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Methyl Bromide Emissions from Agricultural Fields: Bare-Soil, Deep Injection

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The environmental fate and transport of methyl bromide (MeBr) in an agricultural field after deep injection (66 cm) is described and compared to a recent experiment where MeBr was injected at a shallow (25 cm) depth, and the surface was covered with high-density polyethylene plastic. Three independent methods were used to estimate the total MeBr lost after application, i.e., the appearance of soil Br-, the flux chamber, and micrometeorological methods. Peak MeBr volatilization rates occurred during the first 24 h, but relatively high rates continued for more than 7 days after application. Diurnally, the largest volatilization rates occurred from midnight to early morning during periods of decreasing barometric pressure, and the volatilization rate decreased when the barometric pressure was increasing. Due to deep injection, coolertemperatures, and smallerthermal gradients, the total MeBr mass emitted from the field was significantly less than a previous experiment. The total emissions estimate obtained from the Br- data was 239 kg or 21%. The estimates obtained from the direct flux measurements were found to range from 1.9% to 4.9%. The percent mass recovery ranged from 81% to 84% of the applied mass, with an average value of 82%. The discrepancy between Br- and direct flux measurements was attributed to losses from the shank fracture during or immediately after injection. It is importantto understand how deep injection affects MeBr emissions so that the total fumigant loss from agricultural fields can be minimized.

Introduction

There is concern that methyl bromide (CH_3Br, MeBr) and other halogenated gases emitted into the atmosphere are destroying the stratospheric ozone layer (1). Although 90-95% of the ozone loss is thought to be from chlorinated compounds (2), attention has been focused more recently on MeBr, because bromine is believed to be 40 times more efficient in breaking down stratospheric ozone on a per atom basis. As a result of the U.S. Clean Air Act, MeBr is scheduled for phase-outbytheyear2001. MeBr is also one oftheprimary fumigants used to control nematodes, weeds, and fungi in an important segment of agricultural production (3). A conservative economic assessment of the impact from an elimination of MeBr (4) demonstrates that there will be large annual **monetary losses** to the agricultural community. These annual losses will have pronounced effects in California and Florida, which are primary users of MeBr (4), and a partial list includes the following: tomatoes ($350 million), ornamentals ($170million), tobacco ($130 million), peppers ($130 million), strawberries ($110 million), and forest seedlings ($35 million).

This has caused considerable interest in estimating various natural and anthropogenic sources of MeBr. For example, recent estimates indicate that 50-80% of the bromine gas is produced naturally by marine plankton while agricultural fumigation contributes between 15 and 35% (2). Biomass burning may contribute up to 30% (5) to the global burden, and there have been suggestions that the oceans may act as a net sink for bromine gases (6). Deposition onto soil together with microbial degradation may be another important pathway for removing MeBr from the atmosphere (7). Much additional information is needed to reduce the uncertainty of these estimates. It is important to accurately determine the amount of MeBr released into the atmosphere from agricultural use since the current estimates are large (i.e., 15-35%). Furthermore, if the agricultural contribution is actually much smaller, then a phase-out of MeBr will have little effect on ozone depletion since bromine gases will continue to exist in the atmosphere due to natural and non-agricultural sources. For this scenario, the agricultural community needlessly suffers an economic loss. Therefore, it is important to (1) determine the fraction emitted into the atmosphere to reduce the uncertainty and (2) develop improved methods for reducing emissions of any fumigant to the atmosphere, thereby minimizing negative environmental effects.

There have been several recent experiments conducted to obtain information on MeBr emissions from typical agricultural operations. These studies use various methods for estimating the total emission and include the appearance of Br- in fumigated soils (8), micrometeorological flux (9, 10) and enclosed-chamber (11-13) methods. Each method has advantages and disadvantages that can make comparisons between experiments somewhat difficult. The Br- appearance method assumes that the difference between the mass applied and mass degraded (i.e., Br- production) was released into the atmosphere. An advantage is the ease in analyzing the Br- content of soils. A disadvantage is the large number of soil cores necessary to obtain an accurate field-scale estimate of degradation at all depths (8). Meteorological flux methods (9, 10) are fairly complex, require numerous measurements of MeBr concentration and other meteorological parameters, and may require assumptions concerning the behavior of the atmosphere. These methods are reasonably well tested, provide a field-scale average total emission rate, and provide information on the dynamics of the volatilization process. The flux-chamber method (11-13) is one of the simplest methods for measuring pesticide flux, but it suffers from several disadvantages. The flux is only measured over a small area, causing the estimated flux rate to be highly variable; the flux estimates are sensitive to the placement of the chambers relative to the position where MeBr is injected (i.e., closeness to the source); and the chamber can affect the area sampled, especially the local temperature and relative humidity. These factors can have a tremendous effect on experimental uncertainty (13).

