

CONSTRUCTION OF A REACTIVE SURFACE BARRIER TO REDUCE FUMIGANT
1,3-DICHLOROPROPENE EMISSIONS

WEI ZHENG,*†‡ SHARON K. PAPIERNIK,§ MINGXIN GUO,†‡ ROBERT S. DUNGAN,|| and SCOTT R. YATES‡

†Department of Environmental Sciences, University of California, Riverside, California 92521, USA

‡U.S. Department of Agriculture–Agriculture Research Service, Soil Physics and Pesticides Research Unit, George E. Brown, Jr., Salinity Laboratory, Riverside, California 92507

§U.S. Department of Agriculture–Agriculture Research Service, North Central Soil Conservation Research Laboratory, 803 Iowa Avenue, Morris, Minnesota 56267

||U.S. Department of Agriculture–Agriculture Research Service, Animal Manure and Byproducts Laboratory, 10300 Baltimore Avenue, Beltsville, Maryland 20705

(Received 30 September 2004; Accepted 24 January 2005)

Abstract—Halogenated fumigants have been used extensively in production agriculture to control soilborne pests. These types of pesticides are highly volatile and are prone to affect air quality and imperil public health. In the present study, a chemical tarp approach, termed a reactive surface barrier (RSB), was developed to reduce the emission of fumigant 1,3-dichloropropene (1,3-D) from the soil surface. The agrochemicals thiourea and allylthiourea were tested as active reagents for the construction of a RSB, where these soil amendments react with 1,3-D to form nonvolatile isothiuronium ions at the soil surface and, thereby, impede fumigant emission into the atmosphere. The feasibility of the method largely depends on the reactivity of 1,3-D and the RSB agrochemicals in soil as well as on the mobility, persistence, and toxicity of the transformation products. Therefore, the reaction kinetics and transformation mechanism of 1,3-D by thiourea and allylthiourea were studied comprehensively in aqueous solution and soil. A catalytic process occurring at the surface of soil colloids facilitated the reaction between 1,3-D and thiourea in amended soils. The rate of 1,3-D transformation in thiourea-amended soil increased with decreasing soil moisture or increasing thiourea amendment level. In a field trial, a thiourea RSB reduced cumulative 1,3-D emissions by more than 80% relative to that in bare soil surface. The present results clearly indicate that this chemical remediation technology has great potential to control the emissions of volatile halogenated organic contaminants and to mitigate atmospheric pollution.

Keywords—Fumigant 1,3-Dichloropropene Reactive surface barrier Atmospheric emission Chemical remediation

INTRODUCTION

Atmospheric pollution by volatile and semivolatile halogenated hydrocarbons is of particular concern, because these ubiquitous contaminants present a potential threat to public health [1–3]. Moreover, the release of some volatile halogenated compounds often is associated with the depletion of the stratospheric ozone layer, because the massive loss of ozone in the polar stratosphere is catalyzed by halogen radicals derived from volatile halogenated compounds [4–6]. Generally, these types of compounds are introduced to the environment through anthropogenic activities, including agricultural uses (halogenated pesticides), industrial release (halogenated solvents), and improper disposal of chemical wastes, and as a result of chlorination by-products [7] or degradation intermediates of various halogenated organic chemicals.

Soil fumigants are highly volatile pesticides that are widely used to control soilborne pests before planting a variety of economically important crops. Most registered (e.g., methyl bromide, 1,3-dichloropropene [1,3-D], and chloropicrin) and proposed chemical fumigants (e.g., methyl iodide and propargyl bromide) are halogenated aliphatics. Each of these halogenated fumigants has a very high vapor pressure that fa-

cilitates their diffusion through the soil, resulting in effective soil disinfection. The rapid movement of fumigants in soil also may lead to high emissions from the soil surface into the atmosphere. Therefore, it is necessary to seek efficient strategies and develop feasible technologies to control the atmospheric emission of fumigants.

Fumigant emissions can be controlled by physical containment (diffusion barrier) and by enhancing abiotic and biotic degradation processes. One of the most common physical containment strategies is the use of plastic film to cover the soil surface after fumigation. Modification of soil degradation capacity is another important alternative in reducing the volatilization of soil fumigants. Numerous studies have shown that incorporation of composted manure into soil may increase fumigant degradation through stimulating the growth and activity of fumigant-degrading microorganisms [8–11]. Application of effective remediation reagents to degrade soil fumigants by chemical processes is becoming an attractive approach to reduce atmospheric emissions. Recently, a chemical remediation technology, termed a reactive surface barrier (RSB), has been proposed as a means of impeding fumigant emission from the soil surface [12]. In this approach, a thin-layer RSB is constructed by applying reactive agrochemicals to the soil surface so that fumigant vapors are intercepted and rapidly degraded at the soil–air interface, thereby significantly reducing atmospheric emissions. Therefore, the crux of the technology is the choice of appropriate agrochemicals to accelerate the transformation of fumigants on the soil surface, detaining the reaction products in soil for gradual mineralization.

* To whom correspondence may be addressed (wzheng@ussl.ard.usda.gov).

Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government.

Considering that most fumigants are halogenated aliphatic compounds, it is very helpful to select suitable reactants according to the common reaction mechanisms and characteristics of volatile halogenated compounds. In general, halogenated aliphatic compounds undergo two types of transformations in the environment: Nucleophilic substitution and reductive dehalogenation. For monohalogenated and dihalogenated compounds, the bimolecular nucleophilic substitution (S_N2) reaction is believed to play a primary role in the dehalogenation process of these halogenated contaminants in the presence of certain nucleophiles [13,14]. The fumigants methyl bromide and methyl iodide, for instance, can be dehalogenated by some sulfur species in the aquatic environment via a S_N2 reaction [3,15,16]. For polyhalogenated compounds, reductive dehalogenation can occur through several mechanisms, such as hydrogenolysis (the replacement of a halogen with a hydrogen), dehydrodehalogenation (the loss of a halogen and a hydrogen from an adjacent carbon to form a C-C double bond), reductive α -elimination, and reductive β -elimination (dihaloelimination to form a C-C double bond) [17–19]. For example, the fumigant chloropicrin undergoes reductive degradation in the soil environment [20] and in mixture with metam sodium [21] via a sequential hydrogenolysis process.

Numerous reports have shown that some naturally occurring nucleophiles, such as sulfur species, have high reactivity with a variety of halogenated compounds [13,14,17]. Thus, chemical remediation using sulfur species is being investigated to eliminate halogenated contaminants in water and soil. For example, destruction of chlorination by-products with sulfite [7] and dechlorination of chloroacetanilide herbicides by ammonium thiosulfate [22] are suggested as currently available and acceptable technologies for the treatment of these contaminants in water. Thiourea and allylthiourea, which have been proposed for use as nitrification inhibitors [23], accelerate the transformation of halogenated compounds, such as methyl iodide [15]. Nitrification inhibitors are a group of agrochemicals used to minimize fertilizer nitrogen loss by limiting the rate of oxidation of ammonium to nitrate and, thereby, to increase the efficiency of fertilizer usage and reduce nitrate leaching. Therefore, the use of thiourea and allylthiourea as reactants in a RSB has great potential to control atmospheric emissions of fumigants in agricultural fields.

