Accelerated Degradation of Methyl Iodide by Agrochemicals

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The fumigant methyl iodide (MeI, iodomethane) is considered a promising alternative to methyl bromide (MeBr) for soil-borne pest control in high-cash-value crops. However, the high vapor pressure of MeI results in emissions of a significant proportion of the applied mass into the ambient air, and this may lead to pollution of the environment. Integrating the application of certain agrochemicals with soil fumigation provides a novel approach to reduce excessive fumigant emissions. This study investigated the potential for several agrochemicals that are commonly used in farming operations, including fertilizers and nitrification inhibitors, to transform MeI in aqueous solution. The pseudo-first-order hydrolysis half-life ($t_{1/2}$) of MeI was ~108 d, while the transformation of MeI in aqueous solutions containing selected agrochemicals was more rapid, with $t_{1/2} < 100$ d ($t_{1/2} < 0.5$ d in some solutions containing nitrification inhibitors). The influence of these agrochemicals on the rate of MeI degradation in soil was also determined. Adsorption to soil apparently reduced the availability of some nitrification inhibitors in the soil aqueous phase and lowered the degradation rate in soil. In contrast, addition of the nitrification inhibitors thiourea and allylthiourea to soil significantly accelerated the degradation of MeI, possibly due to soil surface catalysis. The $t_{1/2}$ of MeI was <20 h in thiourea- and allylthiourea-amended soil, considerably less than that in unamended soil ($t_{1/2} > 300$ h).

KEYWORDS: MeI; methyl iodide; iodomethane; degradation; transformation; nitrification inhibitor; fertilizer; soil; agrochemical

INTRODUCTION

The fumigant methyl bromide (MeBr) has been used extensively in California and other parts of the world to control plant pathogens such as nematodes, soil-borne diseases, and weeds in economically important crops such as strawberries and nursery stock (*1*). Because of its stratospheric ozone depletion potential, MeBr has been scheduled for elimination in the United States and other developed countries by the year 2005 (*2*). The impending phase-out has resulted in an intensive search for alternative fumigants and the development of other integrated pest management strategies to replace MeBr. Methyl iodide (iodomethane, MeI) is often referred to as the "drop-in replacement" because its fate and transport characteristics and effectiveness as a biocide are similar to those properties for MeBr (*3*). MeI has a distinguished advantage over MeBr in that its atmospheric lifetime is only 4−8 days, compared with 0.4−0.9 years for MeBr (*4*). Therefore, it is unlikely that MeI will reach the stratosphere and contribute to ozone depletion (*5*, *6*), although the volatilization of MeI may be similar to that of MeBr. In laboratory soil columns, cumulative MeI emissions ranged from ~30 to 70% of the applied MeI for polyethylene-tarped soil application (*7*). Although MeI is not considered an ozone depleter, excessive MeI emission into the ambient air

may be hazardous to workers or nearby residents due to its moderate toxicity and suspected carcinogenicity. Massive exposure of MeI can lead to pulmonary edema (*8*).

Generally, the most important environmental problem associated with the use of soil fumigants is atmospheric emissions. This is due to their high vapor pressure that allows them to readily volatilize and enter the atmosphere. Further compounding the problem is that fumigants are often applied at levels that exceed that required to control the target organisms, to compensate for losses due to volatilization and degradation. This ensures adequate pest control but increases the risk of air, surface water, and groundwater contamination. To minimize the negative impact of fumigants on the environment, many management strategies have been proposed to reduce fumigant emissions. For instance, covering the soil surface with impermeable plastic films and sealing the soil surface with water has been shown to reduce fumigant volatilization (*9*, *10*). However, use of impermeable films may cause unintended problems such as worker exposure for those removing a film after a relatively short fumigation (i.e., cover) period. If a film is removed from a field before extensive fumigant degradation has occurred, the gas trapped under the film could be released at high concentrations (*11*, *12*). Other methods of fumigation have also been explored to reduce fumigant emissions, such as deep injection or application via drip irrigation, both of which increase the soil residence time by increasing the travel distance to the soil

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surface or by reducing gas-phase diffusion (*13*, *14*). Soil conditions (such as soil temperature and soil moisture content) and physical−chemical properties (such as soil type and organic matter and clay contents) generally play a significant role in determining the fate of fumigants in soil by influencing the rate of abiotic and biological degradation reactions (*15*, *16*). Previous studies investigated the potential for application of organic waste at the soil surface to reduce fumigant volatilization. Incorporation of composted manure into soil was found to significantly stimulate the growth and activity of fumigant-degrading organisms, causing accelerated fumigant dissipation (*17−19*). Application of nucleophilic compounds such as ammonium thiosulfate (ATS) at the soil surface has been shown to reduce fumigant volatilization by rapid transformation via abiotic reaction with halogenated fumigants (*20*, *21*). Currently, very little information is available concerning the effect of other agrochemicals on the rate of fumigant degradation in soil and water.

Agrochemicals such as fertilizers are applied worldwide to enhance agricultural production, and their use is increasing. Nitrification inhibitors (NIs) are a group of agrochemicals used to limit the rate of fertilizer nitrification and increase fertilizer efficiency. They help to reduce nitrate leaching to groundwater and decrease N loss as N_2O or N_2 (*22*). Use of NIs with N fertilizers has been proposed as a management technique to reduce N leaching and improve N uptake by plants (*23−25*). The use of these agrochemicals may alter the soil chemical and biological conditions, which may also influence fumigant degradation.

