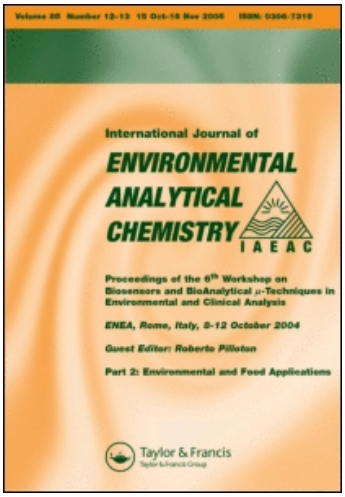


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# Studies on Speciation of Antimony in Soil Contaminated by Industrial Activity

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# STUDIES ON SPECIATION OF ANTIMONY IN SOIL CONTAMINATED BY INDUSTRIAL ACTIVITY

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Antimony is a toxic trace element of growing environmental interest due to its increased anthropogenic input into the environment. Very little is known about the chemical and biological behavior of antimony compounds in soils and sediments. Three soil samples with substantially elevated Sb concentrations (area contaminated by extensive industrial use of Sb compounds), and a soil standard reference material have been analyzed by using conventional single and sequential extraction procedures in order to get information about the chemical forms and availability of Sb in the soil. The antimony concentrations in the extraction solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS). Additionally, Sb(III) and Sb(V) were determined in some extracts by using high-performance liquid chromatography coupled on-line to the ICP-MS (HPLC-ICP-MS).

The total Sb concentrations were in the upper mg $kg^{-1}$ range, but only small amounts were found to be easily available from the soils. The main antimony was bound to relatively immobile Fe and Al oxides. Substantial amounts were also found in the alkaline and EDTA extracts, indicating association of Sb to organic substances. Although contamination was caused by the production of Sb(III) compounds, Sb(III) was not dedected in any of the extracts. The behavior of Sb(III) (as Sb(III) tartrate and $Sb_2O_3$) and Sb(V) (as $Sb(OH)_6^-$) added to the soil samples was investigated in detail.

*Keywords:* Antimony; Sb(III); Sb(V); speciation; HPLC-ICP-MS; soil

## INTRODUCTION

Antimony is a widely distributed toxic trace element, found in the lithosphere mainly associated with arsenic as sulfides or oxides. In general, the natural occurrence of Sb in soils is low (<1mg $kg^{-1}$).[1] Considerably elevated antimony concentrations, which might pose a toxic hazard, were found in regions with sub-

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stantial antimony deposits or in areas contaminated by anthropogenic activity, e.g. up to 1% Sb was found in surface sediments near a copper smelter and concentrations up to 260 mg Sb $kg^{-1}$ were found in soils taken from an area close to lead smelting operations.[2,3] Maximum Sb concentrations in surface soils and plants close to an antimony smelter were found to be 1489 mg kg-1 and 336 mg kg-1, respectively.[4] Antimony can also enter the environment as a pollutant from extensive industrial use of Sb compounds (production of flame-retardant, batteries, antiparasitic drugs, etc.).[5]

Hardly anything is known about chemical forms, transformations, and biological effects of antimony compounds in soils, sediments and the affiliated aquatic environment. Selective extraction and spiking experiments have indicated, that in sediments Sb tends to be associated with immobile hydrous oxides of Mn, Fe, and Al,[2,6,7] and can be adsorbed to humic acid.[8] Factors influencing Sb sorption include substrate surface charge, chemical form of Sb and surface interactions. Sb(III) as $Sb(OH)_3$ and Sb tartrate is sorbed avidly to MnOOH, $Al(OH)_3$, and FeOOH. Both species are also adsorbed by humic acid in accordance with Langmuir type isotherms, whereas only limited uptake was observed for Sb(V) as $Sb(OH)_6^-$. In soil contaminated with $Sb_2O_3$, due to antimony smelting operations, Sb was found largely in immobile forms only extracted from the soil with *Aqua regia*.[9] Since Sb(III) compounds are more toxic than Sb(V) ones and are listed as possible cancerogenic substances, analyses of antimony in environmental samples demand the discrimination between the two oxidation states in order to assess the toxic hazard.[10,11]