The present research aims to characterize the rapid transformation of 1,3-D by thiourea and allylthiourea to provide valuable information for the construction of a RSB with these agrochemicals to reduce the atmospheric emission of 1,3-D. The fumigant 1,3-D is a highly volatile halogenated fumigant widely used in the United States as an alternative to methyl bromide. Because 1,3-D is classified as a B2 carcinogen (probable human carcinogen), human exposure to the fumigant via inhalation or ingestion is a toxicological threat. Therefore, it is important to minimize atmospheric emissions of 1,3-D to protect air quality and human health.

MATERIALS AND METHODS

Chemicals and soils

The 1,3-D standard (Telone II, 50.5% *cis* isomer and 46.9% *trans* isomer) was donated by Dow AgroSciences LLC (Indianapolis, IN, USA). Thiourea (purity, 99%) and 1-allylthiourea (purity, 98%) were purchased from Aldrich Chemical (Milwaukee, WI, USA). Commercial chemical products used in the field were obtained from the manufacturers. An InLine®

formulation of 1,3-D (an emulsifiable concentrate of 1,3-D containing 61% 1,3-D and 33.3% chloropicrin) was provided by Dow AgroSciences LLC. Thiourea was obtained from Spectrum Chemical (Gardena, CA, USA).

The soil used in the incubation study was an Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralf) that was collected from the University of California, Riverside Agricultural Experiment Station (Riverside, CA, USA). Fresh soils were sampled from the top 15 cm (A horizon) of a field that has no history of fumigant application. Moist soils were passed through a 2.0-mm sieve without complete air-drying and were stored at low temperature before use. Soil organic carbon content was 0.92%, and pH was 7.2.

Batch experiments

The first set of batch experiments was conducted in phosphate buffer solution (pH 6.9) to measure the kinetics and mechanisms of reaction of 1,3-D with thiourea and allylthiourea. Serum bottles (125 ml) sealed with Teflon®-faced butyl rubber septa served as reactors. In the sealed system, reactors contained 100 ml of thiourea or allylthiourea buffer solution (1.0 mM). Kinetics experiments were initiated by spiking the reactors with 1,3-D stock solution, yielding an initial concentration of 0.5 mM. Control experiments were concurrently carried out in phosphate buffer solutions containing only 1,3-D to determine the hydrolysis of the fumigant. All reactors were vigorously shaken for 2 min and then incubated at $25 \pm 0.5^\circ\text{C}$ in the dark. Aliquots (0.5 ml) were withdrawn periodically from triplicate bottles and extracted by ethyl acetate (3.0 ml) and anhydrous sodium sulfate (2.5 g), followed by analysis via gas chromatography (GC).

To identify primary transformation products and to elucidate the reaction pathway of 1,3-D with thiourea, two derivative processes were conducted before the extraction: Aliquots of reaction mixtures were adjusted to pH 10 and heated at 60°C in a water bath for 30 min, and aliquots of reaction mixtures were methylated using excess methyl iodide (0.1 M) in alkaline solution (pH 10) and then heated at 60°C for 30 min. After cooling to room temperature, all treated samples were extracted with ethyl acetate, followed by analysis via GC–mass spectrometry (MS).

The second set of batch experiments was designed to investigate the degradation of 1,3-D in soil amended with thiourea and allylthiourea. Thiourea and allylthiourea stock solutions were added separately to soil and thoroughly mixed in a plastic bag. Samples (10 g dry wt) of the amended soil were weighed into 21-ml headspace vials and then spiked with 1,3-D at 0.5 mmol/kg. Unamended soil samples were prepared similarly and used as controls. Sterilized soil was achieved by autoclaving soil twice at 121°C before treatment with 1,3-D. All sample vials were sealed with Teflon-faced butyl rubber septa and incubated in the dark at $25 \pm 0.5^\circ\text{C}$. Triplicate vials were sacrificed periodically for analysis by removing them from the incubator, chilling them in a -21°C freezer for 3 h, and extracting with ethyl acetate (10.0 ml) and anhydrous sodium sulfate (8.0 g). Aliquots of the ethyl acetate extracts were transferred into GC vials and then refrigerated until the end of the experiment, when all samples were analyzed for 1,3-D concentration by GC. Preliminary experiments showed that the 1,3-D recovery using the above-described procedures ranged from 95 to 105%.

To determine the influence of the thiourea amendment level on the degradation rate of 1,3-D, soil samples were premixed

with different thiourea stock solutions to generate initial concentrations of 0, 0.5, 1.0, and 2.0 mmol/kg of thiourea. All samples were spiked with 0.5 mmol/kg of 1,3-D. Thus, the initial molar ratios of thiourea to 1,3-D were 0:1, 1:1, 2:1, and 4:1. For these soil samples, the gravitational moisture content was 10% (wt/wt). Another experiment was carried out to determine the effect of soil moisture variation on the rate of 1,3-D transformation in thiourea-amended soil. Amended soils were preadjusted to different initial water contents by air-drying or adding water, yielding gravimetric soil water contents of 3, 5, 10, 14, and 18%. In this experiment, the initial concentrations of 1,3-D and thiourea were 0.5 and 1.0 mmol/kg, respectively. All treated samples were incubated at $25 \pm 0.5^\circ\text{C}$ in the dark. Triplicate soil samples were extracted periodically and analyzed using the procedure described above.

Field experiments

A field experiment was conducted at the University of California Agricultural Experiment Station in Riverside from December 9 to 16, 2002. Raised beds (15 cm high, 50 cm across the top, with 20-cm furrows) were constructed mechanically. A drip line was installed at the center of each bed at a depth of 15 cm. Rows (5 m long) were treated with different practices, including bare soil surface; bed tarped with high-density plastic polyethylene (HDPE), bare furrows; bed tarped with Hytibar plastic, bare furrows; and bed and furrows treated with a thiourea RSB. Duplicate rows were used for each tarp, and all treatments were arranged in a completely randomized design. Beds receiving HDPE were tarped mechanically. Hytibar was laid manually. The RSB was constructed by spraying 4 L of thiourea solution (~ 2.6 mol) on the top, side, and furrow of each bed before fumigation. InLine was premixed with water and delivered through the drip lines into all plots. The application rate of 1,3-D was approximately 0.35 mol in each plot. Following fumigant application, freshwater was flushed through the drip irrigation system to rinse the lines.

