Short communication

Antimonate sorption in soils increases with ageing

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Summary

It is unclear to what extent sorption of antimony (Sb) in soils proceeds over long time scales. This study was set up to monitor slow reactions (7 days to 6 months) of Sb in Sb(V)-spiked soil samples during aerobic incubation. The solid-liquid distribution coefficients (K_D) increased by factors of 3 to 6 between 7 and 190 days after spiking, depending on the soil. This increase in K_D value, hereafter named the Sb ageing factor, increased with increasing amorphous iron and aluminium hydroxide concentration and decreasing pH of the soil samples. Finally, ageing factors were highest in topsoils and could be important in preventing Sb from migrating downwards into groundwater bodies.

Keywords: antimony, antimonate, sorption, ageing, soils, risk assessment

Highlights:

- Quantification of antimonate ageing in soils.
- Topsoils could prevent downward leaching of Sb on the long-term.
- Ageing of Sb increased in soils with increasing amorphous iron and aluminium hydroxide concentration and decreasing pH.
- Slow sorption reactions reduce Sb mobility in soils.

Introduction

Antimony (Sb) is potentially toxic to aquatic species and plants at elevated concentrations (Nam *et al.*, 2009; Oorts *et al.*, 2008). Sorption kinetics of the more oxidized, pentavalent antimony (Sb(V)) on pure minerals and in soils is typically biphasic, i.e. an initial fast sorption phase is followed by a prolonged slower sorption phase. Studies of Sb(V) sorption on ferrihydrite, iron (Fe)-hydroxide coated sand and in soil samples with a wide range of soil properties showed that added Sb(V) concentrations initially decrease quickly (~minutes to hours), while a slow decrease in Sb(V) concentrations is noted over prolonged equilibration times (~hours to days) (Cai *et al.*, 2015; Fan *et al.*, 2013; He *et al.*, 2014; Martínez-Lladó *et al.*, 2011; Zhang *et al.*, 2014).

The risk assessment of Sb often relies on studies with freshly Sb-spiked soils (~weeks) (Tschan *et al.*, 2010). These freshly spiked soils bear little relationship with soils affected by historical contamination, therefore ageing studies are recommended to translate short-term data to field conditions (Degryse *et al.*, 2009; Smolders *et al.*, 2009). As far as known, only Zhang *et al.* (2014) studied long-term Sb(V) sorption in soils for up to one month. Long-term changes in sorption of the antimonate analogues phosphate (P(V)) and arsenate (As(V)) are well reported and soluble element concentrations in soils can decrease by a factor ~3 (P(V)) and ~2 (As(V)) for differences in reaction time between ~one week and ~3 months (Barrow, 1983; Wang *et al.*, 2017).

In this study, changes in Sb sorption over time were monitored and related to the variation in soil properties along a sampled soil profile up to 3 m depth, to identify possible mechanisms

of Sb ageing. Soil samples were spiked with Sb(V) and incubated under field-moist, aerobic conditions for up to 6 months. It is hypothesized that the mobility of added Sb(V) will significantly decrease in the long-term, similar as observed for other oxyanion forming elements.

Materials and methods

A 3 m deep soil profile was excavated in a Stagnic Luvisol under agricultural grassland in NE France (Crespy-le-Neuf, 48°24'11''N, 4°37'44''E). Nine soil samples were collected from different depths to obtain samples with a gradient in properties affecting oxyanion sorption, as demonstrated in Verbeeck *et al.* (2017, 2019). Samples were 2 mm sieved, air-dried and homogenized with a mortar. The pH, soil organic carbon (OC), effective cation exchange capacity (eCEC), carbonate content (CaCO₃) and amorphous Fe, aluminium (Al), manganese (Mn) and associated phosphorus (P) were determined with standard methods in duplicate, fully described in Verbeeck *et al.* (2017) and briefly repeated in the Supporting Information.

