Environ. Sci. Technol. **1999**, *33,* 1213−1217

Sorption of Fumigants to Agricultural Films

SHARON K. PAPIERNIK,*,†
JIANYANG GAN,†
JAMES A. KNUTESON,‡ AND
SCOTT R. YATES†

Soil Physics and Pesticides Research Unit, U. S. Salinity Laboratory, 450 West Big Springs Road, Riverside, California 92507-4617, and Ecosystem Fate and Exposure Assessment, DowElanco, 9330 Zionsville Road, Indianapolis, Indiana 46268-1053

Plastic tarps are often used in soil fumigation to contain chemicals in the soil to increase efficacy and decrease emissions of fumigant vapors. This research has shown that plastic films have a significant capacity to sorb fumigant vapors and that the sorption is largely reversible. We tested three agricultural films (polyethylene and two high-barrier films) with four soil fumigants (methyl bromide, chloropicrin, 1,3-dichloropropene, and propargyl bromide, a potential alternative to methyl bromide). We observed significant sorption of all fumigants to all the films at field-relevant concentrations. Partition coefficients (sorbed/vapor-phase concentration) ranged from <1 dm^3/m^2 film for methyl bromide to $\sim$200 dm^3/m^2 film for chloropicrin. Sorption isotherms were linear, indicating that the film may be a large sink for fumigant vapors. Sorption of most fumigants was very rapid, with the bulk of the sorption occurring within the first few minutes of contact. Desorption was also rapid, with most desorption occurring within minutes after the film samples were removed to fresh air. First-order rate constants for desorption were $\sim$0.5 to 1.5 min^{-1}. Sorption/desorption may be important in reducing emissions and determining worker exposure and should be considered in measurements involving agricultural films.

Introduction

Soil fumigants are used to control nematodes, weeds, and fungi in soils to be planted with fruits and vegetables. Soil fumigants are volatile compounds that are dispersed through the soil in the gas phase. Because of their high volatility, emission from the soil surface can account for a significant portion of the applied fumigant. Concentrations in air following fumigation have surpassed regulatory health limits (*1*).

Plastic films are often used in the fumigation of greenhouse and field soils to contain the fumigant in the soil in order to increase efficacy and reduce emissions of fumigant vapors. The soil surface is covered immediately following fumigation, typically using a low-density or high-density polyethylene (LDPE or HDPE) tarp. It has been reported that these plastics are permeable to soil fumigants (*2*−*5*). Laboratory (*6*−*8*) and field studies have indicated that emissions from fumigated soils covered with polyethylene films may be high: Methyl bromide emissions of >50% of the applied mass have been reported for treated soils covered with LDPE (*3*, *9*) and HDPE (*5*, *10*). Polyethylene tarps have also been reported to be permeable to other fumigants such as methyl iodide (*5*, *7*), 1,3-dichloropropene (1,3-D) (*5*, *11*), and chloropicrin (*5*). In a typical field application, the plastic tarp is removed after a cover period of 5−10 days. The discarded film is either taken to landfills or collected by a recycler.

Because methyl bromide has been implicated as an ozone-depleting chemical, it is scheduled to be phased out in the U. S. by the year 2005 (*12*). Research on the use of films other than polyethylene has indicated that some films are less permeable to soil fumigants (*3*, *5*, *11*) and can drastically reduce the emissions of methyl bromide vapors to the atmosphere (*10*, *13*). One high-barrier film, Hytibar, has been reported to be virtually impermeable to methyl bromide, methyl iodide, 1,3-D, and chloropicrin (*5*). Hytibar is a coextruded film that has a layer of copolymer ethyl vinyl alcohol between two layers of polyethylene; the middle copolymer layer imparts a much lower permeability to the film than polyethylene alone (*4*).

There is little information available concerning the sorption of organic pesticide vapors to plastics. Steinwandter and Schlüter (*14*) observed sorption of organochlorine pesticide vapors to polyethylene sheets which accounted for up to 100% of the pesticide mass added to the reaction vessel, so that the PE-sorbed concentrations ranged from 0.003 to 0.01 mg/m^2. The sorption of pesticides and other organics in aqueous solution to plastics has been better characterized. The sorption of several insecticides and fungicides to agricultural films was measured by Nerín et al. (*15*). They observed slow sorption of some pesticides on LDPE and other plastics, which could account for >90% of the pesticide mass; sorption occurred over several days. Vuik et al. (*16*) measured the loss of two fungicides from aqueous solution and observed no sorption of oxamyl on PE film, but ∼40% of the etridiazole was adsorbed. Sorption of pesticides in aqueous solution to LDPE, HDPE, and other plastic tubing has been reported to be insignificant (that is, not affecting the measured aqueous concentrations) (*16*−*18*), but some sorption of pesticides to LDPE and HDPE tubing has been observed (*19*). Sorption of chlorinated hydrocarbons in aqueous solution to polyethylene and other plastics has also been reported (*20*−*22*).

