

Irrigation, Organic Matter Addition, and Tarping As Methods of Reducing Emissions of Methyl Iodide from Agricultural Soil

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ABSTRACT: Methyl iodide (MeI) is increasingly being used as a highly effective alternative to the soil fumigant methyl bromide. Due to its volatile and toxic nature, MeI draws wide attention on its potential atmospheric emission following field fumigation treatment. Using soil columns that make it possible to determine emissions and gas phase distribution of soil fumigants, we studied MeI behavior in two soils differing in organic matter content. Additionally, the effectiveness of surface irrigation and tarping with virtually impermeable film (VIF) was assessed. In the lower organic matter, bare soil (control), emissions of MeI were rapid and high (83% of total). Although the peak emission flux was reduced by irrigation, the total loss was very similar to the control (82%). Tarping with VIF dramatically reduced emissions (0.04% total emissions). In the higher organic matter soil, degradation rate of MeI was increased around 4-fold, leading to a significant reduction in emissions (63% total emissions). The work suggests that surface tarping with VIF would be highly effective as an emissions reduction strategy and would also result in the maintenance of high soil gas concentrations (important for pest control). Ripping of the tarp after two weeks led to an immediate spike release of MeI, but, even so, the flux rate at this time was almost 20 times lower than the peak flux rate in the control. Even with tarp ripping, the total emission loss from the VIF treatment remained low (6%).

INTRODUCTION

Methyl iodide (MeI, iodomethane, CH₃I) was reported as a potential alternative to the stratospheric ozone-depleting fumigant methyl bromide (MeBr) in the mid-1990s.^{1,2} It is degraded rapidly by photolysis and has an estimated atmospheric lifetime of <10 days, compared to 1.5–2 years for MeBr.³ Importantly therefore, it is not considered to contribute to degradation of the Earth's ozone layer. In this regard, its emissions from soil are of less concern than those of MeBr. Nevertheless, MeI fumigation does have the potential to increase human health risks through direct inhalation of the MeI gas and due to the potential of its constituent volatile organic compounds to contribute to the formation of near-surface ozone. At 20 °C, MeI has a water solubility at of 14 g L⁻¹, a vapor pressure of 400 mmHg, and a dimensionless Henry's constant (K_H) of 0.21. It has a boiling point of 42 °C.⁴ Compared to other MeBr alternatives, the properties of MeI most closely match those of MeBr, suggesting it may be the most promising alternative to MeBr for soil fumigation. Indeed, based on its pest control efficacy, it has been suggested that it may constitute a direct replacement.⁵ As a preplant soil fumigant, MeI can be used alone, or in combination with chloropicrin (CP) to control plant pathogens, nematodes, insects, and weeds on crops such as strawberries, tomatoes, peppers, ornamentals, turf, trees, and vines.⁶

To reduce atmospheric emissions of soil fumigants, several strategies have been proposed and shown to be successful for fumigants such as CP and 1,3-dichloropropene.⁷ Briefly, such strategies fall into three categories: (i) enhancing degradation of the fumigant within the soil by the application of either a chemical amendment such as ammonium thiosulfate, or organic material; (ii) restricting the upward soil diffusion of the fumigant by

reducing air filled porosity via soil compaction or addition of irrigation water; and (iii) restricting the diffusion of the fumigant across the soil-air interface by the use of plastic coverings such as high density polyethylene (HDPE) or virtually impermeable film (VIF). However, a paucity of information exists relating to the effectiveness of such approaches in the reduction of MeI emissions.

As the product 'Midas' (Arysta LifeScience, NC), MeI is commercially available in formulations with CP at ratios of 98:2, 50:50, 33:67, and 25:75 (MeI:CP). It is registered in USA, Japan, and Turkey, with registration pending in New Zealand, Australia, Morocco, Mexico, Guatemala, Costa Rica, and Argentina.⁸ Currently, its use in US agriculture is receiving significant focus due to its recent registration. In October 2007, the United States Environmental Protection Agency (USEPA) approved the one year registration of MeI as a soil fumigant under highly restrictive provisions governing its use. In October 2008 the one-year time-limited registration was converted to a conditional registration.⁶ Recently (May 2010) California announced its proposed decision to become the forty-eighth US state to register MeI.⁸ Concern over the use of MeI as an agricultural fumigant is based on its potential to cause serious health effects. The Material Safety Data Sheet for MeI states that health effects associated with the chemical are potentially severe (cancer causing). More specifically, it states that MeI has been shown to cause cancer in animals and may be linked to cancer in humans as well as to damage of the central nervous system. Highest potential risk of MeI exposure

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occurs during fumigation events and is therefore most likely to affect agricultural workers and local populations in the vicinity of such events. In spite of its recent registration and health risk concerns, the behavior of MeI, particularly its potential for release from soil to air, has received relatively little attention.

