

Coupling of Soil Solarization and Reduced Rate Fumigation: Effects on Methyl Iodide Emissions from Raised Beds under Field Conditions

Daniel J. Ashworth,^{*,†,‡} Scott R. Yates,[†] Lifang Luo,^{†,‡} Sang R. Lee,^{†,§} and Richeng Xuan^{†,‡}

[†]USDA-ARS, United States Salinity Laboratory, 450 West Big Springs Road, Riverside, California 92507, United States

[‡]Department of Environmental Sciences, University of California, Riverside, California 92521, United States

ABSTRACT: Using field plots, we studied the effect on methyl iodide (MeI) emissions of coupling soil solarization (passive and active) and reduced rate fumigation (70% of a standard fumigation) in raised beds under virtually impermeable film (VIF). The results showed that for the standard fumigation and the passive solarization + fumigation treatments, emissions from the nontarped furrow were very high (~50%). Emissions from the bed top and sidewall of these treatments were relatively low but were increased in the latter due to the longer environmental exposure of the VIF covering with the coupled approach (increased tarp permeability). Overall, this approach offered no advantage over fumigation-only in terms of emission reduction. With active solarization + fumigation, the large application of hot water during solarization apparently led to severely limited diffusion causing very low total emissions (<1%). Although this suggests a benefit in terms of air quality, a lack of diffusion could limit the pesticidal efficacy of the treatment.

KEYWORDS: *passive solarization, active solarization, iodomethane, virtually impermeable film, air quality*

■ INTRODUCTION

Methyl iodide (MeI; iodomethane; CH₃I) is a chemical fumigant used as a preplant agricultural pesticide. It is currently registered in Japan, Mexico, Morocco, New Zealand, Turkey, and Uruguay, although its 2007 registration in the USA was withdrawn in 2012. As a replacement for the banned fumigant methyl bromide, MeI has proved to be highly effective in the control of plant pathogens such as weeds, fungi, and nematodes.^{1–3} However, concerns exist over the potential for a large proportion of the MeI added to soils to be emitted to the atmosphere. Indeed, in the absence of any emission mitigation strategy, approximately 70–80% of applied MeI may be lost by emission,^{4,5} where its potential carcinogenicity and moderate to high acute toxicity for inhalation and ingestion⁶ may cause human health issues. A major gap in our knowledge and understanding of MeI relates to its behavior under field conditions since virtually all of the published research on emissions of this chemical has been performed in the laboratory.

One strategy to reduce emissions is to simply use a smaller mass of the chemical when fumigating soil. This may be effective if fumigation can be coupled with a nonchemical approach to pest control. For example, the coupling of soil solarization and chemical fumigation may be an advantageous approach to killing soil–plant pests prior to cropping.^{7–9} Under favorable climatic conditions, “passive” solarization (covering the soil with plastic film to retain heat within the soil) can elevate soil temperatures to levels sufficient to kill or injure plant pests. To further supplement the heat input to the soil, “active” or “hot water” solarization approaches have been used where water heated by solar radiation is pumped into the soil via driplines.¹⁰ However, major drawbacks with solarization techniques are the dependency upon favorable climatic conditions, and the relatively long time (up to 8 weeks) required to obtain adequate pest control.¹¹ By combining

solarization and fumigation, it is possible that the major drawbacks of both approaches can be overcome. For example, a shorter period of solarization (e.g., 2 weeks) followed by a fumigation period using a reduced application rate may be sufficient to induce highly effective pest control (with the solarization period essentially injuring the pests and making them more susceptible to mortality at lower soil MeI concentrations), as well as a reduction in the mass of MeI lost by emission (due to the lower mass initially applied).

In theory, reduced rate fumigation should lower emissions to the atmosphere; i.e., a lower input should result in lower output. However, in practice, a number of other factors likely impact the degree of emissions from a fumigation event that follows a solarization period. For example, both approaches require covering of the soil with plastic tarp. Therefore, with a coupled approach, the plastic tarp is in the field for a longer period of time than for a fumigation-only approach. In our study we compared a 2 week solarization followed by a 2 week fumigation (total 4 weeks), with a ‘standard’ fumigation time of 2 weeks. The doubling of tarp exposure time in the coupled approach may have a significant effect on the ability of the tarp to retain MeI during the fumigation phase due to environmental stresses on the tarp (e.g., stretching, photodegradation). Moreover, if an active (hot water) method of solarization is employed, the addition of relatively large volumes of water to the soil below the tarp may also impact the emissions of MeI from the soil due to the water blocking gas diffusion within soil pores.

