

## Antimony availability in highly polluted soils and sediments – A comparison of single extractions

Vojtěch Ettler<sup>a,\*</sup>, Martin Mihaljevič<sup>a</sup>, Ondřej Šebek<sup>b</sup>, Zbyšek Nechutný<sup>a</sup>

<sup>a</sup> Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 128 43 Praha 2, Czech Republic

<sup>b</sup> Laboratories of Geological Institutes, Charles University, Albertov 6, 128 43 Praha 2, Czech Republic

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### Abstract

Forest/tilled soils and stream sediments from the highly polluted mining and smelting district of Příbram, Czech Republic, were subjected to single extraction procedures in order to determine the available contents of Sb and As. The results obtained from five widely-used 2-h single extraction tests were compared: deionised water, 0.01 M CaCl<sub>2</sub>, 1 M NH<sub>4</sub>NO<sub>3</sub>, 0.005 M diethylenetriaminopentaacetic acid (DTPA) and 0.1 M Na<sub>2</sub>HPO<sub>4</sub>. The ICP-MS determinations of Sb and As in the extracts were coupled with measurements of pH and Eh and geochemical modelling (PHREEQC-2) to determine their speciation in extracts and possible solubility-controlling phases. According to the speciation calculations, Sb in extracts was present mainly as Sb(V) with the exception of the DTPA extracts from highly organic and acidic forest soils, where Sb(III) species accounted for up to 34% of total Sb speciation. The highest extractabilities were observed for the 0.1 M Na<sub>2</sub>HPO<sub>4</sub> solution (up to 9% of the total Sb and up to 34% of the total As concentration). The other extracting media yielded statistically the same results ( $p < 0.05$ ) with Sb extractabilities below 2% and As extractabilities below 8%. Thus, simple deionised water and 0.1 M Na<sub>2</sub>HPO<sub>4</sub> extractions are preferred for quick estimates of easily-exchangeable and specifically-sorbed Sb, respectively. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Antimony; Arsenic; Soil; Stream sediment; Availability; Single extraction

### 1. Introduction

Numerous recent papers on the distribution, cycling and mobility of antimony (Sb) confirm the increasing interest in this metalloid, which is one of the important anthropogenic contaminants (Lintschinger et al., 1998; Loska et al., 2004; Krachler et al., 2005; Gál et al., 2006). Mining and smelting activities currently represent the principal point sources of Sb in the environment (Flynn et al., 2003; Wilson et al., 2004); however, the growing worldwide usage in automobile brake-lining components, plastics and flame retardants is contributing to increasing amounts of this element in the environment (Krachler et al., 2005). It is generally assumed that the geochemical behaviour and toxicity of Sb are sim-

ilar to those of arsenic (As) (Wilson et al., 2004; Tighe et al., 2005a,b). Similarly, Sb exists in two oxidation states, Sb(V) and Sb(III) and, when dissolved in water, yields the anionic species Sb(OH)<sub>6</sub><sup>-</sup> under oxidizing conditions and the species Sb(OH)<sub>3</sub><sup>0</sup>, Sb(OH)<sub>2</sub><sup>+</sup> and Sb(OH)<sub>4</sub><sup>-</sup> under reducing conditions (Fillela et al., 2002; Gál et al., 2006).

Antimony has been observed to have relatively low mobility in soils (Lintschinger et al., 1998; Hammel et al., 2000; Nakamaru et al., 2006). The immobility of Sb has been documented even in highly polluted soils at some former mining and smelting sites in Britain and New Zealand (Flynn et al., 2003; Wilson et al., 2004). Despite the high concentrations of Sb in mining soils, relatively low concentrations were observed in plants (Hammel et al., 2000) and bacterial biosensors failed in testing the Sb toxicity due to its low availability (Flynn et al., 2003). Exceptionally high Sb accumulations, up to 1423 mg kg<sup>-1</sup>, were

\* Corresponding author. Tel.: +420 221 951 493; fax: +420 221 951 496.  
E-mail address: [ettler@natur.cuni.cz](mailto:ettler@natur.cuni.cz) (V. Ettler).

recently reported in some macrofungi (genera *Chalciporus* and *Suillus*) from Sb-polluted areas indicating that Sb can be mobile in some cases (Borovička et al., 2006). A recent study on soil-like embankments in Swiss shooting ranges contaminated by Pb bullets (with 2–5 wt.% Sb), showed a significant release of Sb during leaching tests, with up to 5 mg Sb l<sup>-1</sup> in aqueous extracts (Johnson et al., 2005).

