MSW-C2, respectively), represented more than 40% of the total organic carbon.

Sorption isotherms of Sb(V) by MSW-C at pH 4.5

The two composts showed a different ability to bind the metalloid, i.e., 0.177 and 0.243 mmol g⁻¹ were the maximum Sb(V) sorption capacities of MSW-C1 and MSW-C2 respectively in the presence of 6.0 mM Sb(V) (Fig. 1a). However, the isotherm shapes were similar for the two MSW-Cs and

Fig. 1 Sorption isotherms (a) and sorption kinetics (b) of Sb(V) by MSW-Cs at pH 4.5



typical of adsorption phenomena directly proportional to sorbate concentration. Both isotherms did not reach a defined plateau (Me_{ads}/Me_{added} ratio increasing) as the Sb(V) concentrations increased, indicating that the saturation of the sites involved in the Sb(V) sorption was not completed (Fig. 1a) (Santona et al. 2006). However, higher Sb(V) concentrations, i.e., > 6.0 mM, could not be employed as the metalloid started to precipitate. These results highlight a substantial affinity of both composts towards Sb(V), in line with some studies reporting a strong association between antimony(V) and soil organic matter (Clemente et al. 2008; Ceriotti and Amarasiriwardena 2009; Wilson et al. 2010).

Given the high chemical complexity of composts, it is reasonable to assume that different mechanisms could be involved in the Sb(V) sorption. In particular, the formation of stable complexes between pentavalent antimony and poly-functional organic ligands, displaying aromatic or aliphatic hydroxyl and carboxyl functional groups, could partly explain the observed results. In this case, Sb(V) sorption by MSW-Cs could have occurred via the establishment of pentagonal or hexagonal rings through Sb-O-C bonds (Tella and Pokrovsky 2012). The non-specific Sb(V) binding to anion-exchange sites on MSW-Cs, e.g., protonated amino functional groups, may have also contributed to Sb(V) sorption (Thanabalasingam and Pickering 1986). Moreover, the Sb(V) interaction with cationic metals within composts [e.g., Fe(III), Mg(II), and Ca(II)], in which the metals act as bridging elements between Sb(V) and other negatively charged functional groups of compost (humic substances in particular), could further explain the observed results (Tighe et al. 2005). In addition, the likely presence in the MSW-Cs of metal-hydroxides physically and/or chemically bound to the organic components (Brown et al. 2012; Zeng et al. 2014) could have contributed to metalloid sorption. Finally, the coprecipitation of Sb(V) with metals could not be excluded. For instance, the Ca(II) involved in outer-sphere complexes (Ca(II) is abundantly present in both MSW-Cs) could be a good candidate for Sb(V) (co)precipitation. In this regard,

Johnson et al. (2005) and Okkenhaug et al. (2011) found that the solid $Ca(Sb(OH)_6)_2$ strongly controls the concentration of dissolved Sb(V) in soil. In the light of these considerations, the higher Sb(V) sorption capacity of MSW-C2 with respect to MSW-C1 could be attributed to the higher content of Ca, N, and Fe in the former compost as well as to a greater total acidity of C2-HA. This could have favored the formation of (i) ternary complexes; (ii) stable complexes with amino functional groups and/or with Fe-oxide surfaces; and (iii) mono and di-esters bonds involving the $Sb(OH)_6^-$ anion and compost components.

In order to better understand the Sb(V) sorption by the MSW-Cs, two types of models, i.e., the Langmuir and Freundlich isotherms, were applied to sorption data.

The Langmuir model assumes homogeneous and monolayer sorption and it is described by Eq. (1):

$$\frac{x}{m} = \frac{KbC}{1 + KC} \quad (1)$$

where b is the maximum monolayer coverage capacity of the sorbent ($mg\ g^{-1}$) and K ($dm^3\ mg^{-1}$) is a constant related to the energy of sorption which quantitatively reflects the affinity between the sorbent and the sorbate.

The Freundlich model is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm can be expressed as:

$$\frac{x}{m} = K_F C^{1/n} \quad (2)$$

where K_F and n are the Freundlich constants related to the uptake capacity and intensity, respectively.