In this work we aimed to assess the potential for this coupling of solarization and reduced rate fumigation to lower

Received: August 20, 2013

Revised: November 26, 2013

Accepted: December 5, 2013

Published: December 5, 2013

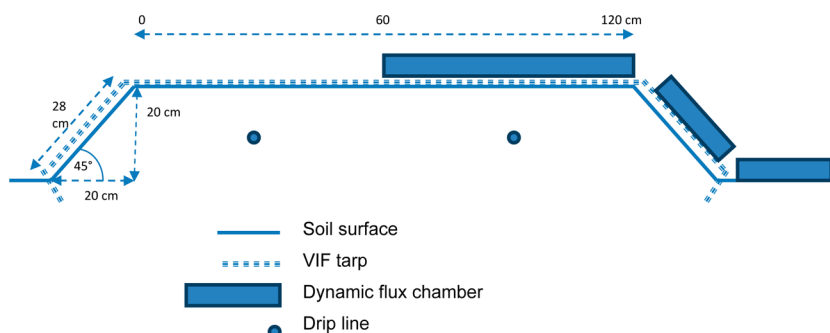


Figure 1. Cross-sectional diagram of raised bed used in field study. Note that flux chamber positions were offset along the length of the bed.

MeI emissions when compared to a standard application rate approach with no presolarization. Specifically, our objectives included the following: (a) to determine field emission flux rates and total emission loss from virtually impermeable film (VIF)-tarped raised beds during a 2 week MeI fumigation at a typical fumigant application rate; and (b) to determine the effects of 2 weeks of presolarization (passive and active) under VIF on the subsequent emission flux rates and total emission loss during reduced rate (70% of the typical rate) MeI fumigation. The effects of the differing application rates, differing tarp exposure times, and differing soil moisture regimes were also evaluated.

MATERIALS AND METHODS

The field experiment was conducted in agricultural field 2B of the University of California—Riverside. The soil at this site is a sandy loam (Arlington series) with a particle size distribution of 75% sand, 18% silt, and 7% clay, a pH of 7.2, and an organic matter content of 0.92%. Prior to the construction of raised beds, the soil was sprinkler irrigated for around 30 h, allowed to drain for 3 days, and then disked to a depth of 20 cm. The gravimetric moisture content of the soil was 9.3%. To construct raised beds (Figure 1), the plowed soil was initially excavated to produce a flat, relatively firm surface of subsoil upon which a wooden frame with dimensions 4 m (*l*) × 1.6 m (*w*) × 0.2 m (*h*) was placed. The excavated plowed soil was then replaced into the wooden frame in approximately 5 cm layers and packed down firmly. After two such layers (i.e., at half the bed height), two drip lines (John Deere Ro-drip, 20 cm hole spacing, 250 L h⁻¹ 100 m⁻¹ drip rate) were placed along the length of the bed. The beds had a uniform dry bulk density of 1.3 g cm⁻³. Upon completion, the wooden frame was removed and the sides of the raised bed were cut to give a 45° angle. For the treatments with presolarization (passive and active), beds were immediately covered with clear ‘HytiBarrier’ virtually impermeable film, VIF (Klerk’s, Richburg, SC; donated by TriCal, Corona, CA), the edges of which were carefully buried around the bed (Figure 1). For the fumigation-only treatment, no tarp was installed at this stage (bare soil).

Starting July 20, 2011, the VIF-covered treatments were subjected to a 2 week period of either passive or active solarization. For the active treatment, a solar collector was constructed (Yates et al.¹⁰) in which water, heated to a temperature of 60 °C via direct solar heating, was periodically pumped through the drip lines in the bed to facilitate increased soil temperatures. Typically, 3–4 L of hot water were administered 2–4 times per day (depending on the frequency with which solar energy heated the water to 60 °C). The daily average addition of hot water was 10.2 ± 2.4 L.

