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Mitigating Iodomethane Emissions and Iodide Residues in Fumigated Soils

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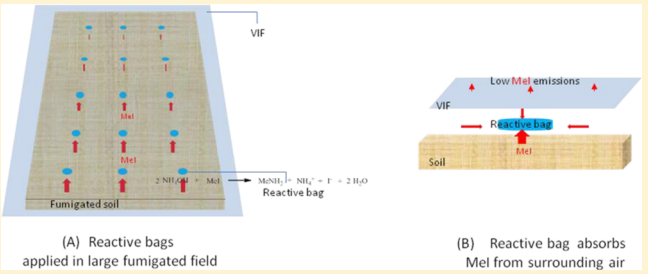
Supporting Information

ABSTRACT: Although long-regarded as an excellent soil fumigant for killing plant pests, methyl bromide (MeBr) was phased out in 2005 in the USA, because it can deplete the stratospheric ozone layer. Iodomethane (MeI) has been identified as an effective alternative to MeBr and is used in a number of countries for preplant pest control. However, MeI is highly volatile and potentially carcinogenic to humans if inhaled. In addition, iodide anions, a breakdown product of MeI, can build up in fumigated soils and potentially cause plant toxicity and contaminate groundwater via leaching. In order to overcome the above two obstacles in MeI application, a method is proposed to place reactive bags containing ammonium hydroxide solution (NH_4OH) on the soil surface underneath an impermeable plastic film covering the fumigated area. Our research showed that using this approach, over 99% of the applied MeI was quantitatively transferred to iodide. Of all the resulting iodide, only 2.7% remained in the fumigated soil, and 97.3% was contained in the reactive bag that can be easily removed after fumigation.



INTRODUCTION

Fumigants are widely used in agriculture (e.g., in the production of strawberries, potatoes, carrots, and egg plants) to control plant pests and soil-borne diseases (e.g., weeds, nematodes, fungi). Historically, methyl bromide (MeBr) has been a very significant fumigant with its worldwide consumption peaking at 6.3×10^4 tons in 1991,[1] and the U.S. alone consumed 2.55×10^4 tons in this year.[2] However, the use of MeBr was scheduled to be phased out in the U.S. in 2005[2] because it possesses a high potential for depleting stratospheric ozone and over 45% of the applied amount could escape into the atmosphere.[1] Without protection from MeBr, it was estimated that U.S. agriculture could suffer a large economic loss of over $1.3 billion a year.[3] Alternatives to MeBr, like 1,3-dichloropropene and chloropicrin, can only partially replace it, because they are not so effective at killing pests and because their use is restricted in some regions (e.g., California township caps on 1,3-dichloropropene use).[4]

Iodomethane (MeI) is similar to MeBr in terms of chemical structure and character. It is similarly effective in controlling pests as a fumigant but does not deplete the stratospheric ozone layer.[5] Therefore, it was considered a promising alternative to MeBr and was expected to replace all MeBr use several years ago.[5,6] It has already been registered as a pesticide in Japan, Turkey, Mexico, Morocco, and New Zealand.[7] Although it was initially registered in 48 states of the U.S. following its 2007 U.S. registration, in 2012 this registration was withdrawn by the manufacturer. The 2007 U.S. registration was highly controversial, especially in California, due to concerns over its impact on human health. The two main concerns were the potential for large emissions (up to 80% of the applied amount[6,8]) of MeI into the atmosphere from fumigated soils, and the potential for residues of iodide (a breakdown product of MeI) to build up in soils. A high level of emissions was a concern because MeI is highly toxic and suspected to be carcinogenic, neurotoxic.[9,10] Excessive iodide residues in soils could be phytotoxic and may potentially leach into, and contaminate, groundwater.

