Theory and Laboratory Study of a Tall Passive Chamber for Measuring Gas Fluxes at Soil Surface

Frank F. Gao, Yan Jin, Scott. R. Yates, Sharon Papiernik, Michael A. Anderson & Marylynn V. Yates


To link to this article: https://doi.org/10.1080/10473289.2001.10464250

Published online: 27 Dec 2011.
Theory and Laboratory Study of a Tall Passive Chamber for Measuring Gas Fluxes at Soil Surface

Frank F. Gao
Delaware Department of Natural Resources and Environmental Control, Dover, Delaware

Yan Jin
Department of Soil and Plant Sciences, University of Delaware, Newark, Delaware

Scott. R. Yates and Sharon Papiernik
Soil Physics and Pesticide Research Unit, U.S. Department of Agriculture Salinity Laboratory, Riverside, California

Michael A. Anderson and Marylynn V. Yates
Department of Environmental Sciences, University of California, Riverside, California

ABSTRACT
A tall passive flux chamber with a height significantly greater than its horizontal dimensions is proposed for measuring fluxes of volatile organic compounds (VOCs) at the soil surface. The main feature of this tall chamber is the presence of a vertical concentration gradient of the target gas in the chamber. The emission and transport behavior of the target gas in the soil-chamber system are analyzed using the diffusion theory. A mathematical model is developed to estimate the flux from the soil into the tall chamber, providing the target gas establishes a detectable vertical concentration gradient in the chamber. To obtain the data required for calculating flux, only two gas concentrations \( C_1 \) and \( C_2 \) at two heights \( h_1 \) and \( h_2 \) within the chamber need to be measured at the end of a short chamber placement time \( t_p \). To evaluate the applicability of the tall chamber for measuring flux, several laboratory tests have been conducted, using \( \text{CH}_2\text{Cl}_2 \) and \( \text{CH}_3\text{Br} \) as the target gases. The results indicate that the proposed tall chamber has promising potential as a method for measuring fluxes of VOCs at the soil surface.

INTRODUCTION
The need for measuring gas fluxes from soils to the atmosphere originated with interests in some agricultural and ecological processes. For example, the measurements of \( \text{O}_2 \) and \( \text{CO}_2 \) fluxes are important in evaluating the respiration of soil microorganisms and plant root systems. The measurements of volatile losses of nitrogen compounds such as \( \text{NH}_3, \text{NO}, \text{NO}_2 \) and \( \text{N}_2\text{O} \) from soils provide information about the nitrogen cycle in agricultural and natural ecosystems, as well as in evaluating efficiencies of fertilizer application. In the last decade or so, environmental concerns have resulted in the need for accurate measurements of fluxes of a variety of gases from soil to the atmosphere. For example, it is believed that \( \text{CO}_2 \) emissions have contributed to the “greenhouse effect” and global warming, that \( \text{N}_2\text{O} \) fluxes have an effect on the depletion of the \( \text{O}_3 \) layer in the lower stratosphere, and that emissions of some pesticides, such as soil fumigants, and volatile organic compounds (VOCs) residing below the soil surface have the potentials to cause health and safety hazards.

In general, there are two major categories of methods for measuring gas fluxes from soils to the atmosphere: micrometeorological methods and enclosure-based methods. The meteorological techniques require that emissions
occur over a large surface area, so that a relatively stable gas concentration gradient can be established and detected above the soil surface. Reviews and comparisons of various meteorological techniques are available. The enclosure-based methods include passive (or closed) and active (or flow-through) chambers, which allow the measurements of gas emissions over small surface areas. In comparison to the meteorological techniques, the important features of the chamber methods are their low cost, simplicity of fabrication, and ease of operation. Their most important feature, perhaps, is their capability for measuring gas emissions over very small surfaces, which allows them to be used in many situ field studies of emissions of VOCs from man-made sources, and in laboratory studies to obtain data necessary for understanding physical, chemical, and biological fundamentals of volatile contaminant transport and fate in soils and at the soil–air interface.

The passive chamber systems have long been used for measuring fluxes of the traditional trace gases, such as NO$_2$, CO$_2$, and CH$_4$. In this method, an open-bottom chamber is placed over the soil surface, covering a surface area ($A$) and creating a closed volume ($V$) above the soil surface. The concentration of the target gas in the chamber increases with time due to the gas flux from the soil matrix into the chamber. By monitoring this concentration increase, the gas flux can be estimated. Various mathematical models have been used to calculate fluxes from the data obtained by closed chambers. For example, a linear model is widely used under the following assumptions: (1) the concentration of the target gas ($C$) in the chamber increases linearly with time ($t$); (2) the gas flux at the soil surface is constant within a relatively short chamber placement period; and (3) there is no concentration gradient of the target gas in any direction within the chamber at any specific time (i.e., the target gas is evenly distributed or well-mixed within the chamber). As noted by many investigators, the closed chamber method with a linear model yields an underestimate of the real gas flux due to the concentration build-up of the target gas in the chamber. To minimize this concentration effect, chamber users employ short chamber placement times to obtain an approximate linear relation between $C$ and $t$ within the chamber. There have also been studies and applications of nonlinear models, which do not require the first two assumptions for the linear model as mentioned above.

