EXECUTIVE SUMMARY
of Report EH 99-02 Entitled

Evaluation of Charcoal Tube and SUMMA Canister Recoveries for Methyl Bromide Air Monitoring

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Hazards Assessment Program

PURPOSE

The Department of Pesticide Regulation (DPR) Environmental Hazards Assessment Program (EHAP) compared two sampling methods, charcoal tubes and SUMMA canisters, for measuring concentrations of methyl bromide in ambient air under varying relative humidity (RH) and methyl bromide concentration conditions. This study was conducted to determine the accuracy of the charcoal tube method and to compare that method to the SUMMA canister method.

BACKGROUND

Methyl bromide is a gas used as a pesticide to control structural and stored commodity pests, and as a preplant soil fumigant to control fungi, insects, nematodes and weeds. It is used extensively in California.

A review of animal studies conducted to evaluate various health effects showed that exposure to methyl bromide in air has the potential to cause neurotoxic and developmental effects. As a result, methyl bromide use practices have been modified to ensure that people will not be exposed to concentrations of methyl bromide in air above a level that is at least 100 times lower than the safe exposure level determined by animal studies. One use practice requires methyl bromide users to maintain specified buffer zones between sites of application and residences, workplaces (including adjacent crop sites), hospitals, schools, and other places where people congregate. Accurate measurements of methyl bromide concentrations in ambient air are essential to establish buffer zones sufficient to protect human health.

Concentrations of methyl bromide in air are currently determined by trapping methyl bromide on charcoal in a tube, extracting it from the charcoal with a solvent and analyzing the resulting liquid with a gas-chromatograph. This charcoal tube method is used because it has been the National Institute of Occupational Safety and Health-approved method since 1975. The SUMMA canister method, which was developed by the U.S. Environmental Protection Agency in the mid-1980s, uses a stainless steel canister under vacuum which, when opened, collects an air sample that is then analyzed directly with a gas-chromatograph.

This study was conducted to quantify the effects of temperature, RH, and methyl bromide concentration on the charcoal method performance and to determine whether using the SUMMA canister method would yield more accurate results.

STUDY METHODS

To test the effectiveness of the two sampling methods, a laboratory system was set up so that a known concentration of methyl bromide in air was being sampled. As with any sampling or testing system, there are a number of uncertainties which must be considered when interpreting results. In this instance, the uncertainties involved the device that controlled the flow of gas; the calibration equipment; the flow of air over the samplers; the amount of time the samplers ran; the pressure within the SUMMA canisters; and the concentration of methyl bromide in the test tank (the stated concentration may vary slightly from the actual concentration). Some of these variabilities are clearly delineated and specified by the manufacturer of the equipment in question; others can be measured. Preliminary tests showed that for SUMMA canisters, the variabilities may result in a discrepancy of as much as 27 percent; for charcoal tubes, the discrepancy may be as high as 15 percent. The higher uncertainty for the SUMMA canister samples is not inherent in the technology, but rather resulted, in part, from the fact that the canisters were set to sample in a manner typical of the way they are used in the field (rather than to minimize variability).

Preliminary tests were run to test the effect of RH on methyl bromide recoveries using charcoal tubes compared to using a Fourier Transform Infrared (FTIR) spectrometer analytical method. The FTIR method is considered the most accurate method for measuring levels of methyl bromide in air in a controlled indoor setting but to date it has not been successfully used under field situations. In addition, a storage stability test was performed to determine whether collecting methyl bromide samples and storing them would impact analytical results using the charcoal tube method. (Storage stability data were already available for the SUMMA canister method.)

Methyl bromide recoveries (the percent of a known amount of methyl bromide detected by a method) using charcoal tubes versus SUMMA canisters were compared at three methyl bromide concentration levels (about 35, 210, and 2300 ppb) each sampled at three RH levels (about 20, 50 and 80 percent) for a total of nine concentration/humidity combinations. These levels were based on the range of values seen in previous field studies.

Statistical analyses were performed on storage stability and concentration/RH combinations. Charcoal tube versus SUMMA canister method recoveries at varying methyl bromide concentrations were compared for samples collected in the laboratory versus samples collected from five previously conducted EHAP field monitoring projects in which the two sampling methods were collocated.

RESULTS AND DISCUSSION

RH comparisons. The preliminary RH tests indicated that charcoal tubes do not perform well at RHs of less than 10 percent and greater than 90 percent. Although of scientific interest, field sampling is unlikely to be conducted under these extreme RH conditions.

Effect of storage. Days of storage had no significant effect on recovery for any of the four combinations of concentration and RH for the two sampling methods.

<u>Effect of methyl bromide concentration and RH.</u> For charcoal tubes, the higher the concentration, the higher the recovery (eight percent more methyl bromide was recovered at the higher concentration sampled). There was no effect of humidities typical of field conditions on recovery.

<u>Effect of sampling method on recovery.</u> There was a significant difference between mean recoveries for the two sampling methods. The mean recovery of the charcoal tube method was 49 percent and of the SUMMA canister method, 78 percent.

<u>Charcoal tube versus the SUMMA canister method.</u> As discussed above, testing the two sampling methods in the lab introduces variabilities not present in actual field sampling. These variabilities lead to discrepancies between the results in the lab compared to actual recovery in the field. These discrepancies should be factored into laboratory recovery rates to arrive at a better approximation of actual recovery in the field.

SUMMA recovery: The uncorrected recovery rate for SUMMA canisters was 78 percent. Factoring in a 27 percent uncertainty factor results in a potential recovery rate close to 100 percent. (Average recovery was lower, but could be the result of bias in the sample preparation procedures.)

Charcoal tube recovery: The uncorrected recovery rate for charcoal tubes was 49 percent. Factoring in a 15 percent uncertainty factor results in a potential recovery rate of 56 percent. That means the actual average recovery by the charcoal methods is not likely to be more than the 56 percent of the total method bromide sampled. This result was substantiated using independent data collected in actual DPR field monitoring where both methods were collocated during sampling.

Statistical analysis indicated that recoveries from the charcoal tube are consistently lower than recoveries from the SUMMA canister.

<u>Quality control</u>. Laboratory testing equipment is checked by spiking a charcoal tube or SUMMA canister with a known amount of methyl bromide. This study showed

that these laboratory-internal quality control spikes are not a good measure of sampling method performance under field conditions because the quality control procedures only address laboratory analytical factors, not sampling, storage and other effects occurring before the samples arrive at the laboratory.

Sampling intervals. Under the field conditions, recoveries were much lower from sampling done with charcoal tubes for six hour periods during the day than during twelve hour periods at night.

CONCLUSIONS

Under conditions typical of field situations, the average recovery was 49 percent for the charcoal tubes and 78 percent for the SUMMA canister. To account for these differences, DPR will review air concentrations listed in past studies and make appropriate adjustments, and will review the methyl bromide sampling methodology used in future studies.

The time samples are stored between collection and analysis had no impact on methyl bromide recovery for either sampling method.

Laboratory-internal control spikes should not be used as a correction factor for samples collected in the field.

The fact that 6-hour sampling with charcoal tubes during the day recovered less methyl bromide than 12-hour sampling with charcoal tubes at night needs further study.