

## Methyl Bromide Emissions from a Covered Field: I. Experimental Conditions and Degradation in Soil

S. R. Yates,\* J. Gan, F. F. Ernst, A. Mutziger, and M. V. Yates

### ABSTRACT

An experiment is described to investigate the environmental fate and transport of methyl bromide in agricultural systems. The experiment was designed to determine the dynamics of methyl bromide movement through soil, degradation, and total emissions to the atmosphere. This is of particular interest because it will allow an assessment of the environmental impacts (i.e., stratospheric ozone depletion) resulting from the agricultural use of methyl bromide. Methyl bromide was applied at a rate of 843 kg in a 3.5-ha (i.e., 240 kg/ha) field at a depth of 0.25 m and covered with a sheet of 1-mil polyethylene plastic. The maximum methyl bromide concentration in the atmosphere occurred at night between 0200 and 0600 h. During the first 3 d of the experiment, the maximum daily concentrations at 0.2 m above the soil surface were 30, 5, and 1 mg/(m<sup>3</sup> of air), respectively. The trend of reduced emissions with time continued until the plastic was removed, when a momentary increase in the methyl bromide emissions occurred. The maximum soil gas concentration 24 h after injection was 30 g/m<sup>3</sup> located at a 0.25-m depth. When the plastic was removed from the field (at 5.6 d), the maximum soil gas concentration was approximately 2 g/m<sup>3</sup> at a 0.5-m depth. A mass-difference method for estimating the total methyl bromide emissions from the soil, based on degradation of methyl bromide to Br<sup>-</sup>, indicates that approximately 39% or 325 kg (±164 kg) of the applied methyl bromide was converted to Br<sup>-</sup> and, therefore, 61% or 518 kg (±164 kg) was lost via volatilization.

**I**N THE USA, methyl bromide (CH<sub>3</sub>Br) is used extensively as a soil fumigant for the control of nematodes, weeds, and fungi and as a postharvest fumigant. Recent research has suggested that methyl bromide can significantly damage the ozone layer (UNEP, 1992) and, as a result of the Clean Air Act, methyl bromide is scheduled for phase-out by the year 2001. The National Agricultural Pesticide Impact Assessment Program has completed an assessment of methyl bromide use and determined that there will be substantial adverse economic impacts on the agricultural community if the use of methyl bromide is restricted. These effects will be most strongly felt in two states, California and Florida, which are the primary users of methyl bromide.

In the *Methyl Bromide Science and Technology and Economic Synthesis Report* (UNEP, 1992), several areas of uncertainty with regard to environmental effects from the agricultural use of methyl bromide were identified. Several important research areas were identified and are summarized as follows: quantifying the methyl bromide mass emitted from agricultural fields, determining the

controlling factors affecting methyl bromide fate and transport under typical field operations including potential atmospheric sinks, determining the accuracy of models to simulate methyl bromide behavior in field soils, and developing alternatives or more efficient management methods to reduce volatile losses of methyl bromide.

One of the most common methods to reduce the amount of methyl bromide leaving the treated soil is the use of plastic films. Although covering the field with plastic can reduce the amount of methyl bromide volatilized by inhibiting the transport from the soil into the atmosphere, the material commonly used (i.e., 0.025 mm or 1 mil high-density polyethylene) is relatively permeable to methyl bromide (Kolbezen and Abu-El-Haj, 1977). Therefore, a significant fraction (i.e., 30–60%) of the applied material can escape the soil zone and enter the atmosphere. If plastic film is not used, however, nearly all of the applied methyl bromide may leave the treated soil zone after a few days when injected at a shallow depth (Majewski et al., 1995).

Any attempt to investigate the environmental fate and transport of methyl bromide must contend with its high vapor pressure, approximately 1420 mm Hg at 20°C, and low boiling point, 3.56°C (Table 1). Because of these properties, methyl bromide exists mainly in the vapor phase under normal temperatures and pressures that occur in the field. The predominant mechanism that induces the spreading of methyl bromide through the soil profile is vapor diffusion (Goring, 1962; Kolbezen et al., 1974; Reible, 1994). After injection, which may involve a short period where pressure-driven flow dominates, liquid methyl bromide vaporizes and methyl bromide moves throughout the soil in response to the phase-change expansion and the initially high gradients near the injection points. As this process continues, methyl bromide quickly approaches the surface where it can escape into the atmosphere. Although diffusion is a primary spreading mechanism in soil, other mass flow processes have been suggested as potentially important in moving gases through the root zone. For example, changes in barometric pressure (Massmann and Farrier, 1992), pressure effects caused from wind at the surface or density sinking (Goring, 1962) may induce a mass flow.

Along with volatilization of methyl bromide at the soil surface, degradation is one of the principle factors removing methyl bromide from the treated area (Gentile et al., 1992; Gan et al., 1994). Principal processes causing degradation in agricultural soils include hydrolysis and methylation. Gan et al. (1994) investigated the effect of soil properties on methyl bromide degradation and sorption in several soils and estimated the degradation half-life for methyl bromide in Greenfield sandy loam (coarse-loamy, mixed, thermic Typic Haploxeralf) to be

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**Table 1. Selected physical properties of methyl bromide.**

Property	Value
Vapor pressure	1420 mm Hg (at 20°C)†
Solubility	13 400 mg/L†
$K_{oc}$	22 mL/(gF <sub>oc</sub> )†
Boiling point	3.56°C†
Specific gravity	3.974 mg/mL†
Molecular weight	94.94 g/mol†
Henry's Constant	0.25‡

† Wauchope et al. (1992).

‡ UNEP (1992).

approximately 8 to 27 d, decreasing with increasing soil depth. There are many other soil and environmental factors that affect methyl bromide movement and degradation in field soils. A review of these is given by Goring (1962).

