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Development of a Methyl Bromide Collection System for Fumigated Farmland

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Recent research has indicated that up to 73% of the methyl bromide (MeBr) applied to agricultural farmland is ultimately emitted to the atmosphere despite the practice of complete coverage of the fields with polyethylene (PE) tarp. To reduce the emission of MeBr, several techniques have been investigated. An alternative that has received little consideration is the collection and recycle or treatment of MeBr emissions. We investigated the potential of using a two-layer tarp system for collecting the MeBr. Laboratory experiments with a small two-layer diffusion reactor were conducted to determine the mass transfer coefficient (K) of MeBr through tarps and to validate a model of the collection system. For PE tarps K was 1.15×10^{-6} m s^{-1} at 20 °C and 5.2×10^{-6} m s^{-1} at 60 °C. K for so-called virtually impermeable films ranged from 4.6×10^{-10} m s^{-1} to 1.3×10^{-8} m s^{-1}. The mathematical model was then used to simulate a full scale fumigant field application. Results indicate excellent agreement between the model, laboratory experiments, and previous field studies. Total emission from the field was a function of the air exchange rate through the swept volume between the two layers, the length of time the field is covered by the collection system, and the mass transfer coefficient of MeBr though the tarps. The results indicate that the proposed two-layer system can be very effective in collecting MeBr emissions from fumigated farmland.

Introduction

Methyl bromide (MeBr) has been commonly used for agricultural purposes since the 1930s as a fumigant to protect stored agricultural commodities, to treat commodities being shipped for international or national trade, and as a fumigant in soil to control arthropods, weeds, bacterial pathogens, parasitic nematodes, and fungi (*1*). Approximately 30,000 tons are used in the United States each year, and about 85% of this is used as a soil fumigant (*2*).

Unfortunately, MeBr has been shown to have significant ozone depleting potential and therefore is subject to regulation by the EPA under Title VI of the Clean Air Act and by the Montreal Protocol for ozone depleting substances. The Montreal Protocol calls for a 50% reduction of MeBr consumption by 2001, a 70% reduction by 2003, and 100% reduction by 2005, based on 1991 consumption levels. Consequently, the EPA froze U.S. production and importation in 1994 at 1991 levels. However, it has allowed the longest time possible under the Clean Air Act before a phase-out in order to facilitate a smooth transition to alternatives. The EPA has indicated that it is working toward a policy allowing the use of methyl bromide in certain cases where alternatives are not found by the year 2001. Great pressure exists to delay the implementation of the Montreal Protocol and continue the use of methyl bromide where the environmental impact can be mitigated (*3*). For commodity fumigation, there is a good potential for collection and recycle or proper disposal of MeBr (*1*). However, the efficient collection of MeBr from soil fumigation poses different challenges.

MeBr is applied to the soil by a professional fumigant applicator usually in liquid form at a typical depth of approximately 25 cm (*1*). The total amount applied is between 240 and 320 kg ha^{-1} (*4*). After injection, MeBr partitions between the gas, aqueous and solid phases where the unitless air to water (mass) partition coefficient is 0.25 (*5*). Immediately following application, the soil is covered with a tarp to reduce MeBr volatilization and to maintain its pest control efficacy. Polyethylene (PE) tarps are typically used because of its physical and mechanical properties as well as its low cost.

Research has indicated that less MeBr is emitted when the entire field is covered, not just the bedded field plots (*6*). Entire fields may be covered by gluing parallel sheets of PE together to form a blanket (*1*). Even so, significant losses to the atmosphere occur, because the tarps are only mildly effective. Recent research has indicated that up to 73% of the applied MeBr is emitted to the atmosphere despite the practice of complete coverage (*6*). This is because of the relatively high diffusivity of MeBr through PE films and its slow biotic and abiotic degradation rates in the soil. Literature reports mass transfer coefficients (i.e., diffusivity/film thickness) ranging from 2.1×10^{-7} m s^{-1} to 4.2×10^{-7} m s^{-1} for usual PE tarps (*7*, *8*). Other tarp materials, which have lower permeability to MeBr, are available but are significantly more expensive (*6*).

Therefore, to reduce emission of MeBr from fields where it has been applied, several different approaches have been considered. These include increased injection depth, irrigation with MeBr application, and coverage with tarps with much lower mass transfer coefficients. Because gas-phase diffusion is the primary transport mechanism in unsaturated soils, deep injection increases the gas residence time. This allows greater time for degradation. In recent research (*9*), this technique decreased the amount emitted from 59% to 15% of the amount applied. However, the experiments also indicated that lower than necessary pest kill occurred as a result. Irrigation has been shown to be an effective method for reducing MeBr emissions because MeBr is water soluble (>17 g L^{-1}) (*10*). With increased water content in the soil, greater mass of MeBr is retained in the water phase and less is emitted. MeBr emissions were reduced by from 59% to 42% while maintaining pest control efficacy (*9*). A promising remedy is the use of so-called “virtually impermeable films” to cover the field. These tarps essentially retain all MeBr in the soil. Research has indicated that the total emission is therefore controlled by time of coverage. Short-term coverage (5 days) will not allow enough time for the MeBr to be degraded in the soil. Consequently, total emissions (emission during coverage period plus emission after cover is removed) will be high (up to 64% of mass applied) unless the fields are kept covered for up to 15 days (*4*). Another disadvantage is the high cost of these films.

