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Assessment of methods for methyl iodide emission reduction and pest control using a simulation model

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ABSTRACT

The increasing registration of the fumigant methyl iodide within the USA has led to more concerns about its toxicity to workers and bystanders. Emission mitigation strategies are needed to protect the public and environmental health while providing effective pest control. The effectiveness of various methods on emissions reduction and pest control was assessed using a process-based mathematical model in this study. Firstly, comparisons between the simulated and laboratory measured emission fluxes and cumulative emissions were made for methyl iodide (MeI) under four emission reduction treatments: 1) control, 2) using soil with high organic matter content (HOM), 3) being covered by virtually impermeable film (VIF), and 4) irrigating soil surface following fumigation (Irrigation). Then the model was extended to simulate a broader range of emission reduction strategies for MeI, including 5) being covered by high density polyethylene (HDPE), 6) increasing injection depth from 30 cm to 46 cm (Deep), 7) HDPE + Deep, 8) adding a reagent at soil surface (Reagent), 9) Reagent + Irrigation, and 10) Reagent + HDPE. Furthermore, the survivability of three types of soil-borne pests (citrus nematodes [*Tylenchulus semipenetrans*], barnyard seeds [*Echinochloa crus-galli*], fungi [*Fusarium oxysporum*]) was also estimated for each scenario. Overall, the trend of the measured emission fluxes as well as total emission were reasonably reproduced by the model for treatments 1 through 4. Based on the numerical simulation, the ranking of effectiveness in total emission reduction was VIF (82.4%) > Reagent + HDPE (73.2%) > Reagent + Irrigation (43.0%) > Reagent (23.5%) > Deep + HDPE (19.3%) > HOM (17.6%) > Deep (13.0%) > Irrigation (11.9%) > HDPE (5.8%). The order for pest control efficacy suggests, VIF had the highest pest control efficacy, followed by Deep + HDPE, Irrigation, Reagent + Irrigation, HDPE, Deep, Reagent + HDPE, Reagent, and HOM. Therefore, VIF is the optimal method disregarding the cost of the film since it maximizes efficacy while minimizing volatility losses. Otherwise, the integrated methods such as Deep + HDPE and Reagent + Irrigation, are recommended.

1. Introduction

Fumigants are a group of highly volatile pesticides used to disinfest soils from soil-borne pests and pathogens before planting crops. A significant fraction (about 20–90%) of applied fumigants can be emitted into the atmosphere after fumigation (Yates et al., 2003), leading to health risks to agricultural workers and nearby populations. Additionally, fumigant emissions can also contribute to ozone formation in the troposphere. In 2010, the U.S. Environmental Protection Agency proposed strengthening the national ambient air quality standards for ozone, reducing the 8-hour primary ozone standard to a lower level within the range of 0.060–0.070 ppm. Under such regulations, pesticide application will need to minimize negative environmental effects while maintaining efficient pest control. Reduction of fumigants emission losses is of great importance in terms of protecting environmental and human health and maintaining crop productivity.

Methyl iodine (MeI) is considered to be an effective alternative to the stratospheric ozone-depleting fumigant methyl bromide (MeBr), and has been increasingly adopted to control soil-borne pathogens (Arysta Lifesciences, 2010). By 2010, 48 states had

Abbreviations: MeI, methyl iodide; VIF, virtually impermeable film; HDPE, high density polyethylene film; LDPE, low density polyethylene; MeBr, methyl bromide; CT, concentration-time index; 1,3-D, 1,3-dichloropropene; CP, chloropicrin; for fumigation treatment: HOM, using soil with high organic matter content; VIF, being covered by virtually impermeable film; Irrigation, irrigating soil surface following fumigation; HDPE, being covered by high density polyethylene; Deep, increasing injection depth from 30 cm to 46 cm; Reagent, adding a reagent at soil surface.

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registered MeI. Compared to other MeBr alternatives, MeI is more volatile and toxic. Therefore, developing effective emission reduction methods is particularly important for MeI.

There have been many experimental efforts to determine the effects of different application methods on reducing atmospheric fumigant emissions. These methods mainly fall into the following categories: 1) covering the soil surface with plastic films to restrict the fumigant diffusion across the soil–air interface, such as low density polyethylene (LDPE), high density polyethylene (HDPE), and virtually impermeable films (VIF) (Yates et al., 2003; Ashworth et al., 2009), 2) reducing the fumigant diffusion rate in soils by decreasing the soil gas-phase pore space via surface irrigation or soil compaction (Gao et al., 2008), 3) adding a soil amendment such as soil organic matter or fertilizer to accelerate the degradation rate of fumigant in the soil (Yates et al., 2011a; Ashworth et al., 2009), 4) injecting fumigants into deeper soil (Ashworth et al., 2009), and 5) enhancing downward fumigant transport through drip-line application (Wang and Yates, 1999). Such experiments have provided much needed scientific information for improving fumigant use and for developing regulations. However, the experimental methods to determine fumigant emissions from soil, especially in the field, are complex, time-consuming, and expensive; and often cannot be suitably replicated.

