Remediation of Methyl Iodide in Aqueous Solution and Soils Amended with Thiourea

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Methyl iodide (MeI) is considered a very promising fumigant alternative to methyl bromide (MeBr) for controlling soil-borne pests. Because atmospheric emission of highly volatile fumigants contributes to air pollution, feasible strategies to reduce emissions are urgently needed. In this study, thiourea (a nitrification inhibitor) was shown to accelerate the degradation of MeI in soil and water. In aqueous solution, the reaction between MeI and thiourea was independent of pH, although the rate of MeI hydrolysis increased in alkaline solution. Substantial increases in the rate of MeI dissipation were observed in thiourea-amended soils. Transformation of MeI by thiourea in aqueous solution was by a single chemical reaction process, while MeI degradation in thiourea-amended soil apparently involved a catalytic mechanism. The electron delocalization between the thiourea molecule and the surfaces of soil particles is energetically favorable and would increase the nucleophilic reactivity of the thiono group toward MeI, resulting in an enhancement of the dissipation rate. The soil half-life for MeI was reduced from >300 h for unamended soils to only a few hours in soil or sand amended with thiourea at a 2:1 molar ratio (thiourea:MeI). The MeI transformation rate in thiourea-amended soil increased with increasing soil temperature and decreasing soil moisture. Therefore, spraying thiourea on the soil surface to form a "reactive surface barrier" may be an effective and innovative strategy for controlling fumigant emissions to the atmosphere and for improving environmental protection.

Introduction

Methyl iodide (iodomethane, MeI) has been increasingly recognized as a promising alternative to replace the effective and popular soil fumigant methyl bromide (MeBr), which is being gradually reduced because of its potential for depleting stratospheric ozone. The complete phaseout of MeBr will begin in the United States and other industrialized countries in 2005 (*1*). Although MeI is chemically analogous to MeBr, MeI has little potential for stratospheric ozone depletion because it is rapidly photodegraded in the troposphere (*2*, *3*). Another distinguishing advantage is that MeI may be applied to soil in a liquid formulation rather than a gas (MeBr), offering a substantial improvement in worker safety.

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Regardless of the chemical used for soil fumigation, emissions to the atmosphere are unavoidable after application to fields because of the chemical characteristics of these compounds, such as low molecular weight and relatively high vapor pressure. For instance, a number of laboratory and field experiments have shown that approximately 21−87% of applied MeBr is lost to the atmosphere after soil fumigation for a range of fumigation techniques (*4*−*6*). Large losses have also been observed for other soil fumigants, especially when applied at shallow depths without any surface diffusion barrier (*7*−*8*). Therefore, management strategies to reduce atmospheric emissions are critically needed.

A wealth of physical, chemical, biological, and integrated management practices have been proposed to control fumigant emissions. Tarping the soil surface with a plastic sheet is a common strategy to impede fumigant volatilization into the atmosphere. However, the effectiveness of tarps to trap fumigants depends on the type of material and thickness and density of the plastic. Use of a virtually impermeable film has been demonstrated to drastically reduce fumigant emissions compared to standard 1-mil high-density poly-ethylene tarp (*9*). Accelerating the ability of a soil to degrade a fumigant is another important strategy to reduce volatilization from the soil surface. Previous research has shown that application of organic wastes may not only promote disease suppressive bacteria to achieve improved pest control (*10*, *11*), but also stimulate the growth and activity of fumigant-degrading microorganisms and potentially lead to increased fumigant degradation (*12*−*14*). Furthermore, accelerating fumigant degradation can also be achieved by application of nucleophilic compounds such as ammonium thiosulfate to soil. Thiosulfate can rapidly degrade and detoxify halogenated fumigants (*15*−*17*) and when placed at the soil surface has provided a barrier to diffusion into the atmosphere. Other agrochemicals such as fertilizers and nitrification inhibitors have been explored to accelerate fumigant degradation in soil and water and to reduce fumigant emissions (*18*). The application of soil fumigant with a simultaneous surface application of an agrochemical, capable of rapidly degrading the fumigant, provides an innovative pest-management strategy to protect the environment at a minimal cost. For this approach to be viable, the chemical added to soil must have relatively low toxicity and can rapidly degrade the fumigant, producing nontoxic transformation products.