A novel method has been proposed to treat MeBr as it is emitted from the soil (*11*). Ammonium thiosulfate, a commercial fertilizer, is applied to the field before it is covered

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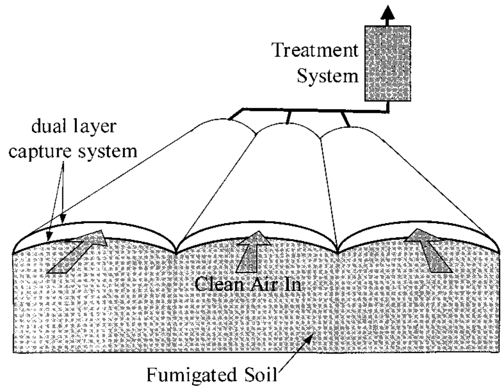

FIGURE 1. Schematic of double layer collection system for application in field fumigations.

with a PE tarp. As MeBr diffuses to the soil surface, the bromide ion was removed a by nucleophilic substitution reaction with thiosulfate. The resulting compound, ammonium methylthiosulfate, is soluble in water, nonvolatile, noncorrosive and low in toxicity (*11*). A field study indicated that 88% less emission than a control (with only PE tarp only) was achieved (*12*).

One alternative that has received little consideration is the collection and recycle or treatment of methyl bromide emissions. Potential treatment systems include adsorption onto activated carbon (*13*), biological degradation (*14*, *15*), or chemical reaction (e.g., with ammonium thiosulfate). To our knowledge, no effective collection method exists for field fumigation. The purpose of this paper is to describe a new method for collecting MeBr from farm fields where MeBr has been applied and to demonstrate through laboratory experiments and mathematical modeling its potential use for mitigating MeBr emissions.

Concept

To reduce the loss of MeBr, fields are usually completely covered with PE. Sheets of PE are rolled out parallel to one another and glued together to form a complete cover (*1*). We are proposing a system where a double layer of tarps is laid on the field and then glued together on the sides (Figure 1). This would provide a channel through which air, provided by a blower and a manifold system, could be used to sweep the collected MeBr into a treatment system. MeBr would diffuse through the lower tarp and be swept into the treatment system. The reduced concentration in the swept volume would minimize the potential for MeBr to be emitted to the atmosphere. The air exchange rate could be adjusted to minimize emission of MeBr.

Materials and Methods

Test Reactor. To test this concept at the laboratory scale, a small diffusion chamber was designed and constructed (Figure 2). The diffusion chamber was composed of three main components each with a 15 cm internal diameter and constructed of carbon steel. The lower and upper chambers (V_1 and V_3, respectively) had a volume of 0.52 L and were open on one end, while the middle chamber (V_2) had a volume of 1.0 L and was open on both ends. Gas sampling ports were located on the sides of each of the chambers. As shown schematically in Figure 2, the three chambers represented the soil, the air channel, and the atmosphere. For specific experiments, the top of the upper chamber (V_3) was removed, which better represented the infinite volume of the atmosphere. During laboratory experiments, neither soil nor water was placed in the lower chamber. Tarps with mass transfer coefficients K_1 and K_2 were located between the three

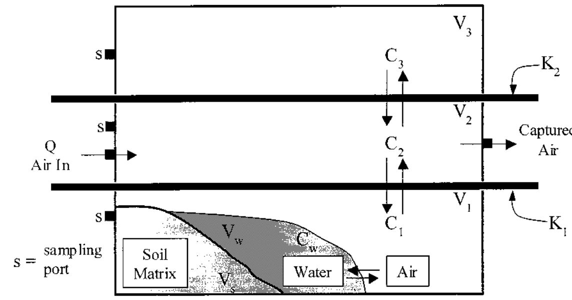

FIGURE 2. Schematic of the diffusion reactor and model concept showing MeBr diffusion and partition between air and water. (Note that during laboratory experiments, neither soil, nor water was placed in the lower chamber.)

chambers. Teflon gaskets were used to ensure a gastight seal between the tarps and the chambers and clamps were used to hold the system together. Air was pushed through V_2 by a peristaltic pump and into 10 L Tedlar bags. Piping connected the reactor and the Tedlar bag was 0.5 cm diameter stainless steel.

