



Study of antimony (III) binding to soil humic acid from an antimony smelting site

Sh Tserenpil*, Liu Cong-Qiang

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guanshui Road 46, Guiyang 550002, China

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ABSTRACT

Soil samples were collected from an antimony smelting site in Guangxi Zhuang Autonomous Region, China, at four locations characterized by different land usage, including two cultivated sites: one formerly cultivated and one uncultivated. Surface soils from all four sites were heavily polluted by toxic metals including antimony (Sb), lead (Pb) and arsenic (As), and their concentrations were 410–3330 mg·kg⁻¹, 410–3690 mg·kg⁻¹ and 200–460 mg·kg⁻¹, respectively. In the uncultivated area metal levels were 1.4–6.2 times higher as compared to the formerly and currently agriculture land. Lower levels at the cultivated sites may have resulted from an accumulation of airborne particles by vegetation and lower contents in the surface soil. However, the elevated mercury (Hg) content may reflect both natural and anthropogenic origins in this smelting site. Soil-derived humic acid (HA) from the smelting site reacted directly with Sb (III) aqueous solutions with concentrations of 12, 71 and 143 mg·g⁻¹. The maximum Sb (III) binding to the soil-derived HA was 253 μmol·g⁻¹ (added concentration of 71 mg·g⁻¹) and showed more binding (up to 50%) at lower Sb content.

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1. Introduction

Antimony has been widely used as an alloy and a chemical compound in approximately 200 substances [1]. Furthermore, Sb is utilized for polyethylene terephthalate plastics as a catalyst, and Sb contamination occurs in bottled water using these plastic containers [2,3].

Sb is a trace constituent in the soil, where concentrations are typically 1 mg·kg⁻¹. However, highly elevated concentrations have been detected in the soil samples from a smelting site 80200 mg·kg⁻¹ [4], shooting ranges 17500 mg·kg⁻¹ (<0.5 mm fraction) [5,6], a previous mining site 15100 mg·kg⁻¹ [7], and in apple orchards (nitric acid extractable fraction was 69 μg·kg⁻¹) [8]. One of the major anthropogenic sources of heavy and toxic metal pollution is fine particulates from smelting industries and the highest Sb contamination is usually found at the smelting sites. Fine particulates with a life time from days to weeks pose a serious health risk and may travel up to 1000 s km [9]. Therefore, metal contamination from the smelters may occur at a significant distance from the point source. The studies concerning Sb pollution in Chinese mining [10,11] and smelting sites [12,13] are limited.

It is known that Sb is associated with soil organic matter [8], oxyhydroxides of iron, manganese and aluminum [14,15] and clay minerals [16]. Both Sb (III) and Sb (V) speciations readily bind to simple organic ligands and complex macromolecules [17–19]. The surveys demonstrated that a significant portion of Sb was associated with organic substances in natural water (35–85% of total Sb) [19–21], sediment and

soil (over 30% added Sb bond to an isolated HA fraction) [17]. Anthropogenic Sb usually presents itself as an insoluble and immobile species in the environment and is confined to the top 30 cm layer rather than accumulating in biological systems or leaching into groundwater [8]. However, Sb is not an essential element in plants and by competing with essential metabolites can even be phytotoxic [22]. Study concerned an effect of Sb on the growth and yield of rice showed that both tri and pentavalent Sb can reduce crop yield [23].

Two main binding sites were proposed for Sb (III) and humic acid binding: 1) a phenolic group forming a neutral complex and 2) a carboxylic group for a negatively charged complex [17]. Moreover, pentamembered bidentate form was suggested for Sb bond with HA via hydroxy-carboxylic groups [19].

In this study, soil properties and Sb contamination level were examined at four locations at Sb smelting site and the capacity of Sb (III) binding to an isolated HA was investigated at site 1. Elemental composition and the chemical nature of HA–Sb (III) composites were compared with parent HA for identification of carboxyl and hydroxyl entities for Sb (III) binding.