This research project was initiated to determine the extent of methyl bromide degradation in soils and volatilization into the atmosphere. The overall project objectives are to determine soil reactions, transport characteristics, volatile emissions, and mass partitioning of methyl bromide after field application. This will allow an assessment of the potential environmental impacts of the agricultural use of methyl bromide. The objective of this article is to describe a field experiment that was conducted to determine the environmental fate and transport of methyl bromide when applied at a shallow depth under a sheet of 0.025-mm (1-mil) polyethylene. This application method is commonly used to treat soil before planting vegetables. The methyl bromide mass degraded to Br<sup>-</sup> and the mass remaining in the field at the completion of the experiment is also reported. This allows an estimate of the total methyl bromide emission from the field to be obtained. An important distinction between the experiment described herein and previous experiments involving methyl bromide is that the necessary informa-

**Table 2. Soil properties for Greenfield sandy loam soil.**

Depth m	Organic matter	Clay	Surface area	pH, H <sub>2</sub> O
	%		m <sup>2</sup> /g	
0-0.3	0.921	9.5	14.4	7.39
0.61-0.9	0.427	14.7	19.8	8.16
1.21-1.5	0.238	4.9	12.7	7.93
1.81-2.1	0.118	3.0	6.2	8.25
2.41-2.7	0.131	3.7	8.0	7.97

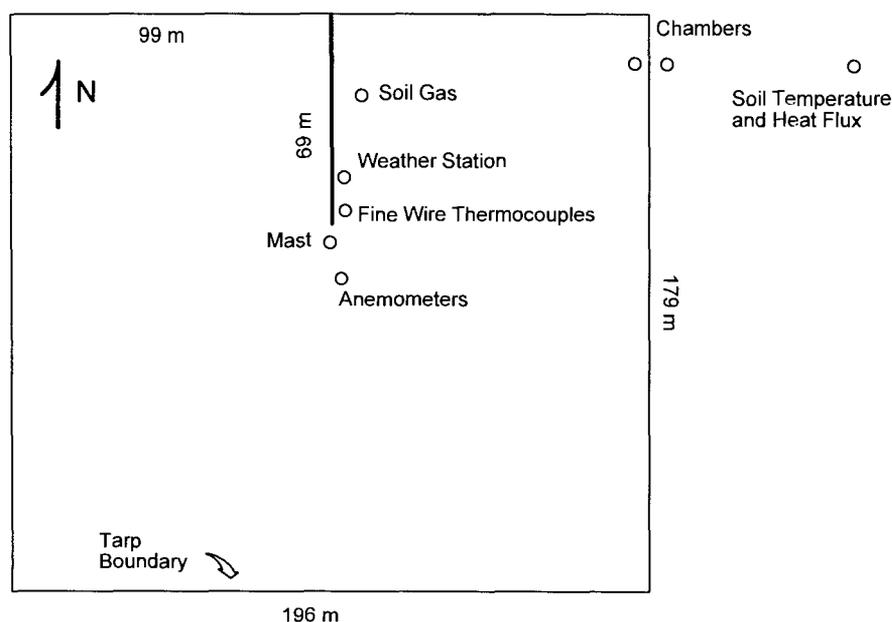
tion to report the mass balance; principally, the mass of methyl bromide converted to Br<sup>-</sup> is obtained. Previous experiments measuring methyl bromide flux failed to provide this vital information along with the mass of methyl bromide remaining in the field, making it impossible to determine whether the estimated emission rates from agricultural fields were accurate.

## MATERIALS AND METHODS

### Experimental Design

The experiment was conducted at the University of California's Moreno Valley Field Station on Field G7, a 4-ha field located in the eastern portion of the station, between 26 Aug. 1993 and 13 Sept. 1993. The adjacent fields were vacant, allowing a determination of the atmospheric transport of methyl bromide off the experimental site (see Yates, 1993) and providing sufficient up-wind fetch so that atmospheric gradient methods could be used to obtain the methyl bromide flux. The soil type in this field is a Greenfield sandy loam and is classified as a coarse-loamy, mixed, thermic Typic Haploxeralf (see Table 2). The field site was sampled to characterize the following properties: soil texture, organic matter content, soil moisture retention and unsaturated hydraulic conductivity, bulk density, porosity, moisture content, surface area, and pH. Figure 1 is a schematic of the experimental layout of the experiment.

Two months before conducting the field experiment, the

**Fig. 1. Schematic of field site. Dimensions are not to scale.**

soil was ripped to a depth of approximately 0.75 m in both the north-south and east-west directions. This was followed by discing to break up the soil large aggregates. Several weeks before applying methyl bromide, the field was irrigated and followed by a waiting period that lasted until the soil water content was near field capacity.

The morning that methyl bromide was applied, the field was cultimulched to break any remaining soil aggregates to further protect the plastic from punctures. After cultimulching, the surface soil had a bulk density of approximately 1.35 to 1.40 gm/cm<sup>3</sup> and was easily compressed.

Methyl bromide was applied to the field by a commercial applicator using a tractor containing two noble plows mounted on the center section of the tool bar with four injection points evenly spaced along each plow. A standard straight shank was located at each end of the tool bar. There were a total of 11 injection points for each panel (e.g., the width of field covered by a single sheet of plastic), spaced laterally approximately 0.25 m apart. During the first north-south pass along the eastern side of the field, methyl bromide was applied to the soil and a 3.6-m (i.e., 12 feet) sheet of 0.025-mm (1-mil) high-density polyethylene plastic was rolled out from behind the tractor and a small portion of each edge buried with a small noble plow located at the end of the tool bar. When the tractor reversed directions for the next pass, one side of the plastic was glued to the previous panel near the buried edge and the other edge was buried. This application method creates a series of panels down the field and a continuous polyethylene cover over the field.

The depth of injection was approximately 0.25 m. The methyl bromide was applied to the field as 99.5% methyl bromide (CH<sub>3</sub>Br) and 0.5% chloropicrin (CCl<sub>3</sub>NO<sub>2</sub>) (USEPA Reg. no. 8536-12-11220). The application rate was approximately 240 kg/ha (i.e., 215 lb/a) to an area of approximately 3.5 ha (i.e., 8.6 acres), for a total applied mass of 843 kg. The 6.5-h application began at 0800 h and continued until about 1430 h. The application process was interrupted for about 30 to 45 min to install various meteorological and atmospheric gas sampling equipment, which were needed to determine the methyl bromide flux. These instruments included: air sampling mast, anemometer mast, weather station, pyranometer, net radiometer, air temperature gradient mast, and air thermometer above and below the plastic.

