
SHORT COMMUNICATIONS

Sampling Mast for Measuring Volatile Organic Compounds in the Near-Surface Atmosphere

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Abstract

Accurate measurement of the atmospheric concentration of volatile organic compounds is essential when estimating the emission rate from the soil surface or in studies relating to worker exposure to volatile compounds. For estimating the surface flux, many methods are available which, in general, require profiles of the concentration during the experimental period. For example, the aerodynamic and the integrated horizontal flux methods require precise determination of the atmospheric concentration so that either the concentration gradients or the concentration profiles can be obtained. The accuracy of this information has a direct effect on the accuracy of the flux measurements. The proposed air sampling device provides a suitable method for measuring the atmospheric concentration of volatile compounds. Two designs are illustrated along with a description of their construction and operation. Their use is illustrated with concentration profiles observed in the field.

VOLATILIZATION is an important pathway for loss of organic chemicals from land surfaces (Taylor, 1978; Cliath et al., 1980; Spencer and Cliath, 1990), and is an especially important mechanism affecting transport to the atmosphere for highly volatile pesticides such as 1,3-D and methyl bromide (Albrecht and Chenchin, 1985; Basile et al., 1986; Gentile et al., 1992). Volatilization of organic chemicals during their use, or following their disposal is an important source of organic pollutants to the atmosphere.

When an organic chemical is mixed into the soil, volatilization involves desorption of the chemical from the soil, movement to the soil surface and vaporization into the atmosphere. When an organic substance is highly volatile, the desorption step is probably of lesser importance in slowing the volatilization rate. Soil-incorporated chemicals volatilize at a rate that depends on the rate of movement away from the soil surface through the atmospheric boundary layer, the effective vapor pressure within the soil, and the rate of movement through the soil to the surface. Vapor density of a chemical in soil is a reflection of its inherent vapor pressure, its water solubility, and its adsorption to the soil. Temperature effects also are important, and increases in the vapor density of about three to four times for each 10°C increase in temperature have been observed (Taylor and Spencer, 1990).

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The purpose is to describe a sampling device that can be used to determine the concentration of volatile compounds in the near-surface atmosphere. The sampling device can be used to measure a full spectrum of chemicals, provided that a suitable trapping method is used.

Theory

One of the most common methods for estimating the volatile flux from a soil surface is the aerodynamic method (Parmele et al., 1972; Majewski et al., 1989). This method uses atmospheric gradients of wind speed, temperature, and concentration to provide a measurement of the flux. The method requires a spatially uniform source and a relatively large upwind fetch to provide assurance that the gradients are fully developed. The fetch requirements are generally assumed to be from 50 to 100 times the height of the instruments (Munro and Oke, 1975; Rosenberg et al., 1983). Although originally developed for neutral atmospheric conditions, the method can be extended to stable and unstable atmospheric conditions by incorporating empirical relations that adjust the flux for these conditions.

The aerodynamic equation is

$$F_z(0) = -k^2 \frac{(c_2 - c_1)(u_2 - u_1)}{\phi_m \phi_c \ln(z_2/z_1)^2} \quad [1]$$

where k is von Kármán's constant (i.e., 0.4; unitless), u is the wind speed [m/s], z is height above the soil surface [m], c is the concentration of the volatile compound [kg/m^3] and ϕ_m and ϕ_c are the stability corrections for momentum and the volatile compound [unitless]. The stability corrections can be related to the Richardson's number, which can be obtained using gradients in the wind speed and temperature or the Monin-Obukhov stability length. Numerous stability corrections have been proposed (see Fleagle and Businger, 1980; Brutsaert, 1982; Rosenberg et al., 1983).

The integrated horizontal flux method (Denmead et al., 1977; Wilson et al., 1982; Majewski et al., 1990) can be used to estimate the surface flux of a volatile chemical when the concentration profile in the atmosphere is known as a function of height.

$$F_z(0) = \frac{1}{L} \int_0^\infty u(z) c(z) dz \quad [2]$$

This formulation relies on principles of mass balance, that is,

$$\int_0^L F_z(0) dx = \int_0^\infty u(z) c(z) dz \quad [3]$$

Equation 3 states that the mass emitted from the surface upwind from a sampling point is equal to the mass that passes through a vertical plane of sufficient height to capture all the mass (i.e., of infinite extent) located at the sampling point.

