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Mitigating 1,3-Dichloropropene, Chloropicrin, and Methyl Iodide Emissions from Fumigated Soil with Reactive Film

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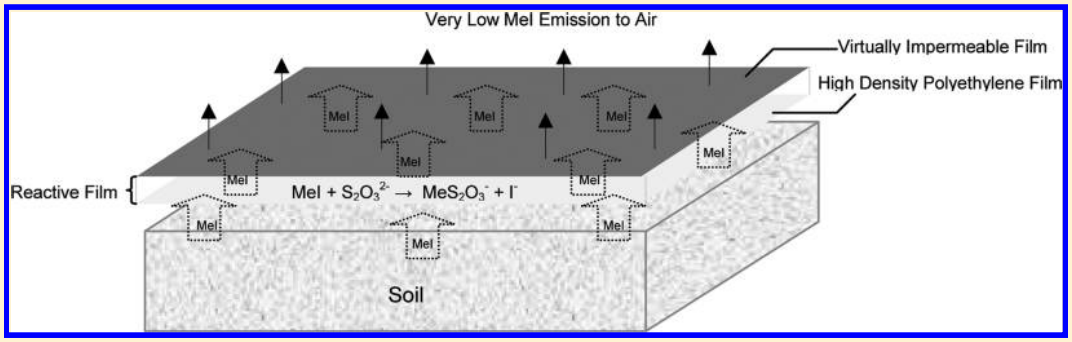

ABSTRACT: Implicated as a stratospheric ozone-depleting compound, methyl bromide (MeBr) is being phased out despite being considered to be the most effective soil fumigant. Its alternatives, i.e., 1,3-dichloropropene (1,3-D, which includes *cis* and *trans* isomers), chloropicrin (CP), and methyl iodide (MeI), have been widely used. High emissions of MeI from fumigated soil likely put farm workers and other bystanders at risk of adverse health effects. In this study, two types of constructed reactive film were tested for their ability to mitigate emissions of 1,3-D, CP, and MeI using laboratory permeability cells. Before activation, these films act as a physical barrier to trap fumigants leaving soil. After activation of the reactive layer containing ammonium thiosulfate solution, the films also act as a sink for the fumigants. Over 97% of *trans*-1,3-D and 99% of the *cis*-1,3-D, CP and MeI were depleted when they passed into the reactive film. Half-lives ($t_{1/2}$) of *cis*-, *trans*-1,3-D, CP and MeI under activated reactive film were 1.2, 1.4, 1.6, and 2.0 h respectively at 40 °C.

INTRODUCTION

Methyl bromide (MeBr) is widely used in agriculture in controlling weeds, insects, nematodes, fungi, and other soil-borne diseases and is generally considered to be the most effective soil fumigant. However, having a high potential for depleting stratospheric ozone, agricultural use is being phased out due to emissions from fumigated soil to the atmosphere. To avoid over \$1.3 billion economic loss from the ban on MeBr use, equally effective alternatives are needed.[1] Mixtures of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) are being used as MeBr alternatives. In 2008, 4.3 × 10^3 tons of 1,3-D and 2.5 × 10^3 tons of CP were used in California.[2] Nevertheless, these chemicals are not a complete replacement for MeBr, and 1.0 × 10^3 tons of MeBr was requested in 2011 for the production of strawberries in USA.[3] Methyl iodide (MeI), having a similar soil fumigant activity but negligible potential for depleting stratospheric ozone, is considered to be an efficacious alternative to MeBr. However, it is highly toxic, and its use may cause significant health risks to people working in fumigated fields and living nearby. Its byproduct, iodide ion (I^-), is phytotoxic and may cause pollution of water resources.

Many studies on fumigants have focused on the reduction of their emissions to the atmosphere. A conventional approach is covering the fumigated field with plastic film. High-density polyethylene film (HDPE), commonly used to mitigate MeBr emissions, has been found to be relatively permeable to CP,[4] and ineffective in reducing 1,3-D and MeI emissions.[5,6] Virtually impermeable film (VIF) can effectively trap the fumigants in the soil[7−9] so long as the soil surface is covered. If soil can substantially transform MeI, a great deal of I^- would be left in soil and could potentially contaminate groundwater and harm plants. However, if soil cannot transform MeI, a large amount of residual MeI would likely escape into the atmosphere when VIF is removed or hole-punched during the planting process. Another emission reduction approach is irrigation. In laboratory soil column tests, 1,3-D emission was reduced 2-fold in columns maintained under simulated irrigation compared to columns of nonirrigation.[10] Under field conditions, irrigation reduced 30−50% of the total emission compared to that without surface irrigation.[11]

Both plastic film and water irrigation maintain fumigants in the soil for longer periods so that fumigant transformation can be maximized. Organic material in soil facilitated 1,3-D transformation.[11] An amendment of organic matter can reduce 1,3-D emissions but is only partially effective because of the

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limited capacity of soil and plants to assimilate the added organic material.[12]

Like organic material, many chemicals can accelerate transformation of these fumigants.[13,14] Ammonium thiosulfate (ATS), among them, has many desirable attributes; it is inexpensive and easy to obtain because it is a fertilizer. It can transform MeI, CP and 1,3-D to relatively lower acute toxic byproducts (eq 1),[15]

$$R - X + S_2O_3^{2-} \rightarrow RS_2O_3^{-} + X^{-} \qquad (1)$$

where, R, X represent $-C_3H_4Cl$, Cl; $-CCl_2NO_2$, Cl and −Me, I for 1,3-D, CP and MeI, respectively.

