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

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ABSTRACT

Microbial-mediated Sb volatilization is a poorly understood part of the Sb biogeochemical cycle. This is mostly due to a lack of laboratory and field-deployable methods that are capable of quantifying low-level emissions of Sb from diffuse sources. In this study, we validated two methods using a $H_2O_2$ -$HNO_3$ liquid chemotrap and an activated coconut shell charcoal solid-phase trap, achieving an absolute limit of detection of 4.6 ng and below 2.0 ng Sb, respectively. The activated charcoal solid-phase trapping method, the most easily operated method, was then applied to contaminated shooting range soils. Four treatments were tested: 1) flooded, 2) manure amended + flooded, 3) 70 % water holding capacity, and 4) manure amendment +70 % water holding capacity, since agricultural practices and flooding events may contribute to Sb volatilization. Volatile Sb was only produced from flooded microcosms and manure amendment greatly influenced the onset and amount of volatile Sb produced. The highest amount of volatile Sb produced, up to 62.1 ng $kg^{-1}$ $d^{-1}$, was from the flooded manure amended soil. This suggests that anaerobic microorganisms may potentially be drivers of Sb volatilization. Our results show that polluted shooting range soils are a source of volatile Sb under flooded conditions, which may lead to an increase in the mobility of Sb. Some of these volatile Sb species are toxic and genotoxic, highlighting the role of Sb volatilization on environmental health, especially for individuals living in contaminated areas exposed to wetlands or flooded conditions (e.g., rice paddy agriculture surrounding mining areas). This work paves way for research on Sb volatilization in the environment.

## 1. Introduction

Antimony (Sb) is a naturally occurring, potentially carcinogenic, toxic metalloid classified as a priority pollutant of interest by the EU and the USEPA (Swedish Chemicals Agency, 2008; USEPA, 2014). Major anthropogenic sources of Sb in soils include mining and smelting activities, coal combustion, the manufacturing and use of ammunition, vehicle brake linings, lead-acid batteries, and flame retardants (Filella et al., 2009; Okkenhaug et al., 2012). Due to the increasing demand for Sb and the widespread contamination that this entails, understanding the biogeochemical cycling and toxicity of Sb are of utmost importance. In the environment, inorganic Sb ($Sb_{IO}$) is predominant and occurs in two oxidation states, as the anionic pentavalent $Sb^{V}(OH)_6^-$ and the neutral trivalent $Sb^{III}(OH)_3$ species (Grob et al., 2018; Johnson et al., 2005; Lewińska et al., 2018; Okkenhaug et al., 2012). Inorganic volatile Sb occurs as the hydride, stibine ($SbH_3$) (Dodd et al., 1992; Howard, 1997; Michalke et al., 2000; Ramesh Kumar and Riyazuddin, 2007). Organic Sb species include soluble pentavalent mono-, di- and trimethylated Sb and volatile trivalent methylated Sb (e.g., Andrewes et al., 2000a; Bentley and Chasteen, 2002; Challenger, 1945; Wehmeier et al., 2004). To date, while most of the research has focused on the behavior of $Sb_{IO}$ in soils, limited work has been done on the methylation and volatilization of Sb, which are key transformations that influence both the toxicity and mobility of metal (loid)s in the environment (Andrewes et al., 2004; Dopp et al., 2006; Duester et al., 2005; Leermakers et al., 2006; Sun, 2010; Sundar and Chakravarty, 2010).

Microorganisms are considered drivers of Sb methylation, given that fungi, bacteria, and archaea can methylate Sb in anoxic and oxic conditions (Andrewes et al., 1999b, 1998; Jenkins et al., 2002; Smith et al., 2002a; Wehmeier et al., 2004). Duester et al. (2005) showed that methylated Sb species were most abundant in the upper horizons of agriculturally influenced soils and may account for up to 1 % of the total Sb ($Sb_t$) in the soil. Similar to arsenic (As) (Arao et al., 2011), the production of methylated Sb species may be enhanced with organic

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amendment when flooded. Grob et al. (2018) showed that after 4 days of flooding, when soils were more reduced ($E_h$ approximately 350 mV), soluble trimethylantimony (TMSbO) was produced in the porewaters of a flooded, manure amended shooting range soil and accounted for up to 7.8 ± 1.1 % of Sb species. The soluble TMSbO may be more mobile than the structurally similar soluble trimethylarsine oxide in soils (Yang and He, 2015). Frohne et al. (2011) showed an increase in $E_h$ reduced the amount of soluble monomethylantimony produced in the porewater of a floodplain soil.

It has been proposed that the microbial methylation of Sb follows the Challenger Pathway, initially formulated for As methylation (Andrewes et al., 1998; Bentley and Chasteen, 2002; Challenger, 1945; Craig et al., 1999; Wehmeier et al., 2004). Here, $Sb_{IO}$ would undergo stepwise oxidative methylation with S-Adenosylmethionine as the methyl donor and a subsequent reduction by glutathione of the non-volatile intermediary species (mono-, di-, and trimethylated antimony) with volatile trimethylstibine ($(CH_3)_3Sb$) as the end-product (e.g., Andrewes et al., 2000a; Bentley and Chasteen, 2002; Li et al., 2016; Wehmeier et al., 2004). Therefore, microbial Sb methylation would lead to the formation of volatile Sb. Volatile $SbH_3$ and $(CH_3)_3Sb$ have been shown to be potent genotoxins (Andrewes et al., 2004), and the pentavalent TMSbO, as dissolved $TMSbCl_2$, was also shown to have genotoxic effects on hamster ovary cells when forcibly taken up (Dopp et al., 2006).

