

Identification of Volatile/Semivolatile Products Derived from Chemical Remediation of *cis*-1,3-Dichloropropene by Thiosulfate

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The prevalent use of soil fumigants has resulted in air pollution in some agricultural regions. Our previous research showed that application of thiosulfate fertilizers at the soil surface may offer an effective and economical approach to reduce the emission of halogenated fumigants via a chemical remediation process. In this fumigant emission-reduction strategy, volatile 1,3-dichloropropene (1,3-D) reacts with thiosulfate to generate a nonvolatile Bunte salt (thiosulfate derivative of 1,3-D). However, the decomposition of the Bunte salt may be associated with the production of perceptible odors. This study investigated the stability of this reaction product in different environmental media. Hydrolysis experiments demonstrated that the thiosulfate derivative was relatively stable in neutral and moderately acidic aqueous solutions. In contrast, the thiosulfate derivative was readily converted to a dialkyl disulfide via a base hydrolysis process in pH 10 buffer solution. In a strongly acidic solution, a mercaptan and a dialkyl disulfide compound were detected as two primary hydrolysis products. In soil, this initial reaction product underwent a series of biotic conversions to generate several volatile or semivolatile organic sulfur compounds. The formation and distribution of four volatile/semivolatile products in the air and soil were detected in different soils treated with the thiosulfate derivative of 1,3-D. This study indicated that odors occurring in soil treated with halogenated fumigants and thiosulfate fertilizers might arise from the generation and release of these and other volatile/semivolatile organic sulfur products. The environmental fate and effects of such volatile/semivolatile sulfur compounds should be considered in the application of sulfur-containing fertilizers in fumigated fields.

Introduction

Soil fumigation is an essential preplant treatment for the production of many economically important crops. The

fumigant 1,3-dichloropropene (1,3-D) has been widely used in California since it was reregistered in 1995. Application of 1,3-D in agricultural production is increasing substantially with the phaseout of methyl bromide, which has been identified as a stratospheric ozone-depleting chemical.

A primary concern associated with the use of soil fumigants is atmospheric emissions (1–4), because these toxic pesticides have relatively high vapor pressures and low boiling points. Most notably, the application rate of fumigants (>100 kg ha⁻¹) is very high, generally hundreds of times greater than that of most of conventional pesticides (5). Fumigant application to large agricultural fields has the potential to adversely impact air quality. Therefore, it is critically important to reduce fumigant emissions to minimize the negative effects of soil fumigation on the environment. Numerous approaches to reducing fumigant emissions have been suggested and tested (4, 6–11). These emission-reduction strategies involve physical, chemical, biological, and integrated practices. Using plastic tarp to cover the soil surface is one of the most commonly adopted strategies to impede fumigant losses. Surface water sealing may be an economically feasible practice to inhibit fumigant emissions (10–12). In addition to these physical containment methods, the amendment of surface soils is receiving increased attention as a potential strategy to reduce fumigant volatilization. For example, incorporating organic materials such as composted manure in the surface soil has been shown to accelerate fumigant biotic and abiotic degradation and thereby reduce the emissions of fumigants (7, 13, 14).

Recently, a chemical remediation technique has been proposed as a promising practice to efficiently reduce the emissions of halogenated fumigants while maintaining pesticidal efficacy or crop productivity (15–18). In this strategy, certain sulfur-containing agrochemicals are sprayed on the soil surface to construct a reactive surface barrier (RSB), in which volatile fumigants are rapidly transformed to nonvolatile products at the soil–air interface (9, 19). Ammonium thiosulfate (ATS), a sulfur fertilizer, reacts with halogenated fumigants (such as methyl bromide and 1,3-D) in soils to form nonvolatile and less toxic ionic products (15–17, 20, 21). Laboratory studies and field trials showed that thiosulfate fertilizers could be an economically acceptable and environmentally beneficial approach to reduce emissions from soil fumigation (15–17). However, these previous experiences revealed that the use of ATS in fumigated fields often resulted in the production of an unpleasant odor, suggesting a need to understand the environmental fate of the reaction products of fumigants and thiosulfate fertilizers. To successfully, effectively, and safely implement the RSB technique, knowledge pertaining to the environmental fate of the reaction products is imperative. Armed with this knowledge, regulators can develop a management tool to direct the correct use of this practice for the control of fumigant emissions.

