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Column System for Concurrent Assessment of Emission Potential and Pest Control of Soil Fumigants

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Abstract

Fumigation for soilborne pest and pathogen control is under close scrutiny because of its potential hazardous effects on the environment and on human health. Therefore, reduced-risk yet effective fumigation practices are imperatively needed. We have developed a column system that allows an integrated evaluation of emission potential and efficacy of fumigants. The system consists of a large, packed soil column and a sampling chamber for measuring fumigant emissions at the soil surface. Nematodes (or other pests) can be inoculated into the column and their survival may be assayed after the treatment. This approach was used to evaluate the emission of 1,3-dichloropropene (1,3-D) and its efficacy against the citrus nematode *Tylenchulus semipenetrans* when ammonium thiosulfate, a 1,3-D degrading fertilizer, was applied at the soil surface. Results closely comparable to field observations were obtained. Compared with field studies, the proposed method is rapid and inexpensive, and thus may be used for screening fumigation practices that have improved environmental safety and pest control performance.

ENVIRONMENTAL PROTECTION is an important impetus for developing reduced-risk pesticide management practices. While an effective pesticide application protocol may be harmful to the environment, a reduced-risk management practice may be not applicable because of its inferior pest control capability. This problem is exemplified by the current situation with the use of fumigants for soilborne plant pest and pathogen control. Soil fumigants are a special class of pesticides that are highly volatile as well as toxic. Although high volatility is required to efficiently disperse the chemical in soil, it also results in significant atmospheric emissions. For instance, excessive emissions of methyl bromide (MeBr) occur after soil injection under different conditions (Yagi et al., 1995; Majewski et al., 1995; Yates et al., 1996, 1998). Because MeBr emissions likely contribute to stratospheric ozone depletion, the production and importation of MeBr are scheduled for phase-out in the USA by 2005. But high air concentrations and excessive emissions have also been reported for fumigants that are currently considered MeBr alternatives, including 1,3-dichloropropene (1,3-D), chloropicrin, and methyl isothiocyanate (MITC) (Albrecht et al., 1986; Leistra and Crum, 1990; van den Berg et al., 1994; Chen et al., 1995; Baker et al., 1996). Lack of consideration for environmental implications during the early development of fumigant application methods has apparently contributed to this dilemma.

In an effort to reduce the environmental effects of fumigation, especially the atmospheric emission of fumigants, various improvements to the existing application methods have been proposed. These include surface tarping with less permeable plastic films (Gamliel et al., 1997; Wang et al., 1997; Yates et al., 1998), drip application (Schneider et al., 1993, 1995; Sipes and Schmitt, 1996; Wang and Yates, 1999), surface irrigation (Jin and Jury, 1995), modified injection patterns (Sipes et al., 1993), and integration through nonchemical methods such as solarization (Chellemi et al., 1994). Some of these methods showed substantially reduced emissions in laboratory columns or field plots, but their effects on pest control are unknown. Clearly, to develop reduced-risk fumigation practices that are also applicable, it is essential to concurrently evaluate environmental behavior and pest control efficacy.

In recent studies on MeBr and alternative fumigants,

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Abbreviations: ATS, ammonium thiosulfate; GC, gas chromatograph.

we developed a column method that allows simultaneous evaluation of fumigant emission and pest control. This relatively inexpensive and rapid approach is especially suitable for screening new fumigation methods that are promising for further field evaluation. In this paper, the schematics and experimental procedures of this methodology are reported, along with a demonstration of its application for evaluating a new 1,3-D fumigation strategy.

Materials and Methods

Description of Column System

The column system consists of two parts, a 70 (h) × 12 cm (i.d.) soil column, and a 5 (h) × 12 cm (i.d.) sampling chamber (Fig. 1). Both the soil column (bottom closed) and sampling chamber (top closed) are made of stainless steel. The soil column is packed with soil, and then sealed together with the sampling chamber to form a gas-tight system. Along the soil columns, gas-tight sampling ports are installed at various intervals to allow injection of fumigant and sampling of soil air. Before use, soil is packed to conditions (e.g., bulk density and moisture content) that are similar to typical field conditions prior to fumigation. When a bulk density of 1.50 g cm^{-3} is used, 11.9 kg of soil (oven-dry weight equivalent) can be packed into the column. During the packing process, sections of soil at selected depths are inoculated with plant parasitic nematodes (or another soil pest) by mixing the soil with nematode inoculum. Nylon screens are used to separate the infested soil layers from the noninfested layers to facilitate precise sampling. The sampling chamber sealed onto the soil column allows continuous collection of fumigant vapor leaving the soil surface. This is achieved by drawing the inside air through sampling tubes using a vacuum so that the fumigant is retained on the adsorbent. The airflow between the inlet and outlet on the sampling chamber is maintained at 100 to 200 mL min^{-1}. In such a system, fumigant dissipation in soil is only attributable to degradation in soil and volatilization from the soil surface.

