

An Approach for Estimating the Permeability of Agricultural Films

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Plastic tarps currently used during soil fumigation to control emissions have been shown to be permeable to fumigant vapors, resulting in appreciable losses to the atmosphere. New low-permeability films are being developed to reduce fumigant emissions and increase efficacy. A rapid, reliable, and sensitive method is required to measure the permeability of various films that may be used in new management practices. This manuscript presents an approach for estimating the mass transfer coefficient (h) of fumigant compounds across agricultural films. The h is a measure of the resistance to diffusion which, unlike other measures of permeability, is a property of the film-chemical combination and independent of the concentration gradient across the film. This method uses static sealed cells; fumigant vapor is spiked to one side of the film and the concentrations on both sides of the film are monitored until equilibrium. An analytical model is fitted to the data to obtain h . This model relies on a mass balance approach and includes sorption to and diffusion across the film membrane. The method was tested using two polyethylene films and a very low-permeability film and showed that the method produces a sensitive and reproducible measure of film permeability.

Introduction

When greenhouse and field soils are fumigated, the soil surface is often covered with a plastic tarp to reduce loss of the chemical via volatilization. Low- or high-density polyethylene tarps (LDPE or HDPE) are commonly used; however, these films have been reported to have significant permeability to MeBr (1–8) and other soil fumigants (7, 9). Plastic films that have reduced permeability to soil fumigants, particularly MeBr, have been developed in response to the call for management practices that reduce emissions and maintain or increase the efficacy of soil fumigants.

Production and importation of MeBr is scheduled to be incrementally reduced in the U.S. beginning in 1999 and is to be completely phased out by 2005 (some uses exempt). As a short-term option, reduced MeBr application rates can partially compensate for decreased availability and higher MeBr prices. With use of high-barrier films the fumigant is contained in the soil at higher concentrations for longer periods of time, resulting in greater efficacy, even at lower application rates. When used with a high-barrier film, MeBr application rates can be reduced by 25–50% (relative to standard application rates) to result in adequate pest control (10–12). A long-term solution will require a replacement for MeBr. Chemical alternatives to MeBr include 1,3-dichloro-

propene (1,3-D), chloropicrin (CP), and propargyl bromide (PrBr, 3-bromopropyne), which is structurally similar to MeBr and is currently being investigated as a potential alternative to MeBr (13). Tarping the soil surface with plastic film is often used to reduce emissions to the atmosphere. To develop fumigation management practices that protect the environment while providing adequate pest control, a rapid, accurate method to measure the permeability of plastic films to soil fumigants is needed.

The permeability of plastic films to gaseous solutes is due to diffusion and is thought to occur by the solute dissolving into the surface of the film, followed by the diffusion through the film and evaporation from the opposite film surface (14). Measurements of film permeability typically use an apparatus where the film being tested is mounted between two chambers, and the permeation of gases through the film is indicated by increasing concentration, pressure, or volume in the receiving chamber.

Kolbezen and Abu-El-Haj (1) described a method for measuring the permeability of plastic films to fumigant vapors under steady state conditions. Their method involved drawing a constant concentration of fumigant through a lower flow-through chamber, while in an upper flow-through chamber, clean air was swept across the surface of a sample of film held between the two chambers. Concentrations in the upper chamber were monitored using an in-line gas chromatograph to measure the quantity of fumigant escaping the source chamber over time. Kolbezen and Abu-El-Haj used this apparatus to measure the permeability of several films to MeBr and CP vapors, all of which had high permeabilities. Because of high dilution of the receiving chamber, this method would probably not be useful for virtually impermeable films. The American Society for Testing and Materials (ASTM) methods for determining the permeability of plastic films involve mounting a sheet of film between two chambers, pressurizing one cell, and monitoring the change in pressure or volume on the opposite side of the film (15). These methods produce variable (15) and relatively insensitive (16) measures of permeability, making them useful only for films with relatively high permeability. Gamleil et al. (16) used the variable volume method and a method similar to that of Kolbezen and Abu-El-Haj to measure the permeability of several films to MeBr. Another disadvantage of these methods is that they measure the flux through the film and produce a measure of permeability which is dependent on the concentration gradient.

Mass transfer follows Fick's laws; diffusion is described by Fick's first law (flux is proportional to the concentration gradient, dC/dx)

$$J_x = -D\left(\frac{dC}{dx}\right) = -hb\left(\frac{dC}{dx}\right) \quad (1)$$

where J_x is the flux in the x direction, and D is the diffusion coefficient. A mass transfer coefficient, h , can be obtained from $h = D/b$, where b is the film thickness (17). If the concentrations are not changing with time, i.e., the system is at steady state, the mass transfer coefficient may be determined by measuring the concentrations on each side of the film and solving for h

$$J = -h(C_r - C_s) \quad (2)$$

where C_s and C_r are the concentrations on the source and receiving side of the film. The h is a measure of the resistance to diffusion. For permeable films such as HDPE, h is high,