In this study, we evaluated the effects of several agrochemicals on MeI degradation. The agrochemicals selected included fertilizers, such as urea, oxamide, and calcium cyanamide, and NIs, such as dicyandiamide (DCD), thiourea, 1-allyl-2-thiourea, ammonium thiosulfate (ATS), sodium diethyldithiocarbamate (Na-DEDTC), and ammonium diethyldithiocarbamate (NH₄-DEDTC). These agrochemicals were chosen because they are nucleophiles and were expected to react abiotically with MeI. The specific objectives of this study were to (i) determine the rate of MeI transformation by these agrochemicals in aqueous solution and propose their reaction mechanism and (ii) assess the rate of MeI degradation in soils amended with these agrochemicals to determine their effectiveness in enhancing the MeI transformation rate. This information will be useful in developing effective management practices to prevent atmospheric emissions and remediate soils contaminated by pesticides.

MATERIALS AND METHODS

Soil and Chemicals. The soil used in this study, an Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf), was collected from the University of California, Riverside Agricultural Experiment Station; the plot has no history of fumigant application. Soil was collected 15 cm from the surface. Moist soils were passed through a 2-mm sieve without complete air-drying and stored at low temperature before use. The soil had a pH of 7.2 and consisted of 0.92% organic matter, 64% sand, and 7% clay.

MeI standard (>99% purity) was purchased from Chem Service (West Chester, PA). Thiourea (99% purity), allylthiourea (98% purity), Na-DEDTC, NH₄-DEDTC, DCD, oxamide, calcium cyanamide, and hydroxylamine (99% purity) were all obtained from Aldrich Chemical Co. (Milwaukee, WI). Urea was purchased from Sigma Chemical Co. (St. Louis, MO). ATS (99.0% purity) was purchased from Fluka Chemical Co. (Ronkonkoma, NY).

Aqueous-Phase Kinetics Experiments. The reaction of MeI with different agrochemicals was first studied in aqueous solutions at 20 ± 1 °C. In these experiments, the disappearance of MeI was measured.

For each nucleophilic agrochemical, a 1.0 mM solution was prepared in deionized water and placed in a 55-mL serum bottle. All bottles were spiked with 1.0 mM MeI and then immediately capped with a Teflon-faced butyl rubber septum and an aluminum seal. At various times, 0.5-mL aliquots were withdrawn from triplicate bottles and transferred to sealed glass vials containing 5.0 mL of ethyl acetate and 3.0 g of anhydrous sodium sulfate. The vials were vortexed for 2 min, and an aliquot of the ethyl acetate extract was quickly transferred to a GC vial for MeI analysis.

Transformation of MeI by Na-DEDTC and NH₄-DEDTC was studied in aqueous solutions with molar ratios (DEDTC:MeI) of 0:1, 0.25:1, 0.5:1, 1:1, 2:1, and 4:1. Samples were prepared, incubated, sampled, and analyzed as described above. At each sampling time, an additional 0.5-mL aliquot of solution was withdrawn from the 1:1 treatment for analysis of iodide ion. The samples were diluted with deionized water and immediately analyzed by ion chromatography (IC).

Soil Incubation Experiment. The kinetics of MeI degradation in soils amended with agrochemicals was investigated. Briefly, separate samples of soil were each premixed with a different agrochemical at 1.0 mmol kg^{-1}. Ten grams of the amended soil (dry weight, gravimetric soil water content 12.5%) was weighed into a 21-mL headspace vial and then spiked with MeI at 0.5 mmol kg^{-1}. Unamended soils were also prepared and spiked in the same way. The vials were sealed with Teflon-faced butyl rubber septa and aluminum seals immediately after spiking and incubated at 30 ± 1 °C in the dark. Triplicate samples were removed at different times and chilled at −21 °C for 3−4 h, and then their seals were removed, 10 g of anhydrous sodium sulfate and 10 mL of ethyl acetate were added, and the vials were resealed. 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 the ethyl acetate extract was transferred to a GC vial and stored in a freezer (−21 °C) until the end of the experiment, when all samples were analyzed for MeI using gas chromatography. Preliminary experiments showed >95% recovery for unamended soil using the above extraction procedures.

The rate of MeI transformation was evaluated in soils containing different initial concentrations of the NIs Na-DEDTC and ATS. Soils treated with Na-DEDTC and ATS at 0, 0.5, 1.0, 2.0, and 4.0 mmol kg^{-1} were spiked with 0.5 mmol kg^{-1} MeI, resulting in initial Na-DEDTC or ATS-to-MeI molar ratios of 0:1, 1:1, 2:1, 4:1, and 8:1. The procedures described above were used for treatment, incubation, and extraction of samples. The rate of MeI degradation in soil was determined from the concentration of MeI remaining as a function of time.