Yagi et al. (II) conducted an experiment to measure the MeBr emission from a southern California field using passive chambers. MeBr was applied at a depth of approximately 25 cm, and the soil surface was covered with polyethylene plastic. The authors obtained 14 estimates of the volatilization rate during the 7-day period and estimated that 87% of the total MeBr applied to the field escaped into the atmosphere. Yagi et al. (12) conducted a second experiment using similar procedures and found that only 34% escaped.

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In a study on strawberries, Majewski et al. (9) obtained estimates of the volatilization rate over a 10-day period and found that 32% of the applied MeBr was emitted into the atmosphere during the first 6 days following application. This value is approximately the same as Yagi et al. (12). The MeBr application rate for this experiment was 392 kg/ha, and the flux density was measured using the aerodynamic method. The reported loss rate fell into the 30-60% range noted in the Montreal protocol, but a mass balance was not conducted.

Yates et al. (8,10,13) (hence termed the "first experiment") conducted an experiment on a 4-ha field where MeBr was applied at a 0.25 m depth, at a rate of 240 kg/ha, and the field was covered with high-density polyethylene plastic. Several independent measurements of the total emission were obtained. From 1872 samples of Br- concentration collected in the field, the total loss from volatilization was estimated to be 61% (±19%). Using the aerodynamic method, 164 volatilization measurements were used to estimate that from 62% (± 11%) to 67% (±6%) of the applied mass was lost to the atmosphere. For the theoretical profile shape and integrated horizontal flux methods, respectively, the estimated total emissions were 61% (±3%) and 70% (±3%). Using flow-through fluxchambers and correcting for temperature effects, the total mass lost from the field was estimated to be 59% (±21%). The average mass recovery using these methods was 867 kg (±83 kg), which was 103% (±10%) of the applied mass (i.e., 843 kg). The range in the mass balance percent (i.e., percent of applied mass that is measured) was in the range 97-108%.

This paper reports MeBr emissions from afield experiment where the fumigant was injected relatively deep and the soil surface remained uncovered. Deep injection is one of the proposed methods for reducing fumigant emission into the atmosphere (14). To date, there have been no comprehensive studies, conducted under typical field conditions, to obtain MeBr emissions rates after injecting deep into soils. The results from this study, therefore, offer important new information that can be used to improve pesticide management and reduce atmospheric emissions.

Experimental Section

Design. The experiment was conducted on an 8-ha field located in the eastern portion of a University of California field station located in Moreno Valley, CA, between May 17 (day 0) and June 13, 1994. The soil type in this field is Greenfield sandy loam and is classified as a coarse-loamy, mixed, thermic, Typic Haploxeralf. With the few exceptions that follow, the field preparation and experimental procedures were similar to those reported in the first experiment (8), which was conducted in an adjacent field.

MeBr was applied to approximately 3.5 ha at the western end of the field using a "track-laying" tractor carrying two shanks that were spaced approximately 1.68 m apart. To improve the sealing of the soil surface and to remove any fractures caused by the shanks, a second tractor followed approximately 5 min behind the injection rig which disced the upper 15 cm of soil and packed the surface soil using a roller packer.

The depth of injection was approximately 0.68 m. The fumigant was applied to the field as 99.5% MeBr (CH_3Br) and 0.5% chloropicrin (CCl_3NO_2) (EPA Regulation No. 8536-12-11220) beginning at 1215 h and ending at 1630 h. A total of 1134 kg of MeBr was applied to the 3.52-ha field, which yields a 322 kg/ha application rate. Since the field was not covered with plastic, much of the auxiliary sampling equipment (i.e., soil temperature, weather station, etc.) was placed at the middle of the field at a position near the eastern end of the treated area. Instruments placed in the center of the treated portion of the field include the air sampling mast and tine-wire thermocouple mast. The instruments placed inside the treated area and near the edge include the anemometer, flow-through chambers, and soil-gas sampling equipment. The entire field, both treated and nontreated areas, was prepared in the same manner prior to initiating the experiment.