Currently, new and innovative remediation technologies including bioremediation, phytoremediation, and chemical remediation have been proposed for use in cleaning polluted soil and groundwater. Chemical remediation is defined here as the use of nucleophilic chemicals and redox agents to destroy pollutants in soil and groundwater systems. For example, hydrogen peroxide and potassium permanganate are common remediation reagents that are applied to destroy many types of chemicals such as fuels, solvents, and pesticides. A variety of naturally occurring nucleophiles have been found to have high reactivity and serve as environmental "reagents" by increasing abiotic degradation of a contaminant (*19*, *20*). Much of this interest has focused on nucleophilic sulfur species because they react strongly with relatively simple halogenated compounds. Some studies have shown that hydrogen sulfide species (H_2S and HS^-), thiosulfate ($S_2O_3^{2-}$), and polysulfides (S_n^{2-}, where $n = 2-5$) can promote the transformation of halogenated aliphatic substrates by inducing bimolecular substitution (S_N2) reactions in groundwater environments (*20*−*23*). Currently, extensive research is being conducted to explore the use of sulfur-containing

nucleophiles to clean up water and soils contaminated by pesticides (e.g., chloroacetanilide herbicides) (*17, 24–25*). In addition, Lippa and Roberts (*26*) have shown that in the presence of bisulfide and polysulfides, chloroazine compounds such as chlorotriazine herbicides can undergo nucleophilic aromatic substitution (S_NAr) reactions, leading to rapid abiotic transformation in hypoxic marine waters (*26*).

Our recent explorations revealed that some sulfur-based agrochemicals, such as thiourea, which has been proposed for use as a nitrification inhibitor (*27–29*), might accelerate the degradation of halogenated fumigants in soil (*18*). Nitrification inhibitors are a group of agrochemicals used to minimize fertilizer N loss by limiting the rate of formation of nitrate from ammonium. There is great potential to use thiourea as a remediation reagent.

The primary purpose of this study was to explore the potential of thiourea to abiotically transform the fumigant MeI in aqueous solution and soil. First, MeI hydrolysis and its nucleophilic transformation in the presence of a thiourea buffer solution at pH ranging from 4 to 12 were determined. Next, the influence of a clay suspension on the reaction between thiourea and MeI was evaluated. Then, the degradation of MeI in thiourea-amended soil was further studied and the mechanism involved in increasing the dissipation rate was clarified. The effects of temperature, moisture content, and soil texture on degradation of MeI in thiourea-amended soil were systematically investigated. The information obtained on fumigant degradation in amended soil will be useful in developing a reactive surface barrier approach to reduce fumigant emissions from the soil surface.

Experimental Section

Chemicals. MeI standard (iodomethane; >99%) was obtained from Sigma Chemical Co. (St. Louis, MO). Thiourea (99% purity) was purchased from Aldrich Chemical (Milwaukee, WI). All chemicals were used as received.

Clays and Soils. The clays used were a Na-montmorillonite Swy-1 (Crook County, WY) supplied by the Source Clay Minerals Repository of the Clay Mineral Society at University of Missouri (Columbia, MO) and a kaolinite (Macon, GA) provided by the Ward's Natural Science Establishment, Inc. (Rochester, NY). The soils used in the incubation study were Coachella fine sand (FS) (Coachella Valley, CA), Arlington sandy loam (SL) (Riverside, CA), Sesame sandy loam (SL) (Paso Robles, CA), and Florida organic soil (muck) (Belle Glade, FL). Moist soils were passed through a 2-mm sieve without complete air-drying and stored at low temperature before use. The organic carbon content of the Coachella FS, Arlington SL, Sesame SL, and Florida muck were 0.32%, 0.63%, 1.42%, and 45.8%, respectively, and the pH values were 7.2, 7.4, 5.7, and 7.2, respectively. Silver sand (90 mesh) was obtained from P. W. Gillibrand Co. (Simi Valley, CA) and washed several times with deionized water and then oven-dried at 105 °C.

Aqueous-Phase Kinetics Experiments. The hydrolysis of MeI and transformation by thiourea were carried out in aqueous solution with different pH values at 30 ± 0.5 °C in the dark. All buffer solutions (pH range 4–12) were prepared according to ref *30*. The reaction kinetics of MeI with thiourea was determined in different buffer solutions, in which the initial molar ratio of thiourea to MeI was 1:1. Reactions were initiated by injecting MeI liquid standard using a gastight syringe into 100 mL of thiourea (1.0 mM) buffer solution in a capped serum bottle. The concentration of MeI in the aqueous solution was 1.0 mM. Samples containing only MeI (no thiourea) were also prepared for studying MeI hydrolysis in individual pH solutions. At intervals, 0.5-mL aliquots of solution were withdrawn from triplicate bottles and transferred into sealed glass vials containing ethyl acetate (5.0

mL) and anhydrous sodium sulfate (3.0 g). The vials were vigorously shaken for 5 min, and a portion of the extractant was immediately transferred to a GC vial for MeI analysis.

The influence of clay on MeI hydrolysis and reaction with thiourea was determined in Na-montmorillonite and kaolinite aqueous suspensions at pH 6.9. The clays (0.1 or 1 g) were weighed into 125-mL serum bottles containing 50 mL of thiourea (1.0 mM) buffer solutions. The sample bottles were closed with Teflon-faced butyl rubber septa and mechanically shaken for 10 min. Then, MeI liquid standard was injected into the bottles and vigorously vortexed for 2 min. Control samples containing only clays and MeI were also prepared. The procedures described above were used for incubation, sampling, and extraction of residual MeI.

Soil System Experiments. A series of experiments were conducted to elucidate the reaction kinetics and transformation mechanism of MeI in thiourea-amended soils. In the first experiment, the MeI dissipation rate was determined in thiourea-amended Coachella FS, Arlington SL, Sesame SL, Florida muck, and silver sand at 20 ± 0.5 °C. The initial thiourea:MeI molar ratio was 2:1 for all soils and sand. The soil moisture content for the Florida muck was 40% (w/w), since it contained very high organic matter content and had a high water-holding capacity. For all other soils, the moisture content was 10% (w/w). In brief, separate samples of soil and sand were thoroughly premixed with thiourea at 1.0 mmol kg^{-1}. These amended samples (10 g) were weighed into 20-mL headspace vials and treated with MeI at 0.5 mmol kg^{-1}. Vials containing each soil treated with only MeI were also prepared and used as controls. All treated vials were sealed immediately and then incubated in the dark. Triplicate samples were removed at different times and immediately placed in a −21 °C freezer for 3 h. The frozen sample vials were opened, anhydrous sodium sulfate (8.0 g) and ethyl acetate (10 mL) were added, and the vials were immediately recapped. The samples were vigorously shaken for 1 h and vortexed for 2 min at room temperature in order to attain complete recovery. An aliquot of each ethyl acetate extractant was transferred to a GC vial and stored in a freezer (−21 °C) until the end of the experiment. All samples were analyzed for MeI using gas chromatography. The recovery of MeI by this procedure was shown to be >95% for all unamended soils in preliminary experiments.

In a second experiment, the effect of soil temperature on the MeI dissipation rate was determined in thiourea-amended Arlington SL. The activation energy of reaction (E_a) of MeI degradation in soil amended with thiourea was calculated using the data obtained from this experiment. The treated soil samples were incubated at 4, 10, 20, 30, and 40 °C with variation of <0.5 °C. Aliquots were periodically extracted into ethyl acetate using the procedure described above, followed by GC analysis.

In the third experiment, thiourea-enhanced MeI degradation was determined in the Arlington SL at different moisture contents to characterize the influence of soil moisture. Arlington SL was adjusted to different initial water contents by air-drying or adding water and then treated with thiourea at 1.0 mmol kg^{-1} and MeI at 0.5 mmol kg^{-1}. The final water contents in amended soil were 2%, 5%, 8%, 12%, and 16% (w/w). All treated samples were incubated at 20 ± 0.5 °C. Dissipation of MeI in these soil samples was measured by determining the residual MeI concentration at different times using the procedures described above.

To elucidate the primary mechanism and to determine whether thiourea-facilitated MeI transformation is solely abiotic, MeI degradation was carried out in nonsterilized and sterilized soil. Sterilized Arlington SL was achieved by autoclaving soil twice at 121 °C before adding sterilized chemical solutions. The treatment procedures described
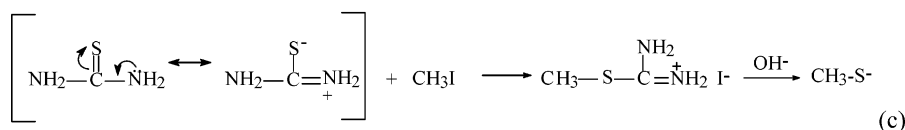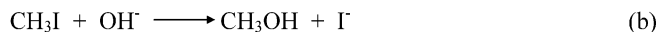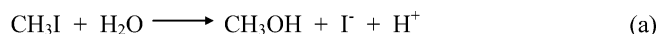
SCHEME 1

$$CH_3I + H_2O \longrightarrow CH_3OH + I^- + H^+ \qquad\qquad (a)$$

$$CH_3I + OH^- \longrightarrow CH_3OH + I^- \qquad\qquad (b)$$

$$\left[NH_2-\overset{\overset{S}{\|}}{C}-NH_2 \longleftrightarrow NH_2-\overset{\overset{S^-}{|}}{C}=\overset{+}{N}H_2 \right] + CH_3I \longrightarrow CH_3-S-\overset{\overset{NH_2}{|}}{\underset{+}{C}}=NH_2 \; I^- \xrightarrow{OH^-} CH_3\text{-}S^-$$

$$(c)$$

TABLE 1. Pseudo-First-Order Kinetics Constants for MeI Hydrolysis and Second-Order Reaction Kinetics Constants of MeI with Thiourea in Different pH Aqueous Solution at 30 $\pm$ 0.5 °C

