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Agricultural soil fumigation as a source of atmospheric methyl bromide

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ABSTRACT **Methyl bromide (MeBr) is used increasingly as a biocidal fumigant, primarily in agricultural soils prior to planting of crops. This usage carries potential for stratospheric ozone reduction due to Br atom catalysis, depending on how much MeBr escapes from fumigated soils to the atmosphere and on details of atmospheric chemical reactions. We present direct field measurements of MeBr escape; 87% of the applied MeBr was emitted within 7 days after a commercial fumigation. Covering the field with plastic sheets retarded MeBr escape somewhat but first-day losses were still 40%; thicker sections of sheets were relatively more effective than thin sections. We also measured gaseous MeBr concentrations versus depth in the soil column; these profiles display diffusion-like evolution. In soil, MeBr is partitioned among gas, liquid, and adsorbed solid phases. Calculated soil inventories agreed only roughly with applied amounts, probably due to nonequilibrium partitioning (during the first 30 min) and to uncertainties in partitioning coefficients. Fumigated fields may release less MeBr if they are covered by more gas-tight plastic films, if injection techniques are improved and injection is deeper, and if soil moistures, organic amounts, and densities are greater than in the soil studied here.**

Stratospheric ozone is being reduced, evidently by chemical reactions driven by chlorine and bromine (1). Largest losses are observed over Antarctica, extending north to 60° south. Smaller but significant decreases are also seen at middle and high latitudes in both hemispheres (2). Although the evidence of chlorine-driven ozone destruction is much more abundant than for bromine, a very high efficiency of ozone destruction by bromine has been theorized by Yung *et al.* (3) who also noted that the reaction $ClO + BrO \rightarrow Br + Cl + O_2$ becomes more important as atmospheric chlorine amounts increase. Indeed, the potential for ozone destruction per Br atom in the stratosphere may be 30–60 times that for a Cl atom (4). Br atoms are carried upward into the stratosphere in organic molecules such as MeBr and the two halons, CF_3Br and CF_2BrCl; stratospheric photooxidation of these organic compounds releases Br atoms.

The contribution of halons to the bromine flux, F_s, that enters the stratosphere is relatively well known (7.2×10^6 kg of Br per year in 1990) because the halons are totally synthetic, their industrial production and emission rates are known and they are inert in the troposphere (5, 6).

The contribution from MeBr to F_s, on the other hand, is poorly quantified at present. Natural sources, principally oceanic surface waters, are known to inject MeBr into surface air but are not well quantified (7, 8). Currently, the global atmospheric content, B, of MeBr is $2 \pm 0.5 \times 10^8$ kg. If reaction with tropospheric OH radicals (7–9) is its major sink, the atmospheric residence time, T, for MeBr is 2 ± 0.5 years. In an assumed quasi steady state, the total surface source = B/T or 0.6 to 1.7×10^8 kg/year (7–9). While much of the MeBr upward flux may be removed by tropospheric OH, thus limiting its contribution to F_s, the amount that reaches the stratosphere may still exceed the contributions from CF_3Br and $CBrClF_2$.

Concern arises over synthetic MeBr because its worldwide industrial usage has increased from 4.2×10^7 to 6.3×10^7 kg/year between 1984 and 1990; these figures exclude MeBr used as a chemical intermediate. Eighty percent of this usage is as an agricultural soil fumigant prior to planting (10). MeBr is a broad-spectrum fumigant biocide against arthropods, weeds, nematodes, fungi, and bacterial pests, apparently cost effective when applied to soils before planting; it is being used in many countries (10). Thus there is a significant and growing potential for atmospheric MeBr to increase, depending on the fraction of MeBr that escapes from soils during and after fumigations and on the size of the natural sources (7, 8). In soils, MeBr may be removed by physical hydrolysis, adsorption to soil particles, and microbiological and transport processes (11, 12). Moisture and organic matter in soils should enhance dissociation rates but it is very difficult to estimate how much MeBr will be decomposed in these ways or through biological cleavage, and hence, how much will escape from soils. Direct measurements are needed.