In light of its recent registration, and its planned registration review in 2013,⁶ it is important to determine the risks associated with MeI use and so accurate experimental data quantifying soil-air emissions under a range of conditions are required. A further requirement is that strategies designed to reduce emissions are assessed in terms of their potential to mitigate air pollution and human health risk. The aim of this work was to address these requirements using an established laboratory column approach.

MATERIALS AND METHODS

Materials and Soils. Methyl iodide standard (>99% purity) was obtained from Sigma Chemical Co. (St. Louis, MO), Acetone Optima and ethyl acetate from Fisher Scientific (Fair Lawn, NJ), acetonitrile from Burdick and Jackson (Muskegon, MI), and Anasorb CSC charcoal tubes from SKC Inc. (Eighty Four, PA). The VIF (Hytibar) was donated by Klerk's Plastic (Hoogstraten, Belgium), had a thickness of 1.5 mil (0.038 mm), and has a MeI diffusion resistance (R) value⁹ of 700 h cm⁻¹ (25 °C) under low relative humidity conditions (i.e., a mass transfer coefficient, *h*, of 0.0014 cm h⁻¹). Soils were collected from two fields on a farm near Buttonwillow, CA (thermic Typic Haplargids; Milam series). Both were a sandy loam (around 60% sand, 30% silt, and 10% clay) of pH 7.8. The primary difference between the two soils was organic matter content since composted green waste material was previously applied to one of the fields. Consequently, the organic matter content increased from 2.09 to 3.16%. The higher organic matter soil is abbreviated here using the term HOM.

Column Study. Duplicated stainless steel soil columns (12 cm diameter × 150 cm length) were used to study the vertical distribution and surface emissions of MeI following a simulated shank injection at 30 cm soil depth. The design and setup of the columns has been described previously.^{7,10} Soils were packed into the columns to a bulk density of 1.5 g cm⁻³, and volumetric moisture contents ranged from 13% at the surface to 19% below 60 cm. The top of the columns was sealed with a stainless steel flux chamber to trap headspace gas. The columns were housed in a controlled temperature room where the ambient temperature was adjusted so as to produce a realistic diurnal temperature regime through the soil profile. At 5 cm depth, soil temperature ranged from 23 to 32 °C. Below 30 cm depth, the columns were insulated to reduce temperature fluctuation in this region. At time 0, 80 μL (182.4 mg) of MeI was injected into the center of the soil column at 30 cm depth. Immediately, a vacuum (80 mL min⁻¹) was applied to the flux chamber to sweep headspace gas vapors through in-line charcoal tubes that were initially sampled every 2 h during the day (7 a.m. to 7 p.m.) and 12 h overnight. At later times, the sampling period was extended since lower MeI emissions were expected. Backup tubes were used to check for MeI breakthrough. All sampled tubes were capped on both ends and stored at -19 °C. After 1, 2, 3, 4, 7, 14, and 15 days, the soil gas distribution of MeI was determined. A 250 μL sample of soil gas was withdrawn at intervals along the soil profile, using a gastight syringe, via sealable ports in the side walls of the columns. Each sample was dispensed into a glass, 12 mL GC-headspace (GC-HS) vial and immediately capped

with a Teflon-faced septum. Samples were stored at room temperature for a maximum of 24 h prior to analysis by GC-HS.

In addition to comparing MeI behavior in the control and HOM soils, two methods of sealing the soil surface (with plastic tarp or irrigation water) were also tested using the control soil to determine their potential for emission reduction. Tarping was carried out using Hytibar film. In this treatment, the effect of tarp ripping on subsequent emissions of MeI was assessed. On Day 14, a hooked implement was inserted via a sealable port in the side of the surface mounted flux chamber and the tarp ripped several times. Emissions were then further monitored over the following 2 days. All other treatments were ended on Day 14, at 338 h. For the irrigated treatment, 1 cm of water was added to the soil surface 30 min before fumigant application and then again after 1, 2, 3, and 4 days. Irrigation water was added using a custom-built, pronged irrigation device (which added water uniformly over the soil surface) inserted via the port in the side of the flux chamber.

At the end of the experiment, selected columns were destructively sampled to determine the residual MeI concentrations in the soil solid phase. The primary objective of this procedure was to establish whether the two soils differed in their ability to retain MeI, which would consequently affect emission potential. From the center of the soil column, 12.5 cm deep cores of soil were removed throughout soil profile and placed into clean plastic bags. According to an existing method,^{11,12} the samples were then subjected to overnight aeration to release any residual gas phase MeI and to air-dry the soil. Immediately following aeration, soil samples were ground to pass a 2 mm sieve and homogenized, and a 10 g subsample was weighed into a 20 mL glass vial. Following addition of 10 g of anhydrous sodium sulfate and 10 mL of ethyl acetate, samples were shaken for 30 min before 1.5 mL of supernatant was transferred to an amber GC vial for analysis. Selected soil samples were further analyzed as above but using acetonitrile as the extractant. During a 24 h extraction these samples were heated at 80 °C in a water bath, with periodic mixing using a vortex mixer.

