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Reactive Films for Mitigating Methyl Bromide Emissions from Fumigated Soil

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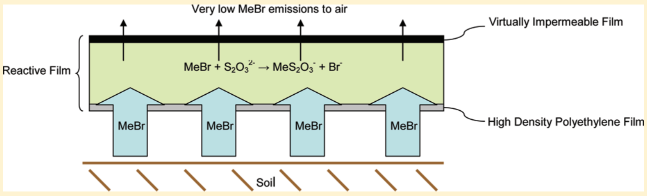
ABSTRACT: Emissions of methyl bromide (MeBr) from agricultural fumigation can lead to depletion of the stratospheric ozone layer, and so its use is being phased out. However, as MeBr is still widely used under Critical Use Exemptions, strategies are still required to control such emissions. In this work, novel reactive films (RFs) were designed and their efficacy in limiting loss of MeBr from soil was tested. A reactive layer, containing dry ammonium thiosulfate (ATS), was sandwiched between two layers of plastic film, the lower layer being HDPE (high-density polyethylene film, which is permeable to MeBr) and the upper layer HDPE or VIF (virtually impermeable film). MeBr diffusion through, and transformation by, the RFs were tested in a stainless-steel permeability cell. Although ineffective when dry, the RFs substantially depleted MeBr when activated with water to produce ATS solution. MeBr half-life ($t_{1/2}$) was around 9.0 h at 20 °C in the presence of activated RF, and was sensitive to temperature ($t_{1/2}$ 15.7 and 2.9 h at 10 and 40 °C, respectively). When the upper film layer was VIF, less than 0.15% of the added MeBr diffused through the film, with the remainder being transformed within the reactive layer. These findings indicate that such films have good potential to reduce MeBr loss from fumigated soils to the atmosphere.



INTRODUCTION

Methyl bromide (MeBr) is an excellent fumigant, acting as a biocide against arthropods, weeds, nematodes, fungi, and bacterial pests.[1] In 1990, its worldwide industrial usage reached 6.7 × 10^4 tons per year, with 94% used as fumigant.[2] Because about 50% of the used MeBr is ultimately released into the atmosphere where it can lead to depletion of stratospheric ozone,[2] the 1995 Montreal Protocol mandated that developed countries eliminate MeBr use by 2010, with developing countries expected to discontinue MeBr use at an unspecified later date.[3]

The plan to eliminate MeBr production and use could have severe economic implications for farmers and growers. The National Pesticide Impact Assessment Program (NAPIAP) estimated that the ban of MeBr without effective alternatives would cause annual economic losses of over $1.3 billion in the United States, with most of the losses from soil fumigation, especially tomato and strawberry production.[4] Therefore, although as early as March 1993 USEPA had already announced that MeBr was scheduled to be phased out by the year 2001,[5] the date of complete phase out was changed to January 1, 2005 with processes for special exemption permitted under the Montreal Protocol.[6] For example, in strawberry production alone, 1.3 × 10^3 tons of MeBr was needed for preplant soil fumigation in 2009,[7] 1.1 × 10^3 tons of MeBr is requested in 2010,[8] and 1.0 × 10^3 tons MeBr will be requested in 2011 [9] under the critical use nomination process.

The best approach to completely phase out MeBr use is to find alternative fumigants that will not destroy stratospheric ozone but have a wide biocidal spectrum of efficacy. Several other fumigants are registered for use in the U.S., such as 1,3-dichloropropene, chloropicrin, methyl isothiocyanate, and methyl iodide (MeI). However, because 1,3-dichloropropene, chloropicrin and methyl isothiocyanate have only relatively narrow spectra, none of them alone can replace MeBr. MeI has a very similar molecular structure and physicochemical properties to MeBr and is generally regarded as the most hopeful alternative to MeBr. However, health concerns over the use of MeI exist because it has been identified as a carcinogen, neurotoxin, and endocrine disruptor, and its use will result in significant risks for workers and the general population.[10] In addition, on the one hand, these fumigants are volatile organic compounds and can contribute to air pollution, e.g., near surface photochemical smog. Therefore, their use may be restricted by regulations, e.g., 1,3-dichloropropene use was restricted by township caps on ∼40−62% of total strawberry land in California in 2008.[9] On the other hand, they have lower vapor pressures, higher boiling points, and lower Henry's Constants than MeBr.[11] While these properties reduce their potential for emission to the atmosphere, they also indicate that these alternatives have a greater potential to remain in soil and may cause contamination of groundwater.[8] Overall, there appears to be no ideal alternative to MeBr. Therefore, the most promising approach may be to investigate technologies that would significantly reduce, or eliminate, the loss of MeBr from fumigated soil.

