Degradation and Phase Partition of Methyl Iodide in Soil

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Methyl iodide (CH_3I) was recently proposed as a direct replacement for methyl bromide (CH_3Br) in soil fumigation, but no information exists on its behavior and safety in the environment. In this study, we compared CH_3I and CH_3Br for their transformation and phase partitioning in soil and characterized processes that affect the dissipation of CH_3I from water. In moist soil, the adsorption coefficient K_d of CH_3I is greater, and the Henry's law constant K_H is smaller, than that of CH_3Br. In the same soil, CH_3I was about twice as persistent as CH_3Br, and the persistence decreased with increasing soil organic matter content. Chemical reactions, likely nucleophilic substitutions on soil organic matter, were identified as the predominant pathway through which CH_3I and CH_3Br were degraded under the concentrations studied. In water, CH_3I degraded to I_2 and I^- under 254-nm UV irradiation and dissipated rapidly ($t_{1/2} = 26$ h) through volatilization and photohydrolysis under outdoor conditions.

Keywords: *Methyl iodide; methyl bromide; degradation; adsorption; photohydrolysis; volatilization*

INTRODUCTION

The impending phase-out of methyl bromide (bromomethane, CH_3Br) as a soil and commodity fumigant, if not replaced with equally effective alternatives, will cause substantial economic damage to the agricultural communities (Ferguson and Padula, 1994). Intensive research is currently being conducted for identifying and developing replacements for CH_3Br. The few remaining fumigants and nematicides, including 1,3-dichloropropene, chloropicrin, and methyl isothiocyanate, all have narrower spectra of activity than CH_3Br (Noling and Becker, 1994). This implies that combinations of two or more of these chemicals may have to be used to achieve a broad control.

Recently, methyl iodide (iodomethane, CH_3I) was proposed as a potential candidate as a direct replacement for CH_3Br in soil fumigation (Becker et al., 1995; Sims et al., 1995; Ohr et al., 1996). In extensive laboratory and field-plot trials, CH_3I was shown to be equivalent to or more efficient than CH_3Br for controlling a wide variety of soil-borne pests including weeds, nematodes, and fungi (Becker et al., 1995; Sims et al., 1995; Ohr et al., 1996). Methyl iodide has also been tested on a small scale for controlling various pests in stored products (Muthu and Srinath, 1974). The main advantage of CH_3I over CH_3Br is that it degrades quickly in the troposphere via photolysis and therefore is unlikely to contribute to ozone depletion (Rassmussen et al., 1982; Solomon et al., 1994). The estimated lifetime for CH_3I in the atmosphere is only 4−8 days compared with 1.5−2 years for CH_3Br, and its estimated ozone depletion potential (ODP) is only 0.016 compared with 0.6−0.7 for CH_3Br (Solomon et al., 1994; Ohr et al., 1996). However, CH_3I is not a registered pesticide, and most aspects of its environmental behavior are essentially unknown. To predict the environmental acceptability of developing this chemical into a commercial fumigant, it is imperative that its transformation and partitioning behavior in the soil−water−air system be characterized. Understanding of these processes is also critical for designing optimum application techniques that would require minimal chemical input while maintaining adequate efficacy for controlling target organisms.

Table 1. Some Physical−Chemical Properties of Methyl Iodide and Methyl Bromide

property	CH_3I	CH_3Br
molecular weight	142	95
specific gravity (g mL^{-1})	2.28 (20 °C)	1.73 (0 °C)
vapor pressure (mmHg)	398 (20 °C)	1600 (20 °C)
boiling point (°C)	42.4	3.6
solubility in water (%)	1.4	1.34

Some of the basic physical−chemical properties of CH_3I are listed along with those of CH_3Br in Table 1. CH_3I is structurally analogous to CH_3Br, and in comparison to CH_3Br, CH_3I has a similar water solubility, lower vapor pressure, and higher boiling point and molecular weight. In this study, we compared CH_3I and CH_3Br for their persistence and degradation mechanisms in selected soils under aerobic and sterilized conditions and their partitioning between air−water phases and soil−water phases. The inclusion of CH_3Br in the study allows logical predictions about the environmental fate of CH_3I due to the great similarities between these two compounds and the fact that abundant data are already available for CH_3Br. CH_3I photohydrolysis in and volatilization from water, and their contributions to its persistence in water, were also investigated.

MATERIALS AND METHODS

Chemicals and Soils. CH_3I with a purity of 99.5% was purchased from Chem Service (West Chester, PA), and CH_3Br with a purity of 99.5% in a lecture bottle was purchased from Matheson Gas Products Inc. (East Rutherford, NJ). Before use, CH_3Br was introduced into a Teflon sampling bag, and CH_3Br in the bag was used as the stock gas. At room temperature and 1.0 atmosphere, the vapor density of CH_3Br in the sampling bag was determined to be 3.8 mg mL^{-1}. Aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline used in the degradation study were purchased from Aldrich Chemical Co. (St. Louis, MO).

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S0021-8561(96)00413-X

Table 2. Some Physical−Chemical Properties of Soils Used in This Study

soil type	OM (%)	clay (%)	pH (H_2O)
Greenfield sandy loam	0.92	9.5	7.4
Carsetas loamy sand	2.51	11.0	7.3
Linne clay loam	2.99	25.1	7.2
nursery potting mix	9.60	4.0	6.2

The physical−chemical properties of the four soils are given in Table 2. The Greenfield sandy loam (Moreno Valley Field Station, University of California, Riverside) was used in previous field and laboratory studies on CH_3Br (Gan et al., 1994; Yates et al., 1996a,b), and the nursery potting mix (1:1 mix of topsoil and fir sawdust) and Carsetas loamy sand (Coachella Valley Field Station, University of California, Riverside) were used in some of the experiments for testing the efficacy of CH_3I (Becker et al., 1995; Ohr et al., 1996). Before use, moist Greenfield and Carsetas soils and the potting mix were passed through a 2-mm sieve without air-drying to protect the microbial activity. Air-dried Linne clay loam (Santa Barbara, CA) was passed through a 2-mm sieve and then wetted to 18% water content and incubated at room temperature for 4 weeks before use. The final water content was readjusted to 12% for Greenfield and Carsetas soils and to 18% for Linne clay loam and the potting mix. The higher water content used for Linne clay loam and the potting mix was necessary because of their higher clay or organic matter contents.