Process-based mathematical models are relatively simple and cost-effective alternatives to expensive laboratory and field experiments and have been long used to simulate pesticide transport and fate (Jury et al., 1983). There are numerous computer programs such as CHAIN-2D (Šimunek and van Genuchten, 1994), HYDRUS 1/2/3-D (Šimunek et al., 2008), and SOLUTE (Yates, 2006) available to simulate volatile pesticide transport by including a description of the volatilization process at the soil–air interface. Analytical solutions are also available to estimate soil concentrations, exposure estimates and volatilization losses from soil, provided that the soils are relatively homogeneous and gas-phase diffusive transport is the dominant process (Yates, 2009).

However, a relatively small number of efforts have been attempted to evaluate models for simulating fumigant transport and fate, and to determine the influences of different emission reduction methods on emissions. This is due, in part, to lack of observational data (Shinde et al., 2000; Wang et al., 2004, 2007; Cryer, 2005). The comparison of mathematical simulations to experimental measurements enables determination of a model's ability to represent the actual fumigant behavior in soils and at the soil–air interface. Wang et al. (1997) simulated MeBr emissions from a field experiment by considering diurnal temperature effects. They found that the model produced relatively accurate total emissions but inaccurate timing of peak emission rates. Yates et al. (2002) and Yates, (2006) reported that when the volatilization boundary condition combined soil and atmosphere processes, the SOLUTE simulation model provided more accurate descriptions of the instantaneous emission rates for MeBr and a herbicide (Triallate).

Little is known of the effects of emission reduction strategies on pest control efficacy. Using a numerical model, Wang et al. (2004) evaluated 1,3-dichloropropene (1,3-D) efficacies for controlling nematodes for various soil types, field geometry configurations, application depths, and application rates. Their results showed that validation is an extremely challenging task for these types of studies. Luo et al. (2011) determined MeI dose-response curves for three types of soil pests (i.e., nematode, weed seed, and fungus) and tested a 2-D model by comparing the simulated and observed results. The model simultaneously predicted MeI volatilization, degradation, soil concentration and percent mortality for nematode, weed seed and fungus. Overall, the model satisfactorily predicted MeI movement as well as the soil zone where the three types of pests were controlled.

The objective of this study was to predict MeI transport and fate under sevaral emission reduction strategies and simultaneously predict the resulting efficacy against three types of soil pests using a simulation model. Specifically, the model was evaluated against experimental measurements of emission rates and loss for four emission reduction treatments: 1) control, 2) using soil with high organic matter content (HOM), 3) being covered by VIF (VIF), and 4) irrigating soil surface following fumigation (Irrigation). Extensions of the model allowed simulating a broader range of emission reduction methods, including 5) being covered by HDPE (HDPE), 6) increasing injection depth (Deep), 7) HDPE + Deep, 8) adding a reagent at soil surface (Reagent), 9) Reagent + Irrigation, and 10) Reagent + HDPE.

2. Methodology

2.1. Simulation model

To simulate fumigant fate and transport with consideration of variably-saturated soils and variable soil temperature, three governing processes: water flow, heat transport, and solute fate and transport were considered. For fumigant transport, the governing equation describes the phase partition between liquid, gas, and solid phase, convection, dispersion, diffusion and degradation processes. Degradation was described using a first-order decay reaction, and included the ability to specify different degradation rates in each phase (liquid, gas, and solid). The governing equation for solute transport was written as follows (Šimunek and van Genuchten, 1994):

$$\eta\frac{\partial C_g}{\partial t}+\theta\frac{\partial C_l}{\partial t}+\rho_b\frac{\partial C_s}{\partial t}=\frac{\partial}{\partial z}\left[D_g\frac{\partial C_g}{\partial z}+D_l\frac{\partial C_l}{\partial z}-q_zC_l\right]-\eta\mu_gC_g-\theta\mu_lC_l-\rho_b\mu_sC_s \tag{1}$$

where C_g and C_l are gas- and liquid -phase concentrations (μg mL^{-1}), respectively; C_s is solid-phase concentrations (μg g^{-1}); D_g and D_l are liquid- and gas-phase diffusion coefficients in soils (cm^2 s^{-1}), respectively; μ is a first-order degradation coefficient (s^{-1}); θ, ρ_b, and η, respectively, are water content (cm^3 cm^{-3}), bulk density (g cm^{-3}), and air content (cm^3 cm^{-3}); q is the Darcian flux density (cm s^{-1}); and the subscripts: l, s, and g indicate liquid-, solid-, and gas- phases, respectively.

The partitioning between liquid- and gas-phase was assumed to obey Henry's Law and the partitioning between liquid- and solid-phase was assumed to be equilibrium adsorption as follows:

$$C_g = K_hC_l \tag{2}$$

$$C_s = K_dC_l \tag{3}$$

where K_h is the Henry's law constant (dimensionless), K_d is the linear equilibrium sorption coefficient (cm^3 g^{-1}).

