

## Aerodynamic Measurements of Methyl Bromide Volatilization from Tarped and Nontarped Fields

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### ABSTRACT

Methyl bromide (MeBr) is used extensively in agriculture as a soil fumigant and there is growing concern over the role it may play in the depletion of stratospheric ozone. Methyl bromide is applied using various techniques and very little is known about how much of the applied fumigant volatilizes into the atmosphere after the application. This field study was designed to estimate the post-application methyl bromide volatilization loss rates from two different application practices. The fields were approximately 6 km apart in Monterey County, California, and were treated in conformity with local practices as of 1992. The MeBr was injected at a depth of 25 to 30 cm. One field was covered simultaneously with a high-barrier plastic film tarp during the application, and the other was left uncovered, but the furrows made by the injection shanks were bedded over. Volatilization fluxes were estimated using an aerodynamic-gradient technique immediately following the completion of the application process and continued for 9 d for the tarped field and 6 d for the nontarped field. The cumulative volatilization losses from the tarped field were 22% of the nominal application within the first 5 d of the experiment and about 32% of the nominal application within 9 d including the one day after the tarp was removed on Day 8 after application. In contrast, the nontarped field lost 89% of the nominal application by volatilization in 5 d. The volatilization rate from the tarped field was shown to be significantly lower than the nontarped field at a 95% confidence level.

IN RECENT YEARS, there has been growing concern over the role MeBr may play in stratospheric ozone depletion. This concern is based on the fact that bromine, one source of which is the photochemical conversion of MeBr, has been shown to play a definite role in the depletion of stratospheric ozone (Wofsy et al., 1975; Solomon et al., 1992) and in particular in the chemistry of the polar ozone hole (Mellouki et al., 1993). Furthermore, it has been shown that bromine, on a per molecule basis, is 30 to 100 times more efficient than chlorine as an ozone depleter (Wofsy et al., 1975; Prather et al., 1984; Pyle et al., 1991; Albritton and Watson, 1992; Solomon et al., 1992). Because of this, MeBr has recently been categorized as a Class 1 ozone-depleting chemical by the U.S. Environmental Protection Agency. The United Nations Environmental Program and Montreal

Protocol (1992), in a similar move, also recommended listing MeBr as an ozone-depleting chemical and called for a 25% reduction in its worldwide use by the Year 2000.

Part of the concern over MeBr in the atmosphere results from uncertainties in identifying and ranking natural and anthropogenic sources, as well as natural sinks, in determining the total global budget of MeBr and its lifetime in the atmosphere. Furthermore, the goal of identifying important anthropogenic sources is to prescribe ways to decrease these sources, and thus the overall MeBr burden to the atmosphere. Recent studies have concluded that, of the possible natural sources, the marine environment may be a major contributor to the atmosphere of bromoalkanes, including MeBr (Sturges et al., 1992, 1993; Methyl Bromide Global Coalition, 1993). This contribution of MeBr to the atmosphere may be as much as 40 to 50 million kg per year worldwide, even though both production and removal processes are operating simultaneously in the oceans (The United Nations Environmental Program and Montreal Protocol, 1992). The oceans are also an important sink (Butler, 1994), and have been found to be supersaturated with methyl bromide (Singh et al., 1983; Khalal et al., 1993; Butler, 1994). A reduction in anthropogenic methyl bromide emissions into the atmosphere will not result in an immediate decrease in methyl bromide concentrations because of the buffering capacity of the oceans.

Important anthropogenic sources of MeBr include agricultural uses (Maw and Kempton, 1973; Sturges et al., 1992), biomass burning, which occurs primarily in the southern hemisphere (Sturges et al., 1992; Manö and Andreae, 1994), and automobile exhaust emissions, although this source is declining in importance because of the increasing use of unleaded fuels (Bauman and Heumann, 1988; Sturges et al., 1992). Of these sources, agricultural use of MeBr has the greatest potential for contributing significantly to the total global burden. Use of MeBr in agriculture, as a preplant soil fumigant for the control of nematodes, soil-borne pathogens, weeds, and other biological pests, accounts for about 80% of all uses worldwide, about 63 million kg per year in 1990 (Andersen and Lee-Bapty, 1992). Furthermore, if a substantial proportion of the MeBr used per year in agriculture volatilizes (about 50 million kg based on 1990 use data), agricultural use could be comparable to the marine environment in the magnitude of its contribu-

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**Table 1.** Select soil properties for the tarped and nontarped fields.

	Tarped	Nontarped
Soil type		Salinas clay loam
Soil texture		Silty clay loam
% Sand	19	16
% Silt	46	37
% Clay	35	47
% Organic C	1.40	2.30
Bulk density, Mg m <sup>-3</sup>	1.26	1.37
pH	7.2	6.6

tion to the total global budget of MeBr (Sturges et al., 1992).

The purpose of this study was to determine the extent of MeBr volatilization by measuring its volatilization flux from fields fumigated using commercial agricultural application regimes. These data could then be used to refine the estimated contribution of agriculturally used MeBr to the total atmospheric burden and to suggest application regimes that would minimize emissions from treated soil. This paper reports the results of MeBr volatilization fluxes from a field covered with a high-barrier plastic film tarp and another that was not covered.

## METHODS

The fields were located approximately 6 km apart in Monterey County, California, and were treated in conformity with local practices as of 1992. One field was simultaneously covered with a high-barrier plastic film tarp during the application, and the other was left uncovered. Both fields were fallow with similar plow histories and were previously planted with head lettuce (*Lactuca sativa* L.). The soil type was salinas clay loam and both fields had similar moisture contents of about 16%, and similar physical characteristics (Table 1). The covered area was a 3.93 ha (approximately 174 by 226 m) fallow field (Fig. 1) surrounded by similar fallow fields. The fumigant, a 67/33% by weight MeBr/chloropicrin (CCl<sub>3</sub>NO<sub>2</sub>) mixture, was injected into the soil at a depth of 25 to 30 cm as a liquid

