A Dynamic Two-Dimensional System for Measuring Volatile Organic Compound Volatilization and Movement in Soils

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ABSTRACT

There is an important need to develop instrumentation that allows better understanding of atmospheric emission of toxic volatile compounds associated with soil management. For this purpose, chemical movement and distribution in the soil profile should be simultaneously monitored with its volatilization. A two-dimensional rectangular soil column was constructed and a dynamic sequential volatilization flux chamber was attached to the top of the column. The flux chamber was connected through a manifold valve to a gas chromatograph (GC) for real-time concentration measurement. Gas distribution in the soil profile was sampled with gas-tight syringes at selected times and analyzed with a GC. A pressure transducer was connected to a scani-valve to automatically measure the pressure distribution in the gas phase of the soil profile. The system application was demonstrated by packing the column with a sandy loam in a symmetrical bed–furrow system. A 5-h furrow irrigation was started 24 h after the injection of a soil fumigant, propargyl bromide (3-bromo-1-propyne; 3BP). The experience showed the importance of measuring lateral volatilization variability, pressure distribution in the gas phase, chemical distribution between the different phases (liquid, gas, and sorbed), and the effect of irrigation on the volatilization. Gas movement, volatilization, water infiltration, and distribution of degradation product (Br\(^{-}\)) were symmetric around the bed within 10%. The system saves labor cost and time. This versatile system can be modified and used to compare management practices, estimate concentration–time indexes for pest control, study chemical movement, degradation, and emissions, and test mathematical models.

Gas emission from the soil to the atmosphere is now an international interest due to concerns for environmental quality. Chemicals of interest range from organics such as pesticides (Seiber et al., 1996), solvents, hydrocarbon fuels, oils, and industrial byproducts to inorganics such as mercury from agricultural, industrial, or waste sites. Emissions of other important gases such as CO\(_2\), N\(_2\)O, NO\(_x\), and CH\(_4\) are also of interest for a better understanding of their global cycle (Rochette et al., 1997; Thomson et al., 1997; Woodrow and Seiber, 1991) and some have enhanced the inlet and outlet (Gao et al., 1997, 1998). These chambers cannot measure small-scale spatial variability of volatilization either associated with soil surface conditions (e.g., bed–furrow system) or soil variability (e.g., cracked soil).

Calculations based on simulation models suggest that there is a significant time lag between gas injection and the peak of volatilization (Chen et al., 1995). Therefore, gas flux within the soil should be understood so that chemical movement in the gas and liquid phases can be estimated along with any associated degradation product. This knowledge will assist in predicting the future release of these chemicals to the atmosphere.

However, chambers are usually installed directly at the soil surface without any measurement of gas movement occurring in the soil profile (Russell et al., 1998). Likewise, if the gas flux is measured in the soil, there is often no information concerning surface emissions (van Bochove et al., 1998). Only a few experiments have been conducted that simultaneously measured emission and gas movement in the soil profile. Gan et al. (1997) investigated the importance of soil surface condition on the volatilization and distribution of methyl iodide in a laboratory soil column. This study was limited to one dimension and uniform conditions were maintained throughout the experiments. Yates et al. (1997) compared methyl bromide volatilization and distribution in the soil profile for different field application techniques. However, the volatilization flux chambers did not allow the study of small-scale spatial distribution. Therefore, a system that allows the study of spatial and temporal distribution of volatile compounds in the soil associated with its emission under complex and variable conditions is needed.

Spatio–temporal study of chemical movement and volatilization requires numerous samples. Automated measurement decreases labor requirement and the chance of random and systematic errors compared with manual sampling. Wang et al. (1999a) developed an automated system to measure the emissions of highly volatile compounds from an active chamber. They used a datalogger to control a solenoid valve system to switch from one chemical trap to another. Each chemical trap represented one time interval. McGinn et al. (1998) measured soil respiration with an automated system. Five chambers were connected to a CO\(_2\) gas analyzer.