A wooden walkway was placed from the field edge to the sampling equipment to allow personnel to enter the field without tearing the plastic. The walkway was constructed by gluing 0.5 m wide strips of 4-mil plastic to the top of the 1-mil polyethylene plastic, and overlaying this with 0.4 m wide pieces of plywood (1.25 cm or 0.5 inch). To prevent the wind from moving the wood, it was secured to the 4-mil plastic

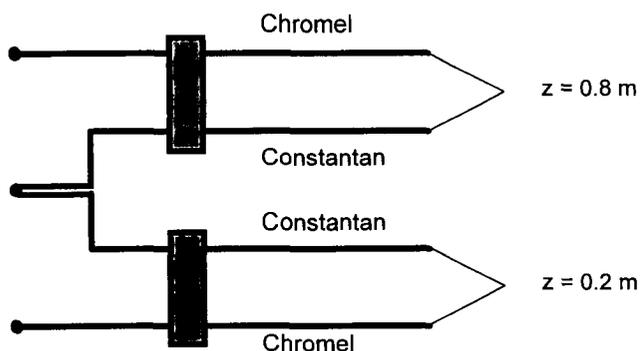


Fig. 2. Wiring diagram of fine wire thermocouples used to make differential temperature measurement in the atmosphere. Resolution is 0.006°C.

using duct tape (attached to the sides of the wood and across the wood). The orientation of the walkway was along a low-probability wind direction, to minimize the walkway's effect on the concentration or wind-speed data. The plastic remained on the field for approximately 5.5 d after application. During removal, which lasted from approximately 1400 to 1700 h on Day 5, atmospheric gas sampling continued. Samples of the polyethylene material and associated condensation were analyzed for adsorbed methyl bromide and Br<sup>-</sup>.

### Meteorological Measurements

Before initiating the experiment, all meteorological instruments were calibrated. The pyranometer (LI-200S, LI-COR, Accuracy:  $< \pm 5\%$ ), wind speed sensing devices (CWT-1806, C.W. Thornthwaite Assoc., Transmitter-Unit, Accuracy:  $\pm 1$  counts/timing cycle) and the net radiometer (Q-6, Radiation and Energy Balance Systems, Accuracy: not provided) were returned to the manufacturer for cleaning and calibration. The soil and air temperature instruments (CS107, Campbell Scientific, Accuracy:  $< \pm 0.1^\circ\text{C}$   $-24 < T < 48^\circ\text{C}$ ) were calibrated using constant temperature environmental chambers.

Wind speed measurements were taken using six Thornthwaite anemometers positioned at 0.1, 0.3, 0.7, 1.5, 2.3, and 3.1 m above the field surface. The anemometer mast was located approximately 8.5 m south of the sampling mast (see Fig. 1). Three replicated air temperature measurements were obtained at 0.2 and 0.8 m above the field and differential air temperatures were obtained using six 76.2- $\mu\text{m}$  diam. (0.003 inch) Type E (chromel-constantan) fine wire thermocouples (FWTC3, Campbell Scientific). To obtain a direct measurement of differential temperature, the probes were wired as shown in Fig. 2. After measuring the data logger panel temperature for a reference, a single-ended voltage measurement of the fine wire thermocouple located 0.2 m above the soil surface and attached to the low side of a data logger channel was obtained. Next, a differential voltage measurement across both the 0.8- and 0.2-m fine wire thermocouple was obtained using the thermocouple at 0.2 m as a temperature reference. A differential temperature value was obtained by subtracting the temperature at 0.8 m from the temperature at 0.2 m. This procedure has no inherent offset error (Campbell Scientific, 1991) and has a resolution of 0.006°C. Four additional air temperature measurements were taken at 0.2 and 0.80 m using two CS207 (Campbell Scientific, Accuracy:  $\pm 5\%$   $0 < \text{RH} < 90\%$ ;  $\pm 0.2^\circ\text{C}$   $0 < T < 50^\circ\text{C}$ ) and two HMP35C (Vaisala, Accuracy:  $\pm 3\%$   $0 < \text{RH} < 100\%$ ,  $\pm 0.1^\circ\text{C}$   $-24 < T < 48^\circ\text{C}$ ) relative humidity and temperature sensors. These were housed in white louvered covers and mounted on a weather station mast. Barometric pressure was obtained using a Vaisala, PTa427 Barometer having  $\pm 50$  Pa (0.5 mbar) accuracy.

Soil temperature and heat flux measurements were taken at 0.05 and 0.1 m below the soil surface. Additional soil temperature measurements were taken at 0.15-, 0.20-, 0.30-, 0.40-, 0.50-, 0.80-, and 1-m depths. The temperature probes could not be installed in the treated area before application due to the tractor-mounted injection shanks used to apply methyl bromide. Also, since methyl bromide is highly toxic and digging in the treated soil soon after application is dangerous, these measurements were taken approximately 10 m from the eastern edge of the field site in an area that was prepared identically to the field site, including the addition of a sheet of polyethylene at the soil surface. In addition, two white air thermometers (Campbell Scientific CS-108) were used to measure the air temperature above and below the plastic. One probe was placed under the plastic on top of the soil surface

and the other was laid on top of the plastic and they were neither shielded from direct sunlight nor aspirated.

The meteorological data were collected using Campbell Scientific 21X Data Loggers at 2-min intervals so that higher frequency phenomena could be observed. The high-frequency data were subsequently averaged to coincide with the sampling interval for the methyl bromide air samples collected on the mast. The data loggers were networked together using multi-drop interfaces (Campbell Scientific MD-9) and coaxial cable so that incoming meteorological data could be observed in real time. A computer program was developed to continuously monitor each data logger, collect data transmitted to the computer, conduct rudimentary error checking on the incoming data stream and alert field personnel if the data were not within a specified interval.