	hydrolysis coefficient		reaction coefficient	
pH	k_1 (h^{-1})	$t_{1/2}$ (h)	$k_{2'}$ (mM^{-1}h^{-1})	DT$_{50}$(h)^a
4.0	1.80($\pm$0.13) $\times$ 10^{-3}	384.8	1.79($\pm$0.03) $\times$ 10^{-2}	56.0
6.9	1.82($\pm$0.14) $\times$ 10^{-3}	380.8	1.81($\pm$0.02) $\times$ 10^{-2}	55.2
9.0	2.67($\pm$0.17) $\times$ 10^{-3}	259.6	1.98($\pm$0.07) $\times$ 10^{-2}	50.5
10.0	6.03($\pm$0.19) $\times$ 10^{-3}	114.9	4.01($\pm$0.21) $\times$ 10^{-2}	24.9
12.0	6.56($\pm$0.19) $\times$ 10^{-3}	105.7	4.54($\pm$0.23) $\times$ 10^{-2}	22.0

^{a} The time of 50% MeI dissipation obtained from eq 4.

above were applied for spiking, incubation, sampling, and analysis of residual MeI concentration.

Gas Chromatograph Analysis. The concentration of MeI was analyzed using a Hewlett-Packard HP 6890 GC equipped with a microelectron capture detector and a DB−VRX capillary column (30 m $\times$ 250 μm $\times$ 1.4 μm, J & W Scientific, Folsom, CA). A 2.0-μL aliquot of ethyl acetate extractant was automatically introduced into a split/splitless injection port at a split ratio of 25:1. The GC conditions were 1.0 mL min^{-1} carrier gas flow rate, 220 °C inlet temperature, and 280 °C detector temperature. The oven temperature was held at 50 °C for 1 min and then increased at 15 °C min^{-1} to 140 °C and kept at 140 °C for 1 min. Under these conditions, the retention time of MeI was 3.96 min.

Results and Discussion

MeI Transformation by Thiourea As Related to Solution pH. Initial experiments focused on the reaction kinetics of MeI with thiourea in five different pH aqueous solutions (pH 4.0, 6.9, 9.0, 10.0, and 12.0). In all solutions containing thiourea, the dissipation of MeI increased significantly compared to the corresponding MeI-only solution (see Figure S-1, Supporting Information). For instance, after a 5-day incubation, approximately 70% of the MeI had disappeared in the pH 4.0 thiourea solutions compared to approximately 20% in pH 4.0 buffer solutions without thiourea. The main reaction mechanisms involved in MeI dissipation in the thiourea solution were hydrolysis including neutral hydrolysis (Scheme 1a) and base-catalyzed hydrolysis (Scheme 1b) and a nucleophilic substitution reaction with thiourea (Scheme 1c).

MeI underwent hydrolysis in aqueous solution via an S$_N$2 nucleophilic substitution reaction. In general, the hydrolysis reaction is treated as pseudo-first-order kinetics and the rate constant is measured as the slope of the plot of ln[pesticide] vs the reaction time (31). The rate constants and half-lives of MeI hydrolysis in different pH solutions are presented in Table 1. For pH > 6.9, the MeI hydrolysis half-life significantly decreased as pH increased. These results demonstrate that the rate of MeI hydrolysis is pH-dependent. It also indicated that the base-catalyzed pathway for MeI is quite significant at high pH solution because OH$^-$ is a much more reactive nucleophile than H$_2$O; accordingly, MeI hydrolysis rate increased.

Because of the electron donating properties of the amino group, thiourea in aqueous solution can be represented as a resonance structure (Scheme 1c). The thiono group of thiourea possesses some nucleophilic reactivity in aqueous solution. It can attack MeI via the bimolecular nucleophilic mechanism by breaking the C−I bond and forming a C−S bond (Scheme 1c). Therefore, the MeI dissipation rate in a thiourea solution would be the sum of the rates of the several concurrent reactions

$$\frac{-d[MeI]}{dt} = (k_a[H^+] + k_N + k_b[OH^-])[MeI] + \\ k_2[MeI][Thiourea] \quad (1)$$

where k_a, k_N, and k_b represent the rate constant for acid-catalyzed, neutral, and base-catalyzed hydrolysis process (31) and k_2 is the second-order rate constant. Exact integration of eq 1 would be difficult. However, the reaction between MeI and thiourea is much faster than MeI hydrolysis (see Figure S-1, Supporting Information). Further, if one is only interested in the reaction kinetics between MeI and thiourea, the equation could be simplified to a second-order reaction. This expression represents the rate of S$_N$2 nucleophilic substitution in terms of initial MeI and thiourea concentrations. Equation 1 would be converted to

$$\frac{-d[MeI]}{dt} = k_{2'}[MeI][Thiourea] \quad (2)$$

Upon rearrangement and integration and for an equal initial concentration of MeI and thiourea, eq 2 becomes