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Several methods of reducing emissions of MeBr from soil have been tried, e.g., using plastic films such as LDPE (low-density polyethylene film), HDPE, and VIF to trap and retain the residual MeBr in the soil and allow it to become transformed;[12−14] addition of organic amendments [15] or ammonium thiosulfate (ATS) [16] to the surface soil to promote MeBr transformation; addition of ammonium hydroxide under agricultural film to transform MeBr;[17] or absorption of residual MeBr onto activated charcoal with subsequent recycling or destruction in ATS water solution.[18] Although MeBr may be transformed quickly in some soils and its total emission losses can be reduced to less than 4% when the fumigated field is covered with VIF for 10 to 15 days,[13] its transformation rate varies depending on soil type ($t_{1/2}$ ranging from 5 to 28 days [19]). Therefore, it is possible that VIF would be removed for crop planting before MeBr is completely decomposed, leading to the residual fumigant vapors immediately entering the atmosphere. The main problem with soil organic amendment is that the soil/plant system can only assimilate a certain quantity of organic material, and this amount may be too low to obtain a satisfactory MeBr transformation rate.[15] Although ATS can quickly transform MeBr, it has been shown that following a MeBr application of 112 kg ha^{-1}, a large amount (660 kg ha^{-1}) of ATS is needed to transform residual MeBr in soil [16] and little is known about the health effects of the resulting breakdown products. Moreover, to promote MeBr transformation, ATS must be sprayed onto the field before MeBr is injected into the soil. In this case, once MeBr is injected, its reaction with ATS would rapidly compromise its efficacy as a fumigant. The issue of bromide ion production following MeBr transformation in soil [20] is a further potential problem associated with traditional MeBr use. The accumulation of such soluble ions may cause plant toxicity and groundwater contamination.[21] Overall, it seems that a system that allows for (a) MeBr efficacy toward pests; (b) containment of the MeBr within the soil; and (c) ultimately, transformation of the MeBr away from the soil, would be a useful tool in limiting environmental damage caused by Critical Exemption Use of MeBr.

As plastic films are widely used during fumigation practices, and ATS is an excellent chemical to transform residual fumigant MeBr, this work aimed to (i) design novel reactive films (RFs) incorporating ATS which can transform MeBr as it diffuses through them; (ii) test RF efficacy in eliminating MeBr at differing temperatures using permeability cells; and (iii) test how the amount of ATS in the film affects an RF's ability to mitigate MeBr emission.

■ MATERIALS AND METHODS

Chemicals and Plastic Film. Methyl bromide was donated by Soil Chemical Co. (Hollister, CA 95024). Ammonium thiosulfate (purity 99%) was purchased from Sigma-Aldrich Co. A 1 mil (0.0254 mm) HDPE film (Dow Chemical Company, Midland, MI) and a 1.5 mil (0.0381 mm) Hytibar VIF (Klerk's Plastics, Inc.) were used for construction of the RFs. These two films have mass transfer coefficients (e.g., permeability) of 2 cm h^{-1} and less than 0.01 cm h^{-1}, respectively. Paper tissue was purchased from Horizon Industries (Tyler, TX).

Permeability Cells. Permeability cells were prepared as described previously.[22] Briefly, the stainless steel cell was composed of one source chamber and one receiving chamber, each 4.0 cm deep and 12.0 cm inside diameter. The two chambers were fitted together with an RF (see below for RF construction details) sandwiched between them and sealed with epoxy and adhesive aluminum tape. In the center of each chamber's side wall was a sampling port, which was plugged with a Teflon-faced silicon septum through which MeBr could be injected into the source chamber at the beginning of the experiment. During the experiment, a gastight syringe was used to sample MeBr gases via these ports from both the source and receiving chambers, to determine the rate of gas diffusion across the RF. For each RF, triplicate samples were tested.