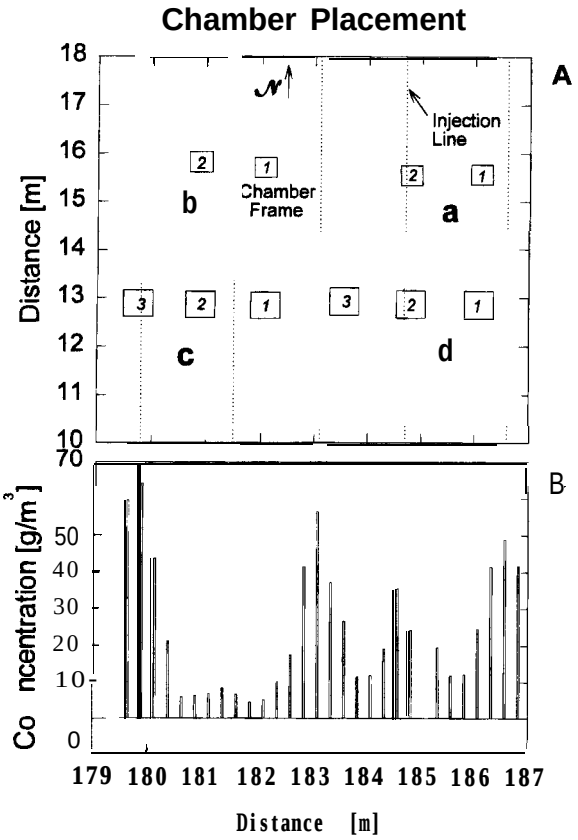

FIGURE 1. (A) Schematic of chamber sampling area. Four chambers were used, one at each location a-d. Squares with a number indicate tbe position of a chamber frame. The chambers were moved between frames after each sample was collection. Dotted lines indicate the position of injection lines. (B) Soil-gas concentration at25 cm depth along a transect near the chambers appnximately 28 h after injection. Peaks indicate the location of shank passes.

The rotating air sampling mast with flowmeters described by Yates et al. (15) was modified to hold nine charcoal sampling tubes at 0.05,0.10,0.30,0.50,0.70,1.1,1.5,2.0, and 2.6 m above the soil surface. This supplied the atmospheric concentration data required by the aerodynamic (9, 10), theoretical profile shape (10,16), and integrated horizontal flux (10,16) methods. A detailed description of the experimental procedures is given by Yates et al. (10). Four flow-through flux chambers (13) were used during this experiment to estimate the volatilization rate and were placed at various distances away from the shanks. At two sites (see sites a and b in Figure lA), a new chamber design (17) was used. The chambers were moved after each sample period between two frames set into the soil. This was done to minimize the effects on the local microclimate caused by the presence of the chamber. At sites c and d, two chambers used by Yates et al. (13) were used. During the first 11 sampling intervals, the chambers were moved among the three frames. Afterwards, to facilitate comparison between the new and old style chambers, the chambers were kept in the same relative position (i.e., positions 3 at locations c and d were no longer used). The position of the injection points relative to the flux chambers were obtained 28 h after injection by sampling the soil-gas concentration along a transect perpendicular to the injection lines (Figure 1B).

Results and Discussion

Weather Conditions. The weather conditions were variable throughout the experiment with predominantly cool and