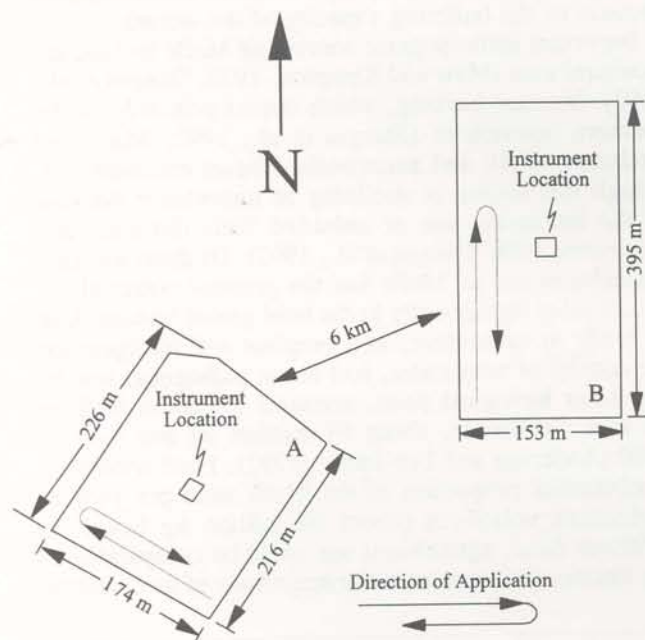
at a rate of 392 kg ha<sup>-1</sup>. A total of 1539.7 kg of fumigant was applied. The application rig used 11 shanks spaced at 30.5 cm intervals. The injection area was immediately covered with a 0.00254 cm (1 mil) thick by 3.35 m wide high-barrier plastic tarp. Each successive tarp swath slightly overlapped the previous swath, and this seam was sealed with glue and pressure. The ends of each tarp swath were covered with soil, and the entire edge of the treated area was also tarped and sealed to prevent edge leakage of the fumigant. The application was done in an east-west orientation (Fig. 1) between 0815 and 1320 h on 26 October. A reinforced path from the edge to the center of the tarped field was made by gluing several 1 m wide layers of the tarp material. This was done to prevent the tearing of the tarp and the subsequent release of MeBr during equipment setup and sample changing. On 3 November, the entire tarp was removed between 1350 and 1520 h.

The nontarped field was a 6.03 ha (approximately 153 by 395 m) fallow field surrounded by similar fallow fields. The fumigant, a 98/2% by weight MeBr/chloropicrin mixture, was injected as a liquid at a rate of 202.7 kg ha<sup>-1</sup> at a depth of 25 to 30 cm. A total of 1222.2 kg of fumigant was applied. The application rig used four shanks spaced at 1.02 m intervals and simultaneously bedded the soil over the furrow made by the injection shanks. The application was done in a north-south orientation (Fig. 1) between 0929 and 1338 h on 27 October. These applications were done several weeks after the normal fumigation period and were the only ones being done in the area that we were aware of. This timing minimized any background contamination as much as possible.

Immediately following the completion of the fumigant application, air concentration and meteorological measurement equipment was moved to the center of each field (Fig. 1). Holes in the tarp created when the instrument and sensor masts, and guy wire stakes were sunk into the soil through the tarp were sealed with duct tape, as per standard practice.

The meteorological instrumentation included measuring wind speed at six heights (20, 30, 50, 80, 125, and 200 cm) above each field with rotating cup anemometers, wind direction at 200 cm, dry and wet bulb air temperatures at 40, 75, and 140 cm, net solar radiation at 100 cm, and soil temperature at -1, -2, -5, -10, -25, and -50 cm. Meteorological measurements were recorded electronically with a data recorder and were averaged over 5-min periods.

Air concentration measurements were taken at the same heights as the wind speed measurements, but on a separate mast. Air was pulled through a primary, secondary, and backup charcoal-filled, glass sampling tube (no.226-16 SKC West, Inc., Fullerton, CA) placed in series at each height. Air flow rates (~100 mL min<sup>-1</sup>) were measured at the beginning and end of each sampling period by momentarily attaching a rotameter, via Tygon tubing, to the intake of each primary cartridge. At the end of each sampling period, each tube was tightly capped, properly labeled, and stored on dry ice for shipment to the laboratory where all the tubes were stored at -20°C until analyzed. The air above the tarped field was continuously sampled starting at 1400 h, 26 October until 1755 h, 4 November, except for 2-h breaks near midday on 28 and 29 October and 1 November. There was also a sampling break from 1300 h, 30 October, to 1315 h, 31 October, because of heavy rain. Sampling on 2 and 3 November ended at about 1900 and 2200 h, respectively, and commenced the following day at about 0600 h. The air above the nontarped field was sampled continuously starting at 1350 h, 27 October, until 1615 h, 1 November, with 2-h breaks near midday on 29, 30, and 31 October. The sampling periods for the first 24 h of both fields were about 2 h in duration and the remaining sampling periods



**Fig. 1.** Field dimensions and instrument locations for the tarped (A) and nontarped (B) fields.

Table 2. Select meteorological measurements, atmospheric stability calculations, air concentrations, and resulting volatilization flux values for each sampling period for the tarped field.