Spiking, Sampling, and Analysis. MeBr was first introduced into a vacuumed Teflon gas sampling bag, from which 75 mL of MeBr vapor was then transferred into a 1.0-L glass cylinder using a syringe. After equilibration for 30 min, 25.0 mL of gas was transferred into the source chamber of the permeability cell with a gastight syringe. The initial MeBr concentration in the source chamber was about 12 mg L^{-1}. At predetermined time intervals, 250 μL of gas was sampled from the source and receiving chambers with a gastight syringe and transferred into a 12.1 mL headspace vial which was immediately capped with a Teflon-faced butyl rubber septum and an aluminum seal.

Samples were analyzed on an HP6890 GC-μECD (gas chromatograph equipped with a microelectron capture detector) with an interfaced Agilent Technologies G1888 Network Headspace Sampler. The headspace sampler was used at 80 °C, with a 5.0-min equilibration and a 1000-μL sample loop. The GC was equipped with DB-VRX fused silica capillary column (J&W, Folsom, CA) which was 30-m long, 0.25-mm i.d., and 1.4-μm in film thickness. Its operation conditions were as follows: helium carrier gas flow rate 1.4 mL min^{-1}; injector temperature 240 °C; detector temperature 280 °C; and oven temperature program: 45 °C held for 1.0 min at the beginning, then increased to 80 at 2.5 °C min^{-1}. Under these conditions, the MeBr retention time was 2.70 min. Calibration standards for the GC analysis were prepared from *n*-hexane MeBr solution at seven concentrations in headspace vials and were analyzed at the beginning of each set of samples.

Preparation of the Reactive Film. The basic principle of the RFs was that the MeBr would react with thiosulfate in aqueous solution [16] and hence be transformed (eq 1) within the film.

$$CH_3Br + S_2O_3{}^{2-} \rightarrow CH_3S_2O_3{}^{-} + Br^{-} \qquad (1)$$

Although sodium thiosulfate could also be used for this purpose,[16,23,24] ATS was selected for these experiments, being much easier to dissolve in water (1.0 mL water can dissolve over 1.8 g ATS at 21 °C). As for the tissue paper, used to introduce and maintain sufficient water within the film to facilitate the MeBr-ATS reaction, several kinds of paper were tested. The selected paper was able to hold sufficient water to dissolve three times the amount of ATS required to react with the applied quantity of MeBr. To construct an RF, two pieces of plastic film were used, either both HDPE, or one HDPE and one VIF. The lower layer (facing the MeBr source) of the RF was always HDPE. Above the HDPE was a single layer of tissue paper holding a certain amount of dry ATS (either 44.2, 88.5, or 132.7 g m^{-2}, i.e. 1:1, 2:1, or 3:1 ATS:MeBr molar ratio based on the commonly used rate of MeBr in soil, 280 kg ha^{-1} [13]), followed by another single piece of tissue paper, and finally a second layer of plastic film (either HDPE or VIF). For the nonactivated RF, the construction was kept dry. For the activated RF, water (132.7 g m^{-2}) was added to the tissue paper layers. As a control film for this experiment, cells were set up with only the two layers of plastic

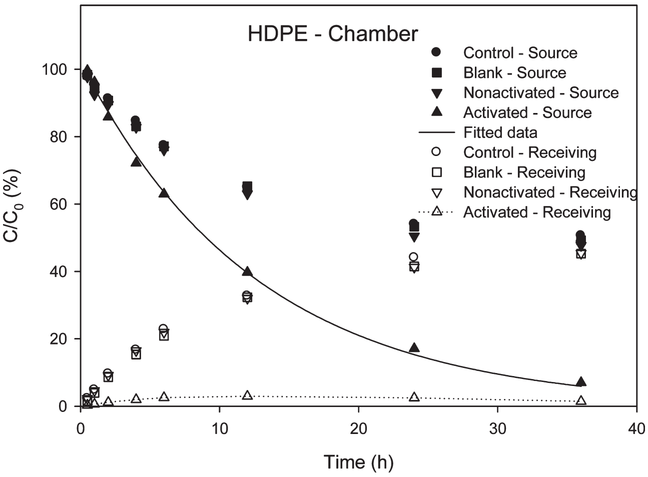

Figure 1. MeBr diffusion through HDPE-RF from the source chamber to the receiving chamber and disappearance in the source chamber at 20 ± 1 °C over time.

film. As a blank RF, cells were set up without ATS, but including the water and tissue paper.