Abbreviations: GC, gas chromatograph; VOC, volatile organic compound; 3BP, propargyl bromide (3-bromo-1-propyne).
Both studies show that highly accurate and reproducible measurements could be obtained from automated systems. Therefore, an automated system for the study of a spatial and temporal volatile organic compound (VOC) emission associated with VOC movement in soil would be ideal.

This paper describes the design of an automated sequential laboratory flux chamber for measuring the volatilization of chemicals at the soil surface associated with the chemical movement in the soil profile. An example of application of this system is also provided in the paper.

**MATERIALS AND METHODS**

**Considerations in the System Design**

The purpose of developing such a system was to study how management practices influence the small-scale spatial variability of fumigant volatilization associated with the chemical movement in the soil profile. The system consists of a two-dimensional soil column with a flux chamber attached to the top and partitioned into several sections. To be useful, the system had to meet certain criteria: (i) The soil column had to be at least 0.5 m deep and the column had to be thick enough to minimize gas flux along the walls. (ii) The soil column had to be completely gas tight and leak proof with many sampling ports. (iii) The soil column connected to the volatilization chamber had to allow for different surface and lower boundary conditions, and a change of conditions during the course of the experiment. (iv) Volatilization and soil gas pressure needed to be continuously monitored. (v) Sorption and desorption of the chemical on the different materials used to build the chamber needed to be minimized. (vi) The system design had to be flexible so that different scenarios could be tested.

Additional criteria were needed for the flux chamber: (i) The chamber had to cover the entire cross section of the soil column. (ii) The chamber can be subdivided into several independent sections, each section having its own flow rate. (iii) No stagnant air zones inside the chamber should develop. (iv) The flow should have minimal turbulence. (v) The inlets and outlets of the sections needed to be large enough so that no pressure deficit occurs. (vi) Inlet tubing had to be long enough to control loss by back diffusion and connected to a chemical trap to prevent contamination of the air flowing in the chamber.

A photo of the volatilization chamber above the soil column is shown in Fig. 1. Because of the complexity of the system, each component is discussed separately.

**Soil Column and Chemical Distribution Measurement**

The soil column was made of 12-mm-thick acrylic (Plexiglas) with inner dimensions of 0.6 m wide, 0.6 m high, and 0.025 m thick. One side of the column can be removed so that soil sampling can be performed at the end of the experiment. Stainless steel screws every 5 cm and 20-mm-thick foam were used to seal together both sides of the column. Silicone was applied on the inside of every joint. Self-adhesive aluminum tape was positioned on the outside of every joint and on the joint with the flux chamber to ensure a gas-tight seal. A gas-tight inlet was used on each side of the column, above the soil surface, to apply water using a Mariotte bottle setup, if needed. The Mariotte bottle system maintains a constant pressure head (i.e., water height at the soil surface). Four equally spaced outlets were placed at the bottom of the column. The outlets were gas-tight when the valves were closed. If desired, they were opened to release internal pressure during irrigation and drainage and to capture the VOC that would move to a deeper depth. The chemical can be applied in the system either through any sampling port in the soil profile, through the irrigation water at the soil surface, or through the air inlet in the atmosphere above the soil surface.

Chemical distribution in the gas phase was sampled at selected times by hand at 62 sampling ports placed in a radial pattern on one side of the column. The sampling ports were made of a 2-mm brass tube fitting (Swagelok Part no. B-100-6; San Diego Valve and Fittings Co., San Diego, CA) with the inner side sealed with a 3-mm-thick by 3-mm-diameter Teflon face septa (Supelco, Bellefonte, PA). The connection to the acrylic was made using a 10-32 threaded hole, and a
plastic gasket was inserted between the acrylic and the fitting to prevent leakage. Gas-tight syringes of 100 μL (pressure lock series; Alltech Associates, Deerfield, IL) were inserted into sampling ports to withdraw 50-mL soil gas samples. The samples were kept frozen at −71°C in 8.8-mL headspace vials (2-7199; Supelco) until analysis could be made using a headspace autosampler (Model 7000; Tekmar, Cincinnati, OH) and a GC following the technique described in Papiernik et al. (1999) and Gan et al. (1995).