Following the solarization period, the bare treatment was covered with VIF and served as a typical fumigation-only approach with MeI application at a rate of 112 kg ha⁻¹. For the passive and active solarization treatments, the original VIF covering was left in place for the subsequent reduced rate fumigation. These treatments were fumigated at a MeI rate of 78.4 kg ha⁻¹ (70% of the fumigation-only treatment rate). To fumigate the beds, each drip line (2 per bed) was

connected to an amber glass solvent bottle containing 3 L of water mixed well with 39.5 g (100% rate) or 27.7 g (70% rate) of MeI. Upon pressurization of the bottles (~10 psi), the fumigant solution was applied to the beds over a period of 20 min (bottles were pretested to ensure safe use under pressure). Following the application, 2 L of clean water were added to each bottle and also applied to the beds to flush any residual MeI from the bottles and tubing. Fumigation took place at 12:00 h on August 4, 2011. During preparation of the fumigant solutions, the fumigation event itself, and subsequent sampling trips to the field, full-face respirators, heavy duty coveralls, gloves, and boots were worn to protect against MeI exposure.

Emissions of MeI from the soil were measured in each bed using dynamic flux chambers (60 cm long × 20 cm wide × 4 cm high) constructed from galvanized sheet metal. On the bed top and sidewall, the chambers were attached to frames glued onto the VIF. In the furrow, the chamber was sealed to a frame with a lip that was inserted 2 cm into the soil. Pipes running from a region around 30 m upwind of the study site were connected to the inlet of the flux chambers and facilitated the sweeping of clean air through the chamber at a rate of 17 L min⁻¹ using an industrial vacuum pump. This flow rate was checked daily to ensure its consistency. At the outlet of the chamber, a Teflon tube was used to draw a subsample of the air flow (~100 mL min⁻¹) through Anasorb CSC charcoal tubes (SKC, Eighty Four, PA) housed within an enclosed sampling box. Subsample air flow was recorded using Flo-Sen #4 flow sensors (McMillan Co, Georgetown, TX) connected to a 21X datalogger (Campbell Scientific, Logan, UT). Initially, each charcoal tube was sampled for a period of 3 h (day and night) before the 21X switched a solenoid valve to begin sampling of the next charcoal tube. Up to four charcoal tubes could be sampled consecutively in this way (total of 12 h) without human intervention (e.g., overnight). Later in the experiment, when emission fluxes were expected to be lower, a 6 h sampling period was used. Backup charcoal tubes were also used to check for fumigant breakthrough although all were subsequently found to contain nondetectable levels of MeI (i.e., no breakthrough). Tubes were collected at 07:00 and 19:00 h each day, capped, and placed at -60 °C prior to extraction and analysis.

After 14 days of fumigation, a series of cross-shaped cuts in the VIF along the bed top was made. At approximately 15 cm either side of each drip line position, a series of cross-shaped cuts (approximately 40 cm apart) along the length of the bed were made. This was done to simulate the effect on emissions of a grower cutting the film to allow crop planting. Cuts beneath the chambers (total of two cuts for each chamber) were performed by removing the chamber, quickly making the cuts, and immediately replacing the chamber onto the frame. Emissions monitoring from the bed top was then continued for a further 30 h.

To determine the effect of soil moisture content on the degradation kinetics of MeI in the Arlington soil, 10 g samples of soil with a gravimetric moisture content of 2, 5, 10, or 20% were placed into 20 mL glass vials and approximately 100 μg of MeI were added. The vials were immediately capped with Teflon-faced septa and placed at 25 °C. At time 0 (i.e., immediately after capping), 2, 6, 10, 20, and 30 d, triplicate samples for each moisture treatment were removed to a freezer (-19 °C) to prevent further degradation. At the end of the

