Effect of Environmental Conditions on the Permeability of High Density Polyethylene Film To Fumigant Vapors

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Soil fumigation in greenhouses or agricultural fields often includes tarping the soil surface with polyethylene (PE) films to contain the fumigant in the soil and reduce emissions to the atmosphere. Previous research has demonstrated that PE films are permeable to methyl bromide and other fumigant compounds. In these experiments, the effect of temperature, fumigant mixtures, condensed water, and field aging on the permeability of high-density polyethylene (HDPE) was determined. Mass transfer coefficients (h, a measure of permeability) of the fumigants methyl bromide, 1,3-dichloropropene, propargyl bromide, and chloropicrin across HDPE films were determined. In these studies, temperature and HDPE film type had the largest impact on the h of fumigant compounds across HDPE films. Other factors investigated, including fumigant mixtures, condensed water on the film, and field aging of UV-stabilized film, did not have a significant impact on h. The results of these experiments suggest that the permeability of an intact piece of an agricultural film will increase with increasing temperature but is relatively constant despite changes in other environmental conditions.

Introduction

Methyl bromide (MeBr) has been implicated as an ozone-depleting compound and is scheduled to be phased out in the United States and other developed countries in 2005 (*1*). Other soil fumigants currently on the market are under investigation for their impacts on air quality. For example, 1,3-dichloropropene (1,3-D) was temporarily banned in California because of its potential toxicity in air (*2*) and its use is currently restricted in California. Continued use of soil fumigants in agriculture will require that their use comply with increasingly stringent environmental regulations.

Soil fumigation in greenhouses or in agricultural fields often involves covering the soil surface with a plastic film immediately following application to provide a barrier to fumigant volatilization; these tarps are kept on the soil surface for several days. Volatilization of soil-applied fumigants is dependent on many factors, including climatic variables, soil conditions, the method of fumigation, and surface cover. Low-density or high-density polyethylene films (LDPE or HDPE) are most commonly used in fumigation of soil with methyl bromide (*3*), but these films are reportedly permeable to methyl bromide (*3*−*10*) and other soil fumigants (*10*, *11*).

To be useful in field applications, films must maintain their integrity through application and throughout the cover period under a wide variety of environmental conditions. To reduce emissions, they must also maintain their imperme-ability to fumigant vapors under field conditions. Experiments to assess the volatilization of soil fumigants from a soil surface overlain by plastic film have been conducted in the laboratory for methyl bromide (*3*, *9*, *10*), methyl iodide (*10*), 1,3-dichloropropene (*12*), and chloropicrin (*11*). Field trials have also been conducted to measure the volatilization of methyl bromide (*5*, *7*−*10*, *13*, *14*), methyl iodide (*10*), and 1,3-dichloropropene (*15*) from the soil surface when covered with different plastic films. Polyethylene films are inexpensive and generally rugged in the field, and they have been used in soil fumigation for many years.

The permeability of LDPE and HDPE has been reported to increase with increasing temperature (*4*, *16*), so that the flux of soil-applied fumigant through these films is increased by a factor of ∼2 for each 20 °C increase in temperature (*13*). The flux of MeBr through HDPE is positively correlated with the ambient temperature, resulting in a diurnal flux pattern with a maximum daily flux occurring around noon (*17*). The impact of temperature on the permeability of HDPE to other soil fumigants has not been established.

Water vapor often condenses on the underside of surface tarps during field application. It has been speculated that condensed water may act as an additional barrier to diffusion, reducing the apparent permeability of HDPE to fumigant compounds. The diffusion coefficient of MeBr in water is about 10 000 times smaller than the diffusion coefficient in air (*18*), which accounts for the slower diffusion of MeBr in moist soil than in dry soil. The impact of condensed water on film permeability has not been quantitatively investigated.

During MeBr fumigation in the U.S., the HDPE film typically remains intact in the field for 2−5 days, when the tarp is removed for planting or punctured for placement of seedlings. When the tarp remains on the soil surface, emissions continue beyond 5 days (*19*), and increasing the cover time may decrease cumulative emissions. Exposure to field conditions during the cover time may alter the perme-ability of HDPE and other films. In California, MeBr fumiga-tion is typically carried out when air and soil temperatures and solar radiation are relatively high and soil moisture is low. These conditions may alter the physical properties of the film over time. The impact of exposure to field conditions on the permeability of plastic films to fumigant compounds has not been assessed.