Partition Coefficients K_H and K_d. A headspace method modified from Rao et al. (1989) was used for measuring the air−water partition coefficient K_H and the adsorption coefficient K_d. Blank headspace vials (121 ± 0.5 mL, Supelco Co., Bellefonte, PA), vials containing 20.0 mL of deionized water, and vials containing 55.0 g of soil with known water content were spiked with 200 μL of saturated CH_3I vapor (over the surface of liquid CH_3I in a closed 1-L flask) or 500 μL of CH_3Br gas and immediately capped with Telfon-faced butyl rubber septa and aluminum seals. The vials were kept in the dark and at room temperature (21 ± 1 °C) for 24 h. During the equilibration, all of the vials were occasionally shaken by hand. Preliminary experiments showed that the 24 h equilibration under the above conditions was adequate for achieving equilibrium. At equilibrium, an aliquot of the headspace (500 μL) was withdrawn using a gastight syringe (Supelco) and transferred to the bottom of a 8.7-mL headspace vial (Supelco), and the vial was immediately capped. Preliminary tests showed that the sample transfer was quantitative and reproducible. The sealed vials were then analyzed for CH_3I and CH_3Br content on a Tekmar 7000 headspace autosampler (Tekmar Co., Cincinnati, OH) in tandem with an HP5890 GC (Hewlett-Packard, San Fernando, CA) equipped with an electron capture detector. Headspace autosampler conditions were 90 °C equilibration temperature, 10-min equilibration time, and 100-μL sample loop. The GC parameters were REX-624 capillary column (Restek Co., Bellefonte, PA), 40 °C oven temperature, 170 °C injection port temperature, 240 °C detector temperature, and 1.1 mL min^{-1} column flow rate (helium). Calibration curves were made by analyzing blank vials spiked with known quantities of CH_3I or CH_3Br under the described conditions.

The concentration in the water phase (C_w) was calculated from the difference between the measured headspace concentrations (C_a) in the blank vials and vials containing water. The dimensionless K_H was then obtained using

$$K_H = C_a/C_w \quad (1)$$

The C_w for vials containing soil and water was obtained using C_a and the calculated K_H in eq 1, and the concentration adsorbed on soil, C_s, was calculated from the C_a, C_w, and volume of the three phases. Since degradation during the equilibration process may cause an overestimation of K_d, the production of I^- and Br^- was measured for the vials containing soil samples at the end of the equilibration. The soil was mixed thoroughly with 25 mL of deionized water, and extraction of the soil−water solution was made under vacuum through a Büchner funnel. The extracts were measured for I^- concentrations on an Accumet 25 pH meter (Fisher Scientific, Pittsburgh, PA), with an iodide-specific electrode (Fisher Scientific), or for Br^- concentrations on a QuikChem AE automated flow injection ion analyzer (LaChat, Milwaukee, WI). A correction factor based on the degraded fraction was then introduced to adjust the calculated C_s. The adsorption coefficient K_d (milliliters per gram) was then obtained using the expression

$$K_d = C_s/C_w \quad (2)$$

Degradation in Soil and Reaction with Aniline. Degradation of CH_3I and that of CH_3Br were compared in the four selected soils under the same conditions. CH_3Br bromide degradation in the Greenfield, Carsetas, and Linne soils was studied previously under unsterilized conditions (Gan et al., 1994) but was determined again in the current study under the presented concentrations to provide a comparison for CH_3I. To elucidate the degradation mechanism, degradation kinetics of CH_3I and CH_3Br was followed in both sterilized and unsterilized soils. For unsterilized treatments, 8.7-mL headspace vials were filled with 11.2 g of Greenfield sandy loam or Carsetas loamy sand (with 12% water content) or 9.4 g of the potting mix or the Linne clay loam (with 18% water content). Less soil was used for the latter two soils because of their low density. Five microliters of acetone solution containing 46 μg μL^{-1} CH_3I or CH_3Br was injected into the soil using a syringe, and the vials were immediately sealed with septa and caps. The initial concentrations, on a dry soil weight basis, were 23 mg kg^{-1} for the Greenfield and Carsetas soils and 29 mg kg^{-1} for the potting mix and Linne clay loam. These concentrations approximate the concentration during the first few days in top soil layers following a typical CH_3Br fumigation under tarped conditions (Abdalla et al., 1974; Kolbezen et al., 1974).

For sterilized treatments, soils were autoclaved twice at 121 °C for 30 min and the soil water content was readjusted to the same values as used in the unsterilized group. Small headspace vials filled with the sterilized soil (11.2 g for Greenfield or Carsetas soil and 9.4 g for Linne soil or potting mix, wet weight) were spiked with the same amount of CH_3I or CH_3Br and then sealed with septa and caps. All of the treated sample vials were incubated in a constant temperature room (24 ± 1 °C) in the dark. At different time intervals after treatment, three replicate samples were removed, and after 5.0 mL of ethyl acetate was added into the sealed vial through the septum using a syringe, the soil−solvent mixture was mechanically shaken for 1.0 h. An aliquot of the ethyl acetate extract was then quickly transferred into a GC vial containing a small amount of sodium sulfate salt, and 2 μL of the sample was injected into the GC from an autoinjector. The same GC conditions as described above were used in the analysis. The recovery of CH_3I or CH_3Br from freshly spiked soil samples using these sample preparation procedures was 95−101%.