2. Materials and methods

2.1. Sampling and site description

The present study was conducted at a recently abandoned Sb smelting site (108°03' E, 24°43' N), which operated from 1996 to 2008 located near Jinchengjiang City, Hechi, in Guangxi Zhuang Autonomous Region, China. The area within the vicinity of the smelter is currently used for agricultural cultivation.

* Corresponding author.

E-mail address: tserenpil.sh@gmail.com (Sh. Tserenpil).

Sampling sites included an uncultivated, a cultivated and a former vegetable gardening site, in order to compare the extent of contamination.

Site 1 is a fallow farmland did not cultivate during the last 5 years due to a dramatic decrease of harvest following the initiation of smelting operation.

Site 2 is an uncultivated site, near the mountain base.

Site 3 and **Site 4** are currently under cultivation.

In October 2009, soil samples were collected from 0–5 cm, 5–20 cm, 20–30 cm and 30–40 cm depths at sites 1 and 2, while surface soils were taken from sites 3 and 4 at 0–10 cm. Samples were kept in pre-cleaned glass bottles and stored in a refrigerator at 4 °C until the analysis.

2.2. Methods

2.2.1. Soil analysis

The determination of soil physico-chemical parameters of soil included data relating the soil pH, texture distribution, pH buffering capacity (pH BC) (Fig. 1), pH-dependent cation exchange capacity (CEC), total organic carbon (TOC) and particulate organic matter (POM). Soil pH, pH BC, CEC and TOC were determined with air dried and pulverized samples (texture analyses conducted on the native soils) by following established methods [24–26]; pH dependent CEC and pH BC were investigated by a modified Ag-TU method [27]. TOC was converted to total organic matter (TOM) based on the assumption that organic matter contains 58% organic carbon [28]. Sb, As and Pb concentrations were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Platform ICP, Micromass Instruments Corporation, Manchester, UK) after a high pressure digestion of 10 mg soil sample with 1.0 ml of HNO₃, 0.5 ml of HF [10]. Reference materials of the soil (GBW07404) and sediment (GBW07305) were analyzed for the quality control of the analyses and blank reagent examined to exclude laboratory contamination. For the determination of total Hg an instrumental (Lumex RA 915, Lumex, USA) analyses was carried out. Controlled heating in an oxygenated decomposition furnace was used to liberate Hg and its vapor was measured directly by Hg lamp. Exchangeable or weakly bonded Sb fraction in soil was determined using single extraction procedures by 1 M NH₄NO₃ for 2 hours [29].

2.2.2. Isolation and characterization of humic acids and HA-Sb (III) constituent

HA was isolated from site 1 (depth of 30–40 cm) using a sodium hydroxide (NaOH) extraction after demineralization of soil by hydrochloric acid (HCl) [30]. For HA purification, the alkaline suspension was first decanted then followed by centrifugation at a high speed of 10000 rpm. HCl/HF treatment was not employed to avoid a destruction of HA molecular structure and as an ash content was not high. The isolated

soil-derived HA was freeze dried for further analysis and a study of Sb binding to HA.

Antimony (III) potassium tartrate hemihydrates, C₄H₄KO₇Sb (analytical reagent grade, Tianjin, China) was used for preparing Sb stock solutions. Four serial samples each containing 1000 mg of soil-derived HA were dissolved in NaOH solutions and freshly prepared aqueous solutions containing 12, 72 and 144 mg of Sb were added to the individual trails and one trail without Sb addition. Added amounts of Sb were chosen to provide a higher level than the adsorption maxima of 53 μmol·g⁻¹ HA found by Pilarki et al. [52] and an assumption that the maximum level reached up to 1000 mg·kg⁻¹ soil. The mixtures were stirred and kept at 40 °C for 15 minutes before filtration. Formed new composites, when added 12, 71 and 143 mg of Sb and without Sb addition herein labeled S1, S2, S3 and humate, respectively, precipitated from ethanol to give dense amorphous particles, which were washed several times with ethanol and centrifuged before freeze drying.