The objectives of the present experiments were to determine the effect of temperature, fumigant mixtures, condensed water, and field aging on the permeability of HDPE films to fumigant vapors. Mass transfer coefficients (h, a measure of permeability) of the fumigants methyl bromide (MeBr), 1,3-dichloropropene (1,3-D), propargyl bromide (PrBr), and chloropicrin (CP) across HDPE films were determined to indicate the impact of these environmental conditions on HDPE permeability.

Materials and Methods

Chemicals and Plastic Films. Methyl bromide in a lecture bottle (99% purity) was obtained from Aldrich Chemical Co. Propargyl bromide (97% purity), a potential alternative to MeBr, was obtained from Fluka. Chloropicrin (98% purity) and 1,3-D (47% *Z*- and 51% *E*-1,3-D) were obtained from Chem Service.

Two samples of high-barrier 1.0 mil (0.025-mm) thick HDPE film, which is commonly used in current soil fumiga-tion practices, were supplied by Tri-Cal, a local commercial fumigation contractor. Film HDPE1 was used for determining

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the effect of temperature, fumigant mixtures, and condensed water on permeability, and the film was used in its new condition. Film HDPE2 was UV-stabilized; this film was used to assess the impact of field conditions on film permeability.

Permeability Tests. A detailed discussion of the apparatus and methods used for these permeability tests are given elsewhere (*20*, *21*). Briefly, gastight stainless steel cells were constructed so as to hold a sample of a film between two chambers. Fumigant vapor is spiked to the chamber on one side of the film (source chamber), and vapor samples are collected from both the source chamber and the receiving chamber (measuring fumigants that have permeated through the film) at several times after spiking. Experiments were conducted in controlled temperature rooms with variability ± 0.5 °C. All equipment was equilibrated at the appropriate temperature before each experiment was initiated.

To assess the impact of field conditions on film permeability, a sample of HDPE2 was applied to the soil surface in a field plot in Riverside, CA from May 23 through June 27, 2001. At 7-day intervals, samples of HDPE2 were removed from the field, and the permeability was tested at 20 °C in the laboratory. The effect of temperature on the permeability of HDPE1 was assessed by determining the h of each fumigant compound at temperatures of 20, 25, 30, 35, and 40 °C. The effect of fumigant mixtures on film permeability was determined by spiking cells with mixed fumigant vapor and with each compound in isolation. The effect of fumigant mixtures was determined at 20 and 40 °C.

To determine the effect of condensed water on the permeability of HDPE1 to fumigant compounds, varying amounts of liquid water were applied to the film surface facing the source chamber after the permeability cell was assembled. In one treatment, water was applied in a continuous layer of 3 mm on the film surface by injecting 34 mL of water into the top (source) cell, taking care not to wet the stainless steel sides of the cell. For other treatments, steam was generated using a distillation apparatus with the condenser removed. The assembled cell with the bottom plate removed was positioned approximately 20 cm above the steam outlet to avoid excessive heating of the film. Air was passed through copper coils in an ice bath, and the cooled air was passed through the receiving chamber to result in condensation on the lower film surface. Very little water was condensed on the stainless steel walls of the cell. The mass of water in the cell was determined gravimetrically. The bottom plate was sealed to the remainder of the assembly with epoxy. Permeability of the film with condensed water was determined at 20 °C.

Spiking, Sampling, and Analysis. For tests with mixed fumigants, pure standards of chloropicrin (7 μL), 1,3-D (50 μL of a standard containing 47% *Z*- and 51% *E*-1,3-D), and propargyl bromide (50 μL) were placed in a screw-top 150-mL Erlenmeyer flask, capped with a mininert sampling valve, and allowed to equilibrate to provide a mixed vapor source. Saturated MeBr vapor was prepared by transferring MeBr from a lecture bottle directly into an evacuated Teflon gas sampling bag. An aliquot (20 mL) of the headspace in the mixed vapor source flask was injected into the source chamber of each permeability cell. A needle was placed in a second port of the source cell to allow air to escape from the source cell during injection so that injection did not pressurize the cell. Immediately following injection of the mixed fumigant vapor, the pressure-relief needle was removed from the port, and 3 mL of saturated MeBr vapor was spiked to the source chamber of each permeability cell. For tests with a single fumigant, the same procedure was followed except that the vapor of only one chemical was spiked to the cells. Vapor sources were prepared by transferring $\sim$7 μL of liquid CP, $\sim$50 μL of liquid PrBr, or $\sim$50 μL of liquid 1,3-D to 150-mL serum bottles which were capped immediately