In practice, MeI could either be injected into soil through tractor rigs followed by an immediate tarp cover over the field or be applied by a drip irrigation system under tarps.[11] The tarps are used to prevent MeI from being instantly lost to the atmosphere. Under the 2007 U.S. registration, USEPA permitted the use of high density polyethylene film (HDPE) for this purpose. However, under the more stringent requirements imposed under the California regulations, CDPR (California Department of Pesticide Regulation) required a covering of virtually impermeable film (VIF) or other highly retentive films[12] to reduce emission of MeI and thus minimize the health risks to workers and nearby residents.

The molecular structure of organic material in soils contains functional groups such as -NH-, -SH, and -OH.[13] Such groups can act as nucleophiles and thus effectively decompose MeI, but, in general, neither the amount nor the activity of these

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groups is sufficient to degrade the relatively large amount of MeI added during the fumigation process. The half-life of MeI in different soils has been found to vary from 13 to 43 d.[13,14] In an attempt to reduce this half-life (and thereby potentially reduce emissions), agricultural chemicals or organic materials have been used as soil amendments to enhance MeI decomposition. Amendments of chemicals, e.g., thiourea, allylthiourea, and ammonium thiosulfate in soils, reduced the half-life of MeI from 12.5 to 0.7 d,[15,16] while an amendment of sandy loam soil with 10% cattle manure reduced it from 32 to 4 d.[14] Although these enhanced degradation approaches could significantly mitigate MeI emissions into the atmosphere, a major drawback is the large amount of the degradation product, iodide (I^-), which would remain in soils after fumigation.

In our previous studies, we first used bases to decompose residual MeBr in soils and thereby mitigate MeBr emissions into the atmosphere.[17] Then, we designed a reactive film which was filled with ammonium thiosulfate solution to trap and absorb residual MeBr or MeI in soil.[18,19] In view of reducing fumigants emissions, both approaches are potentially useful. However, under field conditions, the former approach can result in a large amount of residual bromide ion in the fumigated soils. Similarly, if this approach is used for MeI, it is imaginable that a significant amount of iodide ion can occur in soils after fumigation. A problem also exists for the latter approach because the large size of reactive film required to cover a field can be heavy and inconvenient to apply. An approach to MeI degradation and emission reduction that overcomes these issues is required.

This study aimed at (i) testing the ability of ammonium hydroxide (NH_4OH) in decomposing MeI in aqueous solution and soils at different temperatures; (ii) evaluating the ability of NH_4OH in accelerating MeI degradation under HDPE and VIF to reduce MeI emissions; (iii) designing a reactive bag for removing iodide ions following the breakdown of MeI; and (iv) testing the efficacy of this reactive bag in mitigating residue of MeI and iodide in soil under VIF cover.

EXPERIMENTAL SECTION

Materials and Soil. Iodomethane (ReagentPlus, 99.5%) was purchased from Sigma Chemical Co. (St. Louis MO). Ammonium hydroxide (d 0.89) was purchased from ACROS (Fair Lawn, NJ). Potassium iodide, diethyl ether (anhydrous, Et_2O), and *n*-hexane (95%, optima grade) were purchased from Fisher Scientific Co. (Fair Lawn, NJ).

Arlington sandy loam soil was collected from the University of California, Riverside Agriculture Experimental Station. After being passed through a 2-mm sieve, the fresh soil (pH 7.2, 1.08% organic matter and 1.25% moisture) was stored in a 4 °C cool room in a plastic bag for future use.

Standard HDPE (1 mil, Dow Chemical Company, Midland, MI) and Hytibar VIF (1.5 mil, Klerk's Plastics, Inc.) plastic films were used in the experiment. According to Papiernik et al.,[21] typical methyl iodide resistance values for HDPE ranged from 0.25 to 1.39 h cm^{-1}. For VIF, values ranged from 42 to 1261 h cm^{-1}, indicating the much greater impermeability of VIF to methyl iodide vapor.

MeI Degradation in NH_4OH at Different Temperatures. A half milliliter of 1.0 M NH_4OH sealed in 2.1-mL GC-vials, which were stored in temperature controlled incubators (4, 20, and 40 ± 1 °C), was first spiked with 10 μL of 7.0 mM MeI stock solution in Et_2O and then placed in the original incubators. After certain time intervals, triplicate vials in each temperature treatment were removed from the incubators, and the residual MeI in the NH_4OH was extracted with 1.0 mL of *n*-hexane.