A volatile surface boundary condition was used to simulate the volatilization process

$$\left.\left(D_e\frac{\partial C_l}{\partial z}-q_zC_l\right)\right|_{Z=0} = h\left(C_g-C_{\text{air}}\right)\big|_{Z=0} \tag{4}$$

where C_{air} is gas concentration in the atmosphere (μg mL^{-1}); $D_e = D_l + K_h\,D_g$ is effective dispersion coefficient (cm^2 s^{-1}); h is a mass transfer coefficient (cm s^{-1}) defined as $h = D_g^{\text{air}}/b$, where D_g^{air} is the binary gas diffusion coefficient in the air (cm^2 s^{-1}) and b is the thickness of a stagnant boundary layer at the soil surface (cm) (Jury et al., 1983).

The degradation rate, Henry's Law constant, vapor diffusion coefficient, and film permeability are temperature-dependent. To account for temperature effect, the Arrhenius equation was used in model simulations to calculate a value for these parameters at a specific temperature and time:

$$\beta_T = \beta_r e^{-E_a \frac{(T-T_r)}{RTT_r}} \tag{5}$$

where β_T is a temperature-dependent parameter; β_r is the reference value for the parameter at a reference temperature; E_a is the activation energy for the parameter β_T (J mol^{-1}); T_r is the reference temperature (K); and R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

To quantitatively evaluate organism exposure to pesticides, a concentration-time index, CT, which is the integral of concentration over time was used:

$$\mathrm{CT}(t) = \int_0^t C_T(x,y,z,t)\mathrm{d}t \tag{6}$$

A logistic dose–response curve was used to describe the relationship between organism mortality, y, and CT:

$$y = \frac{100\%}{1 + \left(\frac{\mathrm{CT}}{\mathrm{CT}_{50}}\right)^{-p}} \tag{7}$$

where p is the slope at the inflection point of the logistic curve, CT_{50} is the effective CT required to give a 50% mortality.

2.2. Experiment description

A complete description of the laboratory soil column experiments with simulated shank injection of MeI is given by Ashworth et al. (2011). Soils were collected from two fields on a farm near Buttonwillow, CA (fine-loamy, mixed, thermic Typic Haplargids; Milam series). The primary difference between the two soils was organic matter content since composted green waste material was previously applied to one of the fields, elevating organic matter content from 2.09 to 3.16%. The laboratory experiments were designed to reproduce the field soil and environmental conditions. Briefly, soil was packed into cylindrical (12 × 150 cm) stainless steel columns, maintaining field-measured bulk density and moisture content of the soil. Near-surface soil temperatures were manipulated by programming the ambient temperature of the room in which the column experiments were conducted. A stainless steel flux chamber placed on the surface of the soil column was swept with clean air to channel emitted fumigant through sorbent tubes after MeI injection at 30 cm depth.

The experiments compared HOM, Irrigation and VIF treatments to a Control (bare soil). The higher organic matter soil was used for HOM treatment and all other treatments used the lower organic matter soil. For the VIF treatment, the plastic film was applied over the soil surface and a seal was created between the soil column and the flux chamber using epoxy resin, producing a leak-free barrier. On day 14, the VIF was ripped via a sealable port in the sidewall of the flux chamber. Irrigation was performed by inserting a pronged irrigation device into the volatilization chamber and evenly distributing 1 cm of water onto the soil surface. This was performed 3 h after application of the MeI, and repeated daily for the first five days of the experiment.

2.3. Simulation scenarios and parameterization

MeI emission and pest control for other scenarios listed and described in Table 1 were also evaluated. Model simulations of the column experiments were carried out using Hydrus1D (Šimunek et al., 2008), modified to include various fumigant-related processes, such as temperature-dependent properties of the surface tarp and removal of the tarp at a specified time.

The relevant experimental conditions and model parameters are given in Table 2. These simulation parameters included the properties of soil, fumigant and film (if applicable) and initial and boundary conditions. The parameters were obtained from either a direct experimental measurement or from the literature, when a measured value was not available. Default soil hydraulic properties and heat transport properties for the sandy loam soil in Hydrus 1D were used for all simulations.

Specifically, the first-order degradation rate constant was 0.0026 h^{-1} for the untreated soil based on the experimental measurement (Ashworth et al., 2011). The activation energy of the first-order degradation rate constant was estimated from the data reported by Zheng et al. (2004). Henry's constant was 0.23 (dimensionless) at 25 °C (Gan and Yates, 1996). The activation energy of Henry's constant was not reported in the literature, so the value of MeBr was substituted for MeI (Yates et al., 2003) because of the similarity between MeI and MeBr. Sorption coefficient was set to be zero based on the measurement of Gan et al. (1996). MeI binary gas diffusion coefficient, D_{ab}, and its activation energy were estimated using Fuller correlation (Reid et al., 1987). Tortuosity of soil pore space was calculated using the Moldrup et al. (2000) method, which was implemented in Hydrus1D.

