Environ. Sci. Technol. **2008,** *42,* 4434–4439

Soil Chamber Method for Determination of Drip-Applied Fumigant Behavior in Bed-Furrow Agriculture: Application to Chloropicrin

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Received January 15, 2008. Revised manuscript received March 6, 2008. Accepted March 28, 2008.

To overcome the environmental impacts of soil fumigant use, emission reduction strategies such as tarping can be adopted. There is a need to experimentally quantify the effectiveness of such strategies, preferably in a low-cost manner. We report the design and initial testing of a laboratory soil chamber approach for quantifying the soil distribution and emissions of fumigants from bed-furrow agricultural systems. As far as possible, field conditions (e.g., soil type, bulk density, moisture content, temperature) were maintained in the experiments. In studying the drip application of chloropicrin using this system, very good data reproducibility was observed between replicates, allowing confidence in the experimental design. For control chambers, high emissions, around 60% (of the total added), were observed due to the near-surface (5 cm depth) application. When the soil beds were tarped using high-density polyethylene (HDPE) or semi-impermeable film (SIF), emissions were reduced to around 40% due to an accumulation of chloropicrin below the tarp. The approach offers an inexpensive potential alternative to studying fumigant emissions from bed-furrow systems in the field and suggests that less permeable tarps would be required to drastically reduce chloropicrin emissions.

Introduction

In response to the current phasing out of methyl bromide, use of the soil fumigant chloropicrin (CCl_3NO_2) is expected to increase markedly. As a preplant pesticide treatment, chloropicrin exhibits a broad efficacy controlling nematodes, bacteria, fungi, insects, and weeds, and it is used either by itself or in combination with another fumigant (typically 1,3-dichloropropene). It is used extensively prior to the planting of high cash crops, such as strawberries, where the economic benefits of high yield are most acute. Chloropicrin has a vapor pressure of 2.4 kPa (at 20 °C), a boiling point of 112 °C, a density of 1.65 g mL^{-1} (at 20 °C), and a solubility of 1.6 g L^{-1} (at 20 °C) (*1*). Although applied to soil as a liquid, chloropicrin quickly converts to a gas in warm soil and diffuses through the soil pore space to effect its pesticidal treatment. Within the soil, the half-life of chloropicrin has been determined to be between 0.2 and 4.3 days with 68−92% of this degradation due to the presence of soil microbes (*2*). In addition, and in common with other fumigants, chloropicrin gas is readily lost from the soil to the atmosphere (*3*). It is essential that this loss is quantified in order to then address the associated environmental impacts of chloropicrin emissions. For example, due to their toxic nature fumigants may pose a respiratory risk to agricultural workers and nearby populations. In the United States, release of volatile organic compounds (VOCs) from fumigated soils is federally regulated since they are thought to be a precursor to formation of near-surface ozone (photochemical smog), particularly in areas of California (*4*). Moreover, the use of the fumigant chloropicrin has recently been shown to affect the greenhouse gas balance by increasing the soil emission of nitrous oxide (*5, 6*).

A balance must therefore be found between the advantages associated with pesticide use (e.g., increased crop health/yield and, hence, economic return) and the deleterious environmental impacts. One way to accomplish this is to adopt strategies that allow for the necessary quantities of fumigants to be used while reducing the extent of fumigant loss from the soil to the atmosphere. This can be achieved by covering the soil surface with plastic tarps after the fumigant has been applied. Thus, a physical barrier to diffusion of the fumigant from soil to air is established and emissions are reduced (*7*). A number of different tarps from various manufacturers are currently available and vary in their ability to retain fumigants within the soil. Generally, these tarps are designated, in order of supposed increasing impermeability, as LDPE (low-density polyethylene), HDPE (high-density polyethylene), SIF (semi-impermeable film), VIF (virtually impermeable film), or TIF (totally impermeable film). Other, metallized tarps with supposedly high impermeability are also marketed. However, these designations are somewhat arbitrary, and permeability testing of films within our laboratory (unpublished data) has shown that this order of increasing impermeability can at times be erroneous. Therefore, there is a genuine need to not only determine the extent to which tarping can reduce the emissions of agricultural fumigants from soil but also relate this reduction to some meaningful characteristic of the tarp (e.g., a measure of its permeability).

