

# Methyl Bromide Emission from Fields Partially Covered with a High-Density Polyethylene and a Virtually Impermeable Film

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Recent field studies in the interior valley of southern California have indicated that 56–73% of methyl bromide (MeBr) used in soil fumigation is lost to atmospheric emission when the fields are covered completely with a high-density polyethylene (HDPE) film. The emission can be reduced to less than 5% when a virtually impermeable film or Hytibar is used to cover the fields. This study was conducted to determine MeBr emission from bedded field plots where only the beds were covered with a HDPE or a virtually impermeable plastic film. The results provide an assessment on MeBr emission from field beds partially covered with the HDPE film and the suitability of using a virtually impermeable film for emission reduction. Methyl bromide gas was applied to replicated field beds covered with either a HDPE or the Hytibar film. The films were removed 6 days after MeBr application. Replicated soil cores were taken from different locations of the field beds, 20 days after MeBr application, for the determination of soil bromide ion concentrations. The total amount of MeBr degraded from each plot was calculated from the measured bromide ion concentrations, and the potential emission was determined as the difference between the amount of applied and that of degraded. Results indicated that the potential emission from this bedded system was about 95% for the HDPE treatment and 90% for the Hytibar-covered plots. Regardless of the small improvement with the virtually impermeable film, the experiment clearly indicates that partially covering the field with either a HDPE or a virtually impermeable film would result in unacceptably high emission losses.

## Introduction

Because of its high volatility and potential of destroying stratospheric ozone (1, 2), soil fumigation with methyl bromide ( $\text{CH}_3\text{Br}$ , MeBr) often requires a field to be covered with plastic films either before or at the time of fumigation. However, field studies indicate that 21–87% of applied MeBr is lost to the atmosphere after soil fumigation (3–7). A series of field experiments conducted in the interior valley of southern California have also consistently shown that 56–73% of the applied MeBr is lost to the atmosphere by the time of film removal (6, 8, 9). The large emission loss is attributed primarily to the ineffectiveness of the high-density

polyethylene (HDPE) films to restrict MeBr movement into the atmosphere, although they have been widely used due to their low cost and favorable mechanical properties for field application. A recent field study indicates that MeBr emission can be reduced to less than 5% when the field is completely and continuously covered with a virtually impermeable plastic film (Hytibar) for more than 10 days (9). This new plastic film also appears to have the physical and mechanical properties that are similar to the HDPE films, making it feasible for field use.

Agricultural soil fumigation with MeBr or other fumigants such as 1,3-dichloropropene (1,3-D) is an important practice in controlling soil-borne plant pathogens and nematodes (10) for many vegetable or fruit crops such as tomatoes, bell peppers, and strawberries. These crops are often planted in preshaped beds on which irrigation, fertilizers, and pesticides are delivered. Soil fumigation for these crops are often performed for the preshaped beds prior to planting, and only the fumigated beds are covered with the HDPE films for emission reduction. Schneider et al. (11) obtained a uniform concentration distribution for 1,3-D in a pineapple bed covered with a HDPE film when the chemical was applied either with drip irrigation or by direct injection. However, no information is available in the literature on fumigant emission under a bedded system or when the field is only partially covered with plastic films. It is likely that MeBr emission from a bedded system may be larger than the 56–73% range as compared to the continuous or complete cover with the HDPE films. It is also important to determine if the virtually impermeable film or Hytibar is effective in significantly reducing MeBr emission when only the field beds are covered with the film, as compared to the continuous or complete cover.

Methods of determining MeBr emission under field conditions often use following approaches: (i) meteorological-based concentration profiles, (ii) flux chambers, and (iii) bromide ion ( $\text{Br}^-$ ) appearance method. The  $\text{Br}^-$  appearance method offers a simple and accurate indirect estimation of MeBr emission because MeBr degrades to the simple mineralized form of  $\text{Br}^-$  that can be easily and accurately analyzed in the laboratory. Although the converted  $\text{Br}^-$  may be subject to leaching or plant uptake, soil sampling to sufficient depths and before the plant regrowth would eliminate the possibility for unaccounted MeBr losses. Previous mass balance studies have also indicated that the remainder of applied to emitted MeBr was lost to soil degradation as the simple mineralized form of  $\text{Br}^-$ , since near 100% mass balance was obtained (6, 9). This method is especially suitable for small plot studies where soil variability is less of a problem and direct flux measurement with chambers would be prohibitively expensive.