### Air Monitoring

To collect air samples above the fumigated field, which could be analyzed for methyl bromide, a base and removable sampling mast were constructed and placed in the center of the field. The sampling mast base, described in detail by Yates et al. (1995), was installed in the ground by puncturing the plastic, installing the base in the soil, and sealing the hole by gluing a layer of plastic over the hole and around the bottom of the mast base. The base was connected to a vacuum source located outside the treated area of the field. Three interchangeable light-weight masts were designed to be inserted into the mast base. The masts held charcoal sampling tubes at heights of 0.1, 0.2, 0.5, 0.8, 1.2, and 1.6 m above the field surface. The charcoal sampling tubes were placed on the mast at a remote off-site field station and carried to the field. Once there, the new mast was inserted into the mast base and the air flow rate through each sampler was adjusted to 100 mL/min using a ball flow meter. The charcoal tubes were custom made ORBO tubes (Supelco Co., Bellefonte, PA), which contained 350 and 175 mg 20- to 40-mesh coconut-based charcoal in the front and rear adsorption beds, respectively, which were sandwiched between three glass wool plugs in 70 by 10 mm (o.d.) glass tubing. The sampling regimen required positioning two tubes in series: a primary tube followed by a backup tube for checking methyl bromide breakthrough. Methyl bromide in the air was adsorbed to the charcoal by drawing air through the sampling tubes via a vacuum system connected to the rear end of the tubes series. Air sampling tubes were changed at 2-h intervals except between the hours of 2200 and 0600, when a 4-h interval was used. The charcoal sampling tubes were placed in a freezer and ultimately transported to the laboratory for analysis. A detailed description of the method used to analyze the charcoal sample tubes is given by Gan et al. (1995b) and the details of the error analysis resulting from sample handling is given by Gan et al. (1995a).

### Methyl Bromide Gas Sampling below the Plastic and in Soil

Periodically throughout the experiment, subsurface gas samples were collected at gas piezometers located along the wooden walkway. Two or three samples were collected in the air space between the plastic and the soil surface and after the plastic was removed, at approximately 0.03 m deep in the soil. Four replicated soil gas measurements were taken in the treated area at depths of 0.25, 0.50, 1.0, and 1.5 m. In addition, soil gas samples were collected at 0.25-, 0.50-, and 1.0-m depths for distances up to 1 m away from the edge of the treated area.

Before removing the plastic from the field, the gas concentra-

tion in the air space below the plastic in the first 10 panels on the east side of the field was measured to determine the variability in the methyl bromide gas concentration as a function of panel location.

### Bromide Ion Sampling and Analysis

To determine the methyl bromide mass converted to  $\text{Br}^-$ , numerous soil cores were taken to a maximum depth of 7 m. For background  $\text{Br}^-$  concentration, four cores to a depth of 2 m and one to 3 m were taken in the center of the field before applying methyl bromide. The  $\text{Br}^-$  concentration was measured using an ion selective electrode and an Accumet 25 pH meter (Fisher Scientific Co.) at 0.3-m depth increments. After the experiment, 25 cores to a depth of 5 m and five cores to 7 m were taken randomly in the field. These cores were sectioned at 0.1-m intervals from the surface to a depth of 1.0 m and at 0.2-m intervals from 1 to 7 m. Compared with the posttreatment  $\text{Br}^-$  concentration, the magnitude of the background  $\text{Br}^-$  concentration and its variability were higher than expected; therefore, upon completion of the experiment, 30 additional samples to 7 m were obtained in soil adjacent to the field site, which had the same soil type, and cropping and irrigation history. These data were included to improve the accuracy of the background  $\text{Br}^-$  concentration.

### Determination of Methyl Bromide Loss during Sample Collection and Handling

A number of laboratory studies were conducted to determine appropriate methods for handling, capturing and transporting methyl bromide before beginning the field experiment. These were conducted to minimize any errors from material losses in the sampling tubes, collection methodology, transportation, etc. In addition, other studies were conducted to determine the adsorption of methyl bromide to various materials such as PVC plastic, Teflon, vinyl, tygon, lexan, polyethylene, stainless steel, and aluminum used in field studies. This was done so that materials that have low adsorption could be used wherever possible in the experiments. At temperatures from approximately 25 to 50°C, and concentration ranging from 100 to 2500  $\mu\text{L/L}$  (vol/vol), significant adsorption was observed for tygon, polyethylene, and vinyl. Therefore, other materials were used where possible for the sampling equipment. Under the same conditions, adsorption to the other materials was negligible.

Breakthrough and stability studies were conducted before using activated charcoal tubes to collect methyl bromide from air samples (Gan et al., 1995a). The number of ORBO charcoal tubes, placed in series, needed for accurate sampling without allowing any significant breakthrough were determined for various flow rates and sampling intervals, and were used as guidelines throughout the experiment. The stability of methyl bromide in charcoal tubes under various temperatures and moisture conditions was also investigated so safe handling procedures were created and followed to minimize the loss of methyl bromide due to degradation during sampling, transport, and storage before analysis.

## RESULTS AND DISCUSSION

Shown in Fig. 3 are the wind speed and wind direction data during the first 7 d of the experiment, where integer values on the abscissa indicate midnight. The solid dots in Fig. 3A indicate the interval average wind speed at 1.5 m above the soil surface where the averaging periods coincide with the mast sampling intervals. The dotted

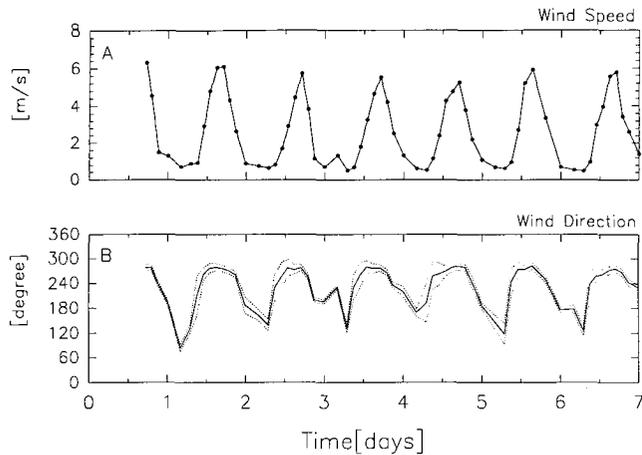


Fig. 3. (A) Wind speed (m/s) at 1.5 m above the soil surface and (B) direction (degrees clockwise from north) during the first 7 d of the experiment. Circles indicate the average value for the mast sampling interval. The dotted lines indicate 1 SD.