For the volatile boundary, a boundary layer thickness (b) of 0.5 cm was used to calculate mass transfer coefficient (h) for the non-tarped treatments (Jury et al., 1983). For HDPE and VIF, mass transfer coefficients from Papiernik et al. (2011) were used to determine b and its activation energy (Table 2). After removing VIF at 14 days, b was changed from 370,531 cm (for VIF) to 0.5 cm (for bare soil). The atmosphere boundary for water, solute and heat transport was used for the soil surface and non-flow boundary was used for the bottom end of the soil column (Šimunek et al., 2005).

The survivability of three types of soil-borne pest was predicted based on the dose–response curves from Luo et al. (2011). Specifically, for Eq. (7), the CT_{50} for citrus nematodes, barnyard weed seeds, and fungi were 13.1, 185.9, and 1194.6 μg h mL^{-1}, respectively and p for citrus nematodes, barnyard seeds, and fungi were 1.55, 4.89, and 13.1, respectively.

Table 1
Description of various MeI emission reduction strategies. Application depth is 30 cm except for Deep, which is 46 cm.

#	Treatment	Description
1.	Control	Bare surface.
2.	HOM	Previously adding composted green waste material to the field, elevating organic matter content from 2.09 to 3.16%.
3.	VIF	Covering soil surface with virtual impermeable film (VIF) and removing the film at 14 days.
4.	Irrigation	Being Irrigated 1 cm water each day at 10:30 am for 5 days (rate was 2 cm h^{-1}).
5.	HDPE	Covering soil surface with high density polyethylene film (HDPE).
6.	Deep	Increasing injection depth from 30 cm to 46 cm.
7.	Deep + HDPE	Combining treatments 5 & 6.
8.	Reagent	Adding a reagent at top 3 cm soil, with a MeI degradation rate 100 times of that of Control.
9.	Reagent + Irrigation	Irrigating the soil surface with 2 cm water and adding the same reagent as listed in treatment 8.
10.	Reagent + HDPE	Combining treatments 5 & 8.

Table 2
Experimental conditions and simulation model parameters for model simulations for ten treatments of MeI fumigation. The surface area of the column was 113.1 cm^2.

Treatment/Data Type	Properties	Value	Units
MeI properties	Henry's law constant at 25°C[a]	0.23	dimensionless
	Binary Gas diffusion coefficient at 20°C[c]	370.5	$cm^2\ h^{-1}$
	Binary water diffusion coefficient at 20 °C	0.115	$cm^2\ h^{-1}$
Activation energy for T-dependence	Binary Gas diffusion coefficient[c]	4403	$J\ mol^{-1}$
	Henry's law constant[d]	26080	$J\ mol^{-1}$
	Degradation rate constant[e]	39700	$J\ mol^{-1}$
Heat transport	Initial soil temperature with depth	25–22	°C
	Temperature range	19–32	°C
Initial concentration	Initial mass, 150 μL of MeI	182.4	mg
	Initial water content:		
	0–15 cm deep,	10.5	$cm^3\ cm^{-3}$
	15–30 cm deep,	13.5	$cm^3\ cm^{-3}$
	30–45 cm deep,	18	$cm^3\ cm^{-3}$
	45–60 cm deep,	21	$cm^3\ cm^{-3}$
	>60 cm deep,	24	$cm^3\ cm^{-3}$
All Treatments	Organic matter content	2.7	%
(unless other data provided)	Sorption coefficient	0	$cm^3\ g^{-1}$
	Degradation rate constant[b]	0.0026	h^{-1}
	Injection depth	30	cm
HOM	Degradation rate constant[b]	0.0100	h^{-1}
Irrigation	Irrigated 1 cm water each day at 10:30 am for 5 days (rate was 2 cm h^{-1})		
VIF properties	EquivalentBoundary Layer Thickness, b_{ref} (cm)[f]	370,531	cm
	Arrhenius Equation Activation Energy, E_a, for b[f]	102,000	$J\ mol^{-1}$
HDPE properties	Equivalent Boundary Layer Thickness, b_{ref} (cm)[f]	92.5	cm
	Arrhenius Equation Activation Energy, E_a, for b[f]	26,577	$J\ mol^{-1}$
Deep	Injection depth	46	cm
Reagent	Degradation rate constant for top 3 cm soil	0.0026* 100	h^{-1}

[a] Gan and Yates, (1996).
[b] Ashworth et al. (2011).
[c] Reid et al. (1987).
[d] Yates et al. (2003) (the same as MeBr).
[e] Zheng et al. (2004).
[f] Papiernik et al. (2011) (Film FM5 for HDPE, the midpoint of the b range@20 °C was used).

3. Results and discussion

3.1. Methyl iodide emission

3.1.1. Comparison between observations and simulations

Simulated emission fluxes of MeI for the Control, Irrigation, HOM, and VIF treatments, together with the measured values, are shown in Fig. 1. The relatively simple trend in the emission fluxes for the Control, Irrigation and HOM treatments (i.e., large, very early, initial peak, followed by rapid decline in emissions and then tailing) was well reproduced by the model. The simulated peak time was consistent with that of measurement for each treatment (occurred very rapidly, 2–4 h sample period after fumigation except for the VIF treatment). However, it is clear that the magnitude of the peak emission rate was underestimated for the Control but was within the standard error bars, around 27% less than the measured mean value. Similarly, the simulations also underestimated the peak for the HOM and Irrigation treatments, about 5% and 33% lower than the measured peak values, respectively. The root mean square errors for emission fluxes were 28.6, 7.7, 8.5, and 3.6 μg $m^{-2}\ s^{-1}$ for the Control, HOM, Irrigation, and VIF treatments, respectively.