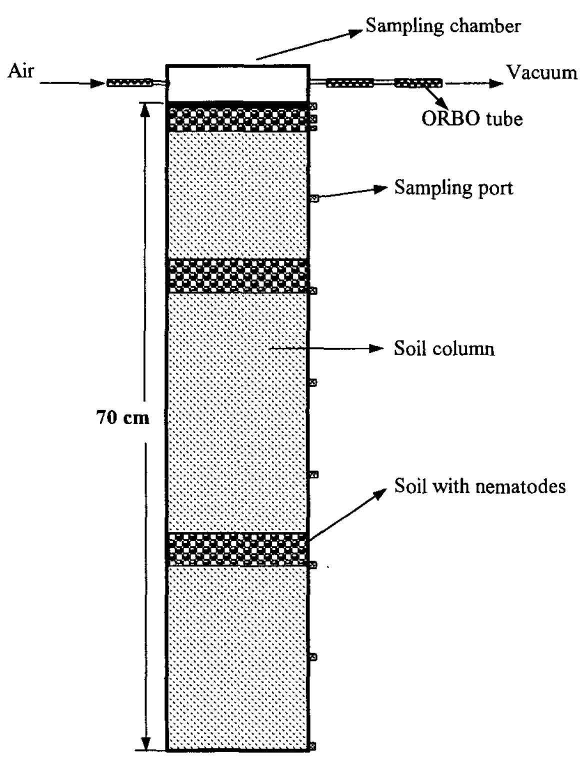

Fig. 1. Schematics of the enclosed column system for integrated fumigant volatilization and efficacy evaluation.

Experimental Protocol

Treatment. After the column system is prepared, a selected fumigant can be injected into the soil at a desired depth. The actual injection amount and depth can be determined according to the experimental objectives. For instance, if the effect of injection depth is evaluated, the fumigant can be injected in similar columns at different depths; e.g., 20, 30, or 40 cm from the surface. Consequently, differences in fumigant emission loss and in nematode control efficacy can be directly correlated with injection depth.

Emission Measurement. After the fumigant is injected into the soil column, sampling tubes on the sampling chambers are periodically replaced with unused tubes, and fumigant concentration in the sample tubes is quantified. While many adsorbents can be used to trap organic vapor, sampling tubes containing activated carbon are inexpensive and have large capacities for most fumigants. When carbon tubes are used, different sampling intervals need to be used for different fumigants to minimize breakthrough (Gan et al., 1995). For instance, short intervals (<2 hours) must be used for MeBr, while long intervals (>4 hours) may be used for 1,3-D, MITC or chloropicrin. Fumigant concentration in the sample tubes can be determined on a gas chromatograph (GC) with an electron capture detector for MeBr, 1,3-D and chloropicrin, and a nitrogen–phosphorus detector for MITC. Solvent extraction and headspace analysis are commonly used for sample preparation. In solvent extraction, carbon granules are removed from the glass tube and shaken in carbon disulfide (Eller, 1984) or acetone (van den Berg et al., 1992) for 30 to 60 min. An aliquot of the solvent extract is then injected into the GC for quantification. In headspace analysis, the carbon granules are heated in a closed headspace vial with a solvent (e.g., benzyl alcohol or ethyl acetate), and a fraction of the headspace is introduced into the GC via a transfer line for quantification (Woodrow et al., 1988; Gan et al., 1994). Headspace analysis is automated and less time-consuming; when optimized, the sensitivity is considerably better than that of solvent extraction. Solvent extraction, on the other hand, does not require expensive equipment, and the prepared extracts can be repeatedly analyzed. For GC analysis, a column equivalent to the 30 m × 0.32 mm × 1.4 mm RTX-624 column (Crossbond 6% cyanopropylphenyl–94% dimethyl polysiloxane, Restek Co., Bellefonte, PA) allows elution of all fumigants in <6 min. When combined with the automated headspace analysis, a total of 100 to 250 samples can be analyzed within a 24-h time period (Gan et al., 1994). Volatilization flux is calculated from the amount of fumigant recovered for a given time interval. Integrating fluxes over the entire sampled time gives the total fumigant volatilization loss.