Clearly, to determine the flux using Eq. [1], atmospheric

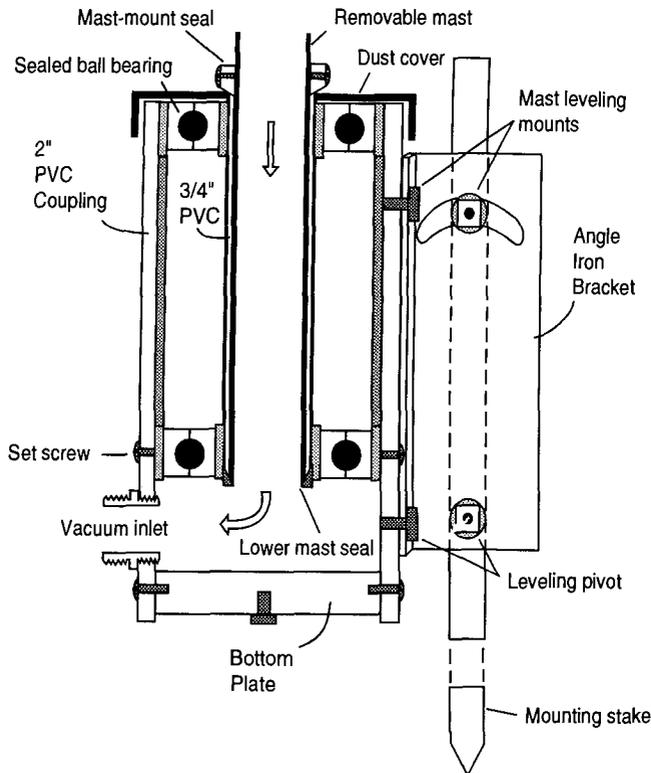


Fig. 1. Schematic of the rotating mast-base housing.

concentrations at a minimum of two heights are necessary so that the concentration gradient can be estimated. Under ideal conditions, however, more heights should be sampled so that the concentration profiles can be used when determining the gradients, which can help in identifying any errant data points. To use the integrated horizontal flux method, the concentration profile at several heights must be determined.

Materials and Methods

A sampling mast was developed that allows simple measurement of the atmospheric concentration of volatile gases over land surfaces. A rotating design was sought to minimize disturbance of the air stream from the sampling equipment. The design incorporates removable masts, so that the sample collectors can be mounted at a remote location and quickly placed into a supportive base between sampling intervals. This minimizes the time interval that the air is not sampled as well as the experimenter's exposure to toxic vapors; which can be extremely important for highly volatile and toxic compounds such as methyl bromide.

Shown in Fig. 1 and 2 is a simplified rotating sampling device for measuring the atmospheric concentration. The device consists of two parts: a rotating mast base (Fig. 1) and a removable hollow stainless steel mast (Fig. 2).

Mast Base Housing

The mast base housing consists of a rigid section of polyvinyl chloride plastic pipe with walls thick enough to be threaded, a diameter large enough to hold a set of 51 mm (2 inches) sealed bearings, and long enough to securely hold a 3 m mast of 19 mm (3/4 inch) tubing.

The walls of a 165 mm (6.5 inch) length of 51 mm (2 inch) schedule 40 plastic pipe were doubled in thickness by cementing it into 51 mm (2 inch) polyvinyl chloride couplings. Increasing

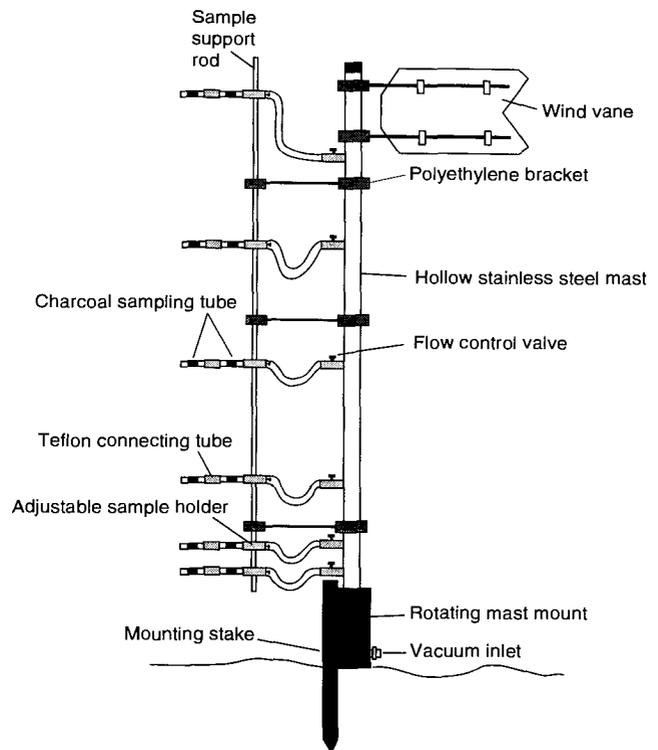


Fig. 2. Schematic of the removable stainless steel sampling mast.