Analytical. At the initiation of experiments, 6.7 mL of air was withdrawn from the lower chamber and then replaced by 6.7 mL MeBr (high purity grade, Aldrich, Milwaukee, WI). This provided an initial concentration of approximately 45 g m^{-3} in V_1. Gas samples were taken immediately from each chamber of the reactor and periodically throughout the course of the experiment, as necessary. Gas samples were analyzed for MeBr by a Hewlett-Packard 5890 Series II gas chromatograph (GC) equipped with a flame ionization detector. The GC was fitted with a Supelcowax 10 capillary column (30 m $\times$ 0.53 mm $\times$ 1 μm; Supelco, Bellefonte, PA) and was operated isothermally at 65 °C with helium as a carrier gas. Samples (0.3 mL) were withdrawn for each gas analysis using a separate 1 mL syringes for each chamber. The maximum number of samples for each experiment was less than 20 from each chamber. Therefore less than 1.2% of the mass was removed for sampling purposes during each experiment. Tedlar bags were periodically changed. Immediately after removal, the bags were sampled and analyzed by the same procedure as for the vessel.

Model Development

A mathematical model was developed to analyze experimental data and determine diffusivity of MeBr through sample films. The model included three chambers (Figure 2), and dynamic mass balances were written for each chamber. The concentration of MeBr was assumed to be homogeneous within each one of the chambers of the diffusion reactor. The model was also used to simulate field fumigation and the proposed collection system. In these cases, since it could no longer be assumed that the concentration of MeBr was homogeneous over the length of the field, a plug flow was assumed, and the system was modeled as multiple diffusion reactors in series along the sweep air path. It was further assumed that diffusion of MeBr did not occur between adjacent chambers so that transport of MeBr between adjacent chambers only occurred in the swept volume where the rate was directly proportional to the exchange rate. Since, the MeBr concentration gradient along the path of the sweep air is very small, this assumption is fully justified. The MeBr concentration entering the first swept volume was set to zero, and the initial concentration of MeBr in the soil (i.e., gas and aqueous phases) was set to be the same in each compartment. The total mass emitted from the system was the sum of all the atmosphere compartments, V_3.

TABLE 1. Table of Parameters

parameter	diffusion coeff determination	flow experiments closed top	flow experiments open top	fit of Wang et al. (4) data	field simulations
K_1 mass transfer coeff of lower tarp	experimentally determined; see Table 2	1.15×10^{-6} m s^{-1} (diffusion expts @ 20 °C)	1.15×10^{-6} m s^{-1} (diffusion expts @ 20 °C)	4.28×10^{-6} m s^{-1} (diffusion expts @ 50 °C)	various
K_2 mass transfer coeff of upper tarp	0	same as K_1	same as K_1	0	same as K_1
a surface area of tarp	1.89×10^{-2} m^2 (measd)	1.89×10^{-2} m^2 (measd)	1.89×10^{-2} m^2 (measd)	16.7 m^2 (Wang et al. 1997)	various
h_1 depth of volume 1	2.6×10^{-2} m (measd)	2.6×10^{-2} m (measd)	2.6×10^{-2} m (measd)	1.0 m (estimated from Wang et al. 1997)	1.0 m (estimated from Wang et al. 1997)
h_2 depth of volume 2	2.6×10^{-2} m (measd)	5.3×10^{-2} m (measd)	5.3×10^{-2} m (measd)	10^{10} m	5×10^{-2} m
h_3 depth of volume 3	N/A	2.6×10^{-2} m (measd)	10^{10} m	N/A	10^{10} m
E air exchange rate	0	various	various	0	various
θ water content	0	0	0	0.16 (Wang et al. 1997)	0.16 (Wang et al. 1997)
ϵ soil porosity	N/A	N/A	N/A	0.3 (assumed)	0.3 (assumed)
K_La mass transfer coeff	N/A	N/A	N/A	100 s^{-1} [a]	100 s^{-1} [a]
H MeBr Henry's constant	N/A	N/A	N/A	0.25 (unitless) (Gan et al. 1996)	0.25 (unitless) (Gan et al. 1996)
R MeBr degradation rate	N/A	N/A	N/A	3.6×10^{-6} s^{-1} (data fit)	3.6×10^{-6} s^{-1} (data fit)
n no. of reactors in series	1	1	1	1	15

[a] K_La chosen to provide continuous equilibrium between water and air phase.

In developing the model equations, equilibrium of MeBr between the aqueous and gas phases was assumed. Therefore, MeBr was removed from the soil gas-phase either by diffusion through the lower tarp or by absorption into the aqueous phase. Consequently, the gas-phase concentration of MeBr in the soil compartment can be written as

$$\frac{dC_{1,i}}{dt} = K_1\frac{(C_{2,i} - C_{1,i})}{h_1\epsilon} - K_La(C_{1,i} - C_{w,i}H)\frac{\theta}{\epsilon} \tag{1}$$

where $C_{1,i}$ is the gas-phase concentration of MeBr in the soil, or lower chamber of diffusion reactor i and i ranged from 1 to n, K_1 is the mass transfer coefficient through the lower tarp, $C_{2,i}$ is the gas-phase concentration of MeBr in the swept volume of reactor i, h_1 is the depth of the soil, ϵ is the porosity K_La is the mass transfer coefficient multiplied by the interfacial area between the gas and aqueous phase (set large enough to ensure equilibrium), $C_{w,i}$ is the aqueous phase concentration of MeBr in reactor i, θ is the volumetric water content, and H is the gas/aqueous partition coefficient defined as

$$H = \frac{C}{C_w} \tag{2}$$

Degradation of MeBr occurs in the aqueous phase; therefore, the aqueous phase concentration in the soil can be modeled as

$$\frac{dC_{w,i}}{dt} = K_La(C_{1,i} - C_{w,i}H) - RC_{w,i} \tag{3}$$

where R is the degradation rate of MeBr in the aqueous phase. It was assumed that all degradation occurred in the aqueous phase and that no adsorption to the soil matrix occurred.

