

Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges

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ABSTRACT

The aim of this study was to determine whether or not Sb and other elements (Ni, Cu, Bi, Tl, and Hg) originating from Pb alloy (2–5 wt. % Sb) bullets become more soluble as a result of weathering and what mechanisms possibly control their solubility. Samples were taken from bank material behind the targets at seven Swiss shooting ranges. The samples were dried, sieved, analyzed, and subjected to leaching experiments. Total average concentrations of Sb ranged from 0.5 to 13.8 g kg⁻¹. In the leaching experiments, Sb was almost exclusively present in solution as the oxidized species Sb(V) in concentrations of up to 5 mg L⁻¹. The Ca mineral Ca[Sb(OH)₆]₂ is suggested to control dissolved Sb(V) concentrations in soils at high concentrations. Oxalate extractions suggested that approximately 50% of Sb [predominantly Sb(V)] in the <0.5-mm fraction was adsorbed to Fe (hydr)oxides and possibly other minerals, such as calcite, that are soluble at pH 2. However, it is possible that only a fraction of the oxalate-extractable Sb(V) is reversibly bound to mineral surfaces. It was concluded that the release of Sb is significant and considerably higher than the other elements under investigation and that the mechanisms controlling Sb mobility should be further investigated.

MANY OUTDOOR SHOOTING RANGES are contaminated with spent bullets that corrode and release heavy metals and metalloid species to the soil environment. Bullets generally have cores made of a Pb–Sb alloy with an Sb content of between 2 and 5 wt. %. Other elements such as As, Bi, or Ag may be present, because poor-quality Pb is used for the production of bullets. In addition the jacket housing may contain Cu or Ni alloy (Guy and Pate, 1973; Randich et al., 2002). The 5.6-mm Gw Pat 90 bullet, used in Switzerland, and the heavier GP 11 bullet, which it is replacing, contain approximately 95% Pb, 2% Sb, 3% Cu, and 0.5% Ni. In Switzerland, it is estimated that 400 to 500 Mg of Pb and 10 to 25 Mg of Sb annually enter the soil as a result of shooting practice at more than 2000 ranges, a majority of which are 300-m rifle ranges (Anonymous, 1997). The contamination is greatest in the top 20 to 30 cm of the embankments that act as stop butts behind the targets. As the bullets corrode, metals are released to the soil. Concentrations of Pb average 10 g kg⁻¹, though values up to 10 wt. % of Pb have been found in the top 20 cm (Basunia and Landsberger, 2001; Wersin, 2003; Knechtenhofer et al., 2003). The high Pb levels have given rise to fears that Pb may contaminate surface and ground waters (Wersin, 2003; Astrup et al., 1999; Craig et al., 1999).

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However, this depends on the soil properties. Knechtenhofer et al. (2003) have recently found that movement of Pb, Sb, and Cu are strongly retarded in top 10 cm of a soil with 15% organic carbon and pH (water) of 3.6.

To date, few studies have been made to assess the mobility of Sb. One of the earliest studies, performed by Fahrenhorst (1993), showed that at clay pigeon shooting ranges soil-water concentrations of Sb exceeded those of Pb in neutral soils, despite the far higher solid-phase Pb content, while in acidic soils the opposite was true. Soil-water concentrations of Sb ranged between 0.5 and 133 µg L⁻¹ in the top 30 cm. Laboratory soil leaching tests, however, yielded Sb concentrations in the low mg L⁻¹ range. A similar pH dependence and concentration range was observed in preliminary laboratory leaching experiments on soil samples taken from 300-m rifle ranges (Oschwald et al., 2002; Gresch and Wettstein, 2002).

An insight into the geochemical properties of Sb may help to explain the observed solubilities. Antimony, like As, is in group (15) and exists in environmental systems in predominantly (III) and (V) oxidation states. In the pH range of most natural aquatic systems, the predominant species are Sb(OH)₃ and Sb(OH)₆⁻, respectively. The species of Sb(III) and Sb(V) have been determined in concentration ranges of 0.0003 to 0.01 and 0.01 to 0.3 µg L⁻¹, respectively, in fresh and estuarine waters (Andreae et al., 1981; Strohal et al., 1975; Middelburg et al., 1988; Filella et al., 2002). In all oxic aqueous systems investigated to date, Sb(V) is the predominant redox species (≥90% of total dissolved Sb).