To elucidate the degradation pathways, CH_3I and CH_3Br reactions with a model nucleophilic compound, aniline, were studied. Solutions containing 5 mM aniline and 0.5 mM CH_3I or 5 mM aniline and 0.5 mM CH_3Br were prepared in deionized water and filled into 125-mL serum bottles. Bottles containing deionized water were treated with the same amount of CH_3I or CH_3Br and used as controls. All of the bottles were sealed with Teflon-faced butyl rubber septa and aluminum caps and kept at 24 °C in the dark. Four replicates were used for each chemical−substrate combination. At different time intervals, 100 μL of the incubated solutions was withdrawn using a gastight syringe and transferred into 8.7-mL headspace vials for analysis on the headspace GC. During the experiment, the bottles were inverted to eliminate loss due to gaseous diffusion through the septa. To identify reaction products, at the end of the 25-day incubation, 10 mL of the aniline sample was extracted with 10 mL of ethyl acetate in a separatory funnel, and an aliquot of the organic phase was injected into a HP 5890GC−5971 MSD (Hewlett-Packard). The GC/MS spectra of eluted peaks were compared to that of aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline. The GC

conditions were HP-5MS (30 m × 0.25 mm × 0.25 μm, Hewlett-Packard), 250 °C injector temperature, and 1.04 mL min^{-1} flow rate (helium). The oven temperature was initially 50 °C (0.01 min) and then ramped at 4 °C min^{-1} to 190 °C.

Photohydrolysis. The photohydrolysis of CH_3I was carried out under artificial UV irradiation using a system similar to that of Castro and Belser (1981). A 2300-mL flask (28 cm in height) was filled with deionized water containing 1.0 mM CH_3I, and a quartz tube [bottom-sealed, 1 cm (i.d.) × 22 cm (l)] was suspended in the solution, with the bottom of the tube hanging about 4 cm from the bottom of the flask. Adhesive aluminum tape was used to carefully seal the flask opening around the quartz tube. A shortwave pencil lamp emitting UV at 254 nm (4500 μW/cm^2, 5-cm lighted tube, Fisher Scientific) was then inserted into the quartz tube, with the tip of the lighted tube positioned about 5 cm from the flask bottom. After the UV lamp was lit, a stream of air was directed into the quartz tube to dissipate some of the heat generated by the lighted lamp. To differentiate photohydrolysis and normal hydrolysis, a flask filled with 1.0 mM CH_3I solution but not exposed to UV irradiation was used as the control. Both flasks were kept at room temperature (21 ± 1 °C) and wrapped with aluminum foil. At different time intervals, 0.2 mL of the UV-irradiated or the control solution was sampled using a gastight syringe and analyzed on the headspace GC. Ten milliliters of the solution was simultaneously removed using a long-needle syringe and measured for I^- concentration using the electrode method. During a preliminary experiment, formation of I_2 from CH_3I was visually observed after exposure to the UV source. To quantify the fraction of I_2 in the solution, an excessive quantity of sodium bisulfite ($NaHSO_3$) was added into the same sample to reduce I_2 to I^- (Moran et al., 1995), and a measurement of I^- was repeated. The increase in I^- concentration before and after the reduction reaction was assumed to be due to I_2. Precautions were used in handling samples to avoid any significant loss of I_2 due to volatilization. After each sampling, to prevent volatilization loss of CH_3I and I_2 from the flask, deionized water was added back to fill the flask (to eliminate any headspace), and the needle puncture was carefully sealed with adhesive aluminum tape.

Volatilization from Water. Volatilization of CH_3I from open-surface deionized water was measured under indoor and outdoor conditions. In the indoor experiment, four bottom-sealed glass cylinders [12.5 cm (i.d.) × 32 cm (h)] were filled with 0.2 mM CH_3I water solution to 30 cm depth and placed in a vacuum hood. Two of the cylinders were kept static, and the other two were continuously stirred at a low speed with a magnetic bar on a stirrer. Samples of solution (0.5 mL) were removed with a pipet and transferred into 8.7-mL headspace vials for analyzing CH_3I content on the headspace GC. In the outdoor experiment, two such cylinders filled with 0.2 mM CH_3I were placed directly under sunlight, and the dissipation of CH_3I in the water was followed as in the indoor study. The average temperature during the 6-day outdoor experiment was 14 °C, with the highest 26 °C and the lowest 4 °C. At the end of each experiment, samples were also analyzed for I^- concentration. In both studies, the unaccounted fraction of CH_3I was assumed to be lost by volatilization.

RESULTS AND DISCUSSION

Phase Partition. The partition of a chemical between air and water phases, represented by its Henry's law constant, K_H, is extremely important in determining the pathway over which a chemical moves in the soil−water−air environment. As a rough rule, at 50% water saturation, the transport of compounds with $K_H \gg 10^{-4}$ is vapor phase diffusion dominated and those with $K_H \ll 10^{-4}$ is liquid diffusion dominated (Jury et al., 1991). The vapor phase diffusion of a chemical is approximately 10^4 times as fast as its liquid phase diffusion (Jury et al., 1991). Reported K_H values for CH_3I are not directly available. From its vapor pressure and solubility, the dimensionless K_H was calculated to be 0.21 at 25 °C (Mutziger, 1996). The reported K_H for CH_3Br is 0.244 at 20 °C (Goring, 1962). Our measured K_H values for both CH_3I (0.21) and CH_3Br (0.30) at 21 °C agreed well with the calculated or reported values (Table 3). With a K_H of 0.30 at 21 °C, CH_3Br transport in soil is predominantly driven by its vapor phase diffusion, which is responsible for its deep penetration and rapid volatilization consistently observed in numerous field and laboratory studies (Abdalla et al., 1974; Kolbezen et al., 1974; Van Wambeke et al., 1980; Yates et al., 1996a,b; Gan et al., 1996). With a K_H of 0.21 at 21 °C, the movement of CH_3I in soil can also be expected to be dominated by gas phase diffusion and, therefore, to be very fast.