Volatile Sb has been detected in microbial incubations (Andrewes et al., 1999a, 1998; Craig et al., 1999; Jenkins et al., 1998b, 2000; Smith et al., 2002b; Wehmeier and Feldmann, 2005), and one anaerobic soil incubation (Meyer et al., 2008). It has also been found in a few environmental compartments with low $E_h$, such as landfills (71 μg Sb $m^{-3}$ of landfill gas) (Feldmann, 2002; Feldmann et al., 1994; Feldmann and Hirner, 1995), sewage sludge fermenters (14 μg Sb $m^{-3}$ sewage gas) (Feldmann and Hirner, 1995; Hirner et al., 1998; Kim et al., 2010; Michalke et al., 2000; Wehmeier et al., 2004; Wehmeier and Feldmann, 2005), geothermal systems (29 mg $m^{-3}$ as $SbH_3$) (Hirner et al., 1998; Planer-friedrich and Merkel, 2006), and a wetland peat bog (Wickenheiser et al., 1998). Lastly, TMSbO extracted from airborne particulate matter has been reported, suggesting the potential for further transport (Zheng et al., 2000). Given the range of microorganisms and environmental compartments shown to volatilize Sb, it can be assumed that this phenomenon is widespread.

However, significant knowledge gaps exist about Sb volatilization, which is likely attributed to a lack of methods that are capable of sampling volatile Sb and the associated challenges with applying these methods in the field. The sampling of metal(loid) gases in the laboratory and field can be done by direct sampling (e.g., syringes) (Mestrot et al., 2013), cryogenic trapping (CT) and focusing (Feldmann et al., 1994; Feldmann and Hirner, 1995), polymers bags (Haas and Feldmann, 2000), solid-phase microextraction (Maher et al., 2018; Smith et al., 2002b; Wehmeier et al., 2004; Wehmeier and Feldmann, 2005), liquid chemotrapping and solid-phase trapping on sorbent tubes (Mestrot et al., 2009; Vriens et al., 2014a, 2014b). Most of these methods are challenging and/or expensive to apply in the field, or have significant field limitations, leading to delays in the progress of volatile Sb cycling research. For example, the quantitative technique CT-GC-ICP-MS requires gases to be preconcentrated by cryofocusing and cryotrapping at low temperatures (−80 °C and −196 °C), severely restricting its viable application in remote areas (Feldmann et al., 1994; Feldmann and Hirner, 1995; Jenkins et al., 1998b; Mestrot et al., 2013). The use of polymer bags, although more accessible for field sampling, is not ideal because the volume sampled is fixed, thereby limiting representative sampling of environmental conditions. Additionally, significant loss of $(CH_3)_3Sb$ onto the bag surface has been reported (Haas and Feldmann, 2000). Finally, solid-phase microextraction, a technique commonly used in laboratory-based experiments, strongly depends on the partitioning of the gaseous phase onto the solid phase and suffers from large matrix effects (Mestrot et al., 2013; Smith et al., 2002b; Souza-Silva et al., 2015). The review by Mestrot et al. (2013) provides further details on the advantages and disadvantages of field-based methods for sampling volatile arsines, since many of the same concepts can be applied to volatile Sb.

A sampling technique with a low limit of detection (LOD) is needed to advance research on Sb volatilization, which must also be compatible for laboratory- and field-based studies. Liquid and solid-phase trapping techniques are ideal as labile species are chemically captured in or sorbed on a stable matrix, allowing for long-term monitoring and storage. Nitric acid traps have previously been used in cultures of *Scopulariopsis brevicaulis* (Jenkins et al., 1998a). However, this method had a low trapping efficiency (51 %) and was not validated for laboratory or field applications (Jenkins et al., 1998a). Solid-phase trapping techniques, such as silver nitrate ($AgNO_3$) silica-gel and activated carbon solid-phase traps have been used and can be transported much more easily in the field. While $AgNO_3$-impregnated filters and activated carbon have been shown to work effectively to trap arsines and $SbH_3$ in the environment and workplace (Carder et al., 1990; Colabella et al., 1988; Mestrot et al., 2009; Pedersen, 1988), these methods have never been validated for $SbH_3$ nor tested for $(CH_3)_3Sb$. First, to validate a method, known concentrations of $SbH_3$ and $(CH_3)_3Sb$ need to be produced, typically by hydride generation (HG) (D'Ulivo, 2012; Dodd et al., 1992; Howard, 1997; Koch et al., 1998; Shaw, 1967; Ulivo et al., 2007). After these gases are derived, they are subsequently trapped in or onto the trapping matrix and the recoveries are assessed.

The objective of the present study was to develop methods to quantify volatile Sb species and $Sb_t$ for laboratory and field-based applications. We tested the capability of our developed method to trap volatile Sb and investigated Sb volatilization from a contaminated Swiss shooting range soil and evaluated the influence of flooding and common agricultural practices (manure amendment) on Sb volatilization.

## 2. Methods

Information about the chemicals, materials and instrumentation used for experiments can be found in S1 of the supporting information.

### 2.1. Liquid Chemotrapping

The experimental design for liquid chemotrapping was modified from Vriens et al. (2014) with the addition of $H_2O_2$ to the liquid chemotraps. For HG, a 50 mL air-tight flat-bottomed reactor vessel with a suba-sealed cap sidearm for $NaBH_4$ injection and gas impinger heads with frits (Frit size: ISO P160, nominal diameter: 100–160 μm) with a gas outflow port was used (Fig. 1a). The reactor vessel was connected to a $N_2$ gas source. The gas outflow was attached to three liquid chemotraps, by Pt-cured tubing, set in series to prevent potential carry-over or insufficient trapping (Fig. 1a). Each liquid chemotrap contained 3 mL of 69 % $HNO_3$ and 3 mL of ≥30 % $H_2O_2$ in a 15 mL corning tube inside of a 100 mL borosilicate glass bottle, which was filled with ultrapure water to avoid back pressure. Validation of the liquid chemotrapping method was conducted with three experimental replicates for $SbH_3$ and $(CH_3)_3Sb$.

For the production of volatile Sb species, 10 mL of 600 μg $L^{-1}$ Sb solutions from potassium antimony$^{III}$ tartrate hydrate ($Sb^{III}$) or trimethylantimony$^{V}$ dibromide ($(CH_3)_3SbBr_2$) solutions were freshly prepared from the corresponding 1000 mg $L^{-1}$ stock solution and mixed with 10 mL 5 M HCl in the reactor vessel. The $(CH_3)_3SbBr_2$ dissolved standard is hereafter referred to as soluble trimethylated Sb, TMSbO. A total of 3 mL of 2 % $NaBH_4$ (w/v) in 4 % NaOH (w/v) at 3, 7, and 11 min was injected into the reactor vessel side-arm (Fig. 1a). The reactor vessel was connected to $N_2$ (150 mL $min^{-1}$) for 15 min. The $N_2$ outflow, containing the HG-product gases, was flushed through the liquid chemotraps. For $Sb_t$ and Sb speciation analyses, the liquid chemotrap samples were diluted to 1 % $HNO_3$ and stored at 4 °C until further ICP-MS and HPLC-ICP-MS analysis (refer to Mestrot et al. (2016) for instrument settings). The remaining HG solution in the reaction vessel was

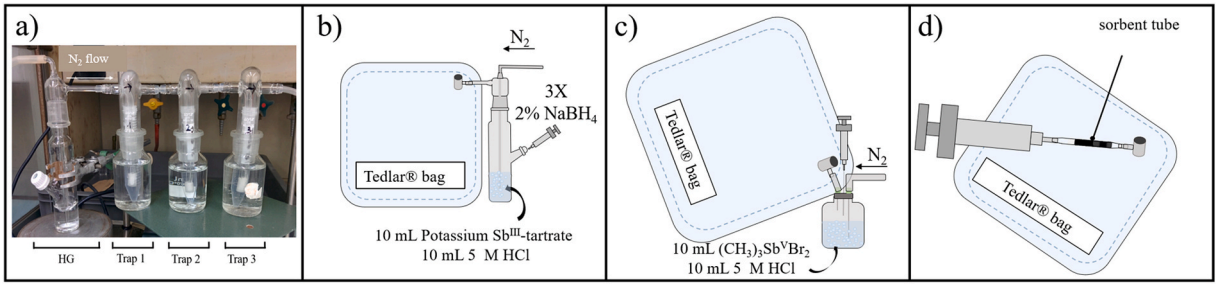


**Fig. 1.** Experimental setup for a) the HG reaction and trapping of volatile Sb in the liquid chemotraps, b) HG and production of volatile $SbH_3$ with a 50 mL reactor vessel, c) HG and production of $(CH_3)_3Sb$ with the smaller 30 mL reactor vessel and d) the trapping of volatile Sb on solid-phase traps by an airtight syringe.

measured for $Sb_t$ to calculate the HG efficiency (n = 3).

A negative HG control reaction, containing ultrapure water instead of an Sb standard solution, was used to determine the Sb background concentration and the absolute Sb LOD, ($Avg_{Blk}$+ 3.3 x $SD_{Blk}$, n = 3), where $Avg_{Blk}$ is the average blank trap and $SD_{Blk}$ is the standard deviation (SD). After 10 days of storage, the traps were measured for $Sb_t$ and Sb speciation (as time zero). At 18 days, Sb speciation was remeasured to test the stability of $SbH_3$ and $(CH_3)_3Sb$ in the liquid chemotraps.

### 2.2. Antimony Speciation in Liquid Chemotraps

Liquid chemotraps were analyzed for Sb speciation using anion exchange HPLC-ICP-MS, following the methods described by Mestrot et al. (2016) and Grob et al. (2018). The mobile phase was 150 mM ammonium tartrate in 4 % MeOH at pH 5 adjusted with HCl, a flow rate of 1 mL $min^{-1}$, injection volume of 50 μL, and column temperature of 20 °C. The different species ($Sb^V$, TMSbO, and $Sb^{III}$) were separated isocratically using a Hamilton PRPX100 anion exchange column (4.6 × 150 mm (PEEK), Reno, NV).

### 2.3. Solid-phase Trapping

For the derived $SbH_3$, the same HG experimental design was followed as the liquid chemotrapping method. For $SbH_3$ and $(CH_3)_3Sb$ HG, a less concentrated 300 μg $L^{-1}$, $Sb^{III}$/TMSbO standard was used (Fig. 1b). For $(CH_3)_3Sb$ HG, a smaller 30 mL reactor vessel was used (Fig. 1c). The smaller reactor vessel had a PTFE septum with needle syringes for the $N_2$ in- and out-flows (200 mL $min^{-1}$) (Fig. 1c). The gas outflow for $SbH_3$ and $(CH_3)_3Sb$ HG was connected to a 5 L Tedlar® bag using NOVOsil™ tubing (Fig. 1b and c) for 15 min 3 L of gases were produced (Fig. 1b and c) and immediately stored in a dark room for less than 5 hours before the trapping experiments. As before, blank HG reactions were included to determine the LOD (3.3 x $SD_{Blk}$), and the remaining HG solution was collected and measured for $Sb_t$ (n = 3) to assess HG efficiency.

Two types of solid-phase traps were tested for $Sb_t$ recovery, a 1 % $AgNO_3$ impregnated silica-gel solid-phase trap, and an activated coconut-shell charcoal (AC) solid-phase trap. The $AgNO_3$ silica-gel solid-phase traps were chosen based on their ability to trap volatile As species (Mestrot et al., 2011, 2009) and under the assumption that Sb and As have similar chemical properties. The AC solid-phase traps were chosen, since AC had previously been applied to trap $SbH_3$ and $AsH_3$ in workspaces (Haring and Compton, 1935; Varma et al., 1980). It is hypothesized that the silica-gel trap immobilizes volatile As species by $AgNO_3$-dependent oxidation (Křepelka and Fanta, 1937), although this has not yet been confirmed (Mestrot et al., 2009). The AC, with a high surface area and variable functional groups, likely traps volatile Sb by adsorption (Rehman et al., 2019). Both traps consist of two layers of sorbent material (silica-gel or activated charcoal), a filter plug, and silica wool. The $AgNO_3$ silica gel solid-phase traps were prepared according to Mestrot et al. (2009) and there was no further treatment of the AC solid-phase traps after acquisition from the manufacturer.

