TRANSPORT OF FUMIGANT COMPOUNDS THROUGH HDPE AND VIRTUALLY IMPERMEABLE FILMS
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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, but these films are reportedly permeable to methyl bromide (MeBr) and other soil fumigants. 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 impermeability to fumigant vapors under field conditions.

In these experiments, we used static sealed permeability cells (1) to determine the mass transfer coefficient ($h$) of fumigant compounds through HDPE and other 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 (2). The impact of environmental conditions on the $h$ of fumigants across HDPE was determined; the factors examined included temperature, fumigant mixtures, condensed water on the film surface, and exposure of the film to field conditions.

Details of the apparatus, procedures, and analysis are given elsewhere (1, 2). This method uses static sealed cells in which 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. An example of the data obtained and model regression results are given in Figure 1.

Results indicated that 1-mil HDPE is permeable to fumigant compounds, and fumigant vapors are transported across the film relatively rapidly. For the two HDPE tested, the $h$ for chloropicrin (CP) is 1.5 to 2 times greater than that of MeBr; the $h$ for propargyl bromide (PrBr) is about 3 to 4 times greater and the $h$s for cis- and trans-1,3-D are approximately 5 and 10 times greater than MeBr, respectively. Polyethylene film, which has been widely used in soil fumigation, has high permeability to MeBr alternatives, so its utility for containment of these compounds is limited. 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.
Investigation of the effect of environmental conditions on the permeability of HDPE indicated that temperature and HDPE film type had the largest impact on the $h$ of all fumigant compounds through HDPE. Other factors investigated had a much smaller or insignificant impact on HDPE permeability.

**Temperature.** An increase in $h$ of fumigants across 1-mil HDPE with temperature was observed. The increase was approximately linear, and all fumigants showed an increase in $h$ of 1.5 to 2.5 times per 10°C increase in temperature from 20 to 40°C. This increase in permeability with temperature has the potential to have a large impact on emissions. Diurnal variation in fumigant flux density from the soil that has been observed in field studies (flux density is much higher during the day than at night) has been attributed primarily to a higher diffusion rate of fumigant through the plastic at higher temperatures.

**Fumigant mixtures.** Fumigants were spiked to permeability cells in a mixture of compounds (MeBr, PrBr, CP, cis- and trans-1,3-D) and each compound was also spiked in isolation. Fumigants exhibited the same $h$ when spiked alone as when spiked in mixture. These results indicate that fumigants behave independently in terms of their transport through HDPE when applied in mixtures (for example, in formulations containing CP).

**Exposure to field conditions.** A sample of a UV-stabilized 1-mil HDPE (designated HDPE2 in Table 1) was placed on the soil surface of a field in Riverside, California from May 23 through June 27, 2001. Samples of the film were collected weekly for 4 weeks and the permeability determined at 20°C. Results indicated no appreciable change in the $h$ of any compound as a result of field aging. In these studies, the permeability of UV-stabilized HDPE was not affected by exposure to field conditions typical of fumigation in southern California.

**Condensed water.** During fumigation, water condenses on the underside of the film surface. To determine the effect of this condensed water on the permeability of HDPE film, water was applied to the film surface facing the source chamber of the permeability cells. Droplets approximately 1 to 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. In either case, the $h$ of fumigant compounds was not impacted by the presence of a water film on the surface of the plastic.

**Virtually impermeable films.** Preliminary results for virtually impermeable films indicate $h$s that are several hundred to several thousand times less than those for HDPE1 (Table 1). Other films tested, including mylar and Safety4 film (manufactured by Dow) showed no measurable concentrations of any fumigant in the receiving chamber after 60 days. Column studies have indicated the potential for emissions reduction with the use of VIFs.
Figure 1. Diffusion of methyl 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. Solid symbols indicate MeBr concentrations in the receiving cell (measuring MeBr that has traversed the film) and open symbols represent concentrations in the source cell (cell to which fumigant vapor was spiked). Lines indicate regression to model of Papiernik et al. (2001) to determine the mass transfer coefficient.

Table 1. Mass transfer coefficients ($h$) for fumigants through plastic films. Values are $h$ for film HDPE1 (1-mil HDPE) compared to $h$ for each film. Results for BromoStop and Hytibar are preliminary and have not been fully verified.

<table>
<thead>
<tr>
<th>Fumigant</th>
<th>HDPE2†</th>
<th>4-mil HDPE</th>
<th>BromoStop</th>
<th>Hytibar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Bromide</td>
<td>0.6</td>
<td>2.7</td>
<td>250-1250</td>
<td>3000</td>
</tr>
<tr>
<td>Chloropicrin</td>
<td>0.6</td>
<td>2.5</td>
<td>20,000+</td>
<td>ND‡</td>
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<tr>
<td>Propargyl Bromide</td>
<td>0.6</td>
<td>3.1</td>
<td>500-1000</td>
<td>6500</td>
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<tr>
<td>cis-1,3-D</td>
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<td>3.6</td>
<td>1500-5000</td>
<td>500,000</td>
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<tr>
<td>trans-1,3-D</td>
<td>0.7</td>
<td>2.8</td>
<td>1250-5000</td>
<td>200,000</td>
</tr>
</tbody>
</table>

†Film HDPE2 is a UV-stabilized HDPE film with a thickness of 1 mil.
‡ND – no permeability detected in >60 days.

References: