Methyl Bromide Alternatives – Meeting the Deadlines

Reducing Fumigant Emissions After Soil Application

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ABSTRACT

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Volatilization and soil transformation are major pathways by which pesticides dissipate from treated agricultural soil. Volatilization is a primary source of unwanted agricultural chemicals in the atmosphere and can significantly affect fumigant efficacy. Volatile pesticides may cause other unique problems; for example, the soil fumigant methyl bromide has been shown to damage stratospheric ozone and will soon be phased

out. There is also great concern about the health consequences of inhalation of fumigants by people living in proximity to treated fields. Because replacement fumigants will likely face increased scrutiny in years ahead, there is a great need to understand the mechanisms that control their emission into the atmosphere so these losses can be minimized without loss of efficacy. Recent research has shown that combinations of vapor barriers and soil amendments can be effective in reducing emissions. In this paper, some potential approaches for reducing fumigant emissions to the atmosphere are described.

Soil fumigants have been used throughout the world for decades to control soilborne pests prior to planting various food crops. Soil fumigants have been implicated in causing various environmental problems. Methyl bromide (MeBr), one of the widely used soil fumigants, depletes stratospheric ozone and restrictions have been placed on the future production and use of this chemical. Ethylene dibromide and dibromochloropropene (DBCP) contaminate ground water systems, and DBCP remains a problem decades after its use in soil fumigation ceased (24).

Estimates of losses as a result of the MeBr withdrawal vary, but the USDA National Agricultural Pesticide Impact Assessment Program (1) determined that it could be in excess of \$1.5 billion in annual lost production in the United States (1,6) if suitable MeBr replacements are not found. This has led to an intense search for nonchemical alternatives and chemical replacements for MeBr. The most promising chemical alternatives identified thus far include 1,3-dichloropropene (1,3-D), chloropicrin, and methyl isothiocyanate (MITC). However, these alternatives are less effective than MeBr in controlling plant pathogens (26). Therefore, it is likely that combinations of two or more chemicals in large quantities will have to be used to achieve similar pest control efficacy, and this in turn may lead to significant emissions of these chemicals.

Recent field experiments have demonstrated that emissions from soil fumigation are significant and can vary from 20 to 90% of the total applied fumigant (2,3,7,21,25,31–35,38–41,43). These studies have shown that many chemical, soil, and environmental factors affect emission losses. To achieve sufficient emission reduction, these factors must be controlled or mitigated during and after soil fumigation.

A thorough understanding of the fate and transport of soil fumigants is necessary to develop efficient emission control measures. Generally, three factors must be balanced to reduce emissions while maintaining pest-control efficacy: containment, degradation, and soil-gas distribution (i.e., effective dosage). This paper describes how containment and enhancing degradation can be used to reduce fumigant emissions to the atmosphere.

Containment. Containment is the retention of fumigant in the soil environment long enough for efficient control of pests. Containment is needed due to the high vapor pressure of all agricultural fumigants. Because of the high vapor pressure, a large fraction of the fumigant exists in the vapor phase at temperatures and pressures that normally occur in the field. Without adequate containment, a significant fraction of the fumigant will quickly be lost to the atmosphere. When emission losses are high, the applicator will need to compensate by using larger quantities of fumigant compared with low emission-loss fumigation.

Plastic films. One of the most common methods of containment is the use of plastic film to cover the soil surface after fumigation. A variety of physical-chemical properties of the film and environmental factors affect the permeability of plastic film. Some films provide a better diffusion barrier to certain fumigants than others. For example, the commonly used high-density polyethylene (HDPE) provides some resistance to MeBr and chloropicrin, but offers little resistance to 1,3-D diffusion. The permeability of two types of film to several fumigants is shown in Figure 1 in which larger mass transfer coefficient values indicate less resistance to diffusion (29) and, in general, higher emission rates.

The mass transfer coefficient, h , shown in Figure 1 is an intrinsic property of the plastic film and is a measure of the permeability (29). The emission rate through film, however, depends on h and the difference in fumigant concentration across the film. The soil emission rate depends on factors affecting fumigant diffusion to the soil surface, the emission rate through the film, and properties of the atmosphere that enhance or inhibit transport away from the soil surface in the air space above and below the film. Impermeable films trap fumigation gases at the soil surface, promoting

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higher soil concentrations and lower emissions. When the film is permeable, the concentration at the soil surface is nearly the same as the concentration above the film, which results in higher emissions. Total emissions can be reduced from more than 60% of the applied MeBr using HDPE to less than 5% using a virtually impermeable film (VIF) (34,44) under ideal conditions. The permeability of a film also depends strongly on ambient temperatures (Fig. 2). Permeability increases 1.5 to 2 times for every 10°C temperature increase (19,28,42).