Derived $SbH_3$ and $(CH_3)_3Sb$ were trapped by connecting a solid-phase trap to the Tedlar® bag and simultaneously connecting an airtight syringe to the other end of the solid-phase trap (Fig. 1d). A fixed volume of 300 mL, equivalent to 300 ng of $SbH_3$, $(CH_3)_3Sb$ or blank HG gas (referred to as blank traps), was slowly drawn from the Tedlar® bag through the solid-phase trap, and into the syringe. Trapping experiments for the $AgNO_3$ silica-gel traps were performed only once, in triplicate. The AC solid-phase trap validation tests were performed in triplicate on 3 separate days for $SbH_3$ and 4 separate days for $(CH_3)_3Sb$. The solid-phase traps were stored at room temperature in the dark until digestion and $Sb_t$ analysis. No Sb speciation analysis was done for the solid-phase traps.

The remaining volume of gas in the Tedlar® bags was measured to calculate the exact concentration of $SbH_3$ and $(CH_3)_3Sb$ produced during the HG reaction. Finally, breakthrough tests were performed in triplicate, for each Sb species produced by HG by connecting two traps in series. The experiment was performed with the same set-up as the solid trapping experiment (Fig. 1b and c), but 1 L of gas, equivalent to 1000 ng of $SbH_3$ or $(CH_3)_3Sb$, was passed through the solid-phase traps.

### 2.4. Solid-phase Trapping: Total Sb Analysis

Two digestions were tested for the $AgNO_3$ silica gel solid-phase traps, an aqua regia microwave-assisted digestion, using 6 mL of 32 % HCl and 2 mL of 69 % $HNO_3$, and a fluoroboric acid digestion using 2 mL of 48 % $HBF_4$ and 6 mL of 69 % $HNO_3$ digestion. Both digestions were done in closed Teflon vessels at 175 °C. For $Sb_t$ analysis of the AC solid-phase traps, the silica wool was removed to reduce blank Sb levels (supporting information S2 and Fig. S1). The contents of the AC solid-phase traps were digested using the same aqua regia digestion as the $AgNO_3$ silica-gel solid-phase traps.

Method blanks and blank traps were included with each digestion. For a detailed description of the procedures and microwave program, refer to the supporting information S3 and Table S1. Digested samples were stored at 4 °C until ICP-MS analysis (parameters listed in Table S4). Antimony was detected at *m/z* 121 using In (*m/z* 115) as an internal standard. To prevent $Sb_t$ carryover, 1:1:5 $H_2O_2$:$NH_4OH$:ultrapure water and 1 % HCl +0.7 % $HNO_3$ rinse solutions were used between samples for 50 and 60 s, respectively.

### 2.5. Incubation Experiments

In January 2018, 2 kg of the upper 10 cm of a contaminated Cambisol (IUSS Working Group WRB, 2014) was sampled in a combat shooting range (Laupen, Switzerland). The plant cover was removed, and the soil was sieved to <2 mm and stored at 4 °C until the start of the experiment.

An aliquot of the soil was digested and analyzed for multielement analysis (supporting information S4.1 and Table S2) and $Sb_t$ (supporting information S4.2 and Table S1). For QC, certified reference materials

(NIST 2711 and NIST 2709a) and method blanks were processed. The QC and the soil samples were digested in triplicate.

Soil incubations were carried-out in 500 mL acid-washed and autoclaved Erlenmeyer flasks fitted with gas impingers (Fig. 2). Inflow air was 0.45 μm filtered and passed through an AC solid-phase (inlet) trap. On the outlet port, an AC solid-phase (outlet) trap and a diffusor air pump (600 mL $h^{-1}$), which was modified to create a negative pressure in the microcosm, were connected together and ran for the duration of the experiment. Pt-cured silicon tubing was used to connect the AC solid-phase traps with the microcosm.

Flasks with 100 g of soil were incubated, with four different treatments in triplicate at 30 °C, to promote microbial growth, and at 70 % relative humidity for 42 days (Fig. 2). The four treatments consisted of: 1) flooded, 2) 5 % manure (w/w) + flooded, 3) 70 % soil water holding capacity (WHC), and 4) 5 % manure (w/w) + 70 % soil WHC. For the flooded treatment, 150 mL of degassed ultra-pure water was used. The manure used for the incubation was a dried and finely chopped commercially available cow manure (Hauert HBG dunger, AG, Grossaffoltern, Switzerland) with 0.1 ± 0.006 mg $kg^{-1}$ Sb (Table S3). The AC solid-phase traps were harvested after 16 hours and multiple days (7, 14, 21, 28, 35, and 42); traps were stored at room temperature in the dark until further $Sb_t$ digestion. All reported outlet trap values were inlet trap subtracted to account for background contamination. A Students t-test with unpaired samples and a significance interval of 0.05 was used to determine if there are statistically significant differences between the treatments. A sterilized soil treatment was not included due to potential changes in soil properties (e.g., nutrient availability), and rapid post-establishment of opportunist microorganisms and resistant spores that is incompatible with a 42-day incubation period (Berns et al., 2008; Nowak and Wronkowska, 1987).

## 3. Results and Discussion

### 3.1. Liquid Trapping Efficiency

The $Sb^{III}$ and TMSbO standard solutions were readily converted to their corresponding volatile Sb species, as the HG efficiencies were 99.92 ± 0.04% (n = 3) for $Sb^{III}$ and 99.92 ± 0.05% (n = 3) for TMSbO.

The trapping efficiencies (supporting information S6, Eq. (1)) were 84.4 ± 1.8% for $SbH_3$ and 103.8 ± 4.0% for $(CH_3)_3Sb$ (Table 1) at time zero, which was defined for measurements taken after 10 days of storage. Significant carryover in the traps was observed for $SbH_3$ (Fig. 3a). The aforementioned efficiency corresponds to the sum of $SbH_3$ captured by three traps in-line (Fig. 3a). During the analysis, the speciation of trapped $SbH_3$ was as $Sb_{IO}$ species: $Sb^{III}$ (approximately 80 %) and $Sb^{V}$ (approximately 20 %). One liquid chemotrap was sufficient to trap all of the $(CH_3)_3Sb$ that had evolved (Fig. 3b), and TMSbO was the sole species detected during the Sb speciation analysis. Both $SbH_3$ and $(CH_3)_3Sb$ are likely oxidized during trapping in the liquid matrix to $Sb_{IO}$ and TMSbO, respectively. Since there were no $Sb_{IO}$ species observed in the speciation analysis of the $(CH_3)_3Sb$ traps, trapped $SbH_3$ and $(CH_3)_3Sb$ can be successfully differentiated. The absolute LOD for the liquid chemotrapping experiments, determined by blank traps, was 4.6 ng (absolute in ng since the blank value depends on the volume sampled).