MeI in *n*-hexane was determined using a Hewlett-Packard HP 7890 gas chromatograph (GC) equipped with a micro-electron capture detector (μECD). A DB-VRX capillary column (30.0 m × 250 μm × 1.4 μm, J&W Scientific, Folsom, CA) was used under the following conditions: the flow rate of carrier gas helium was at 1.0 mL min^{-1}; the inlet and detector temperatures were 240 and 290 °C; and the oven was held at 90 °C. Under these conditions, the retention time of MeI was 2.01 min. The limit of detection was 4.5×10^{-10} g mL^{-1}. A calibration curve consisted of seven MeI standards of known concentrations, which covered the MeI concentration range of the analyzed samples.

A simple pseudo-first-order kinetic model was used to fit the relationship between MeI concentration C (mM) and reaction time t (h). From this regression analysis, an apparent reaction rate constant k (h^{-1}) was obtained. Actual reaction rate constants (k_{corr}) and half-lives ($t_{1/2,\ corr}$) of MeI in solutions were corrected (Supplemental equations S3 and S4) because MeI was volatile and the vial was only partially filled with aqueous solutions.

The activation energy E_a (kJ mol^{-1}) of the reaction between NH_4OH and MeI, based on the Arrhenius equation, was obtained by fitting the relationship between the reaction rate constant k (h^{-1}) and the reaction temperature T (Kelvin).

MeI Degradation in NH_4OH-Amended Soil at Different Temperatures. A mass of 10.96 g of soil (adjusted to 9.6% moisture by adding water into the stock soil) was weighed into each of the 20.1-mL vials. The vials were capped with a Teflon-faced butyl rubber septum and aluminum seal. The vials were spiked with 70 μL of NH_4OH with a syringe through the septum and then kept in temperature controlled incubators (4, 20, 35, 50 ± 1 °C). The resulting soil sample contained 10% moisture and 1.0 M NH_4OH in the aqueous phase. After 1 h of temperature equilibration in the incubators, the vials were further spiked with 7 μL of 70 mM MeI stock solution. The vials were shaken so that MeI was evenly distributed in the soil. At certain time intervals, triplicate vials in each temperature treatment were moved into a freezer (−20 °C) and stored for analysis.

Ten milliliter of *n*-hexane was injected into the frozen soil in each vial. After the soil thawed at 20 °C, the mixture was vortexed for 2 min. An aliquot (1.0 mL) of organic solution was transferred into a 2.1-mL GC vial using a gastight syringe for analysis on a GC-μECD as mentioned above.

MeI Degradation under HDPE and VIF Cover in the Presence of NH_4OH. Permeability cells[20] were used in this experiment. Briefly, a piece of either HDPE or VIF was mounted between two chambers of stainless steel (each 12.0-cm inside diameter and 4.0-cm deep) to create a sealed permeability cell. The join between the two chambers was sealed with epoxy glue and adhesive aluminum tape. Thus the internal space of the permeability cell was separated into two equal size chambers by the plastic film (HDPE or VIF). In the center of each chamber's wall was a port which was plugged with a Teflon-faced silicon septum. Through a port on the under side of the film (referred to as the source chamber), 8.0 mL of 30% NH_4OH (or water in the control experiment) and 25.0 mL of MeI gas (the air in a 1.0-L glass cylinder was spiked with 7.0 μL MeI and was equilibrated for over 30 min at 20 ± 1 °C) were injected in sequence at the beginning of the

experiment. The initial concentration of MeI spiked in the source chamber was 0.60 ± 0.015 mg L^{-1}. At predetermined time intervals, 250-μL gas from both the source chamber and receiving chamber (on the opposite side of the film) was transferred into two separate 12.1-mL headspace vials, which were immediately capped with Teflon-faced butyl rubber septum and an aluminum seal. Permeability cells were used in triplicate for each film at 20 ± 1 °C.