Containment is imperative for the continued use of volatile toxic compounds. Use of high-barrier plastic films appears to be a promising method for reducing emissions of soil-applied fumigants. The effect of these new agricultural films on the emission and efficacy of fumigants is vital to the implementation of new soil fumigation practices. The objectives of this study were to provide information on the interactions of fumigants and plastic films by investigating the sorption and desorption potentials of several fumigants on polyethylene tarp and two high-barrier films.

Materials and Methods

Chemicals and Agricultural Films. Chloropicrin (98% purity) and 1,3-dichloropropene (47% cis, 51% trans) were obtained from ChemService. Propargyl bromide (∼97% purity) was obtained from Fluka, and methyl bromide (>99% purity) was obtained from Great Lakes Chemical Co. HDPE film (1.0-mil thickness) was donated by Tri-Cal (Hollister, CA). Hytibar film (1.5 mil) was contributed by Klerk Plastics (Belgium), and a sample of an experimental film (3.0 mil) was provided by DowElanco (Indianapolis, IN). The weight

---

* Corresponding author. Telephone: (909) 369-4802; fax: (909) 342-4964; e-mail: spapiernik@ussl.ars.usda.gov.
† U. S. Salinity Laboratory.
‡ DowElanco.

10.1021/es980877m CCC: $18.00

per unit area of these films were measured as 58 g/m^2 for HDPE, 93 g/m^2 for Hytibar, and 178 g/m^2 for the Dow film.

Sorption of Chemicals to Film. *Time Required To Reach Equilibrium*. Samples of each film (0.35 g) were cut into pieces ~1.5 × 5 cm and placed in glass headspace vials (21.6-cm^3 capacity). Film samples and blank vials, to which no film was added, were spiked with fumigant vapor using a gastight syringe. Fumigant vapor was used to avoid possible cosolvent effects. Therefore, there were only two components present in each vial: the film and the fumigant in the gas phase. Experiments were conducted for each fumigant separately, to eliminate possible interactions between fumigants (*2*). Vials were spiked with vapor to result in headspace concentrations that reflect the soil gas concentrations measured following soil fumigation. Six replicate vials were prepared for each film and blank treatment. Vials were incubated at 20 ± 1 °C.

To determine the time to attain equilibrium for fumigant sorption, headspace samples were collected at 5 min, 15 min, 1 h, 4 h, 24 h, and 48 h after spiking. The time required for equilibrium was determined as the time after which no additional decrease in concentration occurred in the film vials relative to the blank vials. Headspace samples (0.1 cm^3) were collected using 100-μL gastight syringes; a separate syringe was used for each set of film samples to eliminate cross-contamination. Headspace was removed from each vial and transferred to a 21.6-cm^3 headspace vial, which was capped immediately with a Teflon-faced butyl rubber septum and an aluminum seal. Placing the syringe needle deep in the vial and capping the vial immediately after transfer minimized loss of the fumigant (*8*), and good precision was obtained; variability in the fumigant concentration in six replicate blank vials was usually <5% and always <10%. The headspace concentration in each vial was measured by static headspace GC using a Tekmar 7000 headspace autosampler attached to a Hewlett-Packard 5890 GC following the general method of Gan et al. (*23*).

Determination of Sorption Coefficients. Equilibrium sorption measurements were made similarly, using 0.35-g samples of each film. Appropriate volumes of the fumigant vapor were spiked to each 21.6-cm^3 vial using a gastight syringe to result in four different fumigant concentrations. Methyl bromide was spiked to achieve equilibrium headspace concentrations of 2−20 μg/cm^3 in the film samples; 1,3-D, 0.09−0.8 μg/cm^3 for the cis isomer and 0.05−0.5 μg/cm^3 for the trans isomer; chloropicrin, 0.07−2 μg/cm^3; and propargyl bromide, 0.5−3.5 μg/cm^3.

