METHYL BROMIDE VOLATILIZATION AND DOWNWIND FATE

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There has been a growing concern over the role methyl bromide may play in stratospheric ozone depletion, partly because of the fact that bromine, one source of which is the photochemical conversion of methyl bromide, is 20-60 times more active than chlorine in depleting ozone (Mellouki et al., 1993). As a result, methyl bromide has been categorized as a Class 1 ozone-depleting chemical by the US EPA, and the United Nations Environmental Program has called for at least a 25% reduction in its worldwide use, if not an outright ban, by the year 2000 (UNEP, 1992).

An important anthropogenic source of methyl bromide emissions to the atmosphere is agriculture. Its use as a pre-plant soil fumigant for the control of nematodes, soil-borne pathogens, weeds, and other biological pests accounts for about 80% of all the methyl bromide uses worldwide (about 63 million kg in 1990 [Andersen and Lee-Bapty, 1992]). It has been shown that at least one-third, and perhaps more, of the one million-plus kg of methyl bromide applied as a soil fumigant in California volatilizes, even when it is injected into the soil and confined with a plastic tarp (Yagi et al., 1993, 1995; Majewski et al., 1995).

An important consideration in discussions concerning methyl bromide is the possible role sinks might play in reducing the mixing ratios of this material in the atmosphere and thus possibly reducing its mixing ratios and ozone-depleting potential in the stratosphere. Possible sinks include the following: 1) Chemical/photochemical breakdown; 2) wet deposition in rain and fog water; and 3) dry deposition of vapors. We conducted downwind sampling of methyl bromide volatilizing from a tarped 15.6 ha field commercially treated by Tri-Cal, Inc., with 392 kg/ha of Tricon (67% methyl bromide/33% chloropicrin) under relatively dry conditions (i.e., no rain or fog), focusing on possibility 3). Possibility 2) was not considered in this design, and other investigators have provided evidence that possibility 1) is negligible, at least in localized application-release situations. To help discern the importance of 3), we sampled air through charcoal-filled glass tubes (average of 100 ml/min, 4 hours for each sampling period) attached to multiple-height flux masts placed at several locations, including near the center of the field and at several downwind locations (Figure 1), and measured concentration profiles were compared with those predicted by a computer-based dispersion model. Furthermore, we assayed surface samples of downwind soil for methyl bromide and related the measured residues to airborne concentrations over the soil.

The concentration profiles for methyl bromide in air at a station 5 meters downwind from the edge of the treated field showed, in general, a decrease with height up to 2 meters, whereas further downwind (139 and 441 meters from the edge of the field) the concentration profiles, in general, showed little change or a slight increase with height up to 2 meters. Using the meteorological data from the field and the vertical flux as the source strength in the US EPA's SCREEN-2 dispersion model, we obtained methyl bromide concentration profiles for the downwind stations that showed a marked decline in concentration with height. This makes sense in light of the fact that the source for methyl bromide was at ground level and as a result of this concentrations would be greatest near the ground. Comparing the modeled concentration profiles with our field results suggest that some methyl bromide may have been removed by the soil/plant surfaces located in the intervening distance between the treated field and the downwind stations (Figure 2). This possibility is further emphasized by employing a technique first reported by Parmele et al. (1972), who determined horizontal flux off-site by obtaining the product of concentration and wind speed at several heights. Using our field and model concentrations and measured wind speeds from the field, horizontal flux profiles were quite different for the modeled and field results (Figure 2). The SCREEN-2 model, which does not allow for sinks, indicated that horizontal flux does not change with height (i.e., a vertical line), whereas horizontal flux profiles based solely on the field data indicated a definite increase with height in most cases. Parmele et al. (1972) saw field profiles similar to ours and concluded that the surfaces downwind of the treated field had adsorbed some of their test pesticides from the overlying plume.

Parmele et al. (1972) obtained support for their supposed downwind terrestrial sinks when they analyzed downwind surfaces (i.e., bare soil and straw-covered soil) and found residues of their test pesticides. Using a gas chromatographic headspace technique applied to the air samples (Majewski et al., 1995) (i.e., benzyl alcohol elution of soil samples in sealed headspace vials), our own analyses of dry surface soil taken near the downwind air sampling stations showed the presence of methyl bromide, confirmed by mass spectrometry, at levels in the range 15-150 $\mu g/m^2$. These results were compared to those of an earlier study (Chisholm and Koblitsky, 1943) where surface concentrations at equilibrium were about 2.5 g/m^2 for dry sand, 6.5 g/m^2 for dry clay soil, and 10.5 g/m^2 for dry peat at a methyl bromide partial pressure of about 6.68 torr. Assuming Langmuir adsorption, where the amount of adsorbate on the adsorbent is proportional to the adsorbate partial pressure, and taking a mid-point between sand and clay (i.e., 4.5 g/m^2) for a sandy clay with an organic matter content of about 1-3%, we used a simple proportionation between our field data and the data of the cited study to calculate a concentration range for methyl bromide in field air. Based on our dry soil residue results, the air concentrations responsible for these observed residues fell in the range 100-1,000 $\mu g/m^3$, which compared with the observed air concentrations for the first few sampling periods of the study. Comparing our soil concentrations with our air concentrations and using a plume height of 10 meters at the downwind edge of the field, the soil concentrations represented about 1.5% of the methyl bromide in the plume.