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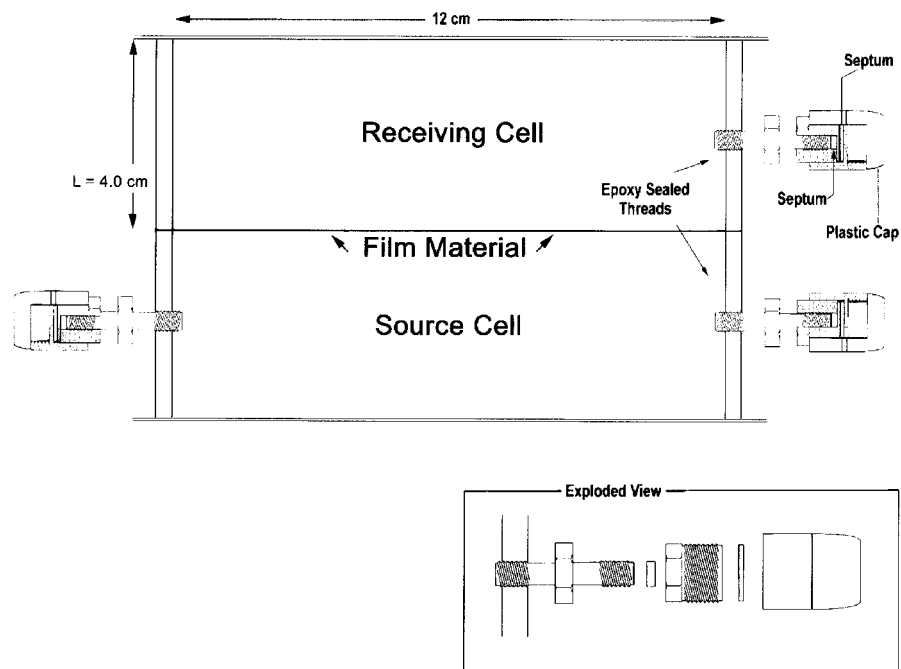


FIGURE 1. Schematic diagram of permeability cells and sampling ports.

while lower values of h indicate a more effective barrier to diffusion. Calculating h provides an intrinsic measure of the permeability of a film to a chemical which is not dependent on the chosen concentration gradient.

This paper describes a method for estimating the mass transfer coefficient of fumigant vapors across agricultural films. Fumigant compounds were spiked to a static sealed chamber and the concentrations in the source and receiving chamber were monitored. For static closed systems such as the permeability cells used in this experiment, the concentration in the receiving chamber increases while the concentration in the source chamber decreases until equilibrium is attained, when the concentrations in the upper and lower chambers are equal. An h was determined from the concentration data using a model which describes solute transport in a two-layered matrix, with the film introducing a boundary condition of reduced diffusion at the interface. The model includes sorption to and diffusion through the film. This method was used to measure the permeability of three films to MeBr, PrBr, and CP. This method requires a minimum of equipment and is especially useful as a screening tool in the development of new management practices for soil fumigation.

Materials and Methods

Chemicals and Plastic Films. Methyl bromide in a lecture bottle was purchased from Aldrich Chemical. Propargyl bromide (97% purity) was purchased from Fluka, and CP (99.9% purity) was donated by Niklor Chemical Company (Long Beach, CA). A sample of HDPE film (1.0 mil thickness) used in current soil fumigation practices was supplied by Tri-Cal (Hollister, CA). Black HDPE (4.0 mil) and silver mirrored Mylar (2.0 mil, surface modified with aluminum on one side) were purchased from a local supplier. These films were chosen for their expected range of permeabilities.

Permeability Cells. Permeability cells (Figure 1) were fabricated from stainless steel cylindrical stock of 12 cm ID. Cells were constructed in two halves, each approximately 4 cm long, sealed on one end by soldering a stainless steel plate to the column. The volume of each half-cell was measured. A piece of the plastic film to be tested was placed between the two half-cells, and epoxy was used to secure the

film and adhere the cell halves together in a gastight seal; adhesive aluminum tape was applied to the outside of the cells to ensure a gastight system. Sampling ports were constructed from brass fittings machined with a center hole, which was plugged with Teflon-faced silicone septa (Figure 1). Ports were installed at the midpoint of each half-cell. Two ports were installed on opposite sides of one half-cell (source chamber); one port was installed in the receiving chamber. The threads of the brass fittings were sealed with epoxy during assembly to prevent leaks during the experiment. Samples were collected by piercing the septum with the needle of a gastight syringe and withdrawing an aliquot of the air within each half of the permeability cell. Between samplings, ports were additionally sealed by tightening a plastic cap containing a Teflon-faced silicone septum onto the brass fitting.

