



CALIBRATION AND TESTING OF A DYNAMIC FLOW-THROUGH CHAMBER FOR FIELD DETERMINATION OF METHYL BROMIDE VOLATILIZATION FLUX

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(First received 3 April 1997 and in final form 30 May 1997. Published September 1997)

Abstract—Accurate emission measurement of highly volatile chemicals such as methyl bromide (MeBr) is a crucial step in assessing their potential for environmental contamination. Use of flux chambers is a simple method for measuring emission rate under field conditions. To validate the applicability of a dynamic flow-through chamber for measuring MeBr emission, we provide a complete presentation of calibration and testing of the chamber. The calibration was made under a controlled system subject to ambient temperature changes. Two field experiments were conducted to test the chamber for measuring MeBr flux under conditions similar to commercial soil fumigation practices. In both the calibration and the two field experiments, the chamber provided accurate emission estimates. The maximum mass balance error was < 10% which is comparable to the micrometeorological method. Because of its simplicity, we believe this dynamic flux chamber can be used reliably in quantifying the emission dynamics of highly volatile chemicals such as MeBr. © 1997 Published by Elsevier Science Ltd.

Key word index: Chamber, volatilization, emission, methyl bromide, flux, fumigation

INTRODUCTION

Methyl bromide (MeBr) is a highly volatile fumigant that has recently been put under scrutiny because of its large potential for depleting stratospheric ozone (Singh and Kanakidou, 1993; Butler, 1996). Field quantification of MeBr emission from soil fumigation has been made with micrometeorological approaches such as the aerodynamic method (Majewski *et al.*, 1995; Yates *et al.*, 1996a) or other approaches such as the *in-situ* flux chambers (Yagi *et al.*, 1993; Yates *et al.*, 1996b). The micrometeorological-based measurements require extensive instrumentation and MeBr concentration measurements at different heights in the air. The treated area also needs to be large to achieve a reasonable fetch. Measuring emission with flux chambers is relatively simple and does not require a large surface area (Mosier, 1990). Two types of flux chambers are often used for the direct measurements of gas emission from the soil. They are static or closed-form chambers (Matthias *et al.*, 1980; Yagi *et al.*, 1993) and dynamic or flow-through flux chambers (Denmead, 1979; Woodrow and Seiber, 1991; Eklund, 1992). Although no significant difference was found on measured N₂O–N flux using either a static

or dynamic chamber (Valente *et al.*, 1995; Christensen *et al.*, 1996), the flow-through type chamber is often the preferred style because of few assumptions required for converting the concentration measurements to emission fluxes (Rolston, 1986).

Although the flux chamber method is probably one of the simplest methods for measuring pesticide volatilization, it could suffer from several disadvantages compared to the micrometeorological-based measurements. First, the chamber method measures only a small fraction of the total surface area for emission, which would cause the measured flux to be very variable. However, the spatial variability can be substantially minimized when the emission surface is covered with a uniform plastic film. Next, the presence of the chamber can affect the area sampled such as the temperature and relative humidity, compared to the rest of the surface area. This effect on local environment is especially large for the static chambers and can be very small for the flow-through type of dynamic chambers if designed properly. Although they have been used in field experiment (Yates *et al.*, 1996b), verification of the dynamic flux chambers for measuring highly volatile organic chemicals such as MeBr is not available in the literature and merits investigation.

The overall objective of this study was to validate the flux measurements from a dynamic flow-through chamber for characterizing MeBr emission under field

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conditions, i.e. covered with polyethylene film after application. Two steps were taken to achieve the proposed objective: (1) to incorporate a highly controlled flow system into the chamber measurement procedures, and (2) to test emission measurements under field conditions with a mass balance by determining MeBr degradation.

MATERIALS AND METHODS

The chamber

The chamber used for this study was designed to create an uniform air-flow pattern inside the chamber, with a design similar to that of Gao *et al.* (1997). The aerodynamic flow was achieved by a gradual expansion and contraction assisted with five separation baffles on both the inlet and the outlet section of the chamber (Fig. 1). The sampling zone is from a 41.5×41.5 cm square opening located between the inlet and outlet transition sections of the chamber. Because the air passing through chamber contained a large amount of MeBr, subsampling from the total flow through the chamber was used to calculate the total emission flux. It was important to place the subsampling port at a location where the MeBr concentration represents the mean concentration in the main flow. For comparison, we sampled from two locations: (1) in the air-flow hose downstream from the chamber outlet and after an air mixing mechanism (see Fig. 1), which will be called Port #1, and (2) at the end of the outlet section of the chamber, which will be called Port #2. To reduce solar heating of the chamber, we covered the chamber with aluminum foil to increase chamber reflectance to incident solar radiation. This was to minimize temperature building up inside the chamber, so that the air passing through the chamber would have temperatures similar to that of the ambient air. Thermocouple temperature probes were installed inside and outside the chamber and the measured temperature difference was less than 1.5°C .