The Efficacy of ATS within RF in Transforming MeBr. In the HDPE-RFs, both plastic films were HDPE. The amount of ATS used in the nonactivated or activated RF was 44.2 g m^{-2}. The experiments were conducted at 20 ± 1 °C.

Effect of VIF and ATS Amount on RF Efficacy. In the VIF-RFs, the upper side film (facing away from the MeBr source) was Hytibar VIF. Activated RFs contained one of three levels of ATS, 44.2, 88.5, or 132.7 g m^{-2}. The experiments were conducted at 20 ± 1 °C.

Effect of Temperature on VIF-RF Efficacy. These activated RFs contained 88.5 g m^{-2} ATS. Permeability cells containing the VIF-RF were kept in 10 ± 1, 40 ± 1 °C isothermal incubators, and a 20 ± 1 °C room.

RESULTS AND DISCUSSION

The Efficacy of ATS within RF in Transforming MeBr. In the permeability cells, MeBr concentrations in both source and receiving chambers changed over time (Figure 1) in response to MeBr diffusion through the film, and potential transformation within the film due to the presence of ATS solution.

In contrast to the activated RF, MeBr gradually diffused through the control, blank, and nonactivated RFs. As the literature indicates, HDPE is relatively permeable to MeBr.[13,22] At 20 ± 1 °C, MeBr reached equilibrium between both sides of the RF in 36 h. In the source chambers, the MeBr concentration equilibrated at 50.6, 49.2, and 47.7% of the initial concentration in the presence of the control, blank, and nonactivated RFs, respectively. In the receiving chambers, the MeBr concentration equilibrated at 48.6, 45.3, and 45.4% of the initial concentration, respectively. The fact that, at equilibrium, concentrations in the source and receiving chambers were very close to half of the initial value in the source chamber, indicates that no transformation of the MeBr took place within the RF. In the presence of activated RF, the rate of MeBr disappearance in the source chamber (via transformation and diffusion through the RF) could be well described using the first-order kinetic regression:

$$C = C_0 \cdot e^{-k \cdot t} \qquad (2)$$

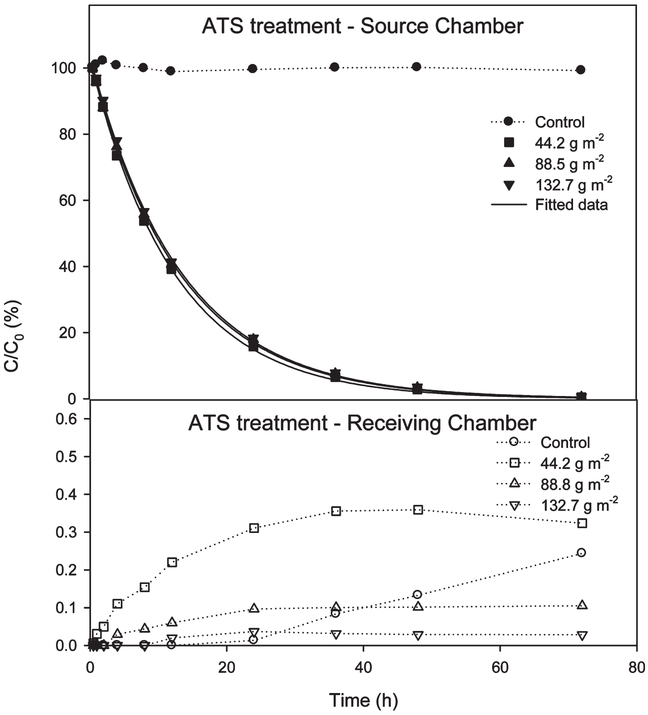

Figure 2. MeBr diffusion through VIF-RFs at three levels of ATS from the source chamber to the receiving chamber and MeBr disappearance in the source chamber over time.