Spiking, Sampling, and Analysis. Methyl bromide vapor was transferred from the lecture bottle to an evacuated Telfon gas sampling bag, giving a saturated vapor source. Methyl bromide (3.0 mL) was spiked to the source chamber of each cell using a gastight syringe. For CP and PrBr, liquid (~7.0 μ L CP, 100 μ L PrBr) was placed in a 125-mL Erlenmeyer flask with a mininert valve screw-cap. The liquid was allowed to vaporize, and 20 mL of the vapor was injected into the source chamber using a gastight syringe. During injection, a needle was placed in the second port of the source chamber to serve as a vent to avoid pressurizing the cell. Experiments were conducted at 20 ± 0.1 °C.

Samples (500 μ L from the receiving chamber; 250 μ L from the source chamber) were collected using gastight syringes and placed in 9-mL headspace vials. Vials were immediately crimp capped with aluminum seals and Teflon-faced butyl rubber septa. Separate syringes were used for the source and receiving cells; syringes were rinsed > 5 times with fresh air between replicate cells. Sampling began 5 min after injection and continued for approximately 8 h for 1-mil HDPE, 30 h for the 4-mil HDPE, and 40 days for the Mylar film. Samples collected from HDPE cells were analyzed the day they were collected. Samples for the Mylar film were stored at -20 °C until the end of the experiment, when all samples were analyzed.

Samples were analyzed using a Tekmar 7000 headspace autosampler interfaced with an HP5890 GC-ECD. The

headspace autosampler conditions were as follows: 90 °C equilibration temperature; 2.0 min equilibration time; 100 μ L sample loop. The GC conditions were as follows: DB-VRX column, 30 m long \times 0.25 mm ID \times 1.4 μ m film thickness; helium carrier gas at a flow rate of 0.6 mL min⁻¹; 230 °C injector temperature; 270 °C detector temperature; and oven temperature program: 35 °C held for 1 min, increasing at 8 °C per minute to 180 °C, held for 0.2 min. Under these conditions, the retention times for MeBr, PrBr, and CP were 7.4, 12.8, and 17.8 min, respectively. Calibration standards for GC analysis were prepared in acetone. Solution (5 μ L) was transferred to 9-mL headspace vials, and standards at seven concentrations were analyzed at the beginning of each set of samples and used for the construction of calibration curves.

Data Analysis. Vapor diffusion between two containers separated by a permeable membrane can be described using two simple coupled differential equations, that is

$$\frac{\partial C_r}{\partial t} + \frac{1}{L_r} \frac{\partial S_r}{\partial t} = D_r \frac{\partial^2 C_r}{\partial x^2} - \mu C_r + Q_r(x, t) \quad (3)$$

and

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

where C is the concentration [mg m⁻³] of the organic compound in the air, L is the length of the chamber [m], S is the mass of adsorbed chemical per film area [mg m⁻²], D is the effective diffusion coefficient [m² d⁻¹], μ is a first-order decay coefficient, and $Q(x, t)$ is any source or sink. The subscripts r and s refer to the receiving chamber and source chamber, respectively. If it is assumed that there is no degradation and that each chamber is perfectly mixed, eqs 3 and 4 reduce to

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

and

$$\frac{\partial C_s}{\partial t} + \frac{1}{L_s} \frac{\partial S_s}{\partial t} = Q_s(x, t) \quad (6)$$

When plastic material is placed between cells, it induces a resistance to diffusion which can be simulated using a mixed boundary condition containing a mass transfer coefficient, $h = D_{film}/b$, that characterizes the resistive nature of the interface. Therefore, the flux across the film is

$$J = h(C_s(t) - C_r(t)) \quad (7)$$

For transport between chambers, $Q(x, t)$ is the J/L with a negative sign indicating mass lost from the system. The solution for the concentration in each chamber when the receiving chamber has an initial concentration of C_0 and the chemical does not adsorb to the plastic film is

$$C_r(t) = \frac{C_{r,0}L_r + C_{s,0}L_s}{L_r + L_s} + \frac{(C_{r,0} - C_{s,0})L_s}{L_r + L_s} e^{-(h(L_r+L_s)t/L_rL_s)} \quad (8)$$

and

$$C_s(t) = \frac{C_{r,0}L_r + C_{s,0}L_s}{L_r + L_s} - \frac{(C_{r,0} - C_{s,0})L_r}{L_r + L_s} e^{-(h(L_r+L_s)t/L_rL_s)} \quad (9)$$

The flux is

$$J = (C_{s,0} - C_{r,0}) h e^{-(h(L_r+L_s)t/L_rL_s)} \quad (10)$$

and the mass transfer coefficient can be estimated at any time, t , using

$$h = \frac{L_s L_r}{(L_s + L_r)t} \ln \left[\frac{(C_{s,0} - C_{r,0})(L_s + L_r R)}{(C_{s,0}L_s + C_{r,0}L_r)(1 - R)} \right] \quad (11)$$

where R is the ratio: $C_r(t)/C_s(t)$ and $C_{s,0} > C_{r,0}$. Equation 11 is useful when one or two concentration measurements are available.