New plastic films that are nearly impermeable to most fumigants are currently available. VIFs are manufactured by coextrusion. A barrier polymer, such as ethylene vinyl alcohol or polyamide, may be incorporated into the center of a polyethylene sheet. Tests in the laboratory have shown that certain VIFs are at least 75 times less permeable to MeBr than the conventional polyethylene films (42) and may be as much as 500 to 1,000 times less permeable (27). In a study conducted outdoors, the permeability of Hytibar was approximately 200 times less than HDPE (36). Similar results have been obtained for other soil fumigants (27). Further testing is needed under the harsh conditions that occur in large agricultural fields to ensure that new VIFs have physical and mechanical properties similar to the conventional plastic films and that they are suitable for field use. There have been reports of difficulties gluing VIF sheets together, and this might affect emissions in field settings.

Table 1 shows some recent estimates of total MeBr emissions for soils left bare and covered with plastic film after application. It is clear that the use of HDPE has a beneficial effect on reducing MeBr emissions, and using VIFs appears to hold great promise for reducing emissions to near zero levels. The use of plastic film is a reliable approach to reduce emissions because the properties and condition of the film are known in advance and are more uniform. Films add to the cost of fumigation, so less expensive barrier methods, such as water seals, may need to be identified.

Depth. The depth of application is also an important factor affecting the rate of fumigant emission into the atmosphere. In general, injecting the fumigant deep into the soil reduces losses to the atmosphere because the concentration gradients that drive diffusion are smaller near the soil surface. However, deep application can also result in inadequate control of soil pests and increased likelihood of contamination of ground water. To demonstrate emission reduction as affected by the depth of fumigant application for bare soil, experiments were performed both in the field and in the laboratory. The laboratory experiments (12) were

conducted using columns with a sealed bottom and 60 cm length. Because fumigants can diffuse freely below this depth in the field, a mathematical model was used to provide estimates of the emissions assuming that the column had an infinite length. The values are reported in Table 2 as corrected emissions and allow comparison of the laboratory and field values. The soil for the laboratory columns was obtained from the small field plots (33). The large field experiments (25,41) were conducted at different locations and times. Significant emission reductions from nontarped soils were observed when the fumigation depth increased (Table 2).

Soil porosity. The rate of fumigant diffusion in the soil gas phase is 10 to 100 times greater than diffusion through the soil liquid phase (18). Therefore, the soil porosity and the continuity of the pore space are important factors affecting the movement, and hence containment of fumigants through soil (15,20,23).

Increasing soil water content is also a means of reducing emissions to the atmosphere because diffusion through the soil water is much less than diffusion through open soil pores (e.g., dry soil). Jin and Jury (16) conducted a laboratory experiment using a 22-cm soil column covered with 1 mil (0.025 mm) of polyethylene film. They found that emissions were reduced by 25% when 4 mm of irrigation water was added to the soil surface. Wang et al. (33) applied irrigation water to the soil surface after

Fig. 2. Effect of temperature on the mass transfer coefficient, h (cm/h), for polyethylene films. Curve marked LDPE ($\circ$, $\square$) is a low-density polyethylene film, the others curves are high-density films (HDPE; $\bullet$, $\blacklozenge$).

Fig. 1. Mass transfer coefficient, h (cm/h), for methyl bromide (MeBr), propargyl bromide (PBr), chloropicrin (Pic), and Telone (1,3-D). Larger numbers indicate higher permeability.

application of MeBr at 25 cm and found that emissions were reduced from 59% to less than 42%.

The placement of the water is important. Using a mathematical model, Jury et al. (17) found that 1 cm of irrigation water uniformly distributed in the upper 10 cm of a soil profile resulted in 66% total emissions. If the same irrigation water was uniformly distributed in the upper 3.3 cm (e.g., wet soil cap), the total emissions were reduced to 29%. Similar observations were obtained in laboratory columns containing a sandy loam. The estimated MeBr emission in soils with low water content (i.e., 6% volumetric water content) was approximately 77% of the applied mass, but when the water content was increased to 18%, emissions were reduced to 62% of the applied mass (14). These results demonstrate the importance of pore-space diffusion in the volatilization process. Increasing water content uniformly does not significantly reduce emissions until the soil is very wet. Creating a saturated layer at the soil surface can significantly reduce emissions. One difficulty, however, is the soil's natural tendency to wick water away from the application point toward dryer soil. The wicking process and gravity drainage tends to produce more uniform soil-water profile and opens soil pores at the soil surface. Multiple water applications would be necessary to refill the surface pores to keep the diffusion barrier intact.