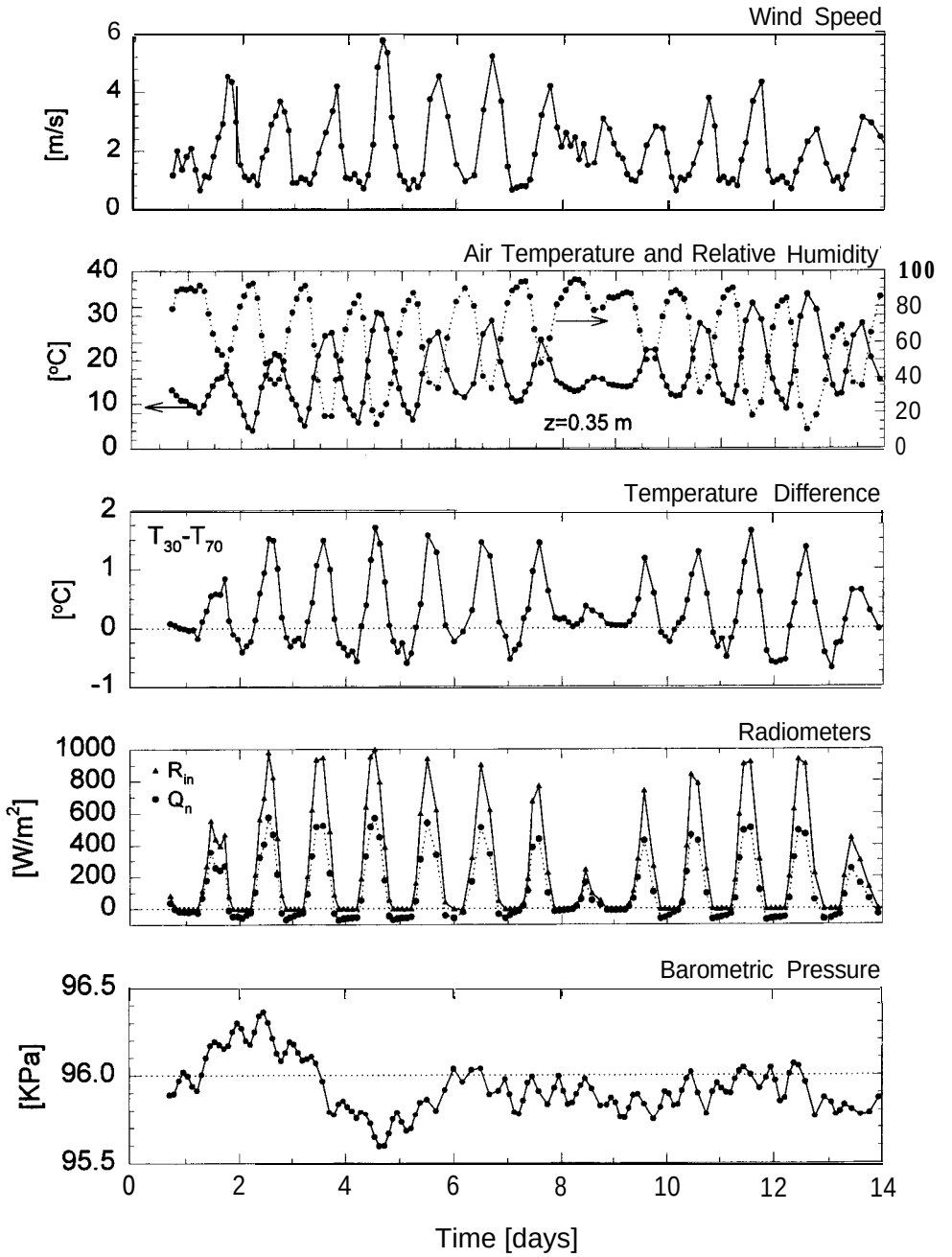

FIGURE 2 Weather data during the first 14 days of the experiment.

cloudy weather occurring during the first 36 h and again on the 8th and 13th days (see Figure 2). During the experiment there were periods of slight precipitation. On day 0 (i.e., May 17) and day 2, respectively, there was 3 and 2 mm of rainfall but no measurable precipitation on the 8th and **13th days. Otherwise, the temperatures were warm, and the sky was relatively** clear. The variable weather is demonstrated in the meteorological data shown in Figure 2, which includes the wind speed, air temperature, relative humidity, air temperature difference between the 0.30 and 0.70 m heights, the incoming radiation, R_{in}, net radiation, Q_n, and the barometric pressure. These data were collected at 5-min intervals throughout the experiment, and the solid dots and triangles indicate the average value when the averaging period coincides with the mast air sampling intervals. The integer values on the abscissa indicate midnight; the day of application is day 0. During the first day there were slight winds, low temperatures, high relative humidity, low incoming radiation (i.e., cloud cover), and an increasing barometric pressure. The highest barometric pressure occurred from approximately noon of day 1 until noon of day 3. This was followed by a trend of lowering pressure and then a relatively constant pressure until the end of the experiment. A maximum change in barometric pressure of approximately 800 Pa occurred over about 48 h.

The weather pattern for this experiment was significantly different as compared to the first experiment. The minimum, median, mean, and maximum values for both experiments are presented in Table 1. Most notably, the first experiment was characterized by greater wind speeds, higher temperatures, and temperature gradients.

MeBr Concentration in Air. Shown in Figure 3 is the air concentration at a height of 0.5 m above the soil surface for the first experiments (dotted lines, open circles) and the current experiment (solid lines and filled circles). At early time, the air concentration during the first experiment was 20 times greater than was encountered during this experiment and indicates potentially greater exposure to persons in or around the field. Also, the reduction in the air concentration as a function of time was much greater during the first

TABLE 1. Comparison of Experimental Conditions Between First and Second Experiment

condition	this experiment				first experiment			
	min	median	mean	max	min	median	mean	max
wind speed (m/s)	0.63	1.54	1.94	5.79	0.49	1.99	2.47	6.32
air temperature (°C)	4.0	14.6	16.6	34.8	13.0	26.2	26.0	39.7
relative humidity (%)	10.6	73.8	65.6	95.2	14.4	46.0	49.8	95.5
air temperature difference: (°C)	-0.69	0.08	0.22	1.70	-0.64	0.43	0.81	2.84
incoming radiation (W/m^2)	0	52.1	230	994	0	278	329	926
net radiation (W/m^2)	-74	11.2	102	575	-70	59	120	502
barometric pressure (KPa)	955.9	959.0	959.2	963.6	956.0	959.2	959.5	964.7