For the VIF treatment, the emission trend was different from other treatments. During the first 14 days, the emission rates were very low, with a maximum peak about 0.02% of that of the control. The ripping of VIF at 14 days caused a marked spike in emission rates from 0.0003 μg $m^{-2}\ s^{-1}$ (at 338 h) to around 30 μg $m^{-2}\ s^{-1}$ (at 340–344 h) according to measurements. The general pattern of higher emissions was reproduced by the model. Nevertheless, in contrast to the other treatments, the model markedly overestimated the measured emission fluxes. This could have been caused by using a value for the mass transfer coefficient that was too high for the piece of film actually used in the experiments. Even so, the model seemed to capture the order-of-magnitude effect of using VIF, that is, a reduction in peak emission rates from the range 100–1000 to 0.1–1.0 μg $m^{-2}\ s^{-1}$. Both the measured and simulated showed a peak in the emission rate quickly after ripping the film, 35.6 and 88.6 μg $m^{-2}\ s^{-1}$ for the measured and simulated curve, respectively.

Cumulative emissions of MeI, expressed as a percentage of the applied mass, are also shown in Fig. 1 (insets). Considering the discrepancies between the measured and simulated peak emission fluxes, the total emission losses are relatively accurately simulated. The difference for the Control and Irrigation was relatively small, about 3–4%. The largest discrepancy was observed for the VIF treatment, 9.6% difference within measured period (400 h). The discrepancy became larger when the simulation time increased to 663 h, resulting in a total emission loss of 23.6% (i.e., 18.9% difference). The large variation in the measured emission values (Table 3) indicates that the experimental uncertainty may mainly contribute to the discrepancy. After 14 days, a considerable amount of MeI still resided in the soil (according to the measured MeI degradation rate, about 41.2% of applied MeI remained in the soil). This led to a large amount of MeI escaping into air after ripping.

The above results suggest that the simulation model, properly parameterized, provides reasonably accurate MeI emissions that are obtained from laboratory experimentation. The model provided the same ranking as the experimental measurements in efficiency of peak emission flux reduction (i.e., VIF > Irrigation > HOM) and total emission loss reduction (i.e., VIF > HOM > Irrigation). The HOM treatment led to a higher degradation rate, about four times that of the control soil. However, the quick emission of MeI after application resulted in limited reaction time and only a 20% reduction in total emission. Similarly, the irrigation treatment did

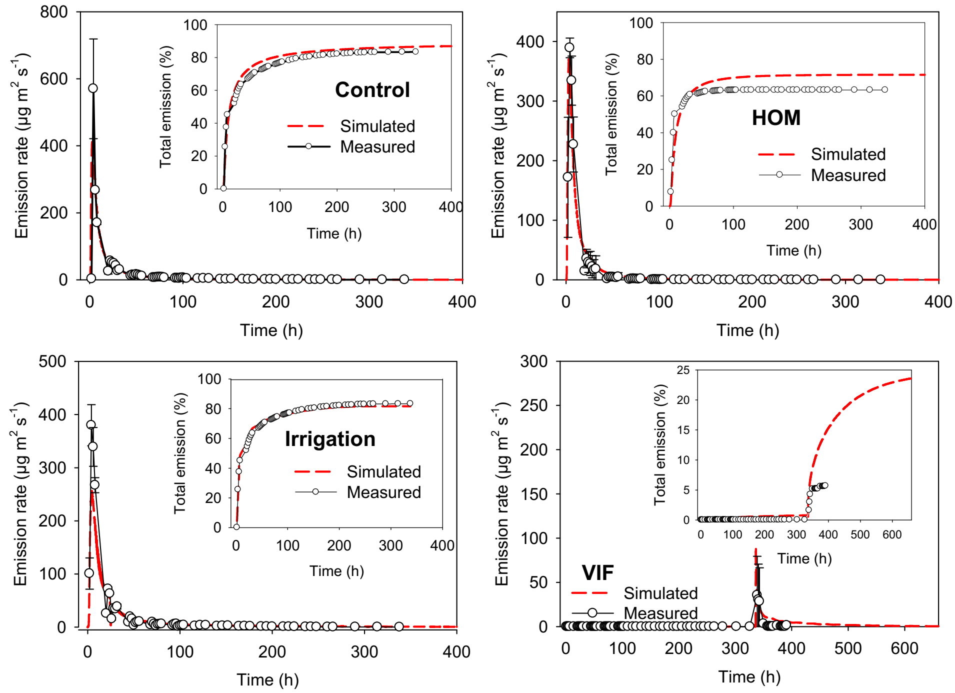

Fig. 1. Measured and simulated MeI emission fluxes for the Control, Irrigation, HOM, and VIF treatments.

not lead to a considerable reduction in MeI emissions, despite reducing the maximum peak emission flux by about 35% relative to the Control. Ashworth et al. (2011) suggested that the initial 1 cm irrigation was insufficient to effectively form a barrier of water-filled pore space for MeI due to rapid MeI emissions.