Date	Time on	Run time	Period	Air temp. at 75 cm, °C	Differential air temp., °C	Wind speed at		Air concentration at		Ri	Phi(m)	Phi(c)	Flux $\mu\text{g m}^{-2} \text{s}^{-1}$
						40 cm	140 cm	40 cm	140 cm				
													$\text{m s}^{-1}$
													$\text{ng m}^{-3}$
26 Oct.	14.00	02.00	A	18.03	-0.257	9.58	10.32	1109	431	-0.016	0.928	0.786	78
26 Oct.	16.15	02.03	B	16.51	-0.040	4.70	4.99	779	346	-0.016	0.928	0.785	20
26 Oct.	18.30	02.02	C	14.31	0.150	2.05	2.27	1899	999	0.106	1.393	1.632	10
26 Oct.	20.45	02.04	D	12.84	0.226	2.70	3.08	1268	530	0.053	1.229	1.340	19
26 Oct.	23.02	02.09	E	12.11	0.232	1.49	1.62	3327	995	0.526	2.111	2.866	5.0
27 Oct.	01.19	02.01	F	11.49	0.070	1.72	1.80	1765	726	0.353	1.880	2.468	2.0
27 Oct.	03.30	02.21	G	12.20	0.018	2.70	2.93	676	334	0.012	1.061	1.016	8.0
27 Oct.	05.58	01.57	H	12.84	0.015	3.08	3.34	1222	380	0.008	1.039	0.970	25
27 Oct.	08.20	02.00	I	13.80	-0.267	1.61	1.68	811	112	-2.217	0.302	0.185	90
27 Oct.	10.34	02.12	J	16.80	-1.116	3.24	3.41	736	349	-1.358	0.353	0.224	91
27 Oct.	13.02	03.58	A	15.27	-0.645	10.75	11.42	309	47	-0.049	0.825	0.661	36
27 Oct.	17.15	04.07	B	13.54	-0.043	4.76	5.02	413	166	-0.023	0.903	0.753	10
27 Oct.	21.36	04.00	C	13.09	0.029	3.91	4.12	468	224	0.021	1.101	1.097	5.0
28 Oct.	01.40	04.30	D	12.78	0.060	1.27	1.36	No data		0.317	1.824	2.373	6.0†
28 Oct.	06.20	04.23	E	13.49	-0.085	1.71	1.80	386	173	-0.296	0.559	0.395	11
28 Oct.	13.00	04.10	A	13.91	-0.216	2.68	2.86	219	78	-0.235	0.594	0.427	11
28 Oct.	17.30	04.12	B	12.63	0.115	1.43	1.57	577	229	0.202	1.617	2.018	2.0
28 Oct.	22.00	04.00	C	11.22	0.206	0.82	0.98	535	209	0.279	1.761	2.265	1.0
29 Oct.	02.20	04.05	D	10.87	0.310	5.31	5.80	452	116	0.043	1.191	1.270	12
29 Oct.	06.45	04.03	E	13.71	0.173	11.96	13.60	238	82	0.002	1.012	0.911	31
29 Oct.	13.00	04.00	A	17.34	-0.057	10.78	11.75	239	83	-0.002	0.989	0.870	20
29 Oct.	17.20	04.00	B	14.82	0.137	2.57	2.83	632	258	0.069	1.282	1.437	6.0
29 Oct.	21.40	04.05	C	13.42	0.191	1.64	1.88	850	290	0.118	1.424	1.687	6.0
30 Oct.	02.00	04.00	D	14.19	0.410	4.19	4.69	299	88	0.056	1.239	1.358	7.0
30 Oct.	06.20	04.00	E	15.09	0.089	4.88	5.34	270	110	0.014	1.072	1.038	7.0
30 Oct.	13.09	04.00	F	-	-	No data		No data		-	-	-	7.0†
31 Oct.	13.15	04.00	A	17.52	-0.763	6.50	8.07	337	135	-0.010	0.950	0.815	46‡
31 Oct.	17.35	03.58	B	11.71	0.239	1.05	1.50	No data		0.040	1.181	1.251	27†
31 Oct.	21.55	06.30	C	9.91	0.311	1.22	1.69	320	57	0.051	1.218	1.320	8.0‡
01 Nov.	04.35	02.10	D	8.41	0.376	1.03	1.65	398	16	0.034	1.155	1.202	19‡
01 Nov.	06.55	04.00	E	13.27	-0.987	1.95	2.28	78	37	-0.324	0.545	0.383	7.0‡
01 Nov.	13.00	04.05	A	17.93	-0.825	6.77	8.48	51	25	-0.009	0.954	0.820	6.0‡
01 Nov.	17.25	04.00	B	13.87	0.193	3.33	4.11	124	52	0.011	1.054	1.002	6.0‡
01 Nov.	21.40	04.05	C	11.00	0.369	1.11	1.70	209	58	0.037	1.167	1.225	7.0‡
02 Nov.	01.50	04.30	D	9.27	0.634	0.91	1.42	240	30	0.086	1.336	1.531	6.0‡
02 Nov.	06.40	04.00	E	14.42	-0.734	1.57	1.86	202	106	-0.289	0.562	0.398	14‡
02 Nov.	11.00	04.00	A	19.42	-1.278	9.35	9.80	56	24	-0.211	0.612	0.443	6.0
02 Nov.	15.09	03.56	B	15.34	-0.352	8.00	8.46	41	24	-0.058	0.803	0.636	2.0
03 Nov.	06.10	03.55	A	12.56	-0.506	2.14	2.23	162	59	-1.993	0.312	0.193	18
03 Nov.	10.15	03.30	B	21.43	-1.225	4.36	4.58	30	13	-0.828	0.413	0.271	4.0
03 Nov.	13.50	03.55	C	21.45	-0.073	4.98	6.10	237	153	-0.002	0.990	0.870	12
03 Nov.	17.50	04.05	D	12.64	0.884	2.19	2.87	842	241	0.064	1.265	1.405	26
04 Nov.	06.15	03.30	A	8.94	-0.182	5.08	6.23	111	38	-0.005	0.975	0.850	11
04 Nov.	09.50	04.00	B	19.99	-1.086	6.79	8.00	29	8	-0.025	0.895	0.744	4.0
04 Nov.	16.55	01.00	C	12.89	0.080	4.02	4.79	30	2	0.005	1.024	0.938	3.0

† Flux values for these periods estimated as the average of the measured fluxes for that day.

‡ Flux values for these periods estimated using wind speed data from the nontarped field.

were about 4 h in duration. The sampling periods and applicable meteorological information are given in Tables 2 and 3.

Samples were analyzed using a head-space gas chromatographic technique described by Woodrow et al. (1988), but with some important modifications. The contents of each sampling tube were emptied into separate 22-mL glass headspace vials (Perkin-Elmer, Norwalk, CT), 2.6 mL benzyl alcohol (99%; Aldrich Chemical Co., Milwaukee, WI) was added to each vial, and the vials were immediately sealed with crimped caps containing Teflon-lined silicone rubber septa (Perkin-Elmer). Each vial was thermostatically heated at 60°C for 15 min in the Model HS-100 headspace instrument (Perkin-Elmer), the internal pressure of each vial was raised to 103 kPa (gauge) with helium, and the equilibrated headspace was sampled for 0.01 min by the headspace instrument. The temperature of the HS-100 sampling needle was maintained at 100°C and the transfer line at 150°C.