The objective of this study was to determine MeBr emission from bedded field plots where only the beds were covered with a HDPE or a virtually impermeable plastic film. The study provides information on MeBr emission from a bedded system partially covered with the HDPE film and the suitability of using a virtually impermeable film for emission reduction under a bedded field.

## Experimental Section

**Plot Design and MeBr Application.** Eight experimental plots, four for the HDPE treatment and four for the Hytibar, were randomized in a field block located at University of California

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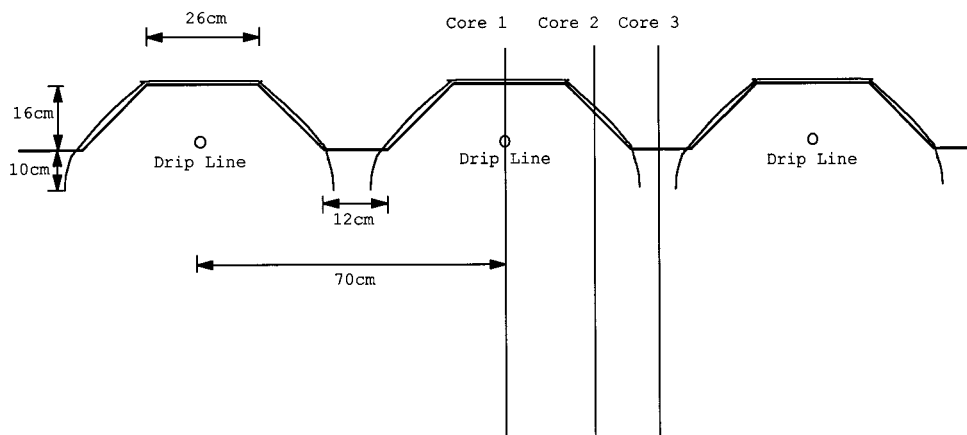


FIGURE 1. Schematic of the cross-section of a bedded field plot showing the bed dimension, plastic cover films, drip lines for methyl bromide application, and locations of soil sampling for bromide ion.

Southcoast Agricultural Experimental Station near Irvine, CA. Each plot consisted of three 6-m-long beds with a bed spacing of 0.7 m (Figure 1). A buffer area about 6 m long without MeBr application was used between each plot. One line of subsurface drip irrigation tape was installed at the same time of bed construction. The drip line was later used for MeBr application using the hot-gas injection method. Prior to MeBr injection, each bed was covered with a layer of HDPE film for the HDPE treatment or Hytibar film for the virtually impermeable treatment. The edge of cover films was buried about 0.1 m below the soil surface near the bottom of the bed slope. The cover films were removed 6 days after MeBr application. Following procedures similar to that of Wang et al. (9), MeBr gas was applied on September 11, 1997, through the preinstalled drip irrigation tapes. The application rate was  $11.2 \text{ g m}^{-2}$  for each plot.

**Soil Water Content and Bulk Density.** Soil water content was measured by taking gravimetric core samples at 0.1 m increment to 1 m depth. Six soil cores were taken: two from the bed top, two from the bed slope, and two from the furrow. The location of the six cores was randomly chosen from within the field block. This was to minimize potential spatial variability caused by uneven water movement in the beds. Soil bulk density was determined from the same core samples as for water content measurement and was used for converting the measured  $\text{Br}^-$  concentration to degraded MeBr content in the soil profile.

**Bromide Ion Sampling and Analysis.** To determine MeBr degradation and to estimate the potential emission loss, soil cores were taken with hand-operated augers (7.5 cm i.d.) to a depth of 1 m at 20 days after MeBr application. Three soil cores were taken from the center bed of every plot: one from the bed top, one on the slope, and one in the furrow to determine the spatial variance of MeBr redistribution or its degradation pattern (Figure 1). Taking samples from the center bed would also help in reducing the boundary effect since MeBr diffuses very rapidly in the soil and is prone to boundary interference for small plot studies. Seven samples were separated from each soil core at following depths: 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1 m for analysis of bromide ion concentrations. Small depth increments were used between soil surface and 0.4 m depth. This was to provide a relatively more accurate measurement of the total mass of degraded MeBr since (i) the injection depth or center mass was at 0.15 m and (ii) the surface soils contained more organic materials, which has been shown to enhance the degradation of MeBr as compared to soils at deeper depths (12). A total of 24 soil cores were taken from the MeBr-treated plots. For a background check on the soil's original  $\text{Br}^-$  content, four

