Surface Amendment of Fertilizer Ammonium Thiosulfate To Reduce Methyl Bromide Emission from Soil

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Introduction

Methyl bromide (bromomethane, CH₃Br) has been widely used as a soil fumigant for controlling soilborne diseases (1). Recent studies indicate that 21–89% of the applied CH₃Br escapes into the atmosphere from fumigated fields (2–6). The volatilized CH₃Br contributes to stratospheric ozone depletion (7, 8) as well as imposes acute and chronic toxicological effects on field workers and nearby residents (9). The production and import of CH₃Br are thus scheduled to be discontinued in the United States by 2001 and in other regions at a later time (10, 11). However, currently there are few, if any, effective alternatives for replacing CH₃Br, and the phase out will likely cause substantial economic losses (12). A solution to this is to develop environment-benign strategies that can effectively minimize the atmospheric emission of CH₃Br.

The excessive emission of CH₃Br after injection into soil is caused by its rapid diffusion and relatively slow degradation in soil. For instance, in most soils, it may take less than 1 h for CH₃Br to move from the injection point (e.g., at 30 cm depth) to the soil surface, but it will take more than 5 d for 50% of the applied CH₃Br to degrade (5). To reduce CH₃Br emission, it is therefore essential to either provide a surface barrier to contain CH₃Br in the soil or to modify soil conditions to accelerate its degradation. The commonly used polyethylene film was found to be too permeable to CH₃Br (14, 15), and materials of lower permeability were shown to result in reduced emission (16, 17). Conceivably, CH₃Br emission can also be reduced if its degradation in soil is enhanced. In a preliminary experiment, we observed that CH₃Br was rapidly converted to Br⁻ in sodium thiosulfate or ammonium thiosulfate solution at ambient temperature (18):

\[
\text{CH}_3\text{Br} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_2\text{S}_2\text{O}_3^- + \text{Br}^-
\]

Although any thiosulfate salt can undergo the same reaction, the use of ammonium thiosulfate [(NH₄)₂S₂O₃], or ATS, can potentially have several advantages. First, ATS is currently used as a sulfur and nitrogen fertilizer and is therefore readily available at a low cost. Second, thiosulfate (S₂O₃²⁻) and its transformed intermediate tetrathionate (S₄O₆²⁻) were found to inhibit nitrification of ammonia and hydrolysis of urea, and mixtures of ATS with fluid fertilizers are sometimes used for increasing N efficiency (19–21). And third, ATS is oxidized to sulfate (SO₄²⁻) in soil and is therefore unlikely to hinder performance of subsequent CH₃Br applications or impose threats to groundwater (20).

In this paper, we studied ATS-mediated CH₃Br degradation in soil and demonstrated the potential applicability of surface ATS amendment for reducing CH₃Br emission. This work may serve as the basis for further evaluation of the feasibility and benefits of this approach on larger scales.

Experimental Section

Chemicals and Soils. Analytical grade CH₃Br (Aldrich Chemical Co., Milwaukee, WI) and (NH₄)₂S₂O₃ (Fluka Chemical Co., Buchs, Switzerland) had purity of 99%. Before use, gaseous CH₃Br was liquefied by chilling on dry ice. Thio-Sul (Texas Sulfur Co., Borger, TX), a commercial ATS fertilizer containing 60% of ATS, was purchased from a local farm chemical dealer. The three soils used were Arlington sandy loam (SL) (Riverside, CA), Linne clay loam (CL) (Santa Barbara, CA), and Carsitas loamy sand (LS) (Coachella Valley, CA). The organic matter contents of the Arlington SL, Linne CL, and Carsitas LS were 0.92, 2.99, and 2.53%, respectively, and the pH values were 7.4, 7.3, and 7.2, respectively. Before use, moist soil was passed through a 2-mm sieve without air-drying.