Chemical distribution in the liquid phase (parent and degradation products) can be sampled during the experiment using syringes in the same manner as the gas phase, provided that the soil contained enough water. This would allow the estimate of the chemical movement and the partitioning of the chemical between the liquid and the gas phases in the course of the experiments. The liquid phase was not sampled during this experiment but only at the end of it.

The distribution of the VOC between different phases (liquid, gas, and sorbed on soil particles) can be addressed at the end of the experiment by soil gas and soil sampling. For soil sampling, the soil column was placed in a horizontal position at the end of the experiment after gas sampling because one side of the column was removed. This side was quickly replaced with an impermeable plastic film so that loss of VOC through volatilization was minimal. The plastic film was perforated for soil sampling and the holes were immediately plugged with an aluminum tape (low permeability to gases). The soil samples were quickly placed in gas-tight containers with a solvent to quantify the mass of the original chemical sorbed on the soil particles and present in the liquid phase.

For our example, propargyl bromide (3-bromo-1-propyne; 3BP) was extracted with ethyl acetate (2:1) and the extract was analyzed using a GC. Additional samples can be taken so that the distribution of the degradation product can be measured. For our example, 3BP degrades into Br⁻ ion and was extracted with water (2:1) and analyzed by ion chromato-graphy.

Volatilization Measurement

The design of the flux chamber was done for studying small-scale spatial variability of VOC emission associated with the variability of the soil surface. In our example, the soil surface variability was due to a bed–furrow system with the irrigation applied only in the furrow and the bed covered by a plastic tarp (high-density polyethylene film). This plastic tarp is thought to keep fumigant volatilization to a minimum and thus to increase the efficiency of the fumigation in killing nematodes and other targeted organisms.

The flux chamber was made of the same acrylic plastic as the soil column. For the test described in this paper, the chamber was divided into five sections, each section corresponding to a region of a bed–furrow system. Two pieces of acrylic were used to funnel the air toward the outlet and to avoid any stagnant air space. An acrylic slit of 3-mm-thick plastic was placed into a groove cut into the side of the chamber to separate the sections. Silicone sealant and aluminum tape were used to ensure a gas-tight system.

An automatic sampling system similar to the one described in Wang et al. (1999a) was used to collect emission samples. The different sections of the flux chamber were connected in parallel to a vacuum. Mechanical flowmeters controlled the flow rate in each section. Teflon tubing was used to connect each section to a solenoid valve. The air was coming from inlets. The air inlets consisted of 7-mm-diameter holes in the back of the column 30 mm above the soil surface. This height was chosen so that the soil surface could be ponded with water without affecting the air inflow. Nylon barbed fittings were used to connect 1-m-long vinyl tubing (6-mm i.d.; Tygon, Akron, OH) to the inlets. This length (1 m) was necessary to limit the loss through back-diffusion. The tubing was also connected to a chemical trap (activated charcoal tubes) to prevent inflow air contamination from entering the chamber.

A computer was programmed to turn on and off the solenoid valves sequentially so that only one chamber section was sampled at a particular time interval. The air from the sections that were not sampled was sent directly to a fumigant trap and discarded. During sampling, the effluent from a chamber section flows through stainless steel tubing to the GC (Model 5890; Hewlett Packard, Palo Alto, CA) for chemical concentration measurement. After a predetermined time to purge the tubes, the control circuitry directed the GC to open the sampling loop, collect effluent gases, and measure the VOC concentration.

The volatilization flux density ($J_{VOC}$, mg m⁻² s⁻¹) at the soil surface was calculated as follows:

$$J_{VOC} = F(C_{out} - C_{in})/A$$  [1]

where $F$ is the mean air flow rate (m³ s⁻¹) as controlled by the flowmeter, and $C_{out}$ and $C_{in}$ are the chemical concentrations (μg m⁻³) of the air at the inlet (zero in our case) and at the outlet of the chamber section of a surface area $A$ (m²). To further ensure there would be no cross-contamination, a 5-min purge time was used between samples.