Both Sb(III) and Sb(V) are strongly hydrolyzed and form complexes with sulfide. Antimony(III) forms strong complexes with chloride ions and organic ligands, in particular those with thiol groups (e.g., Anderegg and Malik, 1970; Özer and Bogucki, 1971; Brookins, 1972). Antimony(III) could thus be stabilized by complexation with organic ligands. Many sulfide and oxide minerals containing Sb [in particular Sb(III)] have been identified in rocks and mineral deposits (e.g., Boyle and Jonasson, 1984), yet very little is known of secondary minerals that may form in sediments and soils under ambient conditions. The solubility of Sb(III) may be limited by Sb₂O₃ to approximately 60 µg L⁻¹ (Baes and Mesmer, 1976), while the solubility of Sb₂O₅ is in the molar range at pH 7. Precipitation of minerals like $M(\text{II})[\text{Sb}(\text{OH})_6]_2 \cdot x\text{H}_2\text{O}$ or bindheimite-like minerals $\{M(\text{II})_2[\text{Sb}_2\text{O}_6(\text{O},\text{OH})]\}$, where M represents a divalent cation, are likely for Sb(V) (von Heffter, 1852), but there is no evidence for this in field samples.

Iron (hydr)oxides do appear to be important sorbents for Sb (Ambe, 1987, 1989; Thanabalasingam and Pickering, 1990; Gannon and Wilson, 1986; Enders, 1996) though sorption to Al (hydr)oxides has been reported by Meima and Comans (1998) and Gannon and Wilson, (1986).

Generally, Sb(III) binds to solids more strongly and over a wider pH range than Sb(V). Sorption is pH dependent. Depending on experimental conditions Sb(V) is almost completely sorbed at pH values below 7, while Sb(III) sorbs to pH values of at least 10. Blay (2000) investigated the sorption of Sb(III) and Sb(V) to components of a soil matrix including α -FeOOH, Fe₂O₃, kaolinite, montmorillonite, and illite. He found that Sb sorption to Fe (hydr)oxide was the strongest and most probably inner sphere for both Sb species. Sorption to clays was quite weak and most probably outer sphere. In sequential extractions of a soil he found that more than 90% of leachable Sb was bound to the "poorly crystalline Fe oxide" and the "crystalline Fe oxide" fractions. Antimony has also been found in association with Fe and Mn oxides in lake sediments (Müller et al., 2002; Chen et al., 2003).

The mobilization of Sb depends primarily on the corrosion of the bullets, oxidation of Sb(0) to Sb(III) and Sb(V), and processes that control the solubility of Sb(III) and Sb(V). Mineral surfaces are likely to play an important role in the oxidation process, because Sb(III) oxidation in homogenous solution with O₂ is kinetically hindered and extremely slow (Leuz and Johnson, 2004). The oxidation of Sb(III) sorbed to Mn oxides has been reported (Blay, 2000; Belzile et al., 2001). This reaction appears to be quite fast, in the order of hours to days, depending on experimental conditions. Measurements of rates of oxidation of Sb(III) by amorphous Fe oxyhydroxides have been made (Belzile et al., 2001), though the mechanism is unclear.

Because very little is known of geochemical behavior of Sb, the aim of this study is to obtain preliminary information on the solubility and oxidation state of Sb in contaminated embankment samples and to define further fields of research.

MATERIALS AND METHODS

Materials

Unless otherwise stated, experiments were performed in vessels that had been previously leached in acid solutions (3% HCl) and rinsed three times in deionized water. Deionized water (Milli-Q; Millipore, Billerica, MA) was used in all experiments. All chemicals were of ultrapure quality.

Sampling

Samples were taken from seven 300-m shooting ranges (Sites A–G) in Switzerland. The embankments were sampled at random on the side facing the targets, where the most contaminated soils are generally located (Anonymous, 1997). The term "soil" is perhaps misleading as the embankments were all artificial barriers that are often disturbed due to maintenance and erosion. Approximately 5 kg of material were taken with a shovel at 10 locations in each embankment to a depth of approximately 20 cm. In the laboratory, subsamples (2.5 kg) were dried at room temperature to constant weight and sieved into the following fractions: >10, 5 to 10, 2 to 5, 0.5 to 2, and <0.5 mm. These were then weighed. Whole bullets and bullet fragments were removed by hand from the >10- and 5- to 10-mm fractions and weighed. The three finer fractions were ground to <0.5 mm.