The sampled headspace was analyzed using a gas chromatograph (Perkin-Elmer, Model Sigma-2000) equipped with a  $^{63}\text{Ni}$  electron-capture detector (350°C) and a 30 m  $\times$  0.32 mm (i.d.) porous layer open tubular (PLOT) column coated with a 10- $\mu\text{m}$  thick layer of PoraPlot Q and equipped with a 2-m long particle trap at the detector end of the column (Chrompak, The Netherlands). The PLOT column was held at 85°C for 8 min and then heated at 10°C  $\text{min}^{-1}$  to 200°C, which was maintained for 1 min before cycling back to the 85°C starting temperature. The head pressure of the PLOT column was held at 172 kPa (gauge), which resulted in a MeBr retention time of about 7 min. Methyl bromide samples were quantitated by comparing responses with those of standard injections from samples prepared by spiking clean charcoal tubes with varying amounts of a 0.1 mg  $\text{mL}^{-1}$  methanolic solution of MeBr (Chem Service, West Chester, PA). The results for each charcoal tube were expressed as mass MeBr per volume of air sampled.

Table 3. Select meteorological measurements, atmospheric stability calculations, air concentrations, and resulting volatilization flux values for each sampling period for the nontarped field.

Date	Time on	Run time	Period	Air temp. at 75 cm, °C	Differential air temp., °C	Wind speed at		Air concentration at		Ri	Phi(m)	Phi(c)	Flux
						40 cm	140 cm	40 cm	140 cm				
													µg m <sup>-2</sup> s <sup>-1</sup>
													— m s <sup>-1</sup> —
													— ng m <sup>-3</sup> —
27 Oct.	13.50	02.18	A	16.85	-0.343	7.97	10.25	2278	1386	-0.002	0.988	0.868	270
27 Oct.	16.15	02.00	B	15.04	-0.036	5.32	6.73	3249	1193	-0.001	0.997	0.880	370
27 Oct.	18.30	02.08	C	14.88	0.105	2.54	3.26	2574	1344	0.007	1.035	0.962	100
27 Oct.	20.45	02.00	D	14.72	0.100	3.24	4.07	2313	892	0.005	1.026	0.942	140
27 Oct.	22.55	02.00	E	14.49	0.110	3.36	4.21	2614	1012	0.005	1.027	0.944	160
28 Oct.	01.06	02.00	F	14.35	0.155	2.57	3.22	1614	965	0.012	1.062	1.019	44
28 Oct.	03.30	02.00	G	14.14	0.075	2.72	3.47	2227	788	0.004	1.023	0.936	130
28 Oct.	05.45	02.00	H	13.96	0.083	2.06	2.51	1541	951	0.014	1.068	1.031	27
28 Oct.	08.00	02.00	I	15.31	-0.187	3.45	4.24	932	559	-0.010	0.950	0.815	42
28 Oct.	10.15	02.00	J	16.46	-0.525	3.92	4.80	487	269	-0.023	0.901	0.752	32
28 Oct.	12.30	04.00	A	15.85	-0.416	5.94	7.53	433	177	-0.006	0.972	0.845	56
28 Oct.	17.00	04.05	B	14.09	0.204	2.06	2.56	1202	789	0.028	1.132	1.157	18
28 Oct.	21.20	04.00	C	13.29	0.284	1.52	2.01	1632	712	0.040	1.180	1.249	35
29 Oct.	01.40	04.03	D	12.67	0.324	4.34	5.72	1108	606	0.006	1.030	0.952	79
29 Oct.	06.00	04.00	E	14.49	0.414	9.82	12.66	282	137	0.002	1.009	0.906	51
29 Oct.	12.15	04.00	A	18.20	0.166	11.50	14.44	182	81	0.001	1.003	0.893	37
29 Oct.	16.35	04.00	B	15.56	0.615	2.17	2.90	828	349	0.039	1.174	1.238	27
29 Oct.	20.50	04.23	C	14.29	0.661	1.21	1.59	1409	496	0.157	1.519	1.851	14
30 Oct.	01.20	04.00	D	12.67	0.324	5.84	7.33	346	154	0.005	1.026	0.942	33
30 Oct.	05.40	04.00	E	14.49	0.414	5.53	7.04	135	54	0.006	1.032	0.955	14
30 Oct.	12.15	04.00	A	18.20	0.166	7.75	10.01	296	71	0.001	1.006	0.898	63
30 Oct.	16.35	04.00	B	15.56	0.615	2.64	3.67	576	120	0.020	1.095	1.085	45
30 Oct.	20.55	04.15	C	14.29	0.661	1.14	1.94	705	237	0.035	1.160	1.212	30
31 Oct.	01.20	04.00	D	8.57	0.754	1.71	2.49	582	239	0.043	1.189	1.267	20
31 Oct.	05.40	04.00	E	10.46	0.296	3.61	4.77	91	72	0.008	1.039	0.970	2.4
31 Oct.	12.15	04.02	A	20.56	-0.583	6.91	8.48	21	11	-0.008	0.961	0.830	2.2
31 Oct.	16.35	04.00	B	14.01	0.671	1.63	2.18	184	36	0.078	1.309	1.484	4.6
31 Oct.	20.53	06.52	C	10.82	0.610	1.16	1.61	303	100	0.102	1.381	1.611	4.7
01 Nov.	03.55	01.55	D	10.67	0.490	1.20	1.78	121	45	0.050	1.218	1.319	3.1
01 Nov.	06.15	04.00	E	13.68	0.056	1.57	1.88	82	53	0.019	1.093	1.081	1.0
01 Nov.	12.15	04.00	A	20.25	-0.660	7.01	8.74	19	6	-0.007	0.963	0.833	3.0

(µg m<sup>-3</sup>). The third back-up tube in the sampling train was used to determine MeBr breakthrough. If MeBr residues in the back-up tube exceeded 25% of the total residue for all three tubes, then the final result was expressed as a "greater than" number.

The practical MeBr detection limit for the method was approximately 4 µg m<sup>-3</sup>, which was equivalent to 0.1 µg MeBr spiked to a charcoal tube (100 mL min<sup>-1</sup> flow for 4 h). Most of the field samples that contained MeBr were well above this limit, with some approaching 100 µg (~4,000 µg m<sup>-3</sup>). The volume of headspace (the amount of analyte) sampled ( $v$ , µL) during the injection time ( $t$ , min) was estimated from the measured flow ( $q$ , mL min<sup>-1</sup>) through the column and Eq. [1].

$$v = qt \times 10^3 \quad [1]$$

Given the column flow of about 1.8 mL min<sup>-1</sup> during injection (103 kPa) and an injection time of 0.01 min, the volume of headspace injected was typically about 18 µL. At the detection limit, about 9 pg MeBr actually reached the detector (Woodrow et al., 1988). Detector linearity was about three orders of magnitude (0.1–100 µg MeBr spiked to charcoal), allowing quantitation of widely varying sample concentrations. Regardless of field sample concentration, chromatograms did not show any interferences near the MeBr peak. Heating the column to 200°C was effective in clearing the column for the next injection; there was no carryover of interfering material between injections. Standard curves were based on 4 to 8 points, with two to three injections per point, and had correlation ( $r^2$ ) coefficients typically >0.99.

