



Adsorption of methylantimony and methylarsenic on soils, sediments, and mine tailings from antimony mine area



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ABSTRACT

Biogeochemical processes of antimony (Sb) – a chemically similar element as arsenic (As) – in a variety of environment is largely unexplored. Soil and sediment environment are known to control the geochemical fate of several contaminants via a multitude of processes, primarily adsorption. Here adsorption of organic Sb/As on soils, sediments, and mine tailings was investigated. Sorption studies showed that the methylarsenic sorption capacity and rate were greater than methylantimony sorption. For TMSb, MMA, and DMA sorption samples, the highest sorption capacity occurred in the Ferralsol, which contained the highest amount of Fe/Al-oxyhydroxides. The sorption capacity was proportional to the Fe/Al concentration in the environmental matrices (TMSb-Fe: $R^2 = 0.52$, TMSb-Al: $R^2 = 0.69$; MMA-Fe: $R^2 = 0.61$, MMA-Al: $R^2 = 0.76$; DMA-Fe: $R^2 = 0.42$, DMA-Al: $R^2 = 0.59$). The highest amount of TMSb, MMA, and DMA sorption rate was also observed for the Ferralsol with 82%, 97%, and 87%, respectively and that of the lowest values were the mine tailings. The other samples had similar amounts of TMSb/MMA/DMA sorption rate ranging from 5 to 60% of initially added organic species.

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1. Introduction

Antimony (Sb) shares similar toxicity and chemical nature with arsenic (As). The predominate oxidation states for inorganic Sb/As species are Sb/As(III) and Sb/As(V). In addition to inorganic forms, organic forms of Sb/As also exist in nature, typically occurring in agricultural and terrestrial environments as TMSb (trimethylantimony dibromine), MMA (monomethylarsenate), and DMA (dimethylarsenate).

Various metalloids and metals can be converted by a variety of microorganisms to their volatile methyl derivatives [1]. The methyl products have quite different properties (e.g., transportation, toxicological) as compared to the inorganic species from which they are derived. Methylated forms of antimony and arsenic are subject to various biogeochemical processes with natural components [2,3]. Methylantimony and methylarsenic species have been detected in the environment [4]. In the case of many metalloids including antimony (and by inference chemically similar arsenic), microorganisms can reduce and methylate the inorganic compounds to give organometallic species which are stable and mobile in water and air [5]. There is a growing interest in the biomethylation of Sb and As in the environment as the chemical properties and toxicities of methylated species are different from those of inorganic species [6,7].

Previous studies focused on the structural incorporation of inorganic Sb/As into natural sorbents such as clay minerals, metal oxides minerals, and humic acids [8–13]. Other studies have demonstrated that

methylated As sorption maxima on four Ultisol soils are correlated with the clay fraction and Fe-oxyhydroxide contents [14]. Little information is available about methylated Sb and As interactions on environmental matrices. Whereas the methylarsenic reactivity in soil is well established, that of the closely related element antimony is not, and there are no reports of methylantimony in environmental matrices. Because of the widespread distribution and toxicity of methylantimony and methylarsenic compounds, their adsorption by environmental matrices is of considerable interest. We report here, for the first time, the adsorption of trimethylantimony on soils, sediments, and mine tailings from highly polluted mine area. The aim of this study was to compare the relative affinity of methylated Sb/As for environmental matrices and the comparison of adsorption capability would benefit the prediction of Sb/As environmental mobility.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals, solvents, and reagents were purchased from Sinopharm Chemical Reagent Company, China, of analytical-reagent grade or higher purity. All glassware, polyethylene bottles, and sample vessels were previously decontaminated by soaking for at least 24 h in 10% (v/v) nitric acid and were rinsed several times with high purity water before use. The stock solutions of antimony species were prepared using trimethylantimony ($(\text{CH}_3)_3\text{SbBr}_2$, Sigma-Aldrich, 98% purity). The stock solutions of arsenic species were all purchased from the Chinese National Standard Material Center. Stock standard solutions

