Fractionation and Redox Speciation of Antimony in Agricultural Soils by Hydride Generation–Atomic Fluorescence Spectrometry and Stability of Sb(III) and Sb(V) During Extraction with Different Extractant Solutions

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This stability of Sb(III) and Sb(V) species was studied during single extraction from soils by water. EDTA, diluted H_2SO_4 and H_3PO_4, and oxalic acid/oxalate solutions, with and without ascorbic acid, were used as stabilizing reagent of both Sb species. Antimony redox speciation in soil extracts was performed by selective hydride generation–atomic fluorescence spectrometry. Simulated extraction procedures (without soil) showed that, except in oxalate medium, Sb(III) was oxidized to Sb(V), and this reaction was avoided with ascorbic acid. Recovery studies from a spiked agricultural soil showed that no oxidation but sorption of Sb(III) occurred during the extraction process in water and H_2SO_4 medium, and quantitative oxidation in EDTA and oxalate medium. With ascorbic acid, this oxidation was totally avoided in EDTA and partially avoided in oxalate solution. A new sequential extraction procedure was proposed and applied to the fractionation and redox speciation of antimony in agricultural soils, using EDTA + ascorbic acid, pH 7 (available under complexing and moderately reducible conditions); oxalic acid /oxalate + ascorbic acid (extractable in reducible conditions) and HNO_3 + HCl + HF (residual fraction). The proposed extraction scheme can provide information about the availability and mobility of antimony redox species in agricultural soils.

Antimony, a nonessential element for animals and plants, it is a cumulative toxic element that has chemical and toxicological properties similar to those of arsenic (1–3). The toxicity of Sb compounds are strongly dependent on the chemical form and oxidation states, and trivalent Sb compounds is more toxic than pentavalent ones.

Over the years, anthropogenic emission of Sb has resulted in an increasing concentration of this element in the environment. Sb may reach soil by wet and dry deposition following emission from smelters of lead, copper, and nonferrous minerals, and incineration and fossil fuel combustion (4). The natural concentration of Sb in soils ranges from 0.2 to 10 mg/kg with an average of 1 mg/kg (5). Studies of the analytical and environmental chemistry of Sb have increased because this element and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) and the German Research Community (DFG). For agricultural soils, the maximum admissible concentration of Sb in Germany is 5 mg/kg (6).

Because the toxicity of Sb is strongly dependent on its chemical forms and oxidation states, speciation data are required for sound risk assessment and a better understanding of the fate of this element in the environment. In the speciation of Sb, oxidation of Sb(III) to Sb(V) often occurs during sample preparation and analysis (7–12). In a recent study, Krachler and Emons (7) demonstrated that Sb(III) can be easily oxidized to Sb(V) within a few hours. Zheng et al. (8) demonstrated that spiked Sb(III) in a moat water sample was oxidized to Sb(V) within 30 min. However, the spiked Sb(III) could be stabilized by adding 0.26M citric acid to the sample, because of the formation of a Sb(III)–citrate complex. Subsequently, to obtain the original species information, these authors proposed the extraction of Sb from airborne particulate matter with this reagent (9). Others studies on the stability of Sb(III) and Sb(V) showed that Sb(III) remained stable in aqueous solutions with 0.1M lactic acid or 0.05M citric acid,

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stored in polyethylene bottles, for 12 months at 4°C (10). The formed Sb(III)–citrate and Sb(V)–citrate complexes were stable in different matrixes. As an extractant solution, citric acid offers the possibility of preserving the oxidation states of Sb species during the extraction process (8, 9, 11).

The determination of Sb in different soil fractions is necessary in order to assess its mobility and availability to plants. However, the extraction of Sb compounds from soil samples without changing the chemical forms remains a great challenge. Some single and sequential extraction procedures have been proposed to determine the Sb redox species in the available fraction or to perform its fractionation in soils (12–16). Two main problems severely hamper the extraction of Sb compounds from soils. First, low efficiencies in the extraction of Sb from soils have been reported with water (13, 14); 1M ammonium nitrate and 0.05M EDTA, pH 7 (13); 0.2M acetic acid and mixtures of methanol–water (1 + 1; 15); and 1M ammonium acetate (16). Second, no sound approaches and detailed investigations of the stability of Sb species during extraction from soils and further analysis are available. Lintschinger et al. (13) demonstrated that during extraction of Sb compounds with water and EDTA from spiked soils, the added Sb(III) (as Sb tartrate or Sb_2O_3) was immediately sorbed to soils. Under alkaline conditions (extraction with 0.1M KOH), oxidation of Sb(III) to Sb(V) was observed. On the other hand, selective extraction and spiking experiments in sediment showed that Sb tended to be associated or sorbed to immobile hydrous oxides of Mn, Fe, and Al, and the amount of Sb sorbed by the matrix compounds decreased gradually at pH values > 6 (17). Pilarski et al. (18) reported that Sb(III) and Sb(V) are also adsorbed by humic acids that can be present in soils, whereas only limited uptake was observed for Sb(V).