the wall thickness would not be necessary if a stronger material such as steel or aluminum pipe was machined to accept the appropriate bearings. A vacuum tight seal between the upper bearing and the removable mast was made by machining a short bevel on the inside edge of one end of a 127 mm (5 inch) section of 19 mm (0.75 inch) schedule 40 polyvinyl chloride pipe (Fig. 1). The tapered mast-mount seal fit into this bevel and also centered the mast in the upper bearing. The lower end of the mast was sealed and centered in the lower bearing by tapering, machining, and cementing a short section of 13 mm (0.5 inch) schedule 80 polyvinyl chloride pipe into the lower end of the 19 mm (0.75 inch) pipe. A short section of both ends of this pipe was machined and pressed tightly into 25 mm (1 inch) i.d. by 51 mm (2 inch) o.d. sealed ball bearings. This assembly was inserted into the 51 mm (2 inch) section of thick-walled pipe and pressed flush with its top. Three set screws were installed contacting the base of the lower bearing to secure the assembly in the bearing housing (see Fig. 1). A bottom plate made from high-density polyethylene plastic was machined to fit tightly inside the mast-base housing and secured to the housing by three set screws. A dust-rain cover was fitted over the top bearing to provide additional weather protection.

A mounting bracket was constructed from 51 mm (2 inch) angle iron 152 mm (6 inch) long. Slots were cut in both angle iron flanges near one end and pivot holes were drilled in both flanges near the other end. A 610 mm (24 inch) stake (angle iron or steel pipe) was bolted to one flange on the angle iron mounting bracket and the other flange was bolted to the mast base using threaded holes in the mast base (see Fig. 1). This arrangement allowed the mast base to be leveled after the support stake was driven into the soil.

The vacuum inlet was installed into the side of the mast-base housing (below the lower bearing) by drilling a hole and tapping to accept 19 mm (0.75 inch) threaded pipe. A 19 mm (0.75 inch) pipe to standard lawn hose connector was inserted which

allows the use of a yard hose or polyethylene drip tubing to connect the mast-base chamber to a vacuum source. This creates a vacuum in the mast base as well as inside the removable mast.

Removable Stainless Steel Mast

Shown in Fig. 2 is a diagram of the removable stainless steel mast. The mast was constructed from 19 mm (0.75 inch) o.d. stainless tubing primarily due to its strength and resistance to corrosion, although any material rigid enough to support the sampling tubes and wind vane would be suitable. The air passing through the sample collectors should be stripped of the target compound and, therefore, the air entering the mast should be clean.

The removable mast is fully supported by the base housing. A vacuum tight seal is obtained by adjusting the mast-mount seal on the removable mast until it contacts the beveled upper end of the 19 mm (0.75 inch) polyvinyl chloride pipe connecting the bearings when the lower end of the mast is firmly seated against the lower mast seal (Fig. 1). Adjustable brackets made from high density polyethylene clamp the mast at three positions for 2 m masts and at five positions for 3 m masts. Extending horizontally from these brackets are 6 mm (1/4 inch) aluminum rods, which hold a vertical sample-tube support rod, which is made from 5 mm (0.188 inch) stainless steel rod. The top of the mast tube is sealed using a number 3 (20 mm) rubber stopper.

A wind vane mounted on the mast orients the sample collectors into the wind, which minimizes any air disturbance as it passes into the sampling tube. This approach was adopted since a stationary mast may induce unnecessary mixing whenever the wind is blowing in a direction that causes air movement through and around the mast and supporting brackets before entering the sampling tube. Minimization of mixing caused by apparatus is desirable. The wind vane is mounted in a manner similar to the horizontal support rods and can be made from any rigid light-weight material. The wind vanes were mounted 10 cm from the pole of a 3 m mast (Fig. 3) and had a surface area of approximately 0.3 m². The mast contained nine sampling stations connected by individual 3 mm (0.125 inch) i.d. polyethylene drip tubes extending 2 m beyond the mast base to a 10-port quick connector (Fig. 3).