Field Preparation

We conducted a field-fumigation experiment to determine the fraction of the applied MeBr that escapes and to investigate the factors that control this fraction. The study was conducted in a field that was being prepared for commercial strawberry growing near Irvine, California on September 10–17, 1992. MeBr was applied to the field by the personnel and equipment of a professional fumigant applicator; a tractor-pulled device injected liquid MeBr through 10 shanks placed ≈25 cm apart, to a depth of ≈25–31 cm. The fumigant mixture consisted of 75% MeBr/25% chloropicrin (CCl_3NO_2) by weight. The desired rate was 275 pounds (1 pound = 453.6 g) of mixture per acre (308 kg/ha; 1 ha = 1×10^4 m^2) but a portion of the field that contained our study site actually received about 305 pounds/acre (342 kg/ha), or 25.6 g of MeBr per m^2. This higher figure was estimated after the application by the professional applicator and it may still be inexact. It is apparently common for flow rates to deviate from programmed values and for this to be discovered after an initial area is fumigated.

Simultaneously, the application device also laid a continuous sheet of plastic over the fumigated soil. The film was of low-density polyethylene (nominal thickness, 0.00254 cm). While laying a sheet, the device applied glue to the edge of the previous sheet and pressed the parallel overlapping edge of the next sheet to seal the seam. The transverse edge of the plastic sheet at the end of each tractor pass was sealed by overfilling large amounts of soil. The usage of these relatively gas-tight films is intended to minimize MeBr emissions and to increase the effectiveness of smaller dosages of MeBr (13). Adjacent parallel sheets overlapped by ≈23 cm and these overlapping edges were sealed by glue. It is common to leave

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the plastic film in place for ≈2 days; in this experiment it was removed 95 h after placement. Table 1 describes the site and its soil.

Flux Measurements

After the MeBr application, we measured its flux from the soil and its concentration versus depth in the soil. Four flux chambers with removable lids were used to measure the fluxes from the surface before and after film removal. Chambers were right circular cylindrical sections of polyvinylchloride pipes (i.d., 30 cm; o.d., 32 cm; vol, 13 liters). For each flux measurement, an initial air sample was taken from inside the open-topped chambers, then the tops were placed, and the buildup of MeBr inside the chambers was monitored by sampling after 10 and 20 min. Removable lids were tightly fitted rims of the same material with tedlar tops. The four chambers were placed at four sites ≈1 m apart; they were sealed on top of the plastic film for the first 95 h after fumigation and then placed into the soil directly below when the film was removed. When the chambers were in place their inside heights were 16–19 cm. Samples were obtained by connecting preevacuated stainless steel cannisters (500 ml) through ultra-torr fittings to steel tubes inside the chambers and were analyzed by flame-ionization gas chromatography using a 105-m 0.53-mm (o.d.) Vocol column.

Our calibration standard is a commercially prepared mixture (Scott Specialty Gases, Plumsteadville, PA) certified to be 49.96 ± 0.50 ppm by volume in pressurized N_2. Two methods were used to inject the standard gas into the column. In one, a known volume of sample was preconcentrated in a glass-bead-packed stainless steel loop at 77 K by pumping away O_2 and N_2. In a direct injection method, the injection loop (2.78 ml) was filled to various pressures with standard gas and onto the analytical column with no preconcentration; pressures were measured with an Edwards Laboratories (Wilmington, MA) barocel absolute pressure transducer. The flame-ionization detector response to MeBr in the range of 1.5–540 μg was quite linear for both the preconcentration and direct injection methods, and data from both methods produced the same calibration line. Field samples taken from the flux chambers were analyzed by the preconcentration method; replicate analyses agreed to within 2%.

Fig. 1 shows the average value of the four fluxes plotted versus time elapsed after the fumigation. Open circles above and below the averages represent the maximum and minimum flux observed at each of the 14 times. Also shown in Fig. 1 is the cumulative emission of MeBr (percent of total applied). During the first 4 days (95 h), emissions were 78% of the applied amount. The second peak occurred between 4 and 4.5 days, just after the polyethylene film was removed. After 7 days, ≈87% of the initially applied MeBr had escaped. The question of validity of this high fraction is discussed below. The highest fluxes observed before film removal were always from the same location and chamber. Fig. 2 shows