Information is not available about Sb extraction efficiency and/or stability of Sb(III) and Sb(V) during the extraction process from soils using diluted H_3PO_4 and H_2SO_4 as extractant solutions, reagents commonly used to extract metalloids such as As and Se (19–21). The present study reports results on the stability of Sb(III) and Sb(V) during the extraction process from soils with water, EDTA, H_2SO_4, H_3PO_4, and oxalic acid/oxalate mixture. The use of ascorbic acid as a stabilizing reagent of both species during these procedures was also studied. On the basis of results obtained from the single extraction, and to obtain information about the mobility of redox Sb species present in soils, a new sequential extraction procedure that allows both fractionation and redox speciation of Sb in soils is proposed. The redox speciation in the soil extracts was based on selective hydride generation–atomic fluorescence spectrometry (HG–AFS). The analytical methodology to determine total Sb in soils and vegetables and to perform its redox speciation in soils by HG–AFS was described previously (22, 23).

Experimental

Chemicals and Reagents

(**a**) *High-quality water (18Ω).*—Obtained from a NANOpure ultrapure water system (Barnstead, Dubuque, IA) and used for all dilutions.

(**b**) *Stock solutions*.—1000 mg/L Sb(III) and 1000 mg/L Sb(V) were prepared by dissolving solid Sb potassium tartrate [$K(SbO)C_4H_4O_6H_2O$; Aldrich, Milwaukee, WI; 99.95% purity] and potassium pyroantimonate [$KSb(OH)_6$; Prolabo, Paris, France, for analysis] in 1% (m/v) ascorbic acid (Merck, Darmstadt, Germany) and water, respectively. These solutions were stored at 4°C in polyethylene bottles. Working solutions of Sb(III) and Sb(V) were prepared daily by an appropriate dilution with 0.1% (m/v) ascorbic acid and water, respectively.

(**c**) *Sodium borohydride solution, 0.7% (m/v).*—Prepared by dissolving $NaBH_4$ powder (Merck) in 0.4% (m/v) NaOH solution (Merck). Solution was prepared daily by just before use or stored for up to 3 days at 4°C.

(**d**) *Citric acid monohydrate*.—Pro-analysis; used to mask Sb(V) (Merck).

(**e**) *Mixture of KI and ascorbic acid*.—Used in the preproduction of Sb(V) to Sb(III) (Merck).

(**f**) *Other solutions*.—To extract Sb compounds from soils were deionized water; 0.05M EDTA, pH 7 [obtained by dissolution of Na_2-EDTA salt (Merck); pro-analysis in water and pH adjusted by addition of NH_4OH (Suprapur; Merck)]; 0.25M H_2SO_4 and 0.30M H_3PO_4, prepared by dilution of the respective concentrate acid (Suprapur; Merck); and the mixture 0.2M oxalic acid + 0.2M di-ammonium oxalate (prepared from oxalic acid dihydrate and di-ammonium monohydrate salts; Merck). These solutions were prepared with or without ascorbic acid.

Apparatus

For HG–AFS Sb determinations, PSA Analytical (Orpington, Kent, UK) Excalibur Millennium Model 10055 atomic fluorescence spectrometer was used. This instrument has a continuous flow system for hydride generation coupled to a commercial dryer membrane (Perma Pure, Toms River, NJ; dryer Model MD-110-12 FP), which is joined to the fluorescence spectrometer. The stibine was purged to the atomization flame by an argon flow; the flame was sustained with H_2 produced in the hydride generation reaction between $NaBH_4$ and HCl, and with H_2 external supply at 30 mL/min. The instrument is equipped with an Sb-boosted discharge hollow cathode lamp (BDHCL; Photron PTY Ltd., Victoria, Australia), operated at 15–20 mA.

Sampling and Pretreatment of Samples

Agricultural soil samples were collected from 5 sites at Puchuncaví Valley, located in Valparaiso region, Chile. This Valley is impacted by the industrial complex "Las Ventanas," where both a smelter and an electro refinery plant of copper ore, as well as a coal-fired thermoelectric plant, are located. Approximately 5 kg portions of soils were taken to a depth of 0–20 cm from each site (composite samples from different

points from ca 1 ha) and were placed in plastic bags. Soils were air-dried and sieved to 2 mm. The <2 mm fractions were stored in polyethylene bottles in a desiccator until analysis.