Recoveries of the trapped Sb species were calculated by dividing the sum of Sb species detected by the HPLC-ICP-MS in the stored traps by the total Sb in the trapping solution at time zero. After 10 and 18 days of storage, the trapped $SbH_3$ was present as $Sb_{IO}$ ($Sb^{III}$ and $Sb^{V}$). At 10 days, 76.2% of the $Sb_t$ was recovered, and at 18 days, 85.1% of the trapped Sb was recovered. The Sb recoveries after the two storage periods were not significantly different ($p > 0.05$) (Table 1).

**Table 1**
Trapping efficiency of liquid chemotraps for $SbH_3$ and $(CH_3)_3Sb$ and stability of the species after 10 and 18 days of storage.

| Volatile Species | Trapping Efficiency (%)[a] | 10 days Recovery (%)[b] | 18 days Recovery (%)[b] |
|---|---|---|---|
| $SbH_3$ | 84.4 ± 1.8 | 76.2 | 85.1 |
| $(CH_3)_3Sb$ | 103.8 ± 4.0 | 70.1 | 63.9 |

[a] Trapping efficiency for liquid chemotrapping is the ratio between the sum of Sb species trapped in the liquid chemotraps versus the total Sb HG standard in the reactor vessel. n = 3 for both species.
[b] Recoveries for days 10 and 18 are calculated based on the ratio of sum of Sb species versus the $Sb_t$ in the liquid chemotrap measured at on day 10.

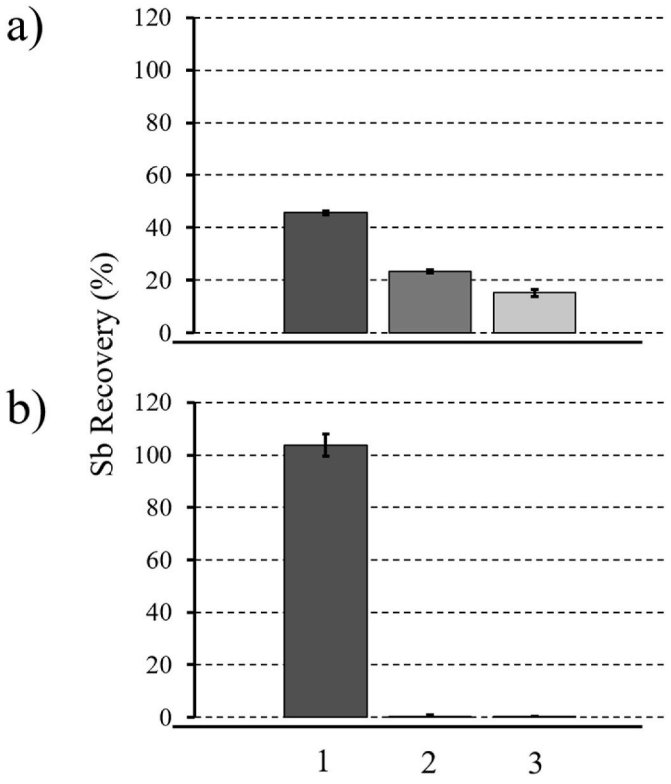


**Fig. 3.** Recovery of three liquid chemotraps connected in series for trapping of a) $SbH_3$ and b) $(CH_3)_3Sb$. Individual traps are numbered on the x axis (labelled 1, 2 and 3). The absolute LOD = 4.6 ng. Bars in panels represent the mean value and error bars, plus one standard deviation (n = 3).

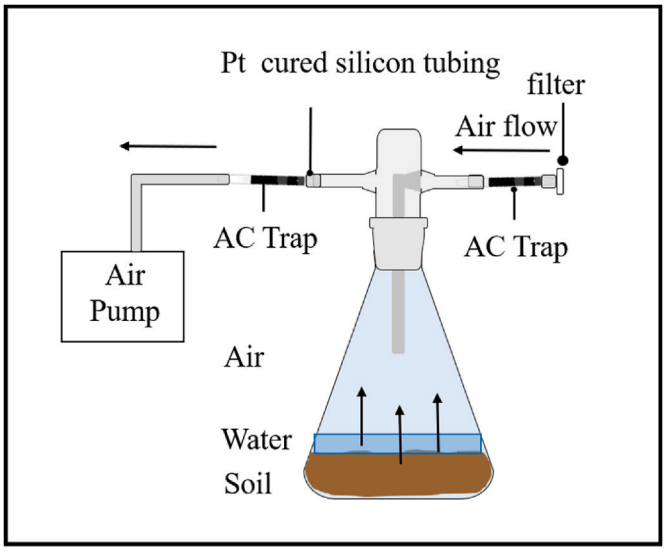


**Fig. 2.** Experimental setup for soil incubations.

After 10 days of storage, the recoveries for the $(CH_3)_3Sb$ traps was 70.1 %, and after 18 days, recovery was 63.9 % (Table 1) ($p > 0.05$). The trapped $(CH_3)_3Sb$ was detected as TMSbO, with no indication of $Sb_{IO}$ at both time points, which suggests that the Sb–C bond persists during trapping; this allows for the identification of $(CH_3)_3Sb$ as TMSbO. However, not all of the trapped $(CH_3)_3Sb$ was recovered after storage, even though no $Sb_{IO}$ was formed. This could potentially suggest that either strong retention on the column results in low recoveries, or that other unidentified Sb species that are not eluted in our method may be present. For instance, $(CH_3)SbH_2$ and/or $(CH_3)_2SbH$ may be formed during HG of TMSbO (Dodd et al., 1992; Koch et al., 1998) or by demethylation with storage and would likely be present in their pentavalent redox state. However, we could not verify this since there are no existing standards to produce $(CH_3)SbH_2$ and $(CH_3)_3SbH$, and they would need to be synthesized (Dodd et al., 1996; Dodd et al., 1992). We can only conclude that for quantitative analysis, Sb should be immediately measured to maximize recoveries.