The rate of MeI (0.5 mmol kg^{-1}) degradation was determined in soils that were pretreated with Na-DEDTC or ATS (1.0 mmol kg^{-1}) at various times to evaluate the influence of aging of the NIs in soil. Soils were amended with Na-DEDTC or ATS and mixed thoroughly and then stored in the dark at 30 ± 1 °C. At different times (0−14 d) after incubation, a fraction of the amended soil was removed, placed in a serum bottle, and spiked with MeI. The same processes as given above were used for spiking, incubation, sampling, and extraction of residual MeI.

Instrumental Analysis. A Hewlett-Packard HP 6890 gas chromatograph (GC) equipped with a micro-electron capture detector was used to analyze the extracted MeI. A DB-VRX capillary column (30 m × 250 μm × 1.4 μm, J&W Scientific, Folsom, CA) was used with the following conditions: 1.0 mL min^{-1} carrier gas flow rate, 220 °C inlet temperature, and 280 °C detector temperature. The oven 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.

A Dionex DX-100 ion chromatograph (IC) equipped with an AS5 column (Dionex, Sunnyvale, CA) and AS40 automated sampler was used to determine iodide ion. The mobile phase consisted of 2 mM NaOH, 4.5 mM Na_2CO_3, and 2% acetonitrile (v/v), and the flow rate was 1.0 mL min^{-1}.

RESULTS AND DISCUSSION

Degradation Kinetics of MeI in Aqueous Solution Containing Fertilizers. Figure 1 shows the disappearance of MeI

Accelerated Degradation of MeI

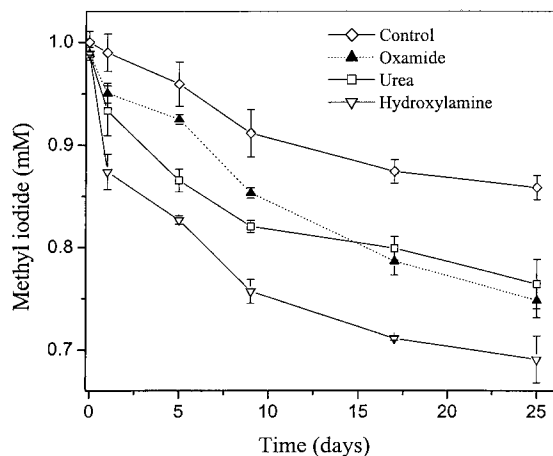*J. Agric. Food Chem.,* Vol. 51, No. 3, 2003   **675**

Figure 1. Disappearance of MeI (1.0 mM) in aqueous solutions containing different fertilizers (1.0 mM). Error bars represent standard deviation of triplicate samples.
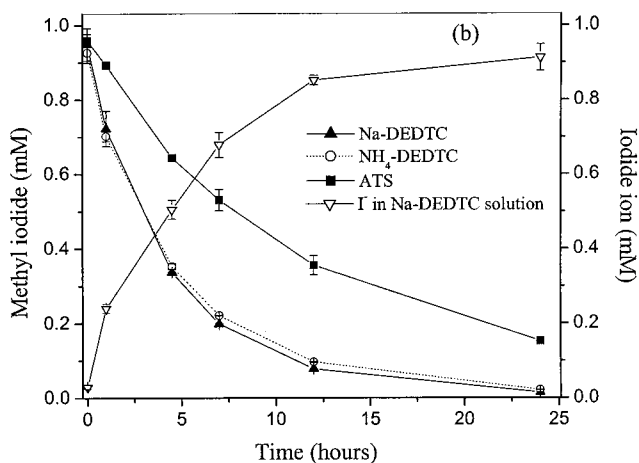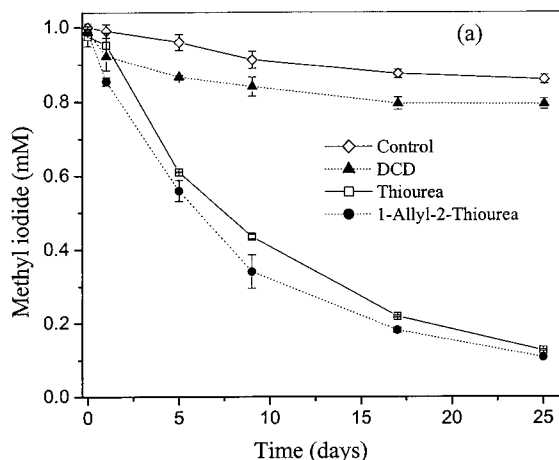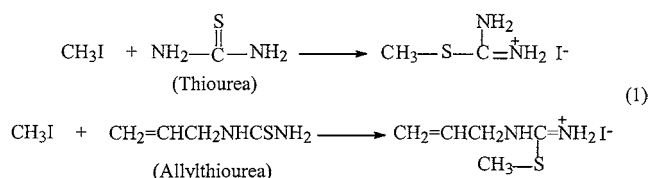

Figure 2. Disappearance of MeI (1.0 mM) in aqueous solutions containing different nitrification inhibitors (1.0 mM). Error bars represent standard deviation of triplicate samples.