The soil-derived HA and obtained HA-Sb (III) composites were investigated by measuring elemental composition (Element analyzer, PE2400 II, USA), ash content by heating at 750 °C for 4 h and the concentrations of total acidic and carboxylic groups of HA were determined by indirect titration [31]. The absorbance ratio of HA extract at 465 nm and 665 nm (E₄/E₆) obtained in 0.05 M NaHCO₃ (30 mg L⁻¹ ash free basis) at visible spectrophotometer (Spectrum 722E, Shanghai Spectrum Instrument Co., Ltd, China). The HA samples were digested using HNO₃ and H₂O₂ for ICP-MS analysis to measure Al, Fe, Mn and Sb concentrations.

3. Results and discussion

3.1. Soil characteristics and heavy metal distribution

The distribution behavior of metals within a soil system is dependent upon geochemical characteristics of soil, which are summarized in Table 1. All the data given are based on the individual soil layers. The typical positive relationship between the concentration of TOM and depth of soil profile was observed at site 2 (uncultivated). But at site 1, the highest concentration was measured at 30–40 cm (1.72% of TOC), which showed plant uptake of nutrients and organic matters was intensive at 5–30 cm during the vegetation. At site 2, the content of TOC ranged from 0.73 to 2.07%, and was inversely related with clay content. This correlation indicated lower content of colloidal organic material (humus) comparing to site 1. Soil pH value fluctuates from 4.59 to 6.92 and increased with depth at sites 1 and 2, a medium to strong acidic character of the surface soils was observed at all sampling sites (Table 1) in the vicinity of the smelter. Strong retention of Sb is expected at low pH (highest sorption 80–100% of Sb appeared at pH < 6.5) [32].

Metals can be mobilized when soil pH changes; however sites maintain their pH in the environment due to the soil BC. Data presented in Table 1 showed a good correlation between soil BC and TOC for the uncultivated site 2, and in addition BC at the surface was higher than those formerly and currently cultivated sites. The pH dependent CEC showed a linear CEC-pH relationship (Table 2) and was negligible on the surface (where pH 4.9) at site 1. The surface soils from the other two cultivated sites possessed a lower (0.8–2.4 cmol·kg⁻¹) CEC than the uncultivated one (3.1–4.9 cmol·kg⁻¹) over pH ranges from 3.1 to 6.2. The properties of the smelting site soil including soil BC, CEC and organic matters distribution, indicated that the sites 1, 3 and 4 affected by agricultural and smelting activities while site 2 was affected solely by the smelter.

Background levels of Sb in Chinese soils varied between 0.8 and 3.0 mg·kg⁻¹ [33]. The present study showed that the surface soils at the sampling sites were heavily contaminated by Sb and its distribution was dramatically decreased with depth from 760 to 2.5 mg·kg⁻¹ and from 3328 to 26 mg·kg⁻¹, at sites 1 and 2, respectively (Table 3). Exchangeable or weakly bonded Sb levels were (only 0.16% of total Sb in the surface) not as high, since it was accumulated at the surface and was negligible at the lower soil horizons. This is in agreement with typical contributions of

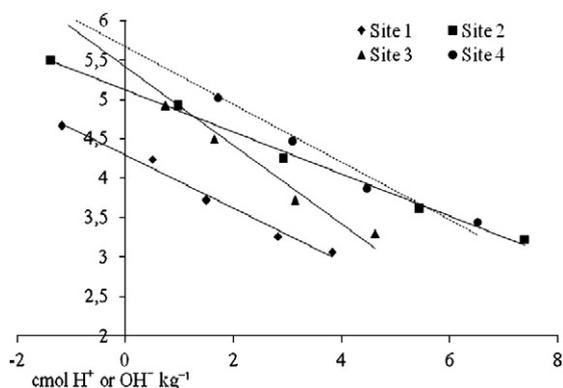


Fig. 1. pH buffering capacity on the surface soils at the sampling sites.

Table 1
Soil properties for the sampling sites.