The aim of the present work is the speciation of antimony in soil samples polluted by a factory producing antimony potassium tartrate (tartar emetic) and antimony potassium citrate for approximately two centuries. The factory was located in the urban area of Marktredwitz, Bavaria (Germany). Antimony compounds were released from the factory into the closed by river with the waste water and were deposited onto the soil via periodically flooding of the area in spring. The geographical distribution of the Sb contamination was estimated during a big project of the Bavarian Government and results of this study will be published elsewhere.[12] Samples for the present work were taken from three locations with highest contamination. Due to the similar history of the contamination within these areas a rather small number of samples were chosen for the benefit of a larger variety in speciation experiments. This should provide primary information which can than be applied for a large number of samples. Established extraction procedures are used for evaluation of the specific phases of the soil in which the antimony compounds are prevalent and to estimate availability of the species.[13,14,15] Sb(III) and Sb(V) are determined in extracts, assumed to be gentle enough to preserve the oxidation state, by using HPLC-ICP-MS.[16] The behav-

ior of Sb(III), which was most probably the primary pollutant, and Sb(V) added to the soils is investigated. As a control for reproducibility of the extraction and determination procedures and for comparison, a soil standard reference material (BCR 143R) is analyzed simultaneously.

## EXPERIMENTAL

### Chemicals and Reagents

Standard stock solutions for antimony(III) (100 mg Sb $L^{-1}$) and antimony(V) (100 mg Sb $L^{-1}$) were prepared by dissolving the appropriate amount of potassium antimonyl tartrate trihydrate (Aldrich, A.C.S) and of potassium hexahydroxyantimonate (Fluka, p.a.) in water. Standard solutions of lower concentrations were prepared daily by appropriate dilution with water. A standard stock solution of $Sb(OH)_3$ was prepared daily by making a saturated solution of $Sb_2O_3$ (Aldrich, 99.999%) in water. The solution was centrifuged and the supernatant solution was diluted with water. The acute Sb concentration of this solution was determined by ICP-MS.

TABLE I Experimental parameters for the determination of Sb(III) and Sb(V) by using HPLC-ICP-MS

| *HPLC* | |
|---|---|
| Column: | Hamilton PRP-X100, 250 × 4 mm, 10 µm |
| Mobile phase: | 20 mM EDTA, 2 mM potassium hydrogen phthalate (KHP), pH 4.6 adjusted with $NH_3$ |
| Flow rate: | 1.5 ml $min.^{-1}$ |
| Injection volume: | 100 µl |
| Detection: | ICP-MS mass 121 |
| ICP-MS | |
| Forward power: | 1200 W |
| Plasma gas: | 15.06 l $min.^{-1}$ |
| Nebulizer gas: | 0.75 l $min.^{-1}$ |
| Auxilliary gas: | 0.78 l $min.^{-1}$ (Ar containing 6% hydrogen) |

All chemicals used for preparation of mobile phase and extraction solutions were of analytical-reagent grade or higher purity. The composition of the mobile

phase and extraction solutions are listed in Table I and Table II, respectively. The solutions were prepared by dissolving the listed compounds in water. The required pH values were adjusted with the acids or bases as stated in Table I and Table II. *Aqua regia* was prepared by mixing the appropriate amount of hydrochloric acid (Merck, Suprapur®) and nitric acid, purified by subboiling distillation. Water was first purified by normal deionization and then by a special cardridge deionization unit (Milli-Q Water Purification System).

TABLE II Experimental parameters for the singel and sequential extractions of the soil samples

| | *Single extractions* | *Ref.* |
|---|---|---|
| | $H_2O$; soil:extractant 1:10, 24 h | 13 |
| | $NH_4NO_3$ 1 M; soil:extractant 1:2.5, 2 h | 14 |
| | EDTA ($NH_4^+$) 0.05 M pH 7.0; soil:extractant 1:10, 1h | 15 |
| | $C_2H_2O_4$ 0.1M + $(NH_4)_2C_2O_4$ 0.175 M; soil:extractant 1:10, 2 h | 6 |
| | $NH_4H_2PO_4$ 0.5 M; soil:extractant 1:10, 2 h | |
| | HCl 0.1 M; soil: extractant 1:10, 2h | |
| | KOH 0.1 M; soil:extractant 1:10, 2 h and 24 h | |
| | *Sequential extraction* | |
| Step 1 | $CH_3COOH$ 0.11M soil:extractant 1:40, 5 h, centrifuged and the supernatant used for analysis; residue washed with 10 ml $H_2O$ | 15 |
| Step 2 | $NH_2OH.HCl$ 0.1 M pH 2 ($HNO_3$) residue from step 1 + 40 ml extractant, 16 h, centrifuged and the supernatant used for analysis; residue washed with 10 ml $H_2O$ | |
| Step 3 | $H_2O_2$, 8.8 M residue from step 2 treated twice with 10 ml $H_2O_2$ for 1 h at 85°C refluxing and reducing to a few ml; residue + 40 ml $CH_3COO^-NH_4^+$ pH 5 ($CH_3COOH$), 16 h,centrifuged and the supernatant used for analysis | |