line in Fig. 3B indicates the standard deviation of the average wind direction. For all the meteorological measurements, data collection continued for approximately 20 d. By this time, the methyl bromide concentration in the atmosphere was no longer detectable except sporadically at a few heights and the meteorological equipment was removed from the field. At the field site, the afternoon winds reached about 6 m/s and generally moved from the west to east (see Fig. 3B). The average wind direction during the afternoon was approximately  $270^\circ$ . A cyclic pattern in the wind direction was observed, with the direction oscillating between about  $110^\circ$  during the night and  $280^\circ$  during the day.

Shown in Fig. 4 are time series of the air temperature (filled circles and solid line) and relative humidity (open circles and dotted line) at 0.2 m above the surface of the field. Daily temperatures averaged  $22^\circ\text{C}$  and ranged from approximately  $17^\circ\text{C}$  to a high of approximately  $35^\circ\text{C}$ . The relative humidity was generally below 80% and averaged approximately 50% at 0.2 m above the surface. On Day 4, an early morning fog, which dissipated by midmorning, was present at the field site. Tem-

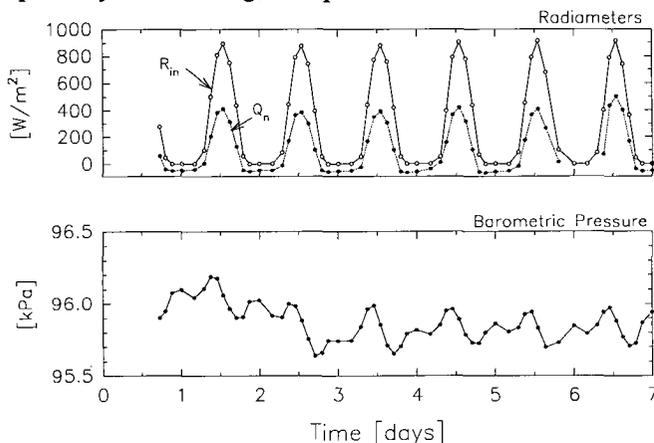


Fig. 4. Air temperature ( $^\circ\text{C}$ ), relative humidity (%) at 0.2 m, and the difference in the air temperature between 0.2 and 0.8 m ( $^\circ\text{C}$ ) during the first 7 d of the experiment. Circles indicate the average value for the mast sampling interval.

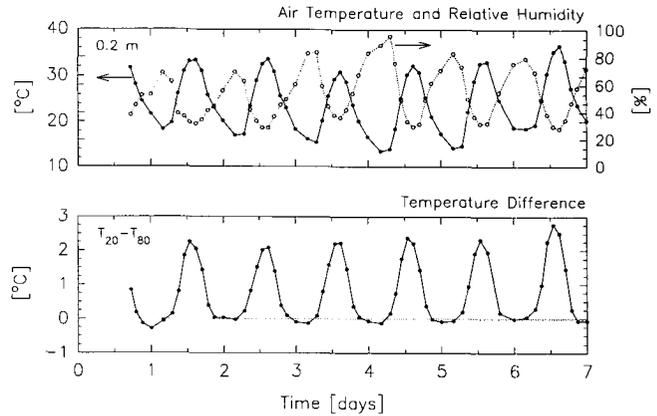


Fig. 5. Incoming solar radiation,  $R_{in}$  ( $\text{W}/\text{m}^2$ ), net radiation,  $Q_n$  ( $\text{W}/\text{m}^2$ ) and barometric pressure (kPa) during the first 7 d. Circles are the average value for the mast sampling interval.

perature gradients in the atmosphere were obtained by averaging three fine wire thermocouple measurements at 0.2 and 0.8 m above the soil surface and is shown in Fig. 4B. Unstable atmospheric conditions are indicated by positive values in Fig. 4B occurred during the day and as much as a  $3^\circ\text{C}$  temperature difference was measured. During the night, neutral to stable conditions were present with the temperature at a height of 0.8 m generally no more than  $0.5^\circ\text{C}$  warmer than at 0.2 m.

Shown in Fig. 5 are time series of the incoming radiation,  $R_{in}$  ( $\text{W}/\text{m}^2$ ), net radiation,  $Q_n$  ( $\text{W}/\text{m}^2$ ), and the barometric pressure (kPa). The clear skies that occurred throughout most of this experiment are indicated by the regular oscillations in both radiation measurements. The barometric pressure, on the other hand, tends to peak near noon and has the lowest values in early evening; overall they seem to have a somewhat irregular behavior. The average, standard deviation and range for the barometric pressure was 96.0, 0.194, and 95.6 to 96.5 mbars, respectively.

The changes in the soil temperature ( $^\circ\text{C}$ ) and heat flux ( $\text{W}/\text{m}^2$ ) are shown in Fig. 6. The soil temperature reached

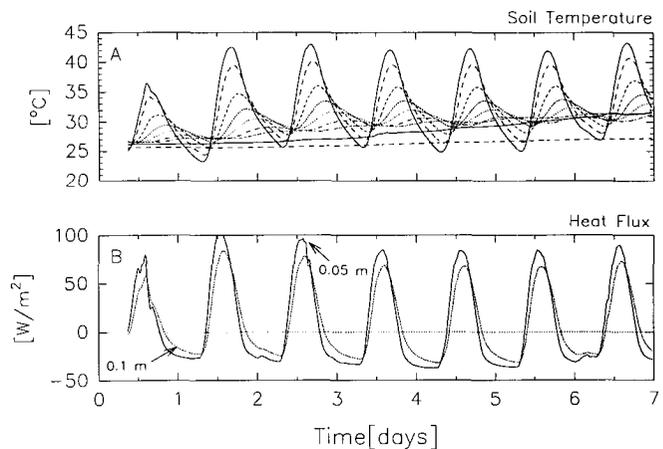


Fig. 6. Soil temperature ( $^\circ\text{C}$ ) and heat flux ( $\text{W}/\text{m}^2$ ). The soil temperature depths were 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.8, and 1.0 m. The largest amplitude is the shallowest depth and amplitude decreases as depth increases.