The concentrations used in this study were similar to those that have been measured in soil gas samples following soil fumigation. In a field experiment using typical application rates of methyl bromide in a HDPE-tarped field, soil gas concentrations of ~10 μg/cm^3 were measured near the soil surface 2 days after application and ~1 μg/cm^3 after 10 days (*24*). Soil gas concentrations on the order of 0.2 μg/cm^3 of total 1,3-D were observed near the soil surface of an untarped field 1.4 days after application in a field study conducted by Wang et al. (*25*). Chloropicrin is used in mixtures with 1,3-D (containing up to 35% chloropicrin) and with methyl bromide (up to 33% chloropicrin), so an estimate of the soil gas concentration expected in field application of these mixtures is 0.07−3.5 μg/cm^3. No estimates of soil gas concentrations that might result from field application of propargyl bromide are available.

Six replicate samples at each concentration were equilibrated at 23.5 ± 0.1 °C for 6 h for chloropicrin, propargyl bromide, and 1,3-D and for 24 h for methyl bromide. The first experiment indicated that these times were sufficient for equilibrium. Headspace concentrations were measured by withdrawing a 0.1-cm^3 aliquot of the headspace in each vial using a gastight syringe and transferring the headspace to an empty 21.6-cm^3 headspace autosampler vial, which was immediately capped with a Teflon-faced butyl rubber septum and aluminum seal. The fumigant concentration was determined by static headspace GC analysis. Calibration standards were prepared by dilution of saturated vapor. The amount of fumigant sorbed to the film was determined from the difference between blank (no film) and film samples for each concentration. Sorption isotherms (plots of sorbed versus headspace concentration) were constructed for each fumigant, and a partitioning coefficient (K) was determined for each fumigant−film combination by calculating the slope of the sorption isotherm via linear regression. Sorption was also calculated on a surface area basis, with the surface area calculated from the mass per unit area for each film. A single piece of film of nominal thickness was assumed so the surface area represented only one face of the film. Regression lines were not forced through the origin.

To determine if the decrease in fumigant concentration was attributable to sorption and not degradation, the equilibrated samples were extracted with hexane immediately following removal of the headspace sample. Hexane (5.0 mL) was added to selected sample vials using a gastight syringe, puncturing the septum so that the vials remained sealed during the extraction step. Sample vials were placed on a shaker table for 2 h. An aliquot of the hexane extract was transferred to a GC autosampler vial and analyzed using GC-ECD. Complete recovery was indicated by equivalent extract concentrations in blank vials (no film) and film sample vials. For samples that showed incomplete recovery of fumigant in hexane, additional equilibrated film samples were extracted with 5 mL of distilled deionized water. An aliquot of the water extract was analyzed on a Dionex DX-100 ion chromatograph to determine the anion concentration in the film sample vials. Transformation of these fumigants results in the formation of Cl$^-$ or Br$^-$, so the presence of Cl$^-$ or Br$^-$ in a sample was used to indicate degradation.

Desorption from Film. An experiment was conducted to determine the desorption of film-sorbed fumigants over short periods of time. Samples of each film were cut into 12-cm-diameter circles and placed in 21.6-cm^3 headspace vials. Film samples were spiked with fumigant vapor so that the total amount added to each vial was the same as for the highest concentration used in the sorption experiment. Six blank vials, which were spiked with the same amount of fumigant vapor but contained no film, were also prepared. Samples were equilibrated as for the sorption experiment.

Following the sorption step, an aliquot of the headspace (0.1 cm^3) was removed from the blank vials and six replicate vials for each film and analyzed by headspace GC. The sorbed concentration at time zero was calculated as the difference in headspace concentrations between the blanks and film sample vials. The vials containing film samples were then decapped and the film was removed and secured to a board in a fume hood using a push pin so that the film surface was continually swept with fresh air in the hood. Six replicate film samples were removed from the board after 2, 5, and 15 min and placed in clean 21.6-cm^3 vials. Hexane (10 mL) was added to extract the film samples; the vials were capped and vortexed for 2 min. An aliquot of the hexane extract was injected onto a gas chromatograph to determine the fumigant concentration, indicating the sorbed concentration. Desorption was fitted to a first-order decay model, and a rate constant (k) was determined for each film/fumigant combination.

Results and Discussion

Sorption Kinetics. Chloropicrin sorption was very rapid and was complete within 15 min after spiking. Sorption of propargyl bromide and 1,3-D was also rapid, with most sorption occurring within 15 min after spiking and was

TABLE 1. Partition Coefficients (C_{Sorbed}/C_{Vapor}) for Fumigant Vapor Sorbing to Agricultural Films

fumigant	HDPE	Hytibar	Dow film
methyl bromide			
K, cm^3/g film	7.4 ± 0.4	12.2 ± 0.3	6.3 ± 0.3
K, dm^3/m^2 film	0.171 ± 0.009	0.45 ± 0.01	0.45 ± 0.02
r^2	0.949	0.988	0.962
chloropicrin			
K, cm^3/g film	205 ± 7	161 ± 3	181 ± 5
K, dm^3/m^2 film	4.8 ± 0.2	6.0 ± 0.1	12.9 ± 0.3
r^2	0.981	0.991	0.989
propargyl bromide			
K, cm^3/g film	46 ± 1	57 ± 2	44 ± 3
K, dm^3/m^2 film	1.06 ± 0.03	2.12 ± 0.08	3.1 ± 0.2
r^2	0.986	0.966	0.910
cis-1,3-D			
K, cm^3/g film	140 ± 11	113 ± 6	119 ± 6
K, dm^3/m^2 film	3.3 ± 0.3	4.2 ± 0.2	8.5 ± 0.5
r^2	0.874	0.937	0.944
trans-1,3-D			
K, cm^3/g film	174 ± 16	133 ± 11	136 ± 11
K, dm^3/m^2 film	3.4 ± 0.4	4.9 ± 0.4	9.7 ± 0.8
r^2	0.843	0.870	0.885

complete within 4 h. Sorption of MeBr on each film was slower than the other fumigants tested; sorption of MeBr took place over several hours and was complete within 24 h.

These sorption reactions appear more rapid than some other previously reported reaction rates for pesticides sorbing to plastics. Steinwandter and Schlüter (*14*) reported that the time required for complete sorption of organochlorine pesticides to plastics was on the order of days; however, the pesticides were added as a liquid so that this indicates the time required for liquid/vapor/sorbed-phase equilibrium. The time required for sorption of pesticides from the aqueous phase to plastic films is variable: Sorption of fungicides to PE film has been reported to occur within the first few minutes of contact, with equilibrium concentrations attained after 4 h (*16*); slow sorption of organochlorine and organophosphorus pesticides to LDPE has been observed, with sorption times on the order of days rather than hours (*15*).

Sorption coefficients. Sorption isotherms were linear, with correlation coefficients > 0.95 in most cases (Table 1). The sorption coefficient (K) is therefore indicated by the slope of the linear isotherm. Chloropicrin showed high sorption onto each film tested, with K ranging from ~160 for Hytibar to ~200 cm^3/g film for HDPE (Table 1). The film-sorbed component accounted for 73−81% of the total chloropicrin added to the closed systems. Calculating partitioning based on the surface area of the films gives K's for chloropicrin ranging from 5 for HDPE to 13 dm^3/m^2 for the Dow film (Table 1). Sorption isotherms based on the mass of the film (Figure 1A) show a different sorption trend than sorption isotherms based on the surface area of the film (Figure 1B), since the weight/unit area for the Dow film is ~3 times higher than for HDPE and almost 2 times higher than for Hytibar. Because Hytibar has layers of HDPE on either side, sorption based on the surface area may be a better method of comparing sorption to different films. Also, surface area is the factor determining the amount of film used in field and greenhouse fumigations.

Hytibar and HDPE showed similar sorption (Figure 1B), suggesting that the HDPE of the coextruded film may be the primary sorbent, with the middle component (ethyl vinyl alcohol in Hytibar) being of secondary importance in determining the sorptivity of this film to chloropicrin. The Dow film showed approximately the same sorption on a mass basis as the other films (Figure 1A), but because of its high weight, sorption based on surface area was much higher than for Hytibar and HDPE (Figure 1B). All of the added chloropicrin was recovered in the hexane extract, so degradation of chloropicrin in contact with these films was negligible.