For field simulations, plugflow conditions were assumed for the air channel formed between the two tarps. The swept volume was therefore modeled as multiple continuous stirred tank reactors (CSTRs) in series. MeBr diffused from the soil (V_1) into the swept volume (V_2) where it was simultaneously carried away by the sweep air and could diffuse to the atmosphere (V_3). Consequently, the equation for the gas-phase concentration in the swept volume can be written as

$$\frac{dC_{2,i}}{dt} = K_1\frac{(C_{1,i} - C_{2,i})}{h_2} - K_2\frac{(C_{2,i} - C_{3,i})}{h_2} + E(C_{2,i-1} - C_{2,i}) \tag{4}$$

where K_2 is the mass transfer coefficient through the upper tarp and h_2 is the average height of the swept volume. $C_{3,i}$ is the MeBr concentration in the upper chamber of reactor i, and $C_{2,i-1}$ is the MeBr concentration in the preceding swept chamber. When i is 1 (first reactor), then $C_{2,i-1}$ refers to the inlet air and the MeBr concentration is zero. E is the air exchange rate, which is defined as

$$E = \frac{Q}{Ah_2} \tag{5}$$

where A is the surface area of the film. Finally, the equation for the gas-phase concentration in the upper volume can be written as

$$\frac{dC_{3,i}}{dt} = K_2\frac{(C_{2,i} - C_{3,i})}{h_3} \tag{6}$$

where h_3 is the height of the upper chamber.

By adjusting the model parameters, the model is used for either fitting laboratory experimental data or simulating field fumigation, both for one tarp, or double tarp situations (Table 1). For example, if K_2 is set to 0, ϵ set to 1, and θ to 1, then effectively there are two chambers and diffusion coefficient experiments could be modeled. Similarly, if K_1 and K_2 are the same but h_3 was made very large, then C_3 is effectively zero under all conditions and the open top flow experiments could be modeled. In all cases, the model equations are solved numerically using Euler's algorithm.

TABLE 2. Mass Transfer Coefficient of MeBr in Tarps Used for the Control of MeBr Emissions

tarp	temp (°C)	mass transfer coeff (m s^{-1})
Barromide SC 30	20	4.6×10^{-10}
Barromide AP 30	20	1.3×10^{-8}
used PE from field (no punctures)	20	2.0×10^{-6}
PE	20	1.1×10^{-6}
PE	50	4.3×10^{-6}
PE	60	5.2×10^{-6}

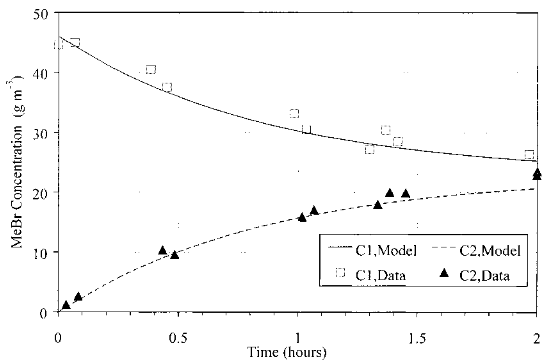

FIGURE 3. Typical run for K_{MeBr} determination through PE tarp. Experimental data (symbols) and model simulations (line). Best fit was $K_{MeBr} = 4.3 \times 10^{-6}$ m s^{-1} at 50 °C. Other parameters as in Table 1.

Results and Discussion

Experimental Determination of the Mass Transfer Coefficient. The mass transfer coefficient of MeBr through various tarps was experimentally determined at 20 °C, 50 °C and 60 °C for PE tarp and at 20 °C for two other tarps (Table 2). The experimental setup proved adequate: duplicate experiments showed less than 5% variation, and the total mass of MeBr was conserved. Excellent agreement was found between the data and the model for all experiments (Figure 3), and these results generally agree with previous work (*7, 8*). In the case of the PE, the mass transfer coefficient increased linearly with increasing temperature over the range investigated. The mass transfer coefficient is related to temperature by the equation

$$K_{MeBr/PE} = 1.0 \times 10^{-7}\ T\ (K) - 2.9 \times 10^{-5}\ (m\ s^{-1})\ \text{for } 293\ K \leq T \leq 373\ K \quad (7)$$

Therefore, greater mass of MeBr will diffuse through the film as temperatures increase in the field. Field temperatures greater than 60 °C have been reported (*4*). Note that according to the film theory, the mass transfer coefficient is equal to the diffusion coefficient divided by the film thickness.