An alternative method for estimating the coefficient h uses the Levenberg–Marquardt nonlinear least squares minimization procedure (18)

$$\min \left(\sum_{i=1}^n [C_r(t_i)_{measured} - C_r(t_i)_{model}]^2 + \sum_{i=1}^m [C_s(t_i)_{measured} - C_s(t_i)_{model}]^2 \right) \quad (12)$$

where h , and possibly other parameters, are determined from the minimization algorithm. The advantage of this approach is that all the collected data can be used to determine h and the method is less affected by measurement or analytical errors. A program was written to perform the minimization. (This program is available from the authors.)

For some film-chemical combinations, adsorption must be considered. However, since the film is not uniformly distributed throughout the cell (e.g., as adsorptive surfaces would be in a porous media), the equilibrium time is also affected by system geometry and gas diffusion to the film surfaces. In addition, the two chambers represent a layered system that is coupled by the film. Therefore, processes occurring on both sides of the film will ultimately affect the equilibrium time. Adsorption can be modeled as a kinetic process at early times that approaches equilibrium at later times

$$\frac{\partial S}{\partial t} = \alpha(k_p C(t) - S(t)) \quad (13)$$

where 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-scale equilibrium adsorption rate parameter. Independent measures of sorption of fumigant vapors to agricultural films (19) showed that the sorption isotherms were linear within the concentration range used in this study. Following the same procedure described above, the solution for the concentration in each chamber when the source chamber has an initial concentration of C_0 and $L_s = L_r = L$ is

$$C_r(t) = \frac{C_0 L}{2} \left[\frac{L + k_p e^{-(\alpha(k_p+L)t/L)}}{L(k_p + L)} + \frac{2h + \alpha(k_p - L) - \sqrt{\beta}}{2L\sqrt{\beta}} e^{-(2h+\alpha(k_p+L)-(\beta)^{1/2})t/2L} - \frac{(2h + \alpha(k_p - L) + \sqrt{\beta}) e^{-(2h+\alpha(k_p+L)+(\beta)^{1/2})t/2L}}{2L\sqrt{\beta}} \right] \quad (14)$$

$$C_s(t) = \frac{C_0 L}{2} \left[\frac{L + k_p e^{-(\alpha(k_p+L)t/L)}}{L(k_p + L)} - \frac{2h + \alpha(k_p - L) - \sqrt{\beta}}{2L\sqrt{\beta}} e^{-(2h+\alpha(k_p+L)-(\beta)^{1/2})t/2L} + \frac{(2h + \alpha(k_p - L) + \sqrt{\beta}) e^{-(2h+\alpha(k_p+L)+(\beta)^{1/2})t/2L}}{2L\sqrt{\beta}} \right] \quad (15)$$

TABLE 1. Mass Transfer and Sorption Coefficients for Fumigants Diffusing through Plastics at 20 °C, Measured Using Triplicate Static Permeability Cells ± Standard Error of the Estimate^a

	methyl bromide	propargyl bromide	chloropicrin
		1-mil HDPE	
<i>h</i> (cm h ⁻¹)	0.37 ± 0.02 (0.38 ± 0.02)	1.48 ± 0.08 (1.47 ± 0.09)	0.65 ± 0.06 (0.65 ± 0.06)
<i>α</i> (h ⁻¹)	0.5 ± 0.4 (2.2)	0.4 ± 0.2 (0.6)	0.9 ± 0.3 (1.0)
<i>k_p</i> (cm)	0.3 ± 0.1 (0.2)	1.2 ± 0.02 (1.1)	1.8 ± 0.2 (1.8)
		4-mil Black HDPE	
<i>h</i> (cm h ⁻¹)	0.14 ± 0.01 (0.16 ± 0.02)	0.48 ± 0.02 (0.46 ± 0.04)	0.25 ± 0.03 (0.24 ± 0.03)
<i>α</i> (h ⁻¹)	0.21 ± 0.09 (0.22)	0.13 ± 0.04 (0.21)	0.32 ± 0.06 (0.29)
<i>k_p</i> (cm)	1.3 ± 0.2 (0.25)	1.3 ± 0.2 (1.4)	3.8 ± 0.3 (4.1)
		Silver Mylar ^b	
<i>h</i> (cm h ⁻¹)	<4.4 × 10 ⁻⁶	<1.3 × 10 ⁻⁵	<2.3 × 10 ⁻⁴
<i>α</i> (h ⁻¹)	2.1 ± 0.9 (2.3)	1.2 ± 0.4 (1.4)	0.8 ± 0.3 (0.9)
<i>k_p</i> (cm)	1.09 ± 0.07 (1.08)	5.2 ± 0.4 (5.2)	11 ± 2 (11)

^a Values for *α* and *k_p* in parentheses are determined independently using eqs 16 and 17; values of *h* in parentheses are determined by nonlinear regression with these values of *α* and *k_p* fixed. ^b No permeation through the film detected; reported *h* is based on detection limit and eq 18. Regression to model to determine *α* and *k_p* fixed *h* at the detection limit and *C₀* at 100%.

where $\beta = -8hL\alpha + [2h + \alpha(k_p + L)]^2$. To make use of eqs 14 and 15, the minimization algorithm shown in eq 12 is necessary.