In comparison to emissions of many soil trace gases, emissions of VOCs from anthropogenic sources have some unique features. First, the soil surface areas of VOC emissions are often limited in size. Examples are accidental leak/spill sites, small waste disposal sites, and small-scale soil incorporation of volatile pesticides. Second, the VOC fluxes are often very intense soon after the compounds are introduced into the soil due to the high mass density of the sources. Examples include accidental leak and/or spill sites and early stages after soil-incorporated application of volatile pesticides. When applying closed chambers to these situations, it is obvious that a closed chamber should have a relatively large volume ($V$) to compensate for the rapid concentration increase of the target VOC gas within the chamber. Assume that the chamber has a height of $H$ and a uniform cross-section area of $A$. The chamber volume can then be given by $V = HA$, which indicates that an increase in either $A$ or $H$ leads to an increase of $V$. An increase in $A$ will not serve the purpose of increasing $V$, since the amount of gas emitted into the chamber is directly proportional to $A$. Thus, increasing the chamber height ($H$) becomes the preferred choice for increasing the chamber volume. However, when the chamber volume is enlarged by increasing the chamber height, a well-mixed condition within the chamber may not be obtained during a short chamber placement time (e.g., 10–20 min), since there exists a vertical concentration gradient within the chamber. The development of a suitable model for the tall closed chamber becomes necessary.

In this study, a closed chamber ($H > 50$ cm) much taller than those commonly used ($H < 20$ cm) has been proposed. The main features of this tall chamber are that it allows a vertical concentration gradient of the target gas to exist within the chamber, and the concentration build-up of the target gas in the chamber is minimized due to the large vertical dimension of the chamber. The emission and transport behavior of the target gas in a simulated soil-chamber system were analyzed with diffusion theory and the principle of mass balance. The proposed tall chamber and its model were tested in a laboratory prototype of the soil-chamber system. The results of the laboratory tests are presented and analyzed.

**THEORY**

We define a tall closed chamber in our study to be an enclosure that has a vertical dimension significantly larger (1 order of magnitude) than its horizontal dimensions. The tall chamber system at the soil surface used for our theoretical analysis is shown schematically in Figure 1. To facilitate our analysis, we make the following assumptions:

1. The chamber placement time ($t_p$) is relatively short (e.g., less than 30 min).
2. The target gas concentration in the chamber is zero before the chamber is placed at the soil surface. After the chamber is placed at the soil surface, there are no sinks, or transformation reactions of the target gas, within the chamber during the short chamber placement period.
The flux of the target gas into the chamber is uniform over the entire covered soil surface. This uniform input creates an upward, diffusion-driven movement of the target gas in the chamber. The vertical dimension of the chamber is large enough and the time frame for the chamber placement is sufficiently short that the diffusion front of the target gas will not reach the top of the chamber. This allows a model of diffusion into a semi-infinite medium to be used as an approximation for describing the gas transport in the chamber.

The governing equation for the upward, 1-dimensional diffusion of the target gas in the tall chamber is Fick’s second law of diffusion:

$$\frac{\partial^2 C(h,t)}{\partial h^2} = D_a \frac{\partial C(h,t)}{\partial t}$$  \(1\)

where $D_a$ is the diffusion coefficient of the target gas in the air within the chamber. Equation 1 is subject to the following initial and boundary conditions for the tall chamber described earlier:

$$C(h,0) = 0$$  \(2\)

$$C(+\infty, t) = 0$$  \(3\)

To solve eq 1, we further assume that the gas flux at the covered soil surface is relatively constant over the short chamber placement period

$$-D_a \frac{\partial C(h,t)}{\partial h} = f_s$$  \(4\)

We make this assumption or simplification based on the following facts: (1) the time frame of the chamber placement (in magnitude of min) is much smaller than the entire VOC emission period of interest, which is usually in the magnitude of days or weeks; and (2) the ample vertical space of the tall chamber allows the target gas to diffuse freely away from the surface within the short chamber placement time. Equation 1 with the conditions of eqs 2, 3, and 4 can be solved using Laplace transform, which gives the following solution:

$$C(h,t) = 2 \frac{f_s}{\sqrt{\pi D_a}} \exp\left(-\frac{h^2}{4D_a t}\right) \frac{h}{D_a} \text{erfc}\left(\frac{h}{\sqrt{4D_a t}}\right)$$  \(5\)

where erfc(x) = 1 – erf(x) is the complementary error function. If at $t = t_p$, a target gas concentration of $C_i$ is measured at a height of $h_i$ above the soil surface in the chamber, eq 5 can be rearranged and used to calculate the flux ($f_s$), provided $D_a$ is known.

$$f_s = \frac{C_i}{2} \left[\frac{t_p}{\pi D_a} \exp\left(-\frac{h_i^2}{4D_a t_p}\right) \frac{h_i}{D_a} \text{erfc}\left(\frac{h_i}{\sqrt{4D_a t_p}}\right)\right]^{-1}$$  \(6\)