Flow Experiments – Closed Top. Flow experiments were conducted to validate the two-tarp concept and verify that a CSTR accurately represented the swept chamber. Experiments were conducted at various air exchange rates from 0 h^{-1} to 2.9 h^{-1} and compared with model simulations using the mass transfer coefficient determined above. The results indicated excellent agreement between the experimental data and the model predictions obtained without any adjustable parameters (Figures 4–6). The mass of MeBr recovered was 102%, 99.8% and 99.6% for air exchange rates of 0, 0.55 and 2.9 h^{-1} respectively. A CSTR accurately represented the middle chamber because the diffusion in gases is much faster than the exchange rate.

Without sweep air ($E = 0$ h^{-1}) equilibrium in the three chambers was reached in approximately 25 h (Figure 4). At nonzero air exchange rates, MeBr diffused into V_2 and was swept into a Tedlar bag for later analysis. MeBr also entered V_3, but at a much lower rate than in V_2 because the MeBr concentration gradient across the upper film remained low, a direct consequence of the sweeping. Hence, C_3 remained low. After an initial peak near the beginning of the run, C_2 also decreased, and therefore a decrease in C_3 was also observed. At $E = 0.55$ and 2.9 h^{-1} the maximum amount of MeBr in V_3 was 4.28 and 0.94% of the amount applied, respectively. Therefore, even at relatively low air exchange rates, most of the MeBr was collected by the system. As will be discussed in the modeling section, MeBr emission and collection are directly linked to the air exchange rate and the mass transfer coefficient through the tarp.

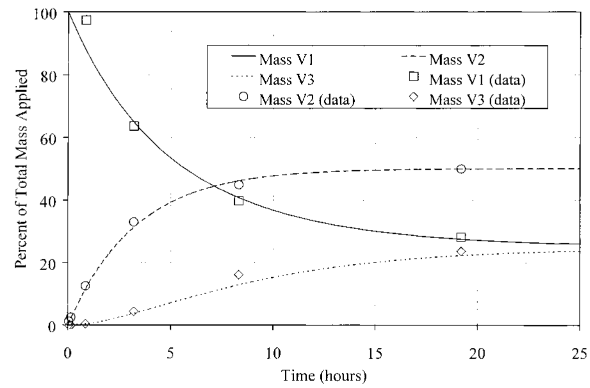

FIGURE 4. MeBr diffusion at air exchange rate = 0 h^{-1}. Closed top experimental data (symbols) and model simulations (line). Other parameters as in Table 1.

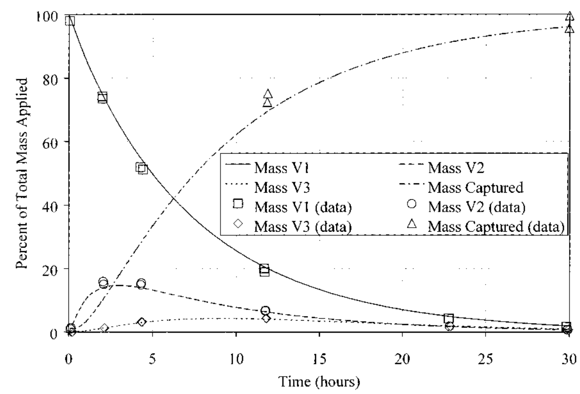

FIGURE 5. MeBr diffusion and collection at air exchange rate = 0.55 h^{-1}. Closed top experimental data (symbols) and model simulations (line). Other parameters as in Table 1.

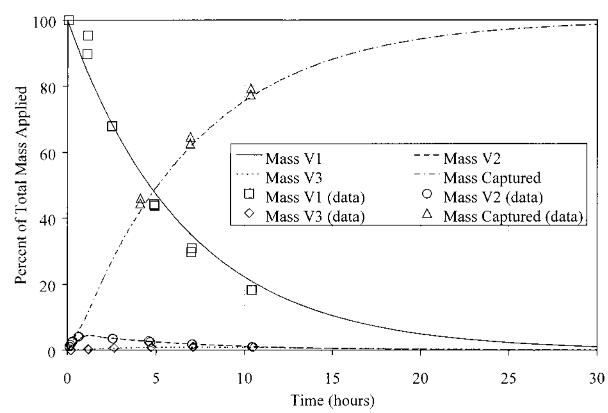

FIGURE 6. MeBr diffusion and collection at air exchange rate = 2.9 h^{-1}. Closed top experimental data (symbols) and model simulations (line). Other parameters as in Table 1.