Alternatively, the parameters may be determined independently for each data set using the early- and late-time data. The equilibrium adsorption coefficient, expressed as

$$k_p = L \left[\frac{C_0 - 2C_{s,\infty}}{2C_{s,\infty}} \right] \quad (16)$$

can be approximated by considering *C_{s,∞}* to be represented by the equilibrium concentration for cells that have reached equilibrium; for cells approaching equilibrium, *C_{s,∞}* was estimated as the mean of the source and receiving cell concentrations in the final samples. The system kinetic parameter may be determined as

$$\alpha = \frac{-L \left(\frac{dC_r}{dt} + \frac{dC_s}{dt} \right)}{k_p} \quad (17)$$

and approximated by considering the change in concentration with time immediately after spiking (i.e., the first few data points) in the source and receiving cells. Fixing the values of *C₀*, *α*, and *k_p* allows for a regression with *h* as the only adjustable parameter.

For situations where the concentration in the receiving cell remains below detectable values, the maximum possible value for the mass transfer coefficient, *h*, can be estimated using

$$0 \leq h < \frac{\epsilon L_r}{t(\bar{C}_s - \epsilon)} \approx \frac{\epsilon L_r}{t\bar{C}_s} \quad (18)$$

where ϵ is the detection limit and \bar{C}_s is the average concentration in the source chamber during the time interval, *t* (in most cases, long after sorption equilibrium has been achieved).

Results and Discussion

The permeability of two HDPE and one Mylar film to MeBr, PrBr, and CP vapors were measured. Concentration data were normalized to the initial source concentration, measured 5 min after injection; *C₀* was fixed at 100% for regression. Mass transfer coefficients are reported in Table 1. As has been observed in laboratory and field studies, HDPE was permeable to fumigant vapors. Both HDPE films produced values for *h* for PrBr and CP that were ~4 and ~1.8 times that of MeBr,

TABLE 2. Mean Mass Transfer Coefficient ± Standard Error for Replicated Cells Containing 1-mil HDPE^a

fumigant	<i>h</i> (cm h ⁻¹)
methyl bromide (<i>n</i> = 4)	0.36 ± 0.03
propargyl bromide (<i>n</i> = 6)	1.45 ± 0.06
chloropicrin (<i>n</i> = 6)	0.62 ± 0.05

^a *h* was determined in each cell individually; the standard error represents the variation between replicates.

respectively (Table 1). Increasing the thickness of the HDPE film decreased the rate of mass transfer for all fumigants (lower *h*, Table 1). The decrease was nearly proportional to the increase in film thickness, and increasing the film thickness by a factor of 4 resulted in an *h* that was ~3 times lower. The Mylar used in this study showed no measurable permeability, with undetectable concentrations in the receiving chamber at all sampling times. Detection limits were ~0.01 μg mL⁻¹ for MeBr and PrBr and ~0.003 μg mL⁻¹ for CP; therefore, *h* is less than 4 × 10⁻⁶ cm h⁻¹ for MeBr, 1 × 10⁻⁵ cm h⁻¹ for PrBr, and 2 × 10⁻⁴ cm h⁻¹ for CP (Table 1), calculated from eq 18. In this study, the Mylar film was placed in the cells with the aluminized side facing the source chamber. Shorter-term investigations of Mylar permeability showed that regardless of the orientation of the film, no MeBr, PrBr, or CP was measured in the receiving chamber after 14 days.

These results are consistent with previously reported measures of film permeability. Kolbezen and Abu-El-Haj (*1*) report several values of permeability coefficients for MeBr and CP diffusing through plastic films. They report permeability coefficients in units of flux/concentration gradient. Converting their units to be consistent with ours, their permeability coefficients become 0.14–0.27 cm h⁻¹ for MeBr diffusing through 1-mil HDPE at 23 °C. At 30 °C, the flux of CP through 1-mil HDPE was ~3 times faster than MeBr. These values and trends are similar to the results of this experiment (Table 1). Other reported values of film permeability (*6, 15*) report permeability coefficients as a flux. Because the flux depends on the concentration gradient, these results cannot be directly compared.

The method provided a precise and relatively rapid means of determining the mass transfer coefficient for different films. Mass transfer coefficients determined in replicated cells containing 1-mil HDPE indicated that the method generates reproducible results; coefficients of variation were <10% for each compound (Table 2).