Table 3. Measured K_H and K_d for CH_3I and CH_3Br (21 ± 1 °C)

parameter	CH_3I	CH_3Br
K_H ($n = 8$)	0.21 ± 0.01	0.30 ± 0.02
K_d(measured) ($n = 6$) (mL g^{-1})		
Greenfield sandy loam	0.09	0.07
Linne clay loam	0.15	0.10
Carsetas loamy sand	0.16	0.09
potting mix	0.55	0.29
K_d(corrected) ($n = 6$)[a] (mL g^{-1})		
Greenfield sand loam	0.08	0[b]
Linne clay loam	0.13	0
Corsetas loamy sand	0.12	0
potting mix	0.46	0.20

[a] Corrected for degradation during equilibration. [b] 0 indicates adsorption below measurable.

The distribution coefficient between soil and water phases, or the adsorption coefficient K_d, has long been established as an important parameter in governing pesticide movement in soil profiles. Assuming CH_3I moves predominantly from diffusion in the vapor phase, its transport can be described by the model (Jin and Jury, 1995)

$$R_g \frac{\partial C_g}{\partial t} = D_s \frac{\partial^2 C_g}{\partial Z^2} - \mu R_g C_g \qquad (3)$$

where C_g is the concentration in soil air, t is time, μ is the first-order degradation rate constant, Z is the distance, D_s is the effective gas diffusion coefficient in soil, and R_g is the retardation factor for gas phase diffusion and is given by

$$R_g = \rho_b K_d / K_H + \theta / K_H + a \qquad (4)$$

where a is soil air porosity, ρ_b is soil bulk density, and θ is volumetric water content.

The measured K_d values for CH_3Br on the selected soils were from 0.07 to 0.39, increasing with soil organic matter content (Table 3). However, measuring Br^- at the end of the adsorption study revealed that a small fraction of the added CH_3Br was degraded during the 24-h equilibration, and more degradation was found in the potting mix than in the regular soils. After correction for the degraded fraction, the amount adsorbed on the Greenfield, Carsetas, and Linne soils was within the range of experimental errors, and K_d thus became negligible (Table 3). Degradation of CH_3I during the 24-h equilibration was less than that of CH_3Br. After correction for degradation, K_d for CH_3I on the tested soils ranged from 0.08 to 0.46. Among all of the soils used, adsorption on the potting mix was the strongest for both CH_3Br and CH_3I. This may be attributed to its very high organic matter content (9.6%).

Small, but non-zero, K_d and K_{oc} values have been reported for CH_3Br by other workers (Arvieu, 1983; Goring, 1962). However, in these measurements, the contribution from degradation during the equilibration to the adsorption was apparently ignored. In numerous adsorption studies of pesticides using batch equilibration techniques based on analysis of chemical remaining in the liquid phase only, degradation has been found to result in overestimated K_d values (Koskinen et al., 1979). As illustrated in this study, correction for degradation is particularly important for compounds that are weakly adsorbed on soil.

Stronger adsorption and smaller K_H of CH_3I combine to indicate that under the same conditions, less CH_3I will be in the soil gas phase than CH_3Br. For instance, in the Greenfield sandy loam, using the estimated K_d and K_H values and assuming a volumetric soil water content (θ) of 0.2 cm^3 cm^{-3}, an air content of 0.2 cm^3 cm^{-3}, and a soil bulk density of 2.6 g cm^{-3}, at equilibrium, about 23% of the total CH_3Br will be in the soil air and 77% in the soil water. In this soil under the same conditions, the distribution of CH_3I in the soil air, water, and solid phases will be 11, 55, and 34% respectively. The effect of K_d and K_H on the movement of CH_3I or CH_3Br in soil via gas phase diffusion may be seen from the interactions of these two coefficients with the retardation factor R_g. For example, substituting the estimated K_d and K_H and the assumed soil parameters in eq 4, the retardation factor R_g for gas phase diffusion in Greenfield sandy loam was calculated to be 2.14 for CH_3I but only 0.87 for CH_3Br. This suggests that under the same soil conditions, CH_3I is likely to diffuse more slowly than CH_3Br, or less volatilization loss of CH_3I will occur if the two chemicals are degraded at the same rate.

It must be noted that despite the differences between the two chemicals, the very high K_H and insignificant K_d of CH_3I still warrant significant volatilization losses of this chemical following a subsoil injection if the soil surface is not covered. Very high emission rates have been reported for CH_3Br under both field and laboratory conditions (Yagi et al., 1993, 1995; Majewski et al., 1995; Jin and Jury, 1995; Yates et al., 1996a,b; Gan et al., 1996). However, since CH_3I has a very short photolysis life time in the air, the emitted CH_3I is not expected to be carried to the stratosphere, where it would contribute to ozone depletion. From this perspective, the rapid movement of CH_3I into the air may be desirable since it would reduce phytotoxicity of CH_3I to plants and potential groundwater contamination.

Degradation in Soil and Reaction with Aniline. As the only irreversible process, degradation of CH_3I and CH_3Br in soil is important in determining the fraction available for volatilization to the air and/or diffusing to the groundwater. As found for 1,2-dibromo-3-chloropropane, CH_3Br, and many other volatile compounds, limited degradation in soil consistently leads to significant volatilization or downward movement of the chemical in the soil (Wagenet et al., 1989; Yates et al., 1996a,b). CH_3Br volatilization losses were found to be directly affected by its degradation rate in soil columns (Gan et al., 1996). Significantly less volatilization was observed in the organic matter-rich Linne soil in which CH_3Br was rapidly degraded to Br^-.

Degradation of CH_3I and CH_3Br in the four soils was determined by measuring the decrease of parent compounds with or without a sterilization pretreatment (Figures 1 and 2). Degradation of both chemicals fits first-order kinetics model in most treatments, with the exception for the degradation of CH_3I in the Greenfield soil (Table 4). At typical field concentrations, it appears that the degradation of both CH_3I and CH_3Br was not drastically affected by sterilization. This implies that under these concentrations these two compounds were mainly degraded chemically in soil.