When $D_a$ is unknown, the tall chamber and eq 5 can also be used to calculate the flux if two gas concentrations of $C_1$ and $C_2$ are measured at two heights of $h_1$ and $h_2$ above the soil surface at $t = t_p$. In this case, eq 5 will give two equations with two unknowns, that is, $f_s$ and $D_a$:

$$C_1(h_i, t_p) = 2 f_s \frac{t_p}{\pi D_a} \exp\left(-\frac{h_i^2}{4D_a t_p}\right) \frac{h_i}{D_a} \text{erfc}\left(\frac{h_i}{\sqrt{4D_a t_p}}\right)$$

$$C_2(h_i, t_p) = 2 f_s \frac{t_p}{\pi D_a} \exp\left(-\frac{h_i^2}{4D_a t_p}\right) \frac{h_i}{D_a} \text{erfc}\left(\frac{h_i}{\sqrt{4D_a t_p}}\right)$$  \(7\)

By solving these two equations simultaneously, the two unknowns in eq 7 can be obtained. Thus, this procedure will be able to calculate the flux, as well as provide valuable information for gas transport (i.e., $D_a$) in the tall enclosure.

**MATERIALS AND METHODS**

**Experimental Setup**

In this laboratory study, an emission-diffusion system, as shown in Figure 2, was designed and constructed to simulate a VOC emission situation. The source chamber for the target gas was a 2-L Pyrex glass bottle with a small injection/sampling port drilled on its wall ~10 cm from the bottom. The effective volume of the source chamber...
(V_s) was 2.23 L. The soil column was 10-cm high, formed by air-dried silty loam or fine sands packed into a glass tube with an i.d. of 5.2 cm, and placed on the neck of the source chamber bottle. The soil surface area of this soil column (A_s) was 21.24 cm². The total volume of the soil layer was 212.4 cm³.

Two diffusion chambers were designed to simulate a tall passive chamber. One chamber consisted of a piece of clear glass pipe, with a total height of 60 cm and an i.d. of 5.75 cm. Another chamber was a clear PVC pipe with the same height but an i.d. of 5.65 cm. The inside diameters of these two diffusion chambers were selected so that they could slide around the glass tube containing the soil layer. The space between the diffusion chamber and the glass soil column tube was sealed with Teflon tape during flux measurement. Due to the 10-cm thickness of the soil layer, the effective height of the two diffusion chambers (H) was 50 cm, resulting in chamber volumes of 1298 cm³ for the glass chamber and 1254 cm³ for the PVC chamber. The outside walls of the diffusion chambers were covered by adhesive aluminum tape to block the light. A removable rubber stopper was used as the top cover of the diffusion chambers.

To minimize possible reaction between the target chemical vapor and the PVC chamber and the rubber, the inside wall of the PVC chamber was sprayed with a chemically inert lubricant (Dry Film Lubricant, Fisher Scientific Co.), and the rubber stopper was wrapped with Teflon tape. A Teflon vent tube with an i.d. of 0.4 cm and a length of 6 cm was installed through the rubber stopper to equalize the barometric pressure between the inside and outside of the chamber. Through the rubber stopper, two pieces of stainless steel tubing (0.6 mm i.d.) were installed at two different heights (h_1 and h_2) above the soil surface as sampling ports (see Figure 2). A twin-syringe set, which consisted of two gas-tight glass hypodermic syringes, was used to draw two 10-mL gas samples simultaneously (i.e., at a placement time of t_p) at h_1 and h_2, as shown in Figure 2. The gas samples were directly injected into an HP 5890A gas chromatograph (GC) equipped with a flame ionization detector (FID) to determine the chemical concentration of the gas samples. The detector (FID) contained a 0.5-mm × 75-m megabore column with the bound phase DB-624 (J & W Scientific, Folson, CA). A 0.5-mL injection-sampling loop was equipped and provided accurate injection volumes but required a gas sample volume of at least 5 mL for loop flushing. Both the injector and oven temperature were set at 90 °C, and the FID temperature was maintained at 250 °C. The GC operation and data acquisition were fulfilled by a computer-operated ChemStation (Hewlett Packard Co.).

**Properties of Chemicals Used**

Two VOCs were used in this laboratory study: CH₂Cl₂ and CH₃Br. CH₂Cl₂ is a colorless solvent commonly used for degreasing and cleaning in industry. This chemical has a relatively high vapor pressure of 440-mmHg at 25 °C and a boiling point of 40 °C at the ambient atmospheric pressure. In a regular laboratory at the ambient pressure and temperature, liquid CH₂Cl₂ can be used to provide a constant vapor source. The chemical used in our experiment was obtained in a liquid form in dark brown glass bottles with a 99.9+% purity (Fisher Scientific Co.) CH₃Br is a biocidal fumigant widely used for various commercial and agricultural purposes, especially for soil fumigation. This chemical is highly volatile with a vapor pressure of 1420-mmHg at 20 °C and a low boiling point of 3.6 °C at the ambient pressure. At the ambient temperature and pressure, CH₃Br exists as a colorless and odorless gas. The CH₃Br used in our experiment was obtained in a compressed liquid form with a 99.54+% purity within a small steel cylinder (Aldrich Chemical Co., Inc.).