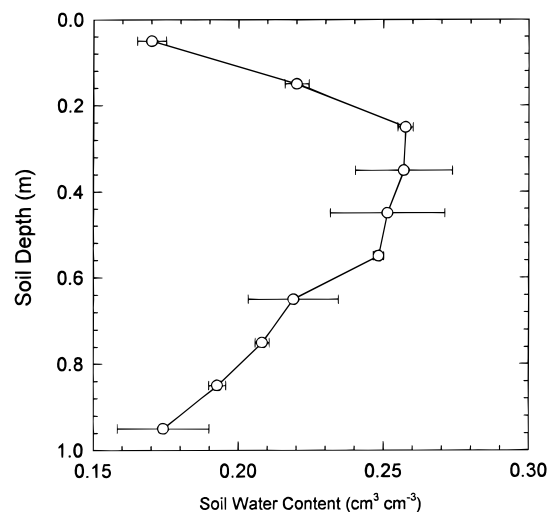


FIGURE 2. Soil water content distribution over depth averaged from different treatments and sampling locations. Error bars =  $\pm \text{SE}$  ( $n = 6$ ).

additional soil cores were taken from the buffer areas where MeBr was not applied. Therefore, a total of 196 samples were used for the determination of  $\text{Br}^-$  concentrations.

Bromide ion from these soil samples was extracted with deionized water at a 1:1 water to soil ratio. After mechanical mixing and separation with a centrifuge, extractions were made by passing the solution through filter papers. The concentrations in the extracts were analyzed with a Dionex ion chromatograph (IC) that has a detection limit of less than  $0.1 \mu\text{g g}^{-1}$ . The amount of degraded MeBr from each sample volume was calculated by converting the measured bromide ion concentration to a MeBr mass on a molar equivalent base. Total degraded MeBr mass from each plot was obtained by (a) calculating the degraded MeBr mass for each of the three sample locations or the area they represent for each depth increment to 1 m and (b) adding the degraded MeBr from the three sample locations and all depths.

## Results and Discussion

**Soil Water Content and Bulk Density.** The volumetric water content was about  $0.22 \text{ cm}^3 \text{cm}^{-3}$  near the injection depth, i.e., 0.15 m depth (Figure 2). The highest water content was in the depth range of about 0.2–0.6 m where it was about  $0.25 \text{ cm}^3 \text{cm}^{-3}$ . Above or below this depth range, the water content decreased (near linearly) to about  $0.17 \text{ cm}^3 \text{cm}^{-3}$ . Because MeBr movement in the soil is primarily driven by vapor-phase diffusion subjecting to a first-order kinetic

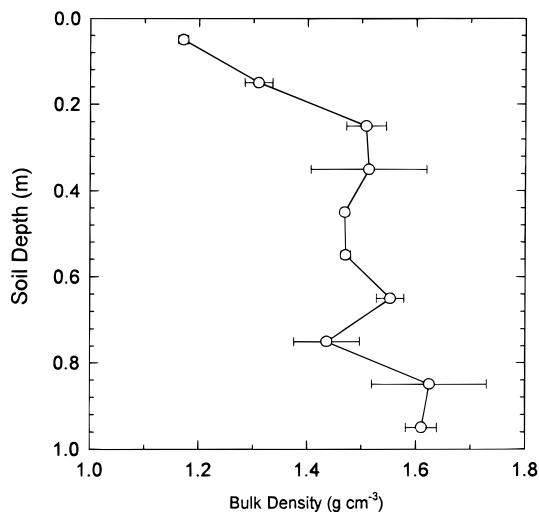


FIGURE 3. Soil bulk density averaged from different plots and sampling locations. Error bars =  $\pm$ SE ( $n = 6$ ).