Table 2 indicates that the Freundlich model described better the equilibrium sorption data of Sb(V) by MSW-C1 and MSW-C2 ($R^2 = 0.968$ and 0.944 , respectively) than the Langmuir equation did ($R^2 = 0.939$ and 0.927 , respectively), suggesting that these sorbents had heterogeneous adsorption sites characterized by different Sb(V) adsorption energies.

Table 2 Langmuir and Freundlich and kinetic model parameters related to Sb(V) sorption by MSW-Cs at pH 4.5

	Langmuir parameters			Freundlich parameters				
	b ($mmol\ g^{-1}$)	K ($L\ mmol^{-1}$)	R^2	K_F ($mmol\ g^{-1}$)	n	R^2		
MSW-C1	0.484	2.066	0.939	0.455	1.008	0.968		
MSW-C2	0.975	1.026	0.927	1.206	0.760	0.944		
	Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation	
	$q = q_{max} - \exp(\ln(q_{max}) - kt)$			$q = q_{max} + q_{max} / (kq_{max}t - 1)$			$y = a + k \ln(t)$	
	q_{max} ($mmol/g$)	k ($mmol/g\ h$)	R^2	q_{max} ($mmol/g$)	k ($mmol/g\ h$)	R^2	k ($mmol/g\ h$)	R^2
MSW-C1	0.186	0.544	0.612	0.191	0.064	0.993	0.348	0.970
MSW-C2	0.243	0.712	0.704	0.246	0.131	0.998	0.188	0.950

Sorption kinetics of Sb(V) by MSW-Cs at pH 4.5

In order to get additional insight into the process of Sb(V) sorption by MSW-Cs, sorption kinetics data were acquired. The kinetic curves were clearly biphasic, highlighting an initially fast sorption step (first 180 min), followed by a slower sorption rate (Fig. 1b); indeed, after 3 hours, more than 75 and 90% of Sb(V) were sorbed by MSW-C1 and MSW-C2, respectively. Subsequently, the adsorption rate slowed down significantly, and during the 3–24 h contact time, the increase in Sb(V) sorption was only 23 and 7.8% for MSW-C1 and MSW-C2, respectively. This suggested that the initial fast rate could be due to the retention of the metalloid on easily accessible (surface) sorption sites. Moreover, this fast step was likely characterized by strong coulombic attraction and/or coprecipitation reactions with accessible cations within composts (e.g., Fe(III), Ca(II), Al(III)) (Mohan et al. 2007; Ahmad et al. 2014). On the other hand, the slow sorption step may be attributed to specific (chemo-) and irreversible sorption (Ahmad et al. 2014; Wang et al. 2015) or to Sb(V) binding with MSW-C sites not easily accessible.

Different kinetic models were used to evaluate the main mechanism involved in Sb(V) sorption by the MSW-Cs, and the fitted kinetic parameters were shown in Table 2. As indicated by the R^2 values, the pseudo-second-order model was the best at describing the Sb(V) adsorption by MSW-C1 and MSW-C2 ($R^2 = 0.993$ and 0.998 respectively), suggesting that the rate-limiting step is a chemical sorption between the Sb(V) and both MSW-C (Mohan et al. 2007; Martínez-Lladó et al. 2011; Xu et al. 2011).

Role of MSW-C humic acids on Sb(V) sorption at pH 4.5

In order to assess the contribution of humic substances to the sorption of Sb(V) by MSW-Cs, sorption experiments were carried out using the HA extracted from both composts. The Sb(V) sorption by HA followed the same trends reported for the sorption and kinetic isotherms of the composts, being equal to ~ 0.017 and 0.059 mmol g^{-1} for HA-C1 and ~ 0.036 and 0.183 mmol g^{-1} for HA-C2, in the presence of 3.0 and 6.0 mM Sb(V), respectively (Fig. 2). The contribution of HA on the overall sorption of Sb(V) was equal to approximately 3.42 and 4.26% for MSW-C1 and 6.98 and 8.24% for MSW-C2, in the presence of 3.0 and 6.0 mM Sb(V), respectively.