## Instrumentation and Procedures

### *HPLC-ICP-MS*

The high-performance liquid chromatographic system consisted of a pump (Beckman 114 Solvent Delivery Module) with a Rheodyne six-port injector valve equipped with a 100 µl sample loop, and an analytical column. A guard column filled with the same stationary phase protected the analytical column. An inductively-coupled plasma mass spectrometer (Elan 5000, Perkin Elmer) was used as chromatographic detector. The HPLC system was connected directly to the nebulizer (Meinhard with Zyklon spray chamber) of the ICP-MS with a short piece of Teflon tubing. The mobile phase was spiked with Rh (10 µg $L^{-1}$) as internal standard to correct for instrumental drift. High concentrated EDTA in the

mobile phase has to be present as ammonium salt instaed of the usually used sodium or potassium salt to prevent blockage of cones of the ICP-MS. Chromatographic and instrumental parameters are summarized in Table I. Masses 103 and 121 were monitored in the graphic mode of the instrument. Data from the ICP-MS were processed with special chromatographic software, that offers routine options for the treatment of chromatographic data, such as data smoothing and trapezian or Simpson integration.[17] Quantification was based either on external calibration curves or on an internal standard addition method. Peak areas were standardized by using the signal for the 10 $\mu g\ L^{-1}$ Rh internal standard.

Total antimony concentrations in aqueous solutions were determined also with ICP-MS. Instrumental parameters of the ICP-MS were the same as used for HPLC-ICP-MS measurements. Prior to analysis standard and sample solutions were spiked with 100 $\mu g\ L^{-1}$ Rh as internal standard and nitric acid was added to give a final concentration of 1%. Extracts containing KOH were not acidified to avoid precipitation of alkaline soluble compounds.



## Sampling and Sample Pretreatment

The contaminated area is located in a housing estate of Marktredwitz. Samples were collected from three residential properties, which were found to be highly contaminated during a previous project; details about sampling and geographical distribution of the Sb contamination will be published elsewhere.[12] Samples were taken in summer by removing the sod (10 cm) in a depth of 10 to 30 and 30 to 60 cm by using a special sampling device (N-MIN drill). From each sampling spot approximately 3 kg soil were immediately homogenized and 400 ml of soil were transferred to a brown glass bottle, the bottle was sealed and transported to the laboratory on the same day. Samples were stored at 4°C.

Aliquots of the samples were air-dried at room temperature and sieved through a 2 mm stainless steel sieve to remove large organic particles and rocks. Approximately 150 ml of these samples were additionally homogenized by using a ceramic mortar and pestle. For speciation of Sb(III) and Sb(V) samples were also used without any sample pretreatment. The standard reference materials BCR 143R (sludge amended soil), BCR 277 (esturian sediment) and BCR 280 (lake sediment) were used without any preparation.

## *Aqua Regia* Extract for the "Total" Sb Concentrations

Aliquots of the dry soil and sediment samples (1000 mg) were accurately weighed into 100 ml round bottom flasks and a few ml of water were added to make a slurry. Nitric acid (2.5 ml) and hydrochloric acid (7.5 ml) were added slowly to avoid losses due to violent reaction. The flasks were shaken carefully to obtain a proper mixture, stored over night at room temperature and then

refluxed for 2 h. After reaching room temperature, the condenser was rinsed with water and 1 ml of HF acid was added to the extraction solution, which was found to be necessary in order to obtain accurate results for standard reference materials. The solution was filtered (Whatman DIN) and transferred to 100 ml volumetric flask. The residual in the filter was washed with 10% nitric acid to give a volume close to 100 ml and the volumetric flasks were then filled up to the 100 ml mark with water. Three extractions were carried out for each sample.