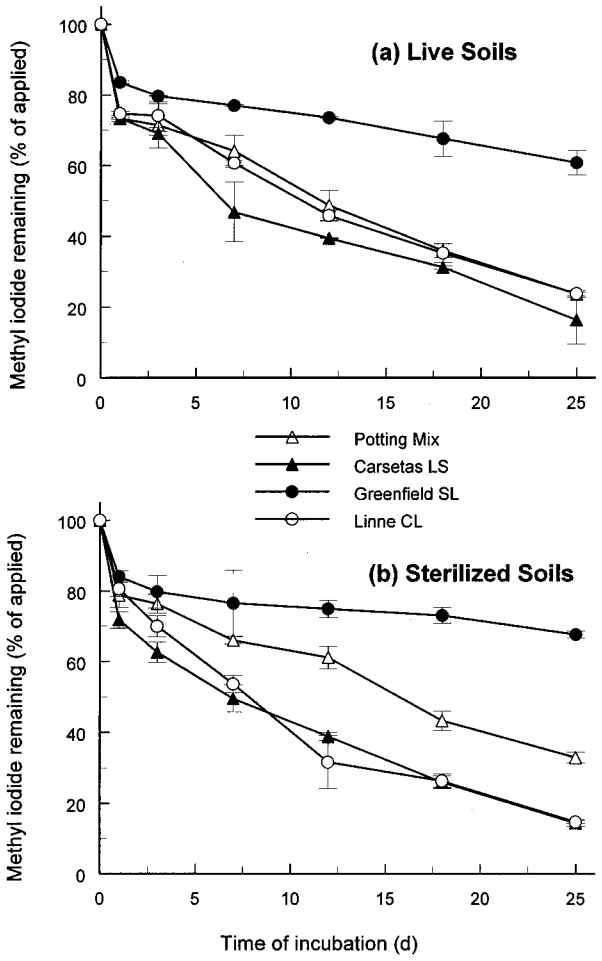

Figure 1. Degradation of methyl iodide in soil.

From their structures, both CH_3I and CH_3Br are typical electrophiles and may undergo bimolecular nucleophilic substitution (SN_2) with H_2O:

$$CH_3X + H_2O \rightarrow CH_3OH + X^- + H^+ \qquad (I)$$

X represents I or Br. The measured $t_{1/2}$ for CH_3Br hydrolysis in water is 20−50 days (Mabey and Mill, 1978; Arvieu, 1983; Herzel et al., 1984; Gentile et al., 1989), and the reported $t_{1/2}$ for CH_3I hydrolysis in water at neutral pH is 50−110 days (Mabey and Mill, 1978; Schwazenbach et al., 1993). The fact that the degradation of both CH_3I and CH_3Br in the organic matter-rich Linne soil and potting mix was considerably faster than their hydrolysis suggests that other reactions were apparently involved. In a few studies, it is established that CH_3Br reacts with nucleophilic functional groups (e.g., $-NH_2$, $-NH$, $-SH$, $-OH$) of soil organic matter in which $-Br$ acts as a leaving group and the organic matter is methylated (Arvieu, 1983; Gan et al., 1994):

$$CH_3Br + OM-NH_2 \rightarrow OM-NH-CH_3 + Br^- + H^+ \qquad (II)$$

Similar mechanisms should also control the degradation of CH_3I in soil.

Table 4. First-Order Degradation Rate Constant (k) and Half-Life ($t_{1/2}$) of CH_3I and CH_3Br in Soils

	k (day^{-1})		$t_{1/2}$ (days)		r^2	
	unsterilized	sterilized	unsterilized	sterilized	unsterilized	sterilized
			CH_3I			
Greenfield sand loam	0.016	0.011	43	63	0.86	0.72
Carsetas loamy sand	0.064	0.069	11	10	0.96	0.98
Linne clay loam	0.053	0.073	13	9	0.98	0.98
potting mix	0.052	0.040	13	17	0.97	0.96
			CH_3Br			
Greenfield sandy loam	0.031	0.034	22	20	0.97	0.97
Carsetas loamy sand	0.116	0.133	6	5	1.00	1.00
Linne clay loam	0.123	0.156	6	4	0.99	1.00
potting mix	0.118	0.103	6	7	1.00	0.99

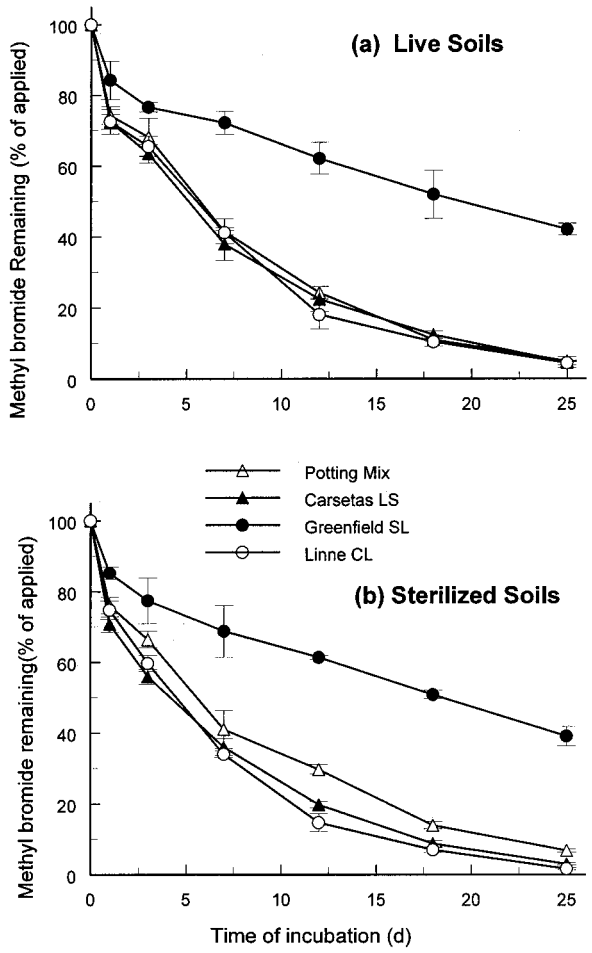

Figure 2. Degradation of methyl bromide in soil.