These results clearly show that HA can have a role in Sb(V) sorption by MSW-Cs in an acidic environment, and that the extent of the sorption can be quite different depending on the HA considered. For instance, the HA extracted from MSW-C2 showed an approx. 70% higher Sb(V) sorption capacity compared with those extracted from MSW-C1 (Fig. 2). The Sb(V) binding to HA could be explained by electrostatic

interactions involving the $Sb(OH)_6^-$ anion and protonated amino functional groups and or by specific chemisorption (e.g., mono and di-esters bonds between $Sb(OH)_6^-$ and hydroxyl functional groups of HA) as previously reported (Thanabalasingam and Pickering 1986; Tighe et al. 2005; Tella and Pokrovsky 2012). In this context, the higher total acidity (in particular of COOH groups) of MSW-C2 HA could partly explain its higher sorption with respect to HA from MSW-C1 (Table 1). Nevertheless, the results obtained highlight the limited role of HA in Sb(V) sorption and indicate that other organic (e.g., non-humic), or inorganic components (metal-hydroxides and cations such iron and calcium) of MSW-Cs are involved in Sb(V) sorption.

SEM-EDX analysis of MSW-Cs-Sb(V) systems

Representative EDX spectra of untreated MSW-Cs and of composts doped with Sb(V) at pH 4.5 (point analyses) were shown in Fig. 3. The spectra of the Sb(V)-doped MSW-Cs always showed a distinct peak at 3.620 KeV which supported the Sb(V) sorption by the MSW-Cs. This peak is due to the combination of the Sb-L α (3.605 KeV) and the Ca-K α (3.691 V) emissions (Russ 1977; Suzuki and Sugi 1978; Suzuki and Sugi 1989) and indicated a certain association of Ca(II) and Sb(V) in both MSW-Cs. This supported the view that Sb(V) sorption by MSW-Cs could involve, to some extent, the formation of ternary complexes where Ca(II) acted as a bridging element between the negatively charged functional groups of MSW-Cs and the $Sb(OH)_6^-$ anion and/or the formation of solid $Ca(Sb(OH)_6)_2$ as previously shown (Johnson et al. 2005; Okkenhaug et al. 2011).

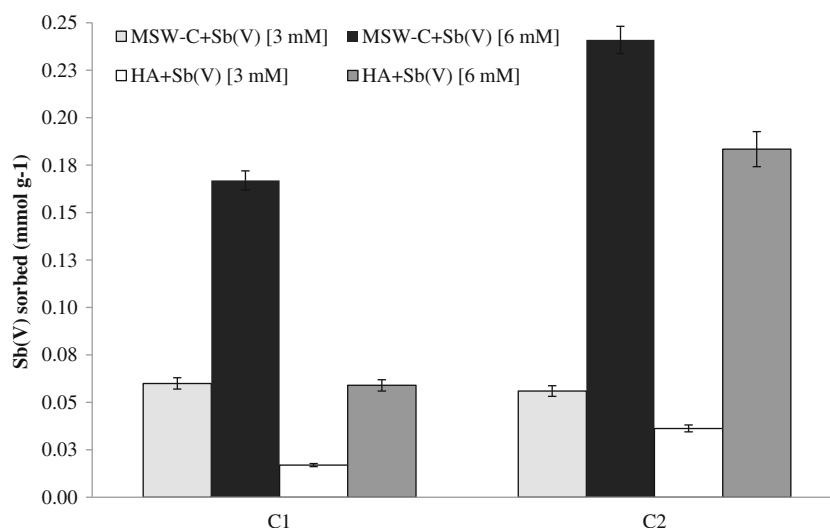
Sequential extraction of Sb(V) sorbed by MSW-Cs at pH 4.5

MSW-Cs doped with Sb(V) were subjected to selected steps of the sequential extraction procedure of Wenzel et al. (2001) to investigate the different Sb(V) pools retained by composts.

The water-soluble Sb(V) fractions (step 1) were negligible in both MSW-Cs when 3 mM Sb(V) was added, while they are accounted for ~ 4.53 and 1.85% of the total Sb(V) sorbed in MSW-C1 and MSW-C2, respectively, when 6 mM Sb(V) was added (Fig. 4). This can be relevant from an environmental point of view since it suggested a substantial stability of the interactions between MSW-Cs and Sb(V) and a limited risk of Sb(V) release from compost to surface and groundwater (Filella 2011).