Directly sprayed on the soil surface before the fumigation process, ATS can form a reactive surface barrier, where 1,3-D can be transformed when it diffuses to the soil surface and comes into contact with ATS.[16,17] The problem with using ATS in this way is that the efficacy of fumigants would likely be compromised as they may be transformed before pests are killed. To overcome this, application of ATS solution through drip irrigation systems permits ATS to be added after a certain time following fumigant addition. Nevertheless, an excessive amount of ATS could be required to transform the applied fumigant[18,19] due to the instability of ATS in soil. In addition, the environmental fate and toxicity of the products formed from fumigant reactions with ATS are unknown.[19]

Recently, a reactive film has been designed and prepared for mitigating MeBr emissions from fumigated soil.[20] Its construction included a permeable under-layer (facing the fumigated soil), an impermeable upper-layer (remote from the fumigants source), and an inner-layer containing solid ATS. When the inner layer was dry, the film was inert to fumigants; when wet, the film became reactive. During the fumigation period, and prior to activating the ATS, the barrier properties of the film were tested by measuring the maintenance of the fumigant concentration within soil. After the fumigation period, water was added to the inner-layer, the ATS dissolved, and the reactive film became activated, that is, capable of transforming of fumigants. Over 99% of MeBr could be transformed when MeBr passed into this film.

A standard agricultural film, HDPE, is less expensive than VIF. To obtain a more cost-effective reactive film, the efficacy of a HDPE-RF was tested in this study. This film consisted of two layers of HDPE and a reactive ATS center layer. A test involved determining the film's effectiveness as a physical barrier to 1,3-D, CP, and MeI movement, followed by a test of the film's ability to deplete the fumigants after activating the ATS center layer. In addition, the efficacy of VIF-RF, in which the upper-lay of HDPE was replaced with VIF, was also tested. All of the experiments were performed in permeability cells.

■ MATERIALS AND METHODS

Reagent and Film. 1,3-D (98.9% purity, including 50:50 *cis-* and *trans*-1,3-D isomers) and chloropicrin (99.9%) were donated by Dow Agrosciences (Indianapolis, IN). MeI (>99%) and ammonium thiosulfate (ATS) (purity 99%) were purchased from Sigma Chemical Co. (St. Louis, MO). Both 1.5 mil Hytibar VIF (Klerks Plastics, Hoogstraten, Belgium) and 1 mil HDPE film (Dow Chemical Company, Midland, MI) were used in the construction of the reactive film. Paper tissue was purchased from Horizon Industries (Tyler, TX) and used in the center layer.

Preparation of Reactive Films. A typical nonactivated HDPE-RF was constructed with two outer layers of HDPE, and an inner layer comprised of two pieces of paper tissue containing 44.2 g m^{-2} solid ATS. In an activated HDPE-RF, the ATS was dissolved in 132.7 g m^{-2} water and absorbed on the tissue paper. In a blank HDPE-RF, there was no ATS. A control RF merely consisted of two layers of HDPE.

In VIF-RF, the under-layer of plastic film was HDPE and the upper-layer was VIF. Either 44.2, 88.5, or 132.7 g m^{-2} of ATS and 132.7 g m^{-2} of water were used in the reactive films.

Permeability Cells. The permeability cell was a cylindrical stainless steel cell, which was composed of one source chamber and one receiving chamber.[21] In these experiments, each chamber was 4.0 cm deep and 12.0 cm inside diameter. The two chambers were fitted together with a film sandwiched between them and the joint was sealed with epoxy resin and an adhesive aluminum tape. The under-layer of the reactive film faced the source chamber. In the middle of each chamber's wall, there was a sampling port which was plugged with Teflon-faced silicon septum. Through the port, 1,3-D, CP, and MeI gases could be injected into the source chamber at the beginning of the experiment and, at certain time intervals, gases could also be sampled from both the source and receiving chambers with a gastight syringe. Experiments were carried out at room temperature (20 ± 1 °C) or in incubators at 10 ± 1 °C and 40 ± 1 °C.

Spiking, Sampling, and Analysis. A 1 L glass cylinder was spiked with 200 μL of 1,3-D, 20 μL of CP, and 7 μL of MeI. After equilibration for 30 min at room temperature, 25.0 mL of the mixed gas was transferred into the source chamber of the permeability cell using a gastight syringe. The initial concentrations of *cis-* and *trans*-1,3-D, CP, and MeI in the source chamber were 2.2 ± 0.055, 1.7 ± 0.043, 0.45 ± 0.011, and 0.60 ± 0.015 mg L^{-1}. At selected time intervals, 250 μL of gas from both the source and receiving chambers was transferred into a 12.1 mL headspace vial using a glass gastight syringe and was immediately capped with a Teflon-faced butyl rubber septum and an aluminum seal. For each reactive film, triplicate permeability cells were tested.