**Experiment 1: Measurement of Constant Flux**

In the first experiment, the tall chamber was used to measure a constant flux created by a constant vapor source of CH₂Cl₂. The purpose of this experiment was to compare the fluxes measured by the tall chamber to a known constant flux, so that the adequacy and accuracy of using the
proposed tall chamber and its model (eq 7) could be evaluated. In the experiment, the soil column was packed with an air-dried loamy silt. The weight of the soil layer was 313.9 g (air-dried). The bulk density (ρ) of the soil layer was 1.48 g/cm³, the porosity (ϕ) was 0.44, and the volumetric air content (α) was 0.43.

At the beginning of the experiment, ~150 mL of liquid CH₂Cl₂ was introduced into the source chamber through the injection port. The port was then sealed with a small rubber stopper wrapped with Teflon tape. After the liquid source was introduced, the source chamber was wrapped with two layers of aluminum foil to block light. With the diffusion chamber off, the system was placed under a fume hood for 16 hr to obtain a constant flux at the soil surface. From the second day, the flux at the soil surface was measured with the tall glass chamber 5 times a day for 4 consecutive days.

For each individual flux measurement, the tall chamber was placed at the soil surface for 5 min (i.e., t_p = 5 min), and two samples at h₁ = 10 cm and h₂ = 30 cm above the soil surface were taken and analyzed to determine the concentrations of the target chemical (C_i and C_j). Immediately after the twin samples (at h₁ = 10 cm and h₂ = 30 cm) were taken, another sample at h = 50 cm was taken to determine whether the diffusion front reached the top of the chamber. The majority of those top samples showed an undetectable concentration of the target gas. A few top samples showed concentrations at very low levels, at least 1 order of magnitude less than those at h₂ = 30 cm. This indicated that no mass accumulation at the top of the chamber occurred during flux measurements. Thus, the diffusion assumption used in the model development was valid during the experiment.

During these 5 days, the weight of the system, including the source chamber, the liquid chemical source, and the attached soil column, was monitored each day to obtain data for estimating the chemical mass loss from the system. After 4 days of flux measurement, the system was set up again using the same procedure, except that the soil surface was sealed with two layers of impermeable plastic film and two layers of adhesive aluminum tape. The total weight of the system was monitored for another 5 days to obtain data for estimating the chemical mass loss from all possible leaks of the system except at the soil surface. During the entire experimental period, the temperature in the fume hood was monitored, and showed a range of 23.9–26.2 °C.

**Experiment 2: Measurement of Changing Fluxes**

In the second experiment, the tall chamber was used to measure fluxes created by two pulse vapor sources of known quantities. The purpose of this experiment was to conduct mass balance comparisons to further evaluate the applicability and accuracy of the tall chamber and its flux model. In this experiment, the soil column was packed with a fine air-dried sandy soil. The weight of the soil layer was 352.5 g (air-dried). The bulk density of the soil layer (ρ) was 1.67 g/cm³, the porosity (ϕ) was 0.37, and the volumetric air content (α) was 0.36. Four emission and mass balance tests were performed: two tests with a known volume of a dense CH₂Cl₂ vapor as the source, and two tests with a known volume of a dense CH₃Br vapor as the source.

In the two tests with CH₂Cl₂, a dense vapor of the chemical was obtained using a gas-tight glass hypodermic syringe, ~1 cm above the liquid CH₂Cl₂ surface in the storage bottle. The density of this vapor at the room temperature (25 °C) and pressure (1 atm) was determined to be 2.26 mg/mL in our laboratory. At the beginning of the first test (Test MC-1), 20 mL of the dense CH₂Cl₂ vapor was introduced into the source chamber through the injection port, and the port was immediately sealed with a rubber stopper wrapped with Teflon tape. Approximately 3 min after the vapor was introduced, two gas samples were taken from the source chamber, using a gas-tight hypodermic glass syringe and a 22-gauge needle, to determine the initial concentration and mass of the chemical in the source chamber. The flux of CH₂Cl₂ at the soil surface was measured with the tall PVC chamber for a 34-hr period—at 0.5-hr intervals for the first 6 hr, at 1-hr intervals for the next 12 hr, and at 2-hr intervals for the final 16 hrs.

In each individual flux measurement, the tall chamber was placed at the soil surface for 5 min (i.e., t_p = 5 min), and two gas samples at h₁ = 10 cm and h₂ = 30 cm above the soil surface were taken and analyzed to determine the concentrations of the target chemical (C_i and C_j). Again, gas samples at h = 50 cm were taken, and the results showed that the diffusion assumption used in the model development was valid during the experiment. After the last flux measurement, two gas samples were drawn from the source chamber and analyzed to determine the final concentration and mass of the chemical in the source chamber. The rubber stopper was then removed, and the source chamber was flushed with air for 12 hr. The system was set up again and the test was repeated (Test MC-2).