The primary objective of this study was to identify the volatile/semivolatile products derived from the primary reaction product of *cis*-1,3-D and sodium thiosulfate and thereby illustrate its transformation process and environmental fate in different media. These studies will be helpful in comprehensively understanding the RSB strategy using thiosulfate fertilizers. The fumigant 1,3-D usually consists of *cis* and *trans* isomers with similar chemical and physical characteristics. Previous studies indicated that the reaction of both *cis*- and *trans*-1,3-D with hydrogen sulfide species produced multiple isomers with same mass spectra and different retention times on the chromatograms (22). To

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reduce the complexity arising from the formation of multiple stereoisomers and to simplify the identification of reaction products, *cis*-1,3-D was selected as a representative fumigant in this study. Sodium thiosulfate was used to avoid the release of ammonia gas resulting from the decomposition of ATS.

Experimental Section

Chemicals and Soils. Pure *cis*-1,3-D (98.9%) and *trans*-1,3-D (98.8%) were donated by Dow AgroSciences (Indianapolis, IN). Anhydrous sodium thiosulfate (>99.0%) was purchased from Aldrich (Milwaukee, WI). High-purity deionized deoxygenated water (prepared by sparging with nitrogen) was used to prepare all aqueous solutions. All chemical reagents were used as received.

Four soils (Arlington sandy loam, Hanford sand, Sesame sandy loam, and Milham sandy loam) as representatives of common soil types in California agricultural fields were used in the study. A description of the soil properties is provided in the Supporting Information. All soils were passed through a 2.0-mm screen without air-drying and stored at low temperature (4 °C) before use. To clarify the role of biotic transformation on the conversion of the reaction product in soil, Arlington sandy loam soil was autoclaved twice at 120 °C for 1 h with a 1-d interval between the first and second autoclaving. Glassware was autoclaved prior to use to inhibit microbial growth.

Aqueous Phase Experiments. The first set of aqueous phase experiments was conducted to determine the reaction kinetics of *cis*-1,3-D with sodium thiosulfate in solution. Briefly, sodium thiosulfate solutions (50 mL, pH~6.0) were prepared in deionized water with initial concentrations of 2.0 and 8.0 mM. Serum bottles sealed with Teflon-faced butyl rubber septa served as reactors. Pure *cis*-1,3-D was spiked into the thiosulfate solutions, yielding an initial fumigant concentration of 1.98 mM. All reactors were vigorously shaken and then incubated in the dark at 25 ± 0.5 °C. At selected intervals, 0.5 mL aliquots of solution were withdrawn from each reactor using a gastight syringe and transferred into a sealed glass vial containing ethyl acetate (3.0 mL) and anhydrous sodium sulfate (3.0 g). Simultaneously, 0.5 mL of N₂ was injected into the reactor to avoid the introduction of headspace. The sealed extraction vials were shaken for 10 min, and then a portion of the ethyl acetate extract was transferred to a gas chromatograph (GC) vial and stored at -20 °C until analysis. All extracts were analyzed by GC with an electron capture detector (ECD). A concurrent control experiment was conducted in aqueous solution without sodium thiosulfate to monitor the hydrolysis of *cis*-1,3-D.

The second set of aqueous phase experiments was conducted to evaluate the stability of the primary reaction product of *cis*-1,3-D and sodium thiosulfate in aqueous solutions of different pH. The preparation and purification of the reaction product is provided in the Supporting Information based on a modified method of Bunte salt synthesis (23). The hydrolytic experiment of the reaction product (2.0 mM) was performed in buffer solutions of pH 2, 7, and 10 (24), and in 0.2 and 2.0 M HCl solutions. At intervals, 0.5 mL aliquots of solutions were withdrawn and extracted using the procedure described above except that the extraction solvent contained 0.5 mM *trans*-1,3-D as an internal standard. Extracts were subjected to GC/mass spectrometric (MS) analysis. All aqueous experiments were performed in triplicate.