Two identical masts are used for an experiment so that sample collector loading and removal can be done off-site during a sampling period and the time spent on the experimental area is minimized. Changing a whole mast of samplers is simply a matter of lifting out the mast containing the exposed samplers and inserting a mast containing fresh sampling media into the mast base (see Fig. 2). The mast illustrated in Fig. 3 requires the additional task of changing the quick connector from the exposed sample mast to the fresh mast. This can easily be accomplished in <30 s.

The rate of air movement through the sample collectors is adjusted using flow-control valves (e.g., brass needle valves) mounted in the hollow mast when using the mast design illustrated in Fig. 2. Flexible tubing connects the sample collectors to the valves. To adjust the flow rate, a ball-type flow meter is placed against the exposed end of the sampling tube (e.g., activated charcoal tubes and polymer tubes such as Tanex-GC; SUPELCO, Inc., Bellefonte, PA) and the needle valve is adjusted until the desired flow rate is attained. Adjusting the flow rate at the start of each sampling interval provides a relatively simple method for sampling volatile compounds in the atmosphere.

A potentially more accurate measure of the flow-rate can be obtained using electronic flow meters, since the flow can be

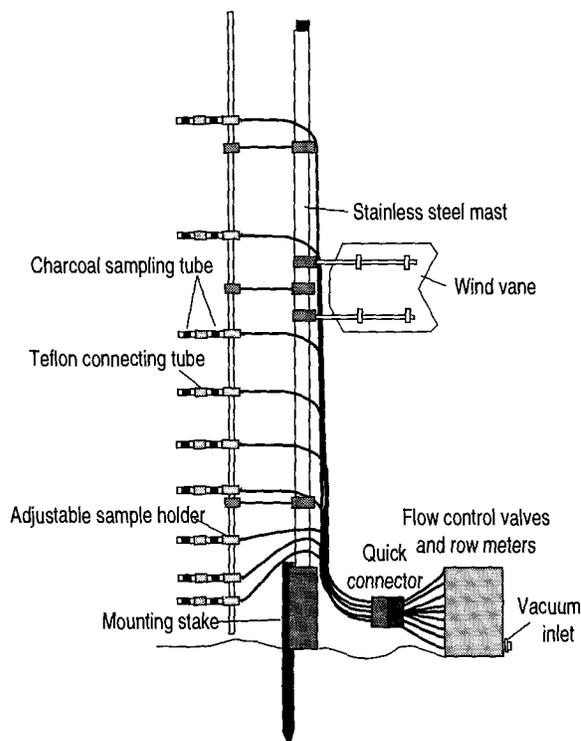


Fig. 3. Schematic of the removable stainless steel sampling mast using electronic flow meters to measure the flow rate.

continuously monitored. A removable, semi-rotating sampling mast using electronic flow meters and supported by the mast-base housing shown in Fig. 1 is illustrated in Fig. 3. Flexible tubing connects the sampling collector to the vacuum source and directs air through a nearby flow meter and flow control needle valve. To enable the mast to be quickly changed in the field, a 10-port quick connector is used to couple the tubes from the mast to the flow meters and flow control valves. A data logger with a display connected to the flow meters allows flow rates to be monitored and adjusted at the mast site.

Experiments Using the Mast Designs

Several experiments were conducted at the University of California's Moreno Valley Field Station that involved using the mast sampling equipment. The field soil at the experimental site is a Greenfield sandy loam and is classified as a coarse-loamy, mixed, thermic Typic Haploxeralf. In each experiment, various pesticides were applied to the bare soil and the atmospheric concentration profiles were obtained.

During Exp. 1, the atmospheric concentration of triallate (S-2,3,3-trichloroallyl di-isopropyl thiocarbamate) and lindane (1,2,3,4,5,6-hexachlorocyclohexane) over a bare soil was obtained during the first few hours after application during June 1990 (see Table 1). The field site is located at the University of California Moreno Valley field station (Field G2). A rotating mast, similar to the mast shown in Fig. 2, was used to measure the triallate and lindane concentrations. The sample collectors were positioned at 10, 20, 50, 80, 120, and 160 cm heights above the field. These heights were selected to provide sufficient data to determine the concentration gradient at a height of 50 cm. The pesticide samples were collected on polyurethane foam plugs held in glass tubes located on the sampling mast. The flow rate through the polyurethane foam was 40 L/min for a 2-h sampling interval (i.e., 4.8 m³ of air was sampled).

For Exp. 2, the methyl bromide was applied to the field

Table 1. Meteorological data for June 1990 experiment.