Where C_0 and C were the MeBr concentrations (mg L^{-1}) at time 0 and t (h) after MeBr injection in the source chamber, k is the first order rate constant (h^{-1}). A k value of 0.0791 h^{-1} ($r^2 > 0.99$) was found. The MeBr $t_{1/2}$ was 8.8 h. MeBr decreased to 7.0% of the initial concentration in 36 h. The greatest concentration in the receiving chamber reached 2.9% of the initial concentration of MeBr in the source chamber during this period. This indicates that 90.1% of the added MeBr was transformed within the RF by reaction with ATS. The lack of MeBr destruction in the control, blank and nonactivated RF treatments indicates that ATS in solution form was required for an effective RF construction to eliminate MeBr.

Effect of VIF and ATS Amount on RF Efficacy. Methyl bromide diffusion through, and transformation in, VIF-RFs containing three levels of ATS are shown in Figure 2.

For the control RF, the concentration of MeBr in the source chamber decreased by 0.5% in the first 24 h, and thereafter decreased even more slowly. The slight reduction in the beginning was likely due to some of the MeBr penetrating HDPE and entering the void between the HDPE and VIF, where it would become trapped due to the very low permeability of the VIF. In the receiving chamber, the concentration did not increase until 24 h, and then increased very slowly. By 72 h, less than 0.3% passed through the control RF. In terms of a mass balance, the presence of close to 100% of the added MeBr at the end of the control experiment indicates that no transformation of the MeBr took place. Compared to HDPE-RF, the replacement of the upper layer HDPE with VIF improved RF efficacy in depleting MeBr, e.g., the loss of MeBr from source chamber to receiving chamber reduced from >2.9% to <0.4% in the RFs of 44.2 g m^{-2} ATS. For all three activated VIF-RFs, the rates of MeBr dissipation were very similar ($t_{1/2}$ around 9 h) despite the 3-fold difference in ATS amount. Because the amount of MeBr that

Table 1. Rate Constant (k) and Half-Life ($t_{1/2}$) of MeBr in Permeability Cells at Three Levels of ATS within The VIF-RF (20 ± 1 °C)

ATS amount (g m^{-2})	k (h^{-1})	r^2	$t_{1/2}$ (h)
44.2	0.0747 ± 0.0011	>0.99	9.3
88.5	0.0808 ± 0.0012	>0.99	8.6
132.7	0.0756 ± 0.0011	>0.99	9.2

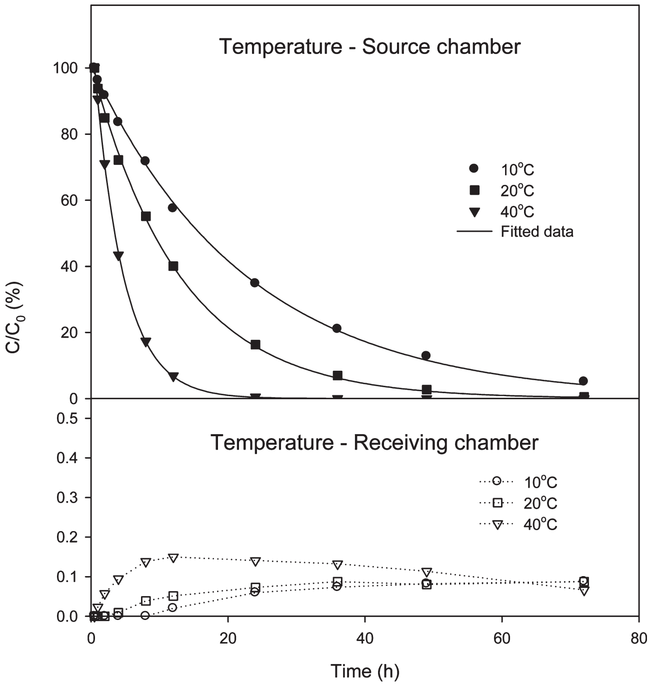

Figure 3. MeBr diffusion through VIF-RFs from the source chamber to the receiving chamber and disappearance in source chamber over time at three different temperatures.

penetrated through RF was limited (<1% as in the case of control), the disappearance of MeBr can be considered a consequence of transformation by reaction with the ATS solution. The MeBr transformation kinetics in the source chamber for these RFs could be fitted with eq 2 (Table 1).