Soil Incubation Experiments. A series of experiments was conducted to investigate the transformation kinetics of *cis*-1,3-D in soil amended with sodium thiosulfate to monitor the formation of volatile/semivolatile products and to elucidate the transformation mechanisms of the reaction product in soils. The first soil incubation experiment was conducted to determine the dissipation rate of *cis*-1,3-D in

Arlington sandy loam amended with sodium thiosulfate and to identify the volatile/semivolatile products. In brief, the soil was premixed thoroughly with sodium thiosulfate in a plastic bag, yielding an amendment rate of 2.0 mmol kg⁻¹ (thiosulfate/soil). Amended soil (10 g dry weight equiv) was weighed into 20-mL headspace vials and spiked with *cis*-1,3-D stock solution, which yielded soil samples with 0.5 mmol kg⁻¹ 1,3-D and a soil moisture of ~10% (w/w). After spiking, each vial was sealed immediately with an aluminum seal and Teflon-faced butyl rubber septum and incubated in the dark at 25.0 ± 0.5 °C. At preselected times, triplicate sample vials were sacrificed for analysis by transferring them into a freezer and chilling at -21 °C for 3 h. To extract 1,3-D residues from soil samples, the frozen sample vials were decapped, and then 10.0 mL of ethyl acetate containing the internal standard (*trans*-1,3-D) was added, followed by immediate recapping. The samples were vigorously shaken for 1 h and vortexed for 2 min at room temperature. After treating with anhydrous sodium sulfate, an aliquot of each ethyl acetate extract was transferred to a GC vial and analyzed via GC/ECD and GC/MS. The degradation of *cis*-1,3-D in unamended soils was determined using a similar procedure. Preliminary experiments showed that the recovery of 1,3-D in unamended soil using the above extraction procedure ranged from 95 to 105%.

The second soil incubation experiment was conducted to determine the transformation of the reaction product of *cis*-1,3-D and thiosulfate in sterile and nonsterile soils. Ten grams (dry weight equivalent) of autoclaved or nonsterile soil was treated directly with the reaction product at 0.5 mmol kg⁻¹ in 20-mL headspace vials. All samples were incubated at 25 ± 0.5 °C in the dark. At selected time intervals, triplicate samples were removed and extracted using the same procedure as described above. The extracts were analyzed by GC/MS.

The third soil experiment was conducted to monitor the release of volatile/semivolatile products derived from further transformations of the reaction product in different soils. Four different soils (10 g dry weight equivalent) were treated directly with the reaction product at 0.5 mmol kg⁻¹ in 20-mL headspace vials. Each treated soil sample was immediately capped with an aluminum seal and a Teflon-faced butyl rubber septum and then incubated at 25 ± 0.5 °C in the dark for 2 d. To determine the volatile products, the air in the headspace of vials was collected using a sampling method similar to that used in ref 25. Briefly, two syringe needles inserted through the septa were used as the inlet and outlet for air flow. Two standard adsorbent tubes (charcoal, ORBO-32, Supelco, Bellefonte, PA) were connected in series using Teflon tubing connectors. The outlet of the tube series was connected to a manifold valve with a flow adjuster (SKC West, Fullerton, CA). The inlet of the adsorbent tube series was connected to the outlet of the headspace vial. Airflow was monitored at the inlet of the headspace vial using a flow meter. During sampling, a continuous and constant air flow (20 mL min⁻¹) was passed through the vials for 0.5 h, and the volatile compounds in the headspace were collected by the two adsorbent tubes in series. No products were detected in the second adsorbent tube, which indicated that no breakthrough occurred under these experimental conditions. Following the sparging, the adsorbent was extracted with 3 mL of ethyl acetate containing a known concentration of *trans*-1,3-D (internal standard) in a 10-mL vial by mixing on a reciprocating shaker for 15 min. A portion of the extract was transferred to a GC vial for analysis via GC/MS. These samples represented the concentration of volatile/semivolatile reaction products in air. The concentration of volatile/semivolatile products adsorbed on soils was analyzed by immediately placing the sparged sample vials into a freezer for 3 h and extracting the soil using the above

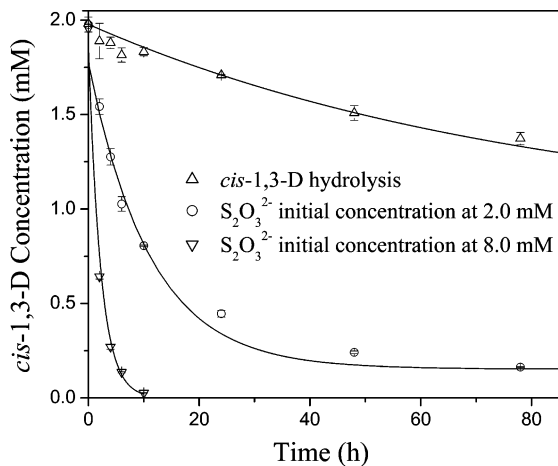


FIGURE 1. Time courses for dissipation of *cis*-1,3-D in sodium thiosulfate solutions at 25 ± 0.5 °C. Error bars represent standard deviations of triplicate samples.

soil extraction method. All soil treatments were performed in triplicate.