For the analysis of MeI on charcoal tubes, a GC-HS method that used benzyl alcohol to release MeI from the charcoal sample has been described.^{13,14} However, in the interests of simplification, we instead used an acetone-extraction method. Following the experiment, MeI was desorbed from the charcoal tubes by separating the two tube sections and dispensing the charcoal into a 12 mL glass vial, adding 4 mL acetone, immediately capping with a Teflon-faced septum, and shaking for 30 min. A 20 μL subsample of the supernatant was then removed from the sealed vial, through the septa, using a gastight syringe and quickly transferred to an amber GC vial containing 980 μL acetone (50 times dilution). A high level of dilution was required due to the high MeI sensitivity of gas chromatography when using a microelectron capture detector (μ-ECD).

MeI Degradation in Study Soils. To determine the degradation kinetics of MeI in the control and HOM soils, degradation studies were performed. To 10 g soil samples (8% gravimetric moisture content) in 20 mL glass vials, a spike of 100 μg MeI was introduced. The vials were immediately capped with a Teflon-faced septum and placed at 25 °C. At 0, 1, 4, 8, 24, 48, 72, 144, 240, and 480 h, triplicate vials were removed and stored in a -19 °C freezer to retard further chemical and biological degradation. For MeI extraction, vials were removed from the freezer, decapped, and 10 g of anhydrous sodium sulfate (to absorb moisture) and 10 mL of ethyl acetate were quickly added

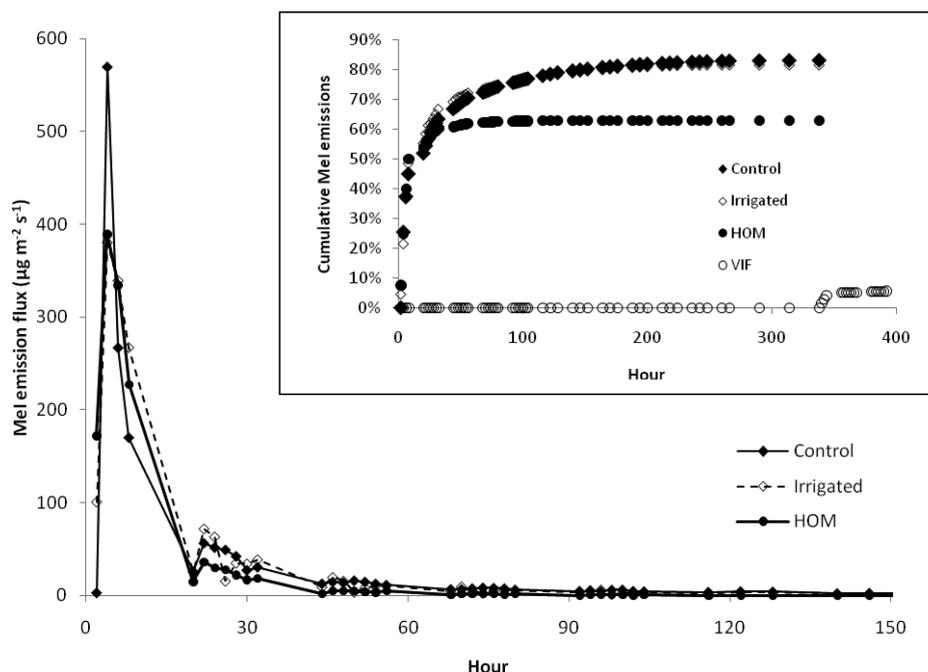


Figure 1. Average MeI emission fluxes from the control, irrigated, and HOM treatments and cumulative emissions (inset) from all treatments. Note that the x axis is shortened to 150 h to improve differentiation of the curves during the early period. Beyond 150 h, in each treatment, continued tailing was observed (this can be seen for the control in Figure 2).

before rapid recapping. The samples were shaken for 1 h before being allowed to settle briefly. A gastight syringe was then used to transfer a 0.5 mL subsample of supernatant from the sealed vial, through the septa, to an amber GC vial for analysis. Preliminary studies revealed that the extraction efficiency of this procedure was 82%. The degradation rate constant and half-life of MeI were calculated according to the first order decay model.