MeI in the headspace vials was determined on an HP6890 GC-μECD combined with an Agilent Technologies G1888 Network Headspace sampler. The GC was equipped with a DB-VRX column (as above). The carrier gas was helium at a flow rate of 1.4 mL min^{-1}. The oven temperature was 80 °C. The temperatures of injector and detector were set at 240 and 280 °C, respectively. The operating conditions of the headspace sampler were as follows: the temperatures of the oven, the loop, and transfer line were 40, 50, and 55 °C, respectively; and the equilibration time of headspace vials in oven was 5.0 min. The sample loop was 1000 μL. Under these conditions, MeI retention time was 3.5 min. The limit of detection was 9.4 × 10^{-7} mg L^{-1}. Calibration standards for the GC analysis were prepared from the stock solution at seven concentrations in headspace vials and were analyzed at the beginning of each set of samples.

Mechanisms of MeI Degradation in NH_4OH. At 20 ± 1 °C, 0.5 mL of 2.5 M NH_4OH (or deionized water in the control sample) in 2.1-mL GC vials was spiked with 10.0 μL of 2.0 M MeI stock solution. At predetermined time intervals, 1.0 mL of *n*-hexane was injected into the vial to extract the residual MeI. After being shaken for 2 min, the organic phase was removed using a syringe. Then, the vial was decapped, the aqueous solution was diluted with 1.5 mL of deionized water, and 1.0 mL of this solution was transferred into an ion chromatography tube.

The extraction and determination of the residual MeI in 2.5 M NH_4OH followed the procedures as described above for the analysis of residual MeI in 1.0 M NH_4OH. All treatments were performed in triplicate.

An 861 Advanced Compact IC equipped with a Dionex column (IonPac, AS14, 4 × 250 mm) and AS40 automated sampler was used for determining concentration of I^- at 20 ± 1 °C. The mobile phase consisted of 0.75 mM Na_2CO_3 and 0.25 mM $NaHCO_3$ aqueous solution at a flow rate of 1.0 mL min^{-1}. The retention time of I^- was 8.9 min. The limit of detection was 1.0 × 10^{-4} mM. A standard calibration curve consisting of eight different concentration standards was used to derive the concentrations of I^-. The standards were prepared from KI and deionized water.

Reactive Bag Preparation and Depletion of Residual MeI in Soil in Permeability Cells under VIF Cover. To prepare a reactive bag, one piece of tissue paper (diameter 11.0 cm) was sandwiched between two layers of HDPE (diameter 12.5 cm). The edge of the double HDPE was heat-sealed. Two milliliters of 30% NH_4OH was injected in the HDPE bag using a syringe, and then the pinhole in the bag was sealed with a small piece of adhesive aluminum tape.

In a permeability cell (as described above), 500 g of soil was weighed into the source chamber, and a reactive bag was placed on the soil surface. VIF separated the permeability cell into two chambers, i.e., the source chamber and receiving chamber. The cell was sealed with epoxy glue and adhesive aluminum tape. The soil was spiked with 60 μL of MeI (equal to 107.96 lb per acre application rate in the fumigated field). At predetermined time intervals, 100 μL of gas from the source or receiving chambers was transferred into a 12.1-mL headspace vial, and the MeI concentrations in the gases were determined on the HP6890 GC-μECD as described above.

After 5 d each permeability cell was dismantled, and the reactive bag was opened, placed in 100 mL of deionized water, and stirred using a glass rod for 10 min. The concentration of I^- in the water was determined after a 10-fold dilution of the sample on the IC as described above. The soil was transferred into a plastic bag. After being mixed thoroughly, 5.0 g of soil was weighed into 10 mL of deionized water in a 20.1-mL head space bottle. The mixture of soil and water was placed on a shaker (Eberbach Co. Ann Arbor, MI) for 30 min. After settling for 1 h, 1.2 mL of supernatant was transferred into a centrifuge tube and centrifuged for 15 min at 13000 rpm. The concentration of I^- in the diluted supernatant (10-fold dilution) was determined by IC. Permeability cells were used in triplicate.

