SHORT COMMUNICATIONS

Automated Sequential Sampler for Collection of Highly Volatile Atmospheric Contaminants

D. Wang,* F. F. Ernst, and S. R. Yates

Abstract

Rapid and accurate measurement of atmospheric concentrations of highly volatile organic compounds is important in obtaining reliable information for the assessment of environmental pollution or the volatilization mechanisms of the chemicals. Nonmechanized sample collection requires intensive labor and effort, and may cause large random or systematic errors. An automated solenoid switching system was developed to assist in obtaining precise environmental concentrations of highly volatile organic compounds. The design, construction, and operation are described in the paper for potential application in similar studies. Using this sampling system, two experiments were conducted to determine atmospheric volatilization flux density of three highly volatile and reactive organic compounds (methyl bromide, 1,3-dichloropropene, and propargyl bromide). The automated solenoid switching system significantly reduced the requirements for labor and time. Results from the two experiments indicate that reliable sample collection was achieved. The automated sampling system was also relatively inexpensive and can be easily modified to accommodate a variety of sources, sampling intervals, and multiple number of solenoid valves.

VOLATILE organic compounds (VOCs) are a main source of air pollution. Fast and accurate measurement of their concentrations in the environment is an important first step to characterize their behavior and dynamics in the ambient air. However, the sampling procedures are often very time consuming and may be subjected to large random or systematic errors during sample collection and handling (Siegrist and Jenssen, 1990). To reduce sampling errors and increase sampling efficiency, Krovetz et al. (1989) used an automated system to collect forest trace gases such as SO_2 and HNO_3 from remote locations. Ham et al. (1995) in their work of characterizing CO_2 flux from a grass field, used a switching system that can collect emission samples from multiple flux chambers.

Recent interest in determining the emission dynamics of methyl bromide (MeBr, CH_3Br) in soil fumigation has led to the development of new sampling methods and procedures that are suitable for highly reactive and volatile organic chemicals such as fumigants. Techniques for collecting samples that would enable the determination of atmospheric emission flux density include a rotating mast (Yates et al., 1995) and passive (Yagi et al., 1995) and active (Yates et al., 1997) flux chambers. Sample collection from either the mast or flux chambers, however, would still be subject to random or systematic errors when performed manually. Further, a continuous sampling scheme would require frequent and over night sample collection from the equipment, making the sampling process a very labor intensive task.

To minimize potential sampling errors and increase sampling efficiency, this paper describes the design and application of a solenoid switching system for automatically collecting environmental samples of highly reactive and volatile organic chemicals.

Materials and Methods

This automatic system for collecting ambient VOC samples used a datalogger to control multiple series of solenoid valves (four in this case) attached to a manifold that was connected to a VOC source (Fig. 1). The datalogger was programmed to turn on the solenoid valves sequentially so the target atmosphere was sampled continuously for fixed time intervals. The VOC contaminants were collected by a series of sampling tubes or trapping media such as activated charcoal (Supelco Co., Bellefonte, PA) that has large absorption capacity to the VOC (Ballesta et al., 1992). As depicted in Fig. 1, the main components used in this system included a vacuum source that was used to pull the vapor source, by way of the vacuum manifold, into the solenoid manifold, and through the currently open solenoid into the trapping media. After the selected time interval, the first solenoid was closed and, simultaneously the second solenoid was opened to allow the vapor source to flow through the second trapping medium. Sampling media were changed before this cycle repeats (i.e., completing a full rotation of the four solenoids). The system required a 24 VDC power supply for switching the solenoid valves, which were controlled with the datalogger through the relay switches. During sample collection, an electronic flow meter was used to record air flow through each collection medium. Because of their relative complexity, the design and components used in the solenoid and vacuum manifolds and the relay switch will be discussed in more detail as follows.