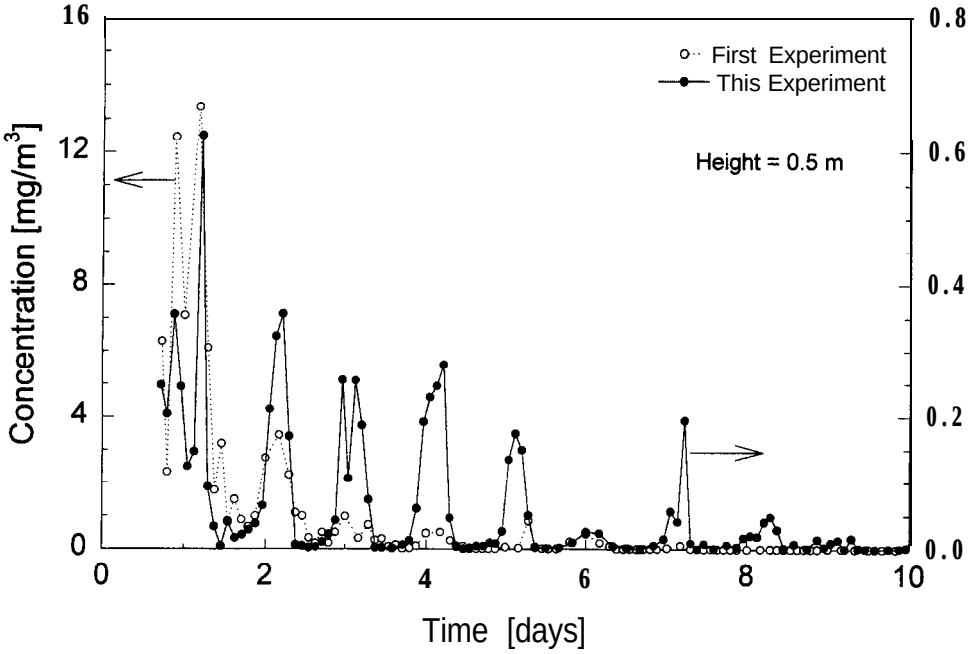

FIGURE 3. Comparison of the MeBr concentration in the air at 0.5 m above the soil surface during the first (dotted line) and this (solid line) experiments. The dotted line corresponds to the left axis. The solid line corresponds to the right axis.

experiment, indicating rapid loss of chemical from the soil. Noting that different axis scales are used to plot the concentration from each experiment, it can be shown that sometime between the fourth and fifth day the air concentrations were approximately the same in both experiments. For this experiment, the maximum concentration at 0.5 m above the soil surface was 0.625 mg/m^3 and occurred approximately 12 h after application. For the first experiment with a shallow injection depth, there were two periods with peak concentrations between 12.4 and 13.4 mg/m^3; the first occurring approximately 4 h after application. Therefore, the depth of application has a delaying effect on the peak air concentration. This has also been observed in laboratory studies (18).

Soil-Gas Concentration near the Flux Chambers. Although the distance between injection points should be spaced 1.68 m apart, throughout the field, the actual placement depends on many factors (i.e., tractor turning radius, positional drift, etc.). To more accurately determine the position of the injection points relative to the flux chambers, a series of soil-gas concentrations at the 25 cm depth were taken along a transect beginning 179 m from the west edge of the treated field. This is shown in Figure 1B where the soil-gas concentration at specified distances from the west edge of the field is presented. Using the locations where the concentration is maximum and noting that the distance between peaks should be approximately 1.6-1.7 m, the position of the shanks can be located. These are shown in Figure 1A as dotted lines. It is interesting to note that, at one of the locations where apeakconcentrationwas expected (i.e., ≈181.3 m), there was only a small increase in the concentration. This may be due to gas venting to the atmosphere during or immediately after injection; plugging of an injector, or a localized phenomenon where the gas did not diffuse as readily as other locations, and the placement of the soil-gas sampling equipment happened to miss the peak.

Flux Measurements. (A) Flux Chambers. The chamber frame locations, shown as squares in Figure 1A, were obtained using a theodolite and should be accurate to within 0.01 m. Since the chambers were moved between frames, their position relative to the injection point changes depending on the sampling interval. In terms of measuring the field-scale average volatilization rate, a fairly representative sample of over-the-injection point and between-the-injection point was obtained. However, when determining the variability of the measured flux rates, the positional effects should be included. With the exception of a few points, the variability between chambers was calculated only using chambers that were positioned similarly with respect to the injection points.

The average volatilization rate as a function of time is shown in Figure 4A. The error bars are reported for every 4th value to enhance legibility. The large error bar on the 3rd data point in Figure 4A is due to the chambers being placed at various distances (i.e., misaligned) from the injection point during this time interval. For the 5th and 6th sample intervals, and all the sample intervals after number 10, chambers a&d and b&c were aligned, reducing the deviation between the measured flux values and resulting in lower variability. The peak flux rate estimated from the chambers, with the exception of one value of 19 $\mu g\, m^{-2} s^{-1}$, was less than 10 $\mu g\, m^{-2} s^{-1}$. The estimate of the total MeBr lost from the field