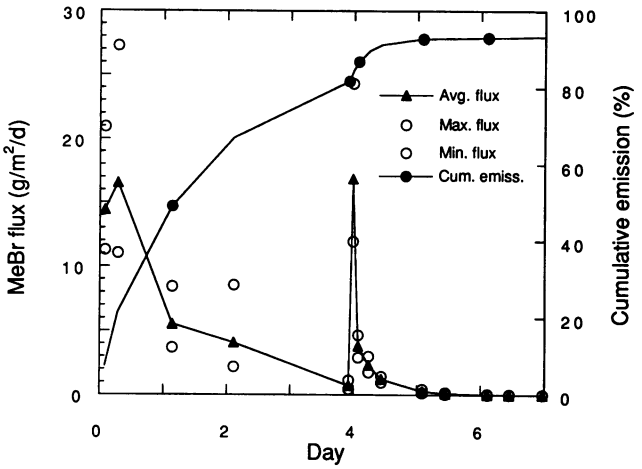

FIG. 1. Left ordinate: fluxes to the atmosphere measured for 7 days after a MeBr soil fumigation. Polyethylene sheets (see text) covered the field for the first 95 h. The solid line connects average of observed fluxes from four subsites; the full range around these averages is indicated (○). Largest fluxes were observed during the first day (d) and immediately after removal of the sheets (end of day 4). Right ordinate: cumulative emission as a percent of initially applied MeBr (25.6 g or 270 mmol of MeBr per m^2). Corrections for area covered by two thicknesses of sheets reduce cumulative emission by 4% (see text).

that film thickness controlled emissions. When the polyethylene film was removed from the field, we saved the circular sections (area, 800 cm^2) that were under the four flux chambers and measured their thicknesses with a micrometer at 10 positions. The thinnest portion of film (1.03 mil or 0.00262 cm) permitted emissions more than twice as large as the thickest portion (1.6 mil). We also found ≈60% less emission from the strips where two sheets of film overlapped and were glued (as described above); such strips covered 7% of the total area of the field. Therefore, we subtract 4% from the final cumulative emission (91%) shown in Fig. 1 to obtain a total loss of 87%.

Soil–Gas Measurements

Concentrations of MeBr in soil gases were measured at five depths (Fig. 3), as follows. Gas samples were extracted from soil-sampling tubes with gas-tight syringes. Tubes with solid concentric rods were hammered into the soil at four sites ≈2 m apart. When the tubes were in place the solid rods were removed. The tube at 10 cm was 1/16 inch stainless steel (1 inch = 2.54 cm) while those at greater depths were 1/8 inch i.d. and 1/4 inch o.d. To the upper ends of the tubes were attached septa within a steel fitting and the sample was obtained as in ref. 14. Gas-tight syringes transferred 5-ml samples to 117-ml serum bottles (with 5 ml of air withdrawn previously), capped with high-density septa. Analysis fol-

Table 1. Some physical and chemical properties of the soil (Sorrento loam) at the study site

Depth, cm	Bulk density, g/cm^3	Total porosity, cm^3/cm^3	Volumetric water content, cm^3/cm^3	Total carbon, %	Total nitrogen, %	pH (1:1 water)
4	1.33	0.497	0.044	0.58	0.053	6.1
10	1.33	0.498	0.089	0.34	0.032	6.2
20	1.47	0.445	0.115	0.38	0.040	6.2
30	1.63	0.385	0.148	0.42	0.041	6.4
60	1.80	0.321	0.181	0.37	0.029	6.4
90	1.74	0.346	0.161	0.15	0.014	6.7

The Sorrento series consists of well-drained soils on alluvial fans and flood plains, formed in alluvium derived from sedimentary rocks. The fumigated field was ≈17 ha in area. Flux and soil measurements were made in a subarea of ≈100 m^2, 25 m from one edge of the field.

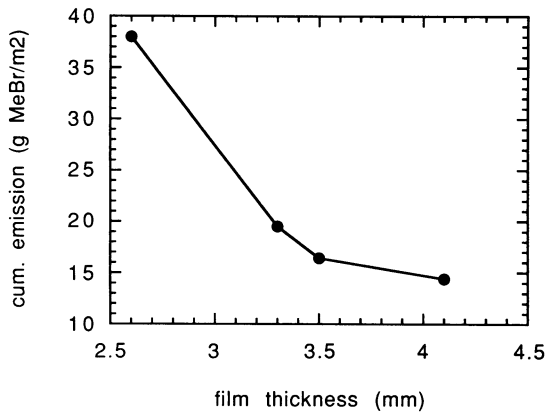

FIG. 2. Measured cumulative (cum) MeBr emissions from the time of fumigation until removal of the polyethylene film (95 h) from four sites on the film, plotted versus the thickness of the film at each site. Measured thicknesses (mean ± SD) were 1.03 ± 0.20, 1.29 ± 0.18, 1.37 ± 0.08, and 1.60 ± 0.26 mil. Emissions from the thinnest section exceeded the initial application rate, implying lateral transport of MeBr under the film.