Sample interval	Sample period	Mean temp.	Mean relative humidity	Wind direction	U† at				
					20 cm	40 cm	80 cm	160 cm	240 cm
2	1200-1400	31.6	34	119	3.0	3.3	3.8	4.2	4.6
3	1400-1600	33.0	21	284	3.6	4.1	4.7	5.2	5.8
4	1600-1800	32.6	19	279	3.4	3.8	4.4	4.9	5.5
5	1800-2000	28.9	32	272	3.0	3.3	3.8	4.3	4.8

† Horizontal wind speed.

as 99.5% methyl bromide (CH_3Br) and 0.5% chloropicrin (CCl_3NO_2 ; EPA Reg. no. 8536-12-11220) at a depth of approximately 25 cm. The application rate was approximately 240 kg/ha (i.e., 215 lb/acre) and the treated area was approximately 3.5 ha (i.e., 8.6 acres), for a total applied mass of 843 kg. During this experiment, the adjacent fields were vacant, which provided sufficient up-wind fetch so that atmospheric gradient methods could be used to obtain the methyl bromide flux. The sampling mast shown in Fig. 2 was constructed so that sample collectors could be positioned at 10, 20, 50, 80, 120, and 160 cm above a 1 mil polyethylene film.

Experiment 3 was conducted in a similar manner as Exp. 2, with the following exceptions. The methyl bromide was injected at approximately 68 cm, to a noncovered soil and the application rate was approximately 324 kg/ha (i.e., 290 lb/acre), for a total applied mass of 1134 kg. For this experiment, the mast shown in Fig. 3 was used and the sample collectors were positioned at 5, 10, 30, 50, 70, 110, 150, 200, and 260 cm above the soil surface.

Methyl bromide was collected on charcoal sampling tubes by passing air at approximately 100 mL/min through the sample tubes (i.e., a total of 0.012–0.024 m^3 of air was sampled). The sampling interval was either 2 or 4 h depending on the time of day. For Exp. 2, the longer interval was during the night; for Exp. 3 it was during the day. Brass needle valves were used to regulate the flow rate for both experiments. A ball-type flow meter was used to measure the flow rate when the mast was first placed in the field during Exp. 2 and electronic flow meters were used to measure the flow rate for Exp. 3.

Results and Discussion

Mast Performance

For the mast shown in Fig. 3, the wind vane will easily rotate the sampling tubes into the prevailing wind at wind speeds as low as 0.4 m/s (0.9 mph). During

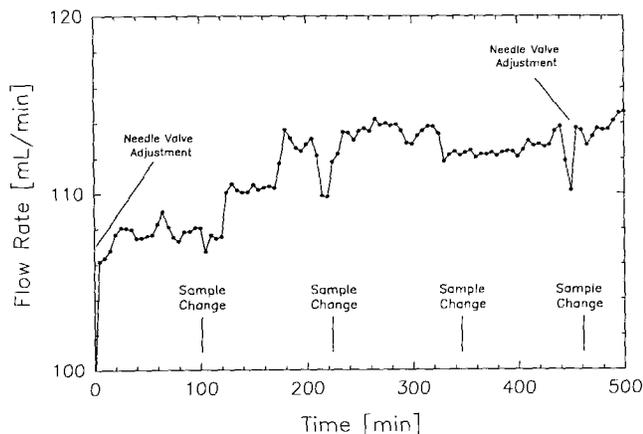


Fig. 4. Variation in flow rate during first four sampling intervals. The flow rate was measured using an electronic flow meter.

testing, constant wind speeds lower than this were difficult to measure so no reliable data is available at lower speeds. The anemometer system (CWT-1806 & CWT-1972; C.W. Thornthwaite & Assoc., Elmer, NJ) used to determine wind speed has a threshold velocity of 0.12 cm/s. Free rotation of $>270^\circ$ (the maximum range during the test period) was observed for wind speeds near 0.4 m/s and, at higher speeds restricted rotation has never been observed. For example, during Exp. 3, which consisted of 3 wk of continuous sampling, the mast was always able to rotate freely. Masts that use their hollow tube for the vacuum supply (Fig. 2) should have a lower wind-speed rotation threshold and no restriction on rotation angle. Sensitivity to winds can be increased by enlarging the wind vane or using longer support rods to move the vane farther from the mast; thereby increasing the torque. Unless very large sample collectors are used on the mast, they will not interfere with the air flow across the vane. Height and number of sample holders can be adjusted to suit experimental needs by moving the holders along the sample support rod using their set screws or by adding more holders to the rod. The mast and base size can be scaled up or down to suit a wide range of experimental requirements. Appropriately sized bases supporting mast heights from 1 to 3 m in length and 19 to 51 mm (3/4 to 2 inches) diameter using samplers flowing 0.1 to 40 L/min have been successfully used in our field experiments for the past 5 yr.