with a gastight seal (Teflon-faced butyl rubber septum and aluminum seal). Fumigant vapor (20 mL) was spiked to the source chamber of each permeability cell to be tested. For cells containing only MeBr, 3 mL of saturated MeBr vapor was spiked to each cell. Spiking resulted in fumigant concentrations similar to those measured in soil following fumigation.

Samples (500 μL from the receiving chamber; 250 μL from the source chamber) were collected using gastight syringes and placed in 9-mL headspace vials. Vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa. Sampling continued for approximately 8 h and were either analyzed the day they were collected or stored at -78 °C until sample analysis.

Samples were analyzed using a Tekmar 7000 headspace autosampler interfaced with an HP 5890 GC-ECD. The headspace autosampler conditions were as follows: 90 °C equilibration temperature; 2.0 min. equilibration time; 100 μL sample loop. For mixed vapor samples, the GC conditions were as follows: one RTX-624 column connected in sequence to two DB-VRX columns; each column being 30 m long $\times$ 0.25 mm I.D. $\times$ 1.4 μm film thickness; helium carrier gas at a flow rate of 0.6 mL/min; 230 °C injector temperature; 300 °C detector temperature; and oven temperature program: 35 °C held for 1 min, increasing at 8° per minute to 90 °C, held for 49 min. Under these conditions, the retention times were as follows: MeBr, 18.5 min; PrBr, 31.2 min; *cis*-1,3-D, 44.9 min; *trans*-1,3-D, 51.0 min; and CP, 53.5 min. Calibration standards for GC analysis were prepared in acetone, and 5 μL of solution were transferred to 9-mL headspace vials. Calibration curves ($\geq$6 concentrations) were constructed for each set of 36$-$50 samples. Because of the long run times, samples were analyzed in random order to avoid systematic bias. When only one compound was being analyzed, one DB-VRX column was used with similar flow and isothermal conditions of 35 °C for MeBr and 100 °C for PrBr, 1,3-D, and CP. Run times for individual compounds were $\leq$10 min.

The concentration data were analyzed using the model described in Papiernik et al. (*20*), which gives the mass transfer coefficient, accounting for sorption to the film. The assembled permeability cell is considered as a two-layer system separated by a membrane that impedes diffusion and is sorptive to the spiked compound. The analytical solution for the concentration in each chamber when the source chamber has an initial concentration of C_0 and the length of both chambers is the same ($L_s = L_r = L$) is

$$C_r(t) = \frac{C_0 L}{2}\left[\frac{L + k_p e^{-\alpha(k_p + L)t/L}}{L(k_p + L)} + \frac{2h + \alpha(k_p - L) - \sqrt{\beta}}{2L\sqrt{\beta}} \right.$$
$$e^{-(2h + \alpha(k_p + L) - \sqrt{\beta})t/2L} - \frac{2h + \alpha(k_p - L) + \sqrt{\beta}}{2L\sqrt{\beta}}$$
$$\left. e^{-(2h + \alpha(k_p + L) + \sqrt{\beta})t/2L} \right] \quad (1)$$

for the receiving chamber and

$$C_s(t) = \frac{C_0 L}{2}\left[\frac{L + k_p e^{-\alpha(k_p + L)t/L}}{L(k_p + L)} - \frac{2h + \alpha(k_p - L) - \sqrt{\beta}}{2L\sqrt{\beta}} \right.$$
$$e^{-(2h + \alpha(k_p + L) - \sqrt{\beta})t/2L} + \frac{2h + \alpha(k_p - L) + \sqrt{\beta}}{2L\sqrt{\beta}}$$
$$\left. e^{-(2h + \alpha(k_p + L) + \sqrt{\beta})t/2L} \right] \quad (2)$$

for the source chamber where $\beta = -8hL\alpha + [2h + \alpha(k_p + L)]^2$. The mass transfer coefficient is h and has units L t^{-1}.