An aerodynamic-gradient (AG) method was used to estimate the MeBr volatilization flux from both fields. This method

depends upon accurate measurements of air concentration, wind speed, and temperature gradients above the center of the treated area. These data provide the average volatilization flux per sampling interval in weight MeBr lost per surface area per time (µg m<sup>-2</sup> s<sup>-1</sup> or kg ha<sup>-1</sup> h<sup>-1</sup>).

The AG MeBr fluxes ( $F_{AG}$ ) were estimated using a modified form of the Thornthwaite-Holzman equation (Thornthwaite and Holzman, 1939) corrected for atmospheric stability conditions (Eq. [2]).

$$F_{AG} = \frac{k^2 \Delta \bar{c} \Delta \bar{u}}{\phi_m \phi_p [\ln(z_2/z_1)]^2} \quad [2]$$

Equation [2] can be derived from the standard forms for the wind and concentration profiles (Monin and Obukhov, 1954) where  $k$  is the von Kármán constant (~0.41), and  $\Delta \bar{c}$  (µg m<sup>-3</sup>) and  $\Delta \bar{u}$  (m s<sup>-1</sup>) are the average pesticide concentration and horizontal wind speed differences, respectively, between heights  $z_1$  and  $z_2$  (m) above the treated surface. The  $\phi$  expressions,  $\phi_m$  and  $\phi_p$ , are stability correction functions of the vertical profiles for wind and pesticide concentration in the surface layer, respectively. For unstable conditions ( $Ri < 0$ ),  $\phi_m = (1 - 16Ri)^{-0.33}$  and  $\phi_p = 0.885(1 - 22Ri)^{-0.40}$  and for stable conditions ( $Ri > 0$ ),  $\phi_m = (1 + 16Ri)^{0.33}$  and  $\phi_p = 0.885(1 + 34Ri)^{0.40}$  (Pruitt et al., 1973).  $Ri$  is a gradient Richardson number that describes the atmospheric stability and is calculated by  $Ri = g(dT/dz)[T(du/dz)^2]^{-1}$  where  $g$  is the gravitational acceleration (9.80 m s<sup>-2</sup>),  $dT/dz$  is the temperature gradient,  $du/dz$  is the wind speed gradient, and  $T$  is the air temperature in degrees Kelvin. Plots of wind speed and air concentrations vs. log height were generally linear.

Evaporative fluxes were calculated using values estimated from regression analysis of the best fit line through these plots. The estimated values used in the flux calculations were always within the linear portion of the plot. A more complete description of this theoretical approach and field requirements are given by Majewski et al. (1989, 1990).

## RESULTS AND DISCUSSION

The general meteorological conditions during treatment of the tarped field on 26 October were warm, clear, and windy, but were cooler, calmer, and overcast during the nontarped field application on 27 October. There was sporadic rain and light drizzle from 28 to 30 October with generally cool air temperatures (average high of 18°C and average low of 11°C). The rains were not from a frontal system, but from isolated cells moving through the area. Sometimes it would be raining at one field and not at the other. A very heavy rainfall occurred near midday on 30 October on both fields. After 31 October the daytime weather was generally clear and warm with cool nights (average high of 23°C and average low of 8°C) and winds varied in speed from light to strong and gusty.

Methyl bromide volatilization losses are summarized in Tables 2 and 3. Figures 2A and B show the MeBr fluxes per period for each field. The high initial volatilization fluxes measured for both fields are typical and have been observed in other volatilization flux field experiments, even with pesticides having much lower vapor pressures (White et al., 1977; Cliath et al., 1980; Glotfelty et al., 1984; Grover et al., 1985, 1988; Majewski et al., 1991, 1993). These initial high fluxes were, most likely, because of residual fumigant on or near the soil surface after the application. Both fields generally exhibited the highest fluxes during the day and the lowest during the late evening and early morning hours. This behavior reflected the generally higher temperatures and wind speed during midday and afternoon periods. On 3 November the tarp was removed between 1350 to 1520 h and a "bloom" of MeBr resulted (Fig. 2A). This bloom was most likely because of the release of accumulated MeBr trapped between the plastic tarp and the soil surface. The volatilization flux, however, rapidly declined after the tarp removal.

Wind speed data for the tarped field were lost from 1300 h, 31 October, through 1100 h, 2 November. The volatilization flux values for these time periods were estimated using wind speed data from the nontarped field because of similar wind speeds at both fields for several days preceding and following these time periods (Fig. 3A). These data were not used to determine if a significant difference existed between the fluxes of the two fields. They were only used to estimate the total volatilization losses from the tarped field. The fluxes for several sampling periods (0140–0610 h, 28 October; and 1735–2133 h, 31 October) also could not be calculated because of loss of the air concentration data. Flux values for these periods were estimated as the averaged flux for each day.

Pesticide volatilization, in general, depends on and is

proportional to the input of solar energy and the stability of the atmosphere. These meteorological parameters and, therefore, the volatilization flux usually follow diurnal cycles that are often maximized near solar noon. Other factors that can influence and change volatilization patterns include the soil moisture content and placement of barriers over the soil surface. In this study, the tarp not only formed a barrier that retarded MeBr emissions into the atmosphere, it also changed the site-related micrometeorological conditions, which may have affected volatilization losses. The most noticeable meteorological differences between the two fields were the net solar radiation, which is the difference between incoming solar and reflected surface radiation, and the air temperature above the fields (Fig. 3A and 3B). The tarp was a semitransparent plastic, and soon after the completion of the MeBr application and tarping, soil water vapor began condensing on the underside of the tarp to form an opaque, highly reflective surface. In contrast, the nontarped field had a very nonreflective surface of dark, moist, clumpy soil. The measured net solar radiation of the nontarped field was consistently greater than that of the tarped field (Fig. 3A). This implies that more of the sun's energy was absorbed by the nontarped soil, which helped drive the volatilization process. The soil transformed part of the incoming solar energy into heat which exchanged with the overlying air, resulting in an increase in air temperature. In contrast, the air temperature over the tarped field was consistently lower by 1 to 6°C. The tarp reflected some of the incoming radiation, but it also trapped much of the transmitted radiation between the soil and the tarp creating a greenhouse-like effect. During the summer months, when most of the MeBr soil fumigation occurs, the air temperature between the tarp and soil, as well as the soil surface temperature, can become much higher than what was observed during this experiment. After the tarp was removed the air temperature above the field actually decreased. This was most likely because of the transfer of the available heat energy in the atmosphere to the soil, which evaporated the accumulated surface moisture.