Table 1. Total MeI Emissions (Mass and Percentage of Total Added) from the Bed Top, Sidewall, and Furrow of Each Treatment^a

	rate (%)	emissions (mg)			
		bed	wall	furrow	total
fumigation only	100	190.1 (150.9)	580.6	37 053.4	37 824.1 (37 784.9)
passive + fumigation	70	1903.2 (1902.7)	7634.3	28 842.1	38 379.6 (38 379.1)
active + fumigation	70	171.6 (171.0)	260.9	4.7	437.2 (436.6)
	rate (%)	emissions (%)			
		bed	wall	furrow	total
fumigation only	100	0.24 (0.19)	0.73	46.9	47.83 (47.78)
passive + fumigation	70	3.44 (3.44)	13.79	52.1	69.34 (69.34)
active + fumigation	70	0.31 (0.31)	0.47	0.01	0.79 (0.79)

^aValues in parentheses are those observed up to the point of VIF cutting (14 days after application).

experiment, vials were removed from the freezer in small batches and the caps removed for the immediate addition of 10 g of anhydrous sodium sulfate (to absorb excess moisture) and 10 mL of ethyl acetate. Vials were then immediately recapped, shaken for 1 h, and allowed to settle, and 1 mL of supernatant was taken for analysis.

To determine the effect of soil moisture content on the partitioning of MeI between the air and liquid phases of soil, a batch study following that of Gan and Yates¹² was performed. In 20 mL glass vials, triplicate 10 g samples of Arlington soil at 2, 5, 10, or 20% moisture content were placed and 400 μg of MeI were added. The vials were immediately capped with Teflon-faced septa and placed at 25 °C for 24 h. After this time, 100 μL of headspace gas were withdrawn from each vial through the septa and dispensed into a sealed gas chromatography vial containing 1 mL of ethyl acetate. The concentration of MeI in the headspace samples, together with an assumed value of 0.21 for the Henry's constant of MeI,¹² was used to calculate the concentration of MeI in the liquid phase of each system. The volume of water in each moisture content treatment was then used to convert the concentration values to masses which were expressed as a percentage of the initial MeI amount added (corrected for 24 h of degradation based on the batch study described above).

Samples of VIF taken from each treatment following the experiment, together with samples taken from the roll (i.e., not used in the field), were subjected to permeability testing using the approach of Papiernik et al.¹³ in which the mass transfer coefficient of a gas through plastic tarps can be readily determined using laboratory permeability cells. The permeability measure, R -value (h cm^{-1}), for each VIF was calculated as the reciprocal of the mass transfer coefficient (cm h^{-1}) of MeI through each piece of tarp.

Charcoal tubes from the field study were extracted by cutting the glass tube and expelling the A and B sections of the charcoal material into separate 10 mL glass vials. To each vial, 4 mL of acetone were added prior to 1 h of shaking and removal of 1 mL of supernatant for analysis. The extraction procedures were performed in a fume hood. Solvent extracts from all studies were analyzed 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 μm 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 was at 240 °C, and the detector temperature was at 290 °C. Under these conditions, the MeI retention time was 3.8 min. Standards were prepared in the same solvent as the extracts and encompassed the range of concentrations present in the extracts.

RESULTS AND DISCUSSION

Total MeI emission losses expressed as both a mass and a percentage of the total amount added are shown in Table 1 for the bed top, sidewall, and furrow regions of each treatment. Although the total emission loss is clearly an important measurement, it does not highlight the maximum potential for air contamination at any given time. This is an important

measure since it can be used to estimate risk to bystanders and local populations in the vicinity of a fumigation event. Therefore, in Table 2, the peak (maximum) emission flux, together with its time from application, is shown for the bed top, sidewall, and furrow regions of each treatment.

Table 2. Peak (Maximum) MeI Emission Flux and Its Time from Application for the Bed Top, Sidewall, and Furrow of Each Treatment

	rate (%)	bed region	peak flux ($\mu\text{g m}^{-2} \text{s}^{-1}$)	time of peak flux (h) ^a
fumigation only	100	bed	0.18	12
		sidewall	3.8	12
		furrow	13.5	30
		bed (post tarp cut)	0.0016	342 (3)
passive solarization + fumigation	70	bed	1.7	9
		sidewall	21.1	15
		furrow	16.8	30
		bed (post tarp cut)	0.000028	345 (6)
active solarization + fumigation	70	bed	0.21	12
		sidewall	0.46	12
		furrow	0.005	30
		bed (post tarp cut)	0.000034	345 (6)

^aNumber of hours from MeI application. Values in parentheses are hours from time of VIF cutting.