Volatilization of 1,3-D was measured using galvanized-steel passive chambers, which have been used successfully for measuring fumigant flux in previous field experiments [24,25]. Chambers were placed on the center of the bed top, the side slope, and the furrow for 30 min; then, an aliquot of the trapped air (100 ml) was withdrawn through a sampling port in the top of the chamber. Each air sample was drawn through an adsorbent tube (XAD-2, containing two beds of adsorbent [40 and 80 mg]) to extract 1,3-D from the airstream. All adsorbent tubes were capped on both ends and stored at -21°C until analysis. Chambers were removed and aerated between sampling times. The content of 1,3-D in each adsorbent tube was determined by using the procedure described by Papiernik et al. [26]. Volatilization fluxes were calculated according to the amount of 1,3-D in the adsorbent tube, X_t (μg); the volume of gas withdrawn from the chamber, V_s (ml); the chamber volume, V_c (ml); the chamber base surface area, A (m^2); and the chamber placement time, t_s (s)

$$\text{Flux} = X_t V_c / A V_s t_s$$

Flux was monitored for 7 d and was integrated over time to give an estimate of the total volatilization as a percentage of the applied dosage. Calculated results for the cumulative emissions were subjected to statistical analyses using a multivariate analysis-of-variance test. More details have been described in similar field experiments [26].

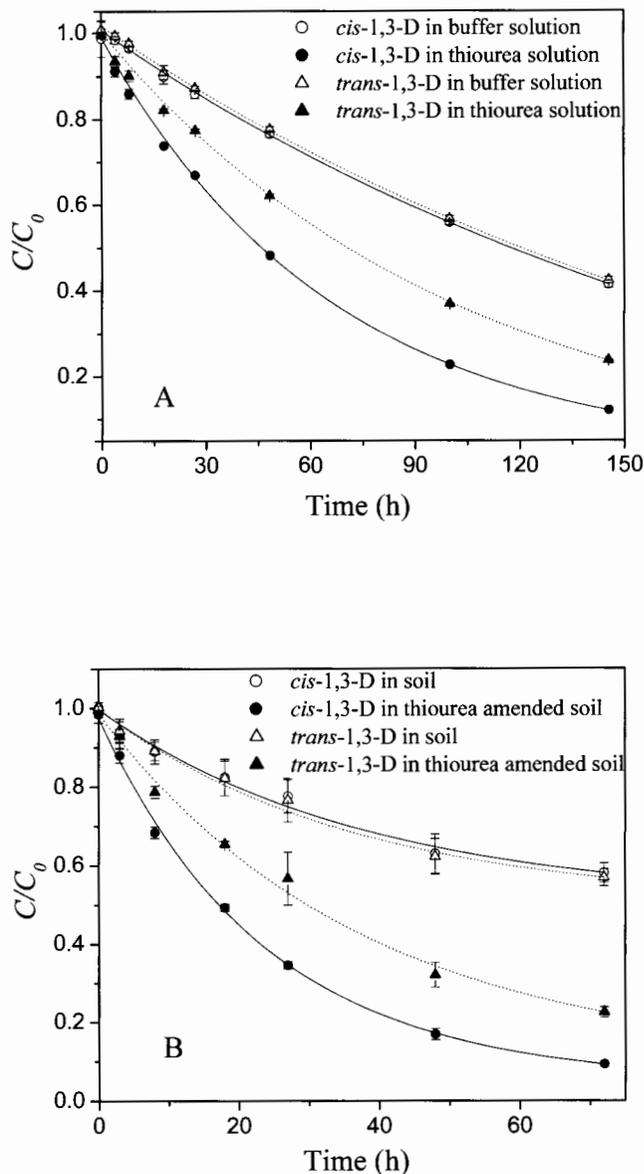


Fig. 1. Disappearance of 1,3-dichloropropene (1,3-D) in phosphate buffer (pH 6.9) and thiourea solution (**top**) and unamended and amended nonsterile soil (**bottom**) at $25 \pm 0.5^\circ\text{C}$ (thiourea:1,3-D, 2:1). Data points are the mean of triplicate samples; error bars indicate the standard error. C_0 = initial concentration of 1,3-D in the solution and soil.

GC and GC-MS conditions

The concentration of 1,3-D was analyzed using a HP 6890 GC (Hewlett-Packard, Avondale, PA, USA) equipped with an on-column injector, a micro-electron-capture detector, and a DB-VRX fused-silica capillary column (length, 30 m; inner diameter, 0.25 mm; film thickness, 1.4 μm ; J&W, Folsom, CA, USA). The GC conditions were a carrier gas (He) flow rate of 1.4 ml/min, an inlet temperature of 240°C , and a detector temperature of 290°C . The initial oven temperature was 50°C for 1 min; the temperature was increased to 80°C at $5.0^\circ\text{C}/\text{min}$ and held for 2.5 min, then increased to 120°C at $25^\circ\text{C}/\text{min}$ and held for 1 min. Under these conditions, the retention times for *cis*-1,3-D and *trans*-1,3-D were 8.03 and 8.87 min, respectively. Data were subjected to analysis of variance, and means were compared by least significant difference.

Transformation products were analyzed using a HP 5890

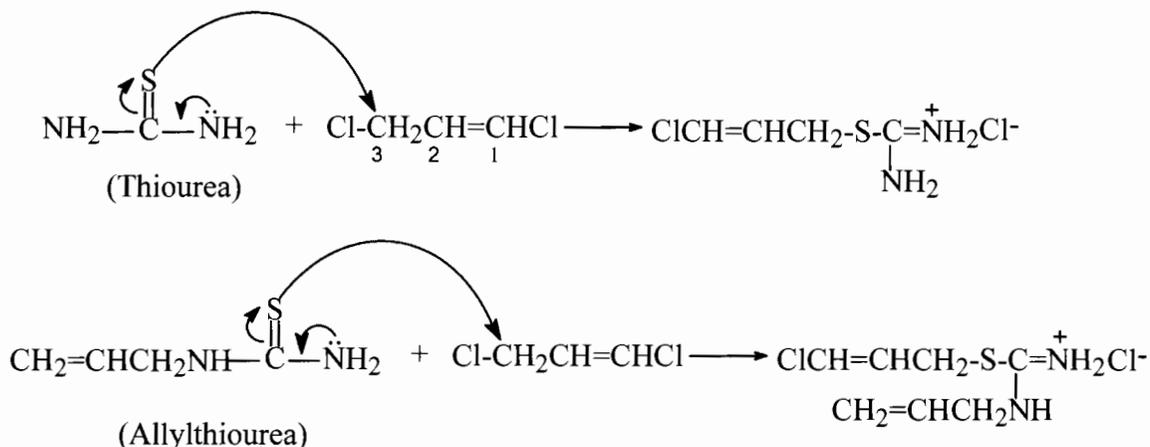


Fig. 2. Chemical reactions of 1,3-dichloropropene (1,3-D) with thiourea and allylthiourea.