Drip chemigation. Measurements of the total volatilization of 1,3-D from recent field experiments have shown that applying fumigant with a drip irrigation system may reduce the emission rate compared with shank injection. Wang et al. (35) conducted a field study to investigate the effect of drip application on total emissions of 1,3-D (applied as Telone II, Dow AgroSciences LLC, Indianapolis). Comparisons were made between shallow drip at a depth of 2.5 cm and covering the bed with HDPE, deep drip at a depth of 20 cm, and shank injection at 30 cm depth. The 1,3-D was injected into the center of the beds with a wing-bladed shank

that entered the soil in the furrow, and the blade cut horizontally into the soil bed. The nozzles injected chemical at several points across the bed at approximately 30 cm below the soil surface. Compared with the 90% total emission observed in shank injection plots, observed emissions were 66 and 57% in shallow- and deep-drip plots, respectively. These results should be interpreted with caution because approximately 80% of the total emissions from the shank plot were lost from the bed furrows. The soil fractures produced by the shank-plow device during the application process were not closed or compacted and provided a preferential diffusion pathway from the point of application to the atmosphere. Using standard shank injection, total 1,3-D emissions were approximately 25% (3) in a study conducted in the Salinas Valley, CA.

Gan et al. (7) conducted a study in the Coachella Valley, CA, on a tomato field where Telone EC was applied to the soil at a depth of 10 cm by a drip system. Two of the treatments included a row-bed configuration and either a bare soil surface or one covered with HDPE. Total emissions were 32% for the bare soil treatment and 24% for tarped soil. These values are similar to those reported by Chen et al. (2,3) for shank injection. From the few published studies, it is not clear if drip chemigation reduces fumigant emissions.

Bulk density. Similar to the effect of increased water content, soil packing can also reduce the soil pore space and, in turn, reduce fumigant emissions. A soil layer with high bulk density acts as a barrier to diffusion. Coupling the use of films with other barrier methods can offer a higher certainty of effective containment compared with using either films or porosity-based methods alone.

Containment alone is insufficient to reduce fumigant losses from soil because emissions are reduced only when the surface barrier remains in place. A balance between containment and soil

TABLE 1. Methyl bromide emissions after application, injection depth 20 to 30 cm

Surface barrier	Laboratory columns (12)		Plot experiments ^a		Field experiments ^b	
	Cover period (days)	Total emissions (%)	Cover period (days)	Total emissions (%)	Cover period (days)	Total emissions (%)
Bare	na	91	na	87	na	89
HDPE	8	59	15	67	4, 5, 8	32 to 66 ^c
Hytibar	8	2 ^d	15	<5	...	...

^a Conducted in small field plots (33,34).

^b Yagi et al. (39,40), Majewski et al. (25), Yates et al. (41), Williams et al. (38).

^c Removed highest and lowest value from available data.

^d Cumulative emissions to 8 days. Total emissions including losses after the tarp was removed were 34% less than high-density polyethylene (HDPE).

TABLE 2. Methyl bromide emissions from bare soil after injection at three depths

Injection depth (cm)	Laboratory columns (12)		Field experiments	
	Total emissions (%)	Corrected emissions (%)	Injection depth (cm)	Total emissions (%)
20	91	82	25	87 ^a ; 89 ^b (25)
30	83	71	60	60 ^a
60	60	38	68	21 ^b (43)

^a Conducted in small field plots (33).

^b Conducted in >2.5-ha field.

TABLE 3. Total emissions (percentage of applied) of 1,3-dichloropropene (1,3-D; applied as Telone II) and methyl bromide following surface application of several rates of ammonium thiosulfate (ATS)

Amendment ^a	1,3-D (7)		Amendment ^b	Methyl bromide (10)	
	Total emissions (%)	Reduction in total emissions		Total emissions (%)	Reduction in total emissions
No ATS	42.9	...	No ATS	61	...
1 ml	16.6	61%	1 ml pretreat	9.5	84%
2 ml	8.4	80%	1 ml posttreat	7.2	88%
3 ml	4.9	89%	...	...	...

^a ATS was applied as 1, 2, or 3 ml of Thio-Sul.

^b Solution was applied as 1 ml of Thio-Sul with 19 ml of water.

degradation must be achieved to reduce the quantity of fumigant in the soil prior to removing the surface barrier (e.g., plastic tarp). In addition, adequate fumigant concentration levels must be maintained in the soil to control pests. Increasing soil residence time by improving containment will increase soil degradation and reduce atmospheric emissions.