$$[MeI] = \frac{[MeI]_0}{1 + k_{2'}[MeI]_0 t} \quad (3)$$

Here, we characterized the speed of reaction by defining a 50% MeI disappearance time (DT$_{50}$) as the time in a given set of conditions (18, 32), which is

$$DT_{50} = \frac{1}{k_{2'}[MeI]_0} \quad (4)$$

In contrast to the hydrolysis at the same pHs, the reaction of MeI and thiourea significantly reduced the persistence of the fumigant in aqueous solution (Table 1). The DT$_{50}$ values of MeI were 6.9, 6.9, 5.2, 4.6, and 5.2 times below that of the corresponding hydrolysis half-life ($t_{1/2}$) at pH 4.0, 6.9, 9.0, 10.0, and 12.0, respectively.

As indicated in Table 1, the dissipation of MeI in thiourea solution increases with increasing pH. The increased rate of MeI dissipation in high-pH thiourea solutions was primarily attributed to the increase in the MeI hydrolysis rate. For example, after 3 days of incubation at 30 °C, the difference in MeI concentration in solutions with or without thiourea was approximately equal for all pH levels (see Figure S-2, Supporting Information). This implies that the reaction between MeI and thiourea was pH-independent and that a change in pH might not significantly affect the transformation

TABLE 2. Pseudo-First-Order Rate Constants for Hydrolysis of MeI (1.0 mM) and Reaction with Thiourea (1.0 mM) in Different Neutral Aqueous Media at 30 ± 0.5 °C

reaction system	rate constant k (h^{-1})	r^2
pure water	1.03 ($\pm$0.13) $\times$ 10^{-3}	0.920
buffer solution (pH = 6.9)	1.82 ($\pm$0.14) $\times$ 10^{-3}	0.962
pure water with thiourea	0.92 ($\pm$0.04) $\times$ 10^{-2}	0.991
buffer solution (pH = 6.9) with thiourea	1.04 ($\pm$0.04) $\times$ 10^{-2}	0.985
1.0 g of Na-montmorillonite suspension (pH = 6.9)	1.93 ($\pm$0.16) $\times$ 10^{-3}	0.921
1.0 g of Na-montmorillonite suspension (pH = 6.9) with thiourea	1.15 ($\pm$0.06) $\times$ 10^{-2}	0.974
0.1 g of Na-montmorillonite suspension (pH = 6.9) with thiourea	1.14 ($\pm$0.07) $\times$ 10^{-2}	0.962
1.0 g of kaolinite suspension (pH = 6.9)	1.96 ($\pm$0.19) $\times$ 10^{-3}	0.916
1.0 g of kaolinite suspension (pH = 6.9) with thiourea	1.11 ($\pm$0.06) $\times$ 10^{-2}	0.973
0.1 g of kaolinite suspension (pH = 6.9) with thiourea	1.13 ($\pm$0.06) $\times$ 10^{-2}	0.975

process in aqueous systems. This result was somewhat contrary to expectations because the intermediate reaction product (isothiuronium salt) may further cleave to methylmercaptide (CH$_3$S$^-$) in alkali solution (*33*). Methylmercaptide is usually considered a powerful nucleophile and would be able to further react with MeI to form dialkyl sulfide. However, the results of these experiments suggest that this process might not actually contribute significantly to the MeI dissipation and the enhancement in MeI dissipation at high pH results primarily from the increased rate of hydrolysis. It was inferred that the transformation process of isothiuronium salt to CH$_3$S$^-$ might be very slow, and only small amounts of CH$_3$S$^-$ were formed in the reaction system. Similar phenomena were reported by Schwarzenbach et al. (*21*), in which the formation and distribution of the reaction products for primary alkyl bromides (RBr) in hydrogen sulfide solution were observed and calculated. They found that only 0.2% dialkyl sulfides were formed.

To determine the influence of buffer salts on MeI dissipation, experiments were conducted comparing the rate of MeI hydrolysis in a buffer solution (pH = 6.9) and a pure-water solution. The results show that MeI hydrolysis was faster in the buffer solution than in the pure-water solution (Table 2). The pH of the pure-water solution sample measured after MeI was completely degraded was about 3.0 (initial pH 6.9). This further demonstrated that hydrolysis of MeI is pH-dependent. Likewise, the difference of the MeI reaction rate with thiourea between in buffer solution and in pure water was also attributed to a reduction in the MeI hydrolysis rate due to a gradually decreasing solution pH as MeI degradation proceeded.