a maximum of approximately 42 to 43°C at a depth of 0.05 m throughout the portion of the study when the plastic was covering the field. At deeper depths, there was a trend of increasing temperature with time, which is due, for the most part, to the heat entrapment caused by the presence of the plastic on the field. At a depth of 0.8 m, the temperature increased by approximately 6°C, at 1 m by about 1.5°C. The plastic was not removed from this part of the field (see Fig. 1) at the same time it was removed from the treated area. Therefore, the soil temperature increase shown in the figure after about 1700 h on Day 5 is not indicative of the soil temperature in the treated area since a decreasing temperature trend would be expected once the plastic was removed. The soil heat flux had a more stationary cyclic pattern, which is probably due to the shallow depth of these sensors (i.e., 0.05 and 0.1 m).

The atmospheric concentration of methyl bromide is shown in Fig. 7 where the methyl bromide concentration ( $\text{mg}/\text{m}^3$  of air) is plotted as a function of time. The insert is an expanded view of the atmospheric concentration beginning at  $t = 2.5$  d. For clarity, only the samples from the 0.2 and 0.8 m heights are shown. The maximum concentrations of methyl bromide in the atmosphere occurred during the first day. Higher concentrations occurred during the night and lower concentrations in the afternoon. This is related, in part, to the wind speed, since at any height  $z$ , the concentration,  $c(z,t)$ , is obtained from

$$c(z,t) = \frac{\text{mass}(z,t)}{u(z) t \Delta x \Delta y} \quad [1]$$

where  $u(z)$  is the horizontal wind speed (m/s) at height  $z$ , and  $(\Delta x \Delta y)$  is the cross-sectional area sampled and is perpendicular to  $u(z)$ . Therefore, higher velocities result in lower concentrations. This is also affected by the atmospheric stability. By the second day, the atmospheric concentrations were 20 to 50% of the first-day values. The decreasing trend continued until the plastic was

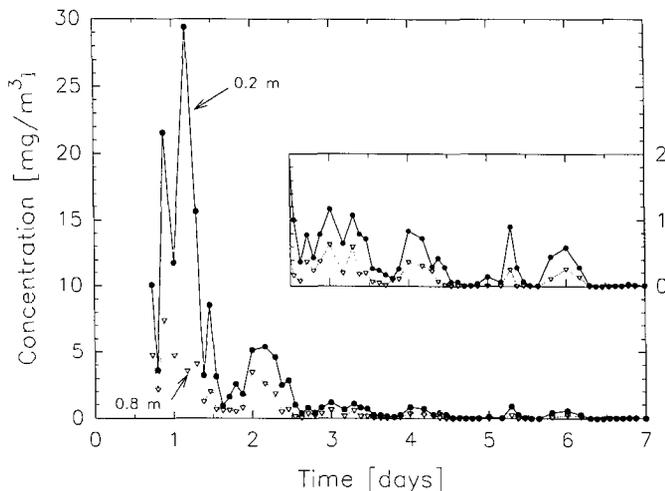


Fig. 7. Methyl bromide concentration in the air ( $\text{mg}/\text{m}^3$ ) at 0.2 and 0.8 m above the soil surface. The plastic was removed after approximately 5 d. Integer values on the abscissa indicate midnight. Insert is an expanded view of concentration data.

removed from the field. At this time, a small surge in the atmospheric emission of methyl bromide occurred. Following this, the emission rate quickly dropped to negligible values.

Shown in Fig. 8 is the methyl bromide concentration in the air space between the plastic and the soil surface for the first 10 panels beginning at the eastern edge of the field. The average value, shown by the dotted line, is  $459 (\pm 172) \text{ mg}/\text{m}^3$ . These data were obtained immediately before removing the plastic and illustrate the variability in the concentration. Many factors contribute to the variability, including: (i) variations in the plastic thickness and/or the amount applied to each strip of the field; (ii) lateral flow effects at the edge of the field, especially for the first panel; (iii) spatial differences in methyl bromide degradation in the field; and (iv) differences in soil texture or the mechanics of applying methyl bromide (i.e., closing the shank fracture), etc. Also shown in Fig. 8 are the air temperatures above and below the plastic. The temperature of the air space below the plastic exceeded 60°C, producing a large downward soil heat flux during sunlight hours. During both the day and night the temperature below the plastic was greater than the air above. During the day and night, respectively, the temperature below the plastic was  $17.6 (\pm 3.9)^\circ\text{C}$  and  $3.2 (\pm 0.8)^\circ\text{C}$  warmer than above the plastic.

Shown in Fig. 9 is a semilog plot of the soil gas concentration as a function of depth for several times after the methyl bromide application. After 1.4 d, a peak concentration of  $30 \text{ g}/\text{m}^3$  was located at the injection depth ( $\sim 0.25 \text{ m}$ ). The peak concentration in the near-surface layer decreased with time, while the concentration at depth increased. After 36 d, the upper 1 m of soil had unmeasurable concentrations, but methyl bromide gas was still detectable at depth. The concentration was  $0.057 \text{ mg}/\text{m}^3$  at 5 m, the lowest depth sampled. The methyl bromide mass in the vapor phase at 36 d was estimated to be 0.04 kg, which is  $<0.005\%$  of the applied mass.