Sampling site and soil depth, cm	pH ^a	pH BC [†] cmol H ⁺ kg ⁻¹ pH ⁻¹	Content in dry weight, %				
			Texture ^b	TOC [‡]	POM ^c	Sb, mg·kg ⁻¹	
Site 1	0–5	4.88	2.69	18.7–73.4–7.9	1.57	0.41	760
	5–20	6.51	4.08	28.2–64.0–7.8	0.81	0.21	30
	20–30	6.90	4.85	26.2–67.9–5.9	1.32	0.18	3.7
	30–40	6.92	4.79	32.8–60.9–6.2	1.72	0.19	2.5
Site 2	0–5	4.59	3.85	19.9–63.2–16.8	2.07	0.60	3328
	5–20	5.46	3.82	29.0–56.9–14.1	1.46	0.21	186
	20–30	6.03	3.62	30.1–56.2–13.7	1.05	0.17	51
	30–40	6.33	2.38	36.3–53.3–10.4	0.73	0.06	26
Site 3	0–10	5.50	2.44	8.8–78.7–12.5	1.69	0.54	413
Site 4	0–10	5.85	2.73	21.9–63.7–14.4	1.82	0.84	497

a: pH in 0.01 M CaCl₂.

b: Clay–silt–sand.

c: Fine particulate organic matter (POM) size of 0.053–0.5 mm.

†BC: Buffering capacity.

‡TOC: Total organic carbon.

mobile Sb concentration (<2%) in the soil [34] and the results by Hammel et al. [35]. Sb and other elements were strongly accumulated in the top 10 cm of acidic soil with high organic content [36]. Steely et al. [8] demonstrated that Sb complexed to HA fraction and trapped in the organic layer of soil. During the transport of metals in soil systems, metal sorption to the solid matrix and formation of complexes with organic materials results in a reduction in the dissolved concentration of metals and this affects the mobilization of metals.

The data were compared to the available information on Sb in the smelting sites. A survey examined topsoil samples in Xikuangshan area, Hunan province where located the world biggest antimony mining and several smelters, and showed Sb levels were up to 2160 mg·kg⁻¹ and soil near an alkaline furnace clinker contained 5050 mg·kg⁻¹ [12,13]. Sb concentration was reported as 1490 mg·kg⁻¹ in the soil at a site close to a working antimony smelter [43], 2900 mg·kg⁻¹ content investigated in the area where smelter had worked for 14 years [44], and Wilson et al. [4] reported the highest concentration of As and Sb at a smelting site, which had been used for 32 years with levels at 2220 and 80200 mg·kg⁻¹, respectively. Differentiation of the contamination level maybe attributed to the smelting technologies and their smelting duration.

Typically, high concentrations of Pb, As and Hg co-occurred with Sb in polluted sites [4,13,45]. Sb, Pb and As levels were varied at four sites with different historical uses. However, distribution trends were similar for these metals, which quantitatively decreased with depth. Only a slight increase of As and Pb concentrations were observed at 20–30 cm depth at site 2. Variation in surface and depth distributions indicated that the pollutant source was smelter emissions, which were transported by the atmosphere and the metals were slowly leached into the subsurface. The highest contamination occurred in the uncultivated soil at site 2 (Fig. 2a). Conversely, lower concentrations were detected in the formerly cultivated (site 1) and the lowest in the cultivated (site 3 and site 4) areas. This may reflect airborne particles accumulated in above ground parts of plants rather than in the soil. One hypothesis is that a significant portion of Sb is confined to HA. Soil from site 2 tends to have a low humic content and the mobility of Sb was higher than at site 1 (Table 3).