Analysis of Soil Samples

The presence of iron was determined in the digested soils by flame atomic absorption spectroscopy. Organic matter was determined by dichromate oxidation followed by potentiometric titration of excess dichromate with Fe(II). The pH values of soils were measured in a 1:2 suspension (soil weight:water volume), using a glass electrode. In the same suspension, redox potential values were measured using Pt and calomel electrodes.

Single Extraction Procedure and Experiments with Spiked Soils

A 1.0 g amount of La Greda soil was weighed accurately (in triplicate) into 50 mL Erlenmeyer vessels, and the extracting solution then was added (10 mL H_2O or 0.05M EDTA, pH 7.0; 20 mL 0.25M H_2SO_4; 0.3M H_3PO_4; or 0.2M oxalic acid/0.2M di-ammonium oxalate monohydrate). The vessel was sealed with Parafilm® and shaken at 150 rpm, at room temperature (horizontal shaker, Junior orbit shaker; Labline Instruments, Melrose Park, IL). Shaking times for extraction of soils with water and EDTA were 24 and 1 h, respectively, and 2 h for extraction by H_2SO_4, H_3PO_4, and oxalic acid /di-ammonium oxalate monohydrate. After extraction, the mixture was centrifuged at 4000 rpm (Kubota 1720, Kubota Corp., Tokyo, Japan) at 10°C, until a clear solution was obtained (30 min) and the supernatant was collected for analysis.

The extraction procedures were also performed with soils previously spiked with Sb(III) and Sb(V) at 100 μg/kg each. For spiking, an aliquot of Sb potassium tartrate and potassium pyroantimonate standard solutions (0.2 mL 500 μg/L) was added to 1.0 g La Greda soil, together with the extractant solution. To evaluate the effect of ascorbic acid on the stability of Sb species during the extraction process, this reagent was added at different concentrations (0.5–2%, m/v) to 0.05M EDTA, pH 7, and 0.2M oxalic acid/0.2M di-ammonium oxalate. With these solutions, spiked and nonspiked soils were extracted simultaneously, under the same experimental conditions previously described. In order to evaluate the stability of both Sb species in the different extractant solutions and to determine the effect of soil matrix, simulated extraction experiments were also performed without soil, under similar conditions, with extractant solutions each spiked with Sb(III) and Sb(V) at 10 μg/L.

Sequential Extraction Procedure

The proposed sequential extraction procedure allows evaluation of Sb in 3 steps: (*1*) available under complexing and moderately reducible conditions; (*2*) extractable in reducible conditions (i.e., moderately mobile) associated with hydrous iron and aluminum oxide compounds; (*3*) residual fraction of extremely low mobility and unlikely to be mobilized at short-term in environmental conditions. The protocol was as follows: 1.0 g of dried soil was accurately weighed (in triplicate) into 50 mL cleaned Erlenmeyer vessels.

In the first step, 10 mL 0.05M EDTA + 0.5% (m/v) ascorbic acid, pH 7.0, was added. The vessel was sealed and the mixture was shaken for 1 h and centrifuged under the conditions previously described. In an aliquot of the supernatant solution, Sb(III) was immediately determined by HG–AFS, under optimized conditions (23). The remaining solution was conserved at 4°C to determine the total Sb concentration. The solid residue 1 was washed with 25 mL saturated NaCl and then resuspended and centrifuged, and the supernatant was discarded.

In the second step, the residue was treated with 20 mL 0.2M oxalic acid/0.2M di-ammonium oxalate + 1.5% (m/v) ascorbic acid and quantitatively transferred to the vessel. In this step, the vessel was shaken for 2 h at room temperature and the mixture was then submitted to the same procedure as the first step. Residue 2 was quantitatively transferred to the PTFE vessel of the high-pressure digestion system and 6 mL concentrated HNO_3 + 8 mL concentrated HCl + 5 mL concentrated HF were added. The vessel was covered and left overnight at room temperature. The system was closed and heated at 170°C for 3 h (controlled heating block, Brainchild, BTC 7020 Model). After cooling, 0.3 g solid H_3BO_3 was added, and the mixture was heated in an open system for 2 h to eliminate excess HF. The soil solution was then filtered and diluted to 50 mL with deionized water. Two blank solutions were prepared simultaneously in the same way. In this last extract soil, only total Sb was determined by HG–AFS under optimum conditions (22). This fractionation scheme was applied to 5 different soils collected from Puchuncaví Valley, impacted by both a smelter and an electro refinery plant of copper ore, as well as a coal-fired thermoelectric power plant.