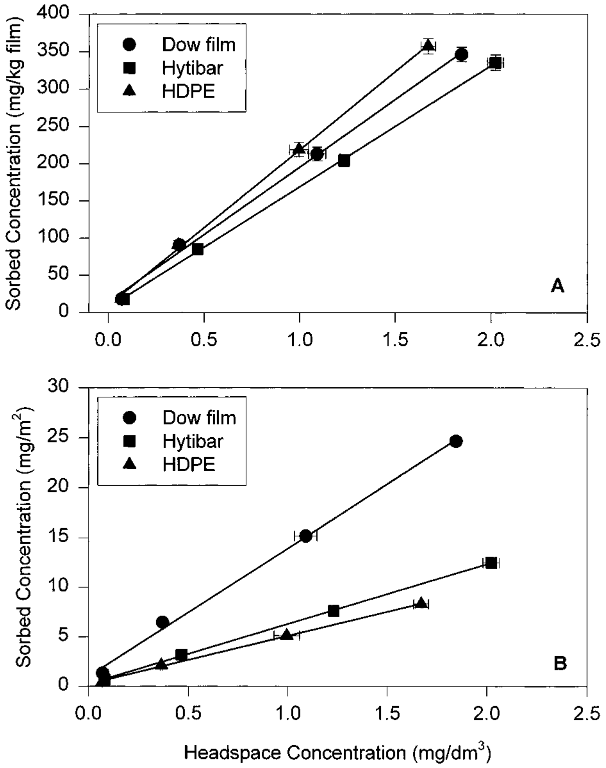

FIGURE 1. Sorption isotherms for chloropicrin based on (A) mass and (B) the surface area of the film. Error bars indicate the standard error of the mean of six replicates.

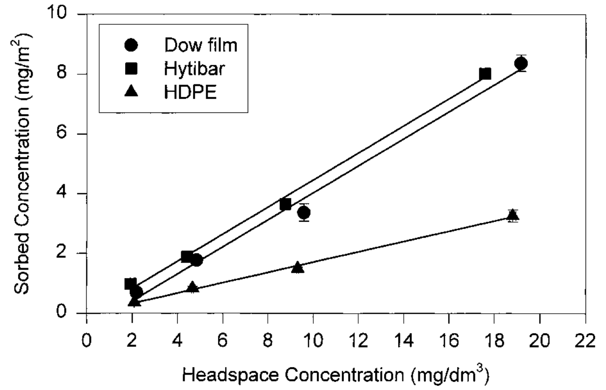

FIGURE 2. Sorption isotherms for methyl bromide based on the surface area of the film. Error bars indicate the standard error of the mean of six replicates.

Sorption of methyl bromide on each film was less extensive than the other fumigants tested. Surface-area-based partition coefficients for methyl bromide ranged from 0.17 for HDPE to 0.45 dm^3/m^2 film for Hytibar and the Dow film (Table 1). Only 7−18% of the total methyl bromide in the vials was sorbed to the film; most remained in the vapor phase. Sorption of methyl bromide (Figure 2) resulted in film concentrations that were an order of magnitude lower than those for chloropicrin (Figure 1). Sorption of methyl bromide to Hytibar and the Dow film was significantly higher than sorption to HDPE when based on surface area (Figure 2), indicating that the coextruded films may contain a phase that is more sorptive to methyl bromide than HDPE is. All of the methyl bromide was recovered in the hexane extract, indicating negligible degradation in 24 h.

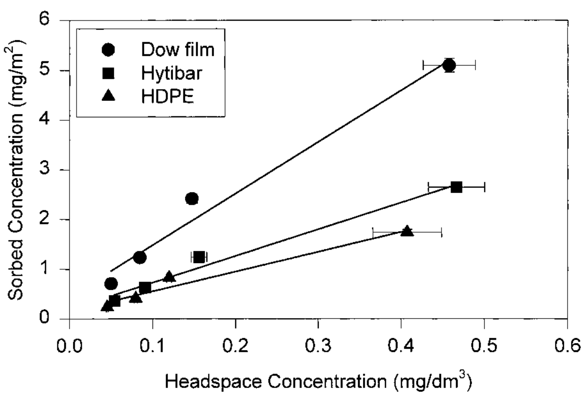

FIGURE 3. Sorption isotherms for *trans*-1,3-D based on the surface area of the film. Error bars indicate the standard error of the mean of six replicates.