For the fumigation-only approach (100% application rate) emissions from the bed and sidewall were extremely low (<1% of the applied amount from both regions combined; Table 1). This illustrates the high effectiveness of the Hytbarrier VIF in preventing MeI emissions. As a means of comparing the permeability of the tarp removed from each of the treatments, the R -values for samples of tarp were determined following the field experiment. For the fumigation-only treatment, the R -value was determined as 3846 h cm^{-1} . This compares to a value of 16 667 h cm^{-1} for the film taken directly from the roll (i.e., not used in the field). Although these values suggest that, during its 2 week use in the field, the permeability of the film increased due to environmental exposure, the field value is still considered very high and indicates that severely limited MeI transfer through the film would be expected. In concurrence, Ashworth et al.⁵ found that MeI emissions were reduced from 82% under bare soil conditions to just 0.04% using the similarly named Hytbar VIF (obtained previously from the same

manufacturer and assumed to have similar properties to Hytibarrier). For other commonly used tarps, low R -values have been observed for MeI. For example, across a wide range of tarps, values of 0.27–1.24 h cm⁻¹ for low density polyethylene and 0.25–1.39 h cm⁻¹ for high density polyethylene have been reported.¹³ Such low resistance values indicate that these tarps would likely result in dramatically greater soil–air emissions of MeI.

Due to the relatively high Henry's constant and vapor pressure of MeI, the absence of tarp, or any other emission reduction strategy, would be expected to yield high MeI emissions from soil. This is borne out for the noncovered, furrow region of the fumigation-only treatment where very high emissions (47%), and a much higher peak emission flux (Table 2), were observed compared to the bed top and sidewall. This indicates that the low permeability of the VIF facilitated the transport of gas (through the soil, and/or in the air space between the soil and the film) to the furrow. The delay in peak emission flux (30 h) for the furrow, compared to 12 h for the bed top and sidewall, supports this hypothesis. Uninhibited emissions from the furrow would have maintained a diffusive gradient toward the region. This level of emissions was lower than that observed in previous studies where a shank injection of MeI to bare soil has been simulated,^{4,5} presumably due to the longer and more tortuous path length from the application point to the bare region (furrow) in this study. The use of impermeable films has been previously shown to facilitate fumigant transport to the furrows of raised bed systems. In laboratory raised bed experiments using Hytibar VIF, 92% to 99% of 1,3-dichloropropene and chloropicrin emissions occurred from the furrow (nontarped) region of the system.¹⁴ Similarly, when compared to the bed top and sidewall, the greatest losses of 1,3-dichloropropene, methyl isothiocyanate, and propargyl bromide have been reported from the furrow region of raised beds under Hytibar VIF.¹⁵

In the passive solarization treatment, emissions of MeI from the furrow region were similar in magnitude to those for the fumigation-only treatment (52% vs 47%, respectively). Again, this indicates the influence of the low permeability of the VIF (covering the bed top and sidewall) in facilitating transport to, and emissions from, the furrow. Although the percentages of emissions from the bed top and sidewall were again relatively low compared to the furrow, they were over 14 times greater than in the case of the fumigation-only treatment. Similarly, peak emission fluxes were much greater compared to the fumigation-only treatment despite the application rate being only 70% in the passive treatment. The reason for this difference is likely related to differences in the length of time the VIF covered the two treatments. In the passive treatment, the VIF was in place from the beginning of the solarization period, i.e., over 2 weeks longer than for the fumigation-only treatment which was bare during the solarization period and then covered with VIF immediately prior to fumigation. Comparison of the R -values for the VIF collected from the two treatments indicates that this longer period of exposure to the environment further compromised the impermeability of the VIF on the passive treatment (R -value of 2439 h cm⁻¹) compared to the fumigation-only treatment and, particularly, the film taken from the roll. Checks were made during the experiment to ensure that no holes formed in the tarps, and so changes in permeability are thought to be due to tarp stretching and degradation, causing a compromise of the polymeric structure of the plastic. Environmental stresses such as

fluctuations in heat, UV light intensity, and wind movement, together with the process of tarp installation, are likely causes of such a compromise. Papiernik et al.¹³ noted that generally R -values decreased due to field use across a wide range of tarps. For a black Hytibar tarp, these workers found that the R -value decreased from 1086 to 618 h cm⁻¹ for tarp taken from the roll and tarp used in the field, respectively.