Redox Speciation and Total Sb Determination in Soil Extracts

The methodology to determine total Sb in soils and the optimization of the redox speciation of Sb in soil extracts by HG–AFS were described previously (22, 23). Briefly, the redox speciation of Sb was carried out in 2 steps. First, Sb(III) was selectively determined in citric acid–HCl medium by standard additions under optimum conditions. The standard addition method was used, considering the matrix effect as previously described (23). To determine total Sb in the soil extracts, a second aliquot of variable volume was treated with KI + ascorbic acid and concentrated HCl. The mixture was held for 30 min at room temperature to prereduce Sb(V) to Sb(III), and then total Sb was determined by a simple calibration. No matrix effect was observed in the total Sb determination by HG–AFS under these conditions (23). The Sb(V) concentration was obtained as the difference between both determinations. To determine total Sb in extracts from step 3, the prereduction of Sb(V) to Sb(III) was accomplished in the same way as previously described, but the mixture was heated at 50°C for 16 h for sample treatment with HF (22, 24).

Results and Discussion

Different reagents have been proposed for the single extraction of different metals and some metalloids (e.g., As and Se) from soil along with a wide variety of protocols and reagents for its sequential extraction (19–21). In this work, the extractant solutions were selected to give environmental information about the availability and association of Sb redox species in soils while evaluating the stability of these species in the extraction processes. In the single extraction, the extractant solutions used were water for the soluble fraction of elements from soils and sediments (25); EDTA for the plant-available fraction (this extractant has been recommended by the "Measurement and Testing Program" of the European Community BCR; 26); diluted sulfuric acid for the As associated with Ca and/or carbonates from soils (20); diluted H_3PO_4 for the speciation of As in soils and sediments (19); and the oxalic acid/di-ammonium oxalate mixture for the trace elements associated with the relatively immobile Fe and Al compounds (the moderately reducible phase; 27).

Recovery of Sb(III) and Sb(V) Species in Simulated Extraction Procedures

To study the stability of Sb(III) and Sb(V) in the extraction solutions, simulated extraction procedures (without soil) were carried out to determine the recoveries of both Sb redox species in the synthetic extracts obtained. Results are presented in Table 1. During the simulated aqueous extraction process, Sb(III) was oxidized to Sb(V). These results are in agreement with those reported of Krachler and Emons (7), who found that Sb(III) aqueous standard solutions with low Sb concentrations were oxidized to Sb(V) within a few hours. The recovery of total Sb was not quantitative from water extracts because of the Sb(III) hydrolysis reaction at neutral pH in this aqueous media (28). However, in the other extractant solutions the total Sb was quantitatively recovered, except for partial oxidation of Sb(III) to Sb(V) occurring in the EDTA, H_2SO_4, and H_3PO_4 media; recoveries of Sb(III) ranged from 27 to 44%. Moreover, EDTA stimulated the complexation of Sb(III) and Sb(V) (14, 29) and partially avoided the oxidation of Sb(III) to Sb(V). Furthermore, in diluted H_3PO_4, Sb(III) was less oxidized to Sb(V). This fact is in accordance with the Eh-pH behavior of Sb under acid conditions (28). The only extractant solution in which quantitative recovery for Sb species occurred was oxalic acid–oxalate medium. Sb(III) was not oxidized to Sb(V) in this medium because of its reducing character and probable stabilization of both Sb species by complexation reaction with oxalate (30).

In light of the Sb(III) instability in the other extractant solutions, the capacity of ascorbic acid to stabilize Sb(III) was further investigated. This reagent is mostly used to prepare Sb(III) standard solutions and to prevent its oxidation during storage. In this study, 0.5% (m/v) ascorbic acid was added to each extractant solution and the simulated extraction processes were performed under the same experimental conditions. Table 1 shows that the presence of ascorbic acid prevented oxidation of Sb(III) in all media, except that Sb(III) was partially oxidized to Sb(V) in water. The long period of extraction (24 h) allowed this oxidation reaction (7, 8). On the other hand, the recovery of total Sb was not modified by the presence of ascorbic acid.

Recovery of Sb(III) and Sb(V) from Spiked Soils

The goal of spiking experiments was to evaluate whether oxidation, reduction, or sorption of the Sb redox species would occur if different compounds were present in the soil matrix during soil extraction. Sb(III) and Sb(V) species were determined in soil extracts obtained from an spiked agricultural soil. Figure 1 shows that the recovery of Sb(III) is dependent on the extractant solution composition. In water extracts, the total Sb recovery was only 50% and the spiked Sb(V) was nearly 100%, which indicated that oxidation of the spiked Sb(III) to Sb(V) did not occur. However, only 6% of the spiked Sb(III) was recovered, showing that this species was sorbed and/or hydrolyzed during the extraction process. This result was consistent with the fact that 96% of added

Table 1. Recovery of Sb(III) and Sb(V) (mean ± standard deviation; *n* = 4) from different extractant solutions with and without ascorbic acid, after simulation of soil extraction procedure (without soil)