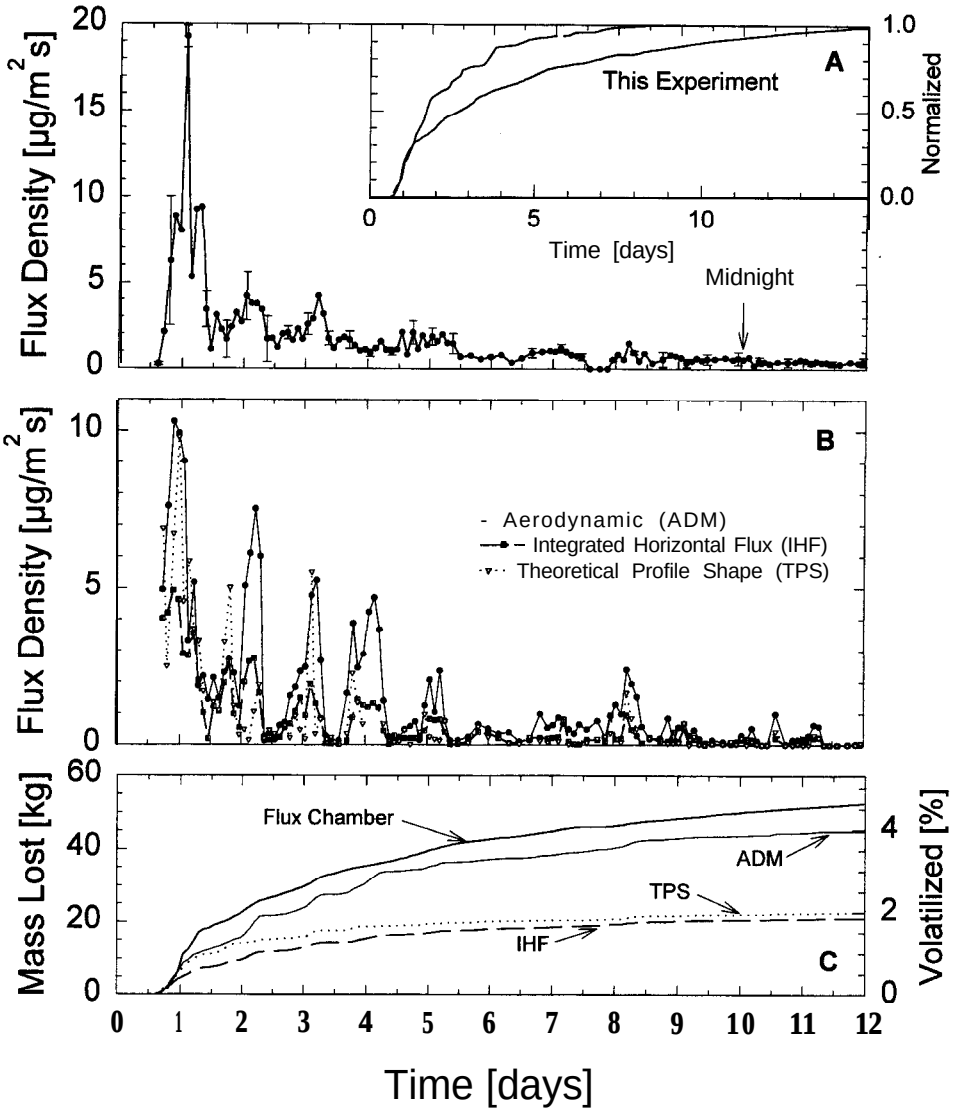

FIGURE 4. Volatilization rata and mass lost during the first 12 days of the experiment. (A) Volatilization rate estimated from four flow-through flux chambers where the error bars indicate the variation between chambers and the insert is the normalized loss rate: (period volatilization loss/total volatilization loss). (B) Volatilization rate estimated from the aerodynamic (solid line; filled circle), the theoretical profile shape (dotted line; open triangle), and the integrated horizontal flux (dashed line; open box) methods. (C) Cumulative mass lost from the field.

was 56 (± 35) kg or 4.9 (± 3)%. The daily percentage of the total amount lost due to volatilization (i.e., 56 kg) after 24,48, 72,120, and 240 h after application, respectively, was 35,49, 61,75, and 91%. This is different from the Erst experiment where after 24, 48, and 120 h, respectively, 39, 67 and 93% of the total 496 kg was lost. This is shown graphically in the inset to Figure 4A where the fractional loss is nearly the same for each experiment during the first 24 h but differs significantly afterwards.

(B) **Micrometeorological Flux** Measurements. An independent measurement of the volatilization rate is obtained from the aerodynamic, theoretical profile shape, and integrated horizontal flux methods. These values use supporting data that are independent of the flux chamber method.

Shown in Figure 4B are three curves of the MeBr volatilization rate that results from the micrometeorological methods. The solid, dashed, and dotted lines, respectively, indicate the result from the aerodynamic, integrated horizontal flux, and theoretical profile shape methods. For the aerodynamic and integrated horizontal flux methods, the lines represent the average volatilization rate as a function of time when several procedures are used for estimating the flux rate. Several methods for combining the data to produce volatilization rates offer additional statistical information on the average behavior of the volatilization rate, reduce the effect of errors or deviations in the basic data, and enable aberrant behavior from any particular combination of data used to estimate the volatilization rate to be more easily identified.

To use the aerodynamic method, concentration and wind speed gradients were obtained both discretely and using the slope of logarithmic profiles that were fitted to the experimental data (10). Using various combinations of these data, a total of seven values of the volatilization rate was obtained for each sample interval. For the integrated horizontal flux method, seven volatilization rates were obtained for each sampling interval; two using a discrete approximation to the integral and five using combinations of the fitted logarithmic profiles to the air concentration and wind speed. A complete description of these procedures is given by Yates et al. (10).