Chemical Analysis. Ethyl acetate extracts were analyzed for *cis*-1,3-D using a Hewlett-Packard (HP) 6890 GC equipped with an on-column injector, a microelectron capture detector (μ ECD), and a DB-VRX column (30 m \times 0.25 mm i.d. \times 1.4 μ m film thickness, J&W, Folsom, CA). The GC conditions were 1.4 mL min^{-1} carrier gas flow rate (He), 240 °C inlet temperature, and 290 °C detector temperature. The initial oven temperature was 50 °C for 1 min; the temperature was increased to 80 °C at 5.0 °C/min, held for 2.5 min, then increased to 120 °C at 25 °C/min, and held for 1 min.

The transformation products were analyzed using an HP 6890 GC in tandem with an Agilent 5975 Mass Selective Detector (MSD) equipped with a HP-5MS column (30 m \times 0.25 mm i.d. \times 0.25- μ m film thickness, J&W, Folsom, CA). Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1} . A splitless injection into a 210 °C injector port was utilized. The initial oven temperature was 50 °C for 4 min, and the temperature was increased to 80 °C at 5.0 °C min^{-1} , then increased to 200 °C at 35 °C min^{-1} , and held for 3 min.

Mass spectrometric analysis was carried out using both full scan and selected ion monitoring (SIM) modes. In the full scan mode, the electron impact (EI) mass spectra were generated using an electron energy of 70 eV, and ions with m/z 50–400 were monitored. The full scan mode was used for the identification of analytes by fragmentation patterns. For improved sensitivity, SIM was used for quantitation. In the SIM mode, the primary ion selected for quantitation was m/z 75 for both 1,3-D isomers and the transformation products. Quantitation was accomplished by comparing the area of the selected ion peak of the analyte of interest with the area of the selected ion peak from the internal standard (*trans*-1,3-D).

Results and Discussion

Transformation of *cis*-1,3-D by Sodium Thiosulfate in Aqueous Solution. Results of aqueous phase experiments conducted to determine the reaction kinetics of *cis*-1,3-D with thiosulfate are shown in Figure 1. The dissipation of *cis*-1,3-D in solution containing thiosulfate was much more rapid than its hydrolysis in deionized water (pH 6.3). For example, *cis*-1,3-D (1.98 mM) was almost completely transformed within 10 h at an initial thiosulfate concentration of 8 mM. In contrast, only ~6% of *cis*-1,3-D disappeared in the thiosulfate-free solution after 10 h of incubation at 25 °C (Figure 1). Moreover, the 50% disappearance times (DT_{50}) of *cis*-1,3-D, calculated according to a second-order reaction

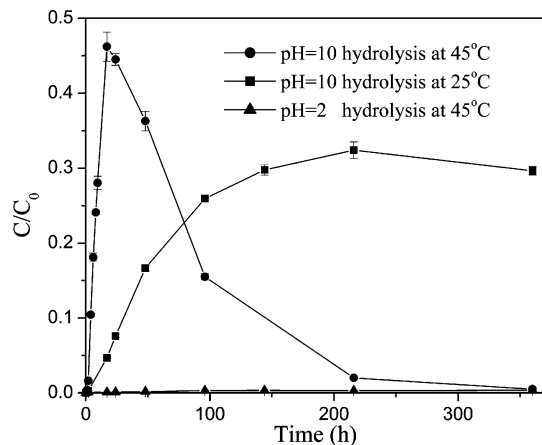
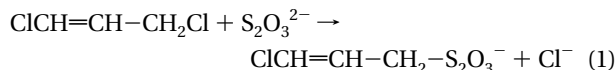


FIGURE 2. Formation of R-S-S-R from hydrolysis of R-S₂O₃²⁻ (2.0 mM) in basic and acidic aqueous solutions. The production of R-S-S-R is normalized to the initial concentration of R-S₂O₃²⁻, C₀ (2.0 mM). Lines are to aid visualization and do not indicate a model fit. Error bars represent standard deviations of triplicate samples.

equation (22), decreased significantly as the concentration of thiosulfate increased in aqueous solution. In comparison with the half-life of *cis*-1,3-D hydrolysis (~155 h), the DT_{50} of the fumigant decreased to 7.3 and 1.4 h in aqueous solutions containing 2.0 and 8.0 mM thiosulfate, respectively.