### Extraction Procedures

Aliqouts of the dry and wet soil samples were accurately weight into 50 ml acid cleaned polypropylene vessels. The extraction solutions were added and the vessels were shaked at ambient room temparature on a horizontal shaker (Edmund Bühler SM). Vessles containing wet samples (used for speciation of Sb(III) and Sb(V)) were purged with Ar prior to shaking. Experimental details are summarized in Table II. After extraction sample solutions were first centrifuged with 3500 rev./min. (Hettich Universal) and aliqots were then again centrifuged with 17.000 rev./min. to obtain clear solutions. Prior to HPLC analyses solutions were filtered through a 0.45 μm filter (Sartorius). The sequential extraction was performed according to the method described by Ure et al.;[15] parameters are listed in Table II. Each extraction was carried out in triplicates. Sample blanks were prepared according to the proposed procedures and concentrations of the extracts were corrected by subtracting the corresponding blank concentrations.



### pH Measurement and CN-Analyses

The pH of the soil samples was determined in a 1 M KCl solution with a ratio between soil and solution of 1:2.5 by using a pH meter (WTW pH 535).

The total carbon and nitrogen content of the soil samples were determined by using a Carlo Erba Element Analyzer Mod. 1106.

## RESULTS AND DISCUSSION

### Speciation by Chemical Extraction Procedures

#### *"Total" Antimony Concentration*

The Sb concentration of the three soil samples (A, B, C) representing the "total" Sb content were determined after *Aqua regia* treatment. They are listed together

with some physical and chemical parameters of the soils in Table III. Concentrations are in the upper mg $kg^{-1}$ range (usually: < 1mg $kg^{-1}$) showing the extensive pollution of the area. Unfortunately, there is no soil standard reference material with certified or indicative Sb concentrations to evaluate the determination method. However, the procedure using *Aqua regia* treatment was validated by analyzing two sediment standard reference materials with indicative Sb concentrations, BCR 277 (4.0 mg Sb $kg^{-1}$) and BCR 280 (1.4 mg Sb $kg^{-1}$). The concentrations in the *Aqua regia* extracts were found to be 3.68 ± 0.11 mg Sb $kg^{-1}$ (92%) and 1.19 ± 0.07 mg Sb $kg^{-1}$ (85%) for the BCR 277 and the BCR 280, respectively. Although soil is a different matrix than sediment it can be assumed that almost all antimony is extracted from the soil with *Aqua Regia.* The soil standard reference material (BCR 143R sludge amended soil), which was used for comparison in this work, contained also a significantly increased amount of antimony (3.5 ± 0.3 mg Sb $kg^{-1}$) which might be due to the amending of the sludge.



TABLE III Total antimony concentrations and some physical and chemical parameters of three soil samples from an area contaminated by industrial activity and a soil standard refernce material BCR 143R (sludge amended soil)

| *Sample* | *Depth cm* | *Color* | *pH* | *C %* | *N %* | *Sb mg $kg^{-1}$* |
|---|---|---|---|---|---|---|
| Soil A | 30–60 | brown | 4.6 | 2.51 ± 0.16 | 0.22 ± 0.03 | 118 ± 20 |
| Soil B | 10–30 | brown | 3.5 | 3.10 ± 0.18 | 0.37 ± 0.03 | 73.4 + 2.5 |
| Soil C | 10–30 | black | 4.2 | 4.82 ± 0.20 | 0.27 ± 0.04 | 196 ± 4 |
| BCR 143 R | | brown | 6.7 | 3.10 ± 0.02 | 0.27 ± 0.02 | 3.5 ± 0.3 |

## Functionally Speciation: Availability of Antimony from the Soil

Soil samples were extracted with three procedures, which are commonly used to asses the availability of heavy metals from soils and sediment: the leachability by water, the determination of mobile trace elements in mineral soils by using an ammonium nitrate extraction, both are recommended by the DIN (Deutsches Institut fuer Normung),[13,14] and the plant available fraction by using an EDTA extractant recommended by the "Measurement and Testing Programme" of the European Community (formerly BCR).[15] The extraction parameters are listed in Table II and results are shown in Figure 1A. The recovery rates represent the mean value of three extractions, absolute standard deviations are indicated by error bars. The RSD's for the water and $NH_4NO_3$ extracts, were relatively high

(8%-21%) due to the low recovery for these extractants. For the EDTA solution, RSD's decreased to 3%-5%.