In contrast to the other two treatments, both total emissions and peak flux from the active solarization treatment were extremely low from all regions of the system (total emissions from the bed top, sidewall, and furrow combined of just 0.79%). Since the VIF on the active treatment was exposed for the same period of time as the passive treatment, these much lower emissions were likely due to a factor other than the condition of the VIF (the R -value for tarp from the active treatment was 2777 h cm⁻¹). The most likely explanation for the low emissions was the addition of water during the solarization phase of the experiment. In total, approximately 143 L of hot water were added during active solarization (daily average 10.2 ± 2.4 L). In the absence of evaporative losses to the atmosphere (due to the VIF cover), drainage was the only potential loss pathway for this water. Although no additional water was added during the fumigation period, the soil at the end of the experiment was markedly wetter than in the other two treatments. At a 0–5 cm depth, volumetric soil moisture content was measured as 0.08 cm³ cm⁻³ in the active treatment compared to 0.02 cm³ cm⁻³ in both the fumigation-only and passive treatments. Similarly, at 5 cm intervals from a 5 to 20 cm depth, moisture contents close to field capacity (0.13–0.15 cm³ cm⁻³) were observed in the active solarization treatment, compared to values of 0.06–0.07 cm³ cm⁻³ for both the fumigation-only and passive solarization treatments. This relatively large water content in the active treatment may have exerted a significant influence on the behavior of MeI gas due to (i) a reduction in diffusion rate of the MeI gas through water filled pores (approximately 10⁴ times slower than in air filled pores); (ii) a greater partitioning of MeI gas into the water phase; and (iii) an enhanced rate of fumigant degradation due to hydrolysis. A combination of these processes likely led to the very low emissions observed in this treatment.

To address the issues of partitioning into the liquid phase and degradation at differing moisture contents, batch experiments were conducted (Figure 2). In the phase partition study, as gravimetric soil moisture content increased from 2% to 5%, 10%, and 15% (equivalent to volumetric moisture contents in the field study beds of 0.03, 0.07, 0.13, and 0.20 cm³ cm⁻³,

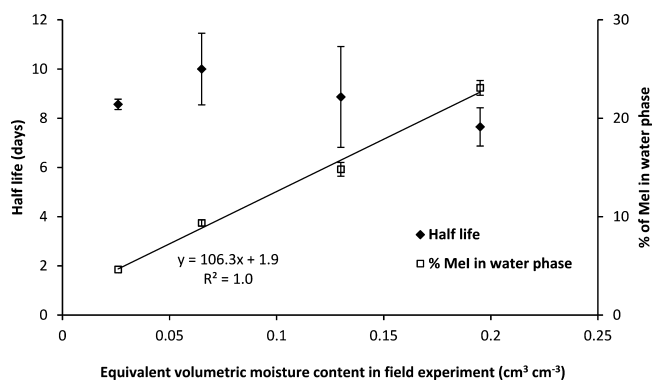


Figure 2. Effect of soil moisture content on MeI degradation half-life and partitioning into the water phase.

respectively), the amount of added MeI that was present in the liquid phase at equilibrium increased linearly from 4.6% to 23.1%. This indicates that air–liquid partitioning of MeI was strongly dependent upon the volume of water present in the system. In relation to the field study, where, at the time of fumigant application, soil moisture content was likely high and heterogeneous (for example potentially very high close to the application drip line), this relationship offers at least a partial explanation for the lower MeI emissions from the bed top and sidewall of the active treatment. However, this effect does not seem to be of sufficient magnitude to explain such dramatically lower emissions from the furrow region of this treatment (0.01% compared with around 50% from the other treatments; Table 1).