Liquid chemotrapping methods have been successfully validated and applied in the field to measure low-level emissions of volatile S, Se and As species (Vriens et al., 2014a, 2014b; Winkel et al., 2010) but never for Sb. This method, now validated for $SbH_3$ and $(CH_3)_3Sb$ speciation, is sensitive and laboratory and field-deployable. Although it is considered to be less suitable for field applications in remote areas, due to the use of glassware, acids, and sampling trains prone to backpressure, the method can preserve the Sb speciation information of the sample.

### 3.2. Trapping Efficiency of $AgNO_3$ Silica-gel and Activated Carbon Traps

The remaining solution in the HG reactor vessel, for all of the $AgNO_3$ silica-gel trap tests, was consistently below the instrumental LOD (<0.006 μg $L^{-1}$ Sb), i.e., 100 % HG efficiency. The recoveries after aqua regia digestion of the $AgNO_3$ silica-gel solid-phase traps were 53.9 ± 0.9 % for $SbH_3$ and 39.3 ± 9.2 % for $(CH_3)_3Sb$. The recoveries for the fluoroboric acid digestion improved for $SbH_3$ to 87.0 ± 2.0 %.The recoveries for $(CH_3)_3Sb$ were 52.7 ± 3.3 % and were, although higher, not statistically different from the aqua regia digestion ($p > 0.05$). Rather than attributing these results to poor trapping efficiency, we hypothesized that trapped $SbH_3$ may form a $Ag_3Sb$ complex with $AgNO_3$ in the traps (Jones, 1876; Shaw, 1967), which may be difficult to digest.

When the AC solid-phase traps were used, the HG efficiency was 99.2 ± 0.2 % for $SbH_3$ (n = 12) and 99.2 ± 0.6 % for $(CH_3)_3Sb$ (n = 9) (Table 2). For $SbH_3$, the AC trapping efficiency was 89.6 ± 3.8% (n = 12, 4 triplicate tests on separate days) (Table 2). For the validation tests of $(CH_3)_3Sb$, when using a 50 mL reactor vessel (Fig. 1b), an initial low trapping efficiency on AC was observed (47.2 ± 12.2%). After replacing the reactor vessel with a lower 30 mL volume (Fig. 1c), decreasing the surface area of the vessel and reducing the potential $(CH_3)_3Sb$ sorption on the glassware, the trapping efficiency was over-estimated (131.2 ± 1.0%). Until this point, an $Sb_{IO}$ calibration curve had been used to quantify the TMSbO standard solution used for the HG reaction and for mass balance calculations. Given that the variable ICP-MS sensitivities have been reported for different Sb-species (Lintschinger et al., 1997), a TMSbO calibration was used to ensure that a reasonable mass balance could be achieved and the recoveries improved to 101.6 ± 3.8 % (n = 3).

To test the Sb-species dependent ICP-MS sensitivity, the instrumental response (counts per second) of two standards was tested: a 10 μg Sb $L^{-1}$ solution as TMSbO and as $Sb_{IO}$ (supporting information S6). For the same Sb concentration, the counts per second were approximately 1.3 times higher when the $Sb_{IO}$ standard was used compared to the TMSbO standard. This effect is unlikely to be caused by the C-enhancement effect (Allain et al., 1991) or volatility differences, since TMSbO would be expected to have a higher signal than $Sb_{IO}$ for both cases. While the reason for the lower signal of the TMSbO standard is currently unknown, it may be due to the sorption of TMSbO on ICP-MS glassware during sample introduction as large carry-over effects were observed. Finally, during the aqua regia digestion, $(CH_3)_3Sb$ would likely demethylate to $Sb_{IO}$. To determine the $Sb_t$ in the AC traps, an $Sb_{IO}$ calibration curve was used to calculate the reported Sb trapping efficiencies (Table 2) to yield rational mass balances (Table 2). The overall AC trapping efficiency for $(CH_3)_3Sb$, using the 30 mL reactor vessel, was 93.2 ± 2.3 % (n = 9, in 3 triplicate tests on different days) (Table 2).

The AC solid-phase trapping technique is reproducible because the SD between tests is less than 4 %, and the method has an absolute LOD of 1.64 ng (n = 9) for $SbH_3$ and 1.63 ng (n = 12) for $(CH_3)_3Sb$. There was no observed breakthrough after trapping 1000 ng (data not shown) for either Sb species. Assuming similar volatilization rates between As and Sb, 1000 ng for breakthrough tests is appropriate for applications in soil, sediment, and water environments (Huang et al., 2012; Jia et al., 2012; Mestrot et al., 2011, 2009; Yan et al., 2020). In extreme environments, such as hot springs and landfills, more volatile Sb has been observed (Feldmann, 2002; Feldmann and Hirner, 1995; Planer-friedrich and Merkel, 2006). However, these fluxes are not likely representative of the soil environment, even though multiple traps could be used to test for the breakthrough.

The AC solid-phase traps, for typical environmental applications, have unlimited sampling volume allowing for long-term monitoring of incubation experiments and/or the sampling of diffuse sources such as soils, sediments, and waters. In addition, the AC solid-phase traps are field-deployable even in remote areas, easy to use and store and do not require acids or $H_2O_2$. These benefits effectively reduce the risks and limitations while working with liquid chemotrapping methods. This is the first report that validates liquid chemotrapping and solid-phase trapping techniques for volatile Sb. We successfully developed two quantitative and sensitive methods to measure volatile $Sb_t$. Both

**Table 2**
Amount of Sb and trapping efficiencies for $SbH_3$ (n = 9) and $(CH_3)_3Sb$ (n = 12) from aqua regia digested AC traps. Average Sb content on the blank traps for the $SbH_3$ was 5.79 ± 0.5 ng (n = 12), and for $(CH_3)_3Sb$ was 5.29 ± 0.5 ng (n = 9). Variability between the traps is likely due to heterogeneity in the trap materials from the manufacturer. The trapping efficiency was calculated as the ratio between the total trapped Sb on the AC in ng versus the total Sb trapped in 300 mL of HG-gas.