From the vapor concentration, it is possible to estimate

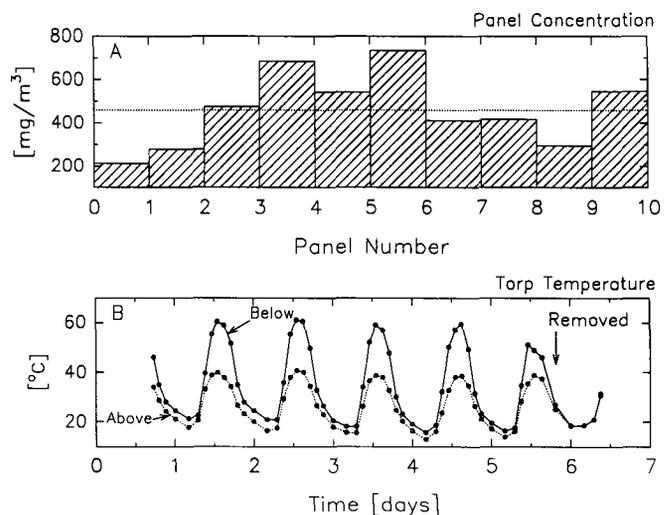


Fig. 8. Methyl bromide concentration [ $\text{mg}/(\text{m}^3 \text{ of air})$ ] in the air space between the soil and the plastic at 5.6 d and the temperature ( $^\circ\text{C}$ ) above and below the plastic.

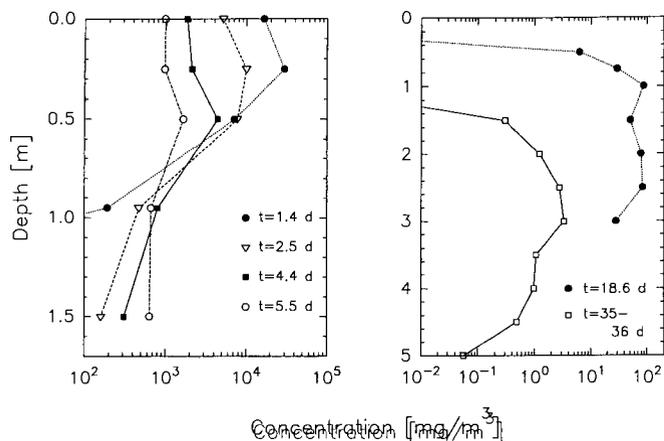


Fig. 9. Methyl bromide soil gas concentration [mg/(m<sup>3</sup> air)] at selected days after application.

the sorbed and liquid phase concentrations, which can then be converted to mass by considering the field size, depth increment, bulk density,  $\rho_b$ , and the water content,  $\theta$ . Assuming that vapor partitioning follows Henry's Law, and using a value of 0.25 for the Henry's constant (UNEP, 1992), the mass of methyl bromide in the liquid phase after 36 d was approximately 0.097 kg. Assuming that the sorbed component follows hydrophobic partitioning, an estimate of the  $K_d$  can be obtained using a value for  $K_{oc}$  of 22, reported by Wauchope et al. (1992) and the  $f_{oc}$  data in Table 2. Using the appropriate values for the liquid phase concentration and  $K_d$  at a specified depth, the methyl bromide mass sorbed was estimated to be 0.13 kg.

The background concentration for the soil  $\text{Br}^-$  (mg/kg) on a dry soil weight basis taken before application is shown in Fig. 10 as open squares. The additional

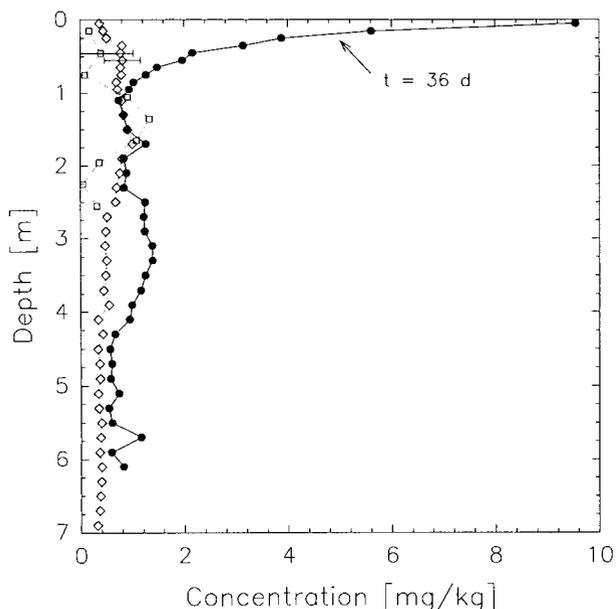


Fig. 10. Bromide ion concentration in mg/kg on a dry-weight basis. Open squares and diamonds are background concentrations, filled circles are concentrations 36 d after application. Insert is an expanded view of the  $\text{Br}^-$  concentration near the soil surface.

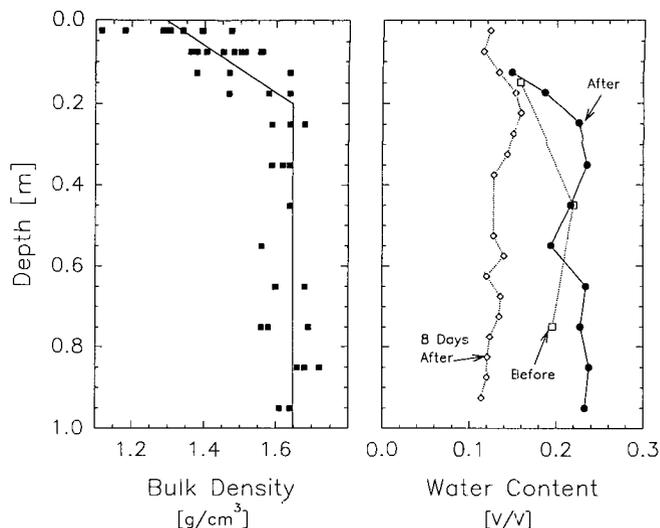


Fig. 11. (A) Bulk density distribution with depth; (B) Soil water content before application (*Before*), after plastic removed from field (*After*) and 8 d after removing plastic.

samples taken in the adjacent field are shown as open diamonds. Also shown on each curve is a bar that indicates an average standard deviation for each curve. The standard deviations were calculated by averaging, over the entire depth of coring, the standard deviations for the  $\text{Br}^-$  concentration at each depth using the 5 to 30 available cores. For the curve denoted by open squares, the value for the average standard deviation is 0.63 mg/kg and for the open diamonds, the value is 0.35 mg/kg.