Similarly, the effect of moisture content on the MeI degradation rate (Figure 2) seemed unable to account for the very low furrow emissions from the active treatment. Across the moisture gradient, the average degradation half-life ranged from around 8 to 10 days. This range of values was slightly below the 12.9 d previously found for the same soil at 12.5% moisture content.¹⁶ Although, on average, degradation was fastest at the higher moisture content (suggesting a possible contributory reason for lower MeI emissions at higher moisture content), one-way analysis of variance (Microsoft Excel 2007) revealed that moisture content was not a significant factor in controlling the MeI degradation rate ($p > 0.05$). In any case, in order to so dramatically mitigate MeI emissions from the furrow of the active solarization treatment, it is considered that much faster degradation than that given by a half-life of 8 days would have been required. The lack of a strong moisture effect on MeI degradation has been observed previously¹⁷ and is consistent with the relatively low rate of its hydrolysis (half-life >100 days¹⁶). Although the degradation rate can be strongly affected by temperature, the higher temperatures observed in the active solarization treatment during the solarization phase (when compared to the passive solarization treatment; data not shown) were not seen during the fumigation phase. Therefore, an elevated level of MeI degradation in the active treatment due to field temperatures was not considered likely.

These findings suggest that the low emissions from the furrow were most likely due to the physical process of excess water blocking the soil pores and effectively preventing gas diffusion. The moisture content of the soil at the end of the experiment was close to field capacity which suggests that gas movement should have been possible because larger pores should have drained of water. However, in recently built raised beds the combination of soil compaction during construction and a lack of macro-biological processes (e.g., plant root growth and earthworm activity) may significantly reduce the volume of large pores. In addition, and perhaps more significantly, the wetting and draining of the soil during active solarization may have led to further consolidation of the sandy loam soil, thereby further reducing pore space. It is considered that the dominance of smaller pores, which would not necessarily have drained under gravity and therefore remained water-filled at field capacity, may have dramatically impacted the effectiveness of MeI transport within the soil. Such a process would have led to poor diffusion of MeI gas to the furrow region and, ultimately, increased degradation of the MeI and low emissions. Although these coupled processes cannot be elucidated in batch studies, several workers have noted the effect of soil irrigation in reducing fumigant emissions and it has been considered as a low cost emission reduction strategy.^{18–20}

An important concern when using relatively long half-life fumigants under impermeable tarps is the potential for spikes in emission fluxes after the tarp is cut for planting. This is particularly a concern for the respiratory health of agricultural workers performing the tarp cutting. However, as shown in Tables 1 and 2, emissions of MeI post tarp cutting were very low (e.g., peak fluxes after tarp cutting were just 0.000028 – $0.0016 \mu\text{g m}^2 \text{s}^{-1}$). This indicates that the MeI had already been emitted (e.g., from the furrow in the fumigation-only and passive treatments), degraded, or had not diffused to the soil surface/tarp interface due to the presence of water (active treatment). A further observation common to all treatments was the greater emission loss from the sidewall when compared to the bed top (Tables 1 and 2). Given the closer proximity of the drip lines to the soil surface than to the sidewall, greater emissions from the bed top would be expected. A possible reason for this may have been MeI gas collecting in the sidewall region due to the buried lip of VIF at the base of the sidewall (Figure 1).

Overall, the percentage of total emissions followed the order passive solarization + reduced rate fumigation $>$ fumigation-only \gg active solarization + fumigation. However, it is also interesting to note the masses of MeI lost by emission (Table 1). For example, comparison of the fumigation-only and passive solarization treatments revealed the total masses of emissions were very similar (37.8 and 38.4 g, respectively), despite the application amount in the passive treatment being lower (70% of the fumigation-only amount). In relation to pest control, passive solarization followed by reduced rate MeI fumigation is viewed as a potential approach to maintain pest control while reducing MeI emissions. All else being equal, this would probably hold true; however, compromise of the VIF during the additional length of time that it was exposed to field conditions in the passive solarization treatment appeared to obviate the reduced application rate in terms of emission reduction. Under such conditions, the fumigation-only approach would seem to be more advantageous due to the shorter treatment time. The dramatic reductions in emissions associated with the active solarization treatment are clearly beneficial in terms of protecting air quality; however, with such apparent limiting of gas diffusion within the wet soil, it is possible that the efficacy of the pest control could be negatively impacted.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: daniel.ashworth@ars.usda.gov. Telephone: 951-369-4802. Fax: 951-342-4964.