Pressure Measurement System

The pressure distribution in the gas phase is important since a pressure gradient may lead to convective gas flux. Pressure gradients may occur from gas expansion after injection and evaporation of a liquid (i.e., fumigant injection), water infiltrating into the soil, or a malfunction of the flux chamber. The pressure distribution was measured using a pressure transducer connected to a 12-port scanivalve and controlled by a datalogger (21X; Campbell Scientific, Logan, UT). Each port was hooked to the back of the column using a hypodermic needle inserted into connector ports.

Rigid wall tubing with a 1.6-mm i.d. was found to be very stable in maintaining pressure. A convective flux due to a transient pressure gradient created during gas sampling was minimized by slowly pulling small 50-μL samples. If larger samples were taken or if the samples were rapidly taken, a pressure gradient could be detected.

Example of System Application

The column was packed by hand with Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralf) to a density of 1.65 kg m⁻³. The soil was initially air-dried and sieved through a 2-mm sieve. The surface condition was a bed–furrow system (Fig. 1), and was 1/2 scale of the proportions used in southern California for strawberry production. One milliliter of liquid propargyl bromide (97% pure) was injected into the center of the column 0.3 m below the bed surface. A 5-h furrow irrigation was applied 24 h after injection with a 20-mm pressure head. A 0.5-mil high-density polyethylene (Trical, Hollister, CA) film (tarp) was used to cover the surface of the bed and the slopes. This is common practice in southern California to install such a tarp over the soil in strawberry, pepper, and tomato production right after fumigation to control fumigant volatilization. However, to save money, growers have a tendency to cover only the bed with the tarp, instead of the entire soil surface. We conducted an experiment to compare the inefficiency of the partial tarp covering and test
different irrigation managements for controlling VOC volatilization to the atmosphere. The example given in this paper represents only one of many tests performed with this system.

The experiment was run for a 9-d period. This corresponds to approximately two to three half-lives of the 3BP in this soil (Yates and Gan, 1998). The air flux was set so that each flux chamber section was completely renewed with fresh air every 10 min. The volatilization flux density in each section was measured every 25 min. This sampling interval was sufficient to capture the peak of volatilization occurring at different times in the different sections. The outlets at the bottom of the column were kept closed during the entire run.

The 3BP distribution in the gas phase of the soil profile was measured many times during the first two days, then once a day. At the end of the experiment, 73 soil samples (approximately 5 g each) were taken on a regular sampling grid (0.07-m interval) for water content, 3BP, and Br⁻ concentration distributions in the profile. The GC concentration measurement followed the method of Gan et al. (1995).

RESULTS AND DISCUSSION
System Testing

It has been suggested that a flux chamber base should be wider than the height of the chamber (Rolston, 1986). Due to the irregular height of the soil surface of our example, the furrow sections were almost three times higher than wide, the bed was about three times wider than high, and the slopes had an irregular shape. It was thus necessary to test if each section had similar flux characteristics. Dense smoke made from burning vegetable oil was injected into each section, so that visual inspection of the chamber performance could be made. Once the smoke was evenly distributed, a vacuum system was applied, creating the same flow rate as for the experiment.

The smoke was completely swept from each section within 1 min and no dead air spaces were produced (i.e., no pockets of smoke remained). The flow in the chamber sections was laminar if the vacuum was kept below 0.15 L min⁻¹. The number of air inlets per section was sufficient since no measurable pressure deficit occurred. Replicate sections produced identical results. Additionally, no smoke could be observed crossing into an adjacent section. These results provide evidence that the chamber worked properly and the sections were well isolated from each other.