	Recovery, %					
	Without ascorbic acid			With 0.5% ascorbic acid, m/v		
Extractant solution	Sb(III)	Sb(V)	Total Sb	Sb(III)	Sb(V)	Total Sb
Water	ND[a]	169 ± 20	85 ± 10	31 ± 1	143 ± 13	87 ± 7
0.05M EDTA pH 7	27 ± 1	173 ± 12	100 ± 1	104 ± 3	102 ± 6	103 ± 3
0.25M H_2SO_4	28 ± 3	165 ± 12	97 ± 1	94 ± 3	99 ± 10	97 ± 6
0.3M H_3PO_4	44 ± 8	161 ± 9	103 ± 1	100 ± 4	95 ± 1	98 ± 1
0.2M $H_2C_2O_4$/0.2M $(NH_4)_2C_2O_4$	104 ± 9	99 ± 5	102 ± 5	98 ± 2	92 ± 5	95 ± 3

[a] ND = Nondetected (LOD Sb(III) 0.017 μg/L; recovery < 0.2%).

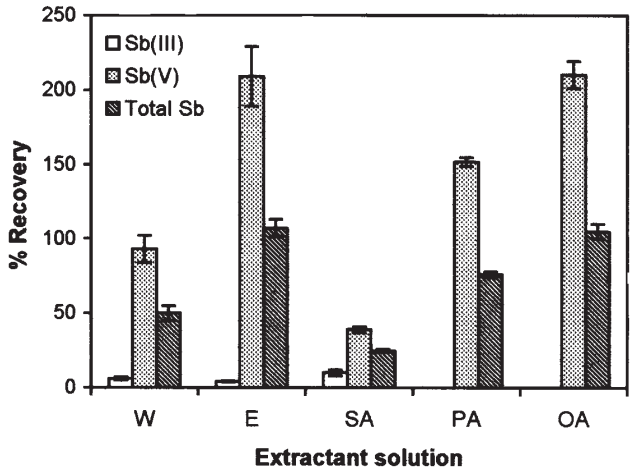

Figure 1. Recovery of Sb(III), Sb(V), and total Sb from agricultural soils spiked with both Sb species (100 μg/kg), extracted by water (W); 0.05M EDTA, pH 7 (E); 0.25M H_2SO_4 (SA); 0.3M H_3PO_4 (PA); and 0.2M oxalic acid/0.2M di-ammonium oxalate monohydrate (OA). Values presented as means ± standard deviation; *n* = 4.

Sb(III) was sorbed after 5 min (13). Binding or reaction sites in soil matrix are responsible for the low recovery of this species. It has been described that Sb(III) is easily adsorbed by Mn, Fe, and Al oxides and the humic acid present in soils (17, 18). Although the percentage of Fe and organic matter in the agricultural soil studies (Table 2) can be considered normal for agricultural-mineral soil (31), its presence explains the observed sorption of Sb(III) by the soil matrix.

In EDTA extracts, the total Sb spiked was quantitatively recovered as Sb(V), demonstrating that in this medium all spiked Sb(III) was oxidized and not sorbed in the soil matrix (Figure 1). Although it has been described that Sb(III) and Sb(V) reacts with carboxylic acids, such as tartaric and EDTA, and form soluble complexes (13, 14, 29), these reactions cannot inhibit the Sb(III) oxidation. The conditional complexation constants for Sb(III) and Sb(V) with EDTA could be similar, because the conditional potential of Sb(V)/Sb(III) couple was not modified by this reagent; therefore, the presence of EDTA, pH 7, is not sufficient to prevent the Sb(III) oxidation by oxygen or other species present in the soil extract or in the soil matrix.

These results are not in accordance with the previous studies performed with 0.05M EDTA, pH 7 (13), where adsorption of added Sb(III) to the soil matrix occurred rather than its oxidation to Sb(V). The difference can be related to the different composition of soils used in both studies; the organic matter content in soil used by Lintschinger (13) was 4 times higher than that in La Greda soil.

In the extraction process with sulfuric acid, the recoveries of Sb(III) and Sb(V) were only 10 and 40%, respectively (Figure 1), indicating that Sb(III) and Sb(V) species were sorbed to soil; as in sulfuric acid medium, the solution pH is low, and the different components of soil, e.g., hydrous oxides and organic matter, have a cationic character (32). Instead, Sb(III) and Sb(V) species, even at pH <1, are present in the neutral and anionic form, respectively (28), so that both species can be sorbed by the different components of soil. The difference in the recoveries of Sb species can be due to the lower affinity between $Sb(OH)_6^-$ and the organic matter, attributed to the stability and structure of the hexa-hydroxy species (18). A different recovery profile was obtained in the extraction process with diluted H_3PO_4. In this case, the recovery of spiked total Sb was 76%, corresponding to 152% of Sb(V). Therefore, Sb(III) was oxidized to Sb(V) and this last species was partially sorbed to soil.