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were prepared in water to give 100 M and all standard solutions were stored in polyethylene bottles at 4 °C. Working solutions were prepared daily by an appropriate dilution. The chromatographic mobile phases were also prepared daily as required prior to analysis by dissolving the appropriate mass of compound in Milli-Q water (18.2 MΩ) and continuously filtered through a 0.22 μm membrane. A 2 m/v NaBH₄, 0.5% m/v NaOH solution was prepared daily and the chromatographic effluent was acidified on-line with 5% HCl.

2.2. Sample characteristics

Samples were collected from Xikuangshan antimony mine, Hunan province, central south of China. The histories of Xikuangshan antimony mining can date back to 1897 and the application of antimony in ammunition boomed during World War I [15]. Anthropogenic Sb enrichment followed closely with those of As in terms of its pollution history and degree of anthropogenic influence on the geochemical cycle [16]. The samples that were studied include top-soils, sub-soils, sediments, and mine tailings with abnormal high metalloid pollution. Samples were air-dried, ground, pass through a 75 μm sieve, and homogenized for characterization. Ammonium oxalate extractions were conducted to determine amorphous Fe-/Mn-oxides, respectively (Table 1).

2.3. Batch adsorption tests

Batch experiments were conducted to determine sorption isotherms at pH 6 with various Sb/As concentrations, ranging from 50 μM to 2 mM. 10 g/L soil/sediment/mine tailing suspensions containing 0.01 M NaCl were placed in 50 mL polypropylene centrifuge tubes and equilibrated at pH 6 for 24 h. The pH values of solutions were measured three times daily and were adjusted with 0.1 M HCl or 0.1 M NaOH at pH 6. The suspensions were centrifuged, and supernatants were collected using 0.22 μm pore size nylon syringe filters.

Sorption kinetics experiments were conducted using a 10 g/L soil/sediment/mine tailing suspension and 0.15 mM TMSb or MMA/DMA in 0.01 M NaCl at pH 6 with 1 mM tartaric or oxalic acid buffer, respectively. The samples were performed for various shaking time (15 min, 30 min, 1, 2, 6, 12, 24, 48, and 96 h). Suspensions were filtered through 0.22 μm pore size filters.

2.4. Analysis of Sb/As species

The concentration of each Sb/As species was analyzed using liquid chromatography-hydride generation-atomic fluorescence spectrometry (LC-HG-AFS) [17,18]. The LC system consisted of a p600 model (LabTech Holdings, Inc., China) with a Hamilton PRP-X100 anion exchange column (250 mm × 4.1 mm i.d., 10 μm). The HG-AFS unit

was a 9800 series (Beijing Haiguang Company, China). The mobile phase contained 5% methanol, 300 mM ammonium tartrate solution for Sb species (pH 4.5), and 15 mM diammonium hydrogen phosphate, 6.6 mM oxalic acid for As species (pH 6.0), respectively, at a flow rate of 1 mL/min. The injection volume of each sample was 100 μL.

Selected separation parameters are presented in Table 2. Calibration curves were obtained with measurements of 1 μg L⁻¹, 2 μg L⁻¹, 5 μg L⁻¹, 8 μg L⁻¹, and 10 μg L⁻¹ standard solutions for TMSb, MMA, and DMA, respectively. The detection limit calculation was based on the following formula: $3 \times s/b$, where s is standard deviation value, and b is linear coefficient of calibration line. Precision was calculated as the percent relative standard deviation from six peak area measurements of the standard solution containing the concentrations of 1 μg L⁻¹ for TMSb, MMA, and DMA, respectively.