The amounts of antimonate extracted from both MSW-Cs treated with $(NH_4)_2SO_4$ (step 2) were also very low ($< 6.5\%$ of the total Sb(V) sorbed) (Fig. 4). Such negligible effect of sulfate on Sb(V) desorption supported the prevalence of specific (inner sphere) binding between Sb(V) and the MSW-C surfaces, while sulfate can only exchange anions forming weaker

Fig. 2 Sorption of Sb(V) by MSW-Cs and respective HA at pH 4.5



(outer-sphere) complexes with positively charged compost functional groups (e.g., protonated amino-groups) (Nagar et al. 2010). The amount of Sb(V) extracted with $\text{NH}_4\text{H}_2\text{PO}_4$ (step 3), which represented the Sb(V) specifically

sorbed, was similar to that extracted in the previous step being equal for both composts to $\sim 7.0\%$ of the total antimonate sorbed, at the two concentrations tested (3.0 or 6.0 mM of Sb(V)). Finally, the Sb(V) fraction released in step 4 (designed

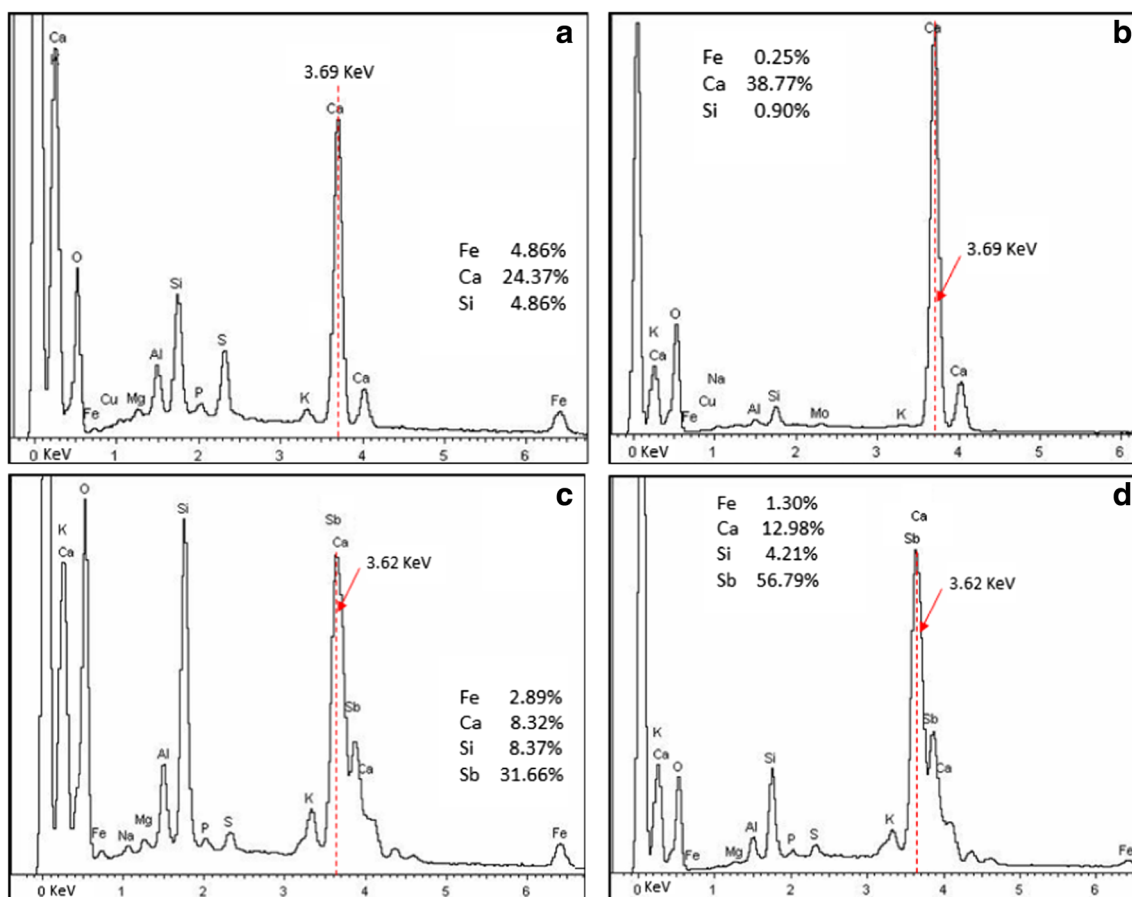
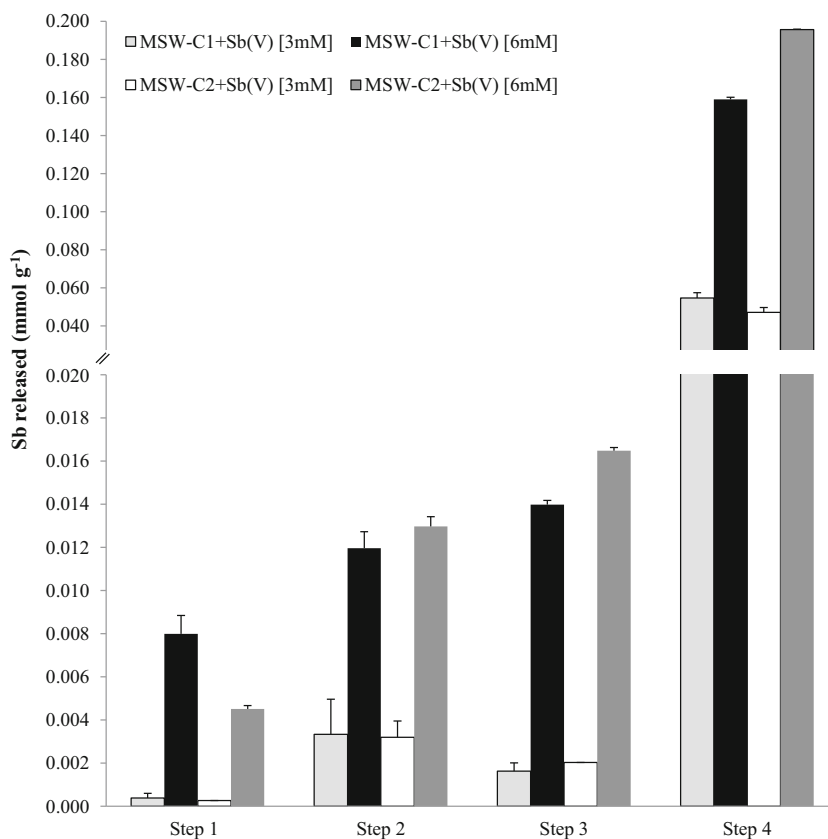