One problem observed during Exp. 3 (using the mast shown in Fig. 3) was the appearance of excessive vibrations when the wind at a height of 2.4 m reached speeds of approximately 6 m/s. To correct this, the wind vane was lowered to a more central position on the mast, which reduced the mechanical stresses sufficiently to end the vibrations. Another potential problem using the ball-type flow meters is the possibility of changes in the desired flow rate occurring during the sampling period from heating effects, vibrations due to wind turbulence, fluctuations in the vacuum system, and possibly other sources. Using electronic flow meters, a continuous record of the flow rate can be obtained. This is shown in Fig. 4 and clearly demonstrates the changes in flow rate that can occur during experiments. No interference from the additional weight of tubes or restriction of rotation by the tubes was noticed during our experiments.

Measuring Concentration Profiles of Moderately Volatile Compounds

Figure 5 is a graph of the atmospheric concentration of triallate and lindane over a bare soil during the first day after application (see Table 1) and illustrates the

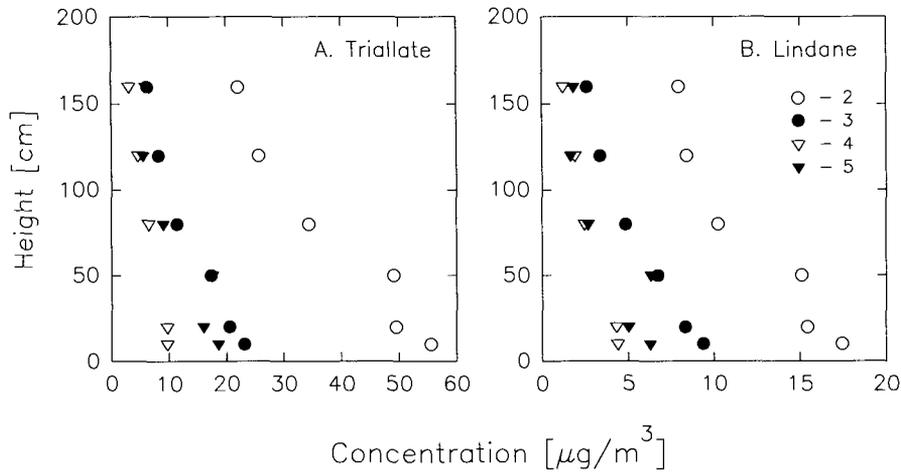


Fig. 5. Concentration profiles of triallate and lindane for the second through fifth sampling intervals during the experiment. The sampling intervals are: \circ = 2, \bullet = 3, ∇ = 4, \blacktriangle = 5.

use of the mast for measuring pesticides with moderate volatility. The vapor pressures for triallate and lindane (Wauchope et al., 1992), respectively, are 1.1×10^{-4} and 3.3×10^{-5} mm Hg, which is nearly seven to eight orders of magnitude less than the vapor pressure for methyl bromide; discussed below. Although the pesticide flux was not determined, this figure provides important information concerning health hazards to workers in and near the field. For example, at 150 cm height, the

concentration of triallate was below $10 \mu\text{g}/\text{m}^3$ 9 h after application. For lindane, the concentration was below $5 \mu\text{g}/\text{m}^3$ after 9 h. Near the soil surface the concentrations are higher. Using information from toxicological studies on each pesticide's effect on humans, or other regulatory information, a reasonable time can be determined before workers are allowed to reenter the field. Also, assuming other necessary information is available, this information can be used to provide estimates for the volatilization rate.