3. Results

3.1. Sorption isotherms

The overall order of the highest TMSb, MMA, and DMA sorption capacity on the environmental matrices was as follows: Ferralsol > Topsoil > Bottom sediment > Surface sediment > Paddy soil > Subsoil > mine tailing (Fig. 1). Sorption isotherms for methylated forms of Sb and As species exhibited L-shaped type isotherms (Langmuir) are shown in Fig. 1. For TMSb, MMA, and DMA sorption samples, the highest sorption capacity occurred in the Ferralsol, which contained the highest amount of Fe/Al-oxyhydroxides (Table 1). Sorption maxima, based on the Langmuir equation $q_e = Q_{\max} b C_e / (1 + b C_e)$, were also the highest for the Ferralsol (Table 3). Notably, the sorption capacity order was approximately proportional to the Fe/Al-oxyhydroxide concentration in the environmental matrices with R² values between oxalate extracted Fe/Al content and TMSb/MMA/DMA sorption of 0.52/0.69, 0.61/0.76 and 0.42/0.59, respectively.

3.2. Sorption kinetics

The sorption kinetics experiments suggested biphasic sorption characteristics: fast initial sorption followed by slow continuous sorption (Fig. 2 and Fig. 3). The first order kinetics model was applied, and initial rate constants were estimated (Table 4). TMSb, MMA, and DMA sorption on these environmental matrices demonstrated a similar trend, but the sorption rate was different. The highest amount of TMSb, MMA, and DMA sorption rate was observed for the Ferralsol with 82%, 97%, and 87%, respectively. The other samples had similar amounts of TMSb/MMA/DMA sorption rate ranging from 5 to 60% of initially added organic species. For the mine tailings, the sorption rate was the slowest. The TMSb, MMA, and DMA sorption rates are also

Table 1
Description and properties of the studied soils, sediments, and mine tailings.

Description	Depth (cm)	pH	Al _{ox} ^a (g kg ⁻¹)	Fe _{ox} ^a (g kg ⁻¹)	Mn _{ox} ^a (g kg ⁻¹)	Corg (%)	Sb (mg kg ⁻¹)	As (mg kg ⁻¹)
1 Ferralsol	0–10	5.3	51	40	0.62	0.64	0.43	4.9
2 Topsoil	0–10	4.9	16	8.2	0.10	10	842	97
3 Subsoil	60–70	7.3	14	6.2	0.07	0.12	12	15
4 Paddy soil	0–10	6.5	11	9.5	0.23	3.0	150	33
5 Surface sediment	0–10	6.5	15	10	0.59	0.09	158	1904
6 Bottom sediment	60–70	6.8	21	23	0.88	0.56	481	4646
7 Mine tailing	0–10	7.2	1	3.5	0.02	– ^b	653	3839

1 is standard Ultisols; 2, 3, and 4 were collected from Sb mine area; 5 and 6 were collected from Pb/Zn mine area; and 7 was collected from Pb/Zn mine tailings.

^a Oxalate-extractable Al, Fe, and Mn.

^b “–” means not determined.

Table 2
Conditions of chromatographic separation.

Parameter	Value
Elution method	Isocratic elution
Flow rate (mL min ⁻¹)	1
Injection volume (μL)	100
Antimony	
Separation column	Hamilton PRP-X100 (250 mm × 4.1 mm i.d., 10 μm)
Mobile phase	300 mM ammonium tartrate + 5% methanol/pH 4.50
Liner range	TMSb: 0.9991–0.9995
Detection limit	TMSb: 0.43 μg L ⁻¹
Precision	1.2–5.3%
Arsenic	
Separation column	Hamilton PRP-X100 (250 mm × 4.1 mm i.d., 10 μm)
Mobile phase	15 mM (NH ₄) ₂ HPO ₄ + 6.6 mM oxalic acid/pH 6.00
Liner range	MMA: 0.9992–0.9996; DMA: 0.9990–0.9995
Detection limit	MMA: 0.35 μg L ⁻¹ ; DMA: 0.39 μg L ⁻¹
Precision	0.8–3.2%

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