In the two tests with CH₃Br, the chemical vapor was obtained by releasing the compressed chemical in the steel cylinder into an air-tight Teflon bag. The density of this vapor at room temperature (25 °C) was determined to be 3.18 mg/mL. At the beginning of the first test (Test MB-1), 10 mL of CH₃Br vapor was transferred, using a gas-tight glass syringe, from the Teflon bag into the source chamber through the injection port. The same procedures as used in Tests MC-1 and MC-2 were followed to determine the
initial concentration in the source chamber, to measure
the flux of CH$_3$Br at the soil surface, and to determine the
final concentration of the chemical remaining in the
source chamber at the end of the test. This test was re-
peated as well (Test MB-2).

RESULTS AND DISCUSSIONS

Experiment 1: Measurement of Constant Flux
The concentrations of $C_1$ and $C_2$ measured at $h_1$ and $h_2$ in
each individual chamber placement were used in eq 7 to
calculate the corresponding flux. It should be noted that
this flux could be the flux at the soil surface only when
the tall chamber has a uniform cross-section area ($A_c$) that
is equal to the covered soil surface area (see Figure 1).
However, the tall glass chamber used in this experiment
had a cross-section area of 25.97 cm$^2$, which was greater
than the soil surface area ($A_s$) of 21.24 cm$^2$. The ratio of
$A_c : A_s$ was 1.223. Thus, the fluxes calculated by eq 7 should
be corrected by a factor of 1.223 to obtain the flux at the
soil surface, assuming a mass balance (or continuity) con-
tion was present at the soil-air interface. The corrected
fluxes at the soil surface during the entire experimental
period are shown in Figure 3. The values of the 20 fluxes
in Figure 3 were from 10.65 to 12.66 mg/cm$^2$-hr, with an
arithmetic mean of 11.93 mg/cm$^2$-hr and a standard de-
viation of 0.47 mg/cm$^2$-hr.

To evaluate the applicability and accuracy of the tall
chamber and its flux model (eq 7), we compared the
fluxes measured by the tall chamber to the flux at the
soil surface determined by mass loss from the system.
Data obtained from monitoring the weight of the sys-
tem during the experiment showed that CH$_2$Cl$_2$ escaped
from the system at a rate of 516.14 mg/hr when the soil
surface was open. When the soil surface was covered,
the loss rate of the chemical from the system was mea-
sured to be 268.35 mg/hr. Thus, the loss rate of the chemi-
cal from the soil surface was estimated to be 247.79 mg/
hr. The mass loss not from the soil surface was likely due
to leakage through the sampling port of the source cham-
ber and the gap between the source chamber neck and
the glass tube holding the soil column. The rate of this
mass loss was constant during the experiment, as shown
by the weight measurement data. Thus, this escaping
loss should not affect the gas flux at the soil surface dur-
ing the experiment.

The ratio of the loss rate from the soil surface ($R_s$) to
the total loss rate from the entire system ($R_t$) was 0.48. We
divided the chemical loss rate from the soil surface by

\[
\frac{R_s}{R_t} = 0.48
\]

Figure 3. Results of Experiment 1.
the soil surface area, and obtained a surface flux of 11.67 mg/cm²-hr. This flux of CH₂Cl₂ is shown as a solid line in Figure 3. It can be seen that the average measured by the tall chamber flux (11.93 mg/cm²-hr) was close to the flux estimated from the mass balance data (11.67 mg/cm²-hr). The 20 tall-chamber fluxes were from 91.3 to 108.5% of the mass-balance flux. The comparison indicates that the tall chamber and its flux model can provide a reasonably precise estimate of the actual flux.

As mentioned previously, eq 7 can provide \( D_s \) values while calculating fluxes. Also shown in Figure 3 were the individual \( D_s \) values estimated by eq 7. The \( D_s \) data were plotted in correspondence to the individual fluxes in the experiment. The 20 \( D_s \) values were from 0.196 to 0.239 cm²/sec, with an arithmetic mean of 0.217 cm²/sec and a standard deviation of 0.011 cm²/sec. The diffusion coefficient of CH₂Cl₂ in the still air, as estimated by the Fuller-Schettler-Giddings method, 23 is 0.105 cm²/sec under our experimental conditions (ambient temperature of 25 °C and ambient atmospheric pressure of 1 atm). The average \( D_s \) measured in our experiment is approximately twice as much as the estimated diffusion coefficient in the still air. This is most likely due to the non-still air environment within the tall chamber during the chamber placement and the acquisition of gas samples. Our experimental system was placed under a fume hood that was ventilated continuously during the entire experiment. The tall chamber was kept outside the fume hood before the placement to maintain a zero-concentration condition in the chamber. For each individual flux measurement, the chamber was brought into the fume hood and placed over the soil surface. The air in the chamber could not reach a still state immediately after the chamber placement. The residual air movement was likely to remain in the chamber during the 5 min placement period. On the other hand, the shaking of the tall chamber caused by the ventilating air in the fume hood could also create small and random air movement in the chamber. The random movement of the air in the chamber, although at a very small scale, could enhance the diffusive transport of the target gas, resulting in a greater or enhanced transport coefficient.