(1.0 mM) in aqueous solution containing the nitrogen fertilizers urea (NH_2CONH_2) and oxamide ($NH_2COCONH_2$). During the 25 d incubation, the disappearance of MeI in aqueous solutions containing these fertilizers was slightly accelerated compared to the control. For instance, after 25 d, about 86% of applied MeI remained in the control samples, while less than 77% remained in solutions containing 1.0 mM oxamide or urea solution (**Figure 1**), indicating a possible reaction between MeI and these fertilizers in aqueous solution. Urea and oxamide contain electron-rich groups ($:NH_2$) which are nucleophiles susceptible to nucleophilic substitution reaction with halogenated fumigants, but little enhancement in the rate of MeI degradation was observed in the two fertilizer solutions. It is surmised that the electron-withdrawing character of the carboxyl ($C=O$) group reduced the nucleophilic activity of the amino group in aqueous solution. Even though the fertilizers urea and oxamide did not drastically accelerate degradation of MeI, the common use of these fertilizers in agricultural systems suggests that residual material may have some effect on the fate of the fumigant in soil.

In previous research it was reported that hydroxylamine (NH_2OH), a product of the catalytic oxidation of ammonia in soil, could degrade and oxidize MeBr to formaldehyde (*26, 27*). **Figure 1** shows that MeI disappeared more rapidly in 1.0 mM hydroxylamine aqueous solution than in the fertilizer solutions and control samples. More than 30% of the applied MeI was degraded in 25 d of incubation, due to a combination of hydrolysis and chemical reaction with hydroxylamine.

Degradation Kinetics of MeI in Aqueous Solution Containing Nitrification Inhibitors. The disappearance of MeI in aqueous solutions of selected NIs is shown in **Figure 2**. With the exception of dicyandiamide (DCD), the rates of disappearance of MeI were considerably higher in solutions containing these NIs compared to the controls. In the 1.0 mM thiourea and allylthiourea aqueous solutions, MeI disappeared rapidly, with less than 13% remaining after 25 d of incubation (**Figure 2a**). After deducting the MeI loss via hydrolysis (14% in the corresponding control sample), the majority of MeI disappearance in thiourea and allylthiourea aqueous solutions was attributed to reaction between MeI and these two NIs. According to the reaction of an alkyl halide converted to an isothiuronium salt by treatment with thiourea (*28*), it can be surmised that the sulfur atom of thiourea and allylthiourea

attacks MeI by breaking the C–I bond and forming a C–S bond:

$$CH_3I \ + \ \underset{\text{(Thiourea)}}{NH_2-\overset{\overset{\textstyle S}{\|}}{C}-NH_2} \longrightarrow CH_3-S-\underset{}{\overset{\overset{\textstyle NH_2}{|}}{C}}=\overset{+}{N}H_2 \ I^- \tag{1}$$

$$CH_3I \ + \ \underset{\text{(Allylthiourea)}}{CH_2=CHCH_2NHCSNH_2} \longrightarrow \underset{\underset{\textstyle CH_3-S}{|}}{CH_2=CHCH_2NH\overset{+}{C}=NH_2} \ I^-$$

Extremely rapid dissipation of MeI was found in aqueous solution containing 1.0 mM Na-DEDTC, NH$_4$-DEDTC, or ATS (**Figure 2b**) compared to the other agrochemicals (**Figures 1** and **2a**; **Table 1**). Complete dissipation of MeI occurred within 24 h in the Na-DEDTC and NH$_4$-DEDTC solution, and less than 20% remained in ATS solution. The MeI degradation half-life, based on a pseudo-first-order rate coefficient, was drastically decreased in Na-DEDTC, NH$_4$-DEDTC, and ATS aqueous solutions (respective $t_{1/2}$ of 0.13, 0.14, and 0.35 d) compared to degradation by hydrolysis ($t_{1/2} = 108.47$ d) (**Table 1**). MeI was dissipated more rapidly in the Na-DEDTC or NH$_4$-DEDTC solution than in ATS solution, with $t_{1/2}$ 2–3 times less than that of ATS (**Table 1**). These results suggest that MeI would be quickly transformed in aqueous systems treated with Na-DEDTC or NH$_4$-DEDTC, which may substantially reduce the risk of off-site transport.

The reaction mechanism between MeI and ATS is postulated to involve conversion to the Bunte salts (*29*) which would

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Table 1. First-Order and Second-Order Degradation Rate Constant and Half-Life of Methyl Iodide (1.0 mM) in Aqueous Solution Containing Different Agrochemicals (1.0 mM)[a]
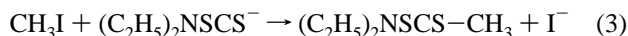
	first-order kinetics		second-order kinetics	
agrochemical	$k_f \times 10^{-1}$ (d^{-1})	$t_{1/2}$ (d)	$\mu \times 10^{-1}$ (mM^{-1} d^{-1})	$t_{1/2}$ (d)
Na-DEDTC	53.93 ± 1.34 (1.00)	0.13	118.32 ± 9.55 (0.99)	0.08
NH$_4$-DEDTC	49.39 ± 1.45 (1.00)	0.14	114.00 ± 8.30 (0.99)	0.09
ATS	19.85 ± 0.37 (1.00)	0.35	34.08 ± 1.75 (0.99)	0.29
thiourea	0.93 ± 0.03 (1.00)	7.47	1.54 ± 0.01 (0.98)	6.51
allylthiourea	1.07 ± 0.04 (1.00)	6.47	2.03 ± 0.01 (0.99)	4.92
DCD	0.08 ± 0.01 (0.88)	83.12	0.14 ± 0.02 (0.71)	69.49
hydroxylamine	0.14 ± 0.02 (0.90)	50.71	0.24 ± 0.3 (0.80)	41.15
oxamide	0.11 ± 0.01 (0.98)	61.18	0.15 ± 0.01 (0.97)	65.79
urea	0.10 ± 0.01 (0.89)	71.96	0.16 ± 0.02 (0.80)	63.69
control	0.06 ± 0.01 (0.91)	108.47	0.08 ± 0.01 (0.91)	130.65