TABLE 1. Effect of Temperature on Mass Transfer Coefficients (cm h^{-1}) of Fumigant Compounds Across 1-mil HDPE

T (°C)	film	methyl bromide	chloropicrin	propargyl bromide	*cis*-1,3-D	*trans*-1,3-D
20	HDPE2[a]	0.63 ± 0.04	1.11 ± 0.09	2.64 ± 0.2	3.7 ± 0.4	5.6 ± 0.8
20	HDPE1	0.37 ± 0.02	0.62 ± 0.07	1.50 ± 0.07	2.0 ± 0.2	3.7 ± 0.3
25	HDPE1	0.45 ± 0.00	0.72 ± 0.07	1.5 ± 0.2	2.6 ± 0.4	4.7 ± 0.8
30	HDPE1	0.62 ± 0.02	1.2 ± 0.1	2.1 ± 0.1	2.8 ± 0.2	4.8 ± 0.6
35	HDPE1	0.76 ± 0.02	1.7 ± 0.2	3.0 ± 0.3	4.9 ± 0.6	6.3 ± 0.7
40	HDPE1	1.0 ± 0.2	2.1 ± 0.4	3.4 ± 1	5.0 ± 2	8.4 ± 5.5

[a] Film HDPE2 is a UV-stabilized HDPE.

Adsorption to the film is modeled as a kinetic process at early times that approaches equilibrium at later times

$$\frac{\partial S}{\partial t} = \alpha(k_p C(t) - S(t)) \qquad (3)$$

where S is the mass of adsorbed chemical per film area [M L^{-2}], k_p [L] is the equilibrium adsorption coefficient defined by the ratio $k_p = S_s(\infty)/C_s(\infty) \equiv S_r(\infty)/C_r(\infty)$ and α [t^{-1}] is the system-equilibrium adsorption rate parameter. A minimization algorithm is used to simultaneously determine h, α, and k_p. The parameters can be determined independently by determining α and k_p from early- and late-time behavior, respectively, and then conducting a regression which includes h as the only adjustable parameter (20).

The permeability of film with water condensed on the source side of the film was determined using the model described above to estimate an effective h for the water-film system. A model including partitioning in the source chamber between the gas and liquid phases (described by Henry's Law), diffusion through the water film, and transport through the plastic film was also developed. This model, which did not include sorption to the film, is presented as Supporting Information. The model includes the h of the plastic film, the initial source chamber concentration (C_0), the depth of the water film (L_w), and the diffusion coefficient of the compound in water (D_w) as adjustable parameters. The Henry's Law constant (K_H) and lengths of the source (L_s) and receiving cell (L_r) chambers are specified.

Results and Discussion

Relative Diffusion of Fumigant Compounds across 1-mil HDPE. 1-mil HDPE is permeable to fumigant compounds, and the compounds are transported across the film relatively rapidly. For both HDPE1 and HDPE2, the h for CP is 1.5 to 2 times greater than that of MeBr; the h for PrBr is about 3 to 4 times greater and the h values for *cis*- and *trans*-1,3-D are approximately 5 and 10 times greater than MeBr, respectively (Table 1). Previous studies have also indicated that HDPE is more permeable to CP than to MeBr (4) and that HDPE has similar permeability to 1,3-D and PrBr (22).