Sorption of propargyl bromide to each film was moderate, with surface-area-based *K*'s ranging from 1 for HDPE to 3 dm^3/m^2 for the Dow film (Table 1). Approximately 40% of the propargyl bromide added was sorbed to the film at equilibrium. As was observed for methyl bromide, Hytibar may contain a phase that is more sorptive than HDPE to propargyl bromide, since the sorption was substantially higher for Hytibar than for HDPE (Table 1). For HDPE and the Dow film, all of the spiked propargyl bromide was recovered in the hexane extract; for Hytibar, ~80% of the mass was extracted. This loss could not be accounted for by production of Br^-, since the water extract showed no detectable Br^-. It appears that there may be some nonextractable component of propargyl bromide sorbed to Hytibar.

Sorption of 1,3-D isomers to each film was high, accounting for 67−83% of the total 1,3-D added. *K*'s ranged from ~3 to 9 dm^3/m^2 for *cis*- and *trans*-1,3-D (Table 1). Sorption coefficients were similar for the two isomers (Table 1). More variability in spiking was observed with 1,3-D than the other fumigants, owing to the difficulties in the preparation and preservation of a saturated vapor source for this compound. This increased variability resulted in less certainty in the calculation of the sorption coefficient (Table 1). Sorption to Hytibar was similar to HDPE, with the Dow film exhibiting higher sorptivity. No degradation of either isomer was observed.

Correlation coefficients for *trans*-1,3-D sorption isotherms were slightly lower than for the other fumigants (Table 1). There was an insufficient number of points to clearly indicate a nonlinear sorption isotherm for *trans*-1,3-D, although there may be some degree of nonlinearity of the sorption isotherm in the concentration range tested (Figure 3).

For each film, sorption determined on a surface-area basis followed the trend chloropicrin (most sorptive) > 1,3-D > propargyl bromide > methyl bromide (least sorptive). These results are consistent with the relative polarity of these fumigants. The aqueous solubilities of propargyl bromide and methyl bromide are similar (*26*); they are more soluble than 1,3-D (*26*) and chloropicrin (*27*), which also have similar solubilities. The results are also consistent with soil sorption studies. Based on the K_{oc} values reported in Wauchope et al. (*27*), chloropicrin would be expected to be the most sorptive and methyl bromide the least sorptive of these three fumigants. In soil sorption studies, propargyl bromide has shown slightly more sorption than methyl bromide (*26*). Sorption isotherms with a large linear range and *K*'s that are inversely proportional to aqueous solubilities can indicate that the sorption is through a partitioning process rather than a specific sorption mechanism (*28*). In this study, isotherms were linear over an order of magnitude change in headspace concentration, *K*'s were generally related to aqueous solubilities, and sorption was reversible, suggesting that the sorption may be due to the dissolution of the fumigants in the film.

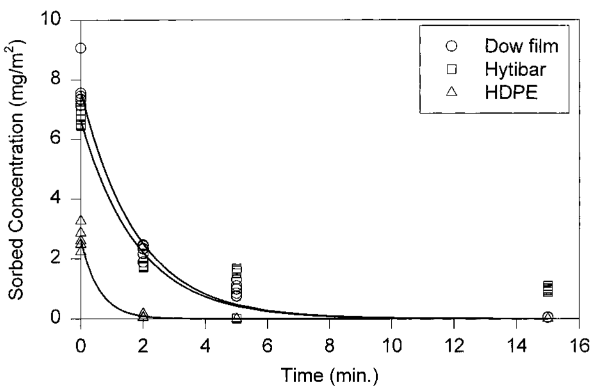

FIGURE 4. Desorption of methyl bromide from plastic film. Six replicates for each film at each time point are shown. Lines indicate first-order kinetics.

TABLE 2. First-Order Rate Constants (min^{-1}) for Fumigants Desorbing from Plastic Film

fumigant	HDPE	Hytibar	Dow film
methyl bromide	1.7 ± 0.4	0.55 ± 0.07	0.56 ± 0.04
chloropicrin	0.55 ± 0.04	0.67 ± 0.04	0.35 ± 0.04
propargyl bromide	1.4 ± 0.3	0.8 ± 0.1	0.38 ± 0.02
cis-1,3-D	1.07 ± 0.03	1.17 ± 0.06	0.50 ± 0.04
trans-1,3-D	1.04 ± 0.04	0.98 ± 0.08	0.44 ± 0.03