Analysis. MeI concentrations of the charcoal filter (soil column experiment) and soil (degradation experiment) extracts were determined using a Hewlett-Packard 7890A GC (Agilent Technologies) equipped with a μ -ECD. The column was a 30.0 m \times 0.25 mm \times 1.4 μ m capillary column (Agilent Technologies) running at a flow rate of 1.0 mL min⁻¹ and using He as the carrier gas. The oven temperature was fixed at 60 °C, the inlet temperature at 240 °C, and the detector temperature at 290 °C. Under these conditions, the MeI retention time was 3.8 min. Standards for the charcoal extract analysis were prepared by injecting differing amounts of MeI (encompassing the range of sample amounts) onto clean charcoal tubes under vacuum (150 mL min⁻¹), prior to acetone extraction using the same procedure as for the samples. Using this approach eliminated the need to apply a mass recovery correction to the sample data. Standards for the soil extracts were prepared in ethyl acetate and encompassed the range of sample values. For the soil gas samples, a Hewlett-Packard 6890 GC (Agilent Technologies) equipped with a μ ECD detector was used in conjunction with a G1888 Network Headspace Sampler (Agilent Technologies). The column was a 30.0 m \times 0.25 mm \times 1.4 μ m capillary column (Agilent Technologies) with a carrier gas of He and a flow rate of 1.4 mL min⁻¹. Oven temperature was set at 50 °C, inlet temperature at 240 °C, and detector temperature at 280 °C. The operating conditions for the headspace sampler were as follows: oven temperature 80 °C, loop temperature 90 °C, transfer line temperature 100 °C, vial equilibration time 5 min, and sample loop volume 0.2 mL. Under these

conditions, MeI retention time was 3.7 min. Five MeI standards encompassing the range of concentrations observed in the soil gas samples were prepared in hexane (1–5 μ L).

RESULTS AND DISCUSSION

Emission fluxes of MeI from the control, irrigated, and HOM treatments are shown in Figure 1. Due to the much lower fluxes observed in the VIF treatment, these data are presented in Figure 2, along with the control as a comparison, using a log scale. If the increased fluxes observed in the VIF treatment following tarp ripping are excluded, the maximum peak in emissions from each treatment occurred very rapidly (in the 2–4 h sample period after fumigation). Indeed, this 2-h period accounted for 21, 28, and 31% of the total recovered MeI in the irrigated, HOM, and control treatments, respectively (8% in the VIF). Compared to other commonly used MeBr alternatives, MeI possesses relatively high Henry's constant and vapor pressure values. This would explain the rapid gas-phase transport from 30-cm depth (the injection point) to the soil-headspace boundary. Compared to the control, which showed the highest maximum peak (570 μ g m⁻² s⁻¹), the maximum peak in the HOM treatment was reduced by 32%, in the irrigated treatment by 33%, and in the VIF treatment by 99.98%. In a previous column study using MeI,¹³ tarping with VIF reduced the maximum emission peak by 82% compared to bare soil. In the same study, potting mix with a high level of organic matter (9.60%) exhibited a maximum emission peak 50% lower than soils with 2.51–2.99% organic matter. Compared to other fumigants applied under similar conditions, the peak fluxes of MeI we measured here were very high. Using identical soil and columns, our previous work⁷ determined the peak emission flux of 1,3-D to be around 14 times lower than found here for MeI (at the same application rate). In the same work, the peak CP emission flux was around 28 times

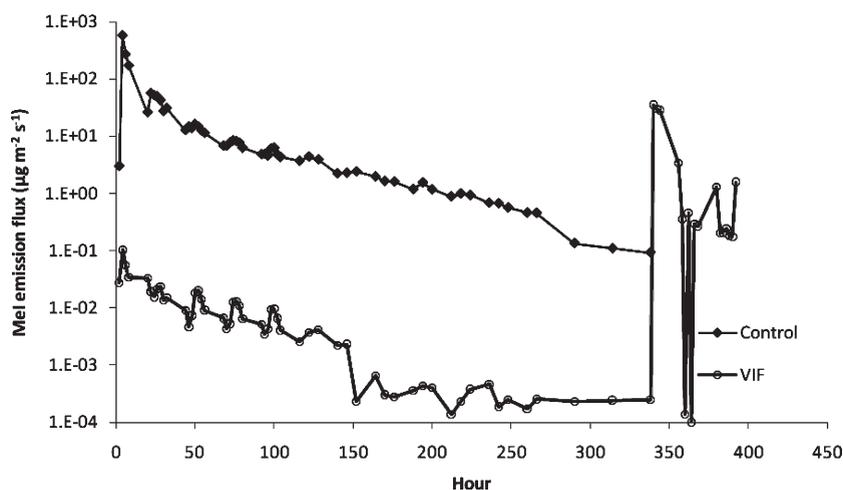


Figure 2. Average MeI emission fluxes from the control and VIF-tarped soil columns. Note logarithmic y axis.

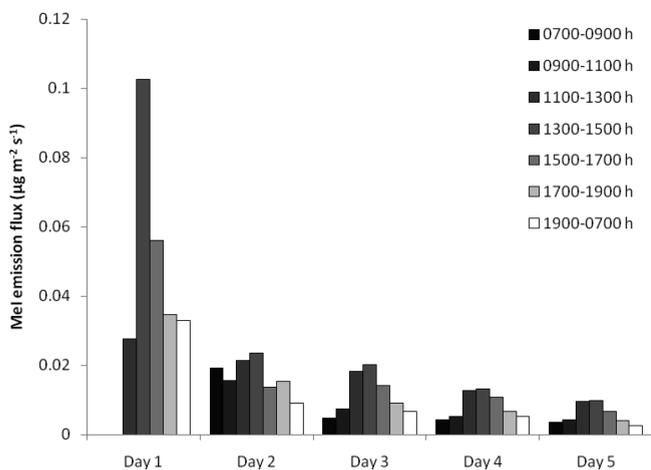


Figure 3. Average MeI emission fluxes for discrete time periods over the first five days in the VIF-tarped treatment.

lower than for MeI (at approximately half the application rate used here for MeI).