In preliminary tests, it was observed that moisture around the VIF could increase its permeability to MeBr. Although less than 0.4% of the total injected MeBr diffused through the activated RF with an ATS treatment of 44.2 g m^{-2}, the rate of penetration was much quicker than that through the control RF. This may be explained by the presence of water in the ATS treatments (i.e., the ATS aqueous solution). When the ATS amount increased, the amount of MeBr which diffused through the RF was reduced, to less than 0.04% in the case of ATS at 132.7 g m^{-2} (Figure 2).

Effect of Temperature on VIF-RF Efficacy. Increased temperature usually increases reaction rate and a plastic film's permeability to MeBr. At different experimental temperatures, MeBr diffusion through the VIF-RF is shown in Figure 3.

With increasing temperature, the rate of MeBr disappearance in the source chamber increased. At 10 °C, 5% MeBr in the source chamber remained after 72 h; at 20 °C, only 0.5% was left; and at 40 °C, no MeBr could be detected. The disappearance rate constants of MeBr in the source chamber could be fitted well with eq 2 (Table 2).

Table 2. Rate Constant (k) and Half-Life ($t_{1/2}$) of MeBr in Permeability Cells Using VIF-RF at Three Temperatures

T (°C)	k (h^{-1})	r^2	$t_{1/2}$ (h)
10	0.0441 ± 0.0008	>0.99	15.7
20	0.0775 ± 0.0021	>0.99	8.9
40	0.2358 ± 0.0026	>0.99	2.9

As the temperature was increased from 10 to 40 °C, the MeBr disappearance rate increased 5.4 times. To characterize the effect of temperature on MeBr disappearance rate in RF, the apparent reaction constant (k) was regressed with temperature according to the Arrhenius equation:

$$\ln k = \ln A - E_a/RT \qquad (3)$$

Where T is the absolute temperature, R is the universal gas constant, A is the pre-exponential factor, E_a is apparent activation energy. T and k were fitted well ($r^2 > 0.99$) and the E_a was 41.4 kJ mol^{-1}. Although the MeBr concentration used to derive the k value was that in the source chamber, not that in the ATS solution within the RF, the E_a in this reaction system is several orders of magnitude higher than that in the case of an HDPE-only system (0.340 kJ mol^{-1}) and a Hytibar VIF-only system (0.243 kJ mol^{-1}), both of which merely act as physical barriers.[25] However, the E_a value for the RF system was close to that found for ATS-treated soil (51.5 kJ mol^{-1}).[16] This indicates the MeBr disappearance was controlled by its reaction with ATS rather than penetration through HDPE or VIF.

On the basis of the observed results, the process of MeBr transformation within such activated RF can be proposed. From the source chamber, MeBr would first have diffused through the HDPE film and reached the inner void of the RF, where it reacted with ATS and was transformed. Despite the peak concentration of MeBr in the receiving chamber being low in all cases (<0.15% of the initial MeBr concentration in source chamber), this can be taken as evidence that the reaction rate between MeBr and ATS was not fast enough to transform all the MeBr that diffused into the void through the HDPE. As diffusion progressed, the MeBr concentration would have gradually decreased in the source chamber and increased in the ATS solution. The residual MeBr in the ATS solution would then have slowly diffused though the VIF. At higher temperature, MeBr diffused much faster through the HDPE, ATS solution, and VIF than at lower temperature, resulting in more rapid diffusion through the RF despite the concurrent increase in the reaction rate between MeBr and ATS. This accounts for MeBr reaching an earlier and higher peak concentration at 40 °C when compared to 20 and 10 °C. With the MeBr concentration in the source chamber decreasing in response to transformation, the diffusion potential would have decreased with the reduction in concentration difference across the HDPE film. Ultimately, this would lead to the MeBr diffusion rate being lower than the reaction rate of MeBr and ATS. In response, the MeBr concentration in the ATS solution would have gradually decreased from its peak. At the same time, the diffusion potential between the inner void and receiving chamber would begin to decrease until the MeBr concentration in the ATS solution became lower than that in receiving chamber. At this point, the MeBr in the receiving chamber would have diffused back to the ATS solution where it would be transformed. However, this was a slow process because of the very low permeability of VIF. Nevertheless, a higher temperature was favorable for MeBr diffusion through the VIF. At 40 °C, the