RESULTS AND DISCUSSION

MeI Degradation by NH_4OH and the Effect of Temperature. It is well-known that both OH^- and $-NH_2$ in soil can enhance MeI degradation.[13] To determine which of these groups dominates MeI degradation in NH_4OH, a series experiments on MeI hydrolysis in different basic aqueous solutions (refer to the Supporting Information) were conducted. The procedures were the same as we previously used for determining MeBr degradation in different bases.[17] In summary, MeI was fairly stable in deionized water but decomposed significantly in basic aqueous solutions, especially in NH_4OH (Table S1). The degradation kinetics can be well represented by using a pseudo-first-order kinetic model. Equation 1 described the degradation rate constant (k_{NH_4OH}) of MeI in 20 °C NH_4OH (Table S1)

$$k_{NH_4OH} = 0.13 \times [OH^-] + 0.18 \times [NH_3]\ h^{-1} \quad (1)$$

where $[OH^-]$ and $[NH_3]$ were the concentrations of OH^- and NH_3 in the reaction solution. As a moderate base with a dissociation constant of 1.76 × 10^{-5} in 25 °C water[24] (i.e., in a 1.0 M NH_4OH solution, the concentration of NH_3 is 1.0 M, and both NH_4^+ and OH^- are 4.18 × 10^{-3} M), NH_4OH mainly exists in the form of NH_3 not as NH_4^+. According to eq 1, MeI was substantially decomposed by NH_3 in NH_4OH. This equation also indicates that NH_4OH is more effective than other bases in enhancing MeI degradation at the same concentration, as the coefficient of $[NH_3]$ was 1.36 times that of $[OH^-]$.

The degradation of MeI and the formation of I^- in 2.5 M NH_4OH could be described very well (r^2 greater than 0.99) by first-order kinetic equations (Table 1). Because both equations had very similar kinetic constants, it can be concluded that MeI was equivalently transformed into I^-. Elevated temperature enhanced MeI degradation (Table 2). At 40 °C, MeI reaction

Table 1. Kinetic Equations of MeI Degradation and I^- Formation in 2.5 M NH_4OH at 20 °C

	fitted model[a]	k (h^{-1})	r^2
MeI degradation	$(C/C_0) = e^{-kt}$	0.317 ± 0.004	>0.99
I^- formation	$(C_r/C_0) = 1 - e^{-kt}$	0.324 ± 0.004	>0.99

[a] C and C_{I^-} were the concentrations of MeI and I^- in NH_4OH at time t; C_0 was the initial concentration of MeI.

Table 2. Model-Fitting Parameter Values, MeI Half-Lives at Different Temperatures, and Activation Energy in 1.0 M NH_4OH

temp (°C)	k (h^{-1})	r^2	$t_{1/2}$ (h)	k_{corr} (h^{-1})[a]	$t_{1/2,\ corr}$ (h)[a]	E_a (kJ mol^{-1}) (r^2)
4	0.0141 ± 0.0005	>0.99	49	0.0178	39	
20	0.120 ± 0.004	>0.99	5.8	0.182	3.8	84.1 ± 7.0 (0.99)
40	0.596 ± 0.011	>0.99	1.2	1.25	0.6	

[a]The calculation of the corrected values of k_{corr} and $t_{1/2,\ corr}$ is described in the Supporting Information.

rate increased to 42 and 4.83 times, respectively, those of at 4 and 20 °C.

MeI Degradation in NH_4OH Amended Soil. An amendment of NH_4OH in soil significantly enhanced MeI degradation, and this was further facilitated with elevated temperature (Table 3).

