Validation and deployment of a quantitative trapping method to measure volatile antimony emissions

Jaime N. Caplette, Matthias Grob, and Adrien Mestrot*

Institute of Geography, University of Bern, Hallerstrasse 12, 3012, Bern, Switzerland

(11 pages, 4 tables, 1 Figure)

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*Corresponding author e-mail: adrien.mestrot@giub.unibe.ch

S1 Materials and Instruments

Two stock solutions of 1000 mg L^{-1} Sb in ultrapure water were prepared from potassium antimony^{III} tartrate hydrate (99.9%) and trimethyl antimony^{V} dibromide ($TMSbBr_2$, 98%) (Sigma Aldrich Inc., St. Louis, USA) solutions Supra-pur HCl (32%) and HNO_3 (69%) produced by distillation (Merck, Darmstadt, Germany) of p.a. grade acids in a clean-air lab were used throughout the experiments. Fluoroboric acid (HBF_4, 48 %) and trace-analysis grade ($\geq$ 30%) H_2O_2 were purchased from Sigma Aldrich Chemie GmbH, Buchs, Switzerland. Ultra-pure water (18.2 M·Ω) from a Millipore Q-Gard® 2 purification system was used throughout the experiments. Silver nitrate ($AgNO_3$, 99.7 %) was purchased from Thermo Fisher Scientific Inc. Ammonium tartrate was purchased from Sigma Aldrich (99.5%, St Louis, MO, USA) and methanol (MeOH, 99.9%) was purchase from Merck Millipore Inc. Sodium borohydrate ($NaBH_4$) was purchase from Sigma Aldrich Inc. (trace metal basis, 99.99%, St. Louis, USA) and NaOH from Carl Roth (99%, Karlsruhe, Germany). Tedlar® bags (5 L), silica gel sorbent tubes (226-10) and activated coconut charcoal sorbent tubes (Anasorb CSC, 226-01, surface area of 180 m^2) were purchased from SKC Inc., Eighty Four, USA. Tubing used for the hydride-generation (HG) experiments were silicon ($Ø_{int}$ = 4 mm, NOVOsil™, Fisher Scientific). Tubing used for the incubation experiments was Pt-cured silicone tubing ($Ø_{int}$ = 3.35 mm, VWR International, Dietikon, Switzerland). PTFE septa (20 mm) for the reactor vessels were purchased from Supelco, Bellefonte, USA. A 100 mL syringe (100MR-LL-GT syringe) was purchased from SGE Analytical Science, Bellefonte, USA. All glassware and microwave Teflon vials before use were soaked overnight in 10% HNO_3 and rinsed with ultrapure water prior to use.

A MARS 6 microwave (CEM, Germany) was used for the digestion of the solid-phase traps. An Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) 7700x series (Agilent Technologies, Waldbronn, Germany) was used for total Sb analysis. For Sb speciation analysis of the liquid chemotraps, an HPLC (1200 Series, Agilent Technologies) was coupled to the ICP-MS. The HPLC column used for Sb species separation was a Hamilton PRP X100 anion exchange column (10 mm, 4.6 x 150 mm (PEEK), Reno, NV.). A temperature- and humidity-controlled incubator was used for the incubation experiments (HPP 260, Memmert GmbH + Co. KG, Buchenbach, Germany) and diffusor air pumps (Eheim air pump 400, EHEIM GmbH & Co. KG, Deizisau, Germany) for continuous head-space sampling of soil incubations.

S2 Antimony in Blank Trap Sections

The Sb background for the entire solid-phase trap (silica wool, AC, and foam) was 9.7 ± 0.5 ng. In order to investigate the high Sb background, the solid-phase traps were separated, and individually digested with aqua-regia (method described in S3 below) (Fig. S1). According to the results and to reduce the Sb background, the silica wool was discarded from the solid-phase traps, and only the foam and AC were digested (Fig. S1).