Sb(V) ageing

Thirty grams air dry soil from each sampling depth was either spiked or not spiked with a KSb(OH)₆ stock solution (Sigma Aldrich, Saint-Louis, USA), to provide a nominal added dose of 42 µmol Sb(V) kg⁻¹. This dose was chosen to examine Sb(V) ageing in the linear sorption range, as suggested by sorption isotherms (Fan *et al.*, 2013; Martínez-Lladó *et al.*, 2011; Verbeeck *et al.*, 2019). Samples were wetted to a gravimetric water content of 21 – 25% and mixed with a spoon. Soil Sb concentration in control and spiked samples was determined by a four acid digestion. Fifty mg of soil was weighed into Savilex Teflon

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beakers. Concentrated HNO_3 (65%), HClO_4 (70%) and HF (48%) were added consecutively, with digestion in a closed system and evaporation near dry between each acid addition step. The residual digest was dissolved in 2.5 M HCl (full protocol in Supporting Information). Solution Sb concentrations were measured by inductively coupled plasma mass-spectrometry (ICP-MS; Agilent Technologies, Santa Clara, USA; no reaction gas or collision cell was used, $m/z = 121$). Control samples were analysed without replicates, spiked samples were analysed in duplicate. A reference sample (PACS-2 marine sediment, National Research Council of Canada, Ottawa, Canada) was included in each analysis batch in duplicate.

The samples were subjected to two drying-rewetting cycles to promote fixation, by (i) drying at 60 °C overnight, (ii) rewetting to the initial water content, (iii) drying at room temperature for three days and (iv) rewetting. Drying overnight at 60 °C did not largely affected Sb sorption kinetics over time, tested up to one month in an additional experiment (Table S1). For 6 months, samples were incubated at 19 ± 2 °C in 50 mL tubes with screw caps, regularly opened and stirred. Final gravimetric water content ranged between 9 – 25 g 100 g⁻¹ oven-dry soil. Immediately after spiking (but before drying-rewetting), after 33 and after 183 days, duplicate samples of 2.5 g (oven-dry basis) were taken, suspended in 25 ml of a 5 mM $\text{Ca}(\text{NO}_3)_2$ solution and centrifuged at 3000 *g* for 30 minutes after 7 days. Antimony, Fe and Mn in solution were measured with ICP-MS after filtering the supernatants over a 0.45 µm filter (Chromafil Xtra PET 45/25; Macherey–Nagel, Düren, Germany) and pH was monitored. Total equilibration time was thus 7, 40 and 190 days.

Antimonate solid-liquid distribution coefficients (K_D , in l kg⁻¹) were calculated as

$$K_D = \frac{M_{\text{soil,added}} - (M_{\text{sol,f}} - M_{\text{sol,c}}) \times V/W}{M_{\text{sol,f}} - M_{\text{sol,c}}} \quad (1)$$

with $M_{\text{soil, added}}$ the added Sb(V) concentration, $M_{\text{sol,f}}$ the final soluble Sb concentration in the 5 mM $\text{Ca}(\text{NO}_3)_2$ extracts of spiked samples, $M_{\text{sol,c}}$ the soluble Sb concentration in the corresponding, non-spiked, control sample, V the volume of the solution (l) and W the mass of oven-dry soil (kg). These K_D values quantify the sorption of the added Sb and are, in case of linear sorption, equal to the K_D of the native Sb (Degryse *et al.*, 2009). Ageing factors of Sb K_D values were calculated as the ratio of the K_D values measured at 40 or 190 days with the mean K_D measured at 7 days of the corresponding soil sample. The ageing factors were then correlated (Pearson's correlation) with soil properties ($\log_{10}$ -transformed when distribution was skewed; summary statistics in Table S2).

Results and discussion

Soil properties are presented in Table 1. The detection limit of soil Sb was $0.4 \mu\text{mol Sb kg}^{-1}$. The certified Sb concentration in the reference sample was $93 \pm 21 \mu\text{mol Sb kg}^{-1}$ whereas $81 \pm 4 \mu\text{mol Sb kg}^{-1}$ was measured (means with 95% confidence interval). Antimony concentrations in the control samples were close to the median value in European agricultural soils, i.e. $2 \mu\text{mol Sb kg}^{-1}$ (*aqua regia* soluble; Reimann *et al.* (2014)), while *aqua regia* soluble Sb is about 35% of total Sb in our soils (data not shown). From the nominal added dose in the long-term ageing experiment ($42 \mu\text{mol Sb kg}^{-1}$), $33 - 39 \mu\text{mol Sb kg}^{-1}$ was recovered (78 – 93 %), calculated as the difference between the spiked and corresponding control sample (Table S3). The coefficient of variation (CV) of the Sb concentration in the spiked soils was always $< 8\%$.