Table 3. Model-Fitting Parameter Values, MeI Half-Lives at Different Temperatures, and Activation Energy in NH_4OH Amended Soil

temp (°C)	k (h^{-1})	r^2	$t_{1/2}$ (h)	E_a (kJ mol^{-1})(r^2)
4	0.0143 ± 0.0008	0.99	48.4	
20	0.103 ± 0.014	0.98	6.7	
35	0.216 ± 0.007	>0.99	3.2	86.1 ± 8.2 (0.99)
50	0.453 ± 0.018	>0.99	1.5	
20[a]	0.00574 ± 0.00033	0.99	120.7	

[a]In nonamended soil.

In the nonamended soil (no NH_4OH spike), the half-life of MeI was 5 d at 20 °C. In the amended soil with 1.0 M NH_4OH in the soil aqueous phase, the half-life of MeI was reduced 20 times compared to the nonamended soil.

The activation energy of MeI degradation in NH_4OH amended soil was very similar to that in NH_4OH aqueous solution (84.1 ± 7.0 compared to 86.1 ± 8.2 kJ mol^{-1}). This indicated that the increasing temperature had a similar effect on accelerating MeI degradation both in soil and aqueous solution.

MeI Degradation and MeI Emissions under HDPE and VIF Cover in the Presence of NH_4OH. In control permeability cells (where the source chamber contained water instead of NH_4OH), containing HDPE, MeI readily diffused into the receiving chamber from the source chamber. The equilibrium of diffusion (where the concentrations of MeI on both sides of the HDPE were the same) was reached within 8 h (Figure 1). In the following 8 h (Figure 1), these concentrations did not reduce significantly. This indicated that MeI was stable in the water-containing cells. In contrast to the diffusion of MeI through HDPE, the chemical could not so easily diffuse through VIF. Indeed, no MeI was detected in the receiving chamber in the first 2 h, and only <4% of the spiked MeI passed through the VIF into the receiving chamber in the following 14 h. Surprisingly, in all cases, the initial concentration of MeI in the source chamber was only ~73% of the total concentration in both chambers after 2 h from MeI spiking. The reason for this might have been that MeI has a much higher molecular mass (191.42) than air (average molecular mass of 28.97). On being spiked into the source chamber, MeI may have at first tended to settle at the bottom of the chamber (due to its higher molecular mass) with some also potentially dissolving in the water. Over around 2 h, and as the result of thermal molecular movement, the MeI might have gradually diffused to reach a uniform concentration within the source chamber.

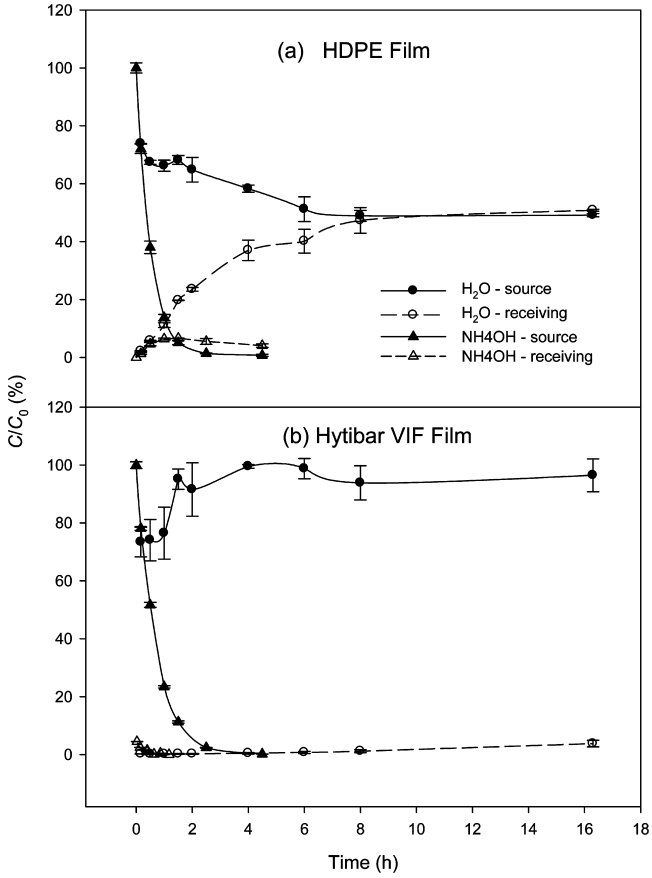

Figure 1. MeI degradation in permeability cell with (a) HDPE film, (b) Hytibar VIF film and diffusion from source chamber (closed signals) through films to receiving chamber (open signals) over time.