**Experiment 2: Measurement of Changing Fluxes**

For the four tests in this experiment (two tests with CH₂Cl₂ and two tests with CH₃Br), we first used eq 7 and the measured concentrations of \( C_1 \) and \( C_2 \) to calculate fluxes. The tall PVC chamber used in this experiment had a cross-section area of 25.07 cm², which was 1.180 times as much as the soil surface area of 21.24 cm². Similarly, the flux values calculated by eq 7 were then corrected by the factor of 1.180 to obtain the fluxes at the soil surface. The surface fluxes for the tests with CH₂Cl₂ (Tests MC-1 and MC-2) were plotted versus time in Figure 4. The surface fluxes for the tests with CH₃Br (Tests MB-1 and MB-2) were plotted in Figure 5.

To further evaluate the capability and adequacy of the tall chamber and its flux model (eq 7), mass balance calculations were conducted for all four tests. The mass of CH₂Cl₂ or CH₃Br lost from the system in each test was calculated using two different approaches: (1) using the initial and final concentrations in the source chamber to calculate the total loss of the chemical from the system \( (M_t) \), where the subscript “t” represents “total loss”, and then using the ratio of \( R_s: R_t \) determined in Experiment 1 to obtain the actual mass loss from the soil surface \( (M_{sd}) \), where the subscript “sd” represents “soil surface loss”); and (2) using the flux data measured by the tall chamber to estimate the mass loss from the soil surface \( (M_m) \), where the subscript “m” represents “measured loss”). The measured mass \( (M_m) \) in each test was actually the total area under the corresponding flux curve (see Figures 4 and 5) multiplied by the soil surface area \( (A_s) \), which can be formulated as

\[
M_m = \sum \frac{f_i + f_{i+1}}{2} (t_{i+1} - t_i) A_s
\]

where \( f_i \) is the flux measured at \( t_i \), and \( A_s \) is the soil surface area. The mass balance calculations and results were summarized in Table 1.

In Test MC-1, the emitted mass from the soil surface measured by the tall chamber \( (M_{sd}) \) was 21.19 mg, which was 96.7% of the mass loss of 21.92 mg from the soil surface \( (M_t) \) estimated by the concentration data from the source \( (M_s) \). In Test MC-2, the emitted mass measured by the tall chamber was 20.28 mg, which was 94.0% of the actual loss of 21.57 mg. In Test MB-1, the emitted mass measured by the tall chamber was 14.16 mg, which was 96.4% of the actual loss of 14.69 mg. In Test MB-2, the emitted mass measured by the tall chamber was 15.09 mg, which was 104.6% of the actual loss of 14.42 mg.

The chemical mass retained in the soil layer at the end of each individual test and the possible degradation loss of the chemical in the soils may alter the above mass recoveries. The alterations, however, will be likely insignificant. In a preliminary test, we found that in the fine sandy soil used in Experiment 2, the equilibrium sorbed-phase-to-gas-phase partition coefficients \( (K) \) were 0.437 (mg/g)/(mg/mL) for CH₂Cl₂ and 0.289 (mg/g)/(mg/mL) for CH₃Br. The sorbed-phase mass is defined in this study as the overall partitioned mass into both liquid and solid phases. If we assume that the gas transport in the soil layer is at a steady state at the end of each test, we can estimate the total mass residing in the soil layer.
Figure 4. Fluxes measured in CH₂Cl₂ tests of Experiment 2.

Figure 5. Fluxes measured in CH₃Br tests of Experiment 2.
At steady state, the governing equation of gas transport in the soil layer is

\[ D_g \frac{\partial^2 C}{\partial z^2} = \frac{\partial C}{\partial t} = 0 \]  

or simply

\[ \frac{d^2 C}{dz^2} = 0 \]  

where \( C \) is the gaseous phase concentration of the target chemical in the soil layer, and \( z \) is the upward dimension with \( z = 0 \) at the bottom of the soil layer and \( z = L \) at the soil surface. Equation 10 is subject to the following boundary conditions:

\[ C \left|_{z=0} = C_{end} \right. \]

\[ -D_g \frac{dC(z)}{dz} \bigg|_{z=L} = f_{end} \]

where \( C_{end} \) is the gaseous phase concentration at the bottom of the soil layer \((z = 0)\) at the end of each test, \( f_{end} \) is the gas flux at the top of the soil layer \((z = L)\) at the end of each test, and \( D_g \) is the gaseous phase diffusion coefficient of the target chemical in the soil layer. The solution of eqs 10, 11, and 12 is

\[ C(z) = C_{end} - \frac{f_{end}}{D_g} z \]  

Thus, the mass of the target chemical in gaseous phase \((M_{gas})\) residing in the soil layer at the end of each individual test is

\[ M_{gas} = a A_s \int_{0}^{L} C(z) \, dz = a A_s L \left( C_{end} - \frac{L}{2 D_g} f_{end} \right) \]  

where \( a \) is the volumetric air content of the soil layer, \( A_s \) is the cross-section area of the soil layer, and \( L \) is the length of the soil layer. The mass in the sorbed phase \((M_{sorbed})\) can be estimated using the following equation:

\[ M_{sorbed} = \rho K M_{gas} \]  

where \( \rho \) is the bulk density of the air-dried soil layer. Thus, the total mass residing in the soil layer at the end of each test \((M_{total})\) is

\[ M_{total} = M_{gas} + M_{sorbed} \]  

Using eqs 14, 15, 16, and the test data, we estimate \( M_{total} \) to be 0.114 mg, 0.092 mg, 0.049 mg, and 0.055 mg for Tests MC-1, MC-2, MB-1, and MB-2, respectively. These estimates alter the mass recoveries in Table 1 to 96.2, 93.6, 96.0, and 104.2% for Tests MC-1, MC-2, MB-1, and MB-2, respectively.