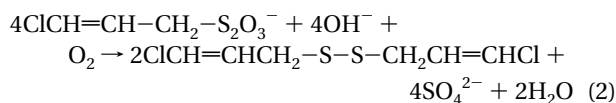
Previous research has suggested that the fumigant 1,3-D is susceptible to nucleophilic dechlorination by thiosulfate via an S_N2 mechanism (17). Thiosulfate, as a nucleophile, may displace chloride at C3 of *cis*-1,3-D to yield a Bunte ion:



In this study, the primary reaction product was also confirmed by LC/MS analysis as a Bunte ion, which is consistent with previously proposed results (17). The mass spectrum for this product at pH 2–3 matches the thiosulfate derivative of 1,3-D with a molecular structure of ClCH=CHCH₂-S₂O₃H (R-S₂O₃H) and a nominal mass of 188. This result suggests that thiosulfate fertilizer used as a chemical remediation reagent converts the volatile fumigant 1,3-D to a nonvolatile Bunte salt.

Stability of Thiosulfate Derivative of 1,3-D (R-S₂O₃⁻) in Aqueous Solution. To evaluate the stability of the Bunte ion reaction product in aqueous media, a series of hydrolysis experiments was conducted under different pH conditions. At pH 10, one major hydrolysis product was detected and identified (Figure S1 and S2, Supporting Information) as consistent with the dialkyl disulfide ClCH=CHCH₂-S-S-CH₂CH=CHCl (R-S-S-R). Also, the mass spectrum compared closely to that previously observed for this compound (22).

The formation of the dialkyl disulfide (R-S-S-R) from the hydrolysis of R-S₂O₃⁻ is illustrated in Figure 2. In basic solution (pH 10) at 45 °C, the concentration of the hydrolysis product R-S-S-R increased rapidly at the beginning of the incubation. The maximum molar concentration of R-S-S-R achieved was approximately 47% of the initial concentration of *cis*-1,3-D, which indicates a stoichiometric hydrolysis of R-S₂O₃⁻. The transformation pathway is proposed as follows:



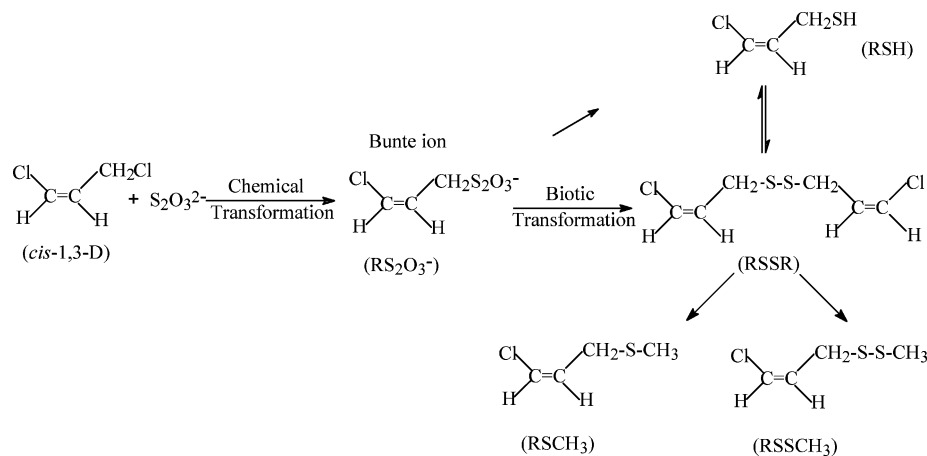
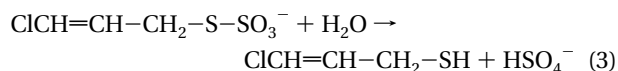


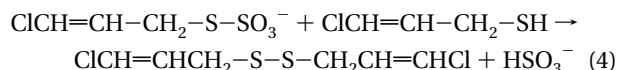
FIGURE 3. Proposed partial pathway of *cis*-1,3-D transformation in thiosulfate amended soil.