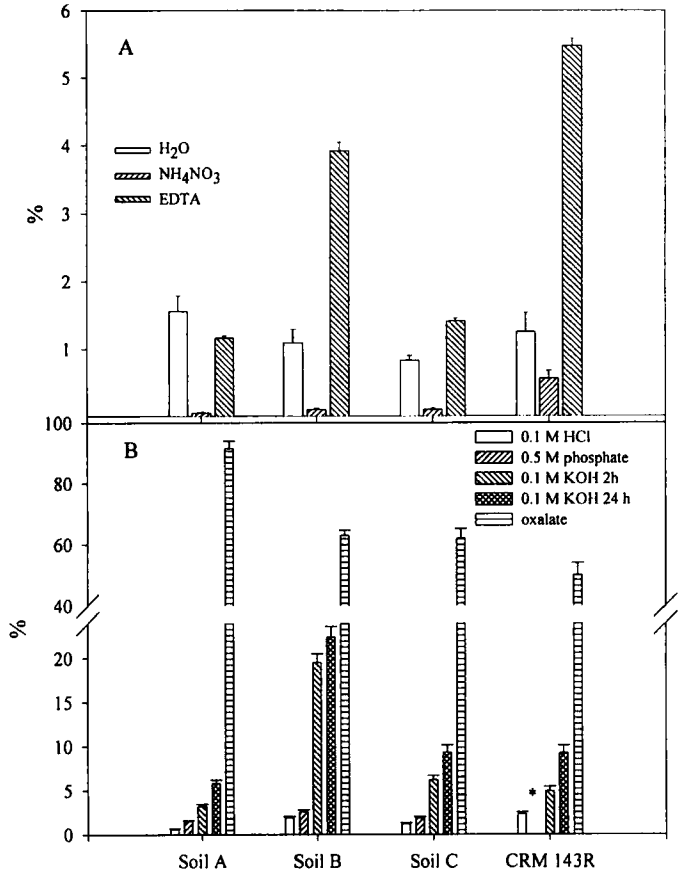


FIGURE 1 Antimony recovery rates from the contaminated soil samples and the soil CRM material using single extraction procedures; **A**: functionally speciation **B**: operationally speciation; experimental parameters see Table II. (* Due to the high Sb concentration of the phosphate blank serious quantification was not possible in this sample)

The Sb concentrations in the 24 h water-leachates were found to be 180 ± 27, 80 ± 15 and 160 ± 13 μg Sb $L^{-1}$ for sample A, B, and C, respectively. Related to the big contamination of the soil samples only small amounts (<2%) were leached with water. Unfortunately, no -data are published in the literature about limiting concentrations of Sb in ground-, drinking- or waste water. However, for arsenic, a chemically similar but more toxic element, 50 μg $L^{-1}$ are tolerated in

drinking water by the WHO.[18] Very low Sb concentrations were found in the ammonium nitrate extracts. In general, this extractant should release metals which are weakly bound electrostaically by ion exchange mechanisms. Because antimony occurs in the soil rather as an anion or non charged species than as a cation the high concentration of ammonium cations did not enhance the release of antimony from the soil. With the EDTA procedure, which is recommended to assess the bioavailable (plant-available) species, significantly increased Sb concentrations were extracted from soil B and the sludge amended standard reference soil BCR143R (Figure 1). EDTA is assumed to extract carbonate-bound and organically-bound fractions of metals by formation of strong chelates. Hence, in soil B and BCR 143R more antimony might be bound to organic matrix. Again, due to the chemical nature of antimony there has to be a different mechanism for the reaction between Sb species and EDTA than complex formation. Though, reactions between antimony compounds, especially Sb(III) ones, with carbonic acids are known. This can increase the availability of Sb from the soil.