Sorption was indicated in the permeability columns by (i) an initial rapid decrease in the source concentration that

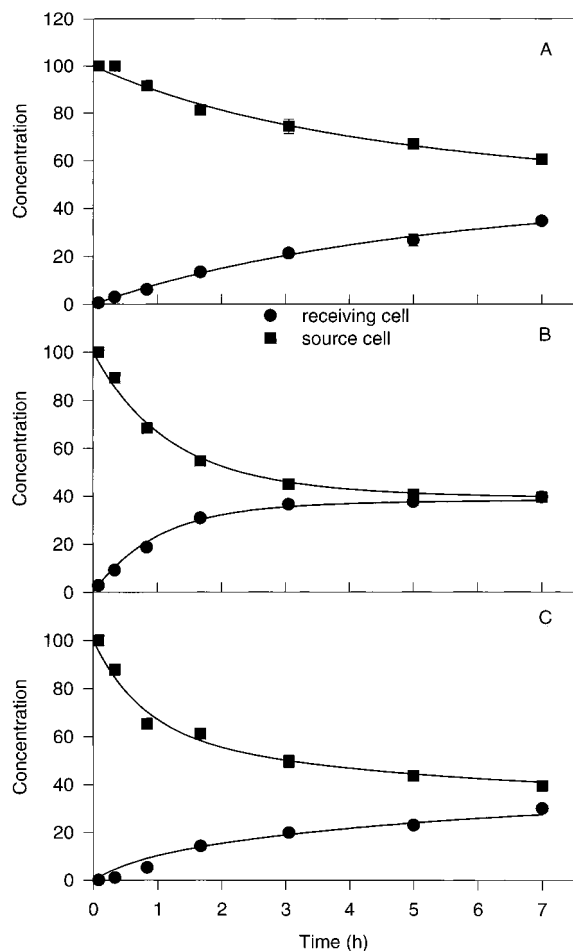


FIGURE 2. Diffusion of MeBr (A), PrBr (B), and CP (C) through 1-mil HDPE at 20 °C. Data points indicate measured concentrations (% relative to source concentration at initial sampling time) in three replicate cells. Lines indicate nonlinear regression to eqs 14 and 15.

is not accompanied by a corresponding increase in the receiving chamber and (ii) an equilibrium concentration < 50% of the initial concentration, because some of the mass is held on the film (Figures 2–4). Sorption is accounted for in the data analysis by the incorporation of a system-scale kinetic parameter (α) and an equilibrium sorption parameter (k_p). While these parameters may be useful for comparing the sorptive potential of different films, they may not be quantitatively applicable as measures of sorption. Several processes are manifested in α , including diffusion to the film surface, sorption kinetics, and system geometry (i.e., length–volume relationships). The timing of sample collection may also impact α because it is strongly affected by the concentration data at early times. For example, because no samples were collected for the Mylar film between 10 min and 0.5 h (Figure 4), the estimation of α for the Mylar films is a lower limit (apparent equilibrium was achieved at least this rapidly). The equilibrium sorption parameter k_p is strongly influenced by the concentration ratio observed at long times. In a previous study reporting equilibrium sorption measurements, sorption followed the trend CP (most sorptive) > PrBr > MeBr (least sorptive) for all films tested, including HDPE (19). The same sorption trend was observed for all films used in these experiments (k_{ps} in Table 1). Sorption experiments (19) showed that fumigant sorption to agricultural films is relatively rapid, with most of the sorption occurring within 15 min, and complete within 4 h (24 h for MeBr). All loss from the gas phase is included in k_p ; therefore, it is imperative that the cells be gastight for equilibrium to be achieved and

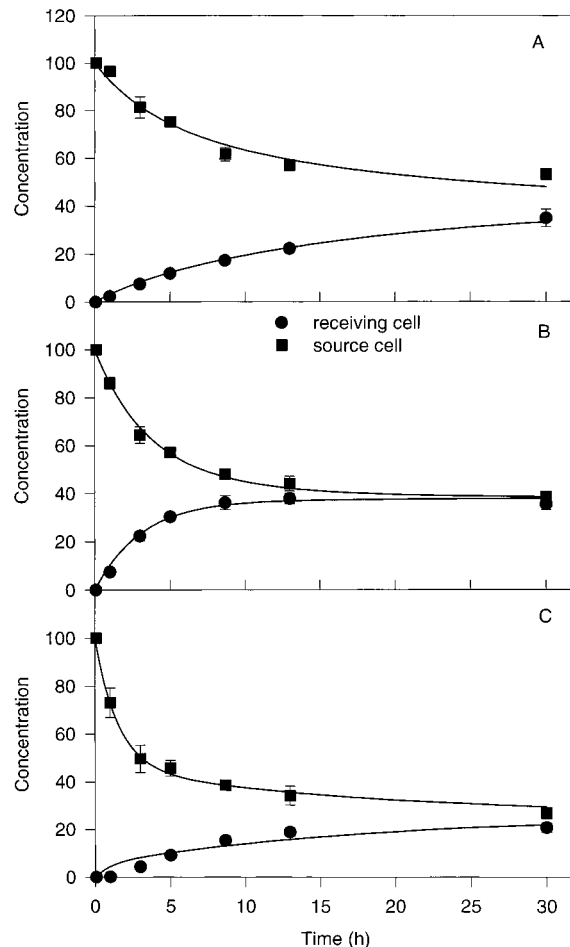


FIGURE 3. Diffusion of MeBr (A), PrBr (B), and CP (C) through 4-mil black HDPE at 20 °C. Data points indicate measured concentrations (% relative to source concentration at initial sampling time) in three replicate cells. Lines indicate nonlinear regression to eqs 14 and 15.

to result in accurate parameter estimation. Our cells were gastight, showing no evidence of leakage during > 40 d (Figure 4, constant concentrations in the source chamber of cells containing a virtually impermeable film).