Following the initial emissions peak, the fluxes in each treatment generally decreased with time, characterized by extended tailing of the curve, to 338 h. Within this tailing, the observed fluctuations in emission fluxes over time were not strongly correlated with the diurnally varying soil temperatures when considered across the entire experiment. Nevertheless, when considered on a day-by-day basis, it was noted that emission fluxes were generally lowest during the night-time period (1900–0700 h) when soil temperatures were low and highest during late morning and early afternoon periods (1100–1300 and 1300–1500 h) when soil warming was evident (data for VIF-covered soil shown in Figure 3). This suggests that soil temperature was somewhat influential over MeI emissions, as would be expected given the positive relationship between temperature and MeI diffusion coefficient in soil. Moreover, for the VIF covered soil, this may have also been coupled with an increase in permeability of the film at higher temperatures.¹⁵

Most effective in the reduction of MeI emission flux was the surface covering of VIF. The low permeability of such films to fumigants generally makes them an excellent strategy for emission

reduction, notwithstanding their relatively high cost. However, one concern over the use of such coverings is the potential for fumigant release following tarp ripping, or removal, prior to crop planting. This is particularly an issue in situations where chemicals with relatively long half-lives (e.g., MeI) are being used. To quantify this potential for emissions, the VIF was ripped on Day 14 of the experiment (Figure 2). This produced a marked spike in emissions from $0.0003 \mu\text{g m}^{-2} \text{s}^{-1}$ (at 338 h) to around $30 \mu\text{g m}^{-2} \text{s}^{-1}$ (at 340–344 h). As a result, emission fluxes from the VIF treatment at this time were greater than those in the other treatments at 338 h (when those treatments were ended). Nevertheless, this maximum peak in the VIF flux was small (almost 20 times lower) compared to the peak emission flux at 2–4 h for the control (bare soil) treatment.

Cumulative emissions of MeI, expressed as a percentage of the added mass, are also shown in Figure 1 (inset). Total loss from the control soil averaged 83%, which is consistent with the large (78%) emission loss of MeI observed from a bare sandy loam soil column study.¹³ However, the loss from the bare soil was much greater than has been observed previously for other soil fumigants such as 1,3-D,^{16,17} CP,¹⁷ and methyl isothiocyanate¹⁸ which are typically in the region of 20–40% total emissions. Despite reducing the maximum emission flux peak relative to the control, the irrigation treatment did not lead to a significant overall reduction in MeI emissions over the course of the experiment (average total loss 82%). The addition of irrigation water was expected to lower emissions by blocking gas phase MeI transport in the water-filled pores close to the soil surface. Such an effect has been observed previously for a number of MeBr-alternative fumigants, e.g. 1,3-D and chloropicrin.^{7,10,19,20} Although 1 cm daily addition of irrigation water for 5 days can be considered a relatively large input, the rapidity of the emissions suggests that only the initial addition (30 min prior to fumigant application) would have had the potential to significantly influence emissions. The data may suggest, therefore, that the initial 1 cm addition was insufficient to effectively form a barrier of water-filled pore space. Moreover, it is considered that the relatively high Henry's constant and vapor pressure values of MeI likely resulted in a more efficient upward gas transfer in the moist soil than might be demonstrated by, for example, 1,3-D and chloropicrin. In particular, the high Henry's constant is likely to have limited the transfer of MeI from the gas phase into the water

phase. Overall, data from the irrigation treatment suggest that a single, large irrigation event immediately prior to fumigation may be most effective at reducing emissions. Subsequent events would likely have little impact. Additionally, these subsequent events may have the undesired effect of increasing the potential for MeI leaching to groundwater.¹²

Relative to the control, the addition of organic material to the soil (HOM) reduced total emissions to around 63%. Higher levels of organic matter in soil potentially reduce fumigant emissions by accelerating the processes of biological and chemical degradation and soil adsorption. Despite work suggesting MeI has a low soil-liquid partition coefficient,²¹ Guo et al.¹² noted that approximately 1.5 months after fumigant application, MeI residues persisted in soil, bound to the soil solid phase. In soil collected from the irrigated and HOM columns at the end of the experiment, no residual MeI was measured using acetone extraction. However, using the hot acetonitrile extraction, residual MeI was detected ($5.8 \pm 0.7 \mu\text{g kg}^{-1}$) at the 25–37.5 cm depth interval (i.e., incorporating the injection point) only in the HOM soil, suggesting that the enhanced organic matter may have been significant in MeI adsorption. Additionally, several workers have reported enhanced degradation of MeI in the presence of added organic matter. For example, Gan and Yates²¹ reported a MeI half-life of 43 days for low organic matter (0.92% OM) soil, compared with 11–13 days for soils with organic matter ranging from 2.5 to 9.6%. Similarly, Guo and Gao²² found that amendment of sandy loam soil with 10% cattle manure reduced MeI half-life from 32 days to 4 days. Chemical, rather than biological, mechanisms are thought to be responsible for MeI degradation,²² with nucleophilic functional groups associated with soil organic matter (e.g., $-\text{NH}_2$, $-\text{NH}$, $-\text{SH}$, $-\text{OH}$) thought to be most significant.²¹