GC (Hewlett-Packard) in tandem with a HP 5971 quadrupole mass-selective detector equipped with an on-column injector. Transformation products were separated using a HP-5MS fused-silica capillary column (length, 30 m; inner diameter, 0.25 mm; film thickness, 0.25 μm ; Hewlett-Packard). The electron-impact mass spectra were generated using an electron energy of 70 eV and were monitored for 1,3-D transformation products at m/z 50–300.

RESULTS AND DISCUSSION

1,3-D transformation by thiourea and allylthiourea

The transformation reactions of 1,3-D with thiourea and allylthiourea were determined in phosphate buffer solution (pH 6.9) and Arlington sandy loam. The time courses for disappearance of 1,3-D isomers in the thiourea aqueous solution are portrayed in Figure 1A along with their hydrolysis. In solution containing thiourea, both *cis*- and *trans*-1,3-D dissipated more rapidly than in the thiourea-free control solution. The accelerated disappearance of 1,3-D is a direct result of the reaction between 1,3-D and thiourea. As such, 1,3-D disappeared much more rapidly in thiourea-amended soil than in unamended soil (Fig. 1B), because thiourea accelerates the transformation of 1,3-D. Very similar trends in 1,3-D dissipation were observed in allylthiourea aqueous solution and amended soil.

Transformation rates of 1,3-D isomers in amended soil and in unamended soil were determined using a pseudo-first order kinetic model. In amended soil with an initial molar ratio of thiourea or allylthiourea to 1,3-D of 2:1, the transformation

rate of each 1,3-D isomer was increased approximately three- to sevenfold compared to the degradation rate in unamended soil (Table 1). Generally, fumigant degradation in soil can be mediated by both abiotic (e.g., chemical transformations) and biotic (e.g., microbial metabolism) processes. In sterile soil, however, 1,3-D degradation usually is attributable only to an abiotic degradation mechanism. The large decrease in k for 1,3-D isomers in sterile versus nonsterile soil (Table 1) indicated that soil microorganisms play a important role in 1,3-D degradation in unamended soil. These results are in agreement with those reported previously [27,28]. The rate of 1,3-D degradation in soil amended with thiourea or allylthiourea was not significantly impacted by autoclaving the soil (Table 1). This implies that the disappearance of 1,3-D isomers predominantly stems from the rapid reaction between the halogenated fumigant and thiourea or allylthiourea in amended soil. This chemical transformation overwhelms the effect of microbial degradation, although the latter contributes significantly to the total 1,3-D degradation in unamended soil.

Proposed reaction mechanism

In amended aqueous solution, 1,3-D is subject to hydrolysis and reaction with thiourea or allylthiourea via a S_N2 nucleophilic substitution process. The thiono group of thiourea and allylthiourea possesses nucleophilic reactivity and may readily attack 1,3-D to form an isothiuronium ion, liberating a chlorine at C3 in the process (Fig. 2).

Because of the nonvolatility of isothiuronium ions (trans-

Table 1. Pseudo-first order rate constants (k) for 1,3-dichloropropene (1,3-D; 0.5 mmol/kg) transformation in soil amended with thiourea and allylthiourea at $25 \pm 0.5^\circ\text{C}$ ^a

Treatment	<i>cis</i> -1,3-D		<i>trans</i> -1,3-D	
	$k(\text{h}^{-1})$	r^2	$k(\text{h}^{-1})$	r^2
Nonsterile soil				
Unamended (0:1)	$7.88 (\pm 0.71) \times 10^{-3}$	0.887	$8.31 (\pm 0.68) \times 10^{-3}$	0.905
Thiourea (2:1)	$3.78 (\pm 0.10) \times 10^{-2}$	0.995	$2.19 (\pm 0.08) \times 10^{-2}$	0.985
Allylthiourea (2:1)	$5.48 (\pm 0.15) \times 10^{-2}$	0.996	$3.10 (\pm 0.10) \times 10^{-2}$	0.992
Sterile soil				
Unamended (0:1)	$3.84 (\pm 0.38) \times 10^{-3}$	0.854	$4.04 (\pm 0.31) \times 10^{-3}$	0.905
Thiourea (2:1)	$3.73 (\pm 0.08) \times 10^{-2}$	0.996	$2.38 (\pm 0.06) \times 10^{-2}$	0.993
Allylthiourea (2:1)	$5.06 (\pm 0.17) \times 10^{-2}$	0.993	$2.93 (\pm 0.10) \times 10^{-2}$	0.990

^a The initial concentration of thiourea and allylthiourea in amended soil was 1.0 mmol/kg. Values in parentheses are the molar ratios of thiourea or allylthiourea to 1,3-D.

formation products in Fig. 2), the emission of 1,3-D may be impeded by the reaction with thiourea or allylthiourea at the soil surface. The isothiuronium ions are relatively stable in neutral aqueous solution, although they may be cleaved to mercaptans under alkaline conditions or by a high-molecular-weight amine [29]. Note that the major reaction products of 1,3-D and thiourea or allylthiourea are polar ions, so two derivatization approaches with GC-MS analysis were employed to identify the transformation products indirectly. A subset of experiments was conducted to deduce the reaction pathway between 1,3-D and thiourea by periodically analyzing extracts of the reaction mixtures that were alkalinized to pH 10 before solvent extraction. These extracts revealed four additional, late-eluting products that were not observed in the chromatograms of the extracts that were not pH-adjusted. Three of these products had different retention times on the total-ion chromatograms but presented the same electron-impact mass spectrum (Fig. 3A), which was consistent with the thioether $\text{ClCH}=\text{CHCH}_2\text{SCH}_2\text{CH}=\text{CHCl}$ (RSR). The reaction product of 1,3-D and thiourea, isothiuronium ion, may be decomposed to thiolate ions (RS^-) in basic solution, which can react with any remaining 1,3-D to form the thioether (RSR) (Fig. 4). Because 1,3-D is a mixture of *cis* and *trans* isomers, three corresponding isomer RSR products (Fig. 4) were determined with different retention times in the GC. Also, partial thiolate ions may convert to a symmetrical disulfide compound $\text{ClCH}=\text{CHCH}_2\text{-S-S-CH}_2\text{CH}=\text{CHCl}$ (RSSR), which was identified via its mass spectrum (Fig. 3B). More definitive studies were conducted by methylating products with excess CH_3I in alkaline solution, followed by extraction into ethyl acetate and analysis via GC-MS. Two major products exhibiting the same mass spectrum (Fig. 3C) were identified as mercaptomethyl-substituted derivatives $\text{ClCH}=\text{CHCH}_2\text{-S-CH}_3$ (RSCH_3), which stemmed from *cis* and *trans* reactants (Fig. 4). Similar results also were observed for the reaction of 1,3-D and allylthiourea (results not shown), supporting the proposed reaction mechanism between 1,3-D with thiourea and allylthiourea described above.