Example of Data Interpretation
Chemical Distribution and Volatilization

Figure 2 shows volatilization flux for the different parts of the bed–furrow system. For the slopes and the furrow, the curves represent the average values of both sides of the bed. Note that the points represent only a small fraction of all the samples. This was done to reduce clutter in the figure. The volatilization fluxes varied across the soil surface. It appears in Fig. 2 that the volatilization flux was higher from the bed than from the furrow. It was first thought that the tarp was not properly installed or it was perforated. If this was the case, then the air could have easily escape from the bed when the irrigation started. This was not the case since the pressure increased near the bed surface (Fig. 3). Also, inspection of the tarp after the end of the experiment indicated that the tarp was installed correctly and there were no holes in the material. We performed other tests with the same system that repeatedly demonstrated that volatilization was higher in the furrow than in the bed before irrigation and the inverse occurred after irrigation. The results in Fig. 2 support part of the assertion, but due to a lack of data prior to 48 h we cannot demonstrate this behavior fully with this experiment. This result indicates that the high-density polyethylene tarp is permeable to 3BP and was less efficient in decreasing chemical volatilization than water. Similar observations were made by Gan et al. (1998) for 1,3-dichloropropene and by Wang et al. (1999b) for 3BP. This information can be useful in planning chamber placement in field experiments and for the use of tarp and irrigation in the field.

The 3BP in the gas phase moved by diffusion from the point of injection when the soil was dry (Fig. 4). Note that the concentration distribution at 24 h is right before the irrigation started. Then, 3BP distribution in the gas phase was compressed by the water infiltrating into the profile. The concentration of 3BP in the gas (Fig. 4) and liquid (Fig. 5) phases became higher with time near the bottom of the column although the soil was still very dry (Fig. 5). This is because 3BP was trapped due to a downward movement of the water, leaving little air space for the gas to escape. This result shows the importance of trapped zones of volatile chemical after irrigation that might occur if a subsurface boundary (e.g., perched water table or hardpan) is present. This also shows that the effect of irrigation on the chemical movement goes beyond the wetting front and this has significance for fumigant management. Also, the Henry’s constant, $K_h$, of 0.05 for 3BP indicates that the moist soil should contain more chemical than the dry soil. However, the furrow section had the highest moisture content for the longer period of time while the concentration of 3BP in both liquid and gas phases were near the detection limit underneath the furrow.
This supports the observation that chemical was lost through volatilization.

**Pressure Distribution on Chemical Movement**

The 3BP concentration in the soil profile moved in an almost perfectly radial pattern (Fig. 4) from the point of injection. As soon as the irrigation started, the movement of 3BP in the gas phase was no longer radial. Figure 3 shows the pressure distribution in the gas phase of half the bed-furrow system at different times. The time corresponds to the number of hours after chemical injection and, in parentheses, the number of hours after the start of the irrigation. The water infiltrating into the profile from the furrows (Fig. 6) caused a pressure gradient in the water phase and in the gas phase. The gas phase was compressed up to $8 \times 10^4$ Pa for a fraction of a second and then up to $1 \times 10^3$ Pa for 2 h after the start of the irrigation before returning to equilibrium again (Fig. 3). The air compression occurred because the air exit at the bottom of the column was closed and the soil surface was ponded in the furrows and covered with a plastic film everywhere else. This caused a significant convective gas flux from the soil surrounding the furrow toward the center of the column and toward the center of the bed near the surface. When the irrigation stopped, the draining water created a negative pressure in the gas phase down to $-1 \times 10^4$ Pa near the furrow for a few seconds and a positive pressure near the wetting front (Fig. 6 at 29.5 h). The pressure gradient was observed for about 2 h (29.5 to 32.5 h) before equilibrating again. Based on the ideal gas law, the negative pressure leads to an expansion of the gas phase and thus to a lower gas concentration. The positive pressure leads to a compression of the gas and to a higher concentration.

Assuming that Darcy’s law is applicable and a linear flow occurs, the average linear gas velocity ($v$, length time$^{-1}$) due to pressure gradient could be calculated as follows (Fischer et al., 1996):
Fig. 4. The propargyl bromide (3-bromo-1-propyne; 3BP) (μg cm$^{-1}$) distribution in the soil gas phase at different times after its injection in the center of the column.