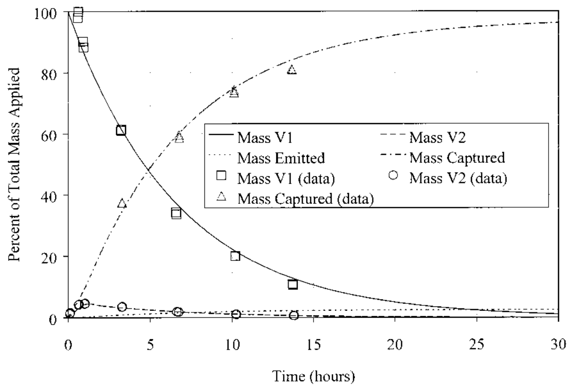

FIGURE 7. MeBr diffusion and collection at air exchange rate = 2.9 hr^{-1}. Open top experimental data (symbols) and model simulations (line). Other parameters as in Table 1.

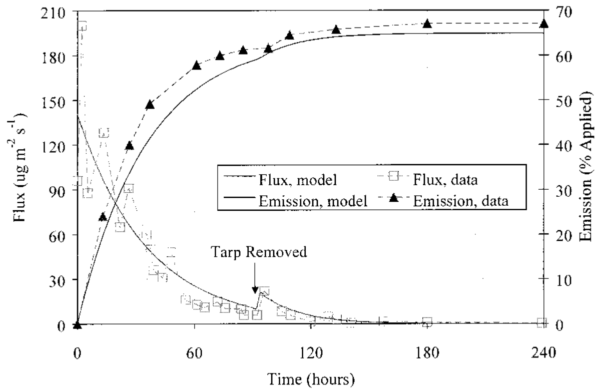

FIGURE 8. Model fitting (thick line) of Wang et al. (*4*) data (symbols, thin line). For model parameters, see Table 1.

Flow Experiments − Open Top. Having confirmed that a CSTR accurately represented the swept chamber and verified that experimental techniques allowed adequate mass balance, experiments were then conducted with V_3 open to the atmosphere. This setup is analogous to field application where the lower volume, V_1, represents the soil, the middle chamber is the swept volume, and V_3 is the air above the farmland. The goals here were to demonstrate the concept of the double tarp with air circulation and again to validate the model for one diffusion reactor. Because V_3 was open to the atmosphere, the actual amount emitted was calculated by the difference between the original mass in the lower volume and the total mass collected. This was justified based on the closure of the mass balance in previous experiments. Tests were conducted at various air exchange rates, and again the results indicated good agreement with the model. A typical run is reported in Figure 7 and compared to the model simulation. The mass of MeBr collected was 96.3%. The curves are similar to close top experiments (Figure 6). However, because V_3 was open to the atmosphere, and therefore C_3 was zero, a greater driving force for MeBr transfer to V_3 existed, and a greater mass entered V_3 but could not diffuse back into the swept volume. The total mass emitted from the system at $E = 0.55$ and 2.9 h^{-1} was 11.9 and 2.6% of the mass applied, respectively. These experimental results demonstrate the great potential for this system for reducing the overall emission of MeBr from farm field fumigations.

Field Simulation Model. Having demonstrated the proof of concept of the two-tarp system for the collection of MeBr from field fumigation, one has to understand how to best implement it in the field. The experimental results suggest that the air exchange rate plays a major role in effective collection; however, other parameters not yet considered in the laboratory experiments need to be integrated in the model. These include partition of MeBr in the soil moisture content, the fact that biotic and abiotic degradation of MeBr occurs, and that the tarp will ultimately be removed from the soil. This is discussed in the next sections: first unknown model parameters (tarp surface area, effective soil volume, water content, porosity, degradation rate, and effective mass transfer coefficient of soil with no tarp coverage) are calibrated using a published set of data of MeBr emission from a field experiment with a single tarp (*4*) and second the efficacy of the proposed two-tarp system is evaluated using model simulations.

Model Fitting of Field Experiment Data. Wang et al. (*4*) conducted a detailed field experiment to study the effect of tarp type and tarp removal time on the emission of MeBr to the atmosphere. The conditions were typical of field conditions where MeBr is applied and, thus, are relevant to simulate in order to determine missing model parameters.

The data presented in their paper from the experiment in which the tarp was left on the field for 5 days were used to determine the model parameters for field simulation. The mass transfer coefficient of MeBr through the tarp, *K*, was obtained from previous experiments (Table 2). The value at 50 °C was used (Table 1) because of the elevated temperatures experienced at the field. The film area and soil water content were given. The effective depth of the soil, h_1, was inferred from concentration distributions in the soil column (*4*). Soil porosity was assumed, although it had little effect on the model results. Only the MeBr degradation rate, *R*, and mass transfer coefficient with no tarp, i.e., after the tarp is removed, were necessary to be fit. All parameters were assumed to be constant, which is an approximation considering the diurnal variations observed by Wang et al. However, if deemed necessary, diurnal changes could easily be introduced in the model parameter to simulate diurnal variations. Here, the purpose was merely to show the validity of the model and obtain reasonable values for MeBr degradation rate *R*, and for *K* without tarp. The results demonstrate good correlation between the average experimental data and the model for both high and low permeable tarps and for different durations of tarp coverage. Only the results of the high permeability tarp, PE, are shown in Figure 8. Interestingly, despite being a relatively simple model, it adequately simulated a quite complex situation.