The transformation kinetics of 1,3-D shown in Figure 1 and Table 1 clearly indicate that the reaction of *cis*-1,3-D with thiourea or allylthiourea was significantly faster than that of *trans*-1,3-D. In the $\text{S}_{\text{N}}2$ nucleophilic substitution reaction, when thiourea attacks 1,3-D at C3, a crowded transition state forms. In the transition state, the potential rotation around the C-C bond of *cis*-1,3-D may be hindered by the chlorine at C1. The greater steric hindrance of the *cis* isomer facilitates its further transformation to generate the *cis* isothiuronium ion. The transition state of the *trans*-1,3-D has higher stability in comparison with the *cis* isomer, and the reaction with thiourea or allylthiourea shows a higher activation energy. Thus, the *trans* isomer was less reactive to thiourea or allylthiourea than the *cis* isomer was.

Effect of thiourea amendment level

Both thiourea and allylthiourea accelerate the transformation of 1,3-D in aqueous solution and soil. Also, these two nucleophiles demonstrated similar reaction mechanisms and reaction kinetics with 1,3-D in amended soil and solution. Considering the feasibility, popularity, and cost of application of these compounds as nitrification inhibitors, thiourea was selected as a reactant for further study.

Because the primary transformation of 1,3-D in thiourea-amended soil was an abiotic reaction process, the transfor-

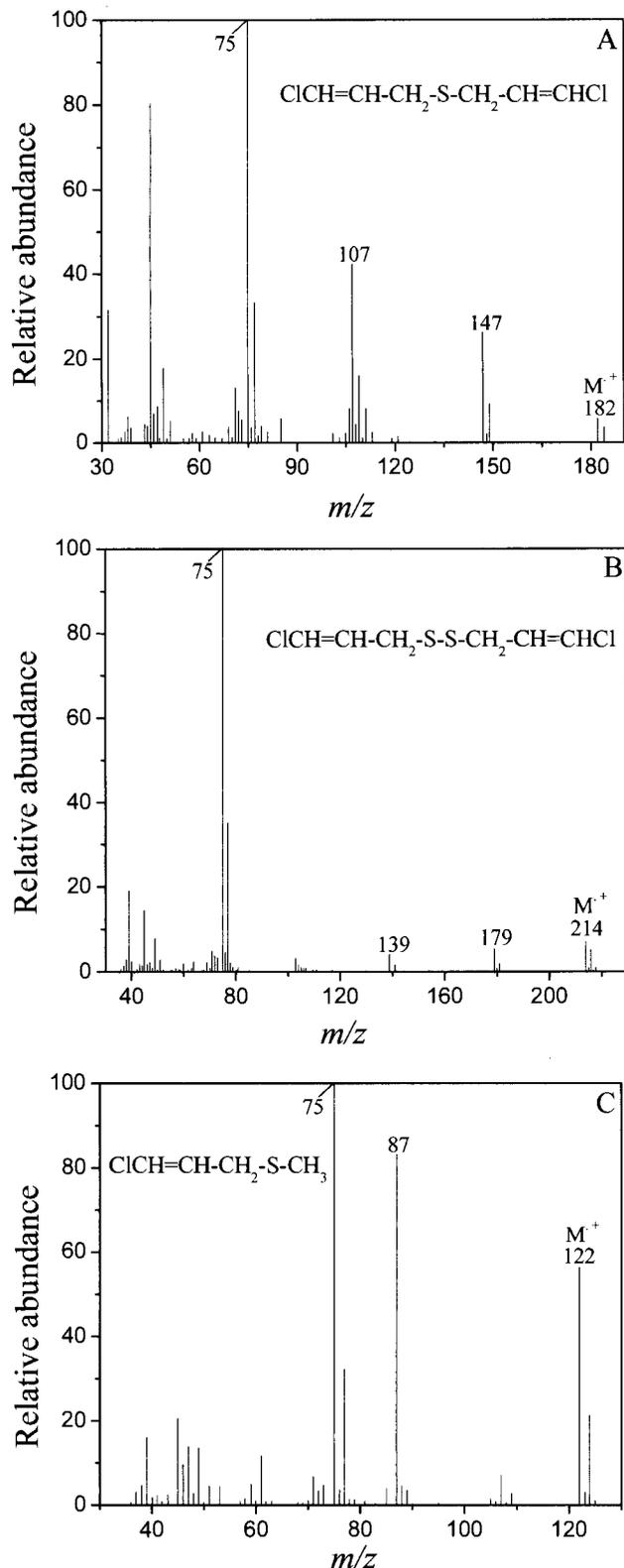


Fig. 3. Mass spectra (electron impact) for major transformation products obtained from the reaction of 1,3-dichloropropene (1,3-D) with thiourea after derivatization treatments. (A) Thioether ($\text{ClCH}=\text{CHCH}_2\text{SCH}_2\text{CH}=\text{CHCl}$). (B) Disulfide compound ($\text{ClCH}=\text{CHCH}_2\text{-S-S-CH}_2\text{CH}=\text{CHCl}$). (C) Methylated product ($\text{ClCH}=\text{CHCH}_2\text{-S-CH}_3$).