| | $SbH_3$ | | $(CH_3)_3Sb$ | |
|---|---|---|---|---|
| | ng on trap [a] | Trapping Efficiency (%)[b] | ng on trap [a] | Trapping Efficiency (%)[b] |
| Test 1 | 233.7 ± 3.6 | 92.7 ± 1.4 | 251.0 ± 2.4 | 96.1 ± 0.9 |
| Test 2 | 273.4 ± 7.6 | 93.7 ± 2.6 | 256.9 ± 4.8 | 95.0 ± 1.8 |
| Test 3 | 240.4 ± 21.8 | 82.4 ± 7.5 | 300.9 ± 14.0 | 88.5 ± 4.1 |
| Test 4 | | | 304.0 ± 2.1 | 89.7 ± 0.6 |
| Average | 249.2 ± 11.0 | 89.6 ± 3.8 | 269.6 ± 7.08 | 93.2 ± 2.3 |

Each test is the average of 3 replicates from the same day. All solid trap results are blank trap subtracted (outlet trap Sb subtracted by the inlet trap Sb). $LOD_{(CH3)3Sb}$ is 1.63 ng and $LOD_{SbH3}$ is 1.64 ng. LOD is calculated as 3.3 x $SD_{Blk}$.

[a] Total Sb ± SD in ng of triplicates.

[b] Recovery ± SD (%) of triplicates of Sb on the trap.

methods are capable of quantifying $Sb_t$ emissions. Furthermore, liquid chemotrapping allows for the elucidation of speciation, and the AC solid-phase trapping method offers optimal transportability and can capture up to 1000 ng Sb on one trap. Given that the AC solid-phase trapping is more promising than the liquid chemotrapping method for field applications, and due to low HPLC recoveries for $(CH_3)_3Sb$ in the liquid chemotrap, we tested the ability of the AC solid-phase traps to capture volatile Sb produced in an Sb-contaminated soil incubation experiment.

### 3.3. Incubation Experiments

The Cambisol tested is a sandy loam with a pH of 6.8 and 75 ± 6.2 mg $kg^{-1}$ Sb (supporting information Table S3). The $C_{org}$ was 2.7 % and the C/N ratio was 21.2. See Table S3 for soil and manure Sb and multi-element information and Grob et al. (2018) for further information on the physical properties of the soil.

In the two treatments with 70 % soil WHC, the amount of volatile Sb that was trapped was lower than the method LOD (4.3 ng, calculation described in Fig. 4 text) in all of the incubators, except for one sampling point in each treatment at different times (approximately 5 ng). Due to the low levels measured in the two samples at one sampling time, we cannot exclude the presence of single point contamination in each of the treatments.

Conversely, Sb was detected on the traps in both of the flooded treatments (Fig. 4a). The manure amended soil produced volatile Sb earlier and volatilized Sb more efficiently than the non-manure amended treatment (Fig. 4a). After 7 days of incubation, volatile Sb was produced from the manure amended treatment, while the first appearance of volatile Sb was observed after 28 days in the flooded treatment. At the end of the experiment, 135.3 ± 56.5 ng volatile Sb was produced from the manure amended + flooded treatment, which is approximately 5 times higher ($p < 0.05$) than the flooded treatment (27.2 ± 14.2 ng volatile Sb).

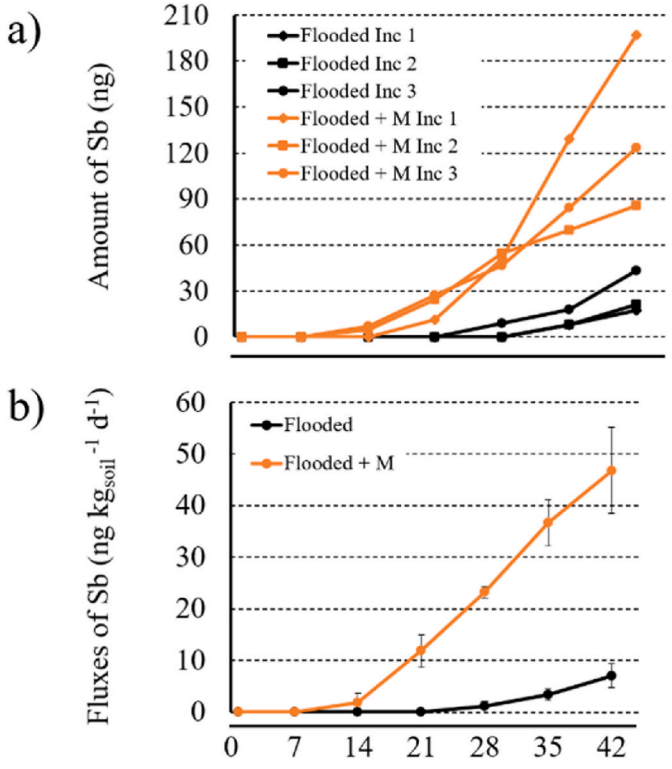


**Fig. 4.** Time series Sb volatilization from flooded soil incubations. On the x axis time (days), and on the y-axis a) cumulative Sb trapped in ng for flooded and 5 % manure + flooded treatments and b) fluxes of Sb (ng $kg^{-1}$ $d^{-1}$) for all treatments. All data plotted are inlet-trap subtracted. LOD of the experiment was 4.3 ng (LOD = 3.3 x $SD_{BT}$). The average of the blank traps during the experiment was 5.5 ± 1.3 ng Sb on the trap (n = 81 traps). For panel a) individual values from each incubator are plotted and for panel b) data points represent the mean value and error bars, plus and minus one standard deviation.

Although great care was taken to ensure homogeneity among triplicates, the production of volatile Sb between replicates was highly variable with some replicate incubators producing 1.5–2.5 times more volatile Sb than the other two (Fig. 4a). This variation between replicates has been previously observed for Sb in soil enrichments (Jenkins et al., 1998b) and for As volatilization (Mestrot et al., 2011, 2009) and could result from the colonization of different microbial communities in different incubators subjected to the same treatment. It also highlights our lack of understanding about the drivers of Sb volatilization.