Samples were analyzed on a Hewlett-Packard HP 6890 A gas chromatograph (GC) equipped with a microelectron capture detector (μECD) and an interfaced Agilent Technologies G1888 Network Headspace Sampler. A DB-VRX fused silica capillary column (30 m × 0.25 mm i.d. × 1.4 μm, J&W, Folsom, CA) was used with the following conditions: helium carrier gas flow rate at 1.4 mL min^{-1}; injector temperature 240 °C; detector temperature 280 °C; initial oven temperature program of 45 °C held for 1 min and then increased to 80 at 2.5 °C min^{-1}. The headspace sampler was used with following conditions: oven 80 °C, loop temperature 90 °C, transfer line temperature 100 °C, and headspace vial equilibration time in oven for 5.0 min. The sample loop was 1000 μL. Retention times of *cis-*, *trans*-1,3-D, CP, and MeI were 11.96, 12.22, 13.58, and 3.79 min, respectively. Calibration standards for the GC analysis were prepared from their stock solution at seven concentrations in headspace vials and were analyzed at the beginning of each set of samples.

Data Analysis. The process of fumigant diffusion from source chamber to receiving chamber through reactive film was described by advection-diffusion equations.

In the receiving chamber:

Table 1. Film Permeability (*h*_s, *h*_r) and Fumigant Degradation Rate (μ_R) within HDPE-RF (at 20 °C, ATS 44.2 g m^{-2})

fumigants	HDPE-RF	equilibrium time (h)	*h*_s (cm h^{-1})	*h*_r (cm h^{-1})	μ_R (h^{-1})	r^2
cis-1.3-D	control	<6	2.05 ± 0.27	2.05 ± 0.27		0.99
	blank	<6	1.86 ± 0.36	1.86 ± 0.36		>0.99
	nonactivated	<6	2.03 ± 0.44	2.03 ± 0.44		0.98
	activated		2.20 ± 0.00	0.65 ± 0.00	69.9 ± 13.8	>0.99
trans-1.3-D	control	<6	3.42 ± 0.48	3.42 ± 0.48		0.99
	blank	<6	3.11 ± 0.70	3.11 ± 0.70		0.98
	nonactivated	<6	3.62 ± 0.82	3.62 ± 0.82		0.98
	activated		3.22 ± 0.00	1.50 ± 0.00	38.3 ± 4.96	>0.99
CP	control	<24	0.466 ± 0.072	0.466 ± 0.072		0.99
	blank	<24	0.400 ± 0.066	0.400 ± 0.066		0.99
	nonactivated	<24	0.426 ± 0.071	0.426 ± 0.071		0.99
	activated		0.918 ± 0.000	0.020 ± 0.00	33.6 ± 9.6	>0.99
MeI	control	<24	0.650 ± 0.048	0.650 ± 0.048		>0.99
	blank	<24	0.594 ± 0.055	0.594 ± 0.055		>0.99
	nonactivated	<24	0.628 ± 0.068	0.628 ± 0.068		>0.99
	activated		1.04 ± 0.00	0.10 ± 0.00	21.1 ± 5.0	>0.99

Table 2. Effect of Different ATS Application Rates on Permeability and Depleting Efficacy of VIF-RF

fumigants	ATS application Rate (g m^{-2})	*k* (h^{-1})	r^2 for *k*	$t_{1/2}$ (h)	*h*_s (cm h^{-1})	*h*_r (cm h^{-1})	μ_R (h^{-1})	r^2 for μ_R	$t_{1/2,\mu}$ (h)
cis-1,3-D	0								292[a]
	44.2	0.354 ± 0.009	>0.99	2.0	2.20	0.02	79.2 ± 9.4	>0.99	0.009
	88.5	0.276 ± 0.008	>0.99	2.5	2.20	0.02	44.5 ± 4.5	>0.99	0.016
	132.7	0.220 ± 0.008	>0.99	3.2	2.20	0.002	29.5 ± 2.8	>0.99	0.023
trans-1,3-D	0								292[a]
	44.2	0.305 ± 0.011	>0.99	2.3	3.22	0.05	38.8 ± 3.6	>0.99	0.018
	88.5	0.245 ± 0.008	>0.99	2.8	3.22	0.01	28.2 ± 2.1	>0.99	0.025
	132.7	0.203 ± 0.020	>0.99	3.4	3.22	0.005	21.8 ± 4.6	>0.99	0.032
CP	0								2009[a]
	44.2	0.136 ± 0.013	0.99	5.1	0.918	0.00001	26.7 ± 10.1	>0.99	0.026
	88.5	0.125 ± 0.003	>0.99	5.5	0.918	0.00001	22.2 ± 1.7	>0.99	0.031
	132.7	0.122 ± 0.008	0.99	5.7	0.918	0.00001	20.9 ± 4.9	>0.99	0.033
MeI	0								7280[a]
	44.2	0.131 ± 0.007	>0.99	5.3	1.04	0.007	21.1 ± 3.4	>0.99	0.033
	88.5	0.117 ± 0.002	>0.99	6.0	1.04	0.007	17.1 ± 1.1	>0.99	0.041
	132.7	0.112 ± 0.003	>0.99	6.2	1.04	0.007	15.6 ± 1.3	>0.99	0.044