Degradation Experiments. Three incubation experiments were conducted in which degradation of CH₃Br in soil as a function of ATS:CH₃Br molar ratio, soil type, and temperature were separately determined. In the first experiment, ATS solutions of different concentrations were added to 10 g (dry weight equivalent) of Arlington 5L in 20-mL headspace GC vials to give four initial ATS concentrations of 0 (unamended control), 0.53, 1.05, and 2.10 μmol g⁻¹. Deionized water was added to adjust the soil moisture to 12% (w/w). Methyl bromide in 5 μL of acetone (1.05 μmol μL⁻¹) was added to the soil to give an initial CH₃Br concentration of 5.3 μmol g⁻¹. In a preliminary study, it was found that adding 5 μL of acetone into the soil had no effect on CH₃Br degradation rates. The treated vials were quickly closed with aluminum caps and Teflon-faced butyl rubber septa and incubated at 20 ± 0.2 °C in the dark. The initial ATS:CH₃Br molar ratios in the above samples were 0.1, 1.1, 2.1, and 4.1. At different times after CH₃Br treatment, three replicate samples were removed from each treatment.
and immediately stored at \(-15^\circ C\). To extract residual CH\(_3\)Br, 10 mL of ethyl acetate was added while the soil was still frozen, and the recapped vials were vortexed at a high speed for 2 min. Previous studies indicate a near 100% recovery for this method (22). An aliquot of the ethyl acetate phase was injected into a GC-ECD (HP 5890, Hewlett-Packard, Norwalk, CT) for detecting CH\(_3\)Br. The GC conditions were as follows: RTX-624 column (30 m \(\times\) 0.25 mm \(\times\) 1.4 \(\mu\)m, Restek Co., Bellefonte, PA), 240 \degree C inlet temperature, 270 \degree C detector temperature, 35 \degree C initial oven temperature (3.5 min) ramping at 20 \degree C min\(^{-1}\) to 200 \degree C, and 1.1 mL min\(^{-1}\) column flow rate. To extract Br\(^-\), soil samples were vortexed at a high speed in 10 mL of 0.1 mol \(L^{-1}\) NaCl solution for 2 min, and a portion of the supernatant was collected after the extract was centrifuged. The concentration of Br\(^-\) was determined on a QuikChem AE ion analyzer (Lachat Co., Milwaukee, WI).

In the second incubation experiment, ATS-enhanced CH\(_3\)Br degradation was measured in the Arlington SL, Linne CL, and Carstas LS. The initial ATS:CH\(_3\)Br molar ratio was 2:1 for all soils, and the soil moisture was 12%. Soils with no ATS amendment were included as controls. The same treatment procedures as described above were used, and disappearance of CH\(_3\)Br in soil with time was similarly determined. To determine the role of soil microorganisms in the enhanced degradation, one set of Arlington SL samples were sterilized by autoclaving at 121 \degree C for 1 h. The sterile soil was similarly treated with ATS and CH\(_3\)Br at 2:1, and the dissipation kinetics was determined.

In the third incubation experiment, ATS-enhanced CH\(_3\)Br degradation was determined in the Arlington SL at different temperatures. The initial ATS:CH\(_3\)Br molar ratio was 2:1, and the soil moisture was 12%. After treatment, soil samples were incubated at 10, 20, 30, or 40 \degree C, and dissipation of CH\(_3\)Br in the soil was determined.

**Column Experiment.** To evaluate the effectiveness of surface ATS amendment for reducing CH\(_3\)Br emission, volatilization of CH\(_3\)Br was measured from soil columns with and without ATS amendment. The column system was used in previous studies for predicting fumigant emission rates and was found to give reproducible estimates (23, 24). In brief, the system was made of a 60 cm (long) \(\times\) 12.5 cm (i.d.) glass column packed with soil and a 5 cm (long) \(\times\) 12.5 cm (i.d.) sampling chamber that was mounted on the top of the soil column. The bottom of the soil column and the top of the sampling chamber were closed, and the junction between the two was carefully sealed. The sampling chamber was connected to a vacuum, and sweep-air of 100 mL min\(^{-1}\) was passed through the sampling chamber to flush volatilized CH\(_3\)Br into ORBO-32 sampling tubes (Supelco) positioned in the flow path.

Three soil columns were packed with the Arlington SL (11,400 g dry weight) to the same soil bulk density (1.55 g cm\(^{-3}\)) and water content (12%). In all columns, a layer of high-density polyethylene film (0.0035 cm in thickness, TriCal Co., Hollister, CA) was placed between the soil surface and sampling chamber to simulate tarped CH\(_3\)Br fumigation. Column A received no ATS amendment, and only 20 mL of water was added to the soil surface at the time of CH\(_3\)Br injection. In column B, 1.0 mL of Thio-Sul was mixed with 19 mL of water and evenly pipetted onto the soil surface 24 h prior to the CH\(_3\)Br injection, and the treatment was considered as pre-ATS amendment. In column C, 1.0 mL of Thio-Sul in 19 mL of water was added onto the soil surface immediately after CH\(_3\)Br was injected, and the treatment was considered as parallel-ATS amendment. The application rate of Thio-Sul in columns B and C equalled 81 mL m\(^{-2}\) as Thio-Sul or 660 kg ha\(^{-1}\) as ATS.