Fig. 5. Soil water content distribution (kg kg$^{-1}$), propargyl bromide (3-bromo-1-propyne; 3BP), and Br$^-$ concentration distributions (mg kg$^{-1}$ of dry soil) in the liquid phase at the end of the experiment.
and in the opposite direction from the water flow). The furrow (i.e., in the same direction as the diffusion flux velocity was up to 0.002 m s\(^{-1}\)).

![Fig. 6. Photos of water infiltrating into the soil at different times (the dark regions indicate wet soil).](image)

\[
v = -k_wk_a\frac{1}{\theta g_\mu g}\frac{\Delta P}{\Delta x}
\]

where \(\theta\) is the volumetric gas content (unitless), \(k_w\) is the air permeability (m\(^2\)), \(k_a\) is the relative air permeability (unitless), \(\mu_g\) is the dynamic gas viscosity (\(\mu g \text{ m}^{-1} \text{ s}^{-1}\)), \(\Delta P\) is the pressure difference between two points (\(\mu g \text{ m}^{-1} \text{ s}^{-2}\)), and \(\Delta x\) is the distance between two points (m). The term \(k_a\) can be calculated with (Moldrup et al., 1998):

\[
K_a = 0.66\theta g_\Phi^2
\]

where \(r_e\) is the equivalent radius of the pore space (m) and \(\Phi\) is the total porosity (unitless). Maximum convective flux was from the furrow to the middle of the bed during the irrigation, which means that the gas was pushed toward the bed. The pressure gradient led to a maximum convective velocity of 0.0008 m s\(^{-1}\) after the irrigation started. Maximum convective flux after the irrigation started was from the middle of the column to the furrow (i.e., in the same direction as the diffusion and in the opposite direction from the water flow). The flux velocity was up to 0.002 m s\(^{-1}\) right after the end of irrigation. The flux values are in the same order of magnitude as in Fischer et al. (1996) for organic volatile compounds in soil. The concentration distribution data are also accurate enough to compare the relative importance of diffusive to convective flux at different times. Convective flux was about 5% of the total cumulative flux during the first two hours of infiltration. This information is useful for modeling purposes.

We are aware that the pressure gradient would probably not have built up in the soil profile if the outlets at the bottom of the column had been opened. This would have sensibly changed the VOC movement and thus its volatilization as well. However, pressure gradients may occur when the water table is near the soil surface, a fast water infiltration rate occurs such as heavy rain from a tropical storm, or a dense layer close to the surface can be found (e.g., dense plow layer, shallow soil with rock underneath).

**Distribution between Phases**

After 216 h (9 d), 3BP distribution in the liquid phase (Fig. 5) was similar to that of 3BP in the gas phase (Fig. 4 at 216 h) but the total mass in the gas phase of the entire column was 5% of the values of the liquid phase. This is in agreement with the Henry’s constant, \(K_h\), of 0.05 for 3BP (Yates and Gan, 1998). This result is important for prediction purposes because \(K_h\) has been developed for a two-phase system (i.e., for equilibrium between liquid and gas phases). These data show that the \(K_h\) value was applicable in this three-phase system (solid–liquid–gas). This observation is important since \(K_h\) is used for model predictions. The distribution between phases also helps in predicting further release of chemicals (e.g., hydrocarbons, VOC) to the atmosphere and to the soil water.

**Distribution of Degradation Product**

The Br\(^-\) concentration distribution after 216 h (9 d) was different from 3BP distribution in the liquid phase and the water distribution (Fig. 5). The shape of Br\(^-\) concentration distribution tended to follow the water infiltration pattern (Fig. 6) with higher values under the bed. When the water infiltrated, the gas was pushed toward the center of the column as suggested by the pressure distribution. After infiltration, it diffused through the water phase because most of the pores were occupied with water and because 3BP has a higher affinity for water than for air (\(K_h\) ~ approximately 0.05). Since the water was moving in the opposite direction to the gas, the water had a longer contact time with 3BP than with other regions of the soil profile. There was less Br\(^-\) near the furrow because the volatilization allowed 3BP to rapidly leave the soil in this area resulting in insufficient time for degradation. The Br\(^-\) concentration underneath the bed was low not only due to the volatilization but also because the water reached this area much later (2 d), resulting in less time for the 3BP to degrade. This type of information may be important for volatile compounds that have degradation products as toxic as the original chemical.