reaction between adsorption and dissolution and a first-order degradation (13), the high water content layer below the injection depth would significantly reduce soil air porosity, therefore, impeding MeBr transport to lower depth in the soil profile. For example, MeBr diffusion coefficient at 20 °C would be reduced from 14.9 cm<sup>2</sup> h<sup>-1</sup> for a water content of 0.17 cm<sup>3</sup> cm<sup>-3</sup> to 5.6 cm<sup>2</sup> h<sup>-1</sup> for water content of 0.25 cm<sup>3</sup> cm<sup>-3</sup>, assuming a soil bulk density of 1.50 g cm<sup>-3</sup>. Furthermore, a large fraction of the vapor-phase MeBr can be partitioned into water phase if the soil water content was high, since at equilibrium liquid-phase concentration is about four times its vapor-phase concentration according to the modified Henry's law constant (14). The overall effect of such a water content distribution may be in favor of MeBr emission loss because most of the applied MeBr would be limited to shallow depths (0–0.2 m) due to the flow impedance and large partition coefficient to soil water, making it readily available to volatilization into the atmosphere. Similar water content distributions were reported in the literature (8). Soil water content was also important to MeBr fate and transport because increasing water content would increase the resistance to MeBr vapor diffusion, enhance its degradation by hydrolysis, and increase the residence time for degradation by soil organic materials.

Soil bulk density is a very important parameter in converting the measured soil bromide ion concentrations to the degraded MeBr mass. The bulk density of this soil was very low near the surface (1.17 g cm<sup>-3</sup>), increased about linearly to 1.50 g cm<sup>-3</sup> at 0.2 m depth, and remained in a narrow range (1.44–1.61 g cm<sup>-3</sup>) to 1 m (Figure 3). Near the injection depth (0.15 m), the bulk density was at 1.31 g cm<sup>-3</sup>.

**MeBr Degradation and Potential Emission.** Bromide ion concentrations in the soil profile decreased from a maximum value at the surface to a value as low as the background concentrations at about 1 m when the beds were covered with either a HDPE or the Hytibar film (Figure 4). Consistent with the soil water content distribution, the reduction in bromide ion concentrations mostly occurred from soil surface to about 0.5 m where the relatively high water content layer might have inhibited MeBr movement to lower depths. The large bromide ion concentrations near the surface may have been attributed to a concurrence of high MeBr gas concentrations under the films or in the surface soil (injection depth = 0.15 m), high soil temperatures near the surface, and large water and soil organic matter contents that could have accelerated MeBr degradation. Soil bromide

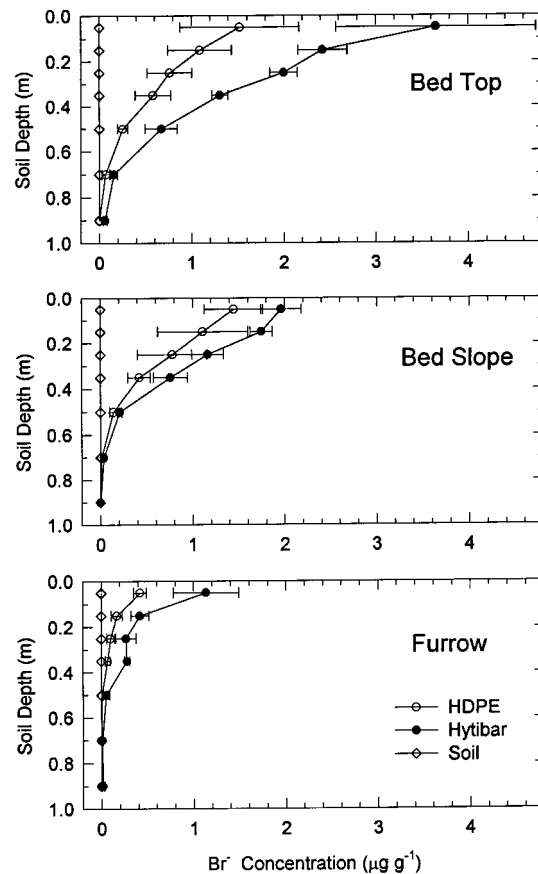


FIGURE 4. Soil bromide ion (Br<sup>-</sup>) concentration distribution under polyethylene (HDPE) or Hytibar film cover at different sampling locations of the field beds. Error bars =  $\pm$ SE ( $n = 4$ ).