Solid-Phase Characterization

The elemental content of the different sample fractions was determined by X-ray fluorescence (X-Lab2000; SPECTRO Analytical Instruments, Kleve, Germany). The Sb content of the bullets was estimated from the Sb to Pb ratio analytically determined in the finer fractions for each site. It was assumed that the Sb to Pb ratio of bullets and the fine material was the same. This procedure was necessary because it was not possible to grind the Pb bullets, yet bullet fragments may contribute significantly to the total Sb concentration. Further, no single manufacturer specification can be assumed for Sb to Pb ratio, as the average age of the bullets at the sites is not known. The <0.5-mm fraction was examined using X-ray diffraction (XDS 2000 diffractometer, Cu-K α -radiation; Scintag, Cupertino, CA). Apart from calcite, quartz, anorthite, muscovite, and chlorite, no further minerals other than cerussite (PbCO₃) in Sample B could be detected.

Leaching Experiments

The <0.5-mm fraction of Samples B to G was equilibrated in water (200 mL) in the dark at different liquid to solid ratios (1–10) for 24 h at 25°C on a rotary shaker (175 rpm). Sample A was not subjected to this procedure because it was found that the bank material was composed of ash with alkaline leachates and was therefore not comparable with the other samples. Preliminary tests over 2 wk had shown that constant concentrations were achieved within 24 h (not shown here). The suspensions were then filtered through a 0.45- μ m nylon filter membrane (Whatman, Maidstone, UK). The pH values, major ion concentrations, Sb(III), and total Sb were determined in the leachates.

Batch desorption experiments were also performed as a function of pH with the <0.5-mm fraction of Sample D. Sample D was chosen because the concentrations of total Sb in the solid phase were relatively low. The procedure was performed at liquid to solid ratio = 10 and solution pH was adjusted using HCl and NaOH. The equilibration time was increased to 48 h.

Oxalate extractions were also performed on these samples in accordance with the method developed by Belzile and Chen (1999). The <0.5-mm sample fractions (0.100 g) were equilibrated on a rotary shaker (175 rpm) at 25°C with 0.1 M Na oxalate (100 mL) adjusted with HCl to pH 2.2 in the dark for 1 h. The samples were then filtered through a 0.45- μ m nylon filter membrane (Whatman) in the dark. Samples were analyzed on the same day as the filtration procedure to preserve the Sb species.

Analysis

Total Sb and Sb(III) concentrations were measured with a hydride generation atomic fluorescence spectrometer (Millennium System; PS Analytical, Orpington, UK) using the method developed by PS Analytical. For the analysis of total Sb varying but known amounts of sample leachate were placed in a polyethylene test tube, HCl (6 mL, 32% suprapure) and KI-ascorbic acid solution (0.4 mL, 3 M KI and 0.57 M ascorbic acid) were added, and the mixture was made up to 20 mL with deionized water. The samples were allowed to react for 30 min in the dark before analysis. The samples were injected into the hydride generation system at a rate of 9 mL min⁻¹ together with the carrier (300 mL 32% HCl with 20 mL of the KI-ascorbic acid solution made up to 1 L with deionized water, 9 mL min⁻¹) and the reductant (0.7% NaBH₄ in 0.1 M NaOH, 4.5 mL min⁻¹). The fluorescence was measured at 217 nm.

Table 1. Concentrations of elements in elevated concentrations in the <0.5-mm fraction of the bank samples.

Site	CaCO ₃	Organic C	Fe	Pb	Sb	Cu	Bi	Ni	Tl	Hg
	wt. %		mg kg ⁻¹							
A	7.3	7.2	8 400	515 800	17 500	4450	5140	770	2150	410
B	33.5	2.9	54 200	111 000	6 000	3050	1130	630	500	125
C	38.0	0.2	16 100	1 450	85	390	6	87	<3	<1.5
D	6.0	1.0	31 800	2 000	100	260	8	81	<3	<1.5
E	13.3	0.6	30 400	35 150	1 880	920	340	180	67	13
F	1.7	3.6	26 200	3 200	110	100	19	54	<3	<1.5
G	25.5	2.0	34 700	1 900	35	160	8	67	<3	<1.5

The analysis of Sb(III) was performed in a less acidic medium. An aliquot of sample (20 mL) was placed in a polyethylene test tube together with Na citrate (5.26 g). The salt was carefully dissolved and the sample was then injected into the hydride generation system at a rate of 9 mL min⁻¹ together with the carrier (0.5 M Na citrate, 9 mL min⁻¹) and the reductant (same as above).