Hg distribution in the soil profiles did not decline with depth (Fig. 2b), like Sb, Pb and As. The concentrations were high in the both surface (0.14 and 0.22 mg·kg⁻¹ at site 1 and 2, respectively) and

subsurface (30–40 cm) (0.11 and 0.30 mg·kg⁻¹), but at 5–30 cm depth its concentrations were low. The background Hg value of Chinese soil was reported 0.065 mg·kg⁻¹ by State Environmental Protection Administration of China (SEPAC) [46] and 0.038 mg·kg⁻¹ by the National Environmental Monitoring Center (NEMC) [47], although Hg concentrations are not uniformly distributed throughout the country, and in certain areas such as southern China, particularly southwestern Hg concentrations are more elevated [48]. Data from this study were higher than stated by SEPAC and NEMC but comparable with regional elevated background levels 0.14 ± 0.05 mg·kg⁻¹ reported by Feng et al. [49]. Meanwhile, Wang et al. [13] studied top soils in Xikuangshan and concluded that Hg content mainly due to the mining and smelting activities. Hence, Hg level at this smelting site may be occurred both naturally and anthropogenically.

3.2. Sb binding to soil humic acid at the smelting site

The environmental distribution of Sb affected by soil HA since its content is a substantial portion of soil organic matter. Other studies clearly suggested that Sb (III) interacted with natural organic matter more than Sb (V) [50,51]. This tendency also showed in the study on the sorption of Sb (III) and Sb (IV) by humic acid [52]. To facilitate the discussion of the fate of Sb in certain locations of smelting area and to study Sb binding to active sites of natural organic matter, soil-derived HA was reacted with Sb (III) in different concentrations.

For HA extraction the soil profile (30–40 cm) at site 1 was chosen that was less affected by agricultural and smelting activities, therefore, this soil has more organic content and a higher CEC. Its concentration accounted for 7.27 g·kg⁻¹ soil (in dry mass), which was 24.56% of the soil TOM. The ash content was found to be 8.8% for soil-derived HA; meanwhile, HA–Sb (III) composites and humate (i.e., S1, S2, S3 and Humate) consisted of 34.0, 35.6, 35.1 and 29.0% ash, respectively (Table 4).

Elemental composition of the extracted HA from the smelting site showed an molar ratio of H/C = 1.5 that was 1.5–2.1 times higher than humic samples used for equilibrium dialysis study [17] for Sb binding to dissoluble humic substances where found a stronger binding sites involved at lower Sb(III)/DOC ratio. Moreover, a ratio of O/C for the obtained HA (0.65) was compared to Aldrich Humic Acid AHA (0.44) and suggesting that the isolated HA has a relatively high content of O-alkyl and carboxylic group, and a low degree of aromatic condensation (higher H/C ratio) [54,55]. Total acidity of the smelting site HA accounted for 558.65 cmol·kg⁻¹ and carboxyl functional group 438.85 cmol·kg⁻¹, which demonstrated the presence of metal binding functional groups. The phenolic hydroxyl group was calculated by the difference between the total acidic and carboxylic group. HA from this site was characterized by its aliphatic nature and the higher concentration of carboxylic

Table 2
Cation exchange capacity (CEC)–pH relationship for site 1.

CEC, cmol·kg ⁻¹ soil	Soil pH				
	6.7	6.0	5.0	4.0	3.0
5–20 cm	2.4	2.1	1.8	1.4	1.1
20–30 cm	4.0	3.9	3.8	3.8	3.7
30–40 cm	4.8	4.6	4.4	4.1	3.9

Table 3
Distribution of Sb, Pb, As and Hg in the soil profiles, $\text{mg}\cdot\text{kg}^{-1}$.

Soil sites and depth	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
	0–5 cm		5–20 cm		20–30 cm		30–40 cm	
Sb _{total} ^a	760	3328	30	186	3.7	51	2.5	26
Sb extractable NH_4OH_3	1.19	5.3	0.01	0.35	0	0.17	0	0.02
As ^b	202	455	48	76	38	86	29	31
Pb ^c	597	3691	93	61	60	72	36	39
Hg ^d	0.14	0.22	0.07	0.20	0.05	0.16	0.11	0.30

The concentration ranges in the uncontaminated soils:

a: $\text{Sb} < 1 \text{ mg}\cdot\text{kg}^{-1}$ [37].

b: $\text{As} \sim 7.2 \text{ mg}\cdot\text{kg}^{-1}$ [39], $\text{As} \sim 11.2 \text{ mg}\cdot\text{kg}^{-1}$ mean concentration for all type of Chinese soil [40].