## Operationally Speciation: Sb Concentrations in Specific Phases of the Soil

With the extraction methods discussed above, only little amounts of the total Sb of the soil samples were recovered. Hence, samples were extracted with some more single extractions and a sequential procedures (Table II) in order to get more information about the concentration of Sb in specific phases of the soil. Results, mean values of three determinations, are shown in Figure 1B and Figure 2 for the single and sequential extractions, respectively. RSD's were found to be <10%, except for soil C which showed a significant increase in RSD's, up to 22%, for the sequential extractions. This might be caused by a larger inhomogeneity of this sample and the smaller amount of soil used in this procedure.

As described by other authors, in all samples the main amount of antimony was associated with relatively immobile iron and aluminum compounds; i.e. in the moderately reducible phase, extracted with a solution containing oxalate as reductant.[6,2] Hydrous iron, manganese and aluminum oxides are positively charged at the pH values most commonly encountered in soils and strongly adsorb anionic compounds. Although in the literature a strong adsorbtion of Sb to MnOOH is described, the Sb in the present soil samples has obviously more affinity to the Fe and Al oxide than to the manganese oxide phase, which is demonstrated by using acidified hydroxylamine hydrochloride (0.1 M) as reducing reagent.[7] This extractant releases metals from the Mn oxide phase with little attack on the Fe oxide phase and compared to the big amounts extracted with oxalate only limited Sb concentrations were found in the hydroxylamine hydrochloride extracts (Figure 2). An important release of Sb from the positively

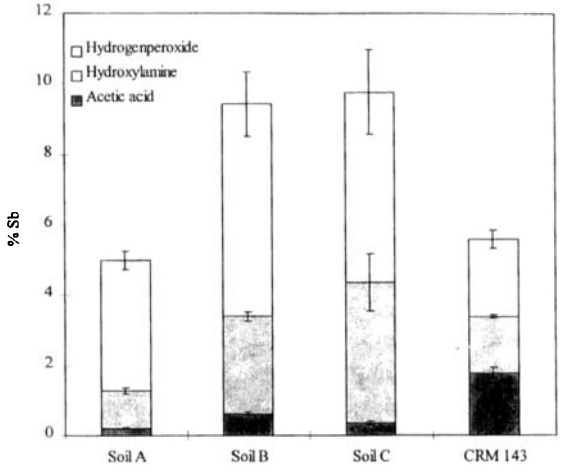


FIGURE 2 Antimony recovery rates from the contaminated soil samples and the soil CRM material using a sequential extraction procedures; experimental parameters see Table II



charged groups of the oxide phases by a competitive exchange with phosphate, present in high concentration, was not observed. The Sb concentrations in a 0.5 M phosphate extract were found to be lower than 2.6% of total Sb for all samples (Figure 1), indicating only small desorption and availability of Sb by anion exchange mechanisms. Significant differences were observed between the different soil samples. In soil A almost all Sb (92%) was found in the oxalate extract, whereas that ones from soil B, C, and the sludge amended soil (CRM 143R) contained only 63%, 62% and 51% of total Sb. This is probably due to a lower content of organic matrix in soil A, which was taken in a depth of 30–60 cm compared to soil B and C which were taken in a depth of 10–30 cm and correlates with the higher EDTA recoveries for organically bound Sb in soil B and CRM 143R (Figure 1A).

As described for arsenic, high amounts of antimony (up to 23%) are also extracted using alkaline conditions (0.1 M KOH) as a result of hydrolysation of organically bound Sb and/or a decrease of the positive charge on the hydrous iron and aluminum oxides, which presumably decreases the sorption of antimony anions.[19] Very little antimony (<0.5%) was found in the acetic acid extracts of the contaminated soils A,B, and C (first step of the sequential extraction), which corresponds to the carbonate phase of the soil (Figure 2). The organic and sulfide phase of the soil, extracted with sodium acetate after oxidation with hydrogen peroxide, contained no significant higher amounts of Sb than the EDTA fraction (Figure 2). Hence, no Sb seems to be present in form of insoluble sulfide compounds.