Fig. 3 Representative SEM-EDX spectra of untreated MSW-Cs (**a, b**) and of composts doped with Sb(V) (**c, d**) at pH 4.5 (point analyses) Note the peak at 3.69 KeV in untreated composts due to Ca-K α emission (**a, b**) and that at 3.62 KeV in composts doped with Sb(V) (**c, d**) due to the

combination of the Sb-L α (3.605 KeV) and the Ca-K α (3.691 V) emissions.

Fig. 4 Sb(V) extracted with H₂O (step 1), (NH₄)₂SO₄ (step 2), NH₄H₂PO₄ (step 3), and NH₄-oxalate (step 4) from MSW-Cs doped with Sb(V) [0.3 and 0.6 mM] at pH 4.5



to detect Sb(V) associated with amorphous Al- and Fe-oxides) was higher than 80% in both MSW-Cs (Fig. 4). The residual Sb(V) fraction (i.e., Sb(V) not extracted) was lower than 0.2% of total antimonate sorbed (data not shown).

These results indicated that very low amounts of antimony(V) could be extracted from the MSW-Cs-Sb(V) systems by using mild extractants. This also implies strong antimony(V) binding to compost solid phases and/or possible Sb co-precipitation with metal cations [e.g., Ca(II)] as suggested by the SEM-EDX results. In this case, the Sb(V) released in step 4 could be partly attributed to the dissolution of Sb/Ca containing precipitates (e.g., Ca(Sb(OH)₆)₂) other than amorphous Al/Fe-oxides.