After 1 d, the concentration of R-S-S-R began to decline gradually. Meanwhile, the hydrolysis solution turned yellow, which implies further decomposition of R-S-S-R. Similar trends were observed when the thiosulfate derivative of 1,3-D was hydrolyzed in pH 10 solution at 25 °C (Figure 2). However, the formation rate of R-S-S-R at 25 °C was less than that at 45 °C, which indicates that the R-S₂O₃⁻ is more susceptible to hydrolysis in basic solution at high temperature.

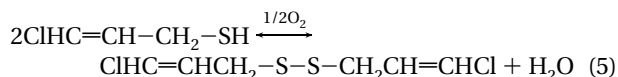
Similar experiments were conducted to evaluate the hydrolysis of R-S₂O₃⁻ in neutral and acidic solutions. The results showed that no appreciable transformation occurred when R-S₂O₃⁻ was incubated in neutral aqueous solution, even at high temperatures (45 °C, data not shown). These observations suggest that the reaction product of *cis*-1,3-D and thiosulfate is fairly stable in neutral aqueous solution. In strongly acidic solution (2.0 M HCl), however, two hydrolysis products (Figure S1, Supporting Information) were detected and identified as a mercaptan (R-SH) and R-S-S-R according to the interpretation of their mass spectra (Figure S2, Supporting Information), which are attributable to the acid hydrolysis of R-S₂O₃⁻. This result indicates that the Bunte ion (R-S₂O₃⁻) can hydrolyze in strongly acidic solution to yield the mercaptan and bisulfate ion:



The mercaptan may further react with remaining R-S₂O₃⁻ to form a dialkyl disulfide compound:



This product R-S-S-R can also be formed through the oxidation of the mercaptan:



The reaction is easily reversed, and the latter can be reduced back to the former. The entire proposed transformation pathway is consistent with previous reports pertinent to the acid hydrolysis of Bunte salts (23, 26).

The hydrolysis of R-S₂O₃⁻ was relatively slow in the pH 2 buffer solution. In contrast to the strongly acidic solution (2.0 M HCl), only small amounts of RSH and R-S-S-R were formed when an identical concentration of R-S₂O₃⁻ was incubated in the pH 2 buffer solution. Examining the stoichiometry of the conversion indicated that the formation

of R-S-S-R only accounted for about 1–2% of the initial concentration of R-S₂O₃⁻ during this experiment (Figure 2). Overall, the thiosulfate derivative of 1,3-D is relatively stable in neutral and moderately acidic solutions. Complete hydrolysis of the reaction derivative is expected to occur only under harsh conditions such as in highly alkaline or acidic solutions.

Transformation of *cis*-1,3-D in Thiosulfate-Amended Soil. The transformation kinetics of *cis*-1,3-D by thiosulfate was further examined in Arlington sandy loam soil. The plot of ln [*cis*-1,3-D] versus time is linear (Figure S3A, Supporting Information), indicating that *cis*-1,3-D transformation in thiosulfate-amended and unamended soils may be well described by first-order kinetics. The dissipation of *cis*-1,3-D was substantially accelerated in the soil amended with thiosulfate compared to the unamended treatment. The half-life of *cis*-1,3-D was reduced from approximately 117 h in the unamended soil to 2 h in the soil amended with sodium thiosulfate at a molar ratio of 1:4 1,3-D:thiosulfate.

In addition to determining the concentrations of *cis*-1,3-D in amended and unamended soils, the formation of nonpolar volatile and semivolatile organic products was also monitored simultaneously by GC/MS. In the unamended soil, no nonpolar fumigant metabolites were detected. In contrast, several organic sulfur products, such as R-SH and R-S-S-R, were identified in thiosulfate-amended soil treated with *cis*-1,3-D. The evolution profiles of some identified products are depicted in Figure S3B (Supporting Information). The experimental results clearly indicate that the initial reaction product, the thiosulfate derivative of 1,3-D (R-S₂O₃⁻), is unstable in soil and may further convert to other organic sulfur compounds. In addition to the dialkyl disulfide (RSSR) and mercaptan (RSH) derived from direct conversion of R-S₂O₃⁻ in the amended soils, a few other organic sulfur compounds including a mercaptomethyl-substituted derivative (R-S-CH₃) and a disulfur-substituted methyl derivative (R-S-S-CH₃) were detected. The mass spectra for these two products are shown in Figure S4 (Supporting Information). Note that these products were not observed in aqueous solution. The occurrence of these two products indicates that the soil provided methyl groups or methyl radicals available as substituted groups. On the basis of these identified products, a tentative partial pathway of *cis*-1,3-D transformation by thiosulfate in soil is depicted in Figure 3.