## Speciation of Sb(III) and Sb(V)

### *Determination of Sb(III) and Sb(V) in Soil Extracts*

The speciation of Sb(III) and Sb(V) was performed with HPLC-ICP-MS described in detail elsewhere.[16] The separation is based on the *in-situ* formation of a Sb(III)-EDTA complex which is separated from the antimonate on an anion exchange HPLC column. A chromatogram of a standard solution containing Sb(III) and Sb(V) (5 $\mu g\ L^{-1}$ each) is shown in Figure 3A. The detection limit of the method ($3\sigma$) was found to be 0.5 $\mu g\ L^{-1}$ for Sb(V) and 0.8$\mu g\ L^{-1}$ for Sb(III). Soil samples were extracted without drying and purged with Ar prior to shaking to avoid possible oxidation during air-drying and extraction. The water leachate, the EDTA, phosphate, acetate, and KOH extracts, which were assumed to be mild enough to preserve the oxidation state, were injected. All solutions contained only antimony(V). When the extracts were spiked with Sb(III) prior to HPLC analyses, recovery rates were close to 100% showing no influence of the soil matrix on the determination method (Figure 3B). Although the contamination originated from the production of Sb(III) compounds its striking that no Sb(III) was found in any of the extracts.



## Spiking Experiments

Spiking experiments were performed by adding a defined amount (30 $\mu g\ Sb\ L^{-1}$) of potassium Sb(III) tartrate, $Sb_2O_3$ or potassium antimonate standard solutions to soil A together with an extractant (water, 0.05 M EDTA, 0.1 M KOH). Samples were shacked and aliquots of the solutions were taken after certain time periods, centrifuged and filtered (0.45 $\mu m$) prior to injecting. Extracts without adding Sb compounds were prepared simultaneously and the recovery rates for the spiked Sb(V) were calculated by subtracting the concentration of these blanks. Results are shown in Figure 4.

It can be seen that Sb(III), as tartrate and dissolved $Sb_2O_3$, was avidly adsorbed to the soil. After approx. 5 min only 4.3% of the added Sb(III) tartrate and 12% of the $Sb_2O_3$ were present in the aqueous phase (Figure 4 A and B). After 10 min no Sb(III) tartrate was found and the recovery of the $Sb_2O_3$ went down to 2% and decreased slowly with increasing time. Oxidation of the added Sb(III) to Sb(V) did not occur, which is shown by a parallel extraction profile for the Sb(V) concentration in the spiked and blank samples. In the presence of EDTA similar results were obtained (Figure 4 C). Although Sb(III) reacts easily with carbonic acids, such as tartrate and EDTA, to form soluble complexes, these compounds are not stable enough to keep the Sb(III) in solution, when they get in contact

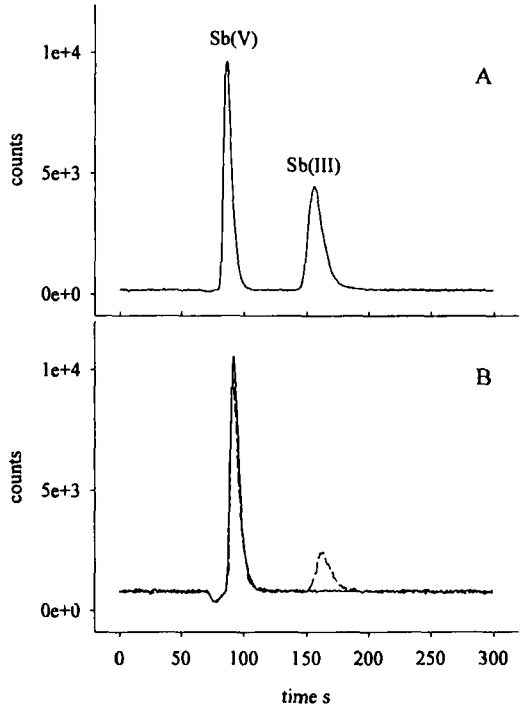


FIGURE 3 Chromatograms of the separation of Sb(III) and Sb(V) using HPLC-ICP-MS; **A**: standard solution containing Sb(III) and Sb(V) (5 μg $L^{-1}$ each); **B**: aqeous extract of soil A, dashed line: same sample solution spiked with 2 μg $L^{-1}$ Sb(III) prior to injection; experimental parameters see Table I



with soil particles. In alkaline solution Sb(III), as tartrate, was adsorbed to the soil immediately to 100% (Figure 4 D). Above pH 11 Sb(III) occurs in aqueous solutions as the tetrahydroxy antimonite anion which seems to enhance the adsorption to the soil. However, with increasing time oxidation to Sb(V) occurred under these conditions, which is in accordance with the Eh-pH behavior of antimony; Sb(III) is more easily oxidized to Sb(V) under alkaline conditions.[20]

Antimony(V) introduced as $KSb(OH)_6$ in aqueous solution was also sorbed from the soil but to a much lesser extent than Sb(III). After 45 min the recovery for the added Sb(V) was found to be 67%. Adding the Sb(V) in presence of the EDTA solution (0.05 M) the recovery rate increased to 74% and under alkaline conditions (0.1 M KOH) no sorption of the Sb(V) from the soil was observed (Figure 4).