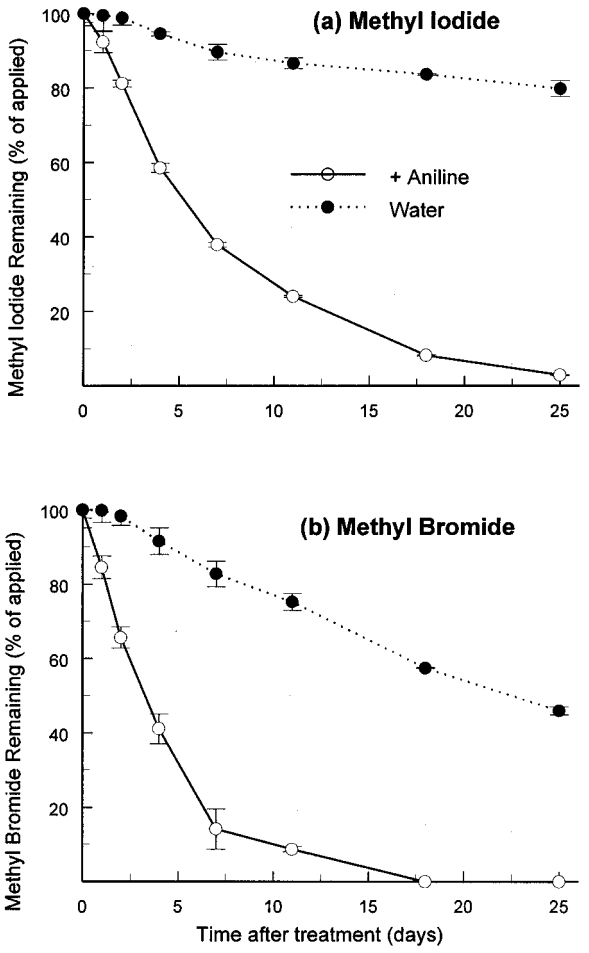

Figure 3. Dissipation of methyl iodide (a) and methyl bromide (b) in deionized water (●) and 5 mM aniline solution (○) at 24 °C.

Close dependence on soil organic matter content was observed in this study in the degradation of CH_3I and CH_3Br under both sterilized and unsterilized conditions (Figures 1 and 2). In the relatively organic matter-rich Linne and Carsetas soils, $t_{1/2}$ values of 9−13 and 4−6 days were obtained for CH_3I and CH_3Br, respectively, while in the Greenfield sandy loam (0.92%), the corresponding $t_{1/2}$ was 43−63 and 20−22 days. It appears that the nature of the soil organic matter is also important in determining the degradation; even though the potting mix contained more organic matter, degradation of CH_3I or CH_3Br in this matrix was not more rapid than that in the Linne and Carsetas soils. It is likely that in the potting mix the organic matter is mostly undegraded plant residues that are less reactive to CH_3I or CH_3Br. The influence of soil organic matter content on CH_3Br degradation has been reported (Brown and Jenkinson, 1971; Brown and Rolston, 1980; Arvieu, 1983; Gan et al., 1994). After measuring CH_3Br degradation in eight soils, Arvieu (1983) found that the $t_{1/2}$ generally decreased with increasing organic matter content in the soil. In a Mandelieu soil with 0.23% organic matter, the $t_{1/2}$ was 49 days, but in a Chevigny soil with 5.11% organic matter, the $t_{1/2}$ was shortened to only 3.6 days. In studying CH_3Br degradation in soils from different depths, Gan et al. (1994) found that the CH_3Br degradation rate constant was highly correlated with soil organic matter content, and the measured correlation coefficient ranged between 0.95 and 1.00.

Reaction of CH_3I and CH_3Br with a model nucleophilic compound provides direct evidence for the proposed soil degradation pathways (Figure 3). In comparison to their hydrolysis, both CH_3I and CH_3Br reacted rather rapidly with aniline, yielding a pseudo-first-order $t_{1/2}$ of 4.9 and 2.9 days for CH_3I and CH_3Br,