Great care had to be taken to avoid sample contamination. Samples were measured in duplicate. Determination limits for Sb(III) and total Sb were 0.1 and 0.04 µg L⁻¹, respectively. Analytical precision was ±15% and the working range was 0.1 to 100 µg L⁻¹. Antimony(V) was estimated by subtracting Sb(III) from total Sb and the determination limit was 0.1 µg L⁻¹. Total Sb concentrations compared well with inductively coupled plasma mass spectrometry (ICP-MS) (SCIEX Elan 5000; PerkinElmer, Wellesley, MA).

The pH was determined with a glass calomel combination electrode (Model 6.0222.100; Metrohm, Herisau, Switzerland) and a Metrohm pH meter (605). The electrode was calibrated with pH-buffer solutions at pH 4, 7, and 10 (Merck, Darmstadt, Germany). Concentrations of Na, K, Mg, and Ca were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Ciros CCP; SPECTRO Analytical Instruments). Lead, Sb, Cu, Ni, Bi, Tl, and Hg were analyzed by ICP-MS (SCIEX Elan 5000). Concentrations of Cl, SO₄, and NO₃ were determined by ion chromatography (Model 761 Compact IC; Metrohm). Carbonate was determined using a carbon analyzer (Model 5000; Shimadzu, Kyoto, Japan).

Model Calculations

Thermodynamic equilibrium calculations were performed with the aid of the computer program MQV40TIT (Furrer, 1995, based on Westall, 1986). Stability constants were taken from Baes and Mesmer (1976), Dzombak and Morel (1990), and Johnson et al. (unpublished data, 2004). The values were corrected for ionic strength by using activity coefficients calculated by the Davies equation.

RESULTS AND DISCUSSION

Solid-Phase Characterization

The concentration of Sb in the <0.5-mm fraction of the contaminated embankment material ranged between 35 and 17 500 mg kg⁻¹ (Table 1). The total elemental concentrations for the whole samples comprising all size fractions (including bullets) were comparable with these values for the highly contaminated Samples A, B, and E but up to 10 times higher for the less contaminated samples. (The total concentrations for Sb are shown in Fig. 1). Thus, in the less contaminated samples, the uncorroded bullets make a significant contribution to the total metal content. The variability between the samples is obviously related to the shooting activity at these ranges, but it is also related to upkeep

maintenance activities and to the extent of weathering of the bullets. Added to this, the contamination is unevenly distributed over the embankment, being highest directly behind the targets. These samples cannot be regarded as representative of the statistical average composition of the banks. Instead, they are grab samples with which to assess the leachability of contaminants. The embankment material is obviously highly contaminated. Apart from the elevated concentrations of Pb, which are to be expected (Table 1), elevated concentrations of Cu, Bi, Ni, Tl, and Hg were also found. These elements are associated with the bullets and are introduced as impurities during the smelting of Pb. Copper, As, Sb, Bi, and Ag are elements typically found in Pb ingots, and are used to identify the source of bullets in forensic cases (Randich et al., 2002). The embankment material did not appear to contain elevated concentrations of As or Ag. Arsenic concentrations ranged between 1 (Sample A) and 14 (Sample E) mg kg⁻¹, while silver concentrations ranged between <3 (Samples C and D) and 32 (Sample A) mg kg⁻¹. It should be noted that the average background concentration of Sb in Swiss soils is 8.6 mg kg⁻¹ (563 samples; Anonymous, 2001), so all samples contained elevated concentrations of Sb.