Both fields exhibited high volatilization fluxes at or near noon each day. The tarped field exhibited maximum flux values during this time. The nontarped field, in addition, showed high fluxes during the early morning sampling periods, for 28, 29, and 31 October just before sunrise, at about 0400 h. The daily flux maxima for the tarped field corresponded to the daily temperature and solar radiation maxima, which also may have affected the permeability of the tarp. Kolbezen and Abu-El-Haj (1977) have shown that the diffusion rate through 1 mil thick high density, polyethylene film doubles for every 20°C rise in temperature. Early morning volatilization increases have been observed for pesticides with much lower vapor pressures over fallow soil (Glotfelty et al., 1984; Grover et al., 1985; Majewski et al., 1993), and have been attributed to the remoistening of the soil surface with the formation of dew. It is unclear if this situation is applicable in this experiment with gaseous MeBr.

The soil temperature-with-depth profiles for both fields were surprisingly similar and were nearly identical to a

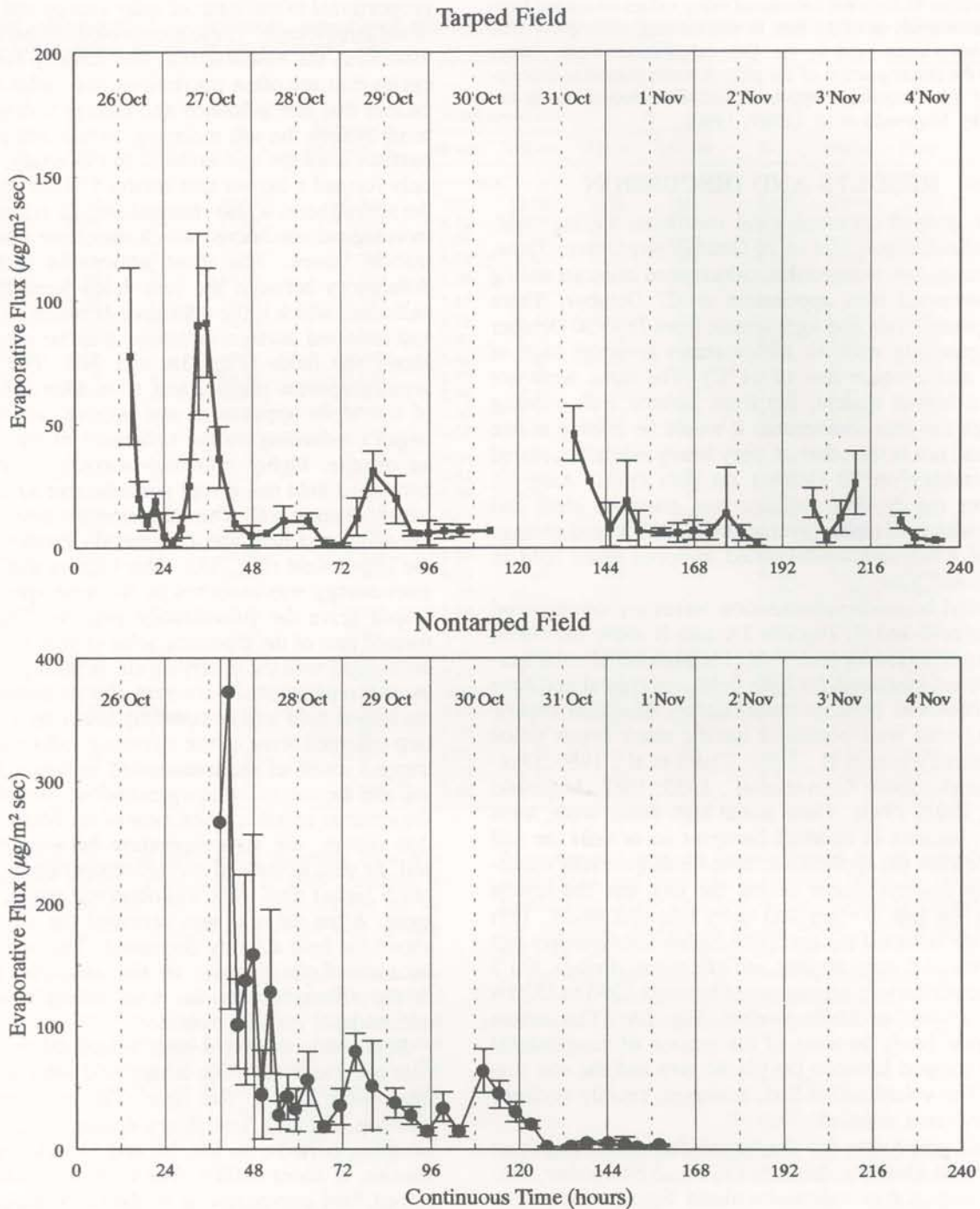


Fig. 2. Methyl bromide volatilization fluxes per period from the tarped (A) and nontarped (B) fields. Methyl bromide was applied to the nontarped field approximately 24 h after the tarped field application.

depth of approximately 25 cm (Fig. 3 B). The nontarped soil at 25 cm only varied between 15 and 16°C while the tarped field soil at the same depth fluctuated between 13 and 17°C. The tarp presented little barrier to incoming solar radiation, but seemed to act as a lid that retained some of the heat under the tarp, which warmed the soil to a greater depth. The soil temperatures under the tarp, as well as the difference in the soil temperature profiles with depth between the tarped and nontarped fields would be expected to be much greater during summer months when the incoming solar radiation is much more intense.