A closed system for chamber calibration

To calibrate the flux chamber, a completely closed system was constructed that included the chamber, a calibration box as MeBr source, and air-flow setups for the chamber and MeBr emission sampling. The source box was constructed with galvanized steel sheet metal (~ 1 mm thick) 61 cm wide \times 62 cm long by 31 cm high. An opening fitting to the dimension of the chamber sampling section (41.5×41.5 cm) was made. The chamber was sealed onto the source box after a layer of polyethylene film (0.036 mm thick) was taped over the opening of the source box. A 1.9 cm diameter flexible hose was used at the outlet side of the chamber to connect to a vacuum which was used to create air flow through the chamber system. A 5 cm diameter hose was connected to the

inlet side of the chamber to channel fresh ambient air into the sampling zone. No measurable vacuum build up was found in the chamber because of the large-sized hose used for the inlet air. Electronic flow meters and a datalogger were used to measure and record air-flow rate through the chamber and the two subsampling ports. An electric fan was installed at the bottom of the source box to mix the injected MeBr. To determine MeBr distribution in the source box and total mass remaining at selected times after application, small Teflon tubes were inserted through a port with their ends at five locations within the box: at center, near one side wall, and at three heights halfway between the center and the wall. The center tube was also used to inject 28.7 g of MeBr into the source. Activated charcoal was used to adsorb MeBr for the emission measurement and MeBr concentration sampling from the source box. All samples were analyzed with a gas chromatograph with a head space sampling unit. The detection limit is less than $1 \mu\text{g}$ and detailed procedures can be found in Gan *et al.* (1995). Thermocouples were also installed in the calibration box to measure air temperature.

Field testing of the aerodynamic chamber for measuring MeBr volatilization

Two field plot experiments were conducted to test the chamber for measuring MeBr emission flux under field conditions. The soil is an Arlington fine sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf) and consists of approximately 64% sand, 29% silt and 7% clay. The volumetric soil-water content was about 18% during both experiments. We used polyethylene films from the same roll used for the chamber testing under the closed system. In the first field study, the chamber was used to measure MeBr flux from a plot (3.6×5.3 m) where MeBr was injected at 60 cm depth at a 32.4 g m^{-2} rate after covering with the plastic film. An air flow and sampling system similar to the calibration setup was used. MeBr emission was measured continuously and the emission samples were replaced at 3 h intervals during the experiment. To determine bromide ion (Br^-) increase from MeBr degradation, soil core samples were taken from nine locations of the plot before and after MeBr injection.

In the second field study, we constructed a replicate of the chamber and both chambers were used during the testing. The sampling procedure was similar to the first field study, however, MeBr was injected at 25 cm depth at a 28.0 g m^{-2} rate after covering with the film. To obtain a mass balance assessment, soil core samples were taken for analysis of Br^- addition from MeBr degradation.

RESULTS AND DISCUSSION

MeBr emission under controlled conditions

Using the closed calibration system, measured maximum daily MeBr emission flux decreased from

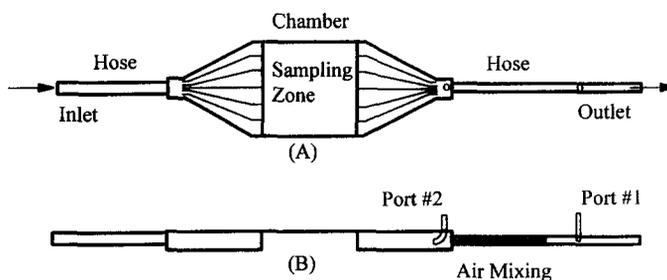


Fig. 1. Schematic of a dynamic flow-through chamber for measuring methyl bromide volatilization flux density: (A) top view, (B) cross-section along the centerline.