The theoretical profile shape method requires a measurement of the air velocity and air concentration at a specific height in the atmosphere (16). The flux density depends on the surface roughness, which was estimated to be 0.3 cm, and the upwind fetch distance, which varied from 88 to 157 m during this experiment. For this experiment, the instrument height varied between 2.3 and 3.2 m, and the ratio of the horizontal to vertical flux (10,16), **Ω,** varied from 10.9 to 11.9. Due to the low MeBr concentration in the air at the

TABLE 2. Total Amount of MeBr Volatilized during the Experiment and Mass Balance

flux method used	no. of values	mess lost from volatilization (kg)	% lost from volatilization (%)	measured – applied mass* (kg)	mess balance* (%)
aerodynamic, discrete method	5	52 (±15)[b]	4.5 (f1.3)	188	83
aerodynamic, profile method	2	35 (± 1)	3.1 (fO.l)	204	82
theoretical profile shape	1	22.8	2.0	217	81
integrated horizontal flux	7	21 (± 2)	1.9 (f0.2)	218	81
flux chamber	4	58 (±35)	4.9 (f3.1)	184	84
soil Br- sampling	2098	239 (±30)[c]	21 (±2.6)[c]		
average[d]		38 (±24)	3.4 (±2)	201	82

* Mass applied, 1134 kg; measured mass remaining, 16 kg; measured mass degraded, 879 kg [standard error: 102 kg). [b] Values in parentheses are standard deviations. [c] Values in parentheses are standard error obtained from Br- data. [d] Excludes estimate using soil Br- sampling.

instrument height, only one estimate of the volatilization rate for each sampling interval could be obtained using this method.

From Figure 4B, all three meteorological approaches produced flux rates less than 11 $\mu g\,m^{-2}\,s^{-1}$. Shown in Figure 4C is the MeBr mass lost from the field during the experiment. It is also shown that the total loss estimated from these methods is in the range of 2-5% of the applied mass. For the micrometeorological methods, the aerodynamic method produced the greatest total loss of approximately 4% and the integrated horizontal flux method produced the least at 1.9%.

The diurnal behavior of the volatilization rate is very different from that reported by Yates et al. (10) where a large peak was reported during the first 24 h, which rapidly diminished thereafter. During this experiment, the peak volatilization rates tended to occur between 0 and 0400 h each day and continued for as many as 10 days. The changes in the volatilization rate tended to follow the changes in the barometric pressure; when the barometric pressure was increasing, the volatilization generally decreased. This has been suggested to be an important process (19). Relatively large peaks continue past 7 days after application, which is also different from the first experiment. By the 12th day, the volatilization rate had reduced to very low levels. This indicates that applying MeBr deeper into soils can be used to minimize the peak volatilization rate, increase the soil residence time, andtherebyreduce totalemissions. The early-time peak is considered to be a principal factor for the large application rates necessary to provide adequate pest control; minimizing this early-time loss should offer a means for reducing application rates.

Another significant difference is the magnitude of the volatilization rate, which was much lower at early times as compared to those reported by Yates et al. (10,13). During the first study, high rates occurred during the first sampling period after injection, whereas in this study, the peak occurred after approximately 12 h, during the sixth sampling period. During the hot and dry conditions in the first experiment, maximum flux values of 120 (flux chamber) and 260 $\mu g\,m^{-2}\,s^{-1}$ (aerodynamic method) were observed which are 6-26 times greater than the 19 (flux chamber) to 10 $\mu g\,m^{-2}\,s^{-1}$ (aerodynamic method) reported here. This is due principally to the reduced gradients near the soil surface resulting from the deeper injection, cooler temperatures, and a reduction in the permeability at the soil surface caused by the soil packing and rainfall. This has been confirmed in a laboratory study (18) where the effect of injection depth was studied under ideal conditions. It was found that increasing the injection depth caused a significant lowering of the surface flux, a delay in the peak flux, and smaller gradients at the surface. The effect of water additions at the soil surface have been suggested as a means for reducing the volatilization rate (14, 20). This has been demonstrated in a laboratory study (21) where a layer of plastic combined with incremental additions of 4 mm of water increased containment of the MeBr over the experimental time frame. Soil packing has also been shown to reduce the flux rate (22). These results suggest that shallow injection with a plastic-covered surface under hot conditions is not as effective in containing MeBr as deep injection under cool and wet conditions.

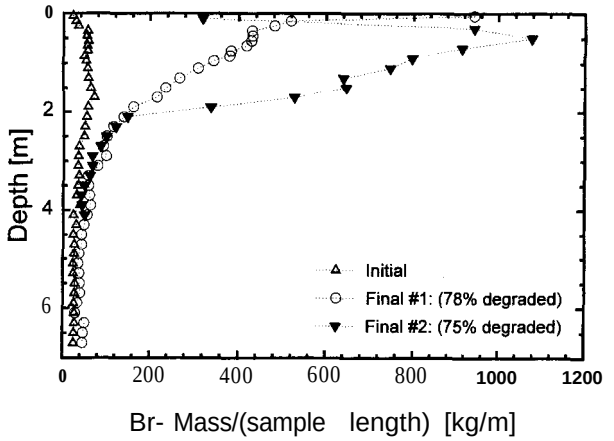

FIGURE 5. Soil Br- concentration before (open triangles), 3 months after (open circles), and 6 months after injection (closed triangles). The concentration is reported as mass per sample-core length to facilitate comparison between the 10 cm cores (final no. 1) and the 20 cm cores (final no. 2) in the upper 1 m of soil.