3.1.2. Simulating a wider range of emission reduction strategies

Simulated emission fluxes of MeI for the HDPE, Deep, Deep + HDPE, Reagent, Reagent + Irrigation and Reagent + HDPE treatments are shown in Fig. 2. Despite reducing the peak emission flux by 40.5% relative to the Control, the HDPE treatment did not cause a significant reduction in total emission. The simulated total emission reduction by HDPE relative to the Control (5.8%) was about the same as the previously observed value for MeI (6%; Gan et al., 1997). The Deep treatment substantially reduced the peak emission flux compared to the control (by 30%). However, a total of about 75.6% of the applied MeI was emitted into air (i.e., a 13% reduction). Again, the data confirms that HDPE alone and deep injection alone are not effective methods for reducing MeI emissions (Ashworth et al., 2009).

Previous study has shown that thiourea accelerated the degradation of MeI in soil and has potential to serve as a reagent when applied at the soil surface. The degradation rate was significantly increased (about 12 times) when the mass ratio (thiourea vs. MeI) was 2:1 (Zheng et al., 2004). Gas phase MeI concentration at soil surface is typically less than 10 μg mL^{-1} (Ashworth et al., 2011). When a reagent is only distributed at the soil surface (e.g., 3 cm), the mass ratio of reagent vs. MeI is likely to be very high. For example, Ashworth et al. (2009) used an application rate of 50 g m^{-2} for ammonium thiosulfate, a reagent of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) (equivalent to 1667 μg mL^{-1} when assuming it is only distributed at the top 3 cm). The higher mass ratio will result in more rapid degradation. Here, we assume a degradation rate of 100 times greater in the top 3 cm

Table 3
Measured and simulated total emission losses of MeI from soil columns. The number in parentheses is the standard deviation of the mean ($n = 2$). The data were not available for the blank.

Treatment	Total emissions				Peak emission			
	Measured (%)	Simulated (%)	Measured reduction (%)[a]	Simulated reduction (%)[a]	Measured (μg m^{-2} s^{-1})	Simulated (μg m^{-2} s^{-1})	Measured reduction (%)[a]	Simulated reduction (%)[a]
Control	83.3 (0.69)	86.9			570.1 (148.6)	417		
HOM	63.2 (2.35)	71.57	24.1	17.6	389.4 (16.4)	370.5	31.7	11.2
VIF	5.7 (4.2)[b]	15.3[b]	93.2[b]	82.4[b]	35.6 (44)	88.53	93.8	78.8
Irrigation	81.6 (3.7)	76.6	2.0	11.9	379.9 (38.8)	256	33.4	38.6
HDPE		81.9		5.8		248.3		40.5
Deep		75.6		13.0		126.6		69.6
Deep + HEDP		70.1		19.3		81.8		80.4
Reagent		66.5		23.5		312.6		25.0
Reagent + irrigation		49.5		43.0		87.1		79.1
Reagent + HDPE		23.3		73.2		93.1		77.7

[a] Compared to the Control.
[b] Within 400 h after fumigation.

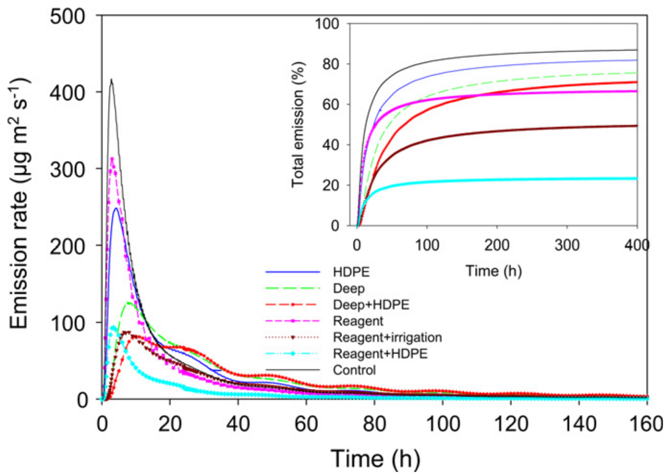

Fig. 2. Predicted MeI emission fluxes for the HDPE, Deep, Deep + HDPE, Reagent, Reagent + Irrigation, and Reagent + HDPE treatments.