We considered degradation loss only for that portion of the chemical sorbed in the soil layer. A laboratory study showed that CH₃Br has a half-life of 38.7 days in the air-dried sandy soil used in this experiment. In a preliminary 24-day degradation test, we found that there was no significant degradation for CH₂Cl₂ in the same soil. Due to the small quantity of chemicals sorbed in the soil layer during the experiment, the degradation loss in this study was neglected.

**General Discussions**

As shown above, the tall chamber and its flux model (eq 7) provide reasonably good estimates of the surface fluxes in both Experiments 1 and 2 conducted in our laboratory. The tall chamber and the flux model should give reasonable estimates of the real fluxes, as long as the assumptions used in the model development are satisfied to a certain degree, and the target gas behaves in the tall chamber with a diffusive nature. Our experiments were conducted in the laboratory under well-controlled conditions, which were set to facilitate the assumptions used in the model development. In both experiments, the chamber placement time \((t_p)\) was kept relatively short (5 min). In Experiment 1,

<table>
<thead>
<tr>
<th></th>
<th>Test MC-1</th>
<th>Test MC-2</th>
<th>Test MB-1</th>
<th>Test MB-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Concentration in Source Chamber (C_0) (mg/L)</td>
<td>21.247</td>
<td>20.788</td>
<td>14.004</td>
<td>13.818</td>
</tr>
<tr>
<td>Initial Chemical Mass (M_0 = C_0 \times V_{sc}) (mg)</td>
<td>47.381</td>
<td>46.357</td>
<td>31.229</td>
<td>30.814</td>
</tr>
<tr>
<td>Final Concentration in Source Chamber (C_{end}) (mg/L)</td>
<td>1.185</td>
<td>1.051</td>
<td>0.555</td>
<td>0.619</td>
</tr>
<tr>
<td>Final Chemical Mass (M_{end} = C_{end} \times V_{sc}) (mg)</td>
<td>2.643</td>
<td>2.344</td>
<td>1.238</td>
<td>1.380</td>
</tr>
<tr>
<td>Total Mass Loss in Test (M = M_0 - M_{end}) (mg)</td>
<td>44.738</td>
<td>44.014</td>
<td>29.991</td>
<td>29.434</td>
</tr>
<tr>
<td>Mass Loss at Soil Surface (M = 0.49 \times M_{end}) (mg)</td>
<td>21.922</td>
<td>21.567</td>
<td>14.696</td>
<td>14.423</td>
</tr>
<tr>
<td>Emission Loss Measured by Tall Chamber (M_m) (mg)</td>
<td>21.195</td>
<td>20.280</td>
<td>14.163</td>
<td>15.092</td>
</tr>
<tr>
<td>Mass Recovery = (\frac{M_m}{M}) x 100 (%)</td>
<td>96.7</td>
<td>94.0</td>
<td>96.4</td>
<td>104.6</td>
</tr>
<tr>
<td>Estimated Mass Retained in Soil Layer (M_{r-total}) (mg)</td>
<td>0.114</td>
<td>0.092</td>
<td>0.049</td>
<td>0.055</td>
</tr>
<tr>
<td>Degradation Loss (mg)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Altered Mass Recoveries (%)</td>
<td>96.2</td>
<td>93.6</td>
<td>96.0</td>
<td>104.2</td>
</tr>
</tbody>
</table>

*Terms used in table: Subscripts “0” and “end” represent the beginning \((t = 0 \text{ hr})\) and the end \((t = 34 \text{ hr})\) of each test; \(V_{sc}\) is the volume of the source chamber (2.23 L); Other terms are self-explanatory or defined in the text.*
a relatively constant flux was maintained at the soil surface during the entire experimental period. Thus, all requirements or assumptions in the model development were met, and then the flux was measured and estimated by the tall chamber and its flux model. In Experiment 2, a changing flux was present at the soil surface in each test. Thus, “a constant flux during the 5-min chamber placement period” was only an approximate condition, and the flux measured should be regarded as an approximate average over the 5-min placement period. However, the mass balance data obtained from all four tests in Experiment 2 indicate that the tall chamber and its flux could still provide reasonably good estimates of the actual fluxes.