A large number of single extraction methods have been proposed in the past few decades for determination of plant-available trace elements (metals, As, Se) in soils and sediments, as was elegantly reviewed by Gleyzes et al. (2002) and Hudson-Edwards et al. (2004). With the exception of the pioneer work of Lintschinger et al. (1998), focused on moderately Sb-contaminated soils, extracting methods simulating the extraction of “available” Sb have not been compared to date. This paper attempts to compare Sb and As extractabilities using five, short-term, single-extraction techniques (H<sub>2</sub>O, CaCl<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, DTPA, Na<sub>2</sub>HPO<sub>4</sub>), which are widely employed in the literature, through application to mining- and smelting-affected soils and stream sediments with Sb concentrations varying from 7 to 2050 mg kg<sup>-1</sup>. The evaluation of the suitability of the individual extraction methods is based on detailed knowledge of the physico-chemical properties (pH, CEC, organic matter content, Fe, Mn and Al oxide content), statistical data treatment and thermodynamic modelling of speciation in extracts and solubility controls.

## 2. Materials and methods

### 2.1. Soils and sediments

Seven environmental samples (forest and tilled soils and stream sediments) from the mining/smelting district of Příbram, Czech Republic, were used for this study. The detailed methodology of soil and sediment sampling and preparation prior to analyses is described in Ettler et al. (2004, 2006). The soils were air-dried and sieved to <2 mm. Stream sediments were passed through a 0.063-mm sieve and air-dried. The samples were ground in an agate mortar (grain size <50 µm; Fritsch Pulverisette, Germany) to obtain consistency between the physical properties of the individual samples and sufficient reproducibility of the digestion/extraction procedures employed. Forest and tilled soils are polluted by fly ash from the primary/secondary Pb smelter (Ettler et al., 2004, 2005a,b). The contamination of stream sediments is related to extensive mining activities in the Příbram polymetallic ore district, where Sb mineralization (mainly antimonite, Sb<sub>2</sub>S<sub>3</sub> and sulphosalts) accompanies the main Pb–Ag–Zn mineralization (Ettler et al., 2006). The general characteristics and physico-chemical properties of the studied samples are given in Table 1. The sample pH was measured in a MilliQ+ deionised water suspension (1:2 v/v) after 1-h agitation using a Schott HandyLab 1 pH meter. The total

Table 1  
Description and properties of the studied soils and stream sediments

Sample	Description	Depth (cm)	TOC <sup>a</sup> (%)	pH <sub>H<sub>2</sub>O</sub> (std. units)	CEC <sup>b</sup> (mmol kg <sup>-1</sup> )	Fe <sub>ox</sub> <sup>c</sup> (g kg <sup>-1</sup> )	Mn <sub>ox</sub> <sup>c</sup> (g kg <sup>-1</sup> )	Al <sub>ox</sub> <sup>c</sup> (g kg <sup>-1</sup> )	Sb (mg kg <sup>-1</sup> )	As (mg kg <sup>-1</sup> )
1	Forest soil	3–6	36.5	3.45	213	8.82	0.31	1.46	705 ± 42.8	336 ± 10.5
2	Forest soil	7.5–11	46.2	3.69	362	2.72	0.09	5.34	31.7 ± 1.38	17.3 ± 2.66
3	Tilled soil	6–13	1.79	5.32	70	2.61	1.21	1.20	46.3 ± 1.85	107 ± 3.97
4	Tilled soil	6–11	2.66	4.43	52	2.84	0.48	1.09	7.72 ± 0.73	29.7 ± 0.07
5	Stream sediment	0–10	3.76	4.97	132	44.8	1.03	1.81	2050 ± 72.8	18767 ± 310
6	Stream sediment	0–10	3.64	6.81	200	8.62	1.45	2.90	11.8 ± 0.43	61.2 ± 9.63
7	Stream sediment	0–10	3.55	6.5	123	9.22	0.43	2.81	207 ± 0.05	383 ± 1.5

<sup>a</sup> TOC – total organic carbon.

<sup>b</sup> CEC – cation exchange capacity.

<sup>c</sup> Oxalate-extractable Fe, Mn and Al.

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