MeI Transformation by Thiourea in Solutions Containing Clay. MeI degradation in aqueous clay suspension with or without thiourea was conducted in a pH 6.9 buffer solution. The dissipation of MeI in aqueous clay suspension was associated with transformation and clay adsorption. Previous research has shown that fumigant sorption in soil is very limited (*34, 35*). Preliminary experiments indicated that MeI dissipation due to sorption to clay was very small, implying that the dissipation of MeI in clay suspension was mainly attributable to hydrolysis and reaction with thiourea. The MeI pseudo-first-order dissipation rate constant in clay suspension with thiourea was only slightly higher than in buffer solution containing thiourea (no clay) (Table 2). This result suggests that clay minerals, such as montmorillonite or kaolinite in suspension, do not increase the rate of reaction between thiourea and MeI or increase the rate of MeI hydrolysis. Gan et al. (*34*) also observed little effect of montmorillonite and kaolinite clays on MeBr degradation in moist samples.

MeI Degradation by Thiourea in Different Soils. The dissipation of MeI was studied in thiourea-amended and unamended sand and soil at 20 ± 0.5 °C. Significant increases of MeI degradation were observed for all four soils and sand when thiourea was added at a 2:1 ratio compared to the
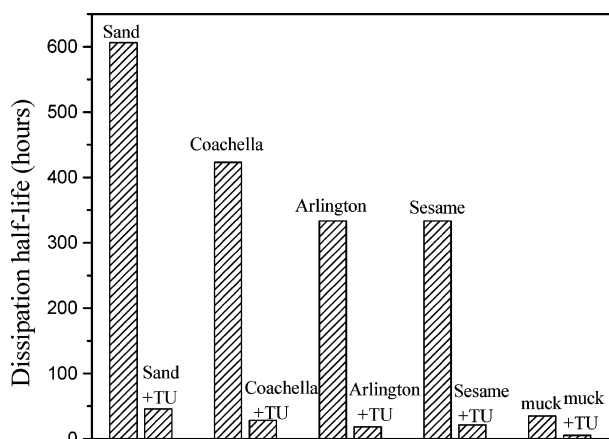

FIGURE 1. First-order half-life of MeI (0.5 mmol/kg) in different soils amended with thiourea at 20 ± 0.5 °C (2:1 thiourea (TU):MeI molar ratio).

unamended control (Figure 1). For example, the MeI first-order half-life decreased by factors of 12, 13, 17, 14, and 5 times, respectively, in thiourea-amended sand, Coachella FS, Arlington SL, Sesame SL, and Florida muck. These large increases in transformation rate imply that MeI degrdation was substantially accelerated by reaction between MeI and thiourea on the surface of soil or sand.

In general, fumigant transformation in soil is primarily attributed to biotic and abiotic degradation. Abiotic degradations such as hydrolysis and nucleophilic substitution often play an important role in fumigant dissipation. Previous studies have indicated that the rate of fumigant degradation was highly dependent on the soil organic matter content and to a lesser extent on other soil constituents such as clay (*34*). For example, in the experiment the dissipation half-life of MeI in Florida muck was only 36 h, significantly less than that in other soils; this is attributed to the Florida soil's extremely high soil organic matter content. Soil organic matter contains a variety of nucleophilic groups, such as $-NH_2$, $-OH$, and $-SH$, which may attack halogenated fumigants through nucleophilic substitution reactions. This results in high rates of MeI dissipation in organic-matter-rich soils such as the Florida muck. Furthermore, the MeI dissipation rate increased when the Florida muck was amended with thiourea. Therefore, Florida muck soil amended with thiourea could be incorporated into other soils as an additive to both increase soil fertility and reduce pesticide pollution potential.

Temperature and Moisture Effects on Amended Soil. Soil temperature and moisture conditions can change drastically both diurnally and over the duration of a soil fumigation. Degradation of MeI in thiourea-amended soils consistently increased with increasing soil temperature (Figure 2). For example, in Arlington SL amended with
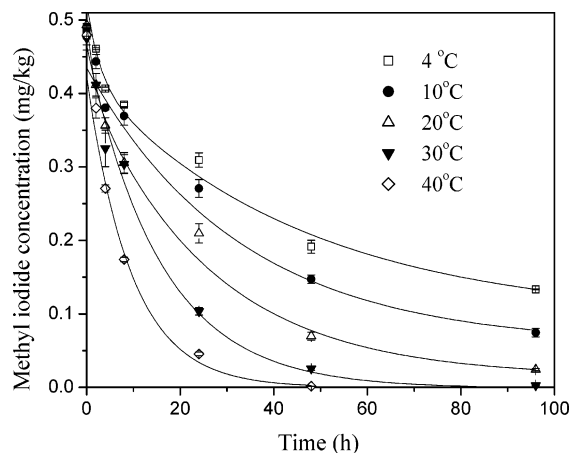
FIGURE 2. Transformation of MeI (0.5 mmol/kg) in thiourea-amended soil at different temperatures. Soil moisture was 10% (w/w), and the thiourea:MeI ratio was 2:1.
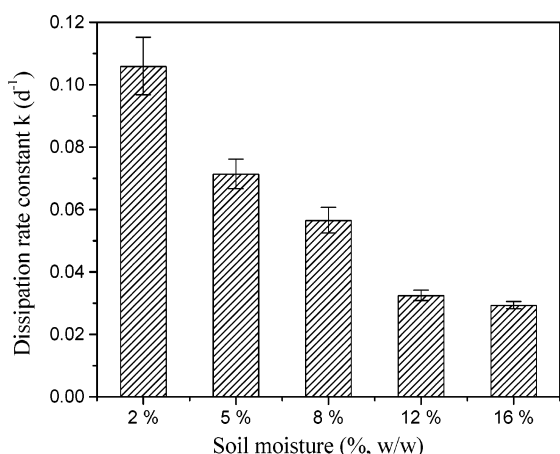