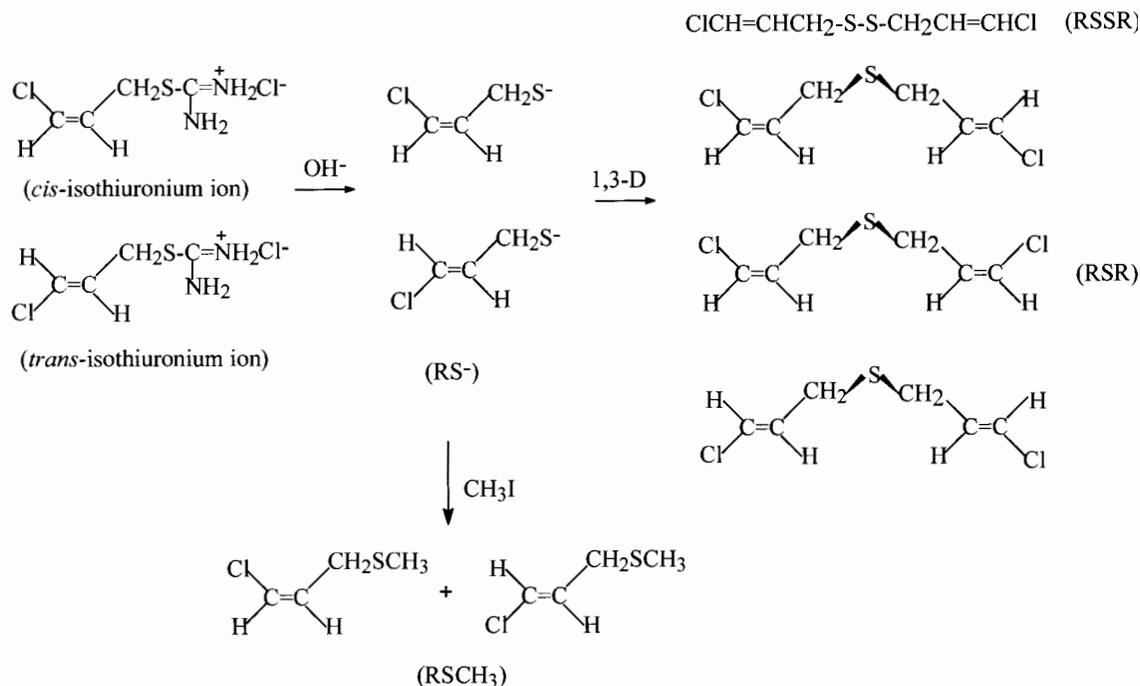


Fig. 4. Proposed transformation pathways of the reaction product of 1,3-dichloropropene (1,3-D) and thiourea (isothiuronium ion) in basic solution.

mation rate depends on the relative ratio of thiourea to 1,3-D. The rates of 1,3-D degradation in soils treated with different thiourea amendment levels are presented in Figure 5. As the initial thiourea to 1,3-D ratio increased, the degradation rate of 1,3-D was increased proportionally in amended soils. For example, the half-lives of *cis*-1,3-D were approximately 88, 33, 18, and 9.3 h when the molar ratios of thiourea to 1,3-D were 0:1, 1:1, 2:1, and 4:1, respectively. Similarly, the half-life of *trans*-1,3-D was reduced from 83 h in the unamended soil to 48 and 31 h when the molar ratio was 1:1 and 2:1, respectively, and reduced further to only 17 h when the molar ratio was 4:1. The dependence of the 1,3-D transformation rate on thiourea level indicates that the effectiveness of a thiourea RSB in reducing 1,3-D emissions will depend closely on the application rate of thiourea on the soil surface. Therefore, multiple factors, such as cost, quantitative control of fumigant volatilization, and crop productivity, should be considered for the application of thiourea RSB technology in agricultural fields.

Effect of soil moisture

Soil moisture can change drastically, both spatially and temporally, during soil fumigation, especially at the soil surface, where irrigation, rain, leaching, evaporation, and many other factors alter the soil water content. The effect of soil moisture on the rate of 1,3-D transformation in thiourea-amended soils was investigated in sealed experimental systems (Fig. 6). At a range of gravimetric soil water contents from 3 to 10%, moisture had no significant effect on the 1,3-D transformation rate. At soil water contents greater than 10%, the transformation rate of 1,3-D decreased. These results are in contrast to the general observation that high water contents favor abiotic reactions and microbial degradation of pesticides [30,31]. The discrepancy may be attributed to a catalytic transformation mechanism of 1,3-D in thiourea-amended soil, as has been observed for the reaction between thiourea and other halogenated compounds in soil [12]. Because organic matter

and clay minerals in soil are electron-rich, the orientation of bonding between the NH_2 group of thiourea and the surface of soil particles will favor electron transfer and result in increased nucleophilic activity of the thiono group. The delocalization of electrons may decrease the reaction activation energy and accelerate 1,3-D transformation in thiourea-amended soil. In amended soil with high water content, water polarization on the surface of soil particles impedes the electron transfer, inactivating the catalytic reaction process.

Typically, the moisture is low at the soil surface in the field because of evaporation, which will facilitate the effectiveness of thiourea as an amendment in the construction of a RSB. After fumigation, volatile 1,3-D is transformed to a nonvolatile isothiuronium ion by thiourea when 1,3-D diffuses upward through the amended reactive layer at the soil surface. There, low soil water content favors the catalytic transformation of 1,3-D by thiourea and improves the fumigant emission control by the RSB.

Reduction of 1,3-D emission by a thiourea RSB

A field trial was conducted to assess the potential for a thiourea RSB to reduce 1,3-D emissions. Before subsurface drip fumigation with 1,3-D, thiourea solution was sprayed uniformly on the soil surface. In bare beds without any treatment, volatilization of 1,3-D from the soil surface occurred immediately, and maximum flux was detected in the first 2 to 3 h after fumigant application for the bed top, side, and furrow locations (Fig. 7). In the thiourea-treated beds, volatilization fluxes were reduced considerably for the whole experimental period (Fig. 7). These results clearly demonstrate that using thiourea as a remediation agent to construct a RSB may effectively control 1,3-D emissions, thereby preventing air pollution by soil fumigation. Emissions measured in these experiments were low compared to those of previous field experiments [24,25], perhaps because of the cool air and soil temperatures existing during the field experiment (range, 2–

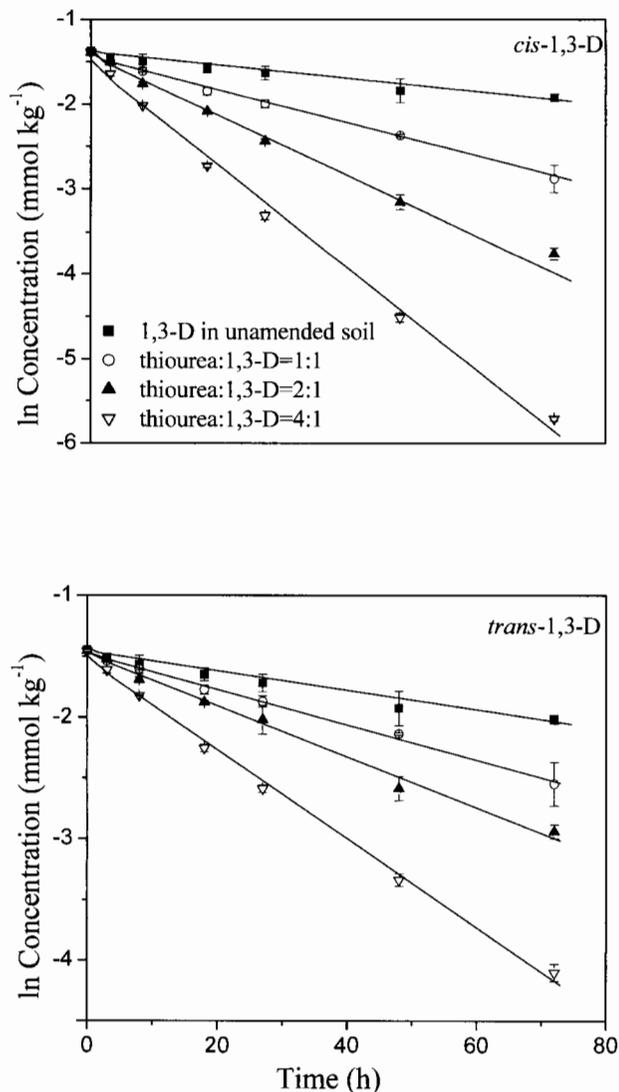


Fig. 5. Degradation of *cis*- and *trans*-1,3-dichloropropene (1,3-D) in soil amended with thiourea at different amendment levels.