The experimental protocol used in this study is considered to be an appropriate and effective approach for evaluating the adequacy of the tall chamber technique. We designed an experimental system and carefully selected two volatile chemicals to generate either a constant flux (Experiment 1) or a flux with a known mass source (Experiment 2) at the soil surface. The tall chamber was then used to measure these fluxes. The comparison of the measured flux with the known flux or the measured mass loss provides good indications about whether the chamber could operate as expected. Flux comparison and mass balance experiments, such as the ones in this study, will enable chamber users to evaluate quantitatively the performance of flux chambers, including both passive and active chambers. For example, similar experimental systems and protocols have been applied successfully in our recent studies on other flux chambers.

The tall chamber and its flux model appear to work very well in this laboratory study, which indicates that this new chamber technique can be an applicable tool for measuring gas fluxes at the soil surface in laboratory studies where experimental conditions can be well controlled. Laboratory experiments on VOC transport and fate in soil have been, and will be, conducted extensively to obtain information about mechanisms that govern VOC behavior in subsurface soil. When a laboratory experiment involves measurement of VOC volatilization rate at the soil surface, the tall chamber and its flux model presented in this study may be chosen as an adequate method. Use of the complicated nonlinear model (eq 7) might be a disadvantage. However, the widespread and easy application of computer programming makes it no longer a problem to use the complicated model.

It is suggested that a tall closed chamber be designed with a height significantly greater than 15–20 cm, the typical height of shallow closed chambers widely used previously. Considering that a very tall chamber might be unstable and difficult to operate in a regular laboratory, a height from 50 to 80 cm is probably a reasonable design range. Theoretically, the two sampling heights \((h_1, h_2)\) can be selected arbitrarily within a tall chamber. This laboratory study shows that an \(h_1\) of 10 cm and an \(h_2\) of 30 cm may be choices of selection. Chamber placement time depends on the diffusion coefficient \((D)\) of the target gas. Methods for estimating \(D\) and the time for the diffusion front to reach a certain height can be found in the literature.

The tall chamber technique may also have a potential to be used in field situations. However, a field environment is often associated with conditions that are not controllable and not consistent with the requirements or assumptions used in our theoretical analysis and model development for the tall chamber. We consider the following to be the two major problems for the tall chamber in the field: (1) radiative heating on the chamber wall, which may create internal circulating convection of the target gas and destroy the diffusive concentration gradient; and (2) vertical air convection driven by the buoyancy due to the variations of temperature and humidity near the soil surface, which may fail the assumption of diffusion-driven transport of the target gas in the tall chamber. The first problem may be avoided by simply applying thermal isolation layer(s) to cover the outside surface of the chamber wall. The second problem, however, cannot be easily overcome because it is not associated with the chamber itself but with the actual thermal and humidity conditions in the field. It should be pointed out that this problem created by the ambient conditions is present when applying any kind of chamber. For our tall chamber, one possible remedy is to add a convection term in the governing equation (eq 1) to include the transport of the target gas along with the thermal convection of air. The mathematical solution for the modified governing equation may be relatively easy and straightforward. However, verification of such a solution or the corresponding flux model will require careful experimental design and a significant amount of laboratory work, which is beyond the scope of this paper.

**CONCLUDING REMARKS**

Previous studies have shown that closed chambers are useful tools for measuring emissions of gases from soil and water to the atmosphere, especially over small surface areas. When measuring intense VOC emissions, a fast and significant mass or concentration build-up will occur within a shallow closed chamber. Under these situations, a shallow closed chamber may become insufficient, unless an adequate flux model is used to account for the nonlinear relation between concentration and time. The tall passive chamber and its flux model proposed in this study may be an attractive alternative to the shallow chamber method. By providing a relatively large chamber volume and recognizing the presence of a gas concentration
gradient in the chamber, a tall closed chamber is considered to be applicable for intense VOC emissions. Operation of a tall chamber is simple, since only a one-time sampling at two different heights in the chamber is required for each flux measurement.

The tall chamber and its flux model were demonstrated to be an applicable tool in laboratory experiments. However, further work needs to be done to verify its applicability in field situations. In addition, sensitivities of sampling and analysis may also limit the applicability of the tall chamber for low-level emissions, where shallow closed chambers and relevant nonlinear flux models may remain preferable. Studies on the applicability of the tall chamber to field situations and comparison of relative applicability and effectiveness of tall and shallow closed chambers under both intense and low-level emission situations are underway in our research group.

ACKNOWLEDGMENTS
The authors thank Drs. J. Gan and F.F. Ernst for their help in the experimental part of this study.

REFERENCES

About the Authors
Dr. Frank F. Gao is a senior environmental engineer with the Air Quality Management Section, Division of Air and Waste Management, Delaware Department of Natural Resources and Environmental Control, 156 S. State St., Dover, DE 19901. Dr. Yan Jin is a faculty member with the Department of Plant and Soil Sciences, University of Delaware, Newark, DE. Drs. Scott R. Yates and Sharon Papiernik are research scientists with the Soil Physics and Pesticide Research Unit, U.S. Department of Agriculture Salinity Laboratory, U.S. Department of Agriculture, Riverside, CA. Correspondence should be addressed to Dr. F. Gao (e-mail address: fgao@state.de.us).