The Sb to Pb ratios were found to be between 2 and 5% and with the exception of Sample F, the ratios were quite similar for the sample fractions 2 to 5, 0.5 to 2, and <0.5 mm (Fig. 2). For Sample G one might speculate that Sb was preferentially leached from the samples, particularly from the finer fractions, but too little is known of the history of this material to allow such an interpretation. The Sb to Pb ratio of 2 to 5% is in

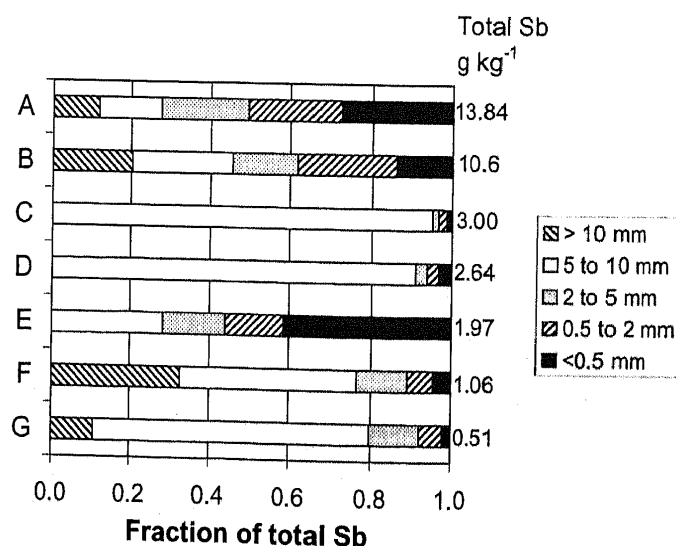


Fig. 1. The distribution of total Sb in fractions of the bank material.

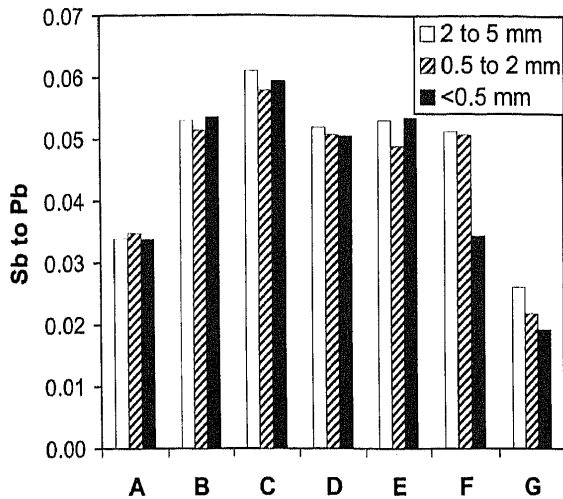


Fig. 2. The ratio of Sb to Pb in the 2- to 5-, 0.5- to 2-, and <0.5-mm fractions of the bank material.

accordance with the composition of the GP11 bullet used at these ranges (Anonymous, 1997).

The distribution of Sb between the different size fractions varies quite widely. In Samples C and D, more than 90% of Sb is found in bullet fragments with less than 3% in the <0.5-mm fraction (Fig. 1), while in Sample E more than 40% of Sb is to be found in the <0.5-mm fraction. The weathering of the bullets is related to the age and type of the embankment material and the physical attributes that might cause bullets to shatter, the climate, and the stability of the bullet. The number of samples is far too small to allow a statistical analysis of the cause.

Figure 3 shows the oxalate-extractable fraction of Sb in the <0.5-mm sample fraction, that is, the Sb that is assumed to be associated with amorphous ferrihydrites (Belzile and Chen, 1999), but could also be associated with acid-soluble components such as carbonates. The amount of total extractable Sb is around 50% in this fraction. This value is close to that found by Blay (2000) using a 0.2 M NH_4 oxalate extraction at pH 3.25. Using the same sequential extraction procedure (Zeien and Brümmer, 1989), Mergenthaler and Richner (2002) found that for the four embankment samples, between 28 and 50% of total Sb was bound to amorphous ferrihydrites. They also found, in contrast to Blay, that a significant

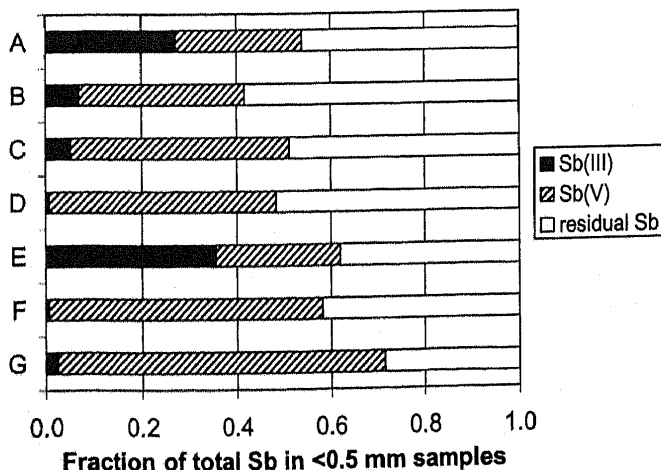


Fig. 3. Oxalate-extractable Sb(III) and Sb(V).