Many field studies have reported that 1-mil HDPE is permeable to MeBr, resulting in emissions of 27−87% of the applied MeBr during standard tarped fumigation (19). Polyethylene film, which has been widely used in soil fumigation, has high permeability to MeBr alternatives (Table 1), so its utility for containment of these compounds is limited. Tarping the soil surface in 1,3-D or PrBr fumigation will likely result in minimal reduction in cumulative emissions (15). The tarp material and application add a significant expense to soil fumigation, and tarping with 1-mil HDPE may not be economically advantageous if emissions reduction is the goal of tarping. Current fumigation with 1,3-D does not routinely use plastic tarp on the soil surface. Since use of 1-mil HDPE alone is unlikely to have a large impact on emissions, other emission reduction strategies are needed for MeBr alternatives. Films with reduced permeability are being developed. Enhanced degradation of fumigant compounds by applica-
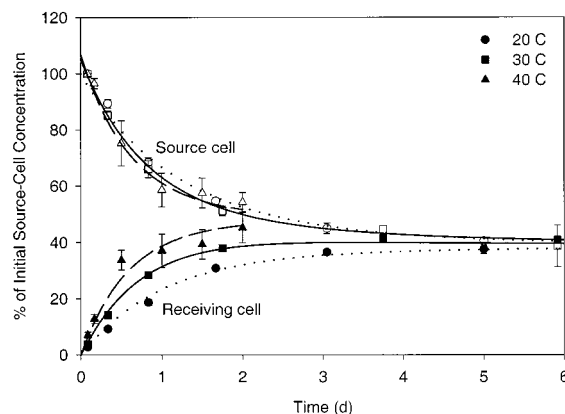

FIGURE 1. Diffusion of propargyl bromide across 1-mil HDPE at 20, 30, and 40 °C. Data points indicate mean of three replicate cells, and error bars indicate standard error of the mean. Open symbols indicate source cell concentrations and solid symbols indicate receiving cell concentrations. Lines indicate regression to model of Papiernik et al. (20) to determine the mass transfer coefficient.

TABLE 2. Temperature Dependence of Mass Transfer Coefficients (h, cm h^{-1}) of Fumigant Compounds Across 1-mil HDPE for Temperatures 20−40 °C

	linear regression	r^2
methyl bromide	$h = 0.032 \cdot T$ (°C) $- 0.31$ cm h^{-1}	0.97
chloropicrin	$h = 0.077 \cdot T$ (°C) $- 1.05$ cm h^{-1}	0.97
propargyl bromide	$h = 0.106 \cdot T$ (°C) $- 0.85$ cm h^{-1}	0.94
cis-1,3-D	$h = 0.166 \cdot T$ (°C) $- 1.54$ cm h^{-1}	0.89
trans-1,3-D	$h = 0.221 \cdot T$ (°C) $- 1.03$ cm h^{-1}	0.90

tion of thiosulfate salts (23) or organic amendments (24) to the soil surface has been proposed as a means to reduce emissions of MeBr alternatives.

Effect of Temperature on h. Fumigants were transported across the film more rapidly with increasing temperature (Figure 1). For all fumigant compounds, h increased with increasing temperature (Table 1). The increase was approximately linear (Table 2). All compounds demonstrated an increase in h by a factor of 1.5−2.5 per 10 °C increase in temperature from 20 to 40 °C. The observed temperature dependence for MeBr is similar to that reported by Chitwood and Deshusses (25), who determined h of MeBr across HDPE at 20, 50, and 60 °C. Their results produce a regression $h = 0.037 \cdot T$ (°C) $- 0.34$ cm h^{-1}. The value of h for MeBr across 1-mil HDPE determined at 20 °C was also similar in both experiments. We determined h to be 0.33−0.37 cm h^{-1} for HDPE1 and 0.63 for HDPE2; Chitwood and Deshusses (25) report an h of 0.40 cm h^{-1}. The results of Kolbezen and Abu El Haj (4) for MeBr and CP diffusion through 1-mil HDPE also agree with our results ±50%. The increase in h with increasing temperature was generally slightly lower in Kolbezen and Abu El Haj (4) than we report here.

This increase in permeability with temperature has the potential to have a large impact on emissions. Diurnal variations in MeBr flux density from the soil surface are
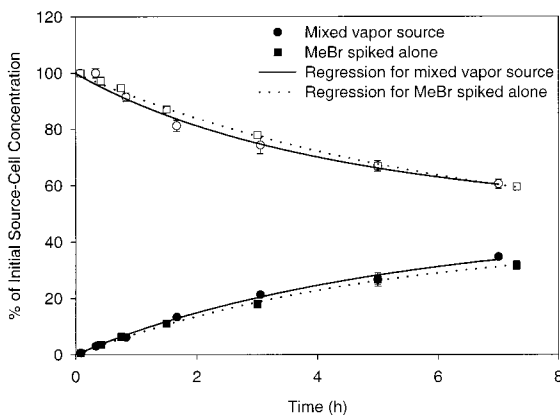
FIGURE 2. Methyl bromide diffusion across 1-mil HDPE determined in cells spiked with mixed vapor or spiked with methyl bromide only. Data points indicate mean of three replicate cells, and error bars indicate standard error of the mean. Open symbols indicate source cell concentrations and solid symbols indicate receiving cell concentrations. Lines indicate regression to model of Papiernik et al. (*20*) to determine the mass transfer coefficient.