The same amount of CH\(_3\)Br (100 \(\mu\)L as liquid, or 170 mg in mass) was injected into each column at 30 cm below the surface. This application rate equaled 140 kg ha\(^{-1}\) (125 lb a\(^{-1}\)). After CH\(_3\)Br was applied, ORBO tubes were changed every 3 h, and the recovered CH\(_3\)Br was analyzed using a reported method (25). Sampling for volatilized CH\(_3\)Br was continued until the concentration fell below the detection limit (0.1 \(\mu\)g per sample tube). At the end of experiment, soil samples were taken from different depths from each column, and Br\(^-\) concentration was measured after extraction.

**Field Plot Experiment.** A field plot experiment was conducted at the University of California’s South Coast Station (Irvine, CA) in September 1997 to determine the effect of ATS application on pest control efficacy. The field was uniformly infested with root-knot nematode Meloidogyne incognita and contained lima beans (Phaseolus limensis) from a previous harvest. Fumigation of CH\(_3\)Br was done by “hot-gas” injection into 600 cm plastic-tarped beds, and the drip line was buried at the middle of the bed at the 25 cm depth. Three treatments were used: standard fumigation, ATS amendment + fumigation, and no fumigation. In the ATS-amended plots, 660 kg ha\(^{-1}\) (as Thio-Sul) was sprayed onto the bed before fumigation. Four plots were used for each treatment, and CH\(_3\)Br application rate was 100 lb a\(^{-1}\) or 112 kg ha\(^{-1}\). Three weeks after fumigation, the germination of lima beans in each plot was counted. Soil was sampled, and nematodes juveniles were enumerated after Baermann extraction. Statistical analysis was performed after log transformation.

**Results and Discussion**

**Enhanced CH\(_3\)Br Degradation in ATS-Amended Soil.** Degradation of CH\(_3\)Br in the Arlington SL was enhanced with the addition of ATS, and the extent of enhancement was dependent on the initial ATS:CH\(_3\)Br molar ratio (Figure 1).

In the unamended soil, about 60% of the initially spiked CH\(_3\)Br remained undegraded after 96 h of incubation, but the fraction decreased to 28% in the 1:1 treatment and further to \(<3\%\) in the 2:1 and 4:1 treatments. As the initial ATS:CH\(_3\)Br ratio increased, the degradation half-life \((t_{1/2})\) of CH\(_3\)Br rapidly decreased. For instance, first-order \(t_{1/2}\) for CH\(_3\)Br degradation was 133 h (or 5 d) in the unamended soil and was reduced to \(<5\ h\) when the ATS:CH\(_3\)Br ratio was increased to 4 (Table 1).

Equal molar concentrations of Br\(^-\) were produced as CH\(_3\)Br was degraded in ATS-amended Arlington soil, indicating that ATS-enhanced CH\(_3\)Br degradation was a complete transformation (Figure 2). At 8 h after application, approximately 0.29 \(\mu\)mol g\(^{-1}\) CH\(_3\)Br was degraded, and 0.27 \(\mu\)mol g\(^{-1}\) Br\(^-\) was produced. The fact that CH\(_3\)Br was near
quantitatively degraded to Br\textsuperscript{-} is significant, since it suggests that other processes, such as adsorption, did not contribute to the observed rapid CH\textsubscript{3}Br dissipation in ATS-amended soils.

Similarly enhanced degradation of CH\textsubscript{3}Br was observed for all three soils when ATS was amended at a 2:1 ratio (Table 1). Compared to the unamended control, degradation of CH\textsubscript{3}Br in ATS-amended Arlington SL, Linne CL, and Carsitas LS was enhanced by 6, 9, and 8 times, respectively. The similar magnitude of enhancement in different soils implies that when ATS is abundant, the rate of CH\textsubscript{3}Br degradation is predominantly controlled by the ATS-CH\textsubscript{3}Br reaction.

Degradation of CH\textsubscript{3}Br in the sterile Arlington SL was not significantly different from the nonsterile soil (Table 1), which suggests that the enhanced CH\textsubscript{3}Br degradation in the ATS-amended soil was chemical degradation. Inoculated nitrifying bacteria were found to transform CH\textsubscript{3}Br (26), and amendment of ammonia fertilizer (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} resulted in a limited stimulation of CH\textsubscript{3}Br degradation in some soils (27). Degradation of CH\textsubscript{3}Br by ammonia oxidation bacteria, however, apparently did not contribute to the grossly enhanced CH\textsubscript{3}Br observed in the ATS-amended soils in this study.