Simulation of Collection System. Using the same parameters used to simulate Wang et al. (*4*) experiments, the model was used to simulate MeBr collection with the proposed two-tarp system for a complete field. A range of air exchange rates was used to demonstrate the effect of this operating parameter on the total MeBr emitted to the atmosphere and on the inlet concentration to treatment system (Figure 9). At $E = 1$ h^{-1} 9.0% of the MeBr was emitted to the atmosphere, while at $E = 10$ h^{-1} only 1.0% was emitted over 10 days. In comparison, the results of Wang et al. (*4*) showed that approximately 50 to 60% of MeBr was emitted when the field was covered with PE for 10 days and between 1.1 and 3.2% when covered with a low permeability material. Thus if the two-tarp system is implemented, significant improvement over present practice can be achieved. In the modeled collection system, the maximum inlet concentration to the treatment system ranged from 6.6 g m^{-3} at $E = 1$ h^{-1} to 0.85 g m^{-3} at $E = 10$ h^{-1}. The highest air exchange rates resulted in the lowest emissions to the atmosphere because C_2 was kept the lowest. Therefore, the potential for it to diffuse through the second film was reduced. Optimal *E* will depend on many factors including the nature of the posttreatment system, energy costs, and regulatory emission allowances.

It is common practice that the tarp is removed from the field 5 to 10 days after fumigation (*4*). After the tarp is removed,

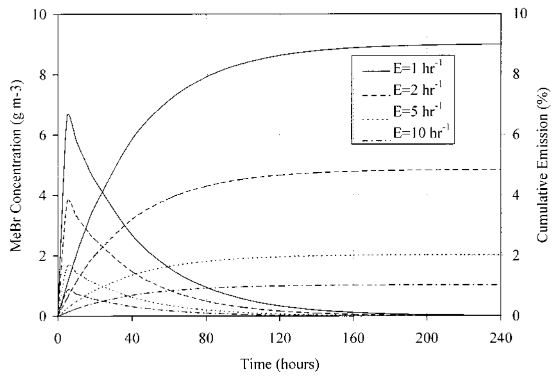

FIGURE 9. Inlet concentration to the treatment system and total MeBr emitted during 10 day collection system operation. See Table 1 and text for specific conditions.

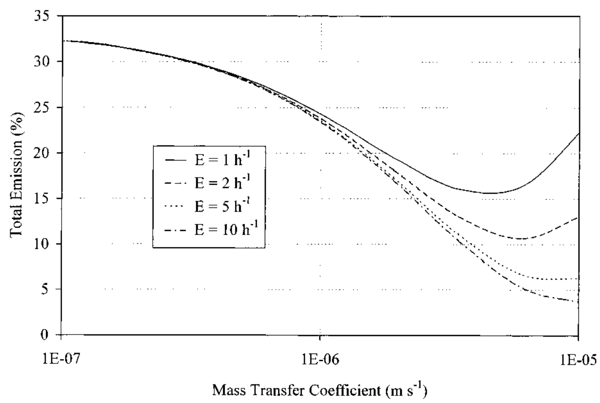

FIGURE 10. Sensitivity analysis of the two-tarp collection system to the mass transfer coefficient of MeBr through the tarp and to the air exchange rate. The cumulative emission is shown. See Table 1 and text for specific conditions; the tarp was removed on day 5.

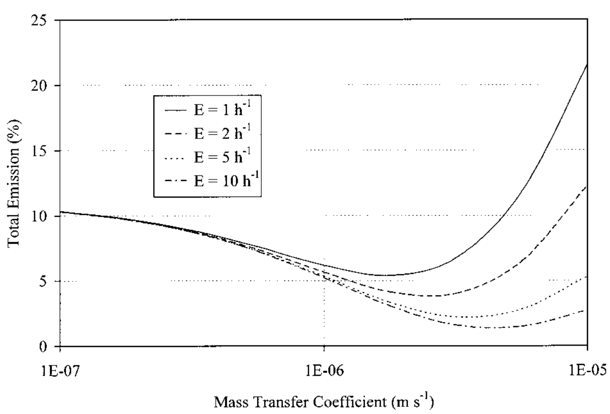

FIGURE 11. Sensitivity analysis of the two-tarp collection system to the mass transfer coefficient of MeBr through the tarp and to the air exchange rate. The cumulative emission is shown. See Table 1 and text for specific conditions; the tarp was removed on day 10.

the MeBr that has not been degraded will freely escape and add to the total cumulative emission. The total emission from the field is therefore a function of the air exchange rate, the mass transfer coefficient of MeBr through the tarps, but also the length of time the tarp covers the field. Therefore, the total cumulative emission was plotted as a function of the MeBr mass transfer coefficient at various air exchange rates and for two different durations of coverage (Figures 10 and 11).