Preliminary results from downwind soil analysis and the concentration and horizontal flux profile shapes for methyl bromide in air at the downwind stations suggest the action of terrestrial sinks to remove some methyl bromide from the overlying plume. However, adsorption of methyl bromide from a plume by soil, and plant surfaces as well, will need to be confirmed with future sampling and analysis in both the field and the laboratory. We accomplished part of this during the 1995 season in a field study that involved sampling air using an array of masts at increasing distances over bare soil downwind of a treated field. Along with the air samples, both bare soil and plant samples, taken from strawberry plants placed near the air sampling stations, were taken for methyl bromide and bromide ion analysis, which is in progress.

References

Andersen, S.O., and S. Lec-Bapty. **1992**. Methyl Bromide Interim Technology and Economic Assessment, United Nations Environment Program.

Chisholm, R.D., and L. Koblitsky. **1943**. Sorption of methyl bromide by soil in a fumigation chamber. *J. Econ. Entomol.*, 36:549-551.

Majewski, M.S.; M.M. McChesney; J.E. Woodrow; J.H. Pruger; and J.N. Seiber. **1995**. Aerodynamic measurements of methyl bromide volatilization from tarped and nontarped fields. *J. Environ. Qual.*, 24(4):742-752.

Mellouki, A.; R.K. Talukdar; and C.J. Howard. **1993**. Abstract submitted to the Methyl Bromide Global Coalition, State of the Science Workshop, 28 October, Washington, D.C.

Parmele, L.H.; E.R. Lemon; and A.W. Taylor. **1972**. Micrometeorolgical measurement of pesticide vapor flux from bare soil and corn under field conditions. *Water Air Soil Pollut.*, 1:433-451.

UNEP. United Nations Environment Program. **1992**. Montreal Protocol Synthesis Report of the Methyl Bromide Interim Scientific Assessment and Methyl Bromide Interim Technology and Economic Assessment.

Yagi, K.; J. Williams; N.Y. Wang; and R.J. Cicerone. **1993**. Agricultural soil fumigation as a source of atmospheric methyl bromide. *Proc. Natl. Acad. Sci. USA*, 90:8420-8423.

Yagi, K.; J. Williams; N.-Y. Wang; and R.J. Cicerone. **1995**. Atmospheric methyl bromide (CH_3Br) from agricultural soil fumigations. *Science*, 267:1979-1981.

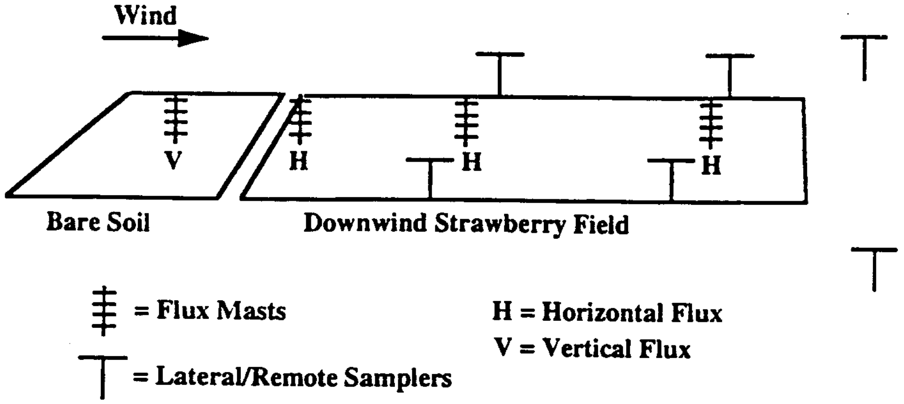

Figure 1. Field layout for the determination of methyl bromide evaporative flux and downwind concentrations.

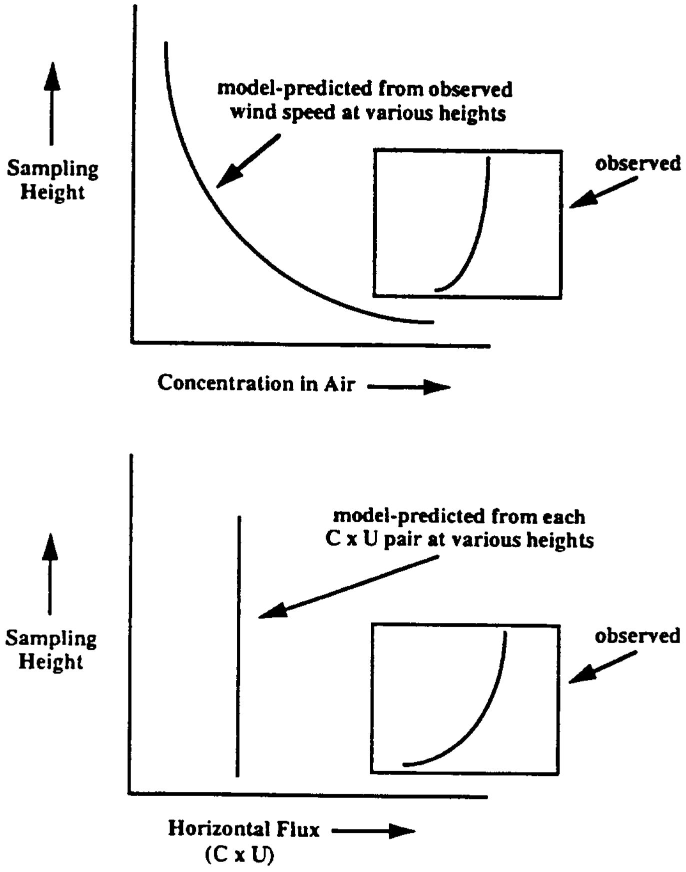

Figure 2. Model-predicted and observed profile shapes for concentration and horizontal flux vs sampling height for downwind stations.