TABLE 3. Effect of Mixture on Mass Transfer Coefficients (cm h^{-1}) of Fumigant Compounds Across 1-mil HDPE

	20 °C		40 °C	
fumigant	spiked alone	spiked in mixture	spiked alone	spiked in mixture
methyl bromide	0.33 ± 0.06	0.37 ± 0.02	1.1 ± 0.1	1.0 ± 0.2
chloropicrin	0.50 ± 0.04	0.62 ± 0.07	2.2 ± 0.3	2.1 ± 0.4
propargyl bromide	1.5 ± 0.1	1.50 ± 0.07	3.1 ± 0.3	3.4 ± 1.2
cis-1,3-D	2.5 ± 0.3	2.0 ± 0.2	4.4 ± 0.2	5.0 ± 2
trans-1,3-D	4.2 ± 0.5	3.7 ± 0.3	6.6 ± 0.7	8.4 ± 5

observed in field studies, where flux density is much higher during the day than at night (*13*). This effect has been attributed primarily to a higher diffusion rate of MeBr through the plastic at higher temperatures (*22, 26*). Other factors, including changes in atmospheric stability, can also produce diurnal variations in flux density from bare and tarped soils (*15, 27*).

Effect of Fumigant Mixtures on *h*. Fumigants diffused across the film at the same rate whether they were spiked alone or in a mixture of fumigant compounds (MeBr, PrBr, *cis*- and *trans*-1,3-D, and CP) (Figure 2). Mass transfer coefficients of fumigant compounds across 1-mil HDPE were not significantly different when spiked in mixture or in isolation at 20 and 40 °C (Table 3). It appears that under the conditions of these tests, the compounds behaved independently and were unaffected by the presence of other fumigant compounds. Kolbezen and Abu El Haj (*4*) reported that MeBr diffused more rapidly when added in combination with CP at temperatures ≤40 °C.

These results are useful in determining the fate of fumigants, which may be applied alone or in mixtures. For example, formulations of 1,3-D often contain CP to increase the spectrum of activity against pests. These results, which indicate that these fumigant compounds traverse the plastic film essentially independently, will aid efforts to model and predict fumigant volatilization using a mass transfer approach.

Effect of Condensed Water on *h*. Fumigant transport across HDPE was determined with ~4 g and ~34 g of water condensed on the film surface. Droplets approximately 1−5 mm in diameter were achieved with condensation of 4 g of water on the film surface. Addition of 34 g of water produced a continuous layer of water 3 mm thick. These permeability
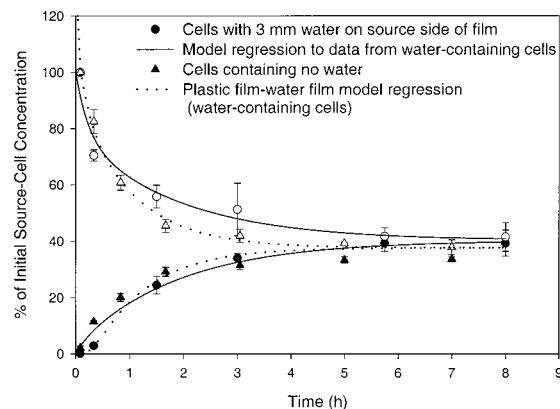

FIGURE 3. Diffusion of *cis*-1,3-D across 1-mil HDPE1 at 20 °C with no water condensed on the film and with a continuous layer of water ~3 mm thick on the source side of the plastic film. Data points indicate mean of three replicate cells, and error bars indicate standard error of the mean. Open symbols indicate source cell concentrations and solid symbols indicate receiving cell concentrations. Solid lines indicate regression to model of Papiernik et al. (*20*) to determine the mass transfer coefficient for the data from the cells containing water. Dotted lines indicate regression of data from cells containing water to the model describing transport through water film and plastic film in series.