[a] The data is from ref 15.

$$\frac{\partial C_r}{\partial t} + \frac{1}{L_r}\frac{\partial S_r}{\partial t} = D_r\frac{\partial^2 C_r}{\partial x^2} - \mu_r C_r + Q_r(x, t) \quad (2)$$

In the reactive layer:

$$\frac{\partial C_R}{\partial t} + \frac{1}{L_R}\frac{\partial S_R}{\partial t} = D_R\frac{\partial^2 C_R}{\partial x^2} - \mu_R C_R - Q_r(x, t) - Q_s(x, t) \quad (3)$$

and in the source chamber:

$$\frac{\partial C_s}{\partial t} + \frac{1}{L_s}\frac{\partial S_s}{\partial t} = D_s\frac{\partial^2 C_s}{\partial x^2} - \mu_s C_s + Q_s(x, t) \quad (4)$$

where *C* is concentration (mg cm^{-3}) of each fumigant in the chamber air at time *t* (h), *L* is the length of chamber (cm), *S* is the mass of adsorbed fumigants per reactive film area (mg cm^{-2}), *D* is the effective diffusion coefficient (cm^2 h^{-1}), μ is a first-order decay coefficient, and *Q*(*x*,*t*) is any source or sink from diffusion. The letters of r, R, and s indicate the receiving chamber, reactive layer, and source chamber, respectively. Assuming the fumigant in the chambers and reactive layer is mixed very well, eqs 2–4 can be reduced to

$$\frac{\partial C_r}{\partial t} + \frac{1}{L_r}\frac{\partial S_r}{\partial t} = -\mu_r C_r + Q_r(x, t) \quad (5)$$

$$\frac{\partial C_R}{\partial t} + \frac{1}{L_R}\frac{\partial S_R}{\partial t} = -\mu_R C_R - Q_r(x, t) - Q_s(x, t) \quad (6)$$

$$\frac{\partial C_s}{\partial t} + \frac{1}{L_s}\frac{\partial S_s}{\partial t} = -\mu_s C_s + Q_s(x, t) \quad (7)$$

Fumigants in the source or receiving chambers did not degrade significantly, but did degrade in the reactive layer. Eqs 5–7 can further be reduced to

$$\frac{\partial C_r}{\partial t} + \frac{1}{L_r}\frac{\partial S_r}{\partial t} = Q_r(x, t) \quad (8)$$

$$\frac{\partial C_R}{\partial t} + \frac{1}{L_R}\frac{\partial S_R}{\partial t} = -\mu_R C_R - Q_r(x, t) - Q_s(x, t) \quad (9)$$

$$\frac{\partial C_s}{\partial t} + \frac{1}{L_s}\frac{\partial S_s}{\partial t} = Q_s(x, t) \quad (10)$$

Table 3. VIF-RF Permeability to Fumigants and Fumigant Degradation Rate at Three Differing Temperatures

fumigants	temp.	k (h^{-1})	r^2 for k	$t_{1/2,s}$ (h)	E_a (r^2) (kJ mol^{-1})	h_s (cm h^{-1})	E_{a,h_s} (r^2) (kJ mol^{-1})	h_r (cm h^{-1})	μ_R (h^{-1})	r^2 for μ_R	$t_{1/2,R}$ (h)
cis-1,3-D	10	0.190 ± 0.012	0.99	3.6	26.6 (0.96)	1.54	31.9 (>0.99)	0.01	30.2 ± 6.3	>0.99	0.023
	20	0.348 ± 0.026	0.99	2.0		2.20		0.02	76.3 ± 26.4	0.99	0.009
	40	0.582 ± 0.028	>0.99	1.2		5.54		0.05	80.5 ± 12.2	>0.99	0.009
trans-1,3-D	10	0.151 ± 0.013	0.99	4.6	28.5 (0.93)	2.39	24.1 (>0.99)	0.01	16.1 ± 3.1	0.99	0.043
	20	0.306 ± 0.027	0.99	2.3		3.22		0.02	39.4 ± 9.3	0.99	0.018
	40	0.507 ± 0.037	>0.99	1.4		6.31		0.06	59.5 ± 11.0	>0.99	0.012
CP	10	0.066 ± 0.006	0.99	10.5	46.0 (>0.99)	0.55	49.6 (0.99)	0.0001	10.2 ± 2.8	0.99	0.068
	20	0.135 ± 0.014	0.99	5.1		0.92		0.0001	26.5 ± 11.1	0.99	0.026
	40	0.432 ± 0.040	0.99	1.6		4.00		0.0001	61.3 ± 16.4	0.99	0.011
MeI	10	0.067 ± 0.002	>0.99	10.3	40.4 (>0.99)	0.47	51.7 (>0.99)	0.003	12.5 ± 1.7	>0.99	0.055
	20	0.123 ± 0.007	>0.99	5.6		1.04		0.007	18.8 ± 3.2	>0.99	0.037
	40	0.350 ± 0.012	>0.99	2.0		3.90		0.03	43.8 ± 4.9	>0.99	0.016