In the permeability cell experiments with NH_4OH amendment, NH_4OH in the source chamber quickly degraded the spiked MeI (Figure 1). The half-lives of MeI under HDPE and VIF were 0.36 and 0.49 h, respectively. Although 93% of the spiked MeI was degraded, 7% diffused through the HDPE due to its permeability. However, VIF permitted very little MeI diffusion to the receiving chamber with more than 99.8% of the MeI being degraded in the source chamber under these conditions.

Depletion of Residual MeI in Soils under VIF Cover Using Reactive Bags. Based on the half-life results obtained above, it can be calculated that half of the spiked MeI would have remained in the soil at five days if no reactive bag was used. However, the reactive bag containing NH_4OH greatly accelerated the degradation of the residual MeI in soil. In 20 h, 97.6% of the spiked MeI was decomposed. Later, the residual MeI in the soil continued to be degraded as shown in Figure 2 (inset). During the degradation, little MeI diffused through the VIF into the receiving chamber. After 5 d, only less than 0.04% remained in the soil, 0.37% diffused through VIF cover into the receiving chamber, and the remainder, over 98.6% of the spiked

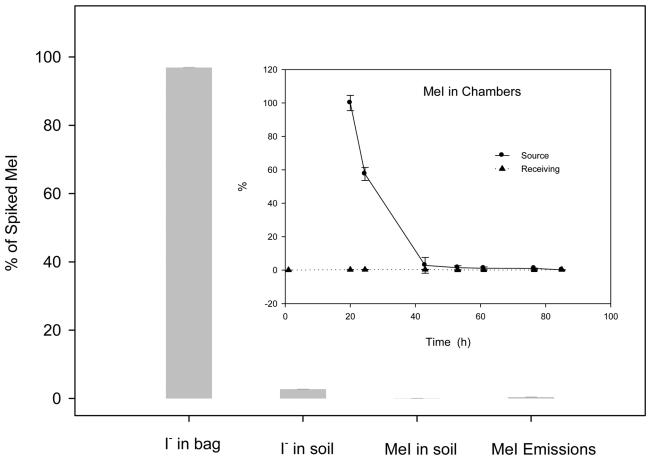

Figure 2. MeI and iodide distribution within the permeability cell after 5 days of MeI spiking (average with standard deviation); and, inset, MeI appearance in receiving chamber (% compared to the spiked amount) and disappearance from source chamber (% compared to the amount at 20 h after spiking).

MeI, was broken down to I^- (Figure 2). Among the total amount of the resulting I^-, 97.3% was contained in the in reactive bag, and only 2.7% was retained in the soil.

Environmental Significance. Soil alone could only moderately decompose MeI. In this study, the half-life of MeI in the Arlington soil was 5 d. Though shorter than the reported values of 12.5−32 d, it is considered long enough for a hypothetical fumigation event to yield a significant amount of MeI emission to the atmosphere.

Ammonium hydroxide was effective at accelerating MeI degradation in both deionized water and moist soil. With an amendment of 1.0 M NH_4OH in the soil aqueous phase, the half-life of MeI was reduced from 5 d to 2.5 h. As indicated by eq 1, the higher concentration of ammonia could result in the quicker degradation of MeI. If the residual MeI was trapped under tarps, e.g., HDPE and VIF, and at the same time, was decomposed by reaction with NH_4OH, MeI emissions could be greatly mitigated, or even prevented entirely, under VIF cover.