[a] Values in parentheses are correlation coefficient *r*.

be relatively stable in neutral aqueous solution:

$$CH_3I + S_2O_3^{2-} \rightarrow CH_3-S-SO_3^- + I^- \quad (2)$$
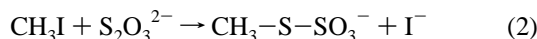
In Na-DEDTC and NH$_4$-DEDTC aqueous solutions, (C$_2$H$_5$)$_2$-NSCS$^-$ exists as a thiolate ion (RS$^-$), which is a strong nucleophile that is susceptible to S$_N$2 nucleophilic substitution reactions with halogenated hydrocarbons. The following reaction between MeI and diethyldithiocarbamate ion in aqueous solution is thus proposed:

$$CH_3I + (C_2H_5)_2NSCS^- \rightarrow (C_2H_5)_2NSCS-CH_3 + I^- \quad (3)$$

As shown in **Figure 2b**, I$^-$ was quantitatively produced as the MeI was consumed in Na-DEDTC aqueous solution.

Fitting a pseudo-first-order kinetic model to the MeI disappearance data showed that as the initial Na-DEDTC or NH$_4$-DEDTC-to-MeI ratio increased, the degradation rate constant of MeI increased (**Figure 3**). For instance, the half-life of MeI in aqueous solution containing 0.25 mM Na-DEDTC or NH$_4$-DEDTC was ~20 h, whereas the half-life was reduced to <0.75 h when the concentration of Na-DEDTC or NH$_4$-DEDTC was increased to 4.0 mM. Wang et al. (*29*) plotted apparent first-order rate constants vs the initial concentration of ATS to attain second-order reaction constants of fumigants in aqueous solutions of ATS; good correlation suggested that the reaction followed second-order kinetics typically exhibited in S$_N$2 reactions. In these experiments, pseudo-first-order degradation constants of MeI were linearly correlated with the initial concentration of Na-DEDTC or NH$_4$-DEDTC in aqueous solution (**Figure 3**), implying that the reaction mechanism between MeI and Na-DEDTC or NH$_4$-DEDTC is an S$_N$2 nucleophilic substitution reaction. Because of the mathematical simplicity of the integrated rate equation for first-order kinetics in comparison with second-order kinetics, a first-order kinetic model is often utilized for comparison purposes in pesticide degradation experiments (*30*).
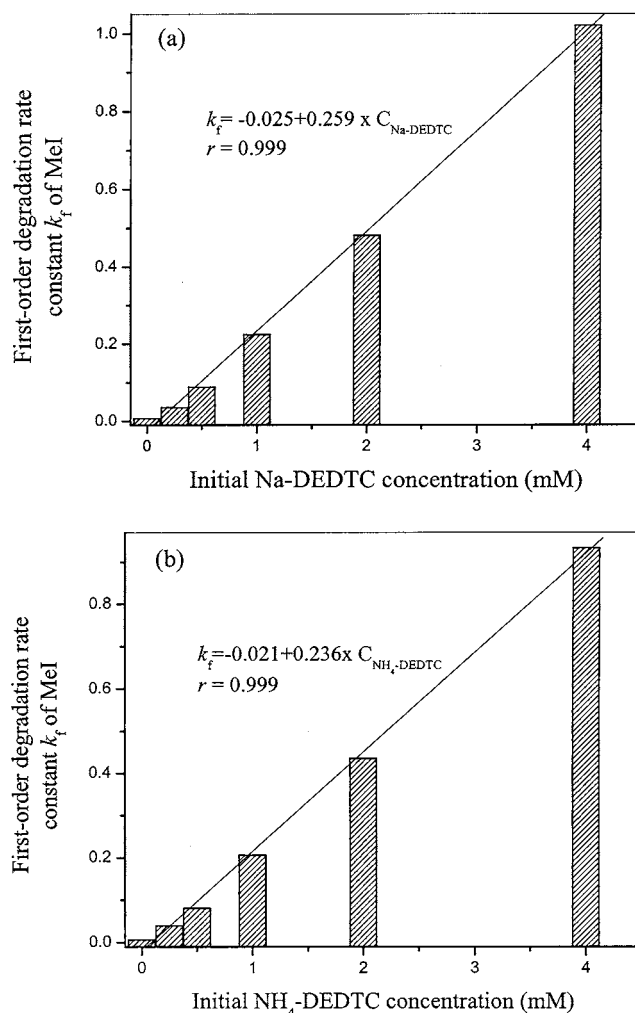
Figure 3. First-order degradation rate constant k_f (h^{-1}) of fumigants (1.0 mM) in aqueous solutions containing varying initial concentrations of Na-DEDTC (a) and NH$_4$-DEDTC (b).