The terms, $Q_r(x,t)$ and $Q_s(x,t)$, include mass transfer coefficients, h_s and h_r (cm h^{-1}), which characterize the fumigant permeability of the under-layer and upper-layer films respectively, and, μ_R (h^{-1}), which is the first-order decay rate coefficient for the reaction of fumigant in ATS solution in the inner layer. The parameters were obtained by fitting eqs 8−10[21] to the experimental data consisting of chamber concentrations using a nonlinear least-squares minimization algorithm.[22] The least-squares minimization algorithm was implemented in a public-domain software program (FilmPC, v. 3.0 which is available at: http://www.ars.usda.gov/Services/docs.htm?docid=21704; verified 4/4/2012). The 95% confidence interval and coefficient of determination (r^2) were obtained and shown in Tables 1, 2, and 3.

To learn how fast the fumigants in the source chamber were depleted by VIF-RFs (acting as a sink), the relationship between the concentration of fumigant in this chamber and reaction time (t, h) was fitted. The simple first-order kinetic model could well describe this relationship. Depletion constant (k, h^{-1}) and half-life of each fumigant ($t_{1/2}$, h) in the source chamber were obtained.

RESULTS AND DISCUSSION

Efficacy of HDPE-RF in Containing and Transforming 1,3-D, CP, and MeI. At 20 °C, *cis*-, *trans*-1,3-D, CP and MeI diffused from the source chamber to the receiving chamber by passing through the control, blank, or nonactivated HDPE-RFs. Within 6 h for *cis*- and *trans*-1,3-D, and <24 h for MeI and CP an equilibrium was reached in gas phase concentration in the two chambers of the permeability cell. With the exception of CP, the equilibrium concentrations were approximately half of the total initial concentration. For CP, the total concentration at equilibrium in the two chambers was 83, 65, and 66% of the initial concentration, respectively, for the control, blank, and nonactivated films. *cis*-, *trans*-1,3-D and MeI were not significantly absorbed by HDPE film, water or tissue paper, whereas CP was partially absorbed by HDPE, as reported by Papiernik et al.[21] In this experiment, CP could also have been absorbed by tissue paper, ATS, and water within the HDPE-RF. Because the total concentration of each fumigant in the chamber remained constant after equilibrium, 1,3-D, CP, and MeI could be considered stable in the presence of HDPE-RF. For each fumigant, the mass transfer coefficient values for different HDPE-RFs were very similar (Table 1).

In contrast, activated HDPE-RF quickly transformed the fumigants, although complete transformation was not reached during the experimental period. Here, the fumigants in the source chamber penetrated the under-layer HDPE and reached the reaction layer where some proportion of each fumigant was transformed. Residual fumigants in the reaction layer then penetrated the second HDPE and reached the receiving chamber. In the source chamber, the concentration of *cis*-, *trans*-1,3-D decreased much more rapidly than CP and MeI. In the receiving chamber, the peak concentration of *cis*-, *trans*-1,3-D, CP, and MeI reached 7.5, 19.8, 0.7, and 3.7% of their initial concentration in source chamber, respectively. As the fumigants were depleted in the inner space of the HDPE-RF, residues in the source and receiving chambers would diffuse into the ATS solution in response to concentration gradients and be transformed. Within the source chamber, the rate of reduction of fumigant was dictated by two factors: the fumigant's diffusion rate through HDPE and the reaction rate between the fumigant and the ATS solution. The concentration of *cis*- and *trans*-1,3-D in the source chamber declined more rapidly than CP and MeI, because the mass transfer coefficients for *cis*-, *trans*-1,3-D for HDPE were much higher, as shown in Table 1.

Overall, nonactivated HDPE-RF did not deplete 1,3-D, CP, and MeI. This means that solid ATS could not transform these fumigants without being dissolved in water; hence it did not effectively trap the fumigants and prevent their emission to the receiving chamber. The activated HDPE-RF, although effective in depleting CP, did not effectively deplete MeI (permitting 3.7% emission) and was even less effective in depleting 1,3-D (permitting up to 19.8% emission). Compared to experiments conducted within a permeability cell, the emissions in field settings will be greater because once fumigants have passed through the film and entered into the atmosphere there is little chance to diffuse into the HDPE-RF for further degradation. Therefore, under field conditions, we could expect that a HDPE-RF barrier would allow some emission of 1,3-D and MeI from the fumigated soil. In an attempt to reduce emissions further, the upper-layer of plastic film of HDPE-RF was replaced with VIF to construct VIF-RF.

Effect of ATS Application Rate on VIF-RF Efficacy. Within the control VIF-RF, < 1, 8, 12 and 20% of MeI, *cis*-1,3-D, *trans*-1,3-D, and CP respectively were absorbed to the film materials. This process took place within the first 10 h of the experiment, after which the concentrations of fumigants remained constant. However, no *cis*-, *trans*-1,3-D or CP were detected in the receiving chamber, and only 0.2% MeI was detected 72 h after spiking fumigants in the source chamber.