The relationship between organic matter and MeI degradation is consistent with measured degradation rates in the present study. Applying the first-order decay model to the measured loss of MeI from soil over time, yielded rate constant (k) values of 0.00264 h^{-1} ($r^2=0.99$) and 0.00993 h^{-1} ($r^2=0.97$) for the control and HOM soil, respectively. Calculating half-lives yielded values of 10.9 and 2.9 d, respectively. Therefore, the rate of degradation in the HOM soil was almost four times faster than the control soil. Interestingly, for the same two soils, we previously determined 1,3-D half-lives of 5.3 and 1.2 d, respectively (i.e., also around four times faster in the HOM soil).¹⁰ The faster degradation in the HOM soil explains the reduction in MeI emissions; however, the alacrity of the emissions appeared to limit the extent to which a beneficial impact was attained. Previously, the same HOM soil was far more effective in reducing total emissions of 1,3-D, responsible for an almost six times reduction (total emissions of 5.7% compared to 33.1% in the control).¹⁰ This greater effectiveness may be attributable to the slower emissions of 1,3-D from the soil when compared to MeI. That is, the contact time between the 1,3-D and soil organic constituents may have been greater than that for MeI, due to the lower Henry's constant and vapor pressure values of the former. Nevertheless, Luo et al.²³ found relatively low MeI emissions (29% total loss) in soil with a high rate of MeI degradation (0.0779 h^{-1} , $t_{1/2} = 8.9 \text{ h}$) induced by soil amendment with citrus roots. Evidently, with such a short half-life, the potential to impact MeI emissions is greatly increased. The results suggest that organic matter enhances MeI degradation, such that soils with higher organic matter contents exhibit lower emissions than soils with lower levels of organic matter. On the other hand, due

to the enhanced degradation, soils high in organic matter may require higher MeI application rates to achieve the same level of pest control as in soils of low organic matter status. Therefore, to maintain both adequate pest control and emission reduction, application of organic materials onto the soil surface is likely to be of significant benefit since degradation occurs only after the fumigant has left the soil. Moreover, application of organic materials beneath plastic film (e.g., VIF) could also be utilized as an approach to limit the spike release of MeI observed upon tarp ripping.

Total emission loss from the VIF treatment prior to tarp ripping at 338 h was 0.04%. Two days after ripping, the total was 6%. Even taking into account the fact that the emissions barrier offered by VIF was ultimately compromised, it would appear that a significant emissions reduction benefit over the other treatments was obtained, both in terms of emission flux rates and total emissions. The reduction in MeI emissions induced by the Hytibar VIF covering was greater than that observed by Gan et al.¹³ These workers reported a series of column experiments to determine soil emissions of MeI under differing surface tarps. For a sandy loam soil, they determined 78, 72, and 52% total emissions of MeI under control (bare soil), polyethylene-tarped and VIF-tarped (Hytibar) conditions, respectively. On the other hand, such a large reduction as was observed here for the Hytibar is consistent with the high MeI diffusion resistance value for this film⁹ and with the large reductions observed for other fumigants applied under this film. For example, Hytibar film has been shown to reduce emissions of the fumigant CP from 82% in a control to just 4%.²⁴ Similarly, Hytibar-induced reductions in the emissions of both CP (from around 21% to just 0.001%) and 1,3-D (from around 41% to 2.4%) have been previously reported.⁷ Similar reductions in methyl bromide emissions were observed by Wang et al.²⁵ in field plots covered with Hytibar (<5%) compared to standard practices using HDPE (>60%). Based on the data available for other fumigants, the large VIF-induced reduction in MeI emissions observed here seems reasonable.

The emission reduction benefit for MeI is further emphasized by the distribution of MeI in the soil gas phase when comparing the control and VIF treatments (Figure 4). The much greater soil gas concentrations of MeI observed under VIF demonstrated the ability of this film to retain the fumigant within the soil. In addition to lowering emissions, this has the effect of increasing the contact time between the MeI and soil pests, thereby maximizing pest kill potential. The relatively very low gas concentrations in the control were due to the rapid and high emissions from the soil surface. Therefore, even at 1 day, gas concentrations were generally below $1 \mu\text{g mL}^{-1}$, compared to $11 \mu\text{g mL}^{-1}$ in the VIF-covered soil. Indeed, even on day 14 under VIF, the gas concentrations were comparable to those in the control on day 1. Ripping of the tarp led to very low gas concentrations on day 15. As others have noted both in column^{12,13} and field¹³ studies, MeI diffuses rapidly due to its high vapor pressure. This is apparent from the day 1 sampling data which shows that MeI had already diffused throughout the profile. This rapid diffusion is consistent with the rapid MeI emissions from the soil surface. In the VIF-covered soil, peak gas concentration was observed close to the depth of injection on day 1. Subsequently, the concentrations generally decreased over time and tended toward a uniform distribution throughout the soil profile. By day 1 in the control, the concentrations tended to increase with depth, presumably as a result of rapid emission