Desorption. Sorbed concentrations for all films decreased quickly when the film samples were removed from the sealed vials, with most desorption occurring within the first few minutes (Figure 4, Table 2). Desorption trends for each fumigant reflected the strength of sorption observed in the sorption study; the film that exhibited the most sorption on a surface-area basis (Dow film) showed the slowest desorption (Tables 1 and 2). Sorption of methyl bromide was similar for the Dow film and Hytibar, with HDPE showing significantly less sorption (Figure 2). Desorption indicated that sorbed concentrations of MeBr on HDPE decreased to nondetectable levels after a 5-min desorption step, whereas after 15 min of desorption, the sorbed concentrations on the Dow film and Hytibar were <1% and ~10% of the time 0 concentrations, respectively (Figure 4). For chloropicrin and the 1,3-D isomers, HDPE and Hytibar showed similar sorption (Figures 1B and 3); for these fumigants, desorption was also similar for HDPE and Hytibar (Table 2). Sorption of 1,3-D appeared mostly reversible, since 15 min of desorption removed most (≳93%) of the sorbed mass. For chloropicrin, the most sorptive fumigant tested, it appeared that there was some resistance to desorption, especially from the Dow film, which maintained a sorbed concentration of ~20% of the time 0 concentration after a 15-min desorption step.

The shapes of some of the desorption curves for Hytibar and the Dow film (Figure 4) suggest that there may be a fast component of desorption (such as from the film surface) that occurs within the first few minutes, followed by a slower desorption that is impeded by the rate of diffusion through the film. This type of desorption is not well-described by a first-order model; however, a detailed characterization of the desorption kinetics was beyond the scope of this paper.

For each film, the extent of sorption of different fumigants to each film observed in the sorption study was not directly related to the rate of desorption. For each film, sorption determined on a surface-area basis followed the trend chloropicrin (most sorptive) > 1,3-D > propargyl bromide > methyl bromide (least sorptive). There was no consistent trend for desorption rates. For HDPE and the Dow film, chloropicrin was the slowest desorbing compound and MeBr the fastest, whereas for Hytibar, MeBr was the least rapidly desorbed compound tested.

The sorption−desorption behavior observed in this study suggests that these agricultural films have a high sorption capacity but the sorption is largely reversible, with little retention of the fumigants on the film when there is a large concentration gradient. Tarping the soil surface with HDPE, which is permeable to fumigant vapors, may still mitigate the flux of fumigant vapors following soil fumigation because sorption−desorption will attenuate rapid flux to the atmosphere. Most of the volatilization loss of MeBr from untarped soils occurs within the first 24 h after application. Soils tarped with HDPE show lower maximum volatilization flux, but volatilization occurs over a longer time so that the cumulative flux may be similar (*6, 8*). If the goal of tarping the soil surface is to decrease maximum air concentrations following fumigation, inexpensive permeable tarps may be sufficient because the sorptive properties of the film will provide a barrier to the rapid flux of vapors, but these tarps may not decrease the total emissions of fumigant vapors to the atmosphere.

The results of this study indicate that agricultural films have the potential to accumulate fumigant concentrations many times the vapor concentration (at least 200 times for chloropicrin) and that the sorbed chemical is readily desorbed. Since stringent air tolerances for fumigants have been established (such as 1 $\mu g/m^3$ or 1×10^{-6} mg/dm^3 for 1,3-D (*1*)), it appears that an investigation of the air concentrations of fumigants that occur during the removal of tarps from fumigated fields is justified to ensure worker and public protection.

All sorption isotherms were linear in the range tested, indicating that the film may be a large sink for fumigant vapors. Sorption may have an impact on measurements involving agricultural films, where a significant portion of the fumigant mass may be adsorbed to the film. Particularly in closed systems where a mass balance is desired, it may be important to consider the film-sorbed component. The effect of sorption on the properties of agricultural films such as permeability requires additional research. Additionally, the impact of the presence of another phase, such as water, on the sorption and permeability of agricultural films is required.

Acknowledgments

We thank P. Zhang and C. Taylor for their assistance in sample preparation and analysis.