lowed several hours later after transport to the laboratory. Storage tests assured reliability over longer periods. Analysis was by flame-ionization gas chromatography, direct injection onto a six-foot OV-101 column, 1/8 inch o.d.

Results appear in Fig. 3. Initial concentrations were highest at 20 and 30 cm, nearest the depth of injection. Upward transport caused the concentrations at 10, 20, and 30 cm to be nearly equal after 1 day (Table 1 shows that soil density decreases toward the surface). At depths below 30 cm, transport was slower. Highest concentrations were observed at 60 cm after 1 day and at 90 cm after 2 days. Concentrations were equal above 60 cm after ≈2 days and were nearly uniform after 4.5 days. Soil gas concentrations after film removal are shown in Fig. 3 *Inset*. In the upper 30 cm, concentrations decreased rapidly in the first 12 h after removal (much of the decrease from day 4.0 to day 4.5 was due to escape to the atmosphere as Fig. 1 shows). The maximum soil concentration was at 60 cm at that time.

These soil–gas measurements are useful to permit a fuller understanding of the physical, chemical, and biological processes in the soil and for a calculation of the soil inventory of MeBr versus time. Fig. 4 shows soil–column integrals of measured gaseous MeBr amounts along with amounts that we calculated to be in liquid phase with the water contents shown in Table 1. Liquid amounts were calculated from gas–liquid partitioning coefficients based on data from ref. 15, the water contents in Table 1, and measured soil temperatures. Partitioning into solid phase was ignored, mostly because available data for water–soil partitioning are disparate (16) and partitioning may depend strongly on soil organic matter type and amount. While the amount of MeBr initially applied was ≈25.6 g/m^2, we found only ≈13.5 g/m^2 in the soil as a gas (including 0.55 g/m^2 in the air under the film but above the soil) at the time of our first measurements, 30 min after application. Calculated soil liquid amounts 30 min after fumigation were 19.8 g/m^2, for a total of 33.3 g/m^2, which is more than was thought to be applied. Several explanations are possible: (*i*) gas–water equilibrium had not been reached by the time of first measurement; (*ii*) >25.6 g of MeBr, possibly 34 g/m^2, was applied; (*iii*) the gas–water partitioning coefficient is erroneously biased toward liquid [note, for example that Haight (15) found less partitioning from gas into fruit juices than into pure water]; (*iv*) spatial variability rendered our sites unrepresentative; and (*v*) there was substantial MeBr in the soil before the fumigation (unlikely because MeBr vanishes after 7 days in Fig. 3).