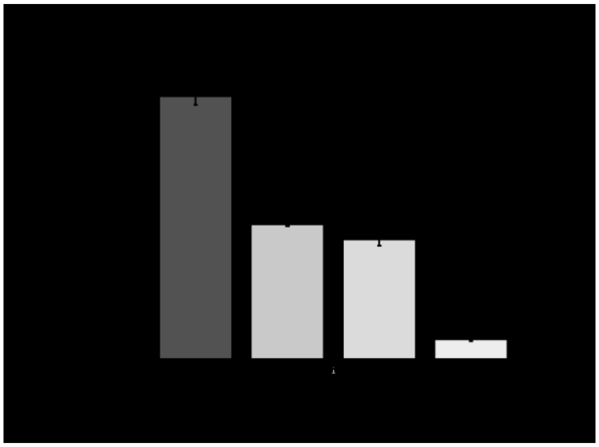

Figure S1. The amount of Sb_t (ng) in the different AC solid-phase trap sections (n = 3). Bars height represent the mean value and error bars, plus one standard deviation. AC: activated charcoal.

S3 Digestion Protocol: Solid-phase Traps

The digestion of solid-phase trap contents was performed using an aqua-regia microwave-assisted digestion, 6 mL of 32% HCl and 2 mL of 69% HNO_3 were added to the samples in closed Teflon vessels. The microwave program is shown in Table S1. Additionally, the silica-gel solid-phase traps were digested using a closed-vessel fluoroboric acid digestion where 2 mL of 48% HBF_4 and 6 mL of 69% HNO_3 were added to the samples using the same microwave program (Table S1). Method blanks and blank traps were digested with each digestion batch. After digestion, samples were cooled to room temperature, transferred to 50-mL corning tubes, filled to 50 mL with ultrapure water and stored at 4°C until analysis. Prior to ICP-MS analysis, a 10-mL aliquot of sample was filtered through a 0.45 µm syringe filter and then diluted 1:1 with ultrapure water .

Stage	Ramp	Hold	Temperature (°C)	Power
1	10	10	120	1200
2	10	40	175	1800

Table S1**.** Microwave program for aqua-regia and fluoroboric acid digestion.

S4.1 Soil Digestion: Multielement

250 mg of finely ground freeze-dried soil was weighed into 50-mL corning tubes. First, 4 mL of 69% HNO_3 was added to the soil, the soil was then left overnight, and the next day 2 mL of >30% H_2O_2 was added to the soil in intervals. The soil was digested following the microwave program in Table S3. Certified reference materials: NIST2709a (San Joaquin) and NIST 2711a (Montana II soil) were used for quality control and recoveries are reported in Table S4.

Stage	Ramp	Hold	Temperature (°C)
1	5	10	55
2	5	10	75
3	5	30	95

Table S2. Microwave program for multi-element digestion of soils.

S4.2 Soil Digestion: Antimony

100 mg of finely ground, freeze-dried soil was weighed onto wax paper and transferred to the Teflon vials. The soils were digested using an aqua-regia microwave-assisted digestion, 6 mL of 32% HCl and 2 mL of 69% HNO_3 was added in closed Teflon vessels. The microwave program is in Table S1. A certified reference material, NIST 2709a (San Joaquin) (n = 3), and method blanks (n = 3) were used for quality control and the recoveries are reported in Table S4.

	Multielement Digestion (S5.1)									Sb Digestion (S5.2)
	Al	Ca	Fe	Mn	Ni	Cu	Zn	As	Pb	Sb
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Blank	<0.0004	<0.001	<0.0004	<0.00001	<0.000016	<0.000103	0.000621	0.000008	<0.001	<0.000021
Manure	391.1 ± 29.6	1459.0 ± 32.9	1255.2 ± 20.0	149.8 ± 2.1	2.4 ± 0.04	40.0 ± 1.6	195.2 ± 0.4	0.6 ± 0.02	5.7 ± 0.4	0.1 ± 0.006
San Joaquin	15037.6 ± 609.2	2371.6 ± 89.6	24176.3 ± 1141.4	496.2 ± 3.1	64.8 ± 0.8	25.9 ± 0.7	80.2 ± 2.3	6.3 ± 0.7	9.5 ± 0.2	1.1 ± 0.02
Montana II	12896.7 ± 498.2	2694.2 ± 68.0	13694.7 ± 327.5	556.1 ± 4.1	13.6 ± 0.1	129.8 ± 2.4	352.0 ± 3.0	90.0 ± 0.6	1328.2 ± 9.1	NA
Laupen	6934.0 ± 226.6	6614.9 ± 348.1	9403.9 ± 300.3	375.5 ± 19.9	22.6 ± 1.7	462.2 ± 161.4	521.4 ± 22.0	8.9 ± 9.4	7717.0 ± 1851.9	75.5 ± 6.2
	recovery (%)	recovery (%)	recovery (%)	recovery (%)	recovery (%)	recovery (%)	recovery (%)	recovery (%)	recovery (%)	recovery (%)
San Joaquin	20.4 ± 0.8	12.4 ± 0.5	72.0 ± 3.4	93.8 ± 0.6	76.2 ± 0.9	76.4 ± 2.1	77.8 ± 2.3	59.5 ± 6.7	54.7 ± 1.3	69.2 ± 1.4
Montana II	19.2 ± 0.7	11.1 ± 0.3	48.6 ± 1.2	82.4 ± 0.6	62.7 ± 0.3	92.7 ± 1.7	85.0 ± 0.7	84.1 ± 0.5	94.9 ± 0.6	*NA*