Enhanced degradation. The rate of degradation of a fumigant in a given soil is another important factor affecting the emission rate and efficacy. Fumigant degradation in soil varies with soil type and organic matter content (9,22,30). However, with reported half-lives on the order of days to months (8,11,44), indigenous soil degradation alone may not be sufficient to significantly affect the emission rate unless amendments are added to soil to enhance degradation. Degradation can affect emission loss to the atmosphere by transforming the fumigant in the soil and making it unavailable for transport to the atmosphere. Hydrolysis, nucleophilic substitution, and microbial degradation are the principal degradation processes removing soil fumigants from agricultural soils.

Organic matter. One approach to reduce fumigant emissions is to enhance the surface soil's capacity to degrade the fumigant before it enters the atmosphere. Various organic amendments were tested to determine if they could accelerate 1,3-D and MITC degradation in soil (5,11). Degradation of 1,3-D and MITC increased significantly in soils amended with organic material. Even for an amendment-to-soil ratio as low as 1:40 (by dry weight), MeBr degradation was two times faster and MITC degradation was four times faster than in unamended soil (13). Compared with native soil, the addition of organic material significantly decreases the degradation half-life of 1,3-D and MITC at all temperatures (Fig. 3). At 20°C, the degradation half-life for 1,3-D decreased from approximately 6 to 2 days when 10% composted steer manure was added to soil (4), presumably due to an increase in biological degradation.

Soil degradation has been shown to have a dramatic effect on total emissions. For example, incorporating 5% composted manure into the top 5 cm of a soil column reduced total MeBr emissions by 18% (13), total 1,3-D emissions by 46% (11), and MITC emissions by 99% (13).

Ammonium thiosulfate fertilizer. A novel method for reducing fumigant emission involves the use of ammonium thiosulfate fertilizer (ATS) to create a zone of high degradation at the soil surface. In ATS-amended soil, MeBr is rapidly degraded into bromide ion and methyl thiosulfate, and the degradation rate was dependent on the molar ratio of ATS/MeBr and soil temperature. At room temperature, the MeBr half-life was reduced from 5 days

to less than 5 h when ATS was added to the soil at a molar ratio four times greater than MeBr (10). Similar enhanced degradation has been observed for 1,3-D, chloropicrin, propargyl bromide, and methyl iodide (37).

Increasing the degradation rate at the soil surface reduces fumigant emissions to the atmosphere. This was demonstrated using soil columns in which MeBr was injected at a depth of 30 cm (10). The total loss of MeBr from the column containing native soil was 61% of the applied dosage, which is in agreement with field measurements (33,34,41). The total emissions were reduced to less than 10% after adding ATS to the soil surface (Table 3). A similar reduction in emissions was observed for Telone (1,3-D) in which the emissions were reduced from 43% to less than 5% after the surface soil was amended with ATS (Table 3) (7). ATS is also effective in reducing emissions of methyl iodide, propargyl bromide, and chloropicrin; however, it is not effective in reducing emissions of MITC or any isothiocyanate precursor (J. Gan and S. R. Yates, unpublished data).

A field study showed that adding ATS (at 640 kg/ha) to the soil surface had no discernible effect on the efficacy of MeBr for controlling nematodes and weeds (10). Because ATS is an inexpensive fertilizer, this approach has promise for field application. Other compounds that may undergo similar nucleophilic substitution reactions are being investigated.

CONCLUSION

Significant short-term emission reduction can be achieved by the use of diffusion barriers. A diffusion barrier increases fumigation efficiency by keeping the fumigant at the target site longer at a higher concentration and provides more time for the fumigant to diffuse through the soil to create a more uniform distribution in the treatment zone. Therefore, less material would be needed for achieving the same level of pest control. Rapid degradation removes the fumigant before it escapes into the atmosphere. Amending the soil with fumigant-degrading material (i.e., organic matter or reactive fertilizer) can enhance fumigant degradation and further reduce emissions. Applying an amendment at the surface reduces fumigant emissions substantially without comprising efficacy. Enhancing soil degradation is especially important in soils with little capacity to degrade fumigants.

Several fumigants have been banned or restricted in recent years. To keep the remaining chemicals available for agricultural use requires a determined effort to reduce their harmful effects on the environment. Future contamination of the atmosphere, ground water, or surface water by agricultural fumigants will likely lead to another round of chemical bans. Protecting the atmosphere from fumigant contamination can be achieved by judicious use of emission control strategies. If the agricultural community adopts the goal of protecting the environment from the harmful effects of fumigant use, in effect, they will be protecting agriculture from the loss of this important class of chemicals.

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Fig. 3. Degradation half-life for Telone (1,3-D) and methyl isothiocyanate (MITC) in amended and unamended soils.

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