c: $\text{Pb} < 20 \text{ mg}\cdot\text{kg}^{-1}$ [38].

d: $\text{Hg} \sim 0.02\text{--}0.026 \text{ mg}\cdot\text{kg}^{-1}$ [41,42].

functional groups nearly 78% (total acidic groups) and was similar to the fulvic acids studied by Ussiri and Jonhson [56]. Hence, in the present study more Sb (III) binding to the studied HA was expected than the adsorption maxima of $23 \mu\text{mol Sb g}^{-1}$ (using inorganic solution) and $53 \mu\text{mol Sb g}^{-1}$ (organic solution) [52]. Nevertheless, it was investigated that Suwannee River Humic Acid (SRHA), which exhibited more functional groups and has a smaller molecule, showed a seven times greater affinity for Sb (III) comparing to AHA [17]. Distribution coefficient for Sb depends on the individual HA, suggesting that different functional groups are involved and different degrees of stabilization by chelation or H-bridges.

Absorbance ratio at 465 nm and 665 nm (E_4/E_6) of the studied HA macromolecule was found identical (Table 4) for both HA–Sb (except S2)

composite and original HA that indicated HA molecular structure unchanged during the association with Sb (III). The E_4/E_5 ratio measured from 5.0 to 5.4, which revealed more aliphatic structure than HA with same origin [57] and comparable to the previously reported data by Steely et al. [8]. The results of elemental analysis, indirect titration and spectrophotometer measurements were in good agreement.

Isolated unpurified HA contained $0.18 \mu\text{mol Sb g}^{-1}$ ($1.89 \text{ mg}\cdot\text{kg}^{-1}$ soil), which was 75.6% of the total Sb in the native soil (see Table 1, site 1 at 30–40 cm depth). It should be noted that the HA sample comprised 0.62% Al, 0.27% Fe and 0.01% Mn, which strongly adsorb Sb but these contents were less than those found for humic materials used in Sb sorption study [32]. S2 and S3, 71 and 143 mg of added Sb (III), respectively, did not show a great difference in ash content; the latter was even slightly low (Table 4). Sb content in HA–Sb (III) composites were measured by ICP-MS and highest binding was found $253.3 \mu\text{mol Sb g}^{-1}$ for S2, 50.4 and $179.3 \mu\text{mol Sb g}^{-1}$ were determined for S1 and S3, respectively. Sb binding reached its maxima when used $71 \text{ mg Sb (III)}\cdot\text{g}^{-1}$ HA. However, in trial S1 50.3% of added Sb (III) bond to HA and in S2 was found 43.2%, but in the trail with the highest concentration of added Sb binding reached only 15.3%. This tendency was in good agreement with earlier published data on conditional distribution coefficients for Sb (III) binding to humic substances [17].

Anthropogenic Sb may be found an adsorbed and chemically bonded to soil organic phases, also there is a new concept that explains metals can be trapped inside voids within HA multifunctional biopolymer as an organic-inorganic nano composite in which HA plays a role as a stabilizer for metal ions [58]. Both carboxyl and hydroxyl entities have contributed in Sb (III) binding to HA and the chemical bonds in these composites will be assessed in due course.

4. Conclusion

All surface soils from the sampling site in the vicinity of Sb smelter were heavily polluted by metals including Sb, Pb and As, and their concentrations were measured $410\text{--}3330 \text{ mg}\cdot\text{kg}^{-1}$, $410\text{--}3690 \text{ mg}\cdot\text{kg}^{-1}$ and $200\text{--}460 \text{ mg}\cdot\text{kg}^{-1}$, respectively. However, the elevated concentrations ($0.11\text{--}0.30 \text{ mg}\cdot\text{kg}^{-1}$) of Hg may be occurred both naturally and anthropogenically in the investigated area. The exchangeable Sb (up to 0.16%) was not as high as it was accumulated in the surface soils. This study showed that aerosol particles from Sb smelter can be result a severe pollution of toxic metals into the local environment and high risk in agricultural plants. HA content at site 1 was accounted for 24.6% of TOM of soil and characterized a high content of carboxylic functional group and its aliphatic character these investigated by chemical and instrumental analysis. The maximum binding of Sb to the isolated soil-derived HA found as $253 \mu\text{mol}\cdot\text{g}^{-1}$ when added 12, 71 and $143 \text{ mg}\cdot\text{g}^{-1}$ of Sb and decreased for higher added amounts. This tendency was in agreement with previously reported data on Sb (III) binding to humic substances. However, its binding capacity was found to be higher than earlier published concentration. This may reflected from the direct reaction in

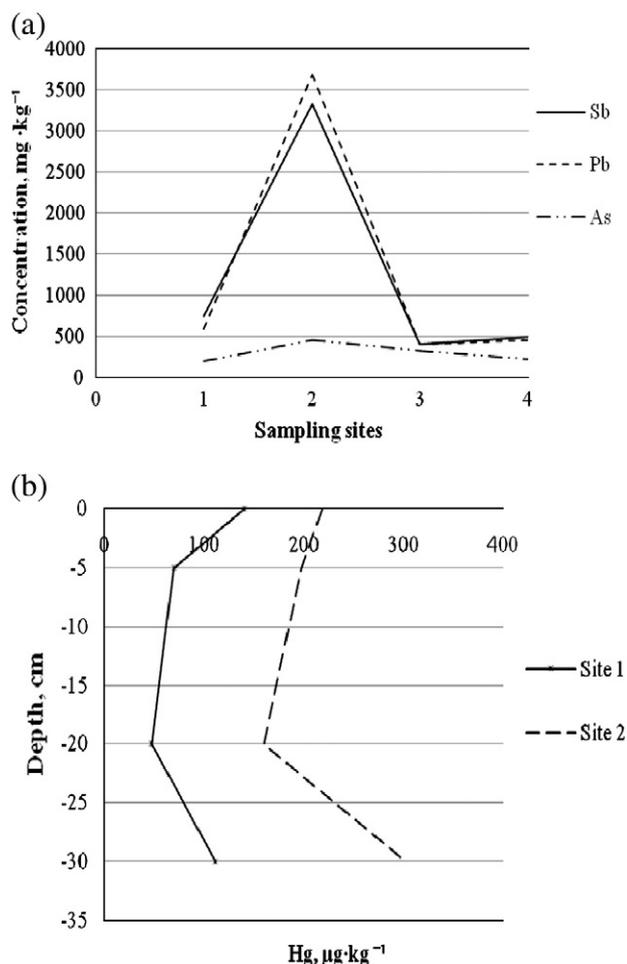


Fig. 2. a) Distribution of Sb, Pb and As in the surface soils at four sampling sites. b) Hg distribution throughout soil profile at site 1 and site 2.

Table 4

Elemental composition, ash and mole atom ratio in soil-derived HA and HA–Sb composites compared to Aldrich humic acid (AHA).

Samples	Elements, % (ash free basis)					Ash, %	H/C	E ₄ /E ₆	Sb, μmol g ⁻¹
	C	H	N	S	O				
HA	48.4	5.9	3.0	0.7	42.1	8.8	1.5	5.1	0.18
Humate	47.9	7.7	2.5	0.6	41.5	29.0	1.9	5.0	-
S1_HA–Sb 12 mg	47.1	6.1	2.5	0.6	43.7	34.0	1.6	5.0	50.4
S2_HA–Sb 71 mg	47.2	6.3	2.6	0.6	43.3	35.6	1.6	5.4	253.3
S3_HA–Sb 143 mg	43.6	5.8	2.2	0.5	47.9	35.1	1.6	5.0	179.3
AHA ^a	57.8	3.7	0.7	4.2	33.6	5.2	0.7	-	-

a: As reported by Arnold et al. [53] for a treated AHA from the soil.

this study and its aliphatic nature characterized by the presence of the high carboxylic moiety.

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