Solenoid Manifold

The solenoid manifold consisted of a length of 3/4 in. (19 mm) Teflon pipe threaded and capped on both ends with standard 3/4 in. PVC caps. A thin Teflon disc (~0.5 mm thick) was fitted between the cap and the pipe to ensure a good seal and eliminate the possibility of sorption of the organic vapor

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USDA-ARS, U.S. Salinity Lab., 450 West Big Springs Rd., Riverside, CA 92507-4617. Received 20 Feb. 1998. *Corresponding author (dwang@ussl.ars.usda.gov).

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Abbreviations: VOC, volatile organic compounds; MeBr, methyl bromide; 1,3-D, 1,3-dichloropropene; PrBr, propargyl bromide; GC, gas chromatograph; HSA, headspace autosampler.

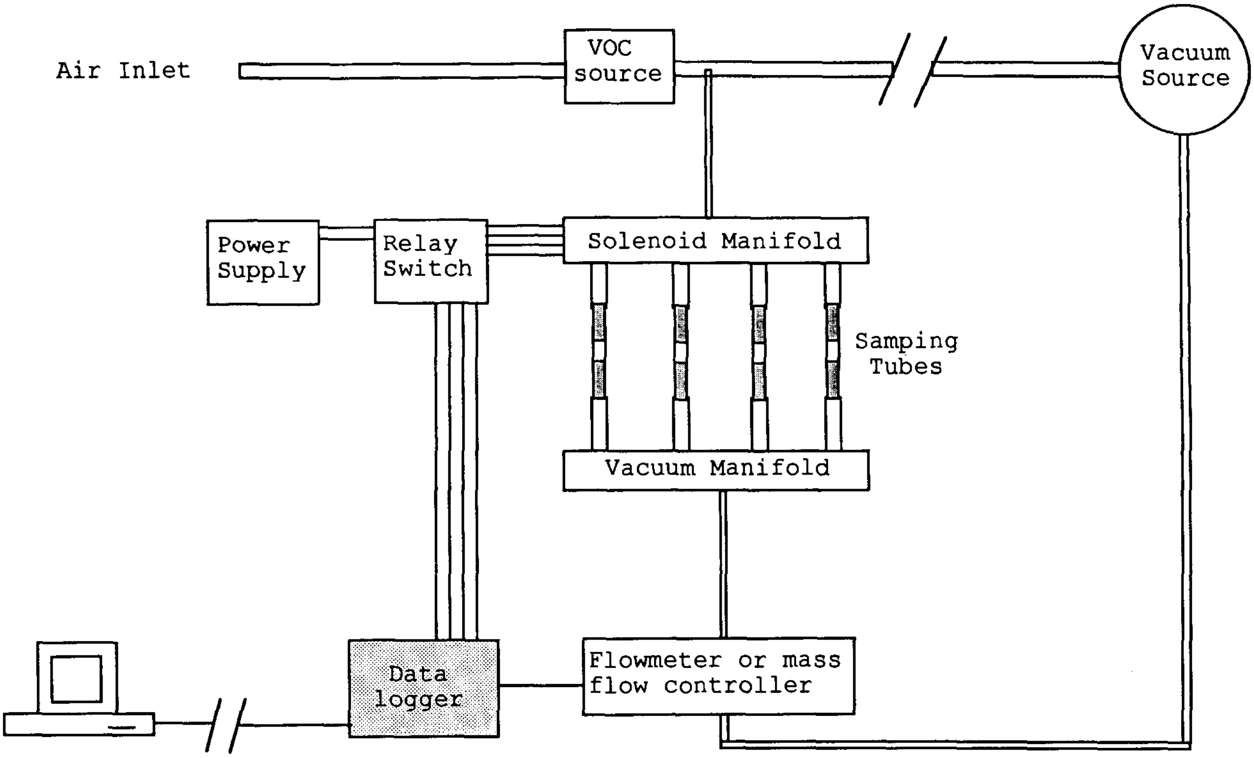

Fig. 1. Schematic of an air flow and solenoid switching system for an automated collection of volatile organic compounds from a contaminated air source.