In the thiosulfate-amended soil, >99% of the applied *cis*-1,3-D disappeared within 1 d. Meanwhile, the dialkyl disulfide (R-S-S-R) was formed gradually and reached a maximum at 4 d (Figure S3B, Supporting information). Obviously, the rapid disappearance of *cis*-1,3-D was not accompanied by a proportional rise of the product R-S-S-R. The lag in the formation of R-S-S-R supports the proposed pathway, in

which the disulfide compound is derived from the further transformation of the thiosulfate derivative $R-S_2O_3^-$ (Figure 3). After 4 d, the concentration of $R-S-S-R$ began to decrease (Figure S3B, Supporting information), which indicates that this product may undergo further transformation in the soil. It is important to note that the amount of $R-S-S-R$ formed was not in proportion to the fumigant loss on a molar basis. The maximum concentration of $R-S-S-R$ only accounted for 3.5% of the initial concentration of *cis*-1,3-D. Other identified products, including $R-S-CH_3$, $R-S-S-CH_3$, and $R-SH$, had maximum concentrations $<0.5\%$ of the initial 1,3-D concentration. These results indicate that most of the thiosulfate derivative $R-S_2O_3^-$ may remain in soil, and only a small portion was transformed to nonpolar volatile and semivolatile organic products. Also, not all potential products were identified by the methods used in this study. Other $R-S_2O_3^-$ conversion processes may exist in addition to the transformation pathways proposed in Figure 3.

Conversion Mechanism of Thiosulfate Derivative of 1,3-D. The thiosulfate derivative of 1,3-D was a primary reaction product of *cis*-1,3-D and thiosulfate in both aqueous solution and soil. Our results showed that the thiosulfate derivative was more susceptible to further transformations in soil than in neutral solutions, producing several volatile and semivolatile organic sulfur compounds. To explore the transformation mechanism of $R-S_2O_3^-$ in soil, a series of sterile/nonsterile soil experiments was conducted.

In general, the transformation of a pesticide in nonsterile soil involves both biological and chemical processes. In sterile soil, however, only abiotic mechanisms contribute to the transformation. Several organic sulfur compounds (such as $R-S-S-R$, $R-S-S-CH_3$, $R-S-CH_3$, and $R-SH$) were detected after $R-S_2O_3^-$ was directly injected into nonsterile soils. In contrast, when $R-S_2O_3^-$ was applied to sterile soil, no products were found until day 4 when a very small amount of $R-S-S-R$ was detected (Figure S5, Supporting information). The concentration of $R-S-S-R$ formed in the sterile soil was much lower than that in the nonsterile soil, suggesting that $R-S_2O_3^-$ is relatively stable in sterile soil and that the transformation of $R-S_2O_3^-$ in soil is primarily attributable to biotic mechanisms. Therefore, it is likely that the stability of the thiosulfate derivative of 1,3-D is strongly dependent on soil microbiological activity. Collectively, 1,3-D first underwent a chemical transformation to form a nonvolatile organic anion in soil amended with thiosulfate fertilizer. The further conversion of the reaction product in soil was primarily a biotic process (Figure 3).

Volatile/Semivolatile Organic Sulfur Products. The further transformation of $R-S_2O_3^-$ in soil resulted in the formation of several organic sulfur compounds, which may enter the atmosphere through volatilization. Moreover, these products may result in noticeable odors because volatile sulfur compounds have relatively low odor threshold values. This study suggests that an unpleasant odor from fields treated with ATS may be associated with the volatilization of these organic sulfur compounds.

The distribution of identified volatile/semivolatile sulfur compounds between the soil and air phases was examined in soils 2 d after treatment with $R-S_2O_3^-$. Figure 4 shows the relative amounts of the four identified volatile/semivolatile organic sulfur compounds in the air and soil phases from four different soils. These results show that at least two organic sulfur compounds ($R-S-CH_3$ and $R-S-S-CH_3$) were detected in the air phase of all four soils. The concentration of $R-S-CH_3$ was significantly higher than that of $R-S-S-CH_3$ (Figure 4). The maximum air and soil concentrations of $R-S-CH_3$ were measured in the Milham sandy loam that has the highest organic matter content and thus may contain more available methyl groups or methyl radicals. Although the total amounts of these two methylated volatile products were very