Compared to the long half-lives (292−7280 h) in pure water, all of the tested fumigants decomposed in ATS solution rapidly (half-lives 0.009−0.044 h). The half-lives of these fumigants in the source chamber ($t_{1/2}$), beneath activated VIF-RFs, were much longer than that in ATS solution ($t_{1/2,\mu}$) (Table 2). Increasing the ATS application rate in the activated VIF-RF had a minor effect on the fumigant elimination rate. Nevertheless, the elimination rate of *cis*-, and *trans*-1,3-D was affected more than that of CP and MeI and likely due to higher h_s values. The $t_{1/2}$ of the *cis*-1,3-D and *trans*-1,3-D in source chamber was prolonged from 2.0 to 3.2 h and 2.3 to 3.4 h respectively when the ATS in the VIF-RF increased from 44.2 to 132.7 g m^{-2}. Therefore, it seems that the fumigant elimination rate decreased with the increasing ATS amount. There was a lack of a strong relationship between the ATS application rate and $t_{1/2}$, and the fact that this occurred whether the values of μ_R were very different at the different ATS application rates (e.g., 1,3-D) or similar (e.g., MeI and CP) indicated that the rate limiting step was not the transformation of fumigants in ATS solution. Rather, the rate limiting step appeared to be the diffusion rate of fumigants through the under-layer of HDPE. This is also supported by the large difference in magnitude between $t_{1/2}$ and $t_{1/2,\mu}$. Compared to HDPE, the smaller value of h_r for VIF increased the fumigant residence time due to an overall lower permeability of VIF-RF than HDPE-RF. In this study, higher ATS concentration resulted in lower μ_R, and this finding suggests that higher ATS application rates are unnecessary in terms of reducing fumigant emission rate.

Activated VIF-RF effectively reduced the diffusion of each fumigant from the source chamber to the receiving chamber (Figure 1). After 72 h, when *cis*-1,3-D in the source chamber was reduced to less than 0.8% of the initial concentration, <0.4% was able to pass through the VIF-RF for the 44.2 g m^{-2} ATS application rate. Increasing the ATS application rate to 132.7 g m^{-2} reduced the *cis*-1,3-D in the receiving chamber to <0.1%. Similarly, *trans*-1,3-D and MeI in the receiving chamber were less than 0.8 and 0.01%, respectively, whereas their concentrations in the source chamber were less than 1.1 and 0.2% of their initial concentrations, respectively. CP did not pass through the VIF-RF until only 0.4% remained in the source chamber. Overall, an activated ATS layer in VIF-RF resulted in a high degree of fumigant transformation, and this, together with the low permeability of the VIF, led to low diffusion rates from the source to the receiving chamber. We believe the results from the permeability cells can serve as a useful approximation of real fields. The amount of fumigant in the receiving chamber can be reasonably regarded as the expected fumigant emissions in the field, because VIF restricts fumigants in the receiving chamber from re-entering the VIF-RF. This is similar to fumigant diffusion through VIF-RF and into the atmosphere.

Effect of Temperature on VIF-RF Efficacy. The effectiveness of activated VIF-RF in eliminating fumigants at different temperatures is shown in Figure 1 for an ATS application rate of 44.2 g m^{-2}. The Arrhenius equation adequately described the relationships between temperature (T) and elimination rate constant (k, h^{-1}) in the source chamber, and T and the mass transfer coefficient of HDPE (h_s) for all the tested fumigants. The activation energies, that is, E_a, and $E_{a,\,h\_s}$, were obtained and reported in Table 3.

The activation energy of VIF-RF (E_a, 24−52 kJ mol^{-1}) for depleting *cis*-, *trans*-1,3-D and CP in the source chamber was similar to that of diffusion through HDPE (E_{a,h_s}), which was in accord with the results of Papiernik, et al.[23] Together with the fact that the elimination rates of all the fumigants in the source chamber were much lower than that in ATS solution, it can be concluded that the rate of fumigant elimination for a VIF-RF was controlled by fumigant diffusion through HDPE rather than reaction between fumigants and ATS solution.