If the residues of I^- in soils were not a concern from the point of view of plant toxicity and leaching to groundwater, the simplest approach to mitigate MeI emissions from the fumigated soil would be to introduce ammonia gas into wet soil under tarps which seal the fumigant within the soil. A significant amount of condensed moisture on the underside of the tarps and moisture in the top soils could immediately adsorb the introduced ammonia gas to form NH_4OH at a high aqueous concentration. As we have shown, this NH_4OH would likely quickly decompose the residual MeI, while the tarp (HDPE or VIF) prevents MeI from escaping into the atmosphere, but a serious defect of this approach is that almost all of the applied MeI would break down and produce an equivalent amount of I^- in soil.

Previously, we have designed a reactive film containing ammonium thiosulfate solution.[18,19] When a fumigated soil was covered with this type of film in laboratory permeability cells, the residual MeI first had to react with ammonium thiosulfate as it passed through the film. Thus, most of the residual MeI was decomposed within the film, and MeI emission into the atmosphere could potentially be greatly reduced. In this process, all the products from this reaction, including I^-, were contained within the film. Therefore, if used in the field, when the reactive film is removed, I^- contained within the film would also be removed. This approach is potentially highly successful in mitigating MeI emissions into the atmosphere and preventing residual I^- build up in soil. However, in practice, it is likely not easy to use such a film in the field because the film would become too heavy after activating the ammonium thiosulfate with water.

In this study, a new reactive bag was constructed. The size of the bag was much smaller than the reactive film described above. It is envisaged that this bag could be used under VIF covering a fumigated field. The role of the reactive bag would be to absorb the residual MeI trapped beneath the VIF. Thus, the size of bag could be modified depending on its application. Additionally, as NH_3 has a lower molecular mass than ammonium thiosulfate, using NH_4OH instead of ammonium thiosulfate solution (as in the reactive film) benefits the preparation of a relatively lighter reactive bag.

In practical terms, we suggest that the reactive bags should be placed on the soil surface, prior to the installation of VIF. Due to its impermeability, the VIF would then trap the applied MeI leaving it available for degradation. Because HDPE is relatively permeable to MeI, MeI will be able to diffuse into the reactive bags where it will react with NH_4OH and be decomposed. The breakdown product, I^-, will be dissolved in the NH_4OH solution and thus confined within the bags. Therefore, instead of entering the atmosphere, most of the residual MeI will be absorbed in the bags, thereby significantly reducing the potential for detriment to air quality from fumigation. When the concentration of residual MeI in the soil air phase is lower than a predetermined (e.g., nonharmful) level, the VIF can be opened and the reactive bags removed from the field for disposal or recycling. In the current permeability cell experiment, after 5 d of adding MeI, 96.9% of the applied MeI was trapped in the reactive bag and decomposed to I^-; 2.7% was decomposed to I^- in soil; a mere <0.37% escaped into the atmosphere; and <0.04% remained in soil as a residue. These results indicate that a system consisting of reactive bags and VIF cover is potentially very effective in mitigating both MeI emissions into the atmosphere and residual I^- in soils.

The process of the reactive bag absorbing MeI was a relatively rapid one. At 20 °C over 97.6% of the applied MeI was degraded in the first 20 h. Because the permeability of the HDPE to MeI increases 1.5 times for each 10 °C rise[21,22] and the reaction rate between NH_4OH and MeI increased 4.83 times when temperature increased from 20 to 40 °C, residual MeI under field conditions would likely be degraded even more rapidly than in this experiment, as under real field conditions the soil surface temperature can easily reach 40 °C.[23] Additionally, there are many other plastic films which are more permeable to MeI than HDPE.[21,22] If such films were used to prepare reactive bags, the residual MeI would again likely be depleted faster.

Overall, the application of plastic film bags containing NH_4OH under VIF cover has shown potential not only in mitigating the emissions of residual MeI into the atmosphere but also in removing most of the resulting I^- from the soil. Additional work is required to assess the effectiveness of these bags under field conditions, for example the size and spacing of the bags required for optimal emission mitigation.

■ ASSOCIATED CONTENT

Supporting Information

A detailed description of the measurement of MeI degradation kinetics in base solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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