Table S3. Average concentration with standard deviation (mg kg^{-1}) (n = 3) of major, minor and trace elements in soil CRMs, Laupen shooting range soil, and manure amendment (top rows) and recoveries of CRMs (%) (bottom rows). NA indicates that the sample was not measured during digestion. Blank refers to method blank ran during the digestion.

S5 ICP-MS Parameters for Sb analysis

	No Gas
RF Power (W)	1550
Carrier gas flow rate (L min^{-1})	1.2
Nebulizer pump (rps)	0.1
Spray chamber (ºC)	2
Make up Gas	0
Lenses	
Extract 1 (V)	-4
Extract 2 (V)	-200
Omega bias (V)	-100
Omega lens (V)	9.9
Cell entrance (V)	-30
Cell exit (V)	-50
Deflect	12.6
Plate bias	-40
Reaction cell	
OctP bias (V)	-8
OctP RF (V)	170
Energy discrimination (V)	5

Table S4. ICP-MS (Agilent 7700x series) instrument settings for total Sb analysis.

S6. Response of Inorganic Sb and TMSbO standards in ICP-MS

As explained in the manuscript, the efficiencies of $(CH_3)_3Sb$ trapped were >100% when the concentration of the TMSbO standard solution for HG reaction was done using an Sb_{IO} calibration curve. Therefore, we determined the ICP-MS sensitivity (counts per second, CPS) for Sb_{IO} and TMSbO standard solutions. The sensitivity was 615 318 ± 0.004 CPS for Sb_{IO} and 492 449 ± 0.005 for the TMSbO, i.e., for the same amount of Sb, the Sb_{IO} has approximately 25% higher ICP-MS signal compared to TMSbO ($Sb_{IO}/Sb_{TMSbO} = 1.25$).

The recoveries for the solid-phase traps (or "trapping efficiencies") are calculated as:

$$\text{Recovery} = (Sb_{trap,actual})/\ (Sb_{trap,expected})\ \text{x}\ 100 \qquad \text{Eq. 1}$$

Where:

$Sb_{trap,actual}$: is the amount of Sb trapped on the AC traps measured by ICP-MS

$Sb_{trap,expected}$: is the amount of Sb expected to be trapped on the AC traps calculated from the equation below.

The amount of Sb expected on the AC solid-phase trap is calculated by:

The actual concentration of Sb standard (measured by ICP-MS), corrected for dilution factor, and then calculated from solution yielding the volatile Sb produced

$$\text{Actual Sb on trap} = ((\text{TMSbO x } V_{std})/V_{gas}) \text{ x } V_{trapped} \qquad \text{Eq. 2}$$

Where:

TMSbO = concentration of TMSbO standard added for HG

V_{std} = Volume of TMSbO standard added to reactor vessel for HG

V_{gas} = amount of gas produced through experiment, this is approx. 3L but corrected for variation by measuring the V of gas in the Tedlar bag after trapping

$V_{trapped}$ = volume of gas trapped on AC traps (300 mL)

When AC solid-phase traps are digested the C-Sb bond is most likely broken, and therefore are measuring Sb_{IO} in the solid-phase trap digests.

Whereas, when the TMSbO standard is measured by ICP-MS this yields a smaller signal than the same concentration for Sb_{IO} in ICP-MS. When the TMSbO standard is corrected for the volume trapped on a solid-phase trap using Eq. 2 the amount of Sb trapped is less.

When comparing the trapping efficiencies using Eq.1 there is an over estimation of Sb trapped on the solid-phase traps because comparing Sb_{IO} measured in the ICP-MS vs. TMSbO measured in the ICP-MS which have higher and lower signals, respectively.