In the oxalic acid extracts, the oxalate medium prevented the sorption of Sb species and allowed the reducing dissolution of Fe and Al oxyhydroxides compounds (33), which are excellent scavengers of metals and metalloids such as As and Sb (12, 27, 34). However, this result was in contrast to results from the simulated extraction process, where Sb(V) was the only species found in the soil extracts.

Table 2. Some chemical characteristics and total antimony extracted by 0.05M EDTA, pH 7, with and without 0.5% (m/v) ascorbic acid, from agricultural Chilean soils[a]

	Chemical characteristics				Total antimony extracted, mg/kg		
Soil	Fe, %	Organic matter, %	pH	pε	Without ascorbic acid (a)	+ 0.5% (m/v) ascorbic acid (b)	Ratio (b)/(a)
La Greda	3.7 ± 0.1	1.2 ± 0.1	6.7	9.3	0.34 ± 0.01	0.49 ± 0.03	1.4
Maitenes	4.7 ± 0.1	1.5 ± 0.1	7.4	9.0	0.31 ± 0.01	0.38 ± 0.01	1.2
Campiche	4.0 ± 0.2	2.6 ± 0.1	7.9	9.4	1.1 ± 0.1	1.9 ± 0.2	1.7
Puchuncaví	3.8 ± 0.1	3.1 ± 0.2	7.3	9.0	0.20 ± 0.01	0.61 ± 0.06	3.1
Nogales	4.1 ± 0.1	2.6 ± 0.1	7.3	9.1	0.020 ± 0.001	0.061 ± 0.005	3.1

[a] Values expressed as mean ± standard deviation; *n* = 4.

Ascorbic Acid as Stabilizing Agent of Sb Species During Extraction

Because of the convenience of disposable extraction procedures used to assess the Sb redox species in the available fraction (EDTA) and relatively immobile Fe and Al compounds (oxalic acid/di-ammonium oxalate), and owing to its significance in the environment, we studied the effect of the ascorbic acid present in these extractant solutions on both Sb species. These experiments demonstrated the effect of ascorbic acid on the extraction efficiency of total Sb and on the stabilization of Sb(III) by these extractant solutions. Figure 2 shows the results obtained in the extraction with EDTA + ascorbic acid. The oxidation of added Sb(III) was certainly avoided by 0.5% (m/v) ascorbic acid; however, the recovery of spiked Sb(III) was 15%, and the sorption of spiked Sb(III) to the soils was not inhibited, which is explained by the sorption process of the anionic Sb(III)–EDTA complex to the soil matrix (14). These results are in agreement with those reported by others, that the soluble complex formed with EDTA cannot retard the sorption of the Sb(III) with soil particles (13). Thanabalasingam and Pickering (17) reported that the maximal Sb(III) adsorption on the hydrous oxides of Mn, Fe, and Al occur at pH 7 to 8 (17). Moreover, Sb(III) and Sb(V) are adsorbed by humic acid, whereas only limited uptake has been observed for Sb(V)(18). Furthermore, as shown in Figure 2A (right axis), the presence of ascorbic acid increases the extraction efficiency of total Sb from this soil.

Table 2 shows that total Sb extraction efficiency was significantly increased ($P = 0.95$) by the presence of ascorbic acid. It has been reported that in ascorbic acid medium, partial dissolution of Fe compounds can occur (33), decreasing the possibility of adsorption and increasing extraction efficiency. Though ascorbic acid avoids the oxidation of Sb(III) extracted from soils by EDTA, the use of this mixture (0.05M EDTA + 0.5% ascorbic acid, m/v) as extractant solution to define the Sb plant available fraction could overestimate this fraction.

Figure 2B presents results obtained in the extraction of spiked soils by acid oxalic/oxalate + ascorbic acid. This extractant solution, containing different concentrations of ascorbic acid, permitted the quantitative recovery of total Sb. Oxalic/oxalate solutions prevent the Sb adsorption to hydrous oxides compounds of soils (13, 27). On the other hand, the extraction of total Sb from nonspiked soil was not modified by the presence of ascorbic acid in the extractant solution (Figure 2B, right axis). There was no significant difference ($P = 0.95$) between the total Sb extracted with or without this reagent. Under the experimental conditions used, the presence of ascorbic acid, even at a concentration as high as 2% (m/v), could not avoid the oxidation of added Sb(III) to Sb(V), and only 75% Sb(III) was recovered by this solution.