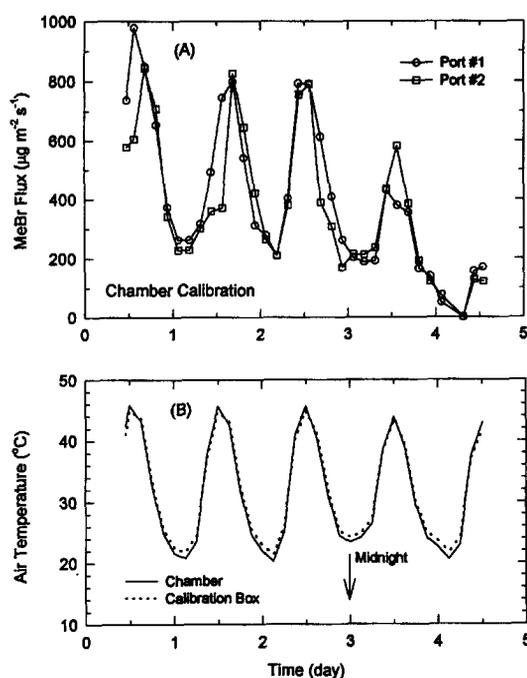


Fig. 2. Methyl bromide (MeBr) volatilization flux measured from two sampling ports of a dynamic flux chamber under controlled conditions (A) and air temperature inside the chamber and the calibration box (B).

about 1000 to 200 $\mu\text{g m}^{-2} \text{s}^{-1}$ in 4.58 days (Fig. 2A). During this time, the cumulative emission loss was 84.3 and 78.0% for subsampling Ports #1 and #2, respectively. MeBr in the source box was distributed evenly both at the beginning and 4.58 days after application. The coefficient of variation between the five locations in the calibration box was, respectively, 3.1 and 6.9% right after and at 4.58 days after MeBr injection. Based on the measured MeBr concentration ($\approx 38.6 \mu\text{g cm}^{-3}$ after 4.58 days) and the effective volume of the source box ($\approx 0.117 \text{ m}^3$), the MeBr mass remaining in the box was 4.52 g which corresponded to 15.8% of the total applied mass. Combined with the measured emission loss, this yielded a mass balance of 100.1 and 93.8% for subsampling Ports #1 and #2, respectively. The near 100% mass balance indicates that this dynamic flux chamber can be used to provide adequate assessment of MeBr volatilization loss under controlled conditions. The small difference between the two subsampling locations was found not to be significant, especially under field conditions where experimental errors tend to be greater than the controlled calibration system. Nevertheless, we recommend subsampling the main flow after thorough mixing or from Port #1 to reduce the potential of either under or over estimating the mean concentration.

Temperature effect on MeBr emission

Measured MeBr flux exhibited strong diurnal variation with high fluxes occurring between noon to

early afternoon hours and low fluxes between midnight to early morning (Fig. 2A). This has been observed in studies using micrometeorological methods (Majewski *et al.*, 1995; Yates *et al.*, 1996a). As indicated by Wang *et al.* (1997), MeBr volatilization flux is influenced by temperature because of a temperature dependency of MeBr diffusion coefficient in air, its Henry's constant, and film permeability. Other factors that may contribute to variations in emission flux include atmospheric instability, and changes in wind speed and ambient barometric pressure. In this calibration system, temperature dependency of MeBr Henry's constant and diffusion coefficient can be neglected because we had only air phase in the source box and a fan constantly mixing the air creating an advective MeBr redistribution inside the box. Therefore, the diurnal variation was mostly caused by changes in film permeability with temperature (see Yates *et al.*, 1996b) which followed the same trend as the measured emission fluxes (Fig. 2B).

MeBr emission under field conditions

With 60 cm injection, measured MeBr flux increased slowly to a maximum of $\sim 50 \mu\text{g m}^{-2} \text{s}^{-1}$ 8.7 days after application (Fig. 3A). The slow increase is reasonable because MeBr needed to travel through 60 cm soil before reaching the surface for emission. It took about 4 days for the applied MeBr to reach the soil surface (under the film). Most emission loss occurred between day 4 and 20 when the average maximum flux was less than $10 \mu\text{g m}^{-2} \text{s}^{-1}$. The overall emission loss was only 83 g or 13.4% of the applied MeBr mass.

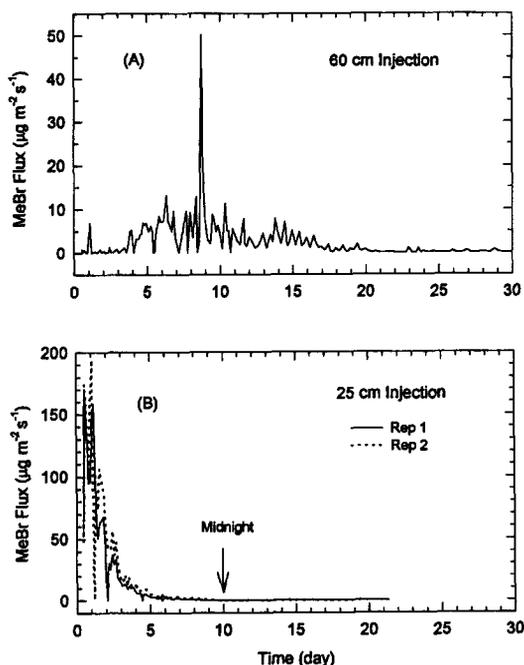


Fig. 3. Methyl bromide (MeBr) volatilization flux measured from a field plot covered with polyethylene film, where MeBr gas was injected at (A) 60 cm and (B) 25 cm.