In addition to simultaneously determining h , k_p , and α via the nonlinear least squares minimization procedure, these parameters were also determined independently by using long-time behavior to approximate k_p and early-time behavior to determine α , then fixing these values and using the model to determine h only. Both approaches produced very similar values for all three parameters for each data set (Table 1).

The effect of sorption on estimated mass transfer coefficients was determined by fixing α and k_p at very low values (10^{-6}) and including h and C_0 as adjustable parameters. For film-chemical combinations demonstrating very little sorption, the inclusion of the sorption terms α and k_p resulted in a negligible change in the nonlinear regression and values of h . For example, for MeBr permeation through 1-mil HDPE, h was the same when α and k_p were fixed at 10^{-6} as when α and k_p were included as adjustable parameters ($h = 0.37$ vs 0.38 cm h^{-1}), and there was little difference in the fit to the experimental data (Figure 5). For more sorptive film-chemical combinations, inclusion of the sorption parameters had a larger impact on h and a substantial improvement in fit to the experimental data. For example, for CP diffusing through 4-mil black HDPE, including α and k_p as adjustable parameters resulted in a much better fit to the data (Figure 6) and a change in h from 0.25 cm h^{-1} ignoring sorption to

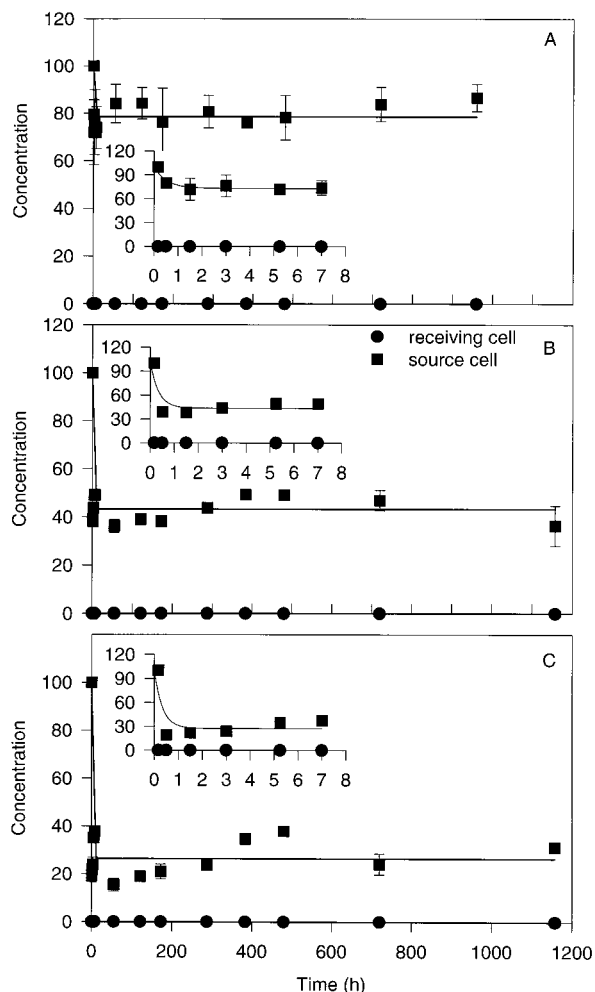


FIGURE 4. Diffusion of MeBr (A), PrBr (B), and CP (C) through 2-mil silver mirrored Mylar at 20 °C. Data points indicate measured concentrations (% relative to source concentration at initial sampling time) in three replicate cells. Lines indicate nonlinear regression to eqs 14 and 15. Insets demonstrate early-time behavior.

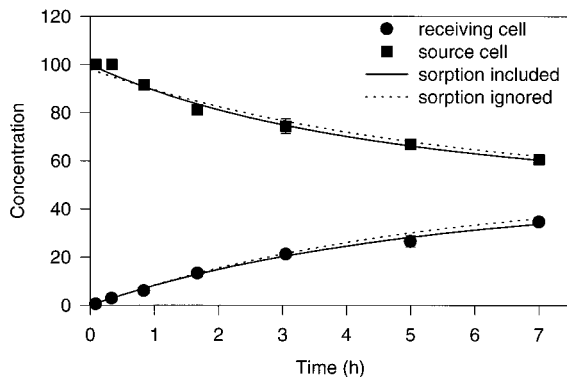


FIGURE 5. For film-chemical combinations demonstrating low sorption, inclusion of sorption parameters has little impact on model results. Nonlinear regression of MeBr data for 1-mil HDPE with (eqs 14 and 15) and without (eqs 8 and 9) sorption terms included in the model.