Literature Cited

(1) Baker, L. W.; Fitzell, D. L.; Seiber, J. N.; Parker, T. R.; Shibamoto, T.; Poore, M. W.; Longley, K. E.; Tomlin, R. P.; Propper, R.; Duncan, D. W. *Environ. Sci. Technol.* **1996**, *30*, 1365−1368.
(2) Kolbezen, M. J.; Abu-El-Haj, F. J. Proceedings, International Agricultural Plastics Congress, San Diego, CA, April 11−16, 1977; pp 1−6.
(3) de Heer, H.; Tuinstra, J. G. M. Th.; Hamaker, Ph.; Van der Burg, A. M. M. *Acta Horticulturae.* **1983**, *152*, 109−126.
(4) Daponte, T. L. F. *Acta Horticulturae.* **1995**, *382*, 56−66.
(5) Yates, S. R.; Gan, J.; Ernst, F. F.; Wang, D.; Yates, M. V. Emissions of methyl bromide from agricultural fields: Rate estimates and methods of reduction. In *Fumigants: Environmental Fate, Exposure, and Analysis*; Seiber, J. N., Knutson, J. A., Woodrow, J. E., Wolfe, N. L., Yates, M. V., Yates, S. R., Eds.; ACS Symposium Series 652; American Chemical Society: Washington, DC, 1996; pp 117−134.
(6) Jin, Y.; Jury, W. A. *J. Environ. Qual.* **1995**, *24*, 1002−1009.
(7) Gan, J.; Yates, S. R.; Ohr, H. D.; Sims, J. J. *J. Environ. Qual.* **1997**, *26*, 1107−1115.
(8) Gan, J.; Yates, S. R.; Spencer, W. F.; Yates, M. V.; Jury, W. A. *J. Environ. Qual.* **1997**, *26*, 310−317.
(9) Yagi, K.; Williams, J.; Wang, N.-Y.; Cicerone, R. J. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 8420−8423.
(10) Wang, D.; Yates, S. R.; Ernst, F. F.; Gan, J.; Gao, F.; Becker, J. O. *Environ. Sci. Technol.* **1997**, *31*, 3686−3691.
(11) Van Wambeke, E. Brighton Crop Protection Conference—Pests and Diseases, Brighton, UK, 1990; pp 563−568.
(12) U.S. Department of Agriculture. *Methyl Bromide Alternatives* **1999**, *5*, 1.
(13) Yates, S. R.; Wang, D.; Gan, J.; Ernst, F. F.; Jury, W. A. *Geophys. Res. Lett.* **1998**, *25*, 1633−1636.
(14) Steinwandter, H.; Schlüter, H. *Chemosphere* **1977**, *6*, 27−34.
(15) Nerín, C.; Tornés, A. R.; Domeño, C.; Cacho, J. *J. Agric. Food Chem.* **1996**, *44*, 4009−4014.
(16) Vuik, J.; van der Poll, J. M.; Vink, R.; de Vos, R. H. *J. Agric. Food Chem.* **1990**, *38*, 328−330.
(17) Papiernik, T. D.; Widmer, S. K.; Spalding, R. F. *Ground Water Monit. Remed.* **1996**, *16*, 80−84.
(18) Schuh, W. M.; Cline, R. L.; Kosse, M. J.; Sletton D. W. *Ground Water Monit. Remed.* **1997**, *17*, 81−90.
(19) Topp, E.; Smith, W. *J. Environ. Qual.* **1992**, *21*, 316−317.
(20) Barcelona, M. J.; Helfrich, J. A.; Garske, E. E. *Anal. Chem.* **1985**, *57*, 460−464.
(21) Parker, L. V.; Ranney, T. A. *Ground Water Monit. Remed.* **1994**, *14*, 139−149.
(22) Parker, L. V.; Ranney, T. A. *Ground Water Monit. Remed.* **1997**, *17*, 115−124.
(23) Gan, J.; Yates, S. R.; Spencer, W. F.; Yates, M. V. *J. Agric. Food Chem.* **1995**, *43*, 960−966.
(24) Wang, D.; Yates, S. R.; Ernst, F. F.; Gan, J.; Gao, F.; Becker, J. O. *Environ. Sci. Technol.* **1997**, *31*, 3017−3022.
(25) Wang, D.; Yates, S. R.; Ernst, F. F.; Gan, J. USDA-ARS, U. S. Salinity Laboratory, Riverside, CA, unpublished data.
(26) Yates, S. R.; Gan, J. *J. Agric. Food Chem.* **1998**, *46*, 755−761.
(27) Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustijn-Beckers, P. W. M.; Burt, J. P. *Rev. Environ. Contam. Toxicol.* **1992**, *123*, 1−164.
(28) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831−832.

Received for review August 25, 1998. Revised manuscript received December 17, 1998. Accepted January 18, 1999.

ES980877M