by the PVC. The brass solenoid valves were connected to the manifold by threading them into tapped 1/8 in. (3.2 mm) NPT holes on the Teflon pipe. Small nylon hose barbs were threaded on to the solenoid outlets, and used to connect the solenoids (with tubing) to the sampling tubes. A barbed vapor hose inlet was mounted on the solenoid manifold with a 1/8 in. NPT, and was used to connect the manifold to the VOC source. The solenoid and manifold materials (brass and Teflon) were chosen to suit the particular application need (i.e., for highly reactive and absorbing fumigants). The size of the manifold and air pathway in the solenoids were selected to facilitate an air flow rate of 100 to 200 mL/min without creating a significant vacuum built up. Materials of the manifold components and their sizes may be substituted to match specific experimental requirements.

The unit cost for the three-way solenoids was about $5 (Table 1). Total cost for the whole solenoid manifold was about $27, which included four solenoid valves and the manifold itself, but not including labor cost.

Relay Switch

The relay switch module had the capability of sequentially switching the solenoid valves for four fixed time intervals. This module consisted of a mounting board and a set of input/output relay switches. Because each switch controlled one solenoid valve, the number of switches was the same as the number of solenoids used in this application (i.e., four). If more than four time intervals are required, this system can be upgraded to six or eight sequences by changing the mounting board and adding two or four more relay switches. Before doing this it is important to consider the length of time the trapping media used can stay in the field or laboratory conditions without significant degradation. It is also important to determine if the datalogger has the capability to control more time intervals (six control ports for the 21X datalogger). The datalogger uses a 5 VDC power signal to activate the switches to control the power supply to the solenoid valves (24VDC).

Both the relay switches and mounting boards were manufactured by Potter & Brumfield (Table 1). Total cost for a four-switch module was about $70.

Vacuum Manifold

The vacuum manifold consisted of a length of 1/2 in. (12.7 mm) PVC pipe with both ends covered with PVC end caps. No specific material was required since VOC contaminants had been removed by the trapping media. Plastic tubing was used to connect nylon hose barbs on the vacuum manifold to the sampling media tubes, and a 1/8 in. NPT hose barb and tubing was used to connect the manifold to the electronic flow meter. To assure an accurate measurement of air flow rate through the trapping media, it is critical that all connections between the vapor source to the flow meter be vacuum tight. Because the materials required for the vacuum manifold were very inexpensive, the total material cost for each manifold was only about $3 (Table 1).

Field Applications

One of the important interests in environmental sampling of VOC contaminants is to determine the contaminant concentrations. Because analytical instruments such as a gas chromatograph (GC) can only detect a finite amount of chemical on a mass basis, the contaminant concentrations on the collection media or in the ambient environment can be calculated as:

$$C_{\mathrm{VOC}} = \frac{M_{\mathrm{voc}}}{F\Delta t} \qquad [1]$$

where C_{voc} is the concentration (M/L^3); M_{voc} is the VOC mass collected during one sampling interval (M); F is the mean

Table 1. Components, vendor, and approximate costs for the automated sampling system.†

Item (model or part no.)	Manufacturer or vendor	Cost ($)
Three-way 24 VDC solenoid valve (Allied cat. V3M7X-1)	C&H Sales Co. 2176 E. Colorado Blvd. Pasadena, CA 91107	5
Teflon solenoid manifold (custom fabricated)	Materials include: Teflon pipe and end caps, brass barbed hose fittings, and supporting metal rods and screws	7
I/O relay switch (P&B model ODC-5; module 4A033)	Siemens Electromechanical Components Inc. Potter & Brumfield Products Div. 200 S. Richland Creek Dr. Princeton, IN 47671	11
Mounting board for 4 switches (P&B model 2104B; module 4A034)	Siemens Electromechanical Components Inc. Potter & Brumfield Products Div. 200 S. Richland Creek Dr. Princeton, IN 47671	26
24 VDC power supply	C&H Sales Co. 2176 E. Colorado Blvd. Pasadena, CA 91107	50
PVC vacuum manifold (custom fabricated)	Materials include: PVC pipe and end caps, nylon barbed hose fittings, and supporting metal rods and screws	3
Electronic flowmeters (model 100)	McMillan Co. P.O. Box 1340 Georgetown, TX 78627	130
Vacuum source (custom fabricated with a Ametek motor: model 116472-00)	Ametek Motor Co. 627 Lake Street Kent, OH 44240	95
Datalogger (21X)	Campbell Scientific Inc. 815 W. 1800 N. Logan, UT 84321	2030