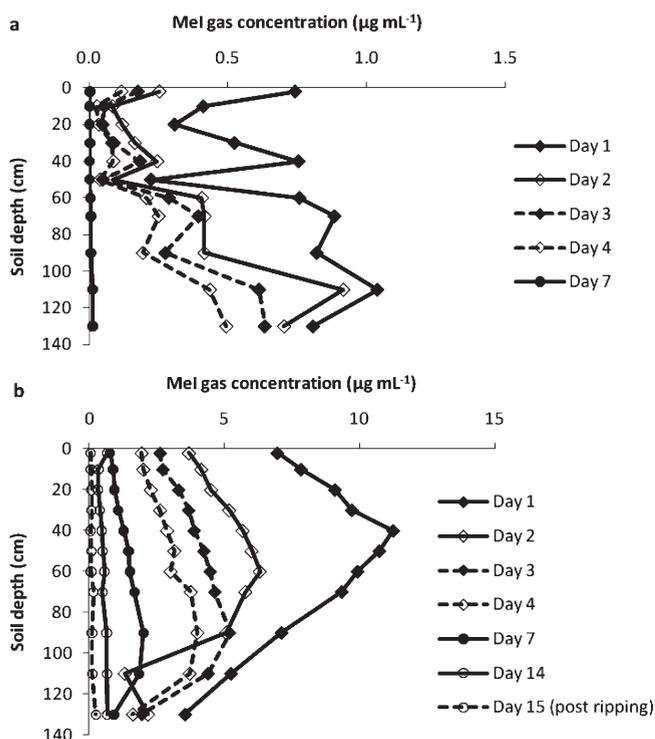


Figure 4. MeI soil gas concentrations throughout the soil profile in the (a) control and (b) VIF-tarped soil columns. Note differing x axes. It is unclear why the 50 cm sampling point in the control soil consistently yielded a relatively low concentration, but it is expected that this value should be more in line with the values observed at 40 and 60 cm depth.

losses at the surface boundary driving the removal of MeI from the near-surface soil. Overall, the low concentrations observed in the control soil may indicate that in the absence of some form of containment, pest control could be compromised.

The data suggest that compared to other registered fumigants, high emissions of MeI from soil to air are likely to occur very rapidly after fumigant application. During this period, health risks to local populations and agricultural workers are likely at their greatest. Due to the rapidity of the MeI emissions and the physical-chemical properties of MeI (both of which limited the effectiveness of irrigation and organic matter enhancement), by far the most effective strategy to reduce emissions was VIF covering. This dramatically limited both fluxes and total losses of MeI and offers the additional advantage of maintaining higher MeI soil gas concentrations and, hence, potentially increasing pest-control efficacy. This suggests that VIF use may offer the potential for using reduced MeI application rates. Overall, to limit environmental and human health risks, VIF should be considered for soil covering during agricultural preplant fumigation with this chemical. Although such films are likely to be more expensive than standard plastic (e.g., HDPE), the potential for using reduced application rates is likely to, at least partially, offset this increased cost and make VIF a competitive option.²⁶