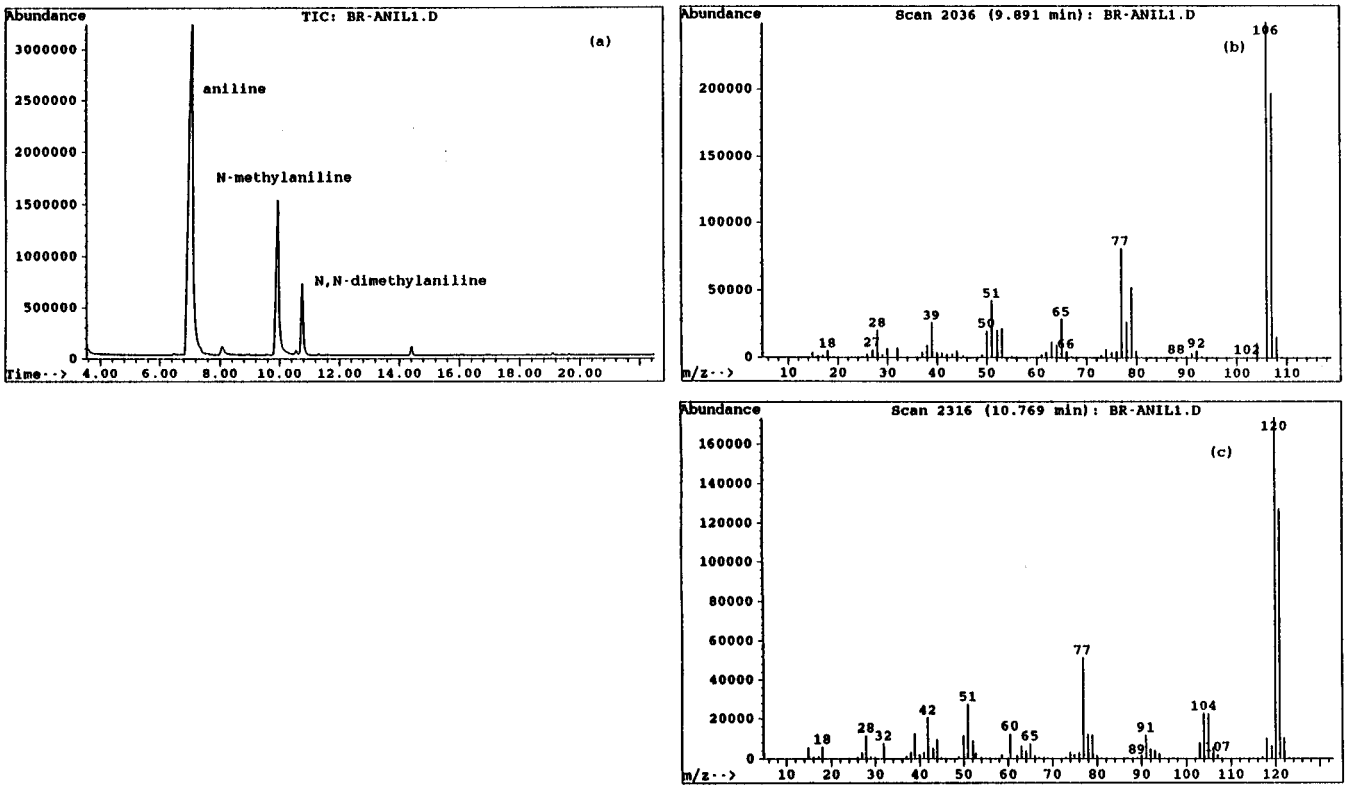

Figure 4. GC/MS profiles of reacted methyl bromide−aniline solution: (a) total ion chromatogram; (b) spectrum of *N*-methylaniline in sample; (c) spectrum of *N*,*N*-dimethylaniline in sample.

respectively. In water at the same temperature (24 °C), the $t_{1/2}$ was about 74 days for CH_3I and 22 days for CH_3Br. As the end products of nucleophilic substitution with aniline, *N*-methylaniline and *N*,*N*-dimethylaniline were positively identified on GC/MS by comparing the spectra of the degradation products with those of the standards (Figure 4). The following reaction equations could thus be presumed:

$$CH_3X + C_6H_5{-}NH_2 \rightarrow C_6H_5{-}NH{-}CH_3 + X^- + H^+ \quad \text{(III)}$$

$$CH_3X + C_6H_5{-}NH{-}CH_3 \rightarrow C_6H_5{-}N{-}(CH_3)_2 + X^- + H^+ \quad \text{(IV)}$$

After 18 days, CH_3Br was completely reacted in the aniline solution, and about 80% *N*-methylaniline and 20% *N*,*N*-dimethylaniline were formed. While in the aniline−CH_3I mixture, after 25 days about 3% of CH_3I was left and 84 and 13% were converted to *N*-methylaniline and *N*,*N*-dimethylaniline, respectively.

It is also likely that under the treated concentrations, original microbial activity in the soil was inhibited due to toxicity of the fumigants. At 5−14 ppb(v), bacterial degradation was believed to cause rapid dissipation of CH_3Br in surface soils (Shorter et al., 1995). A few isolated bacteria, including nitrifying bacteria *Nitrosomonas europaea*, *Nitrosolobus multiformis*, and *Nitrosococcus* oceanus (Rasche et al., 1990) and methane-oxidizing bacteria *Methylomonas methanica* and *Methylococcus capsulatus* (Oremland et al., 1994a), were reported to degrade CH_3Br. In methanotrophic soils, CH_3Br degradation was inhibited at 10 000 ppm, but not at 1000 ppm. Since initial CH_3Br concentrations during a typical agricultural fumigation are 10^4−10^5 ppm (Kolbezen et al., 1974), it is likely that biodegradation of CH_3Br in fumigated fields may be suppressed and chemical degradation is predominant.

Compared to CH_3Br, in the same soil, CH_3I degraded more slowly (at a significance level of 0.95 for all treatments). The calculated $t_{1/2}$ for CH_3I is 1.8−3.1 times that for CH_3Br in the same soil (Table 4). In the Greenfield sandy loam, a $t_{1/2}$ as long as 43 days was obtained for CH_3I in the unsterilized soil. The slower degradation of CH_3I in soil may be controlled by its intrinsic reactivity, as reflected in its slower reactions with aniline and water (Figure 3). In soil fumigation, if application techniques similar to those used in CH_3Br fumigations are adopted for CH_3I, a higher proportion of CH_3I than CH_3Br is likely to volatilize into the air due to this prolonged persistence. The slower degradation of CH_3I in soil may also result in significantly more downward movement, particularly if the soil surface is tarped.

Dissipation of CH_3I in Water. In this study, two pathways, i.e., photohydrolysis and volatilization, were examined under simulated and outdoor conditions to assess their importance in governing the fate of CH_3I in water. CH_3I in water was rapidly photohydrolyzed under UV at a wavelength of 254 nm to produce I^- and I_2 (Figure 5). Formation of I_2 was first noticed visually and later quantified by reduction with $NaHSO_3$ to I^- and measuring the difference in I^- concentration. Additional confirmation of I_2 was accomplished by reacting the samples with water-soluble starch. The ratio of I_2 to I^- in the irradiated solution was about 2.5 (Figure 5). It is known that I^- may be oxidized under light to form I_2. However, irradiating a KI solution (containing 200 ppm I^-) with the same pen-ray lamp for 52 h only converted about 1.6% of the I^- to I_2. Therefore, kinetically, oxidation of I^- to I_2 could not be the main pathway by which I_2 was formed during the exposure study.