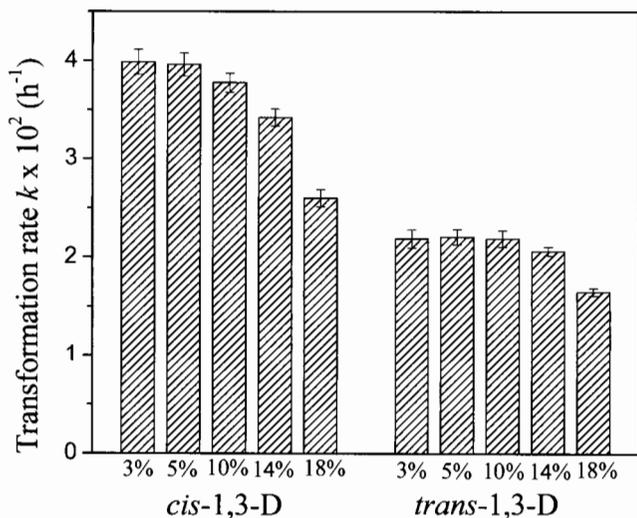


Fig. 6. Effect of soil moisture on the first-order transformation rate constant k (h^{-1}) in thiourea-amended soil at $25 \pm 0.5^\circ\text{C}$ (thiourea:1,3-D, 2:1). 1,3-D = 1,3-dichloropropene.

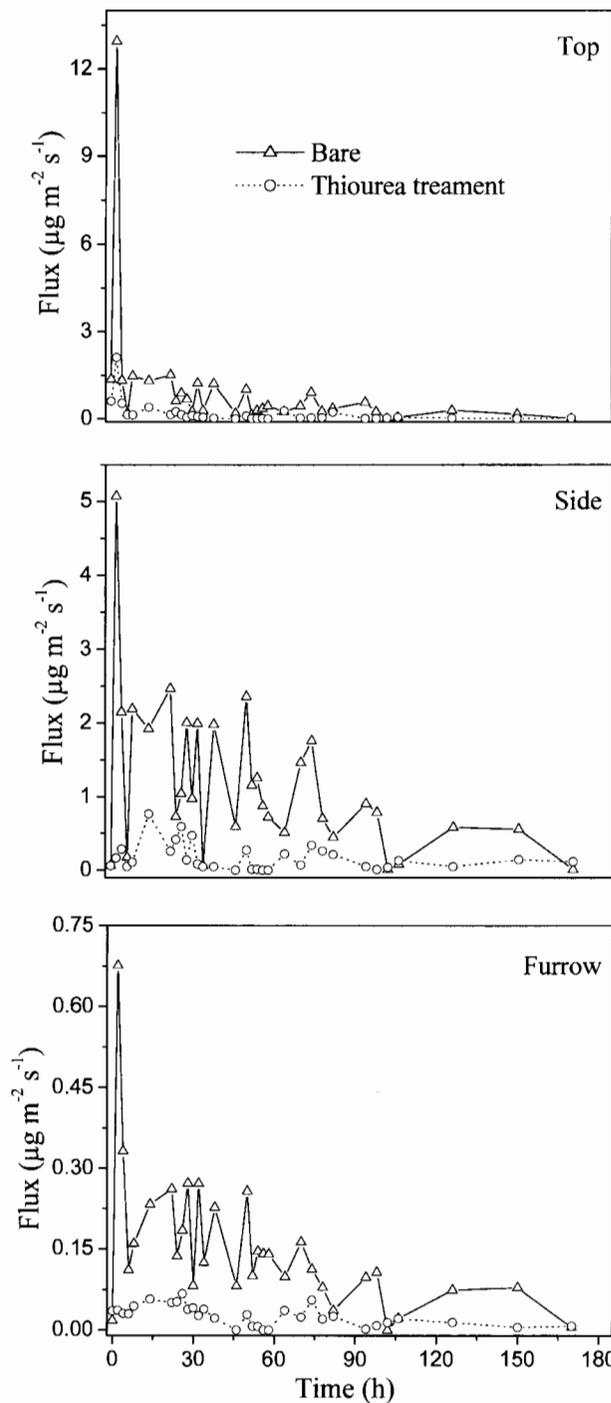


Fig. 7. Volatilization fluxes of 1,3-dichloropropene (1,3-D) from bare beds and surface thiourea-treated beds during the first 7 d after application. Data points indicate the mean of samples from duplicate rows.

22°C), and the high amount of water applied with the drip application, which inhibited gas-phase diffusion.

Cumulative emissions of 1,3-D at 7 d after application for the different treatments are summarized in Table 2. In the beds treated with a thiourea RSB, cumulative 1,3-D emissions were reduced by more than 80% relative to bare beds. Use of a thiourea RSB resulted in a total reduction in 1,3-D emissions similar to HDPE film (a conventional plastic film) and Hytibar film (a new, virtually impermeable film) (Table 2). Because the reaction process occurs only at the soil surface, thiourea

Table 2. Cumulative emissions of 1,3-dichloropropene (1,3-D; % applied) from the bed top, side slope, and furrow measured from the field experiments^a

Treatment	Top (%)	Side (%)	Furrow (%)	Total lost (%)
Bare	2.88A	2.98A	0.34A	6.20A
Thiourea RSB	0.39B	0.31B	0.28A	0.98B
HDPE tarp	2.50A	0.30B	0.10B	2.90B
Hytibar tarp	0.10B	0.10B	0.25A	0.45B

^a Values for 1,3-D between treatments followed by different letters are significantly different ($\alpha = 0.05$) by Tukey's mean separation test. HDPE = high-density plastic polyethylene; RSB = reactive surface barrier.

RSB treatment does not alter the fumigant distribution in the soil profile and, thus, does not affect pest control efficacy. These results indicate that the method of using agrochemical amendments to construct RSBs has great potential in reducing air pollution resulting from soil fumigation and may replace, in part, the use of plastic films to maintain atmospheric environmental quality and pest-control efficacy. Use of a RSB has several advantages compared to use of common plastic tarps, including elimination of the cost of the tarp; its application, removal, and disposal; and reduced worker exposure to fumigants that may occur during tarp removal. To improve the use of RSB technology in fumigated fields, further research is needed to evaluate comprehensively the impact of this approach on the environment, crop productivity, and cost-effectiveness.