† Mention of manufacturer or vendor names does not constitute endorsement by USDA, and similar materials may be substituted in the system.

Table 2. Cumulative emission with concentration samples collected with the automated system.

Treatment	MeBr†	1,3-D†	PrBr†
Flow system test			
Application rate, g	26.12	17.02	20.25
Cumulative emission, g	23.30	16.59	19.90
Emission loss, %	89.20	97.47	98.27
Field experiment			
Application rate, g/m^2	28.01	13.70	NA‡
Cumulative emission, g/m^2	19.04	11.01	NA
Emission loss, %	67.98	80.36	NA

† MeBr = methyl bromide; 1,3-D = 1,3-dichloropropene (cis- + trans- isomers); PrBr = propargyl bromide.
‡ Not apply.

air flow rate (L^3/T); and Δt is the duration of the sampling interval (T).

Other important information in characterizing VOC contaminants is to quantify the volatilization rate under various environmental conditions. When the VOC source is known, the volatilization flux density may be calculated using the measured concentrations:

$$J_{\mathrm{VOC}} = \frac{F(C_{\mathrm{voc,out}} - C_{\mathrm{voc,in}})}{A} \qquad [2]$$

where J_{voc} is the VOC's volatilization flux density (M/L^2-T); C_{voc}, out and C_{voc}, in are VOC concentrations (M/L^3) measured at an outlet and an inlet of a flux chamber covering a surface area of A (L^2).

This automated switching system was applied and tested in two experiments: one was conducted outdoors using an enclosure system similar to that reported in Wang et al. (1997a), and the other was for a field experiment. In the first experiment, a dynamic flux chamber was sealed onto a VOC source enclosure after a layer of polyethylene film was taped over the opening of the enclosure. Three highly volatile organic chemicals were used with the system, and they were methyl bromide (MeBr, CH_3Br), propargyl bromide (PrBr, C_3H_3Br), and 1,3-dichloropropene (1,3-D, including both *cis-* and *trans-* isomers). The physical and chemical properties of the three chemicals can be found in Yates and Gan (1998). Prior to the experiment, fixed amount of each of the three chemicals (Table 2) was injected separately into the enclosure through a self-sealed port. In the second or field experiment, this sampling system was used with flux chambers to measure the atmospheric emissions of MeBr and 1,3-D from field plots. Procedures similar to that of Wang et al. (1997b) were used in the design of the field plots and application of the chemicals. In both experiments, the automated switching system was programmed to 3-h sampling intervals, so that with four solenoids, the sample tubes were replaced every 12 h. Activated coconut charcoal tubes (ORBO-32, Supelco, Bellefonte, PA) were used to absorb the chemicals by passing an average of 120 mL/min air through the trapping media. Air flow through the charcoal tubes was maintained at about 120 mL/min by manually adjusting two needle valves located near the electronic flow meters. To prevent chemical breakthrough, two tubes were used in a series in the enclosure experiment. Three tubes were used in the field experiment because of the potential plastic failure under field conditions. A Hewlett-Packard 5890 GC with electron capture detector was used for the analysis of these VOCs absorbed on each sampling tube. After desorption with benzyl alcohol, injections were made from a Tekmar 7000 headspace autosampler (HSA) equipped with a 7050 sample carrousel. The minimum detection limit of this GC-HSA setup was <1 μg for the three chemicals. More detailed descriptions of sample analysis can be found in Gan et al. (1995). After the determination of total chemical losses from the 3-h interval, Eq. [2] was used to calculate the volatilization flux density of the tested chemicals.