The  $\text{Br}^-$  concentration after 36 d is shown as solid circles. The difference between the ending and initial curves represents the quantity of methyl bromide gas degraded to  $\text{Br}^-$ , which is principally due to hydrolysis and methylation. Peak  $\text{Br}^-$  production occurred near the soil surface, where the organic matter content (see Table 2) and soil temperatures (see Fig. 6) were highest. Contributing to this is the presence of water on the underside of the plastic, which can, through hydrolysis, degrade methyl bromide to  $\text{Br}^-$ . Under windy conditions, the accumulated  $\text{Br}^-$  in the condensate is deposited on the soil surface as water droplets fall from the plastic increasing the  $\text{Br}^-$  concentration at the surface. Shown in Fig. 11 is the bulk density as a function of depth, which is used to convert  $\text{Br}^-$  concentration to mass. Also shown in Fig. 11 is the soil water content in the field while covered by plastic and 8 d after the plastic was removed. The bulk density of the soil above 0.25 m was low compared with the typical condition of this soil as a result of soil preparation to prevent puncturing the plastic. Below 0.25 m, the bulk density near the maximum value commonly observed for this soil, approximately 1.65 gm/cm<sup>3</sup>, and remains fairly constant.

Based on the difference in the concentration vs. depth curves shown in Fig. 10 (i.e., diamonds and circles), the mass of  $\text{Br}^-$  produced by degradation was estimated to be 273 kg. Since the molecular weights of  $\text{Br}^-$  and methyl bromide are 79.9 and 94.94 g/mol, respectively, the measured mass of  $\text{Br}^-$  must be converted to represent the mass of methyl bromide degraded. The standard error

(SE) was obtained by calculating a standard deviation for the 30 differences in the  $\text{Br}^-$  concentration (i.e.,  $C_{\text{Br}^-, \text{end}} - C_{\text{Br}^-, \text{start}}$ ) and dividing by the square root of number of available values. An estimated 325 kg (SE  $\pm 164$  kg) was degraded during the course of this experiment, which represents approximately 39% ( $\pm 19\%$ ) of the applied mass. For completeness, 10 measurements were taken of the  $\text{Br}^-$  ion concentration on the underside of the plastic to determine the mass. It was found that approximately 2.5 g of  $\text{Br}^-$  was present and represents an insignificant fraction of the applied mass.

In the absence of any mechanisms other than volatilization for removing methyl bromide from the field, a method for estimating the total mass lost from methyl bromide emissions at the soil surface can be obtained by subtracting the sum of the mass degraded plus the mass remaining from the mass applied; that is, the total emission rate  $F_z(t)$  is

$$F_z(t) = \int_0^t f_z(0, \tau) d\tau = M_{\text{applied}} - M_{\text{degraded}} - M_{\text{remaining}} \quad [2]$$

where  $f_z(0, t)$  is the instantaneous vertical flux at the soil surface. An estimate of the mass lost from the field due to volatilization is 518 kg, which represents approximately 61% of the total applied mass. The spatial and measurement variability introduces uncertainty into the  $\text{Br}^-$  mass calculation as evidenced by the standard error of  $\pm 164$  kg. Therefore, the true fraction of methyl bromide lost from the field from volatilization also includes uncertainty, that is 61% ( $\pm 19\%$ ). This value is based solely on the soil  $\text{Br}^-$  data since the amount remaining in the liquid, vapor, and sorbed phases was estimated to be  $<0.05\%$ ; or 0.26 kg.

Consideration of the field scale variability of the  $\text{Br}^-$  concentration is important when estimating the total methyl bromide loss based on soil concentration of degradation products. For example, when the estimate is obtained using the five soil cores to a depth of 3 m, which were taken before applying methyl bromide, the total loss is 298 kg or 35.3%. If in addition, the samples from the 30 cores taken adjacent to the field are used to extend the initial distribution below 3 m, the total loss is estimated to be 435 kg or 48.4%. This demonstrates that numerous deep soil cores are needed to adequately estimate methyl bromide degradation in soil.

The percent total emission reported by Majewski et al. (1995) for similar experimental design is 36%, which is approximately 60% of the value found during this experiment. These values are smaller than the results of Yagi et al. (1993), who report a total emission of approximately 87%. Yagi et al. (1993) obtain their data from flux chambers, and neither Majewski et al (1995) nor Yagi et al. (1993) included a mass balance. There are several possible explanations for the differences in the total emission reported in the literature: when flux chambers are used, they may have produced errors due to changes in the local environmental condition above the soil the chamber samples, soil degradation may differ significantly at each field site, the plastic used in each

experiment may have had different permeabilities or possibly other unidentifiable site-specific factors. Failing to conduct a mass balance makes it impossible to determine whether the flux-measurement method produces an accurate total emissions value. Therefore, it is highly advisable to include this vital information in future experiments designed to measure the total emission rate from agricultural fields. In this way, errors in determining the flux can be readily identified.

## CONCLUSIONS

An experiment was conducted to obtain an estimate of the total methyl bromide emissions from an agricultural field. The estimate was obtained from the difference between the amount of methyl bromide applied, the amount degraded to  $\text{Br}^-$ , and the amount remaining in the field ( $<0.05\%$ ). From this information, the total emission is approximately 518 ( $\pm 164$ ) kg or 61% ( $\pm 19\%$ ) where 325 kg or 39% degraded in the soil to  $\text{Br}^-$ .

Conducting a mass balance provides vital information on the accuracy of experiments to determine the total emission of methyl bromide from agricultural fields. This can be accomplished by conducting detailed sampling for  $\text{Br}^-$ , both before application and after the soil concentrations in the field are below detectable levels. Combining the information contained in this article on soil degradation and the mass remaining with independent measurements of the volatilization rate, a complete mass accounting can be obtained. Future experiments designed to measure the methyl bromide volatilization rate should include a mass accounting so that any errors in the determining the flux, the field-scale degradation, or the methyl bromide remaining can be readily identified.

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