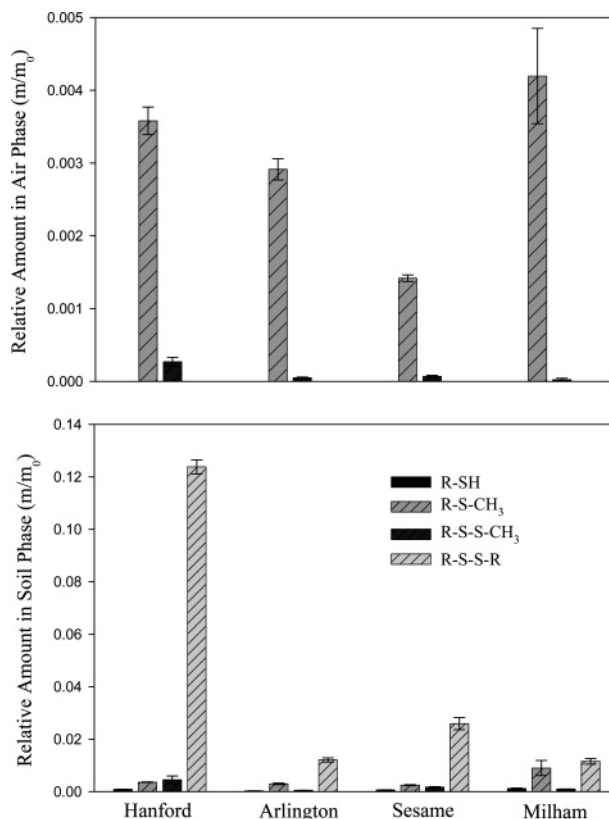


FIGURE 4. Distribution of four identified volatile/semivolatile sulfur-containing products in air and soil phases. The relative amounts are normalized to the initial application rate of $R-S_2O_3^-$ (0.5 mmol). Error bars represent standard deviations of triplicate samples.

small relative to the initial application rate of $R-S_2O_3^-$, the possible impact on air quality should not be ignored because of their odor, low perception threshold, and potential nuisance to farm workers and nearby residents. The concentration of each of these sulfur products was much higher in the soil phase than in the air phase (Figure 4). Also, the compound $R-S-S-R$ was detected as a primary product in all soils. The Hanford sand produced the highest concentration $R-S-S-R$, followed by the Sesame sandy loam, the Arlington sandy loam, and the Milham sandy loam. No strong correlation was observed between the conversion rate of $R-S_2O_3^-$ and soil properties such as soil organic matter content and pH, which further indicates that the transformation of $R-S_2O_3^-$ in soil is primarily a biotic process.

Environmental Implications. Thiosulfate fertilizers react readily with a variety of halogenated organic compounds via a nucleophilic substitution reaction mechanism (27, 28). Thiosulfate has been recommended as a chemical remediation reagent to reduce environmental pollution. For example, in an instantaneous capturing and destruction approach, thiosulfate solution is used as an inexpensive nonhazardous scrubbing reagent to capture methyl bromide from air streams and decompose it into harmless byproducts (29–31). This technology may also be very effective in detoxifying other volatile halogenated contaminants to protect air quality. Our study suggests that the direct farm discharge of scrubber solution may result in the formation of some volatile/semivolatile organic sulfur compounds in soil, although the reaction product may be stable in neutral solution. These results suggest that the waste solution derived from the reaction of halogenated chemicals and thiosulfate should be properly treated to avoid secondary contamination.

This study provides information contributing to a fuller understanding of thiosulfate fertilizers as remediation agents

for halogenated fumigants. The use of thiosulfate fertilizers in RSBs may result in the formation of a small amount of volatile/semivolatile sulfur products. The potential effect of these products on air quality should be considered when assessing this emission-reduction strategy. Also, this information will be very useful for the further development of efficient and comparatively inexpensive strategies for reducing fumigant emissions and in the establishment of regulations regarding the application of chemical remediation techniques in large scale fields and the treatment of waste solutions.

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Supporting Information Available

Soil properties, Bunte salt synthesis, and figures showing selected ion chromatograms of hydrolysis products, EI mass spectra of hydrolysis and transformation products, and transformation of *cis*-1,3-D as well as formation of volatile/semivolatile products in sterile and nonsterile soils amended with thiosulfate. This material is available free of charge via the Internet at <http://pubs.ars.org>.

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