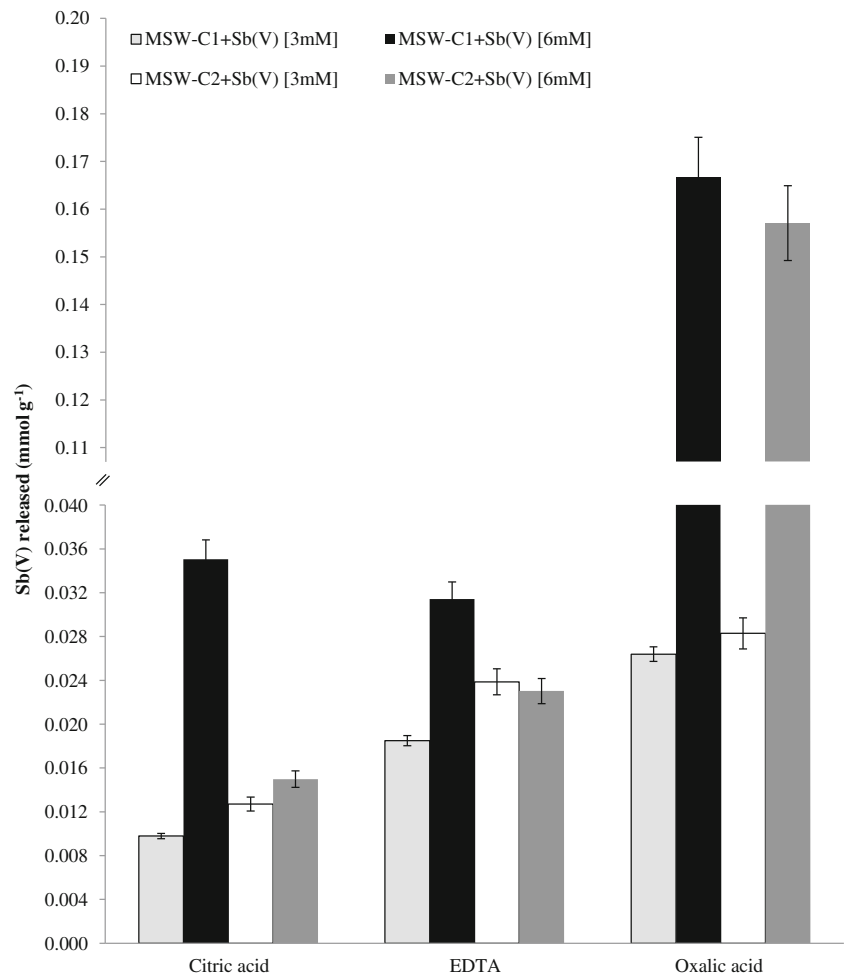
Effect of organic acids on the release of Sb(V) by MSW-C-Sb(V) systems at pH 4.5

In order to better clarify the potential mobility and bio-availability in soil of the Sb(V) sorbed by the composts, MSW-C samples doped with 3 and 6 mM Sb(V) were treated with citric (CA) and oxalic (OX) acids at pH 4.5 and the metalloid released was quantified after 24 h contact (Fig. 5). Citric and oxalic acids are abundantly present in the rhizosphere as products of the biological activity of plants and microorganisms (Stevenson 1994). As such, the Sb(V) release after CA and/or OX treatment

has certain environmental implications. The concentration of the two organic anions (i.e., 1.5 mM) was chosen considering that their concentration in the soil solution can vary from 1·10⁻⁵ to 1·10⁻³ mol L⁻¹ (Stevenson 1994) and that in selected microenvironments, such as rhizosphere and soil sites where decomposing plant residues is enhanced; it can be higher than 10⁻³ mol L⁻¹ (Stevenson 1994). EDTA, which is probably the most efficient metal chelating agent, was selected as a control chemical in order to complex metal cations such as Fe, Al, and Ca, to which Sb(V) could be bounded. In principle, the formation of such EDTA-Me complexes should favor the release of antimonate bounded to the metals.