Fractionation and Redox Speciation of Sb in soils

An environmental risk linked to the presence of one element in soils depends, to a great extent, on the chemical form and its respective mobility. There are no direct methods for speciation of Sb in soils, and little information is available about its fractionation in this matrix (13, 16). On the basis of results obtained in the single extraction procedures, a simplified sequential extraction was proposed to perform the fractionation and redox speciation of Sb in soils. The total Sb concentrations (mg/kg) determined in each fraction of 5 soils are given in Table 3. The Sb percentages extracted in each fraction, relative to the total Sb concentration in soils (previously determined by HG–AFS), are also included. The recoveries of total Sb in the sequential extraction procedure were in agreement with the total concentrations of Sb in soils (91–100%). The Sb available fraction, extracted by EDTA + ascorbic acid, ranged between 3.4 and 18% of the total Sb in soils.

These results show that the mobility of Sb in these soils was low, except for Campiche soil where this fraction reached 18%. The fraction of Sb extracted by EDTA could come from organic and metals compounds containing Sb, which are dissolved by formation of strong chelates between metallic ions with this carboxylic acid. Furthermore, EDTA forms soluble complexes with both Sb species (14, 29). On the other hand, total Sb associated with the relatively immobile Fe and Al

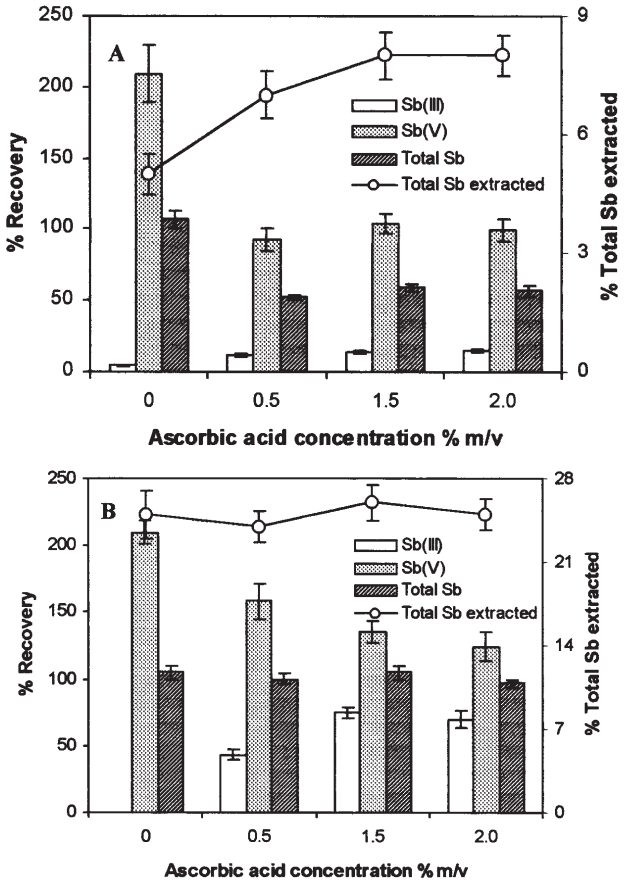

Figure 2. Effect of different concentrations of ascorbic acid in (A) 0.05M EDTA, pH 7 and (B) 0.2M $H_2C_2O_4$ + 0.2M di-ammonium oxalate monohydrate extractant solutions, on the recovery of Sb(III), Sb(V), and total Sb from La Greda agricultural soil spiked with both Sb species (100 μg/kg; left axis); and percentage of total Sb extracted from nonspiked soil (right axis). Values presented as means ± standard deviation; $n = 4$.

Table 3. Total antimony concentration (mg/kg) obtained in fractionation of agricultural Chilean soils and percentage relative to total Sb in soils[a]

		Fractionation of antimony			
Soil	Total Sb	Available	Reducible	Residual	Σ 1-3
La Greda	6.7 ± 0.4	0.44 ± 0.03 (6.6)	0.93 ± 0.08 (14)	4.7 ± 0.2 (70)	6.1 (91)
Maitenes	6.4 ± 0.5	0.40 ± 0.01 (6.3)	1.1 ± 0.1 (17)	4.4 ± 0.3 (69)	5.9 (92)
Campiche	12 ± 1	2.1 ± 0.1 (18)	1.7 ± 0.1 (15)	7.4 ± 0.3 (62)	11 (92)
Puchuncaví	5.5 ± 0.1	0.66 ± 0.01 (12)	0.53 ± 0.02 (9.5)	3.9 ± 0.1 (71)	5.1 (93)
Nogales	1.8 ± 0.2	0.065 ± 0.005 (3.4)	0.17 ± 0.01 (9.3)	1.6 ± 0.1 (89)	1.8 (100)