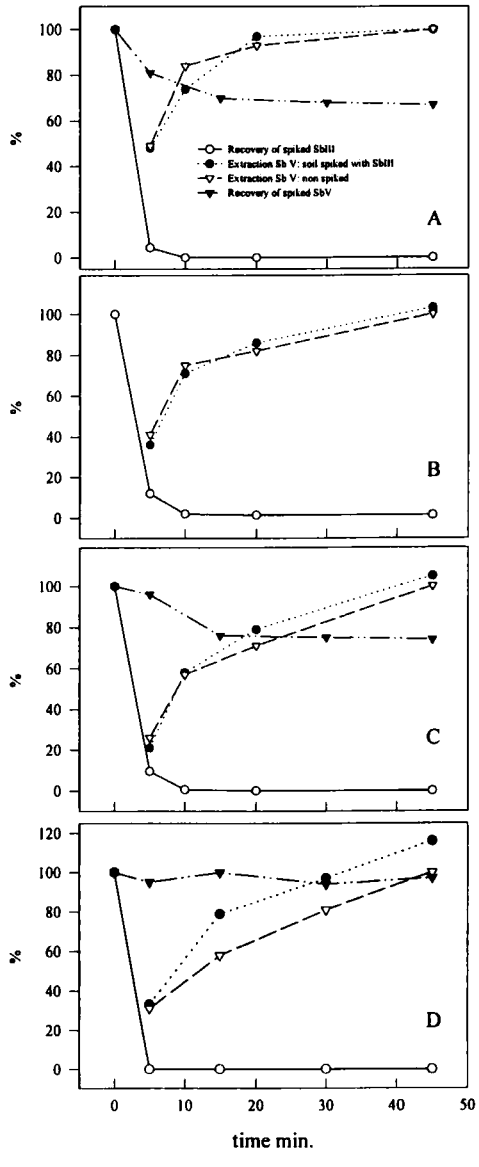


FIGURE 4 Results of spiking experiments with soil A; recovery rates of added Sb(III) and Sb(V), and relative Sb(V) concentrations extracted from the spiked and non spiked samples (standardized by the concentration of the non spiked samples after 45 min.); **A**: Sb(III) tartrate and potassium antimonate added with water; **B**: $Sb_2O_3$ added with water; **C**: Sb(III) tartrate and potassium antimonate added with 0.05 M EDTA; **D**: Sb(III) tartrate and potassium antimonate added with 0.1M KOH. Spiked concentrations 30 µg Sb $L^{-1}$each

## CONCLUSIONS

The results of the present study show that although soil samples were heavily contaminated with antimony its availability from the soil was low. The main amount of antimony was bound to relatively immobile hydrous Fe and Al oxides, i.e. the moderately reducible phase of the soil. Significant amounts of Sb were also associated with the organic matrix of the soil. The ratio between organic and hydrous oxid phase bound Sb seems to be influenced by the presence of potential organic ligands, e.g. soil sample from 10–30 cm depth (close to the sod) and the sludge amended soil contained less oxide bound and relatively more organic bound antimony than the soil sample from 30–60 cm depth.

Although contamination originated from the production of Sb(III) compounds no Sb(III) was detectable in any soil extract. Spiking experiments showed that added Sb(III) (as Sb-tartrate or $Sb_2O_3$) was immediately sorbed from the soil and was not released even in presence of EDTA or under alkaline conditions. A weak adsorption of Sb(V) was also noticed. Oxidation of the added Sb(III) to Sb(V) during extraction was only observed under alkaline conditions.

Considering the low availability of the Sb from the soil and the presence of the less toxic Sb(V) in the extracts the toxic hazard within the contaminated area seems to be of minor importance. However, risk assessment is difficult due to the lack of data about toxicity and biochemical effects of antimony compounds, especially during long time exposure.



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