FIGURE 3. Transformation of MeI (0.5 mmol/kg) in thiourea-amended soil at different soil moistures at 20 ± 0.5 °C (2:1 thiourea:MeI ratio).

FIGURE 4. Comparison of MeI dissipation in thiourea-amended soil and in aqueous solution at 30 ± 0.5 °C (2:1 thiourea:MeI ratio). C_0 is the initial concentration of MeI in the soil and solution.

SCHEME 2

thiourea, the MeI dissipation half-life was approximately 41.8, 31.4, 18.9, 12.1, and 5.5 h, respectively, at 4, 10, 20, 30, and 40 °C. This dependence on temperature demonstrates that thiourea amendments are more effective at degrading MeI in warmer soil. It also indicates that the MeI dissipation rate would peak in the soil surface during the afternoon when the soil temperature is the highest and reaches a minimum before sunrise when the soil temperature is at its lowest. Therefore, a remediation strategy that uses thiourea should account for this behavior. The Arrhenius equation offers a simple method to incorporate the effects of temperature into a mathematical relationship. By fitting the degradation data to the Arrhenius equation, the activation energy (E_a) was calculated to be 39.7 kJ mol^{-1}, with a correlation coefficient (r^2) of 0.987. This E_a indicates that the transformation rate of MeI in thiourea-amended Arlington SL increases approximately 1.8 times with every 10 °C increase in temperature (*36*).

The transformation rate constant of MeI in thiourea-amended soil also varies with soil moisture content (Figure 3). In thiourea-amended Arlington SL, the MeI dissipation rate decreased nonlinearly with increasing soil moisture content. When the soil was very dry (2% moisture, w/w), the MeI dissipation rate was significantly higher than in soil with higher water contents of 5–16% (w/w) (Figure 3). For instance, the MeI half-lives were 6.5, 9.7, 12.3, 21.3, and 23.6 h, respectively, when the thiourea-amended soil moisture contents were 2%, 5%, 8%, 12%, and 16%. In these experi-
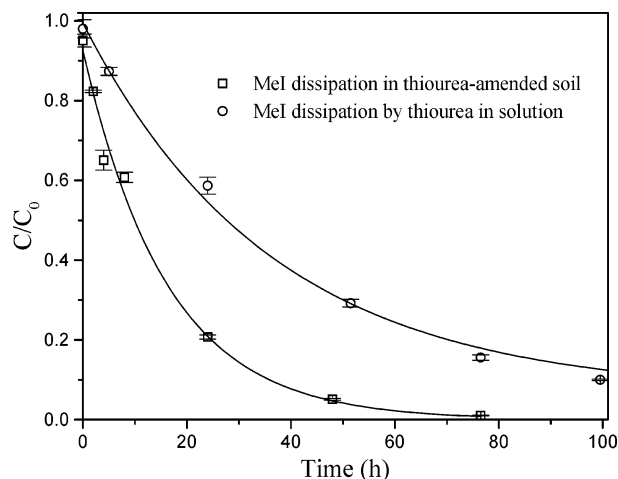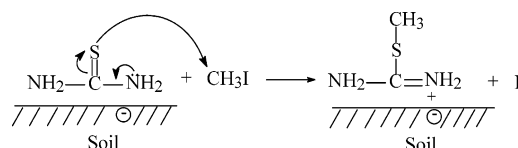
ments, the influence of soil moisture on MeI degradation was minimal when the soil water content was above 12% (Figure 3). Pesticide degradation generally occurs in the soil solution phase, and a moist soil environment favors microbial growth that may stimulate pesticide degradation. Therefore, pesticide degradation has frequently been found to increase with increasing soil moisture (*37, 38*). In the experiment, MeI degradation decreased with increasing soil moisture, suggesting that a special reaction mechanism of MeI with thiourea was involved on the surface of soil particles. Apparently, the dissipation rate of MeI in amended soil did not depend solely on reactions that occurred in the soil aqueous phase but also involved a soil catalytic process (described below). These results suggest that surface application of thiourea might be more efficient than other amendments, because MeI degradation was accelerated in dry thiourea-amended soil.