Present Address

[§]Environmental Measurement & Analysis Center, National Institute of Environmental Research, Environmental Research Complex, Hwangyong-ro 42, Seo-gu, Incheon, 404-708, Republic of Korea.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Ping Zhang for technical assistance throughout the work. They also thank Nydia Celis, Marcelo Altamirano, Richard Austin, and Jim Wood for assistance during the fieldwork.

■ REFERENCES

- (1) 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.
- (2) Becker, J. O.; Ohr, H. D.; Grech, N. M.; McGiffin, 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.
- (3) Waggoner, M.; Ohr, H. D.; Adams, C.; Sims, J. J.; Gonzalez, D. Methyl iodide: an alternative to methyl bromide for insectary fumigation. *J. Appl. Entomol.* **2000**, 113–117.
- (4) 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.
- (5) Ashworth, D. J.; Luo, L.; Xuan, R.; Yates, S. R. Irrigation, organic matter addition and tarping as methods of reducing emissions of methyl iodide from agricultural soils. *Environ. Sci. Technol.* **2011**, *45*, 1384–1390.
- (6) National Institute for Occupational Safety and Health. The registry of toxic effects of chemical substances – Iodomethane. 2008. URL (<http://www.cdc.niosh/rtecs/pa903210.html>) (accessed 08 Aug 2013).
- (7) Frank, Z. R.; Benyephet, Y.; Katan, J. Synergistic effect of metham and solarization in controlling delimited shell spots of peanut pods. *Crop Prot.* **1986**, *5*, 199–202.
- (8) Benyephet, Y.; Melerovera, J. M.; Devay, J. E. Interaction of soil solarization and metham sodium in the destruction of *Verticillium-dahliae* and *Fusarium oxysporum* f. sp. *Vasinfestum*. *Crop Prot.* **1988**, *7*, 327–331.
- (9) Eshel, D.; Gamliel, A.; Grinstein, A.; Di Primo, P.; Katan, J. Combined soil treatments and sequence of application in improving the control of soil borne pathogens. *Phytopathol.* **2000**, *90*, 751–757.
- (10) Yates, S. R.; Ashworth, D. J.; Yates, M. D.; Luo, L. Active solarization as a non-chemical alternative to soil fumigation for controlling pests. *Soil Sci. Amer. J.* **2011**, *75*, 9–16.
- (11) University of California Agriculture and Natural Resources. *Integrated Pest Management for Strawberries*, 2nd ed.; UCANR Publications: Oakland, CA, 2008; p 176.
- (12) Gan, J.; Yates, S. R. Degradation and phase partition of methyl iodide in soil. *J. Agric. Food Chem.* **1996**, *44*, 4001–4008.
- (13) 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.* **2011**, *40*, 1375–1382.
- (14) Ashworth, D. J.; Luo, L.; Xuan, R.; Yates, S. R. 1,3-Dichloropropene and chloropicrin emissions following simulated drip irrigation to raised beds under plastic films. *Environ. Sci. Technol.* **2010**, *44*, 5793–5798.
- (15) Papiernik, S. K.; Yates, S. R.; Dungan, R. S.; Lesch, S. M.; Zheng, W.; Guo, M. X. Effect of surface tarp on emissions and distribution of drip-applied fumigants. *Environ. Sci. Technol.* **2004**, *38*, 4254–4262.
- (16) Zheng, W.; Papiernik, S. K.; Guo, M. X.; Yates, S. R. Accelerated degradation of methyl iodide by agrochemicals. *J. Agric. Food Chem.* **2003**, *51*, 673–679.
- (17) Guo, M.; Gao, S. Degradation of methyl iodide in soil: effects of environmental factors. *J. Environ. Qual.* **2009**, *38*, 513–519.
- (18) 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.
- (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.