After 7 days, 28 to 35 $\mu\text{mol Sb kg}^{-1}$ was adsorbed by the 9 different samples, which relates to an average molar Sb: ($\text{Fe}_{\text{ox}}+\text{Al}_{\text{ox}}$) ratio of 0.001. Antimony spiking did not alter soil pH within 0.2 units and did not affect the slight pH changes during incubation (Table S3). Spiking increased the Sb concentrations in the soil extracts from $\sim 0.0003 \mu\text{M}$ to $\sim 0.4 \mu\text{M}$ Sb (Figure 1). The CV of duplicate analyses ranged between 1 – 46%, with an average of 14%, for the control samples while this was 0.01 – 7 %, with an average of 2 % for the Sb(V)-spiked samples. Upon ageing, the Sb concentrations significantly decreased by a factor of 2 to 3 between 7 and 40 days and by a factor of 3 to 6 between 7 and 190 days. In one control sample (P1_125), the Sb concentration significantly, but marginally, increased, i.e. by a factor of 1.3 between 7 and 190 days (Figure 1). Zhang *et al.* (2014) also found a decrease in soluble Sb concentration by a factor of 2 between 7 and 30 days, at Sb additions of 14.8 mmol kg^{-1} .

Calculated Sb(V) K_D values (Eq.1) are presented in Table 1 and are within the range of previously reported values, i.e. 4 – 5500 l kg^{-1} (Janik *et al.*, 2015). The ageing factors (7 – 190 days) increased with increasing oxalate-extractable Fe and Al concentration in soil and with decreasing soil pH (Figure 2). First, the topsoil horizons of the sampled profile had greater ageing factors than deeper sampled horizons (Figure 2) and had greater oxalate-extractable Fe and Al concentration (Table 1). A larger ageing factor might be explained by a larger fraction of interior binding sites, of, for example, larger particles in soils with higher Fe and Al concentrations. Increased ageing factors (i.e. more fixation) for cationic metals have previously been associated with increased soil Fe concentration (Buekers *et al.*, 2007). Alternatively, the Fe and Al hydroxides in topsoils may be more amorphous and have a

greater microporosity than the hydroxides in subsoils due to more weathering and periodic dissolution/precipitation in topsoils than in subsoils. Increasing microporosity of Fe oxyhydroxides increases ageing reactions of phosphate (Warrinnier *et al.*, 2018). Second, the pH effect on ageing of Sb is in line with its effect on sorption, i.e. sorption of the antimonate anion increases when pH decreases due to increased positive charge (Janik *et al.*, 2015; Leuz *et al.*, 2006; Tighe *et al.*, 2005; Verbeeck *et al.*, 2019). Similar to what was found for antimonate in this study, arsenate ageing factors are also higher in acid soils (Tye *et al.*, 2002; Wang *et al.*, 2017). The small changes in pH for some samples during the incubation do not change this observation, as the ageing factors were also negatively correlated with the initial soil pH ($r = -0.52$ after 40 days; $r = -0.87$ after 190 days; $p < 0.05$ for both).

Based on these observations, it is speculated that Sb(V) ageing is due to solid-state diffusion from initially surface adsorbed Sb(V) to interior binding sites of the Fe and Al hydroxides, similar as suggested for phosphate (Barrow, 1983) and arsenate (Wang *et al.*, 2017). Precipitation of Sb(V) with calcium (Ca) is likely not a mechanism causing Sb(V) ageing in our study, because the Ca–Sb $\log_{10}$ transformed ion activity products are always < -14 (M^3), which is lower than reported solubility products for different possible Ca–antimonate precipitates ($\log_{10} K_s = -9.6$ to -12.6) (Cornelis *et al.*, 2011; Johnson *et al.*, 2005; Oorts *et al.*, 2008). Finally, reduction of the initially adsorbed Sb(V) to Sb(III), which is often reported to sorb more strongly than Sb(V), could result in higher Sb retention (Guo *et al.*, 2014; Leuz *et al.*, 2006; Qi & Pichler, 2016). However, the concentrations of Fe and Mn in the 5 mM $\text{Ca}(\text{NO}_3)_2$ extracts after 40 and 190 days of aerobic incubation remained $< 0.2 \text{ mg l}^{-1}$ (Table S4). This indicates that likely no reducing conditions developed during the 190 days of

aerobic incubation (Hockmann *et al.*, 2014), leaving the redox speciation of the added Sb(V) unchanged.