Mass Balance. Table 2 contains the mass balance information for this experiment. All the direct measurements of flux, i.e., chamber, aerodynamic, integrated horizontal flux, and theoretical profile shape methods, produced values for the total MeBr lost to the atmosphere between 2 and 5%. Since these measurements are in agreement, and sampling continued without break for 22 days, it is unlikely that the sampling procedure missed any significant MeBr once the equipment was in place.

Soil sampling for Br- production, however, tells a different story. When the Br- was measured before and 3 months after the experiment, only approximately 78% of the amount applied was detected as Br- with approxlmately 1% of the original MeBr remaining in the soil. The Br- concentration in the soil 3 months after application is shown as open circles in Figure 5. The open triangles indicate the initial Br- concentration. The mass is reported as mass per unit length of sample to facilitate comparison with a second sampling 6 months after application, which is shown as closed triangles in Figure 5. The second sampling was conducted to verify the accuracy of the amount degraded and was found to be within 3% of the first sampling. This was done because Jury (23) demonstrated that field-scale Br- concentration measurements can be highly variable, and we wanted further evidence that the field-scale Br- concentration was accurate. The nearly equivalent values for the total mass degraded from each sampling indicate that sufficient samples were collected to obtain an accurate field-scale average.

This independent measure of the total volatilization (i.e., 21%) differs from the direct measurement reported above,

and there are at least three possible explanations: (1) the reported mass applied to the field was in error; (2) a systematic error occurred during handling or laboratory analysis that caused the MeBr concentration to be underestimated; or (3) some process occurred that was not measured which allowed MeBr to bypass normal detection. The first possibility is unlikely since the applicators rechecked their figures and no errors were found. The second possibility is also unlikely since the methods for handling and analysis have been extensively developed and tested (24, 25), and the same sampling and analysis procedures have been used for other laboratory and field experiments that have had good mass balances. Furthermore, a systematic underestimation of the air concentration would directly affect the estimated volatilization rate from every method except the aerodynamic method. Since the flux is **estimated** from measured gradients (i.e., differences), a systematic error affecting both values of the concentration would not affect the estimate of the gradients and, therefore, the volatilization rate. Because the aerodynamic method produced similar volatilization rates as the other methods, it is unlikely that a systematic error caused the discrepancy. This suggests that some other process or mechanism was operating.

It can be speculated that these losses occurred during the 4-h MeBr application process, before the sampling instruments were installed in the field, by a process of advective gas transport through the shank fractures. Compared to shallow broadcast injection utilizing 11 injection nozzles (8), only two shanks are used when MeBr is applied deep into soil, each with a single nozzle. The application rate for deep injection (322 kg/ha) is 34% greater than for shallow application (240 kg/ha) and, together with only two nozzles, would produce a much greater pressure at the **injection** point as compared to shallow broadcast applications. For example, the mass exiting a nozzle during deep injection was 7.4 times greater than during shallow injection. Further, since the soil is not immediately covered by plastic, there is a low-resistance pathway between the MeBr source and the atmosphere. The phase change from liquid MeBr (0.055 L/mol) to the gas phase (23 L/mol, at boiling point) would cause a large increase in volume and associated pressure gradients near the source. This would enable MeBr gas to move quickly through the soil cavities caused by the shanks passing through the soil. After 5 min elapsed, the second tractor disced the upper 15 cm of soil and packed the soil surface. If any MeBr gas had moved into the upper 15 cm of soil, it would have been released to the atmosphere during the discing operation. Unfortunately, it would be difficult, if not impossible, to quantitatively measure these types of losses since they would be highly localized and transient in nature. Even if the amount exiting the fracture could be determined, some suitable methodology would be needed to integrate this local effect over the entire field.

The great variation among **recent** experiments measuring the total volatilization of MeBr from fields imply that many factors, including those related to application methods as well as to soil and climatic conditions, together influence MeBr transport and transformation in the soil-water-air system and hence its ultimate volatilization loss from the soil surface. In recent laboratory studies, it was found that injection depth, use of plastic films, water content, and bulk density have pronounced effect on MeBr volatilization after injection into soil (22). In the field, additional processes such as the effects of temperature and barometric pressure may be important.

From comparison of these experiments and others reported in the literature (9,12), the following conclusions can be drawn. The tarp helps to contain the MeBr gas in soil at early times and should be used even for deep injection to offer resistance to direct movement along soil fractures. The effect of injection depth and environmental conditions is important. To minimize volatilization, MeBr should be applied during periods of cool temperatures, relatively deep in moist soil (especially at the surface) under tarped conditions, and the soil surface packed immediately after the application. Injecting MeBr during periods of warm temperature at a shallow depth in dry, loose soil will likely result in higher volatilization rates and, therefore, should be discouraged.

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