For completeness, the second-order reaction rate coefficients, μ, may be found from the following second-order relationship (*31, 32*):

$$\frac{dC}{dt} = -\mu XC = -\mu(C - C_0 + X_0)C \quad (4)$$

where C and X are the MeI and NI or fertilizer concentrations, respectively, C_0 and X_0 are their initial values, and μ is the second-order rate constant. After integrating, the appropriate solution to eq 4 is described as follows:

$$C(t) = C_0 \frac{(X_0 - C_0) \exp[-\mu(X_0 - C_0)t]}{X_0 - C_0 \exp[-\mu(X_0 - C_0)t]} \quad (5)$$

When the experiment is arranged so that the initial concentrations of MeI and NI or fertilizer are equal ($X_0 = C_0$), eq 5 becomes

$$C(t) = \frac{C_0}{1 + \mu C_0 t} \quad (6)$$

When half of the original concentration MeI is consumed, we may insert $C_0/2$ for $C(t)$ and thereby obtain the second-order half-life equation, which is

$$T_{1/2} = \frac{1}{\mu C_0} \qquad \text{for } X_0 = C_0 \qquad (7)$$

Table 1 contains the second-order reaction rate coefficients (μ) and half-lives ($t_{1/2}$) together with relevant pseudo-first-order kinetics for MeI (1.0 mM) in agrochemical aqueous solution (1.0 mM). Both the first-order and second-order kinetic models produced a good fit to the data, especially for some NIs such as Na-DEDTC, NH$_4$-DEDTC, ATS, thiourea, and allylthiourea that rapidly reacted with MeI in aqueous solution. Because of the occurrence of MeI hydrolysis and the possible influence of degradation products on these reaction systems, it is difficult to verify that the reaction between MeI and agrochemicals in aqueous solution follows second-order kinetics. Moreover, the rate of a second-order reaction is dependent on the initial reactant concentrations, whereas the rate of a first-order reaction is not. A more complex equation (e.g., eq 5) for calculating rate coefficients is necessary if the initial concentrations of fumigant and agrochemical in aqueous solution are not equal (*32*). Therefore, for purposes of comparing fumigant degradation under different experimental conditions described herein, the first-order kinetic model is appropriate and relatively easy to use (*29, 33*).

Accelerated MeI Degradation in Soil Amended with Fertilizers. The potential influence of agrochemical application on the rate of the MeI degradation was further studied in soil. Accelerated MeI degradation occurred in soils amended with all agrochemicals tested. **Table 2** shows the first-order rate coefficients k_f (h^{-1}) and corresponding half-lives for MeI (0.5 mmol kg^{-1}) in Arlington sandy loam amended with different agrochemicals.

Incorporation of the fertilizers oxamide, urea, and calcium cyanamide (150 μg of N/g of soil) into Arlington soil was found to moderately increase the rate of MeI degradation. The degradation was about 1.3, 1.5, and 2.4 times faster in oxamide-, urea-, and calcium cyanamide-amended soil, respectively, than in unamended soil. Generally, both microbial and chemical degradation may be involved in fumigant degradation in soil. However, for short-chained halogenated hydrocarbons such as MeBr and MeI, abiotic degradation is often the major factor (*26, 34*), whereas biological degradation has been shown to be important for other fumigants such as MITC (*35*), 1,3-D (*33*), and chloropicrin (*11*). The application of fertilizers to soil can alter the biological and chemical conditions and affect the rate of MeI degradation in soil. Ou et al. (*26*) reported that MeBr degradation was accelerated by liming and applying an ammonia fertilizer as well as through inoculation with an ammonia oxidizing bacterium. When the N fertilizers oxamide and urea are incorporated into soil, they should stimulate the activity of nitrifiers, which may lead to an increased capacity to degrade MeI in a manner similar to that reported for the oxidization of MeBr (producing formaldehyde and bromide ion) by terrestrial and marine nitrifiers (*27, 36*). Moreover, the urea and oxamide dissolved in soil water may react with MeI, so a slight increase in the abiotic degradation of MeI in soils may also be observed. Compared to the degradation rate of MeI in soil amended with urea and oxamide, calcium cyanamide-amended soil showed a higher potential to rapidly degrade MeI. Calcium cyanamide (CaNCN) is also a nitrogen fertilizer, though it is less commonly used than urea. Though calcium cyanamide is essentially insoluble in water, it may undergo partial hydrolysis to the soluble calcium hydrogen cyanamide, which is a source of cyanamide ion. In the presence of cyanamide ion, MeI may be transformed to a disubstituted methyl cyanamide, which may then be hydrolyzed and decarboxylated to a