**System Precision**

Water content, 3BP, and Br\(^-\) distribution were symmetrical within 10%. This demonstrates that the packing was homogeneous and the sampling, extraction, and chemical analysis techniques were precise. The results discussed above were also precise enough to estimate a chemical’s concentration–time index at different distances from the point of injection and to use it for pest management purposes. Differences in the volatilization flux between both slopes were less than 5% (Fig. 2), indicating consistency along the bed–furrow system. However, the differences between the furrow sections were almost 100% at early times and decreased to about 5% at later times. This was due to differences in water infiltration from the furrows. After the irrigation was ended, the furrow with slower infiltration had a lower volatilization rate. After water redistribution, the difference in the water movement in the soil between the furrow sections was minimal, resulting in volatilization...
estimates that were within 5%. Mass balance tests conducted with this system indicated more than 90% recovery.

**Cost Efficiency of the System**

About 600 gas samples were taken to study 3BP movement in the gas phase. The headspace autosampler saved labor cost and time by eliminating extraction with a solvent. More than 2000 samples were analyzed with the automated volatilization system on a 24-h basis. This would have cost considerably more if a chemical trap would have been used (e.g., charcoal tube at $1 each + labor for analysis). Most labor and effort in measuring during nights and weekends is not needed with this system. An additional advantage to this automated system is that it eliminates errors associated with manual sampling of volatilization (e.g., punctuality, possibility of contamination and degradation during storage, and extraction). This would not be possible with a manual system. The pressure transducer with the scanivalve allows a frequency (time and space) of pressure measurement that would otherwise be impossible by hand or very expensive if many transducers are used.

**Potential Applications of the System**

The dynamic volatilization flux chamber presented in this paper can be used to study the movement of volatile compounds under complex scenarios. The soil surface can be changed between experiments and water can be added during an experiment through different irrigation systems and timings. The injection of the chemical can be done anywhere in the soil column. Gas sampling
devices can easily be added, removed, or changed in position between runs. The shape of the soil column can be modified. The automation of the flux chamber to the GC allows a quasi-real-time measurement. The knowledge of degradation product distribution allows the study of chemicals that have complex cycles or chemicals that have secondary products as toxic as the parent chemical.

The system can be used in different ways (Fig. 7) because it is very versatile. This system is actually used in the laboratory to determine time–concentration indexes for nematode population controlled by fumigation. This system is also being used for studying greenhouse gas emissions from soil monoliths under different management applications (Fig. 7). Instead of pressure measurement, the scanvalve is used to sample soil gas in the profile. The system could be used in the field where electricity is available and the GC could be installed in a safe isolated shelter. However, the sampling tubing should be as short as possible or the purge time between samples increased.

CONCLUSION

The system presented in this paper allows the study of VOC movement in gas and liquid phases of the soil profile and the distribution of their degradation products, as well as their emission to the atmosphere. The contribution of different parts of the soil system (spatial variability) to volatilization can be compared with the sectioned flux chamber. This semi-automated system is cost effective compared with the labor and cost needed to measure volatilization with a chemical trap. Also, the interpretation of 3BP and Br₂ in the liquid phase would have been difficult without the knowledge of the water infiltration pattern, available with a transparent acrylic system. This system can be used to compare management practices, estimate concentration–time indexes, increase our knowledge on chemical movement in the soil associated with spatial variability of volatilization, and test models. Our example indicates the potential of irrigation management to control the movement, degradation, and volatilization of fumigants in soil, and the importance of pressure measurements in interpreting gas movement under complex conditions.

ACKNOWLEDGMENTS

The authors wish to acknowledge Richard Austin for his support with electronic equipment and Chris Taylor for his support with chemical analysis.

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