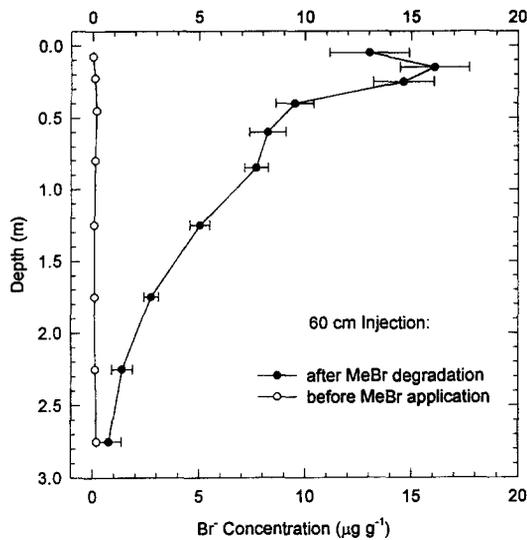


Fig. 4. Soil bromide ion concentration before methyl bromide (MeBr) injection at 60 cm depth and covered with polyethylene film and after degradation.

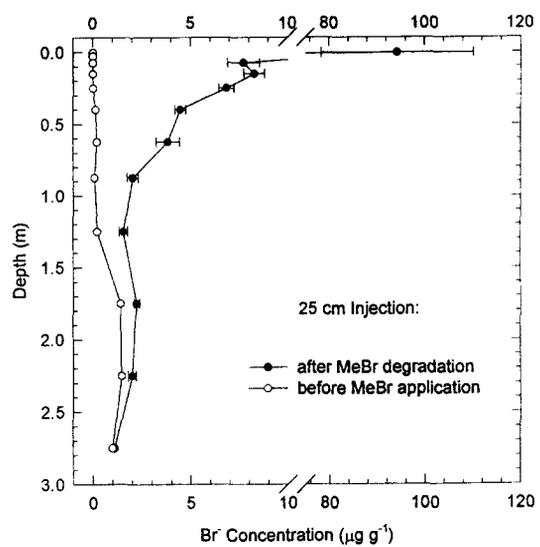


Fig. 5. Soil bromide ion concentration before methyl bromide (MeBr) injection at 25 cm depth and covered with polyethylene film and after degradation.

The total emission was small because most of the applied MeBr had degraded in the soil, which caused the elevated soil Br^- concentrations (Fig. 4). Since soil Br^- was sampled 133 days after MeBr application and the plot was continuously covered with the plastic film, there would be no significant amount of MeBr remaining in the soil profile and the converted Br^- (from MeBr degradation) would all remain in the soil. From the concentration increase in soil Br^- , we calculated that the total degradation would be 528 g or 85.4% of the applied MeBr. Adding the degradation to the cumulative emission loss, we obtained a 611 g total mass or 98.8% mass balance, compared to the amount applied. This is very close to 100% which indicates that the chamber measurement provided an accurate estimate of MeBr volatilization when injected at 60 cm and covered with polyethylene film.

In the second field experiment, the measured MeBr flux reached a maximum of $195 \mu\text{g m}^{-2} \text{s}^{-1}$ (from replicate 2) about 0.5 day after injection at 25 cm depth (Fig. 3B). The fast increase in emission flux was caused by the reduced application depth, i.e., 25 cm vs 60 cm, hence, less travel time to the soil surface. The flux decreased to near zero in less than 10 days and the emission measurement was terminated on day 21. Both chambers followed a similar trend with replicate 1 measuring a total of 322 g or 60.3% cumulative emission and replicate 2 for 393 g or 73.5% emission loss. The measured total emission was comparable to values reported in the literature such as $64 \pm 10\%$ found in Yates *et al.* (1996a) using micrometeorological methods. Difference in measured emission loss between the two replicated chambers may be attributed to variations in film thickness, as indicated by Yagi *et al.* (1993).

The flux variation followed a diurnal pattern in the first 3 days when the flux density was the highest. The diurnal change was attributed to temperature effect on MeBr diffusion coefficient in soil-air phase, its Henry's partition ratio between soil-air and soil-water, and temperature dependency of MeBr diffusion through the polyethylene film.