TABLE 4. Effect of Water on Apparent Mass Transfer Coefficients (cm h^{-1}) Determined at 20 °C

fumigant compound	no water	~4 g water	~34 g water (3 mm)
methyl bromide	0.37 ± 0.02	0.34 ± 0.02	0.31 ± 0.02
chloropicrin	0.62 ± 0.07	ND[a]	0.50 ± 0.7
propargyl bromide	1.50 ± 0.07	1.6 ± 0.1	1.7 ± 0.8
cis-1,3-D	2.0 ± 0.2	2.4 ± 0.2	1.3 ± 0.4
trans-1,3-D	3.7 ± 0.3	4.0 ± 0.8	2.4 ± 1.3

[a] Not determined.

cells had at least one top or bottom plate that was made of clear glass, allowing for visual examination of the film/water surface; observations indicated that there no noticeable evaporation of the water added to the cells during the experiment.

Concentration measurements indicated that there was a very short lag between loss of fumigant from the gas phase of the source chamber and appearance of measurable concentrations in the gas phase of the receiving chamber (Figure 3). This lag is due to partitioning of gaseous fumigants into the liquid phase and diffusion through the liquid phase to the film surface. The model presented in eqs 1 and 2 was used to estimate an overall *h* for the plastic film-water layer system. The model described the data well overall (r^2 for data in Figure 3 was 0.98), but receiving cell concentrations were overpredicted at early times. Presence of a water film, even a continuous layer several mm in thickness, did not significantly impede diffusion of any compound through standard HDPE (Table 4, Figure 3). These results suggest that in all cases tested, the rate of diffusion in the HDPE-water system was limited by the rate of diffusion of fumigant compounds across the film. The observable effect of the water film in these systems is a short delay in the initial appearance of fumigant at the film surface because of the time required for dissolution into and diffusion through the water phase, but this delay (on the order of minutes) does not significantly alter overall mass transfer through the film (Figure 3).

These results are supported by the simulations obtained with the model including a plastic film and water film in series (Supporting Information). D_w was determined by

TABLE 5. Parameters for Permeability Cells Containing a 3-mm-thick Water Film on 1-mil HDPE1 Determined Using the Model Describing Transport through a Water Film and Plastic Film in Series[a]

fumigant compound	K_H[b]	h (cm h^{-1})	exptl D_w[c] (cm^2 h^{-1})	correlation D_w[d] (cm^2 h^{-1})
methyl bromide	0.24	0.37	0.031 ± 0.010	0.043
chloropicrin	0.093	0.62	0.025 ± 0.022	0.030
propargyl bromide	0.037	1.50	0.031 ± 0.016	0.033
cis-1,3-D	0.056	2.0	0.042 ± 0.015	0.030
trans-1,3-D	0.041	3.7	0.038 ± 0.027	0.030

[a] Regression fixed L_w at 0.3 cm and h at the value determined in cells containing no water. [b] Henry's Law constants from ref 32 for propargyl bromide and ref 33 for all other compounds. [c] Diffusion coefficient in water determined by regression to the data obtained in these experiments. [d] Diffusion coefficient in water estimated by correlation techniques. Values are means of the Tyn-Calus method (34) and the Hayduk-Laudie method (35).

regression while fixing the h of the plastic film at the value determined in cells with no water (values in Table 1) and the depth of the water film at 0.3 cm. This resulted in D_w values nearly equal to those estimated by correlation techniques (Table 5). Measured concentrations in the permeability cells, particularly early-time behavior in the receiving cell, were well-described using this model (Figure 3). The model equates the fluxes in the permeability cells, so that the flux out of the source-chamber gas phase is equal to the flux into the water film. Further, the flux out of the plastic film is equal to the flux entering the receiving chamber. Given the Henry's Law constants of these compounds, the concentration in the water phase is 4 (MeBr) to 27 (PrBr) times higher than the concentration in the vapor phase at equilibrium. From these results, it appears that the transport through the plastic film limits the overall rate of mass transfer in these systems, and for the conditions and chemicals studied in these experiments, the concentration gradient in the water layer adjusts to deliver fumigant to the water-plastic film boundary at a sufficient rate and concentration to drive the system at the same rate as if there were no water present.