0.23 cm h^{-1} with sorption. Some films are highly sorptive to organic vapors (19), and the inclusion of sorption parameters in these cases may have a large impact on the value of h . In this study, the Mylar film was significantly more sorptive than the polyethylene films, and sorption was very important in determining the regression and model parameters (Figure 7).

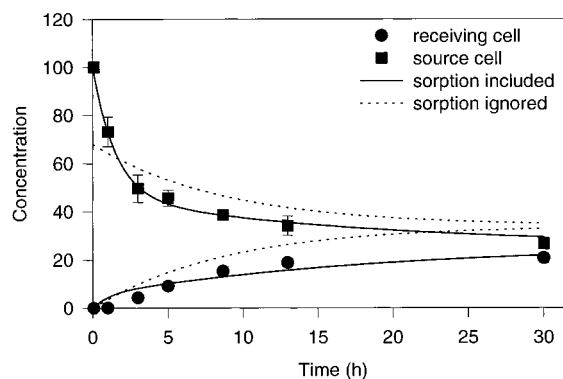


FIGURE 6. For film-chemical combinations demonstrating significant sorption, inclusion of sorption parameters has a larger impact on model results. Nonlinear regression of CP data for 4-mil black HDPE with (eqs 14 and 15) and without (eqs 8 and 9) sorption terms included in the model.

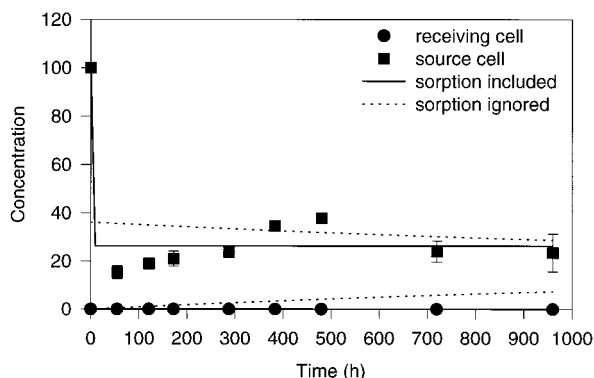


FIGURE 7. For sorptive, nonpermeable films, inclusion of sorption terms in the model has a large impact on the model results. Nonlinear regression of CP data for Mylar with (eqs 14 and 15) and without (eqs 8 and 9) sorption terms included in the model.

Advantages of This Method. This method has several advantages over previously reported procedures to measure the permeation of fumigant compounds through agricultural films. (1) This method provides a measure of permeability that is a property of the film-chemical combination: The mass transfer coefficient is not dependent on the concentration gradient as other measures of film permeability are. (2) Other reported measurements of permeability to fumigants have used very high concentrations (1) or pure fumigant vapor (16), which may not be appropriate in estimating emissions under field conditions. In these experiments, we used fumigant concentrations similar to those measured in the soil following field applications of MeBr (20) and field-relevant concentrations of CP and PrBr. (3) Because agricultural films are sorptive, this method accounts for the sorbed mass and system kinetics, while flow-through cells and ASTM methods measure permeability after sorption equilibrium, under steady-state conditions.

The mass transfer coefficient measured by this method depends only on the film type and temperature, making this method useful for comparisons of film permeability under different management practices, application techniques, and environmental conditions. Since the method requires a minimum of equipment and is easy to employ, it will be useful as a screening tool in the development of new films and management practices. The permeability of an intact sample of a film may not represent the emissions observed in the field, however. Particularly for virtually impermeable films, while the film itself may have very low permeability, glued seams, puncture holes, and edge-of-field borders may provide avenues for significant leakage.

This method will be better suited to determine the mass transfer coefficient for virtually impermeable films than flow-through or ASTM methods. Using flow-through systems, the mass of chemical diffusing across the film is diluted to a great extent by the air stream used to sweep the receiving cell. Therefore, relatively high concentrations are required before an accurate measurement can be made. In the ASTM methods, the permeability of the film must be great enough to produce a measurable change in volume or pressure in the receiving cell. Gamleil et al. (16) report limits of detection for MeBr permeability as $0.05 \text{ g m}^{-2} \text{ h}^{-1}$ for the variable volume method and $0.0005 \text{ g m}^{-2} \text{ h}^{-1}$ for the flow-through system. Because the air in the receiving chamber is only minimally diluted in our method (a sample collected using a gastight syringe is transferred to a 9-mL headspace vial), and because the analytical method is sensitive to low concentrations of these fumigant compounds, our method should produce significantly lower limits of detection than previously reported methods, making it more useful for films with low permeability.

Acknowledgments

This research was partially funded by Dow AgroSciences.

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Received for review June 28, 2000. Revised manuscript received September 30, 2000. Accepted December 11, 2000.

ES0014279