Measured Br^- concentration increase accounted for 534 g or 44.4% of the applied MeBr (Fig. 5). The reduced degradation was attributed to the increased emission flux and reduced MeBr residence time in the soil, compared to the 60 cm application. The mass balance was 104.7 and 117.9% for the two replicated chambers, respectively. The average mass balance error was 11.3% which is in the same error range of meteorological methods (Yates *et al.*, 1996a).

Based on the calibration and field testing results, we believe this design and system configuration of the dynamic chamber can provide accurate emission assessment for highly volatile chemicals such as MeBr under field conditions.

Acknowledgements—This research was sponsored by the USDA Cooperative State Research Service Agreement no. 92-34050-8152. The authors would like to thank Ms Q. P. Zhang and R. LeMert for analyzing MeBr and bromide ion samples in the laboratory.

REFERENCES

- Butler, J. H. (1996) Scientific uncertainties in the budget of atmospheric methyl bromide. *Atmospheric Environment* **30**, i–iii.
- Christensen, S., Ambus, P., Arah, J. R. M., Clayton, H., Galle, B., Griffith, D. W. T., Hargreaves, K. J., Klemmedtsson, L., Lind A.-M., Maag, M., Scott, A., Skiba, U., Smith, K. A., Welling, M. and Wienhold, F. G. (1996)

- Nitrous oxide emission from an agricultural field: comparison between measurements by flux chamber and micrometeorological techniques. *Atmospheric Environment* **30**, 4183–4190.
- Denmead, O. T. (1979) Chamber systems for measuring nitrous oxide emission from soils in the field. *Soil Science Society of America Journal* **43**, 89–95.
- Eklund, B. (1992) Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. *Journal of the Air and Waste Management Association* **42**, 1583–1591.
- Gan, J., Yates, S. R., Spencer, W. F. and Yates, M. V. (1995) Optimization of analysis of methyl bromide on charcoal sampling tubes. *Journal of Agriculture and Food Chemistry* **43**, 960–966.
- Gao, F., Yates, S. R., Yates, M. V., Gan, J. and Ernst, F. F. (1997) Design, fabrication and application of a dynamic chamber for measuring gas emissions from soil. *Environmental Science and Technology* **31**, 148–153.
- Majewski, M. S., McChesney, M. M., Woodrow, J. E., Prueger, J. H. and Seiber, J. N. (1995) Aerodynamic measurements of methyl bromide volatilization from tarped and nontarped fields. *Journal of Environmental Quality* **24**, 742–752.
- Matthias, A. D., Blackmer, A. M. and Bremner, J. M. (1980) A simple chamber technique for field measurement of emission of nitrous oxide from soils. *Journal of Environmental Quality* **9**, 251–256.
- Mosier, A. R. (1990) Chamber and isotope techniques. In *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*, eds M. O. Andreae and D. S. Schimel, pp. 175–187. Wiley, New York.
- Rolston, D. E. (1986) Gas flux. In *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*, ed. A. Klute, 2nd Edn., pp. 1103–1119. ASA, SSSA, Madison, Wisconsin.
- Singh, H. B. and Kanakidou, M. (1993) An investigation of the atmospheric sources and sinks of methyl bromide. *Geophysical Research Letters* **20**, 133.
- Valente, R. J., Thornton, F. C. and Williams, E. J. (1995) Field comparison of static and flow-through chamber techniques for measurement of soil NO emission. *Journal of geophysical Research* **100**, 21,147–21,152.
- Wang, D., Yates, S. R. and Gan, J. (1997) Temperature effect on methyl bromide volatilization in soil fumigation. *Journal of Environmental Quality* (in press).
- Woodrow, J. E. and Seiber, J. N. (1991) Two chamber methods for the determination of pesticide flux from contaminated soil and water. *Chemosphere* **23**, 291–304.
- Yagi, K., Williams, J., Wang, N. Y. and Cicerone, R. J. (1993) Agricultural soil fumigation as a source of atmospheric methyl bromide. *Proceedings of the National Academy of Science* **90**, 8420–8423.
- Yates, S. R., Gan, J., Ernst, F. F., Mutziger, A. and Yates, M. V. (1996a) Methyl bromide emissions from a covered field II. Volatilization. *Journal of Environmental Quality* **25**, 192–202.
- Yates, S. R., Gan, J., Ernst, F. F. and Wang, D. (1996b) Methyl bromide emissions from a covered field III. Correcting chamber flux for temperature. *Journal of Environmental Quality* **25**, 892–898.