fraction (17–44%) was bound to organic material. The results shown in Fig. 3 indicate that apart from Sites E and A most of this extractable Sb is present as Sb(V). These results are in very good agreement with extended X-ray absorption fine structure (XAFS) analyses performed on the same samples by Scheinost et al. (personal communication, 2004). This means that the distribution of Sb between the redox states V and III of the oxalate-extractable fraction was representative of the whole sample as determined by XAFS. At present we do not have an explanation for this observation.

Leachates

Figure 4 shows the concentrations of leached total Sb as a function of water to solid ratio. With one exception, total Sb was composed to more than 99% of Sb(V) and less than 1% Sb(III) for all water to solid ratios. In Sample B, Sb(III) made up 10% of the dissolved total Sb. The leachability of Sb appears to be relatively independent of water to solid ratio for the Samples D, F, and G. For these samples, concentrations remain below 0.5 mg L^{-1} . These samples have relatively low Sb contents (Table 1). Concentrations of total Sb for Samples B and E, which have the highest solid-phase Sb content in this group, are between 3 and 6 mg L^{-1} . Concentrations appear to decrease slightly as a function of the water to solid ratio. Sample C appears to represent an intermediate case because at low water to solid ratios, concentrations are around 4 mg L^{-1} , while at high water to solid ratios they approach values close to those of D, F, and G. The marked decrease of dissolved concentrations as a function of water to solid ratio for Sample C and the less marked decreases for Samples B and E are most probably a result of reduced availability, because much more Sb has to dissolve at higher water to solid ratios.

The most likely explanation for these observations is that a combination of processes is controlling Sb(V) solu-

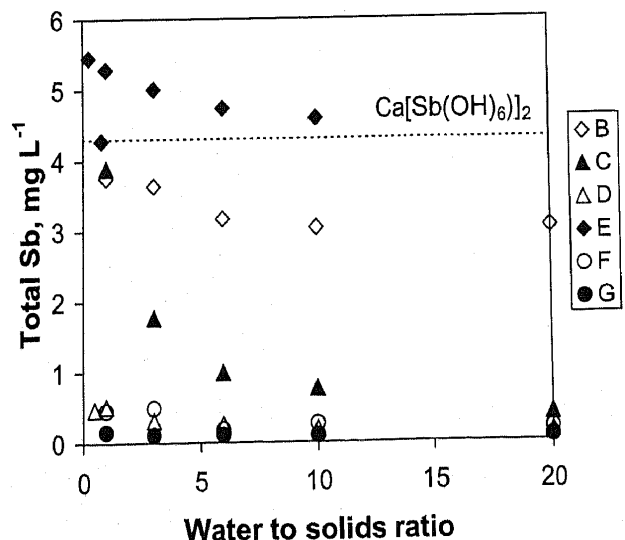


Fig. 4. Leached total Sb concentrations as a function of water to solid ratio. The solubility of $\text{Ca[Sb(OH)}_6\text{]}_2$ was calculated for an average composition of the leachate ($I = 0.005 \text{ M}$, $[\text{Ca}] = 0.0015 \text{ M}$, $[\text{total CO}_3] = 0.002 \text{ M}$, $[\text{SO}_4] = 0.0002 \text{ M}$). It is almost constant over a pH range of 4 to 9.

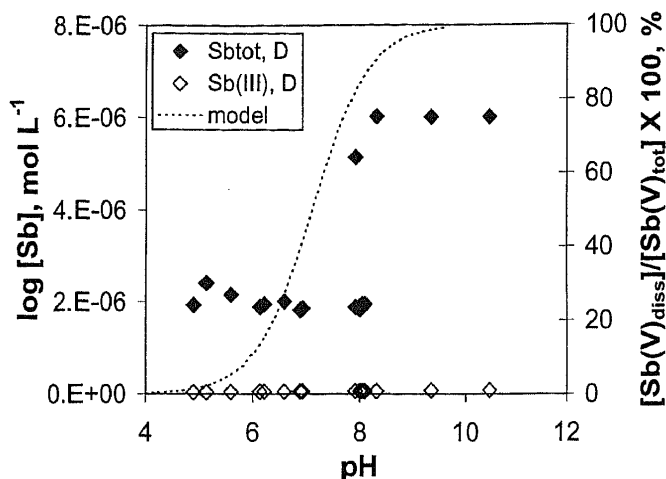


Fig. 5. Solubility of total Sb and Sb(III) as a function of pH for Sample D. The dashed line represents the calculated percentage of total Sb(V) in solution.