Based on similar experiments on the same soil (Grob et al., 2018) and similar soil experiments (Hockmann et al., 2014; Pezeshki and Delaune, 2012; Rinklebe et al., 2020; Weber et al., 2009), we speculate that our experiments were oxygen-depleted within 48 h of flooding. This and the absence of volatile Sb produced in non-flooded treatments (70 % WHC) suggest that the production of volatile Sb in the tested soils may potentially be due to anaerobic microorganisms in the soil. Sterilization of soils has been shown to prevent the production of volatile Sb or As species in previous studies (Andrewes et al., 1998; Edvantoro et al., 2004; Meyer et al., 2007; Smith et al., 2002b; Turpeinen et al., 2002). Furthermore, studies on As volatilization showed production only in flooded soils and enhanced by manure addition (Edvantoro et al., 2004; Huang et al., 2012; Mestrot et al., 2009). This was likely caused by microbial biostimulation due to nutrient addition (Edvantoro et al., 2004). The higher Sb volatilization observed in the manure amended treatment, rather than being introduced from Sb in the manure (see Table S3 for manure Sb concentration), suggests an enrichment of the microbial communities capable of Sb methylation and/or volatilization.

The low efficiency of Sb volatilization, 0.0004–0.002 % of the initial $Sb_t$ in the soil (75.5 mg $kg^{-1}$ of Sb, Table S3), is generally lower than reported As volatilization efficiency (0.002–0.13 %) from rice paddy soils (Mestrot et al., 2009) and Sb volatilization from pure microbial cultures using elemental Sb (0.03–2.30 %) (Jenkins et al., 1998b). However, it is slightly higher than reported Sb volatilization efficiency (0.001 %) from *Cryptococcus humicolus* under biphasic aerobic-anaerobic incubation (Smith et al., 2002b). As a low proportion of the soil Sb was volatilized in our experiment and enhanced with manure amendment this suggests that volatilization of Sb may not be dependent on soil $Sb_t$ concentrations but rather on available Sb. This finding is comparable to observations for non-volatile methylated Sb species detected in soils (Duester et al., 2005) and observations for volatile Sb in the study by Meyer et al. (2007). The latter study, with low Sb (1.3 mg $kg^{-1}$), produced around 166.9 ng of $(CH_3)_3Sb$ equivalent to 370 ng $kg^{-1}$ $d^{-1}$ Sb, around 6 times higher than the fluxes observed in our highest producing incubator (62.1 ng $kg^{-1}$ $d^{-1}$ Sb) (Fig. 4b). The higher volatilization in the alluvial soil may be due to different solid-phase speciation of Sb, potentially resulting in higher bioavailability, higher organic matter content (Meyer et al., 2008), higher experiment temperatures (37 °C) (Vriens et al., 2014b), the strict anaerobic conditions used and/or longer incubation periods (3 months) compared to the same set of properties in our study.

This is one of the first reports of Sb volatilization from a contaminated shooting range soil. Our results show that Sb volatilization is favored in flooded soils and is enhanced by organic matter addition. This indicates that waterlogged environments, even with low Sb (Meyer et al., 2007), are important sources of Sb mobilization into the atmosphere. Volatile Sb has been previously measured in landfill sites (Feldmann, 2002; Feldmann et al., 1998; Feldmann and Hirner, 1995; Jakob et al., 2010), sewage sludge fermentation units (Feldmann and Hirner, 1995; Hirner et al., 1994; Michalke et al., 2000; Wehmeier et al., 2004; Wehmeier and Feldmann, 2005), geothermal hot springs (Hirner et al., 1998; Planer-friedrich and

Merkel, 2006; Stauffer and Thompson, 1984), a peat bog (Wickenheiser et al., 1998) and the incubation of an alluvial soil (Meyer et al., 2007). All of these studies are anaerobic and organic matter rich except for the hot spring. It is apparent from these studies and our work that Sb volatilization may be favored in reduced environmental settings and that high organic matter seems to play a role, making wetlands (e.g., peat bogs), rice paddy fields, and floodplains potential hotspots of Sb volatilization. Furthermore, the vast area covered by these environments potentially makes them very important sources of volatile Sb, contributing to the global biogeochemical cycling of this element. Therefore, further studies should focus on volatile Sb, including the application and advancement of volatile Sb speciation methods, at both uncontaminated and contaminated waterlogged environments in the terrestrial environment, as well as the aquatic environment. All of these diverse settings are recognized to be important sources of volatile species of other metal(loid)s to the atmosphere (Fernández-Martínez and Charlet, 2009; Wang et al., 2014; Zhang et al., 2013).

## 4. Conclusion

In this work, we validated two methods to measure volatile Sb. The liquid chemotrapping technique preserves volatile Sb speciation, which is fundamental for mobility and toxicity studies. The newly developed solid-phase trapping technique using AC solid-phase traps has a lower limit of detection and is suited to measuring volatile Sb concentrations in the field, even in remote areas. Our results are the first to report Sb volatilization from a shooting range soil and demonstrate that volatile Sb production is higher under manure amended and flooded conditions. The findings provide a first indication of favorable conditions for volatile Sb production. With our newly validated and field-deployable AC solid-phase trapping method, we aim to gain further insight about Sb volatilization from diverse environmental compartments to better gauge volatilization inputs into the global Sb biogeochemical cycle. In addition to the identification of sources and their importance, the stability and mobility of volatile Sb species in the atmosphere also remains to be investigated. Finally, further research on toxic volatile Sb species will help shed light on its impact on human and environmental health.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117831.

## Credit Author Statement

Jaime N. Caplette: Conceptualization, Methodology, Writing – original draft and Writing – review & editing, Validation, Investigation, Visualization. Matthias Grob: Conceptualization, Methodology, Validation, Investigation. Adrien Mestrot: Supervision, Conceptualization, Writing – review & editing, Funding acquisition

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