MeBr concentration in the receiving chamber gradually decreased, while at 20 and 10 °C this process was not obvious.

Environmental Implications. To date, plastic films (e.g., LDPE, HDPE, and VIF), are used only as a physical barrier to fumigant release from soil. Fumigated fields are tarped to contain, rather than transform, MeBr in soil. Because of prolonged soil contact time, MeBr efficacy as a biocide is improved and, as a result, MeBr use rate can be reduced.[8,12−14] Tarps also increase the potential for transformation of MeBr with the soil. Overall, the potential for MeBr emission is reduced by tarping. The RF reported here is not only a physical barrier, but also an active sink for MeBr after activated by the addition of water.

Preliminary experiments demonstrated that ATS is very unstable in moist soil. This probably explains why an excessive amount (3.8:1 molar ratio, ATS:MeBr) is needed to deplete MeBr when directly added in soil.[16] Sandwiched between two plastic films within the RF, the ATS in our experiments was not in contact with soil and hence avoided such decomposition. Therefore, because all of the ATS can react with MeBr, only an equal molar amount is required.

The tissue paper within the RF is not able to absorb moisture through the plastic films, so the RF can be kept dry, and therefore nonactivated, for times where only a physical barrier may be desired. As shown by our data, nonactivated RF (i.e., without water) has very limited potential to transform MeBr. Nevertheless, because the edge of the RF can remain unsealed, water can be introduced to, and absorbed by, the paper at a later time to activate the RF. For example, immediately following fumigation, the nonactivated RF may be used while the MeBr is disinfesting the soil. Later, when disinfestation is complete but residual MeBr is still present, the RF can be activated to deplete the fumigant and mitigate emission loss when the film is removed.

In previous work, in order to prolong the retention time, and therefore increase transformation and reduce emission, MeBr was injected into deeper soil.[14] Although this method was effective in reducing emissions on the whole, the residual MeBr in deeper soil was transformed at a much lower rate than that in shallower soil.[26] If film is used to tarp these fumigated fields, the deeper injection would likely mean that a longer period of tarping is required. Otherwise, a large quantity of MeBr will likely diffuse into the surface layer soil and then into the atmosphere after the film is removed. However, if RF is used, the soil would not be a major factor in promoting MeBr transformation, and so the depth of MeBr injection could be decided based on biocidal efficacy rather than emission reduction potential. A shallower injection will reduce the time for all of the residual MeBr to reach the field surface and thus be transformed by the RF.

The timing of activation of the inner reactive layer can be controlled by applying water at the appropriate time (i.e., after MeBr efficacy is achieved). The MeBr transformation rate is controlled only by the RF itself, and the film temperature. As MeBr $t_{1/2}$ under our RFs was less than 10 h at 20 °C, and less than 3 h at 40 °C, the residual MeBr in real field situations would likely be transformed rapidly, because the temperature of the soil surface will often be higher than 40 °C.[27] RF can ultimately be removed from the field taking both excess ATS and any byproduct after the residual MeBr is transformed. It is also possible that the used RF and byproduct might be recyclable. Our results suggest that the RF could potentially be adopted as an important new tool to control MeBr emissions in situations where its use is still permissible (e.g., critical use exemptions). We aim to further assess the ability of our RF to reduce fumigant emissions from soil. We also aim to investigate the practical limitations of applying RF in the field. Important questions relating to the weight and handling of such films, together with the best way to introduce water into the film under different agricultural scenarios (e.g., broadcast and raised bed applications) will be addressed in future studies.

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