While presence of condensed water may not impact tarp permeability, studies have shown that increasing the soil water content decreases cumulative emissions of soil fumigant compounds. The bulk soil diffusion coefficient is reduced in soils with high moisture, and the slower transport from the application depth to the soil surface allows increased time for degradation in the soil. In a soil column study where the soil surface was tarped with PE and the column was exposed to diurnal temperature variations, soil water accumulated at the soil surface; this accumulation resulted from condensed water on the tarp being redeposited on the soil surface and from diurnal heat variation resulting in upward flux of water vapor at night (28). Increased water content at the soil surface had a large impact on cumulative emissions in PE-tarped columns, so that the application of water under 1-mil HDPE was much more effective at reducing cumulative MeBr emissions than was surface sealing with 1-mil HDPE alone (29). These film permeability results indicate that the effect of application of irrigation water on reducing emissions is not due to condensed water on the film reducing the apparent permeability of HDPE, but rather is likely due to the increased water content decreasing the rate of fumigant diffusion in the soil, so that the flux of fumigant from the soil surface to the film is greatly reduced in soils with high water content.

Field studies have also demonstrated the effect of surface irrigation on decreasing MeBr emissions. Field plots irrigated with ~15 mm of water and covered with polyethylene film demonstrated an increased proportion of MeBr degraded in the soil and lower cumulative emissions than nonirrigated plots covered with polyethylene (14). In packed, untarped soil columns, increasing the soil moisture decreased maximum and cumulative MeBr flux from the soil surface and increased the proportion of MeBr degraded in the soil (30).

Effect of Field Aging on h. A sample of HDPE2 was placed on the soil surface of a nonfumigated field in Riverside, CA, and film samples were collected weekly for 28 days. The environmental conditions were monitored at hourly intervals during the exposure period in an adjacent area also covered with HDPE2. During this time, the soil temperature at a depth of 1 cm varied from 20 to 60 °C with a mean of 35 °C. The air temperature ranged from 12 to 37 °C with a mean of 21 °C; net radiation varied from −60 to 490 W m^{-2} with a mean of 123 W m^{-2}; the relative humidity ranged from 9 to 98% with a mean of 64%; and the barometric pressure was 90−96 kPa with a mean of 93 kPa.

Permeability determined at 20 °C indicated no change in the h of each fumigant compound after field aging compared to new HDPE2 film (values reported in Table 1). For example, for MeBr, h was determined to be 0.63 ± 0.04 with no field exposure (Table 1). After 7 days of field exposure, h was 0.56 ± 0.03; after 14 days, h was 0.57 ± 0.04; after 21 days, h was 0.62 ± 0.03; and after 28 days in the field, the h was 0.51 ± 0.02. Linear regression of these values indicated a slope of −0.0034, which was not significantly different from zero. Regression of the h values for the other fumigants indicated similar slopes, all of which were not significantly different from zero ($\alpha = 0.01$). For film HDPE2, permeability was not impacted by exposure to environmental conditions typical of soil fumigation in California. Field aging did not appear to significantly alter the flexibility, color, elasticity, or other physical characteristics of the film, even after 1 month's exposure to relatively high temperatures and intense solar radiation.

If the permeability of the film does not increase with time, increasing the cover time following fumigation has the potential to decrease cumulative emissions. In both laboratory and field studies of MeBr and CP emissions, a spike of fumigant exiting the soil is observed following tarp removal (11, 31). These results demonstrate that for UV-stabilized HDPE films, allowing the tarp to remain intact on the soil surface will reduce the magnitude of the flux to the atmosphere at late times and reduce fumigant emissions. The magnitude of the emission reduction will increase with decreasing film permeability.

In the present studies, temperature and polyethylene film type had the largest impact on mass transfer coefficients of fumigant compounds across HDPE films (Table 1). Other factors investigated, including fumigant mixtures, condensed water on the film, and field aging of UV-stabilized film did not have a significant impact on mass transfer coefficients. The results of these experiments suggest that the permeability of an intact piece of an agricultural film will increase with increasing temperature but is relatively constant despite changes in other environmental conditions. These results will aid in the development of approaches to reduce emissions resulting from soil fumigation.

Supporting Information Available

Model including plastic film and water film in series. This material is available free of charge via the Internet at http://pubs.acs.org.

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