concentrations were consistently higher in the Hytibar-covered plots than in the HDPE plots either directly under the bed top, under the bed slope, or under the furrow. This may indicate that, even with only a partial cover, the Hytibar film was relatively more effective in reducing MeBr emission than the HDPE film, hence keeping more MeBr in the soil and increasing degradation. The magnitude of the bromide ion concentrations for the Hytibar plots was about twice of that for the HDPE plots at either the bed top location (i.e., 3.6  $\mu$ g g<sup>-1</sup> for the Hytibar and 1.5  $\mu$ g g<sup>-1</sup> for the HDPE plots at 0 to 0.1 m) or the furrow location (1.1  $\mu$ g g<sup>-1</sup> for the Hytibar and 0.4  $\mu$ g g<sup>-1</sup> for the HDPE plots). At the bed slope, the differences in bromide concentrations between the two plastic films were not as large as for the bed top or furrow. This may be attributed to soil water regimes at the bed slopes where bi-directional water redistribution may homogenize some of the film effect. Consistent with the gas diffusion theory, the bed top location had more MeBr degradation than the slope or the furrow location because MeBr was applied directly below the bed top. The furrow location had the least MeBr degradation because (i) it was the farthest from the source and (ii) the furrow surface was not covered with the films, thus MeBr gas would be readily lost to atmosphere making it unavailable for soil degradation. The background bromide concentrations were very low and generally below the ICs detection limit (<0.1  $\mu$ g g<sup>-1</sup>). Therefore, there is less interference with bromide ion measurement after MeBr degradation, and concentration differences from the background would only be derived from MeBr degradation. It is also clear that taking soil core samples to 1 m depth was sufficient for the bedded field conditions because the bromide concentrations at 1 m were at or very close to that of the background soil (Figure 4).

**TABLE 1. Methyl Bromide Degradation and Potential Emission under Different Surface Cover Regimes**

variable	partial cover		full cover <sup>a</sup>		
	polyethylene	Hytibar	polyethylene	Hytibar	Hytibar
application rate (g m <sup>-2</sup> )	11.2	11.2	28.0	14.0	14.0
cover duration (day)	6	6	5	5	10
degradation rate <sup>b</sup> (g m <sup>-2</sup> )	0.6 (0.2)	1.2 (0.1)	7.6 (0.9)	8.5 (1.0)	13.3 (1.5)
degradation fraction <sup>b</sup> (%)	5.2 (1.7)	10.4 (1.3)	27.2 (3.1)	61.2 (7.3)	95.4 (11.0)
potential emission (%)	94.8	89.6	72.8	38.8	4.6

<sup>a</sup> Data from Wang et al. (9). <sup>b</sup> Values in parentheses are standard errors; n = 12 for partial cover, n = 9 for full cover.

Converting the measured bromide concentrations to masses, the amount of degraded MeBr was 0.6 and 1.2 g m<sup>-2</sup> for the HDPE or Hytibar plots, respectively (Table 1). The fraction of total degradation was only 5.2% for the HDPE treatment and 10.4% for the Hytibar plots, compared to the application rate of 11.2 g m<sup>-2</sup>. Because emission into the atmosphere and degradation into bromide ions are the only two pathways responsible for MeBr disappearance from the soil, the difference between the amount of application and that of degradation would potentially be lost to atmospheric emission. Therefore, the potential emission from this bedded system was about 95% for the HDPE and 90% for the Hytibar-covered plots, which is even higher than the 89% emission reported for bare soil conditions (5). Regardless of the small improvement with the virtually impermeable film, the experiment clearly indicates that covering the field only partially with either the HDPE or the Hytibar film would result in emission losses much higher than that of covering the field completely with the HDPE films. As indicated by Wang et al. (9), the virtually impermeable film was effective only when the field was covered completely and continuously for at least 10 days, when the total emission was reduced to only 4.6% of the total amount applied (Table 1). This is to allow sufficient time for soil degradation to deplete the applied MeBr, and this 10 day duration may vary according to the local soil conditions, especially the organic matter content. Covering the field for 5 days with the Hytibar film did not significantly reduce the emission loss since a large emission flux occurred at the time of film removal (Table 1). In the case of partially covering the field, the amount of emission may remain unacceptably high even with an extended cover duration with the virtually impermeable film. To significantly reduce MeBr emission, a complete cover with a virtually impermeable film such as the Hytibar for at least 10 days is strongly recommended.

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