Results and Discussion

From the first enclosure experiment, measured volatilization flux density decreased with time for all three chemicals (Fig. 2). The volatilization flux density for MeBr exhibited a very strong cyclic behavior with large emission near noon and lower values at midnight (Fig. 2A). This is consistent with previous field measurements and model simulations by Wang et al. (1997c) and the cyclic behavior was caused primarily by the temperature dependence of the plastic film's permeability to MeBr. The measured maximum flux density during the first 2 d was about 120 μg/m^2-s, which is also consistent with previous results obtained under field conditions for the polyethylene films (Wang et al., 1997b). The volatilization flux density decreased to about 0 after 5 d when about 90% of the applied MeBr had been lost through emission (Table 2). The near 100% loss was expected since no significant degradation was expected to occur in the source enclosure.

For PrBr and 1,3-D, the volatilization flux density was very large right after their application in the enclosure and decreased rapidly to near 0 in 2 d (Fig. 2BC).

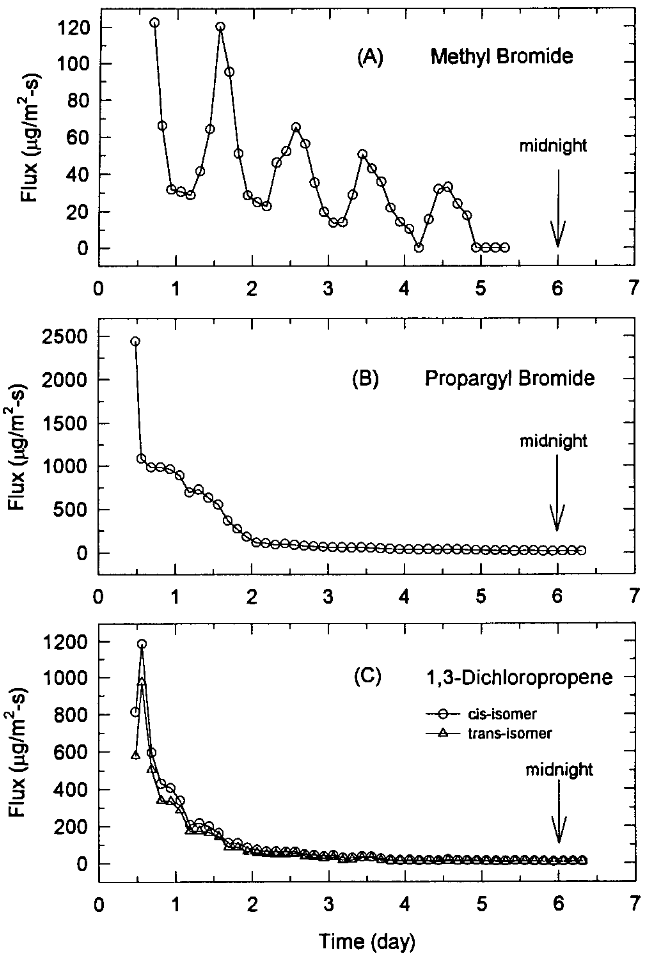

Fig. 2. Volatilization of methyl bromide (*A*), propargyl bromide (*B*), and 1,3-D (*C*) from a source enclosure covered with a layer of polyethylene film.