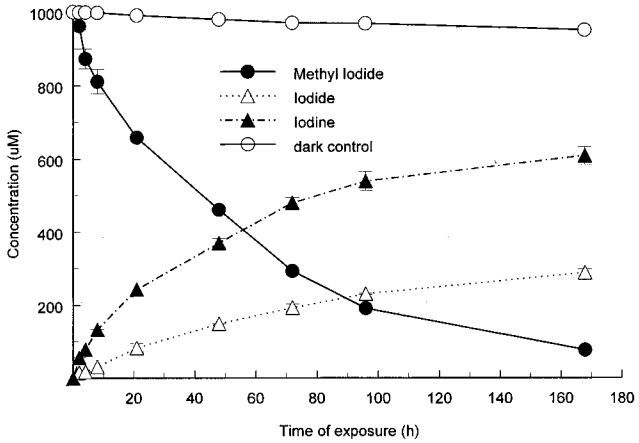

Figure 5. Dissipation of methyl iodide (●) and formation of iodide (△) and iodine (▲) in deionized water under 254-nm UV irradiation.

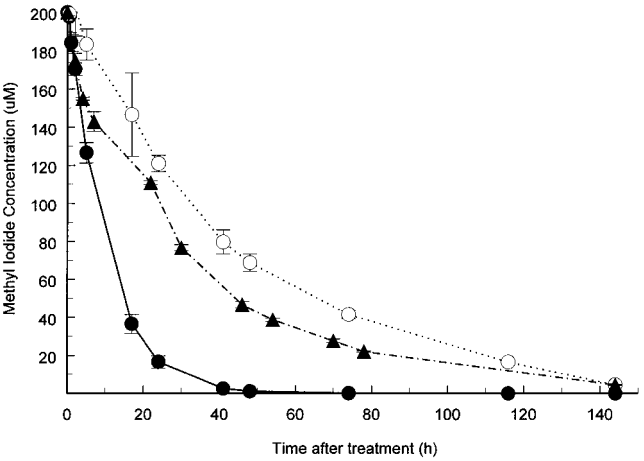

Figure 6. Dissipation of methyl iodide from open-surface water under disturbed, indoor conditions (●), static, indoor conditions (○), and static, outdoor conditions (▲).

From these observations, two independent reactions are likely responsible for the photolytic degradation of CH_3I in water:

$$CH_3I + h\nu \rightarrow (CH_3I)^* + H_2O \rightarrow CH_3OH + H^+ + I^- \quad \text{(IV)}$$

$$CH_3I + h\nu \rightarrow I^\bullet \rightarrow I_2 \quad \text{(V)}$$

Castro and Belser (1981) reported reaction IV as the only pathway by which CH_3Br was photodegraded in water under UV light. Reaction V is similar to the pathway through which CH_3I is decomposed via photolysis in the air (Fahr et al., 1995).

Dissipation of CH_3I from open-surface water was measured under indoor and outdoor conditions (Figure 6). In the laboratory, CH_3I was lost rapidly from the 30-cm deep cylinders, with a first-order $t_{1/2}$ of 29 h under static conditions and 6.5 h under disturbed conditions. At the end of the 6-day indoor experiment, <1% of the spiked CH_3I was detected as I^-, indicating volatilization from the open surface was the main cause for the dissipation. Under outdoor conditions with sunlight irradiation, the measured $t_{1/2}$ was 26 h. At the end of the 6-day exposure, 3.1% of the spiked CH_3I was recovered as I^-, but no I_2 was detectable. Since I_2 produced from photohydrolysis might have escaped during the experiment due to its volatility, the actual contribution from photodegradation in water of CH_3I could be higher. Though not examined in this study, it must be noted that in waters that are rich in nucleophiles, dissipation of CH_3I may be further accelerated. Reaction with HS^- was suggested as an important pathway for removal of both CH_3Br and CH_3I from the solution of a saltmarsh (Oremland et al., 1994b).

Conclusions. Because of the similarities to CH_3Br, after application into soil as a fumigant, CH_3I could be expected to behave similarly to CH_3Br. However, the distribution of CH_3I and CH_3Br between the soil−water−air phases is slightly different, and the difference will result in slower movement of CH_3I in the soil profile and less volatilization from the soil surface on the same time scale. Also, the degradation of CH_3I is considerably slower than that of CH_3Br. The slower degradation of CH_3I determines that, under similar application and soil conditions, the ultimate volatilization loss of CH_3I would likely be greater than that of CH_3Br, and the risk for CH_3I to enter the groundwater would likely be higher. Since volatilized CH_3I is quickly decomposed in the air under light, it will not contribute to ozone destruction. Governed by its high air−water partition ratio (0.22 at 22 °C) and its high photoinduced hydrolysis rate in water, once in water, CH_3I may dissipate rapidly if the water is exposed to air and sunlight. The dissipation half-life for CH_3I in water under exposed, outdoor conditions is in the scale of about 1 day.

ACKNOWLEDGMENT

We thank C. Taylor and Q. Zhang for obtaining some of the data. Property data for Carsetas loamy sand and the potting mix were provided by H. Ohr of the University of California, Riverside. We also thank W. F. Spencer, J. J. Sims, H. Ohr, and J. O. Becker of the University of California, Riverside, for helpful discussions.

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Received for review June 10, 1996. Revised manuscript received October 7, 1996. Accepted October 9, 1996.[⊗] This study was supported by USDA Cooperative State Research Service Agreement 92-34050-8152. Reference to a company name or product does not imply the approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

JF960413C

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1996.