bility, namely the precipitation of solid phases at high concentrations and the sorption to surfaces at low concentrations. Because Ca is the predominant cation in these soil waters (0.002 M), it is possible that such a mineral could precipitate, though it is also possible that Pb antimonate may form in these samples. Recently determined solubility products of the solids $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ ($K_{so} = [\text{Ca}^{2+}][\text{Sb}(\text{OH})_6^-]^2 = 10^{-12.55}$) and $\text{Pb}[\text{Sb}(\text{OH})_6]_2$ ($K_{so} = [\text{Pb}^{2+}][\text{Sb}(\text{OH})_6^-]^2 = 10^{-11.02}$) synthesized in the laboratory (Johnson et al., unpublished data, 2004) allow the calculation of Sb(V) solubilities at equilibrium with these solid phases. Adopting the average leachate composition ($I = 0.005 \text{ M}$, $[\text{Ca}] = 0.0015 \text{ M}$, $[\text{total CO}_3] = 0.002 \text{ M}$, $[\text{SO}_4] = 0.0002 \text{ M}$), the solubilities of Sb(V) in equilibrium with Ca and Pb antimonate at pH 8 are 4 and 300 mg L^{-1} , respectively. In addition to this, the total dissolved Pb concentration would be a little less than 150 mg L^{-1} . It is unlikely that Pb antimonate would control the solubility of Sb, though it may form locally, for example at the surface of corroding bullets. The agreement between the measured concentrations of Samples B and E and the calculated solubility of Ca antimonate is very good. The total solid-phase concentration of Sb in Samples D, F, and G is one to two orders of magnitude lower than that of Samples B and E. The leachate of these samples is clearly undersaturated with respect to Ca antimonate.

The relationship between pH and dissolved Sb(V) and Sb(III) concentrations is shown in Fig. 5 for the <0.5-mm fraction of Sample D. This sample was chosen because the Sb content was sufficiently low to assume that sorption is the dominant solubility-limiting process for Sb. Overall, the dissolved concentrations of Sb(V)

Table 2. Concentrations and pH values of selected components in batch leaching experiments at a water to solid ratio = 1.

Sample	pH	$\mu\text{g L}^{-1}$						
		Sb	Pb	Ni	Cu	Bi	Tl	Hg
B	8.21	3750	20 860	22	100	18	<2	500
C	7.75	3890	180	12	90	2	<2	<20
D	8.59	510	240	18	140	<2	<2	<20
E	7.78	3525	720	15	105	8	<5	<50
F	8.54	450	540	20	84	50	<2	<20
G	8.43	150	4	12	76	<2	<2	<20

are around 100 times higher than the Sb(III) concentrations. Desorption of Sb(V) is observed at pH values above 8. This is in agreement with literature studies of the pH dependence of Sb(V) sorption to $\alpha\text{-Fe}_2\text{O}_3$ and to $\gamma\text{-Fe}_2\text{O}_3$ (Ambe, 1987, 1989). The dotted line shows an estimate of the percentage of Sb(V) in solution using surface complexation constants derived by Dzombak and Morel (1990) from linear-free energy relationships with deprotonation constants. Assuming from Dzombak and Morel (1990) that all the Fe is present as hydrous ferric oxide with a surface area of 600 $\text{m}^2 \text{ g}^{-1}$, a site density of 3 $\text{mmol g}^{-1} \text{ Fe}$, and an Fe content of 3%, a sorption capacity of around 90 mg kg^{-1} is estimated for the embankment samples. Because sorption to Fe (hydro)xides is known to be about 100 times stronger than to clays (Blay, 2000), it is possible that ferric solids provide sufficient sorption capacity for Samples D, F, and G, but that the Sb content of Samples B and E is just too high. The agreement between the model and measured desorption curve is quite good considering the many assumptions. However, it should be noted that only 7% of the total Sb content of the sample is desorbed, while the model would predict 100%. It must therefore be concluded that most of the Sb(V) is not reversibly bound to Fe (hydro)oxide surfaces and may be bound in association with other mineral constituents. Further information is required regarding the binding mechanisms of Sb(III) and Sb(V) to the solid phase.