The graphs have two distinct regions. At a very low mass transfer coefficient ($<3 \times 10^{-7}$ m s^{-1}) cumulative emission is not a function of air exchange rate. This occurs because the lower tarp is effective at trapping essentially all the MeBr and not allowing it to diffuse into the swept volume. Therefore, C_2 is virtually zero irrespective of the air exchange rate, and no MeBr is emitted while the tarp covers the field. Therefore, the total cumulative emission is a function only of the coverage time (the two tarp system is of little use in such case). In the case of tarp removal on day 5, the total emission is about 32%. For the 10 day removal, the greater time has allowed more MeBr to be hydrolyzed, and the total emission is about 10% of the total mass applied. For a 15 day removal (figure not shown), the total emission is about 4%, which excellently agrees with Wang et al. (*4*).

For cheaper films, with higher mass transfer coefficients, the emission is clearly a function of both air exchange rate and mass transfer coefficients as well duration of tarp coverage. Increased mass transfer coefficients allows more MeBr to diffuse from the soil into the swept volume, V_2, and therefore to be collected. Interestingly, the total cumulative emission of MeBr diminishes with increasing mass transfer coefficient until it reaches a minimum. On the other extreme, if the mass transfer coefficient is large and air exchange rate low, MeBr will build up in the swept volume and part of it will diffuse to the atmosphere. Therefore, the cumulative emission increases with increasing mass transfer coefficient at low exchange rates. For extremely permeable tarps, punctured or incorrectly hot-welded tarps ($K \geq 1 \times 10^{-5}$ m s^{-1}), most of the MeBr has diffused through the system within 5 days; therefore, little difference is seen between the 5 day and 10 day coverage at these mass transfer coefficients.

Overall, the results presented and discussed demonstrate that the proposed two-tarp system can be very effective in collecting MeBr emissions from field fumigation and therefore reduce the environmental impact of using MeBr. Further full-scale demonstration and detailed evaluation of the cost-effectiveness of the proposed technique is pending. Even so, there is no doubt that for the long term, environmentally friendly solutions are necessary to protect our environment. However, various concerns about the neurotoxicity of some of the proposed alternatives to methyl bromide or the cost-effectiveness of other replacement alternatives suggest that collection and recycle or disposal of MeBr might be an acceptable solution for critical cases, until better alternatives become available.

Supporting Information Available

Schematic of how experiments were performed. This material is available free of charge via the Internet at http://pubs.acs.org.

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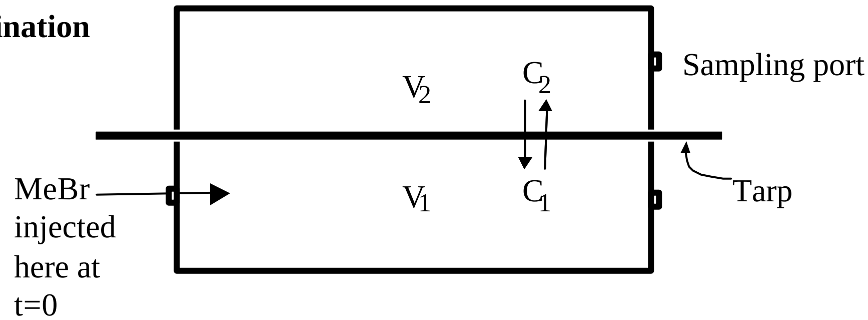
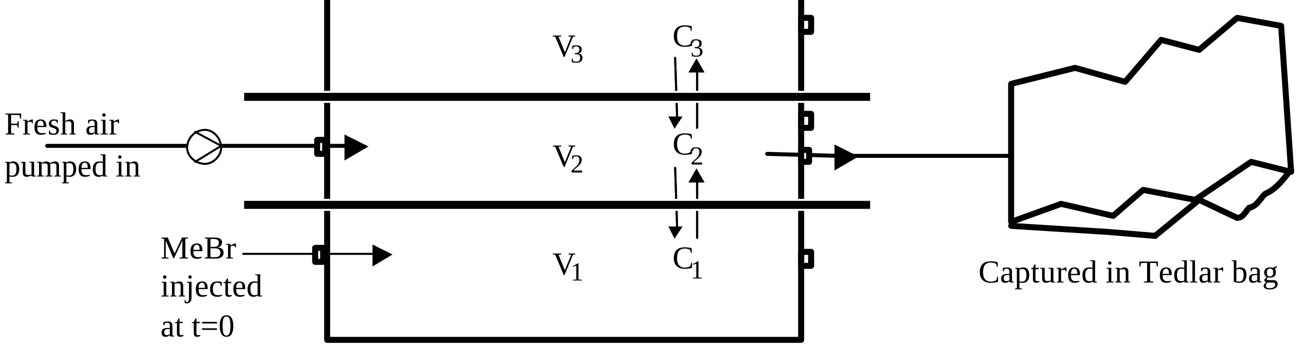
Supporting Information (web only): Experimental Procedures

Diffusion coefficient determination



Flow experiments, closed top



Flow experiments, open top