Sorption of Fumigants to Agricultural Films

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Plastic tarp stories 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 dm3/m2 film for methyl bromide to ~200 dm3/m2 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 ~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 tarpars 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/m2. 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 Nerin 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
per unit area of these films were measured as 58 g/m² for HDPE, 93 g/m² for Hytifar, and 178 g/m² 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-cm³ 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 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 sorption occurring within 15 min after spiking and was complete within 15 min after spiking. Sorption of chloropicrin, propargyl bromide and 1,3-D was also rapid, with most sorption occurring within 15 min after spiking and was complete within 15 min after spiking.

**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-cm³ 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/cm³ in the film samples; 1,3-D, 0.09–0.8 µg/cm³ for the cis isomer and 0.05–0.5 µg/cm³ for the trans isomer; chloropicrin, 0.07–2 µg/cm³; and propargyl bromide, 0.5–3.5 µg/cm³.

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/cm³ were measured near the soil surface 2 days after application and ~1 µg/cm³ after 10 days.

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-cm³ aliquot of the headspace in each vial using a gastight syringe and transferring the headspace to an empty 21.6-cm³ 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-cm³ 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 cm³) 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-cm³ 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...
Sorption of methyl bromide on each film was less extensive 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.

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.

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

<table>
<thead>
<tr>
<th>fumigant</th>
<th>HDPE</th>
<th>Hytibar</th>
<th>Dow film</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl bromide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_c$, cm$^3$/g film</td>
<td>7.4 ± 0.4</td>
<td>12.2 ± 0.3</td>
<td>6.3 ± 0.3</td>
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<tr>
<td>$K_d$, dm$^3$/m$^2$ film</td>
<td>0.171 ± 0.009</td>
<td>0.45 ± 0.01</td>
<td>0.45 ± 0.02</td>
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<tr>
<td>$r^2$</td>
<td>0.949</td>
<td>0.988</td>
<td>0.962</td>
</tr>
<tr>
<td>chloropicrin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_c$, cm$^3$/g film</td>
<td>205 ± 7</td>
<td>161 ± 3</td>
<td>181 ± 5</td>
</tr>
<tr>
<td>$K_d$, dm$^3$/m$^2$ film</td>
<td>4.8 ± 0.2</td>
<td>6.0 ± 0.1</td>
<td>12.9 ± 0.3</td>
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<tr>
<td>$r^2$</td>
<td>0.981</td>
<td>0.991</td>
<td>0.989</td>
</tr>
<tr>
<td>propargyl bromide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_c$, cm$^3$/g film</td>
<td>46 ± 1</td>
<td>57 ± 2</td>
<td>44 ± 3</td>
</tr>
<tr>
<td>$K_d$, dm$^3$/m$^2$ film</td>
<td>1.06 ± 0.03</td>
<td>2.12 ± 0.08</td>
<td>3.1 ± 0.2</td>
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<tr>
<td>$r^2$</td>
<td>0.986</td>
<td>0.966</td>
<td>0.910</td>
</tr>
<tr>
<td>cis-1,3-D</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$K_c$, cm$^3$/g film</td>
<td>140 ± 11</td>
<td>113 ± 6</td>
<td>119 ± 6</td>
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<td>$K_d$, dm$^3$/m$^2$ film</td>
<td>3.3 ± 0.3</td>
<td>4.2 ± 0.2</td>
<td>8.5 ± 0.5</td>
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<tr>
<td>$r^2$</td>
<td>0.874</td>
<td>0.937</td>
<td>0.944</td>
</tr>
<tr>
<td>trans-1,3-D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_c$, cm$^3$/g film</td>
<td>174 ± 16</td>
<td>133 ± 11</td>
<td>136 ± 11</td>
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<tr>
<td>$K_d$, dm$^3$/m$^2$ film</td>
<td>3.4 ± 0.4</td>
<td>4.9 ± 0.4</td>
<td>9.7 ± 0.8</td>
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<tr>
<td>$r^2$</td>
<td>0.843</td>
<td>0.870</td>
<td>0.885</td>
</tr>
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</table>
Sorption of propargyl bromide to each film was moderate, with surface-area-based K’s ranging from 1 for HDPE to 3 dm³/m² 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 dm³/m² 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 in 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 Koc 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.

**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

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**TABLE 2. First-Order Rate Constants (min⁻¹) for Fumigants Desorbing from Plastic Film**

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

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. Stringent air tolerances for fumigants have been established (such as 1 μg/m3 or 1 × 10−6 mg/dm3 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

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Literature Cited