Mechanism of Accelerated MeI Transformation in Thiourea-Amended Soils. A previous study revealed that the reaction between MeI and thiourea occurred more rapidly in soil than in aqueous solution (*18*). In these experiments conducted at an initial thiourea:MeI molar ratio of 2:1, MeI degradation amended Arlington SL soil was significantly faster than in aqueous solution (Figure 4). The enhanced degradation of MeI in thiourea-amended soil may be attributable to a soil catalytic process. Previous studies have shown that clay minerals and organic matter in the soil often play an important role as an electron shuttle to donate electrons (*39, 40*). Hence, the orientational bonding between the thiourea NH$_2$ group and soil surface would favor the electron transfer of the amino group and result in increased nucleophilic activity of the thiono group. The delocalization of electrons between the thiourea and the soil surface may decrease the energy requirement for the reaction with MeI, resulting in an enhanced reaction rate. The catalytic reaction process is assumed as Scheme 2.

The reaction mechanism presented in Scheme 2 can also explain the moisture-dependence of the MeI dissipation rate. When soil moisture increases, the effect of water polarization on the surface of soil particles becomes more significant and

TABLE 3. First-Order Rate Constants for MeI Dissipation (0.5 mmol/kg) in Sterile and Nonsterile Arlington SL with Thiourea Amendment (1.0 mmol/kg) at 20 ± 0.5 °C

treatment	rate constant k_f (h^{-1})	r^2
nonsterile soil	2.07 (±0.21) × 10^{-3}	0.849
nonsterile soil with thiourea	3.25 (±0.17) × 10^{-2}	0.986
sterile soil	2.28 (±0.22) × 10^{-3}	0.869
sterile soil with thiourea	3.97 (±0.31) × 10^{-2}	0.983

may impede the possible electron transfer between thiourea and the soil surface. Therefore, the nucleophilic activity of the thiono group will be decreased, resulting in a low dissipation rate of MeI in amended soil with high moisture.

The transformation of MeI in thiourea-amended soil was observed to be abiotic by comparing the dissipation rate of MeI in sterile and nonsterile soils. In thiourea-amended Arlington SL, the dissipation rate of MeI was not affected by autoclaving the soil (Table 3). This indicates that microbial degradation was not significant in Arlington SL amended with thiourea. Microbial degradation may become important in soils with a long history of soil fumigation since this may produce a population of indigenous microorganisms capable of degrading MeI. In addition, autoclaving soil may alter the chemical and physical characteristics of soil and may affect soil organic matter. Therefore, it is possible for the MeI dissipation rate in sterile soil to increase (Table 3) as more reaction sites are made available. Previous studies have reported that autoclaving soil increases the chemical degradation of a similar fumigant, MeBr (41).

Developing Reactive Surface Barriers. Application of effective remediation reagents to the soil surface, i.e., creation of a reactive surface barrier, could effectively block fumigant emissions to the atmosphere in the same manner as plastic films, although by a different mechanism. Theoretically, this reactive surface barrier would not affect fumigation efficacy deeper in soil because only the top few centimeters of soil would be treated. The effectiveness of emission control would depend on the activity and stability of both the remediation reagents and fumigants. Thiourea could be an ideal reagent in a reactive surface barrier because thiourea degrades MeI rapidly and is relatively stable in soil. Other sulfur species, such as thiosulfate, are easily oxidized to sulfate in soil (42), which would quickly render them ineffective in controlling emissions.

Although the soil moisture content in the field can change both spatially and temporally, the moisture at the soil surface is generally low owing to evaporation. The rate of MeI dissipation in thiourea-amended soils increases with decreasing soil moisture (Figure 3). As MeI diffuses upward from deep soil layers through the treated surface layer, the low surface soil moisture content would promote its reaction with thiourea. Moreover, higher soil temperature at the soil surface during sunlit hours would further increase the fumigant degradation process in thiourea-amended soil.

It may be possible to integrate the strategy of reactive surface barrier control with other management options to further reduce fumigant emissions. For instance, it is well-known that plastic films covering the soil surface after fumigation increase soil temperatures below the film, in addition to providing a diffusion barrier to the atmosphere. The higher temperatures under plastic would increase the rate of reaction between thiourea and MeI and further reduce the emission. However, further research is needed to determine the net effect of integrated practices on fumigant emissions. Research is also needed that addresses the influence of temperature, soil moisture, film permeability, and reactivity on fumigant behavior in agricultural settings. With a complete understanding of the interrelated processes, new fumigation technologies that use reactive surface barriers may be developed.

Acknowledgments

Supporting Information Available

Two figures showing the dissipation of MeI in different pH aqueous solution with and without thiourea and the effect of pH on the reaction kinetics of MeI with thiourea. This material is available free of charge via the Internet at http://pubs.acs.org.

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