At pH 4.5, the organic acids added, which are common and abundant compounds in soil and rhizosphere (Stevenson 1994), were in the form of organic anions (pK₁ = 3.09 and 1.23 for CA and OX, respectively). Citrate and oxalate could be involved in competition phenomena with Sb(V) for the same adsorbing sites on the MSW-Cs, thus causing the release of Sb(V) in solution by means of common anion exchange phenomena. At the same time, these low molecular weight organic acids (LMWOAc) could cause the partial dissolution of compost phases containing Fe(III) oxy-hydroxides or Ca(II) cations and the concurrent release of the Sb(V) bonded to iron nuclei or calcium (Onireti and Lin 2016).

Fig. 5 Sb(V) released from MSW-Cs doped with Sb(V) [0.3 and 0.6 mM] at pH 4.5 after citric and oxalic acids and EDTA treatment



The data obtained highlighted a different capability of the organic molecules to mobilize the Sb(V) sorbed by the MSW-Cs, regardless of the compost type (Fig. 5). Oxalate released 43 and 98% of total Sb(V) sorbed by MSW-C1 and 18 and 65% of total Sb(V) sorbed by MSW-C2, when 3 and 6 mM of Sb(V) were added, respectively. This indicated that MSW-C2 not only was able to adsorb more Sb(V), but it was also capable of a stronger metalloid retention. EDTA and CA showed a lower efficacy, being able to extract <20% of total antimony(V) sorbed in both MSW-Cs when 6 mM of Sb(V) was added. In particular, EDTA gave very low yields of Sb(V), and this is in agreement with several studies which reported low percentages (<4%) of total soil antimony extracted with EDTA (Conesa et al. 2010; Wilson et al. 2010; Filella 2011). However, it should be mentioned that the complexing capacities of EDTA increase significantly from acidic to alkaline pH and this could explain the low amounts of antimony(V) released at pH 4.5.

The higher release of Sb(V) following OX treatment may be attributed to the stronger acidity of oxalic acid, as compared to citric acid, as well as to the strong capacity of OX to

solubilize inorganic phases containing iron and calcium through non-reductive and reductive pathways (Onireti and Lin 2016). This in turn could have caused the indirect release of the Sb(V) bound to such inorganic phases.

The results obtained suggest that the different LMWOAs tested mobilized different Sb(V) pools bound to the MSW-Cs. In particular, CA likely mobilized the Sb(V) involved in the formation of inner or outer-sphere complexes with the MSW-C organic molecules; on the other hand, OX likely mobilized the former Sb(V) pools as well as those more strongly retained by the MSW-Cs, i.e., the Sb(V) (co-)precipitated or bound with calcium as well as that bound to iron oxyhydroxides.

Conclusions

The results from this study indicate that the MSW-Cs investigated are able to act as Sb(V) accumulators in acidic conditions, such as those characterizing many polluted sites. Different processes, most likely interrelated, and different organic and inorganic components of composts

affected the sorption of Sb(V). Irrespective of the compost type, HA had a role in Sb(V) sorption even if it was quantitatively limited.

Importantly, sequential extractions indicated that the majority of the Sb(V) sorbed (approx. 80%) was tightly bound to MSW-Cs through inner-sphere surface complexes and/or immobilized through co-precipitation reactions. This implies that such Sb(V) is not expected to be readily released under natural conditions.

SEM-EDX spectra revealed a certain association of calcium with antimony suggesting the occurrence of $\text{Ca}(\text{Sb}(\text{OH})_6)_2$ precipitates and/or the involvement of Ca(II) in the formation of stable ternary complexes with Sb(V) and compost functional groups. At the same time, this could suggest a minor role of amorphous Fe/Al oxides in Sb(V) binding in the presence of abundant Ca.

Treatment with citric and oxalic acids (commonly occurring plant and/or microbial metabolites) mobilized very different amounts of sorbed Sb(V) indicating the presence of different interaction types between Sb(V) and MSW-Cs, and supporting a possible role of calcium in the sorption processes. Treatment with OX, which has a marked and well-known affinity for calcium, released approx. 65 and 98% of the Sb(V) bound to MSW-C2 and MSW-C1, respectively.

The results presented indicate that the selected MSW-Cs should be tested as alternative and sustainable amendment for the remediation of acidic Sb(V)-contaminated soils.

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