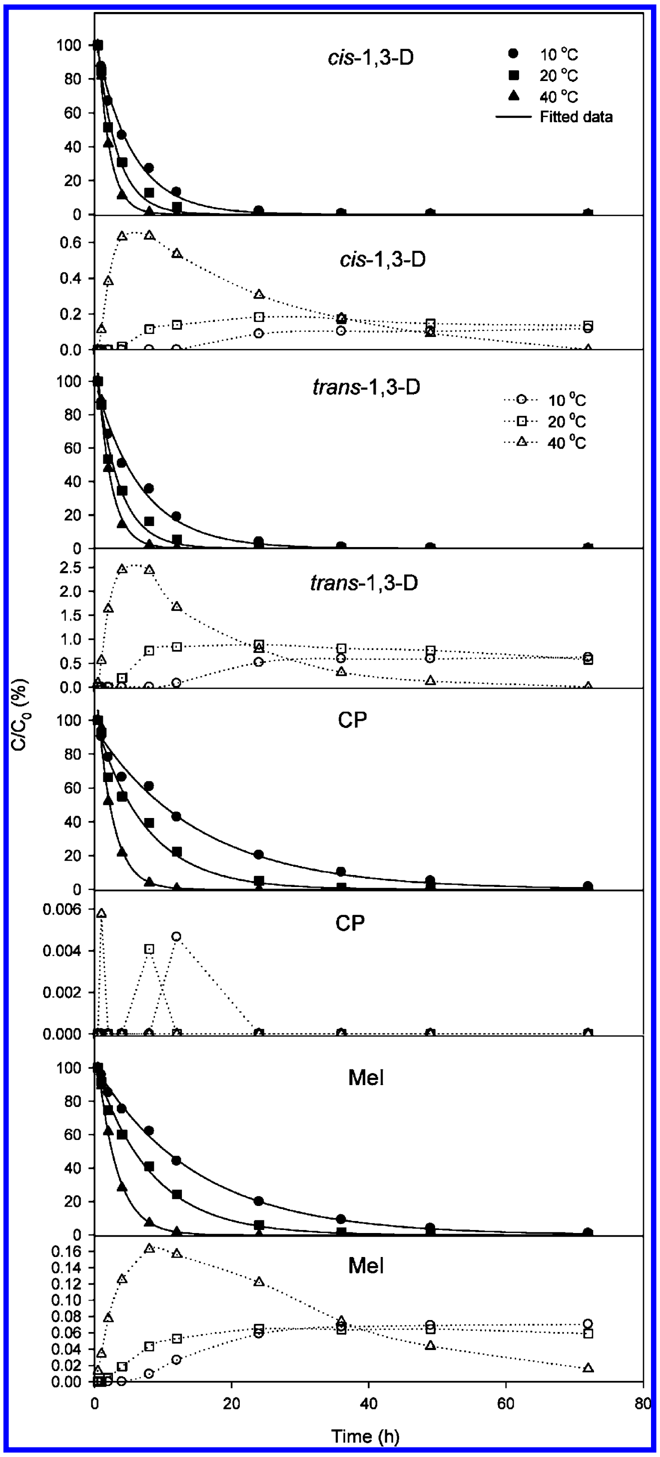

Figure 1. *cis*-1,3-D, *trans*-1,3-D, CP, and MeI diffusion through VIF-RF from the source chamber (closed symbols) to the receiving chamber (open symbols) and disappearance in the source chamber over time at three different temperatures. The ATS application rate was 44.2 g m^{-2}.

Compared with 10 °C, the higher temperature (40 °C) had little effect on VIF-RF emissions of CP and MeI (total emission <0.006, 0.15%, respectively), but did slightly increase emissions of *cis*-1,3-D, *trans*-1,3-D (Figure.1). During the course of the experiment, concentrations of *cis*-, *trans*-1,3-D in the source chamber gradually declined to very low values due to reaction with ATS. The amount of *cis*- and *trans*-1,3-D which diffused to the receiving chamber increased from 0.1 and 0.6%, respectively, at 10 °C to 0.6 and 2.4%, respectively, at 40 °C (Figure.1).

Environmental Implications. Although relatively permeable to MeBr, HDPE has been widely used to cover MeBr fumigated fields to reduce emissions and improve pest-control efficacy. The permeability of HDPE to both CP and MeI is similar to MeBr. HDPE is highly permeable to 1,3-D and is an ineffective emissions barrier. VIF is likely the optimum choice for use as a physical barrier to reduce rapid emissions after fumigation. However, because it merely contains fumigants in soil and does not accelerate transformation, a significant amount of fumigant could escape into the atmosphere upon removal of the film for planting. For a reactive film, the relatively high permeability of HDPE is advantageous as the under-layer plastic film because it allows the fumigants to quickly reach, and be transformed by, the ATS solution. The VIF layer above the ATS, being nearly impermeable, then prevents fumigant diffusion into the atmosphere.

VIF-RF has an optimum structure for trapping and transforming fumigants. When not activated, it acts as a physical barrier due to the impermeable nature of VIF and traps the fumigants within soil without decomposition. This leads to an improvement in the fumigants' pest-control efficacy. When activated by the addition of water, it reacts with fumigants in the inner (reactive) space of the VIF-RF and transforms the fumigants without significant emissions through the VIF. At 20 °C, fumigant half-lives under activated VIF-RF were just several hours, significantly less than that in soil and pure water (from few days to several weeks).[5,15,24] Moreover, higher temperature accelerated the fumigant elimination rate. Because the surface temperature of soils during summer months may easily reach 40 °C or even higher,[25] it would be expected that the fumigants will readily be transformed under field conditions when a VIF-RF is used.

Using VIF-RF to cover fumigated soil may render irrigation unnecessary as a potential approach to reduce fumigants emission. The organic content of the soil also becomes less important in relation to fumigant transformation and, hence, reduced emissions. The time required for tarp covering the field can be greatly reduced, since once pest-kill efficacy is obtained, the residual fumigants can be quickly depleted by the VIF-RF, rather than having to wait for them to dissipate by slow diffusion through the plastic film or be transformed in soil.[26] Therefore, the chance of downward diffusion of the fumigant is reduced and, because the byproducts from the fumigants (e.g., I^- from MeI transformation) are completely contained within the VIF-RF and can be removed with the film before planting, the risk of groundwater contamination from both fumigants and their byproducts can be reduced. Overall, VIF-RF offer a feasible tool to reduce 1,3-D, CP, and MeI emissions when they are used as soil fumigant alternatives to MeBr.