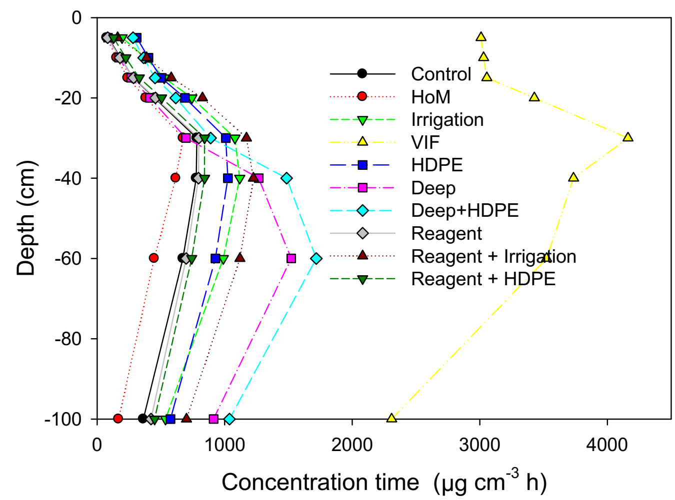

Fig. 3. Predicted MeI concentration-time values along soil depths for the Control, irrigation, HOM, VIF, HDPE, Deep, Deep + HDPE, Reagent, Reagent + Irrigation, and Reagent + HDPE treatments.

soil than that of the control soil. Total emission and peak emission flux were reduced by 23.5% and 25.0%, respectively. The reduction in total emission was more effective than the HDPE and Deep treatments.

There are few studies to determine the effects of integrated management practices on fumigant emissions. Using a simulation model, three types of integrated methods were tested here. When coupling the HDPE and Deep treatments, the total emission reduction was about the sum of each method alone (19.3%). The peak emission rate was only about 20% of the Control. When a reagent was applied together with irrigation at soil surface, less pore space is available for fumigant diffusion, leading to an increased reaction time in the soil and a reduction in emissions (total emission reduced by 43% and peak emission rate reduced by 80%). The Reagent + HDPE treatment significantly reduced the total emission (by 73.2%) and peak emission rate (by 77.7%). Clearly, compared with irrigation (2 cm water), HDPE produced a better barrier for MeI emission when a reagent was available. Interestingly, Xuan et al. (2011) proposed the use of reactive films consisting of a reagent between two films as a method to reduce fumigant atmospheric emission.

It is clear that coupling of different methods can lead to a significant improvement in emission reduction and thus has great potential to mitigate air pollution. For example, irrigation is a common practice and usually required before fumigation. Integration of this method to other emission reduction methods provides a simple and economical mitigation strategy. Though HDPE alone is not very effective in emission reduction, being used together with other methods such as a reactive surface barrier, can lead to a significant reduction in emissions.

3.2. *Pest control*

The predicted MeI concentration-time values in the soil profile for all treatments are shown in Fig. 3. Generally, the CT values were relatively high within about 30 cm below the injection depth. As expected, the HOM treatment reduced the CT values because of more rapid degradation relative to the Control. However, the reduction was not significant in the top 20 cm, probably due to rapid volatilization of MeI into air for any treatment without a surface barrier. The reduction in CT values became more evident with increasing depth. The Deep treatment also slightly reduced the CT values in the top 30 cm but notably raised the values of the deeper soil. Reagent had little effect on the CT values in the soil profile, since enhanced degradation only occurred near the soil surface. With a barrier of water or film at soil surface, the CT values were elevated in the soil profile. The VIF treatment was the most effective to contain MeI in the soil, having at least 3 times higher CT values than other treatments.

Survivability of three types of soil pests with different sensitivity to MeI were predicted (Fig. 4). Overall, control of soil pests was best between 30 and 60 cm. The VIF treatment had the highest efficacy with nearly full control of all three types of pests. Control of fungi within the top 20 cm soil was very limited for other treatments. Fungus control for the Deep treatments (Deep and Deep + HDPE) was the next best, with more than 60% fungi killed within 40–60 cm. Compared to the Control, the HDPE and Irrigation treatments showed an increase in fungus mortality but were still relatively ineffective compared to the VIF treatment. For nematodes and weed seeds, there was also relatively poor control near the soil surface. As expected, the HOM, Deep and Reagent treatments weakened nematode and seed control within the top 30 cm soil relative to the Control. Except for VIF, HDPE, and Deep + HDPE treatments, more than 40% of the seeds in the top 15 m soil were still alive following fumigation. Because citrus nematode is the most sensitive to MeI among the three types of soil pests (Luo et al., 2011), more than 90% of nematodes were killed for all treatments for the top 100 cm soil.

It has been reported that the lethal CT values decrease with soil temperature (Xue et al., 2000) and even temperature alone can suppress soil pests (Yates et al., 2011b). Therefore, modeling soil pest survival can be improved by considering the effect of soil temperature and its synergy with fumigants. Future research is needed to develop a database of organism survival as a function of temperature and fumigant concentration. Moreover, pest control efficacy for different treatments should not be simply compared by using the average pest mortality of the whole profile or any depth. For example, since pest control in the top 15 cm soil is typically the most critical for crop plant growth, especially the early stage, emphasis should be made to increase the CT values in the vicinity of the soil surface. To achieve this, covering the soil surface with impermeable films is a highly effective practice because impermeable tarps at the soil surface maintain fumigant concentrations and simultaneously increase surface daytime soil temperatures up to 14 °C (Yates et al., 2011b); these may act together to enhance the pest control for the surface soil layer.