Soil Air Concentration Measurement. After application, the test fumigant degrades and diffuses in the soil column. Distribution of a fumigant in soil as a function of space and time controls fumigant volatilization as well as pest control activity. Fumigant concentration in soil can be determined indirectly by sampling soil air at different positions and times. Aliquots of soil air (e.g., 0.5 mL) can be withdrawn through the sampling ports using a gas-tight syringe. The sampled air is then transferred into empty headspace vials, and the capped vials are analyzed on a Headspace-GC system for fumigant content.

Bioassay. At the end of experiment, soil columns are dismantled, and soil sections initially inoculated with nematodes (or other pests) are carefully removed. For nematode assay, aliquots (50 cm^3) of soil samples are incubated on Baermann funnels at 23°C. Nematode juveniles are collected for 4 d and enumerated under a dissecting microscope.

Demonstration Experiment

Application of the column methodology was demonstrated in the following experiment, in which an innovative low-emission 1,3-D application strategy was compared with a conventional method. We previously found that ammonium thiosulfate (ATS), a sulfur and N fertilizer, rapidly transformed 1,3-D to less toxic and water- soluble ions in soil. It was thus hypothesized that application of ATS at the soil surface would reduce 1,3-D emission because of the enhanced degradation. However, ATS-induced 1,3-D depletion may render soil fumigation ineffective for controlling plant parasitic nematodes near the surface. To evaluate the feasibility of ATS application for reducing 1,3-D emissions, we prepared multiple columns of identical characteristics and treated them with different amounts of ATS following 1,3-D application. Soil columns were packed using an Arlington sandy loam (Riverside, CA) that was sieved through a 2-mm sieve. The soil had an organic matter content of 0.92%, pH of 7.2, and field capacity of 11% (w/w). Soil bulk density in each column was 1.50 g cm^{-3}, and water content was adjusted to 5% (w/w). Small pieces (≈1 cm) of *Tylenchulus semipenetrans*-infested citrus roots were mixed with soil at a ratio of 1.5 g of feeder roots per 50 cm^3 of soil, and then filled into the column at 0- to 3-, 17- to 20-, and 47- to 50-cm depths.

For soil fumigation, 127 mL Telone II (Dow AgroSciences LLC, Indianapolis) was injected into the soil column at the 30-cm depth using a gas-tight syringe. Telone II contains 0.606 g mL^{-1} *cis*-1,3-D and 0.584 g mL^{-1} *trans*-1,3-D, and the application rate was thus equivalent to 13.0 g m^{-2} as 1,3-D. For ATS amendment, Thio-Sul (Tessenderlo Kerley, Inc., Phoenix) was dissolved in 100 mL water, and the solution was applied to the soil surface immediately after injection of Telone II. Four levels of Thio-Sul were used: 0, 1, 2, and 3 mL of Thio-Sul per column, where level 0 was used as the no-ATS control. Thio-Sul contained 0.794 g mL^{-1} ATS, and the rates were thus equivalent to 0, 64, 129, and 193 g m^{-2} as ATS. Each treatment was replicated in 3 columns, but emission and soil air concentration were measured from only one column for each treatment. A nonfumigation treatment was used as the nontreated control.

Volatilization of 1,3-D was measured simultaneously in the four treatments using a manifold with adjustable flow controllers (SKC West Inc., Fullerton, CA). Sampling was automated by using a programmable data logger and a series of solenoid valves. Airflow rate through the sampling chamber was 200 mL min^{-1}, and the sampling interval was 4 h. Sample tubes were extracted with 4 mL of acetone in small glass vials, and 2 mL was injected into the GC for quantification. Soil air samples were stored in small headspace vials and analyzed by using a headspace-GC method. Volatilization measurement was continued until no volatilization of 1,3-D was detectable. At the end of the experiment, nematode-infested soil sections were removed, and aliquots were enumerated for nematode juvenile population following extraction.