Table 2. First-Order Degradation Rate Constant k_f (h^{-1}) and Half-Life ($t_{1/2}$) of Methyl Iodide (0.5 mmol kg^{-1}) in Arlington Sandy Loam with Different Agrochemical (1.0 mmol kg^{-1}) Amendment

agrochemical	$k_f \times 10^{-3}$ (h^{-1})	$t_{1/2}$ (h)	r
oxamide[a]	3.01 ± 0.34	226.5	0.91
urea[a]	3.44 ± 0.78	195.8	0.75
calcium cyanamide[a]	5.28 ± 0.54	131.3	0.93
NH$_4$-DEDTC	3.87 ± 0.79	179.1	0.87
Na-DEDTC	3.90 ± 0.40	177.7	0.93
DCD	3.83 ± 0.74	181.0	0.79
ATS	39.8 ± 3.9	17.4	0.99
thiourea	42.9 ± 4.4	16.2	0.98
allylthiourea	44.4 ± 2.7	15.6	0.99
control	2.24 ± 0.55	309.4	0.88

[a] Concentration 150 μg of N/g of soil.

secondary amine according to the following reaction:

$$2CH_3I + NCN^{2-} \rightarrow (CH_3)_2-NCN \xrightarrow{H_3O^+ \text{ or } OH^-} (CH_3)_2NH \qquad (8)$$
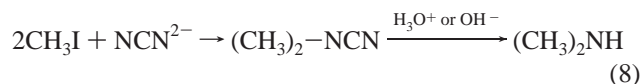
Accelerated MeI Degradation in Soil Amended with Nitrification Inhibitors. The degradation of MeI was further studied in Arlington soil amended with several NIs. The disappearance of MeI in these soils was well-described by first-order kinetics (**Table 2**). While Na- and NH$_4$-DEDTC showed strong nucleophilic substitution activity with MeI in aqueous solution (**Table 1**), amending soil with Na-DEDTC and NH$_4$-DEDTC had a relatively small impact on the rate of MeI degradation in comparison with the degradation in unamended soil (**Table 2**). Further, the level of enhancement in the rate of MeI degradation in amended soil (ATS $\gg$ Na-DEDTC > NH$_4$-DEDTC) was significantly different from the trend in aqueous solution (Na-DEDTC > NH$_4$-DEDTC > ATS) (**Tables 1** and **2**). This difference may be attributable to sorption of Na-DEDTC and NH$_4$-DEDTC to soil, which would reduce the availability of the amendment for reaction. In these experiments, MeI was injected into the soils, where it partitioned between the air, water, and solid phases of soil. Generally, reactions between halogenated fumigants and nucleophilic amendments take place only in the aqueous phase. As sorption decreases aqueous concentrations, the overall reaction rate is decreased. Contrary to the reduced MeI degradation rate in the Na-DEDTC- and NH$_4$-DEDTC-amended soils, MeI degradation in ATS-amended soils remained similar to the degradation rate in aqueous solution. This occurs because ATS is an inorganic chemical and its reactive group (thiosulfate anion, S$_2$O$_3^{2-}$) exists in the aqueous phase of the soil as the ion. This distinguishes ATS from nucleophilic organic chemicals such as Na-DEDTC and NH$_4$-DEDTC, where a large portion of the chemical may be distributed in the sorbed phase.

As the initial Na-DEDTC:MeI and ATS:MeI ratios increased, the degradation rate of MeI was increased in amended soils (**Figure 4**). Increasing the molar ratio of Na-DEDTC to MeI did not proportionally increase the degradation rate of MeI. However, the rate of MeI degradation in ATS-amended soils depended on their molar ratios: when the molar ratio of ATS to MeI doubled, the degradation rate of MeI also doubled. These results further support observations that MeI transformation in ATS-amended soil is abiotic and that the degradation rate depends on the ATS concentration (i.e., second-order reaction). Sorption of diethyldithiocarbamates to soil may have reduced the availability of Na-DEDTC and NH$_4$-DEDTC in the aqueous phase, suppressing the MeI degradation rate in soil.

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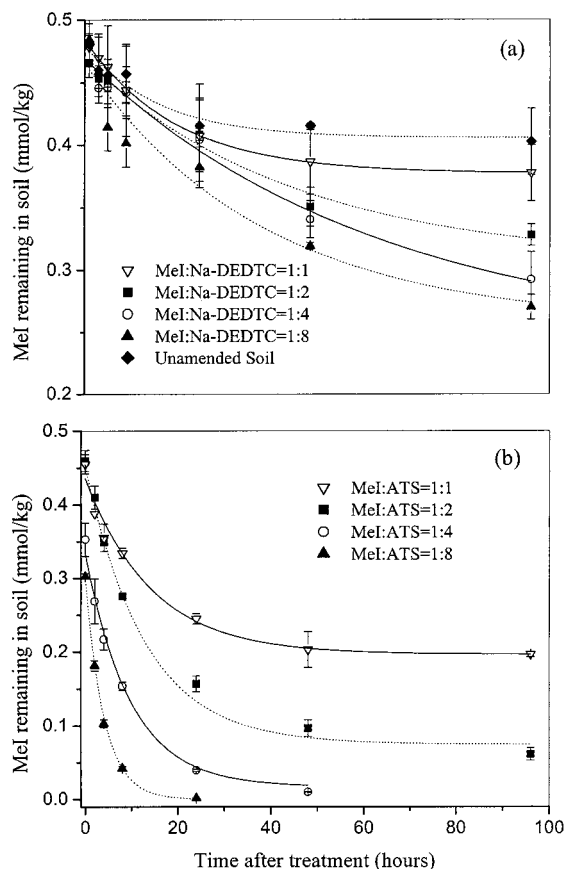
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Figure 4. Degradation of MeI (0.5 mmol/kg) in Arlington soil amended with Na-DEDTC (a) and ATS (b) at different molar ratios. Error bars represent standard deviation of triplicate samples.
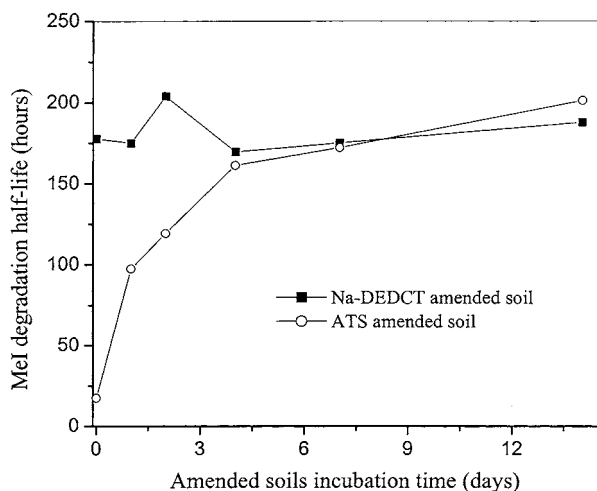