Though the issues associated with using VIF-RF in practical field situations (e.g., how to conveniently introduce water to the reactive layer, how to handle the VIF-RF under differing conditions such as large flat field or raised beds) are mainly future research topics, it appears that a relatively narrow strip of VIF-RF (e.g., 1 m wide) would be most appropriate for field use. In this strip, solid ATS and paper would be sealed between HDPE and VIF, and a small tube connected through which water could be introduced to the inner space of the VIF-RF. With shank injection of fumigants to a field, strips of VIF-RF could then be used to cover certain regions of the field with the rest covered with regular VIF. In raised beds, the edges of the VIF-RF could be kept open and be buried in the furrow alongside the bed. When the residual fumigants need to be removed (i.e., at the end of fumigation period), water could be added to the VIF-RF through the tube located in the strips, or via the furrow in a raised bed application, so that the paper in the VIF-RF could absorb and deliver enough water to the inner space of the VIF-RF to dissolve solid ATS. Because the paper holds the ATS solution, the byproducts together with any excess ATS would remain within the VIF-RF. Using the VIF-RF in narrow strips not only reduces the cost, but also overcomes application and removal problems associated with a relatively heavy film.

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Notes

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REFERENCES

(1) The biologic and economic assessment of methyl bromide. The national agricultural pesticide impact assessment program (NAPIAP), Washington, D.C., 1993.

(2) California department of pesticide regulations. Summary of pesticide use report data 2008 indexed by chemical; CDPR: Sacramento, CA, 2009.

(3) Methyl bromide critical use nomination for preplant soil use for strawberry fruit grown in open fields. http://www.epa.gov/ozone/mbr/CUN2011/CUN2011Strawberry.pdf

(4) 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.

(5) 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.

(6) 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.

(7) 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.

(8) Wang, D.; Yates, S. R.; Gan, J.; Knuteson, J. A. Atmospheric volatilization of methyl bromide,1,3-dichloropropene, and propargyl bromide through two plastic films: transfer coefficient and temperature effect. *Atmos. Environ.* **1999**, *33*, 401−407.

(9) 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 soil. *Environ. Sci. Technol.* **2011**, *45*, 1384−1390.

(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) Yates, S. R.; Kunteson, J.; Ernst, F. F.; Zheng, W.; Wang, Q. Effect of sequential surface irrigations on field-scale emissions of 1,3-dichloropropene. *Environ. Sci. Technol.* **2008**, *42*, 8753−8758.

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

(13) Zheng, W.; Gan, J.; Papiernik, S. K.; Guo, M.; Yates, S. R. Identification of volatile/semivolatile products derived from chemical remediation of cis-1,3-dichloropropene by thiosulfate. *Environ. Sci. Technol.* **2007**, *41*, 6454−6459.

(14) Zheng, W.; Papiernik, S. K.; Guo, M.; Yates, S. R. Accelerated degradation of methyl iodide by agrochemicals. *J. Agric. Food Chem.* **2003**, *51*, 673−679.

(15) Wang, Q.; Gan, J.; Papiernik, S. K.; Yates, S. R. Transformation and detoxification of halogenated fumigants by ammonium thiosulfate. *Environ. Sci. Technol.* **2000**, *34*, 3717−3721.

(16) Gan, J.; Yates, S. R.; Becker, J. O.; Wang, D. Surface amendment of fertilizer ammonium thiosulfate to reduce methyl bromide emission from soil. *Environ. Sci. Technol.* **1998**, *32*, 2438−2441.

(17) Gan, J.; Becker, J. O.; Ernst, F. F.; Hutchinson, C.; Knuteson, J. A.; Yates, S. R. Surface application of ammonium thiosulfate fertilizer to reduce volatilization of 1, 3-dichloropropene from soil. *Soil. Pest Manag. Sci.* **2000**, *56*, 264−270.

(18) 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.

(19) Qin, R.; Gao, S.; Hanson, B. D.; McDonald, J. A.; Trout, T. J.; Ajwa, H. Effect of drip application of ammonium thiosulfate on fumigant degradation in soil columns. *J. Agric. Food Chem.* **2007**, *55*, 8193−8199.

(20) Xuan, R.; Ashworth, D. J.; Luo, L.; Yates, S. R. Reactive films for mitigating methyl bromide emissions from fumigated soil. *Environ. Sci. Technol.* **2011**, *45*, 2317−2322.

(21) Papiernik, S. K.; Yates, S. R.; Gan, J. An approach for estimating the permeability of agricultural films. *Environ. Sci. Technol.* **2001**, *35*, 1240−1246.

(22) Marquardt, D. W. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Indust. Appl. Math.* **1963**, *11*, 431−441.

(23) 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.

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

(25) Yates, S. R.; Gan, J.; Ernst, F. F.; Mutziger, A.; Yates, M. V. Methyl bromide emissions from a covered field: I. Experimental conditions and degradation in soil. *J. Environ. Qual.* **1996**, *25*, 184.

(26) CDPR. Methyl iodide controls are stricter in California. http://www.cdpr.ca.gov/docs/registration/mei_pdfs/mei_chart_12-10.pdf