Results and Discussion

Demonstration Experiment

Application of ATS, even at the lowest selected level, substantially reduced 1,3-D volatilization from soil (Fig. 2). As ATS application rate increased, 1,3-D volatilization proportionally decreased. The total loss of *cis*-1,3-D was 47.5, 14.5, 6.4 and 3.4%, respectively, for the 0, 64, 129, and 193 g m^{-2} ATS treatments (Table 1). The total loss of *trans*-1,3-D for the corresponding treatments was 40.2, 19.6, 10.9 and 6.6%, respectively. After averaging over the two isomers, the total loss of 1,3-D was 42.9, 16.6, 8.4, and 4.9%, respectively, for the four treatments. This represents 61 to 89% reduction in 1,3-D emissions by ATS application (Table 1). Nematode extraction at the end of the experiment showed that for all the fumigated treatments, no citrus nematodes survived at any of the tested depths (Table 2). In the nontreated columns, nematodes were still present at all the depths. ATS application, regardless of the application rate, did not affect the effectiveness of 1,3-D fumigation for controlling the indicator nematodes. Analysis of 1,3-D distribution in soil revealed, however, that the 1,3-D level in

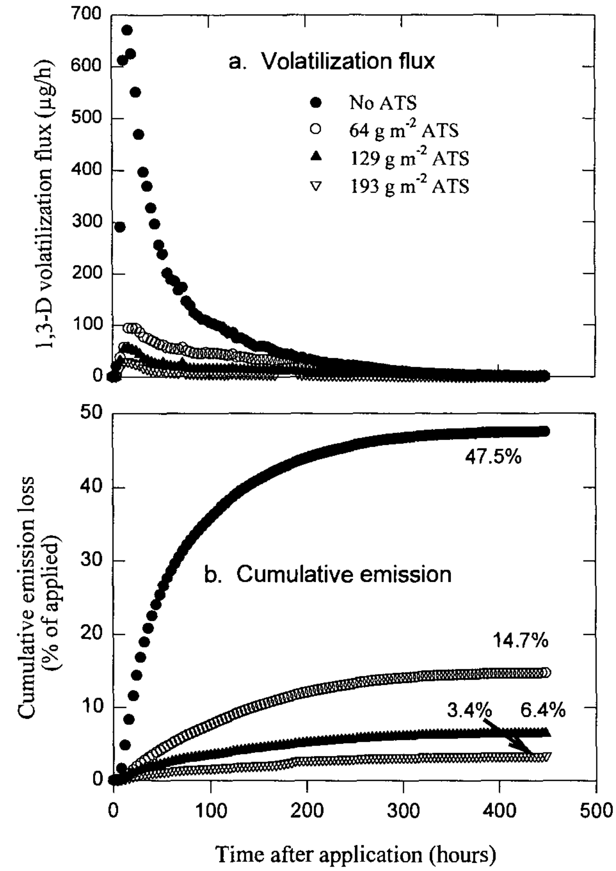

Fig. 2. Effect of ammonium thiosulfate (ATS) amendment (applied as Thio-Sul) on volatilization of *cis*-1,3-dichloropropene (1,3-D) from soil columns following Telone II injection at the 30-cm depth.

Table 1. Effect of ammonium thiosulfate (ATS) application rate on total emission loss (% of applied dosage) of 1,3-dichloropropene (1,3-D), following Telone II fumigation.

Treatment	*cis*-1,3-D	*trans*-1,3-D	Total	Reduction
	%			
No ATS	47.5	40.2	42.9	–
ATS at 64 g m^{-2}	14.5	19.6	16.6	61
ATS at 129 g m^{-2}	6.4	10.9	8.4	80
ATS at 193 g m^{-2}	3.4	6.6	4.9	89

Table 2. Effect of different ammonium thiosulfate (ATS) application rates on citrus nematode *Tylenchulus semipenetrans* survival (nematode juveniles per 50 mL of soil) in soil columns fumigated with 1,3-dichloropropene (n = 3).

	Nematode survival				
	Fumigated treatments				
Depth	No ATS	ATS at 64 g m^{-2}	ATS at 129 g m^{-2}	ATS at 193 g m^{-2}	Control
0–3 cm†	0	0	0	0	800 ± 24
17–20 cm	0	0	0	0	1102 ± 340
47–50 cm	0	0	3 ± 4	0	1240 ± 108

† Depths at which nematodes were inoculated.

surface soil was significantly reduced with ATS treatment (Fig. 3). This effect was less significant in the deeper soil layers. This suggests that although 1,3-D concentration was substantially reduced near the soil surface in ATS-treated columns, the cumulative exposure was still sufficient to kill the nematodes.