The elements listed in Table 1 were analyzed in the leaching experiments (Table 2). It was found in most of cases that total Sb concentrations were higher than for the other components. Lead concentrations were also found to be rather high ($\geq 150 \mu\text{g L}^{-1}$ except for Sample G). All leachates showed Cu concentrations in the range of about 100 $\mu\text{g L}^{-1}$, whereas those for Ni and Bi were considerably lower. Thallium and Hg concentrations were below detection levels, except for Sample B, which showed high Hg levels (Table 2).

Chemical equilibrium calculations were performed for leachate compositions with a water to solid ratio = 1 (Table 3) using thermodynamic data (Nordstrom et al.,

Table 3. Concentrations and pH values of main components in batch leaching experiments at a water to solid ratio = 1

Sample	pH	TOC†	Na	K	Mg	mmol L^{-1}				
						Ca	Cl	SO ₄	NO ₃	HCO ₃
B	8.21	2.22	0.043	0.010	0.25	0.3	0.056	0.198	0.086	1.185
C	7.75	1.58	0.304	0.008	0.2	0.3	0.085	0.260	<0.2	1.279
D	8.59	3.85	0.087	0.016	0.4	1.9	0.197	0.239	<0.2	2.611
E	7.78	2.08	<0.2	0.000	0.23	1.17	0.000	0.000	0.000	0.000
F	8.54	8.49	0.087	0.004	0.1	3.1	0.254	0.229	<0.2	3.263
G	8.43	4.18	0.087	0.012	0.3	2.1	0.085	0.239	0.214	3.237

† Total organic carbon.

Table 4. Calculated solubilities controlled by mineral phases in leachates at a water to solid ratio = 1.

Sample	Element				
	Pb†	Pb†	Cu†	Ni‡	Bi‡
	Solid phase				
	Cerussite	Hydrocerussite	Malachite	NiCO ₃	α-Bi ₂ O ₃
	mg L ⁻¹				
B	0.28	0.40	0.21	0.06	0.83
C	0.29	0.58	0.14	0.16	0.83
D	0.31	0.40	0.23	0.02	0.83
E	0.28	0.62	0.13	0.12	0.83
F	0.31	0.45	0.20	0.02	0.83
G	0.30	0.48	0.2	0.02	0.83

† Stability constants for Pb and Cu taken from Nordstrom et al. (1990).

‡ Stability constants for Ni and Bi taken from Hummel et al. (2002).

1990; Hummel et al., 2002) to check solubility control by solid phases for Pb, Cu, Ni, and Bi (Table 4). The results for Pb indicate that this element may be controlled by the solubility of cerussite or hydrocerussite at Sites C, D, E, and F (compare Tables 2 and 4). In fact, both Pb phases have been frequently reported in bank materials of shooting ranges (Lin, 1996; Murray et al., 1997; Jørgensen and Willems, 1987; Chen et al., 2002). The very high Pb concentrations (20 mg L⁻¹) in Sample B might be due to colloidal particles remaining in the filtrate. All observed Cu concentrations are in the same range as expected from malachite equilibrium. On the other hand, the observed Ni concentrations are generally lower than expected from equilibrium with NiCO₃, which is the stable mineral phase according to thermodynamic calculations. Bismuth also does not appear to be controlled by solid-phase equilibrium with α-Bi₂O₃, but the available thermodynamic data may not be reliable enough to draw a conclusive statement on this aspect.

CONCLUSIONS

These experiments show the potential of the bank material to release heavy metal and metalloid ions. For antimony the mobile fraction appears to be Sb(V) and the precipitation of Ca antimonate may play a role in controlling the solubility. A significant fraction of Sb in the <0.5-mm fraction is oxalate extractable, indicating an association with amorphous ferrihydrites, but also possibly with solid phases, such as carbonates, that are soluble at pH 2. There are indications that only a fraction of Sb(V) is reversibly sorbed to mineral surfaces. In lower soil layers, as Sb concentrations decrease, sorption is likely to become the more important solubility-controlling process. To be able to predict the long-term mobility of Sb at shooting ranges it will be necessary to further elucidate the binding mechanisms of both Sb(III) and Sb(V) in soils and the redox processes that control the oxidation of Sb(III).

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