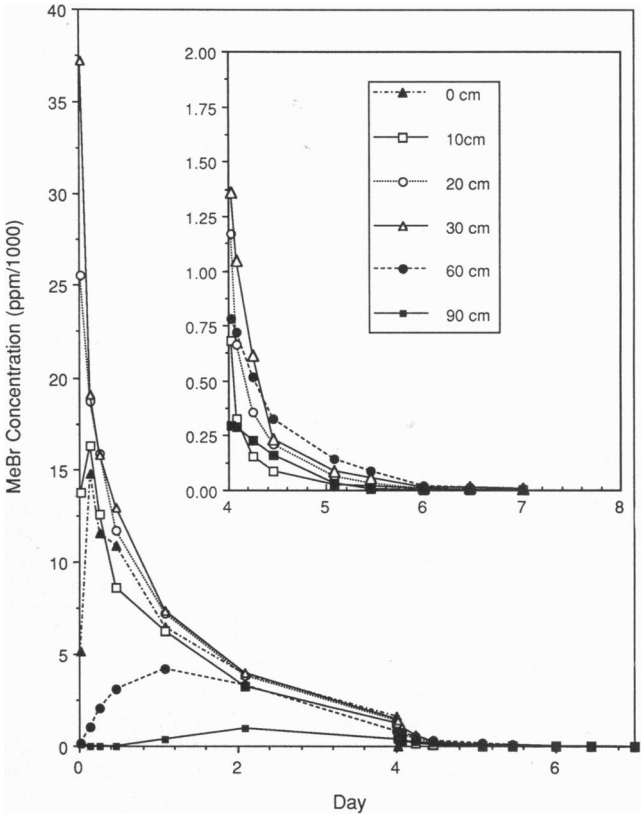

FIG. 3. Concentrations (units, thousands of parts per million by volume) measured at five depths in the soil (averages of four subsites) for 7 days after a MeBr soil fumigation. Initial injection was at 25–31 cm depth. (*Inset*) Results for times after plastic sheets were removed from soil. Zero depth represents samples from the air space between the plastic film and the soil surface (first 95 h only).

Discussion and Conclusions

To summarize the measurements, directly observed fluxes from the soil to the atmosphere, extrapolated to the entire field, amounted to 87% of the total MeBr applied, a higher fraction than is currently assumed (7, 8) but similar to data from greenhouse studies with relatively permeable films (17). If correct, this 87% loss to the atmosphere may also be due

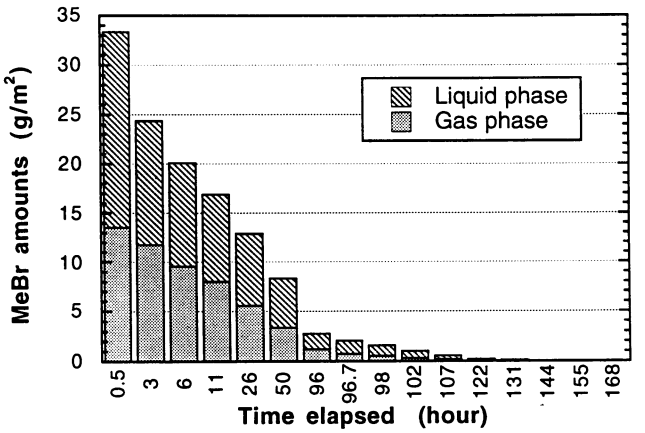

FIG. 4. Measured gaseous MeBr amounts in the soil column (integrals of depth profiles in Fig. 3) and calculated liquid-phase amounts versus time elapsed after fumigation, assuming equilibrium between phases and partitioning as for pure water. Total amount at 0.5 h exceeds amount applied to the soil by 30% (7.7 g of MeBr per m^2) possibly due to transient disequilibrium between phases and salting out effects in soil water (see text).

to the low soil contents of water and organic matter (Table 1) at our site. But our estimated loss may be erroneously high if the amount applied was higher than believed (due to metering errors of the applicator described earlier) or if our sites were not representative because of spatial variations in the soil or the plastic film thickness, for example. The result can be challenged further because the inventory of MeBr calculated from measurements made 0.5 h after fumigation (Fig. 3) exceeds 25.6 of MeBr per m^2. It would be much more satisfactory if the initial inventory calculated from soil measurements were equal to the amount applied. Calculated amounts would equal applied amounts if initial liquid amounts were reduced 40%, either by salting out effects in soil water [as suggested by Haight (15) for impure water] or by lack of gas–liquid equilibrium 30 min after injection. This latter possibility is likely because soil MeBr inventory decreases between days 4 and 7 are within 5% of the measured emissions for that period. Specifically, from day 4.0 through day 7, the directly observed emissions (Fig. 1) were 2.78 g of MeBr per m^2 and the change in soil inventory (Fig. 4) was 2.63 g.

Because it is important to determine accurately the global emissions of MeBr, we emphasize the need for accurate measures of amounts applied per unit area, soil water contents, temperatures, and soil organic parameters. It is also necessary to account for spatial variability in soil conditions and film thickness. Continued significant cooperation from commercial applicators and farmers is needed because the use of representative sites and of modern large-scale fumigation equipment is essential. Also, more reliable gas–liquid partition coefficients are needed to permit accurate calculations of soil MeBr inventories, as is attention to adsorption on solids. Agricultural industry efforts to minimize emissions into the atmosphere can be based on deeper injections, better injection techniques, and the use of less-permeable films and smaller doses (13).

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