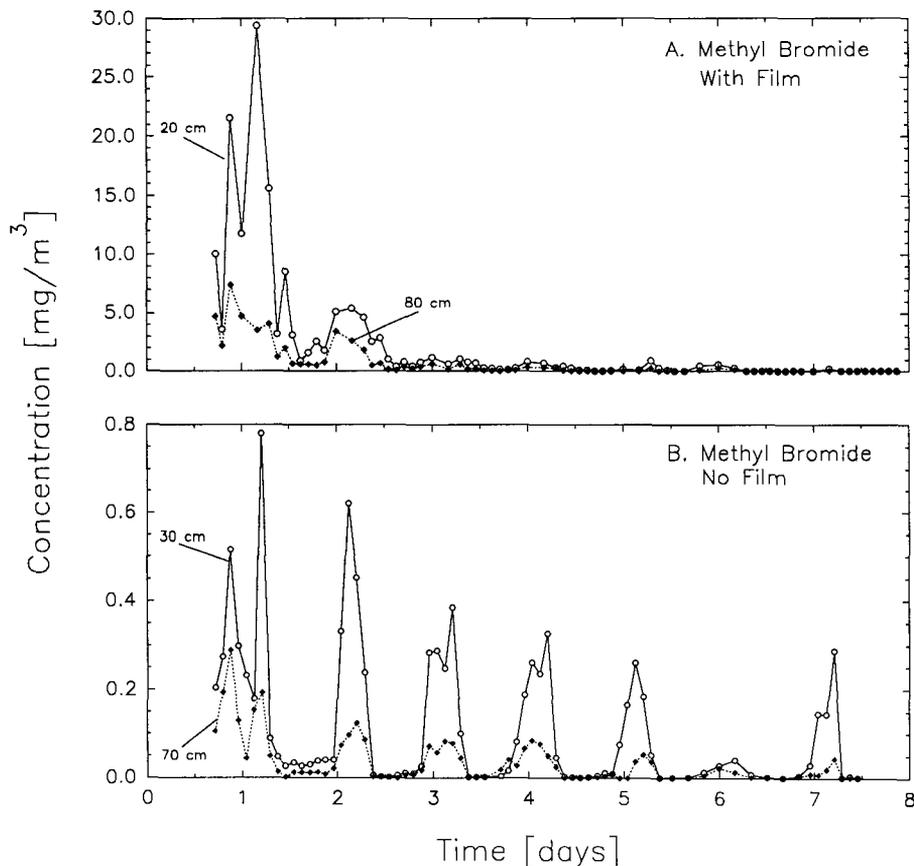


Fig. 6. (A) Time series of the methyl bromide concentration at 20 and 80 cm above a 1 mil polyethylene film during the first 8 d after application and (B) methyl bromide concentration 30 and 70 cm above a bare soil after a deep-injection, noncovered application. Zero time is midnight the day of application.

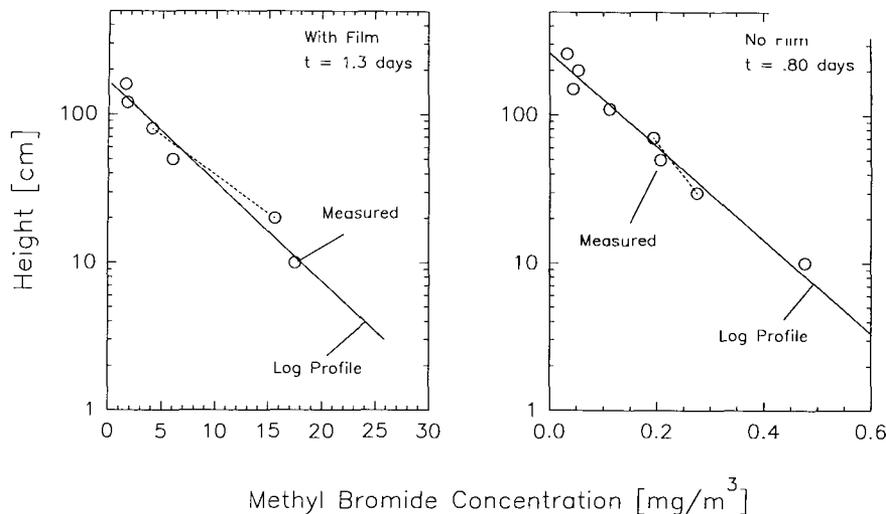


Fig. 7. Concentration profile of methyl bromide where the circles indicate the measured concentrations and the solid line is the theoretical logarithmic profile. The dashed line shows the gradient that results from using only two measured concentrations.

Measuring Surface Volatilization Rate of Highly Volatile Compounds

Shown in Fig. 6A and 6B, respectively, are time series of the methyl bromide concentration measured at 20 and 80 cm over a field covered with a 1 mil plastic film (Exp. 2) and at 30 and 70 cm over a deep injected, noncovered field (Exp. 3). Methyl bromide concentrations and gradients were higher at night compared with daytime values. For Exp. 3, a cyclic pattern was observable for 7 d after application. Coupling this information to gradients of the air temperature and wind speed, provides a method for determining the surface flux of methyl bromide.