Figure 5. Influence of amended soil (1.0 mmol/kg) incubation time on the degradation half-life of MeI (0.5 mmol/kg).

The degradation of MeI in soils was determined in amended soils held for different incubation periods prior to addition of MeI. The MeI degradation half-life was not significantly affected by aging Na-DEDTC in soil for a 0−14-d period before fumigation (**Figure 5**). This implies that the timing of Na-DEDTC application would not affect the degradation of MeI in soil amended with Na-DEDTC. In contrast, the degradation half-life of MeI in ATS-amended soil greatly increased with incubation time (**Figure 5**). This demonstrates that ATS is unstable in soil, because the thiosulfate ion can be easily oxidized to sulfate (*37*), which is not reactive with MeI.

Therefore, to achieve optimum control of fumigant emissions, ATS application should be carried out concurrently with fumigant application because volatilization of fumigants from soil is generally most rapid shortly after fumigation.

A dramatic acceleration in MeI degradation in soil amended with thiourea and allylthiourea was observed. The enhancement was greater than that for the other agrochemicals tested in these experiments (**Table 2**). For instance, the first-order half-life ($t_{1/2}$) of MeI in thiourea- and allylthiourea-amended soil was ∼16 h, significantly less than that in unamended soil (>300 h). Soil application of thiourea and allylthiourea may offer an alternative approach to accelerate the degradation of MeI and reduce the emission of halogenated fumigants into the atmosphere.

Degradation of MeI was greatly enhanced in soil amended with thiourea and allylthiourea relative to the rate of degradation in aqueous solution (**Tables 1** and **2**). Apparently, the rate of MeI degradation in the amended soils did not depend solely on reactions that occurred in the aqueous solutions, but also depended on other soil reaction processes (i.e., catalysis). Owing to the negative charge characteristic of the soil surface, thiourea could be converted to the corresponding thiuronium ions in soil, which would react with MeI to give isothiuronium salt. This would further cleave to mercaptan in alkali soil or in the presence of high-molecular-weight amines in soil. The proposed reaction for thiourea is as follows:
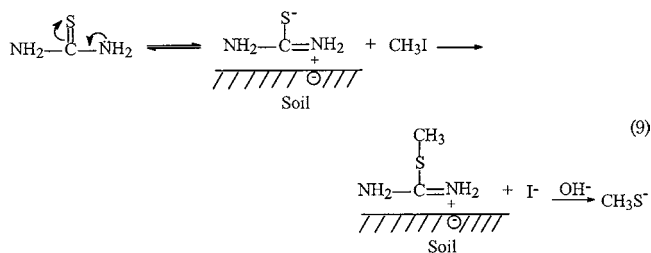
The degradation product, mercaptan, would be available to degrade additional MeI through an S_N2 nucleophilic reaction. Thus, the electrostatic interaction of thiuronium ion with the soil may lower the energy requirements for the reaction with MeI and result in a higher degradation rate of MeI in soil compared to that in aqueous solution. Similarly, enhanced MeI degradation in allylthiourea-amended soil could follow a similar catalytic mechanism in soil. Previous research has indicated that the application of thiosulfate salts to soils may substantially decrease volatilization of halogenated fumigants from soil, and surface application has been promoted as a promising emission control and soil remediation measure (*20, 21*). Soil application of thiourea and allythiourea to increase the rate of MeI degradation may provide an effective tool to prevent and reduce fumigant emissions. To further develop this approach, fumigant degradation and emissions reduction in soils amended with thiourea and allylthiourea needs to be further evaluated under different conditions and for other soils.

ABBREVIATIONS USED

MeI, methyl iodide; Na-DEDTC, sodium diethyldithiocarbamate; NH$_4$-DEDTC, ammonium diethyldithiocarbamate; ATS, ammonium thiosulfate; DCD, dicyandiamide; NI, nitrification inhibitor.

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