[a] Values expressed as mean ± standard deviation; $n = 4$.

compounds, i.e., in the reducible fraction (second step), extracted with oxalic acid and ammonium oxalate solution, represent between 9.3 and 17% of total Sb. In all analyzed soils, Sb was mainly associated to the residual fraction accounted for 62–89% of total content. Sb present in these soils remains as an insoluble and unreactive silicate compound. Although only a small fraction of the total Sb in these impacted soils is available to plants, these concentrations may be sufficient to increase the Sb concentration in plants grown in these soils. The percentage of Sb of the residual fraction correlated inversely to the total Sb concentration in soils ($P = 0.95$; Figure 3). This shows that an important fraction of Sb that arrives to soil from the industrial complex remains associated with the available and/or reducible fraction.

From the redox speciation, Sb(V) was the predominant species in the available the reducible fractions (steps 1 and 2, respectively; Table 4); the species was predicted on the basis of the pε and pH parameters determined in these soils (Table 2) and the respective pε–pH diagram (28). In the first fraction, with the exception of Nogales soil, only 1–4% of total Sb extracted corresponded to Sb(III); instead in the second fraction, the percentage of this species was higher, reaching 5–11%. These results showed that Sb(III) determined in these soils has low mobility and availability and is more associated with the relatively immobile Fe and Al compounds than in the available fraction.

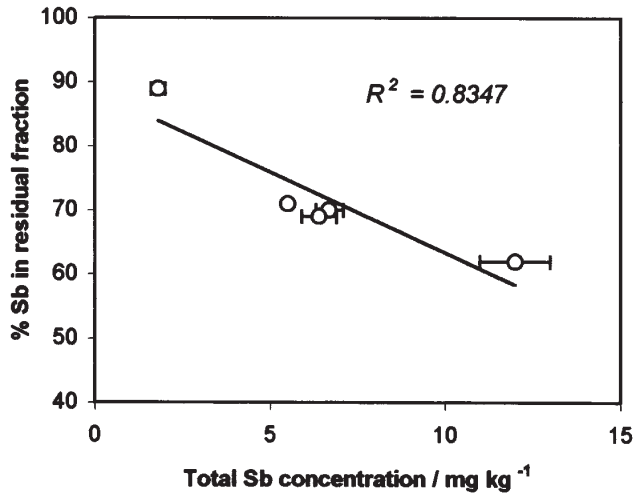

Figure 3. Relationship between percentage of total Sb in residual fraction and total concentration present in soils. Values presented as means ± standard deviation, $n = 4$.

Conclusions

Results of present study showed that Sb(III) was stable only in reducing media as oxalate solutions. Instead, in water, EDTA, diluted H_2SO_4, and diluted H_3PO_4, this species was oxidized to Sb(V) during simulated extraction procedures. However, Sb(III) was stabilized by adding ascorbic acid to the extractant solutions, excepting in the extraction process by water. Spiking experiments performed with an agricultural soil demonstrated that, during the extraction process with water and diluted H_2SO_4, the added Sb(III) is sorbed but not oxidized. Instead, the oxidation of added Sb(III) to Sb(V) occurred in EDTA, diluted H_3PO_4 and oxalic acid/oxalate medium. It can be concluded that redox speciation of Sb in these kinds of agricultural soils, with these last 3 solutions,

Table 4. Percentage of Sb(III) and Sb(V) relative to total Sb, extracted in available and reducible (moderately mobile) fractions from agricultural soils[a]

	Available fraction		Reducible fraction	
Soil	Sb(III)	Sb(V)	Sb(III)	Sb(V)
La Greda	4.0 ± 0.2	96 ± 6	10 ± 1	90 ± 9
Maitenes	3.0 ± 0.3	97 ± 3	5 ± 1	95 ± 9
Campiche	1.0 ± 0.1	99 ± 4	11 ± 1	89 ± 6
Puchuncaví	3.0 ± 0.3	97 ± 2	11 ± 2	89 ± 4
Nogales	29 ± 3.0	71 ± 6	21 ± 2	79 ± 6

[a] Results expressed as mean ± standard deviation; $n = 4$.

can produce changes on the original distribution of species, overestimating the Sb(V) concentrations in the soil extracts. The presence of ascorbic acid in EDTA and oxalic acid/oxalate medium quantitative or partially prevents the oxidation of added Sb(III) during the extraction procedure from soils. The use of these extractant solutions, containing ascorbic acid as a stabilizing agent, allows a more accurate determination of the Sb redox species in the soil extracts. In general, the sequential extraction scheme developed in this work is suitable for the fractionation and redox speciation of Sb from soils and can be applied to evaluate the availability and mobility of Sb redox species in agricultural-mineral soils.

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