Degradation of CH\textsubscript{3}Br in ATS-amended soil increased as the soil temperature was increased (Table 2). The activation energy, E\textsubscript{a}, calculated from the Arrhenius equation, was 51.5 kJ mol\textsuperscript{-1}, and the correlation factor r\textsuperscript{2} was 0.98. From this E\textsubscript{a} value, the average change in CH\textsubscript{3}Br degradation rate per 10°C change in temperature is about 2 times (28). It is known that when soil is covered with plastic sheets, as in CH\textsubscript{3}Br fumigation, temperature at the soil surface is often drastically elevated (5). The high temperature under the plastic cover may, therefore, further facilitate the reaction between ATS and CH\textsubscript{3}Br, resulting in further reduced emission.

**Reduction of CH\textsubscript{3}Br Emission by Surface ATS Amendment.** Rapid CH\textsubscript{3}Br volatilization occurred shortly after CH\textsubscript{3}Br was injected into the soil columns (Figure 3a). However, in ATS-treated columns, the magnitude of volatilization fluxes was greatly reduced as compared to the control column. For instance, the maximum flux detected from the control column without ATS amendment was 1400 μg h\textsuperscript{-1}, while that from the ATS-amended columns was only about 300 μg h\textsuperscript{-1}. The total loss of CH\textsubscript{3}Br from the unamended column was 61% of the applied dosage (Figure 3b), which is in agreement with field measurements (5, 27, 28). The loss was only 9.5% from the column treated with ATS prior to CH\textsubscript{3}Br application and 7.2% from the column treated with ATS after CH\textsubscript{3}Br application (Figure 3b). Under the similar conditions, applying sodium thiosulfate instead of ATS to the soil surface 24 h prior to CH\textsubscript{3}Br treatment resulted in 8.9% emission, while applying sodium thiosulfate immediately after CH\textsubscript{3}Br injection resulted in 9.0% emission.

Analysis of Br\textsuperscript{-} residue in soil columns revealed that the reduced CH\textsubscript{3}Br emission in ATS-amended columns was caused by increased degradation of CH\textsubscript{3}Br to Br\textsuperscript{-}. In the unamended soil column, the Br\textsuperscript{-} concentration was low, averaging only 3.5 mg kg\textsuperscript{-1} for the whole profile (Figure 4). In the ATS-amended columns, Br\textsuperscript{-} distribution patterns were reduced.
characterized with extremely high concentrations (>100 mg kg\(^{-1}\)) near the soil surface (Figure 4). In both ATS-treated columns, the Br\(^{-}\) concentration was greatest near the soil surface and rapidly decreased as the depth further increased, which indicates that the downward movement of ATS in soil was very limited under the used conditions.

**Effect of Surface ATS Amendment on Efficacy.** Compared to the unfumigated plots, CH\(_3\)Br fumigation, with or without ATS amendment, provided effective control over the root-knot nematode M. incognita and lima beans that were used as a weed substitute (Table 3). There was no statistical difference between the standard fumigation and ATS-amended fumigation for nematode control, and the difference for weed control became significant (\(P < 0.05\)) only after log transformation. This indicates that under field conditions, surface ATS application is unlikely to greatly affect the efficacy of CH\(_3\)Br fumigation. The limited effect on CH\(_3\)Br activity could be due to that the applied ATS remained near the surface in the tarped soil, as observed in the column experiment, while most soil pathogens and pests were present in the subsurface layers. In reality, modifying ATS application time, rate, and method may further minimize this impact.

Using an existing fertilizer to minimize the negative effects of a pesticide represents a novel risk-mitigation approach. The potential of using ATS to reduce CH\(_3\)Br emission is of particular significance not only because there is a lack of effective alternatives to CH\(_3\)Br but also because the global use of CH\(_3\)Br as a soil fumigant will likely continue for many years to come. However, to further develop this approach, some other aspects need to be better understood. These include, for instance, the application method of ATS, the economic implication of the integrated practice, and the safety and fate of the reaction products of CH\(_3\)Br and ATS. Most of all, the effectiveness of ATS amendment for reducing CH\(_3\)Br emission should be evaluated at the field scale and under different fumigation conditions.

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**Literature Cited**


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