Shown in Fig. 7 are concentration profiles measured 1.3 and 0.8 d after application of methyl bromide for Exp. 2 and 3, respectively. The open circles are the measured values and the solid line is the logarithmic concentration profile that is commonly assumed to occur and demonstrates that during these sampling intervals, the measured values were approximately logarithmic. Also, the extent of the deviation from the lognormal model is similar regardless of whether ball-type (A) or electronic flow meters (B) are used. A significant advantage of using electronic flow meters (B) is the simplification of collecting samples in the field. Without electronic flow meters, changing sample collectors involves numerous tasks (i.e., removing and installing charcoal tubes, measuring, and adjusting the flow rate at

each height) spanning 5 to 10 min. This can be especially difficult during hours of darkness or inclement weather. Using electronic flow meters and a removable mast, changing samples takes <30 s and requires no adjustment.

The methyl bromide flux can be obtained using Eq. [1]. This is shown in Table 2 for the concentration profile data in Fig. 7. Two cases are considered; when the concentration gradient is taken from the slope of the logarithmic profile and when the two concentrations values indicated by the dashed line in Fig. 7 are used to estimate the gradient. For the sampling sequence shown in Fig. 7A, the two-point gradient produces a flux that is 29% greater than the flux based on the log-profile gradient. For Exp. 3, the two-point gradient produces a flux that underestimates the log-profile flux by about 24%. Since for large-scale field experiments there is no way to obtain an absolute measure of the flux, it is impossible to determine which of these values is closer to the true emission rate. Even so, a higher level of confidence can be placed on the flux values resulting from the log-profile gradient, since the additional concentration measurements lend support to the estimate. When the gradient is based on several values of the concentration, deviations from the logarithmic profile model due to sampling and analytical errors can be more easily identified. Their influence also would be reduced once the logarithmic profile model was fitting to the data; again enhancing reliability.

Table 2. Flux calculation.

	$\frac{\partial u}{\partial[\ln(z)]}$ m/s	$\frac{1000}{T} \frac{\partial T}{\partial z}$ 1/m	$\phi_m = \phi_c \ddagger$	$\frac{\partial C}{\partial[\ln(z)]}$ Concentration at 2 heights mg/m ³	$\frac{\partial C}{\partial[\ln(z)]}$ Profile mg/m ³	Flux from concentration at 2 heights μg/m ² s	Flux from lognormal model μg/m ² s
Exp. 2 (Fig. 7a)	0.068	-0.781	0.659	-8.32	-6.43	208.4	161.1
Exp. 3 (Fig. 7b)	0.338	-0.846	0.936	-0.101	-0.133	6.23	8.21

† T is temperature (K).

‡ $\phi_m = \phi_c = (1 \pm 16 Ri)^{\pm 1/3}$, where Ri is the Richardson's number and the positive sign is used for stable conditions; and $Ri = g/T (\partial T/\partial z)(\partial u/\partial z)^{-2}$, where g is gravitational constant and u is the wind speed.

Conclusions

Accurate measurement of the atmospheric concentration of volatile organic compounds is possible using the air sampling device described herein. This information can be used for measuring the concentration of volatile organics in the atmosphere as it relates to worker exposure or for developing reentry protocols. This information also can be used for estimating the surface flux of pesticides into the atmosphere using methods that require profiles of the pesticide concentration in air during the experimental period (i.e., the aerodynamic and the integrated horizontal flux methods) or for methods that require a concentration at a single height (i.e., theoretical profile shape method; see Majewski et al., 1989); although simpler designs are possible for one-point measurements. Two sampling masts are described, the more complex design requires the use of electronic flow meters and data logging equipment. Although construction of this sampling mast is more expensive and time consuming, its use during field experiments is considerably simpler compared with the mast shown in Fig. 2, and can reduce the number of person-hours necessary to complete a field experiment. In terms of materials, the rotating mast will approximately double the unit cost compared with a stationary mast. The addition of flow meters will add considerably to the overall cost, with each flow meter costing as much as the mast. Constructing the rotating mast will require as much as four times the person hours of the stationary mast. Much of this is offset by the time saved in the field, in both personnel costs and reduced exposure to pesticides. Changing samples with the rotating mast using flow meters takes <1 min. This compares with 10 to 15 min required for a 3 m stationary mast containing double sampling tubes (in series) and nine sampling heights.

Acknowledgments

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