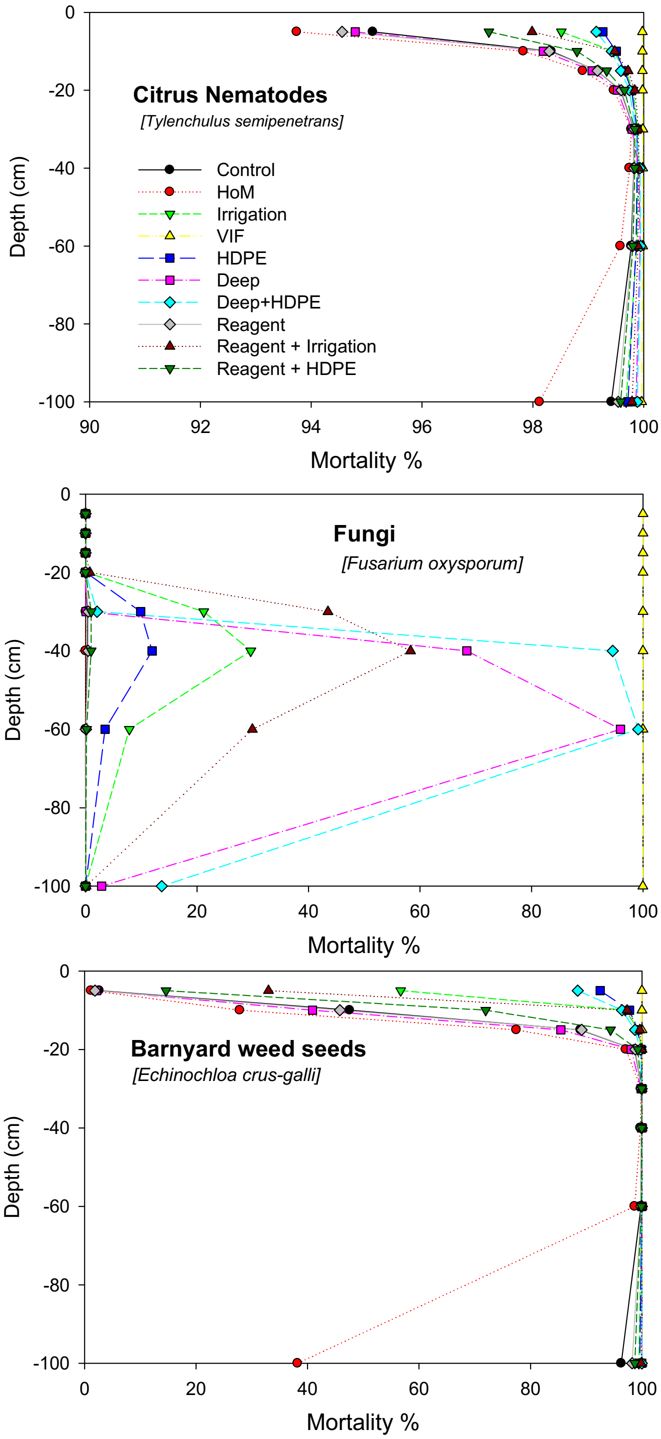

Fig. 4. Predicted MeI mortality of three types of soil pests (citrus nematodes [*Tylenchulus semipenetrans*], barnyard seeds [*Echinochloa crus-galli*], fungi [*Fusarium oxysporum*]) along soil depths for the Control, Irrigation, HOM, VIF, HDPE, Deep, Deep + HDPE, Reagent, Reagent + Irrigation, and Reagent + HDPE treatments (notice the different *x*-axis for citrus nematodes).

4. Conclusions

With the registration of MeI, there is great potential of excessive atmospheric emissions following soil fumigation. This can become a serious concern due to the high toxicity of this fumigant. In this study, numerical simulations were performed to simulate shank injection of MeI in soil and to determine the effects of different emission reduction methods on pest control. The comparisons between the model simulation and laboratory experimentation for the Control, HOM, Irrigation and VIF imply that simulation models provide reasonably accurate emissions of MeI. In summary, the ranking of effectiveness was VIF > Reagent + HDPE > Reagent + Irrigation > Reagent > Deep + HDPE > HOM > Deep > Irrigation > HDPE for total emission reduction, and Deep + HDPE > Reagent + Irrigation > VIF > Reagent + HDPE > Deep > Irrigation > HDPE > Reagent > HOM for peak emission rate reduction. For pest control, the ranking of effectiveness was different from the above. Generally, VIF had the highest pest control efficacy, followed by Deep + HDPE, Irrigation, Reagent + Irrigation, HDPE, Deep, Reagent + HDPE, Reagent, and HOM.

When both atmospheric emission reduction and pest control efficacy are considered, VIF is the best method among nine treatments due to its ability to contain MeI within the soil. When VIF is used, a much lower dosage is required to achieve the same level of pest control, compared to other methods. This should partly offset the cost of VIF since it is expected that VIF is likely to be more expensive than other films such as HDPE. However, attention should be paid to the high emission rate and risk potential when removing the VIF after about two weeks. When VIF is not available, integrated methods such as Deep + HDPE and Reagent + Irrigation, are recommended.

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