To conclude, soils affected by historical contamination could have lower Sb mobility and bioavailability of Sb than recently contaminated soils, similar to other oxyanion forming elements like P, arsenic and selenium (Barrow, 1983; Tolu *et al.*, 2014; Wang *et al.*, 2017). Finally, topsoils are possibly important in preventing Sb from migrating downwards into groundwater bodies. However, further research focusing on the mechanisms underlying these ageing effects could help to improve the understanding and prediction of longterm Sb mobility in soils.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure captions

Figure 1 Semi-log₁₀ plot of total dissolved Sb in a 5 mM Ca(NO₃)₂ 1:10 solid:liquid soil extract of Sb(V) spiked soils (upper points) that were incubated field-moist for up to 6 months. On average, the concentration of Sb in non-spiked, control samples (lower points) did not change significantly with time. Lines connect mean values of duplicate data of each spiked (full lines) or control (dotted lines) soil ($n = 9$). Error bars present one standard error above and below means.

Figure 2 Factor change in Sb K_D (ageing factor; values relative to the day 7 data) increases with (a) increasing Fe and Al hydroxide concentrations, (b) with decreasing pH and (c) is greatest in topsoil samples. Mean values are presented with one standard error above and below presented by the error bars ($n = 2$; error bars not visible when smaller than the marker). Lines are linear regressions when significant and are presented to guide the eye.

Tables

Table 1 Soil properties of soil samples, collected at various depths (depth given in sample name, in cm below surface). Mean values from duplicate analyses are presented (except for Sb_{tot} , which was measured without replicates). The K_D values were calculated at three different incubation times, and means are presented with standard error of duplicate analysis. The pH and Sb in solution are presented for the control soils measured after 7 days.

Sample	pH	OC ^a	eCEC ^b	CaCO ₃	Fe _{ox} ^c	Al _{ox} ^c	Mn _{ox} ^c	P _{ox} ^c	Sb _{tot} ^d	Sb _{sol} ^e	K_D Sb(V) /l kg ⁻¹		
		/g kg ⁻¹	/cmol _c kg ⁻¹	%			/mmol kg ⁻¹		/μmol kg ⁻¹	/nM	7 days	40 days	190 days
P1_10	5.7	39	19	<1	83	23	5.3	8.7	3.4	1.3	86±2	230±5	560±10
P1_25	6.5	8	14	<1	47	25	7.0	3.5	4.5	0.6	110±1	270±1	460±24
P1_35	6.7	3	15	<1	20	30	4.3	0.9	3.9	0.2	140±1	340±1	570±12
P1_60	7.3	1	17	<1	11	34	1.5	0.3	4.4	0.3	110±6	320±9	480±6
P1_125	7.2	<1	19	<1	11	24	14.9	0.5	4.9	0.2	110±1	260±5	400±5
P1_180	7.2	3	15	22	6	10	1.0	1.3	3.8	0.5	51±1	110±1	180±1
P1_200	7.3	2	16	9	8	14	2.4	2.4	4.5	0.4	54±1	120±1	190±1

P1_225	7.3	3	15	7	7	15	0.6	2.0	3.7	0.4	53±1	110±1	180±1
P1_280	7.2	4	18	8	7	12	0.5	1.6	3.6	0.2	56±1	100±1	170±1

^aorganic carbon; ^beffective cation exchange capacity; ^coxalate-extractable Fe, Al, Mn and P; ^dSb extracted with four acid digestion; ^eSb in

solution of a 1:10 solid:liquid 5 mM Ca(NO₃)₂ soil extract of the non-Sb(V) spiked soil