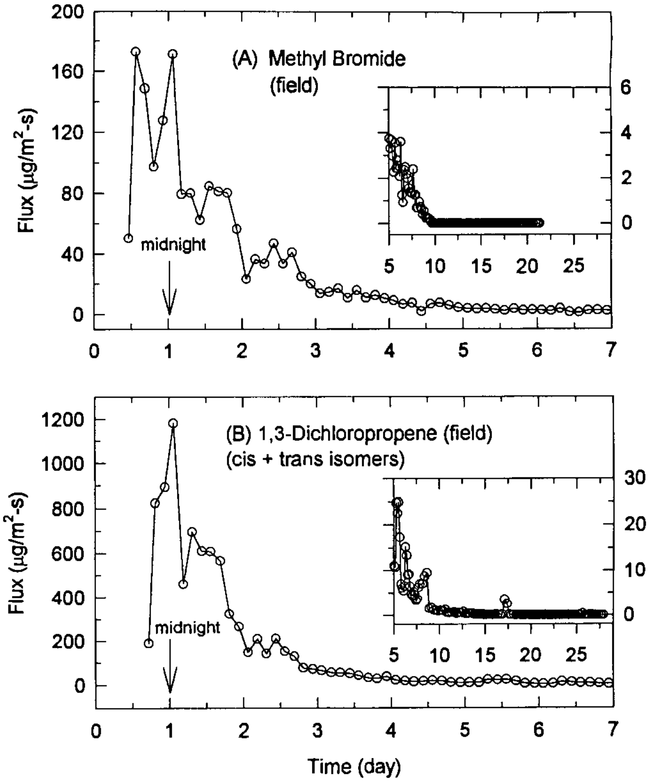

Fig. 3. Volatilization of methyl bromide (*A*) and 1,3-D (*B*) from field plots covered a polyethylene film. Inserts show emission fluxes at a smaller scale from Day 5 to the end of sample collection.

This large initial emission flux was attributed to the large permeability of the polyethylene film to the two chemicals, since about the same molar amount (as MeBr) was applied in the enclosure. To assure no unaccounted chemical losses, the measurements were continued for about 6 d when the absolute flux density reached zero for more than 24 h, and about 100% emission loss had accumulated (Table 2).

Results from this experiment also indicate that the 3-h sampling interval appeared to be adequate in capturing the temporal dynamics of the emission processes for the three highly volatile compounds. The resolution of measured flux density may be improved by reducing the sampling interval to <3 h during the first 24 h after application. However, the total experimental cost may increase very rapidly with very small sampling intervals, and sometimes the extra amount of information gained may not be as critical as reducing the experimental budget.

Under field conditions, this automated switching system was proved to be very efficient and reliable in assisting sample collection on a 24-h continuous basis. Measured MeBr and 1,3-D emissions followed a pattern similar to that in the enclosure experiment (Fig. 3). The maximum flux density was about 170 μg/m^2-s for MeBr and 1200 μg/m^2-s for 1,3-D. Because diffusion to the surface was slower in the soil (than in the air), the emission process continued for about 10 d before the emission rate was below detectable levels. Sample collection with the automated switching system was continued for more than 21 d to capture all emission losses (see inserts of Fig. 3). The system functioned, without failure, for the entire field experiment while the ambient air temperature fluctuated diurnally between 13 to 45°C.

Over the course of the two experiments, more than 500 samples were collected with only two people working on the project, and no sampling error was made. Had the sampling been made manually, human errors would likely occur in the time-critical collection process. Further, samples may be changed a few minutes earlier or later than the scheduled time, whereas the automated sampling always occurs punctually at predetermined time points simplifying data analysis. It also eliminated much of the high requirement for operator's time and effort by allowing measurements to be made through night and weekend hours with little personnel attendance.

The automatic solenoid switching system can be used to collect environmental samples of highly reactive and volatile organic compounds such as soil fumigants. The system is relatively simple to construct and can be easily modified to accommodate a variety of sources, sampling intervals, and multiple number of solenoid valves. For example, when used with appropriate sampling equipment such as the specially designed soil gas probes (Bradshaw et al., 1995) or soil sampling procedures

(Lewis et al., 1994), it may be used to collect VOC samples from the subsurface soil profiles. In applications where maintaining a constant flow rate is critical, the electronic flow meters may be substituted with mass flow controllers. This automated sampling system is also relatively inexpensive and cost effective since the investment of constructing the system is much less than the cost for labor and time of a manual sampling regime. Application of this automated switching system can improve measurement accuracy and assure sample changes occur exactly at predetermined time intervals.

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