Cumulative volatilization losses from both fields show a bimodal distribution when plotted on a logarithmic scale (Fig. 4). Both fields exhibited an initial high loss period of between 16 and 24 h followed by fairly constant, but lower, loss rate for the remainder of the sampling periods. The tarped field lost 22% of the nominal application by volatilization within the first 5 d of the experiment. Approximately half of this loss (51%) occurred within the first 24 h. The total 9-d tarped field MeBr volatilization losses were estimated as 32% of the nominal applica-

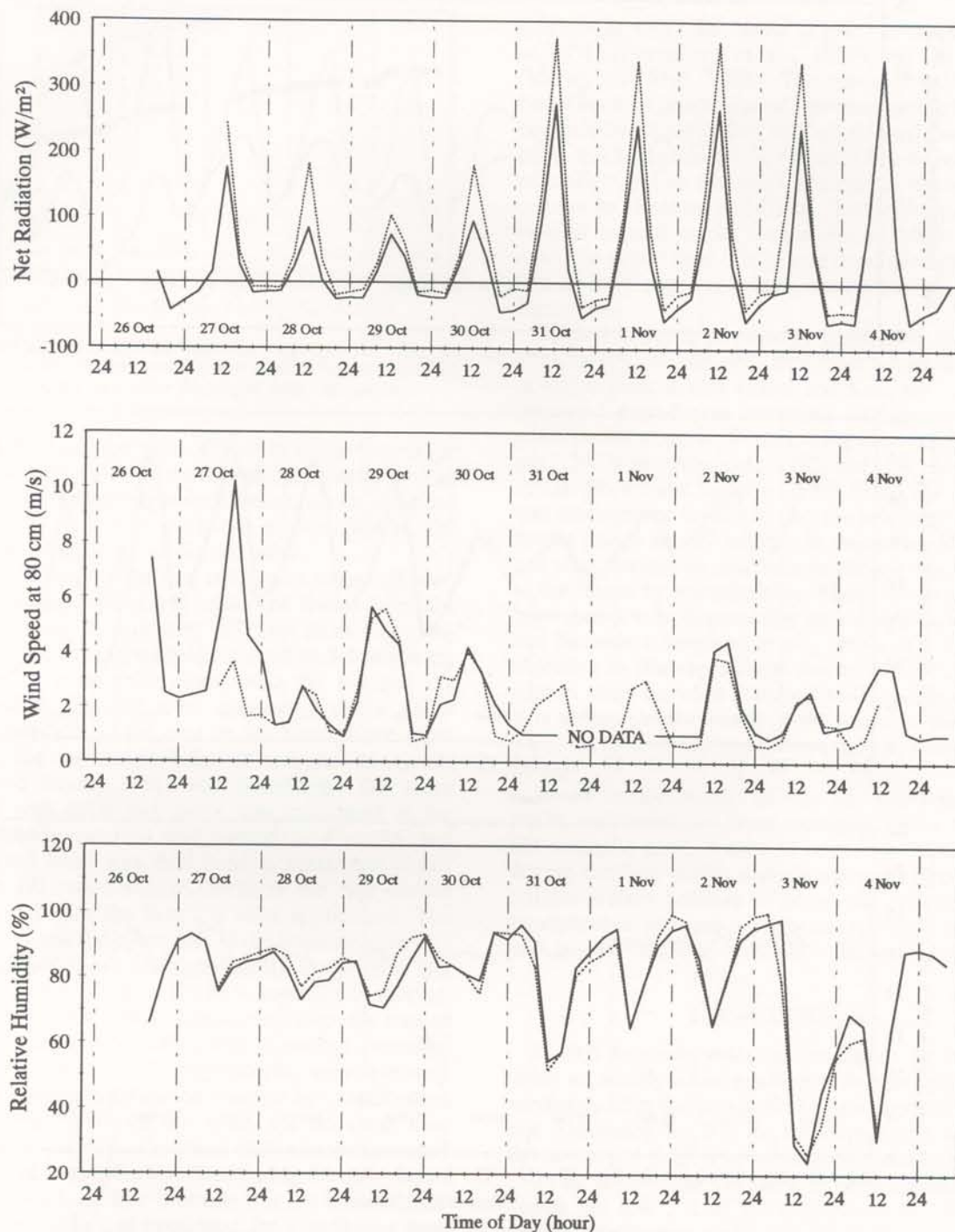


Fig. 3. Net radiation, wind speed, relative humidity, air temperature, and soil temperature at 2 and 25 cm between 26 Oct. and 4 Nov. 1992 for the tarped (—) and nontarped (---) fields. (Continued next page.)

tion. In contrast, the nontarped field lost 89% of the nominal application by volatilization in 5 d, with approximately half of this loss (52%) occurring within the first 16 h. After these initial high-loss periods, both fields exhibited relatively steady cumulative losses throughout the duration of the experiment.

Different MeBr/chloropicrin formulation mixtures were used in this experiment (a 67/33% mixture for the tarped field and a 98/2% mixture for the nontarped field). This was due, in part, because these fields were being

prepared for commercial use using conventional application rates and formulations. The effect of the different chloropicrin concentrations on the gas phase MeBr behavior is thought to be very small. The vapor pressure of MeBr ( $1.89 \times 10^5$  Pa at 20°C) is two orders of magnitude greater than that of chloropicrin ( $3.2 \times 10^3$  Pa at 25°C) and the vapor phase movement of MeBr in soil is much greater than that of chloropicrin. From a practical standpoint, the mobility of MeBr does not appear to be enhanced or retarded with formulations con-





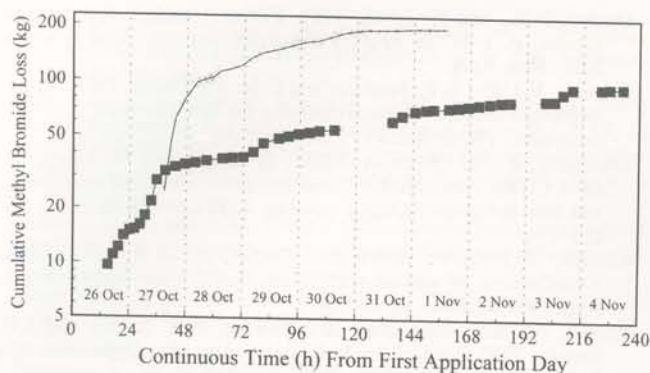


Fig. 4. Cumulative volatilization losses for the tarped (■) and nontarped (◇) fields. Methyl bromide was applied to the nontarped field approximately 24 h after the tarped field application.

soil or tarp thickness because of the very limited coverage of the total surface with the sampling chambers. The AG method for measuring volatilization rates is designed to average the flux over the entire source, that is, the entire treated field area in this situation.