Additionally, the reaction characteristics of thiourea and 1,3-D indicated in the present work suggest that many other halogenated organic compounds also may be degraded via a similar reaction process. Therefore, this chemical remediation technology may be used to control the emissions of many volatile halogenated contaminants and reduce their atmospheric pollution, rendering the significance of the technology (RSB) much greater than the single example presented here.

Acknowledgement—We thank Fred Ernst and Qiao-ping Zhang for invaluable discussions and assistance. The present study was funded by the U.S. Department of Agriculture Methyl Bromide Transitions Program (grant 2003-51102-02043).

REFERENCES

- Aelion CM, Conte BC. 2004. Susceptibility of residential wells to VOC and nitrate contamination. *Environ Sci Technol* 38:1648–1653.
- Montzka SA, Spivakovsky CM, Butler JH, Elkins JW, Lock LT, Mondeel DJ. 2000. New observational constraints for atmospheric hydroxyl on global and hemispheric scales. *Science* 288:500–503.
- Schwarzenbach RP, Giger W, Schaffner C, Wanner O. 1985. Groundwater contamination by volatile halogenated alkanes: Abiotic formation of volatile sulfur compounds under anaerobic conditions. *Environ Sci Technol* 19:322–327.
- Ohr HD, Sims JJ, Grech NM, Becker JO, McGiffen ME Jr. 1996. Methyl iodide, an ozone-safe alternative to methyl bromide as a soil fumigant. *Plant Dis* 80:731–735.
- U.S. Environmental Protection Agency. 2000. Protection of stratospheric ozone: Incorporation of Clean Air Act amendments for reductions in class I, group VI controlled substances. *Fed Reg* 65:70795–70804.
- Sun B, Griffin BM, Ayala-del-Río HL, Hashsham SA, Tiedje JM. 2002. Microbial dehalorespiration with 1,1,1-trichloroethane. *Science* 298:1023–1025.
- Croue J-P, Reckhow DA. 1989. Destruction of chlorination by-products with sulfite. *Environ Sci Technol* 23:1412–1419.
- Dungan RS, Gan J, Yates SR. 2001. Effect of temperature, organic amendment rate and moisture content on the degradation of 1,3-dichloropropene in soil. *Pest Manag Sci* 57:1107–1113.
- Dungan RS, Gan J, Yates SR. 2003. Accelerated degradation of methyl isothiocyanate in soil. *Water Air Soil Pollut* 142:299–310.
- Gan J, Yates SR, Papiernik SK, Crowley D. 1998. Application of organic amendments to reduce volatile pesticide emissions from soil. *Environ Sci Technol* 32:3094–3098.
- Gan J, Yates SR, Crowley D, Becker JO. 1998. Acceleration of 1,3-dichloropropene degradation by organic amendments and potential application for emissions reduction. *J Environ Qual* 27:408–414.
- Zheng W, Papiernik SK, Guo M, Yates SR. 2004. Remediation of methyl iodide in aqueous solution and soils amended with thiourea. *Environ Sci Technol* 38:1188–1194.
- Roberts AL, Sanborn PN, Gschwend PM. 1992. Nucleophilic substitution reactions of dihalomethanes with hydrogen sulfide species. *Environ Sci Technol* 26:2263–2274.
- Loch AR, Lippa KA, Carlson DL, Chin YP, Traina SJ, Roberts AL. 2002. Nucleophilic aliphatic substitution reactions of propachlor, alachlor, and metolachlor with bisulfide (HS^-) and polysulfide (S_n^{2-}). *Environ Sci Technol* 36:4065–4073.
- Zheng W, Papiernik SK, Guo M, Yates SR. 2003. Accelerated degradation of methyl iodide by agrochemicals. *J Agric Food Chem* 51:673–679.
- Gan J, Yates SR, Becker JO, Wang D. 1998. Surface amendment of fertilizer ammonium thiosulfate to reduce methyl bromide emission from soil. *Environ Sci Technol* 32:2438–2441.
- Larson RA, Weber EJ. 1994. *Reaction Mechanisms in Environmental Organic Chemistry*. Lewis, Boca Raton, FL, USA.
- Perlinger JA, Angst W, Schwarzenbach RP. 1996. Kinetics of the reduction of hexachloroethane by juglone in solutions containing hydrogen sulfide. *Environ Sci Technol* 30:3408–3417.
- Arnold WA, Winget P, Cramer CJ. 2002. Reductive dechlorination of 1,1,2,2-tetrachloroethane. *Environ Sci Technol* 36:3536–3541.
- Castro CE, Wade RS, Belser NO. 1983. Biodehalogenation. The metabolism of chloropicrin by *Pseudomonas* sp. *J Agric Food Chem* 31:1184–1187.
- Zheng W, Yates SR, Guo M, Papiernik SK, Kim JH. 2004. Transformation of chloropicrin and 1,3-dichloropropene by metam sodium in a combined application of fumigants. *J Agric Food Chem* 52:3002–3009.
- Gan J, Wang Q, Yates SR, Koskinen WC, Jury WA. 2002. Dechlorination of chloroacetanilide herbicides by thiosulfate salts. *Proc Natl Acad Sci USA* 99:5189–5194.
- Prasad R, Power JF. 1995. Nitrification inhibitors for agriculture, health, and the environment. *Adv Agron* 54:233–281.
- Gan J, Becker JO, Ernst FF, Hutchinson C, Knuteson JA, Yates SR. 2000. Surface application of ammonium thiosulfate fertilizer to reduce volatilization of 1,3-dichloropropene from soil. *Pest Manag Sci* 56:264–270.
- Wang D, Yates SR, Ernst FF, Knuteson JA, Brown GE Jr. 2001. Volatilization of 1,3-dichloropropene under different application methods. *Water Air Soil Pollut* 127:109–123.
- Papiernik SK, Yates SR, Dungan RS, Lesch SM, Zheng W, Guo M. 2004. Effect of surface trap on emissions and distribution of drip-applied fumigants. *Environ Sci Technol* 38:4254–4262.
- Ma QL, Gan J, Papiernik SK, Becker JO, Yates SR. 2001. Degradation of soil fumigants as affected by initial concentration and temperature. *J Environ Qual* 30:1278–1286.
- Zheng W, Papiernik SK, Guo M, Yates SR. 2003. Competitive degradation between the fumigants chloropicrin and 1,3-dichloropropene in unamended and amended soils. *J Environ Qual* 32:1735–1742.
- March J. 1985. *Advanced Organic Chemistry*. John Wiley, New York, NY, USA.
- Gan J, Yates SR, Knuteson JA, Becker JO. 2000. Transformation of 1,3-dichloropropene in soil by thiosulfate fertilizers. *J Environ Qual* 29:1476–1481.
- Parkin TB, Shelton DR. 1994. Modeling environmental-effects on enhanced carbofuran degradation. *Pestic Sci* 40:163–168.