Extrapolation to Field Conditions

A field-plot experiment was carried out in southern California, in which 1,3-D emissions from a loamy sand soil were measured after 1,3-D fumigation (6.0 g m^{-2}) and surface amendment of ATS (32 g m^{-2}) (Gan et al., 1999). Application of ATS resulted in 50% reduction in 1,3-D emission. Nematode assay before and after fumigation showed that ATS application did not compromise 1,3-D's effectiveness for controlling root-knot nematode *M. incognita*. Application of ATS also had no effect on the yield of two tomato cultivars grown in the treated plots (Gan et al., 1999). These results agreed well with the prediction from the above column experiment.

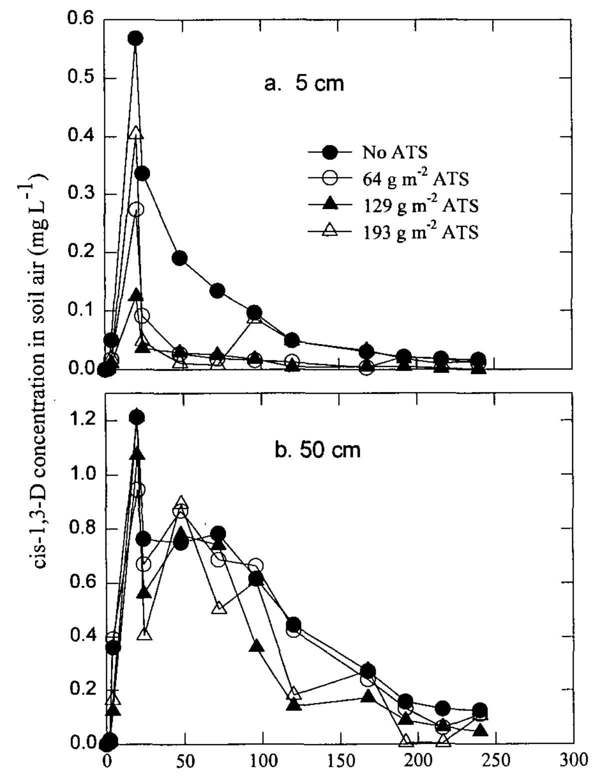

Fig. 3. Concentration of *cis*-1,3-dichloropropene (1,3-D) in soil air at the (*a*) 5- and (*b*) 50-cm depth in soils columns treated with Telone II and different amounts of ammonium thiosulfate (applied as Thio-Sul).

A similar column method was used previously for determining MeBr emissions under different application and soil conditions (Gan et al., 1996, 1997). These studies showed that soil type, bulk density, soil water content and surface cover of polyethylene plastics all had significant effects on MeBr volatilization. When MeBr was injected at the 30-cm depth in a sandy loam of 12% water content (v/v) and the surface was covered with polyethylene film, 37% overall emission loss occurred (Gan et al., 1997). In field studies conducted by other researchers, MeBr emission loss was found to be 36 to 62% (Yagi et al., 1995; Majewski et al., 1995; Yates et al., 1996). This suggests again that when representative conditions are used, the column system can provide close estimates of fumigant emissions under field conditions.

It must be noted that due to the simplicity of columns, certain field conditions are difficult to simulate in a column environment. These include the diurnal temperature variation, changes in relative humidity, wind speed and direction, and soil disturbance created by the mechanical fumigant application. For instance, air exchange at the soil surface in an enclosed column system is much slower than that in a field, which may prevent fumigant to quickly dissipate into the air. This may result in an increased fumigant accumulation near the soil surface that may in return affect the behavior of pathogens or nematodes in the surface layer. Crop growth cannot be studied in a column system. It is known that nematode density in soil and disease incidence cannot be linearly correlated, and information on nematode control from a column study is thus only indicative in nature. Therefore, the reported column methodology should be used as a screening tool for identifying practices that should be further evaluated under field conditions.

Field studies for measuring pesticide volatilization are exceptionally difficult and expensive to conduct, because sophisticated sampling devices and extensive sampling are often required. By comparison, column experiments are rapid and much less expensive. Moreover, since field conditions may vary spatially as well as temporally, it is difficult to correlate field study results with specific variables. In contrast, conditions in columns are well controlled, and observations can thus be related to the tested variables. Although packed columns are frequently used for studying pesticide transport in soil, most reported column methods do not have a biological component; e.g., the control of pest species. The integrated column method shown in this study could be useful for screening fumigant application practices that are improved in both environmental safety and pest control efficacy. Modifications to this system may allow it to be used for evaluating other pesticides and pests (e.g., weeds and fungi).

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