An error analysis of the flux estimation values allowed us to determine if the lower observed fluxes from the tarped field were significantly different from those observed from the nontarped field for the first 5 d following application to each field. Since both the  $\Delta \bar{c}$  and  $\Delta \bar{u}$  values used in Eq. [2] were obtained from a linear regression analysis of the best fit line through the measured data, the standard deviation of each predicted value (Draper and Smith, 1981) was calculated. The error associated with each flux value was calculated at the 95% confidence interval and plotted in Fig. 2A and 2B. A paired *t*-test was then used to determine if any significant difference existed between the flux results from each field for the first 5 d after application. The results of this test indicated that MeBr volatilization flux from the tarped field was significantly lower than that from the nontarped field at the 95% confidence interval.

The placement of a high-density tarp over the treated surface retarded the volatilization of methyl bromide. Over the 9-d period of the experiment, approximately 32% of the nominal application was lost by volatilization from the tarped field. Of this total, 6% occurred after the removal of the tarp. The other 68% was unaccounted for. Since no soil analysis was done during the experiment for residual MeBr or free bromide it is not known if the tarp kept the MeBr gas contained for a sufficient time for other dissipative pathways to occur.

After injection into the soil, MeBr rapidly diffuses radially from the point of injection. Several factors that affect this diffusion are the composition of the soil, the degree of compaction, the moisture content, and temperature (Maw and Kempton, 1973). Gaseous MeBr also can diffuse deeper into the soil and early studies (Drosihn et al., 1968) found that MeBr persisted at significant amounts at a depth of 1 m for as long as 14 d after the tarp was removed. Dissipative routes for methyl bromide other than volatilization include hydrolysis, sorption to soil particles and organic matter, dissolution into soil moisture, and biodegradation. The hydrolysis

half-life in water for MeBr at pH 7 is reported as 38 d at 20°C (Ehrenberg et al., 1974) and 20 d at 25°C (Mabey and Mill, 1978). The reported half-life in soil based upon an unacclimated aqueous aerobic biodegradation half-life is between 1 to 4 wk (Howard et al., 1991). Maw and Kempton (1973) reported that direct hydrolysis of MeBr is a slow reaction that requires strongly alkaline conditions. Rolston and Glauz (1982) compared the results of several model simulations of MeBr dissipation in soil to actual field results and concluded that degradation by hydrolysis is minor, even after 14 d following fumigation.

Methyl bromide can readily transfer its methyl group to carboxyl groups, and to *N*- and *S*-containing groups in soil organic matter (Maw and Kempton, 1973), with increased degradation occurring with increased soil organic matter content. Reported log *K*<sub>oc</sub> values for MeBr are 1.34 (Wauchope et al., 1992) and 1.92 (Montgomery, 1993). Brown and Rolston (1980) found that decomposition mechanisms involving clay particles and soil organic matter play a significant role in degrading MeBr during and after fumigation, but were negligible when compared to the losses by volatilization. Methyl bromide also has been shown to be degraded by both aerobic and anaerobic soil bacteria (Oremland et al., 1994a, b). The primary objective in this experiment was to compare the volatilization rates between a tarped and nontarped field and it is unknown how much of the unaccounted for MeBr was degraded by one or more of the processes described above.

Based on the results of this and previous research, MeBr will volatilize from fumigated soils whether or not a tarp is used. Although meteorological conditions during the time of this experiment were atypical for the Salinas Valley because of lower air temperatures and precipitation amounts, the principal effect of the tarp was to slow the rate of MeBr volatilization from soil.

## CONCLUSIONS

Methyl bromide volatilization fluxes were estimated using an aerodynamic-gradient technique beginning immediately after the completion of the application process and continuing for 9 d for the tarped field and 6 d for the nontarped field. The cumulative volatilization losses from the tarped field were 22% of the nominal application within the first 5 d of the experiment and 32% of the nominal application within 9 d. In contrast, the nontarped field lost 89% of the nominal application by volatilization in 5 d. The volatilization rates during the time the field was tarped were shown to be significantly lower than for the nontarped field at a 95% confidence level. The results of this field experiment show that fields fumigated with MeBr could be tarped if the purpose is to retain MeBr in the soil for a prolonged period of time to increase efficacy. Approximately 50% of the total measured volatilization losses occurred within 24 h after application, however, regardless of whether the field was tarped or not.

Nearly all of the MeBr applied to the nontarped field was accounted for by volatilization, but 68% of the MeBr

applied to the tarped field was unaccounted for. Other dissipative routes include sorption to soil particles and organic matter, dissolution into soil moisture, hydrolysis, and biodegradation. Gaseous MeBr also can potentially diffuse deeper into the soil under tarped conditions and could continue to volatilize from the surface after tarp removal at very low rates for an extended period of time.

Future work is warranted that compares tarp materials of different composition and thickness with the goal of finding a material that best retards the volatilization of MeBr; to investigate application rates, injection depth, and alternate methods of sealing the soil surface (such as spraying water on the surface after injection) as ways of controlling MeBr emissions from soil; and to examine in greater detail the effects that soil composition, moisture content, and temperature have on other dissipative processes such as sorption, hydrolysis, and biodegradation.

The contribution of worldwide agricultural use to the total global MeBr burden is thought to be nearly equal to the contribution from the marine environment. The marine environment, however, complicates the picture because it is both a source and a sink for MeBr, and acts to buffer the MeBr concentration in the atmosphere. The role other sinks such as soil, flora, rainfall, and fog play in affecting the global burden of MeBr is not well understood. Future research could also focus on characterizing the air-sea exchange rate of MeBr and its chemistry in sea water, and identifying the contribution of other important surface and atmospheric sinks. Until the complicated mechanism of MeBr cycling in the global environment is clarified, the ozone-depleting potential of anthropogenic sources of MeBr, such as agriculture, cannot be assessed with certainty.

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