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REFERENCES

- (1) Sims, J. J.; Grech, N. M.; Becker, J. O.; McGiffen, M.; Ohr, H. D. Methyl iodide: a potential alternative to methyl bromide. In: Proceedings of the second annual international research conference on methyl bromide alternatives and emissions reductions, San Diego, 6–8 November 1995. Methyl Bromide Alternatives Outreach: Fresno, CA, p 46.
- (2) Ohr, H. D.; Sims, J. J.; Grech, N. M.; Becker, J. O.; McGiffen, M. E. Methyl iodide, an ozone-safe alternative to methyl bromide as a soil fumigant. *Plant Dis.* **1996**, *80*, 731–735.
- (3) Ruzo, L. O. Physical, chemical and environmental properties of selected chemical alternatives for the pre-plant use of methyl bromide as soil fumigant. *Pest Manage. Sci.* **2006**, *62*, 99–113.
- (4) Ajwa, H. A.; Trout, T.; Mueller, J.; Wilhelm, S.; Nelson, S. D.; Soppe, R.; Shatley, D. Application of alternative fumigants through drip irrigation systems. *Phytopathology* **2002**, *92*, 1349–1355.
- (5) Becker, J. O.; Ohr, H. D.; Grech, N. M.; McGiffen, M. E.; Sims, J. J. Evaluation of methyl iodide as a soil fumigant in container and small field plot studies. *Pestic. Sci.* **1998**, *52*, 58–62.
- (6) USEPA. Extension of conditional registration of iodomethane (methyl iodide). 2009. Available at http://www.epa.gov/pesticides/factsheets/iodomethane_fs.htm (accessed Sept. 21, 2010).
- (7) Ashworth, D. J.; Ernst, F. F.; Xuan, R.; Yates, S. R. Laboratory assessment of emission reduction strategies for the agricultural fumigants 1,3-dichloropropene and chloropicrin. *Environ. Sci. Technol.* **2009**, *43*, 5073–5078.
- (8) Arysta Lifesciences. California announces proposed decision to register Midas for commercial use. 2010. http://www.arystalifescience.us/usa/media/CA_Registration_Press.pdf (accessed Sept. 21, 2010).
- (9) Papiernik, S. K.; Yates, S. R.; Chellemi, D. O. A standardized approach for estimating the permeability of plastic films to soil fumigants under various field and environmental conditions. *J. Environ. Qual.* (accepted, June 22, 2010).
- (10) Ashworth, D. J.; Yates, S. R. Surface irrigation reduces the emission of volatile 1,3-dichloropropene from agricultural soils. *Environ. Sci. Technol.* **2007**, *41*, 2231–2236.
- (11) Guo, M.; Papiernik, S. K.; Zheng, W.; Yates, S. R. Formation and extraction of persistent fumigant residues in soils. *Environ. Sci. Technol.* **2003**, *37*, 1844–1849.
- (12) Guo, M.; Zheng, W.; Papiernik, S. K.; Yates, S. R. Distribution and leaching of methyl iodide in soil following emulated shank and drip application. *J. Environ. Qual.* **2004**, *33*, 2149–2156.
- (13) Gan, J.; Yates, S. R.; Ohr, H. D.; Sims, J. J. Volatilization and distribution of methyl iodide and methyl bromide after subsoil application. *J. Environ. Qual.* **1997**, *26*, 1107–1115.
- (14) Gan, J.; Yates, S. R.; Spencer, W. F.; Yates, M. V. Optimization of analysis of methyl bromide on charcoal sampling tubes. *J. Agric. Food Chem.* **1995**, *43*, 960–966.
- (15) Papiernik, S. K.; Yates, S. R. Effect of environmental conditions on the permeability of high density polyethylene film to fumigant vapors. *Environ. Sci. Technol.* **2002**, *36*, 1833–1838.
- (16) Gan, J.; Yates, S. R.; Crowley, D.; Becker, J. O. Acceleration of 1,3-dichloropropene degradation by organic amendments and potential application for emissions reduction. *J. Environ. Qual.* **1998**, *27*, 408–414.

(17) Gao, S.; Trout, T. J.; Schneider, S. Evaluation of fumigation and surface seal methods on fumigant emissions in an orchard replant field. *J. Environ. Qual.* **2008**, *37*, 369–377.

(18) Gan, J.; Yates, S. R.; Papiernik, S. K.; Crowley, D. Application of organic amendments to reduce volatile pesticide emissions from soil. *Environ. Sci. Technol.* **1998**, *32*, 3094–3098.

(19) Gao, S.; Trout, T. J. Using surface water application to reduce 1,3-dichloropropene emission from soil fumigation. *J. Environ. Qual.* **2006**, *35*, 1040–1048.

(20) McDonald, J. A.; Gao, S.; Qin, R.; Trout, T. J.; Hanson, B. D. Thiosulfate and manure amendment with water application and tarp on 1,3-dichloropropene emission reductions. *Environ. Sci. Technol.* **2008**, *42*, 398–402.

(21) Gan, J.; Yates, S. R. Degradation and phase partition of methyl iodide in soil. *J. Agric. Food Chem.* **1996**, *44*, 4001–4008.

(22) Guo, M.; Gao, S. Degradation of methyl iodide in soil: Effects of environmental factors. *J. Environ. Qual.* **2009**, *38*, 513–519.

(23) Luo, L.; Ashworth, D. J.; Dungan, R. S.; Xuan, R.; Yates, S. R. Transport and fate of methyl iodide and its pest control in soils. *Environ. Sci. Technol.* **2010**, *44*, 6275–6280.

(24) Gan, J.; Yates, S. R.; Ernst, F. F.; Jury, W. A. Degradation and volatilization of the fumigant chloropicrin after soil treatment. *J. Environ. Qual.* **2000**, *29*, 1391–1397.

(25) Wang, D.; Yates, S. R.; Ernst, F. F.; Gan, J.; Jury, W. A. Reducing methyl bromide emission with a high barrier plastic film and reduced dosage. *Environ. Sci. Technol.* **1997**, *31*, 3686–3691.

(26) Martin, F. N. Development of alternative strategies for management of soilborne pathogens currently controlled with methyl bromide. *Annu. Rev. Phytopath.* **2003**, *41*, 325–350.