A major disadvantage of fumigant emission reduction research is that field experiments designed to quantify such processes are expensive and time consuming. This problem can be overcome, to some extent, by designing laboratory experiments in a way that mimics a field situation and produces comparable data. Such an approach, for the shank injection of fumigants, has been reported (*8*), and this compared very well to the data derived from the field experiment that the laboratory approach was designed to mimic (unpublished data). Although column experiments to simulate shank injection of fumigants in ploughed soils are relatively numerous (e.g. *9–12*), little laboratory work has addressed the fumigant emission behavior of drip-applied fumigants in bed-furrow systems. This is critical, particularly in relation to strawberry production, where drip application of fumigants to raised beds under a plastic tarp is commonplace due to the potential benefits it offers in terms of uniform fumigant distribution, economic feasibility, emission reduction, reduced worker exposure, and reduced application amount (*13*). Therefore, the work described in this paper

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10.1021/es800148p CCC: $40.75
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Published on Web 05/14/2008

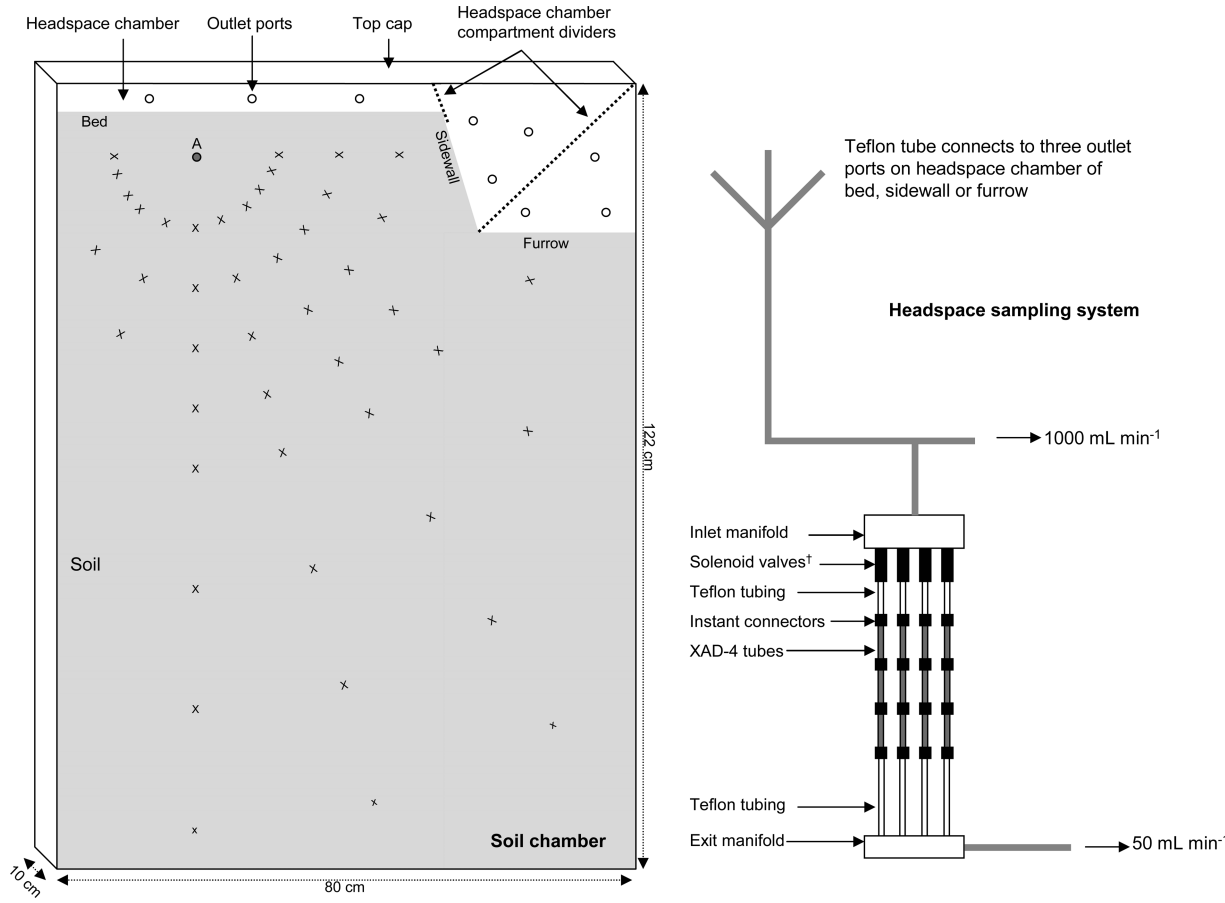

FIGURE 1. Front of soil chamber and headspace sampling system (not to scale). A separate headspace sampling system was used for each sampling chamber compartment (bed, sidewall, and furrow). Four sampling chamber inlet ports (allowing clean air to be drawn across the soil surface) were positioned on the backside of each sampling compartment: A, fumigant application port; x, approximate position of gas sampling ports; †, solenoid valve switching controlled by a Campbell Scientific 21X datalogger.

aimed to (a) design a laboratory chamber that allows for the reproducible quantification of soil gas distribution and surface emission of fumigants applied to bed-furrow agricultural systems under realistic soil conditions and (b) use such chambers to quantify the fate and transport of drip-applied chloropicrin fumigant under nontarped and tarped conditions.

Experimental Section

Chamber Fabrication. Soil chambers were fabricated from sheet aluminum and had final, internal dimensions of 122 × 80 × 10 cm (Figure 1). Front and rear walls of the chambers were made of 6 mm aluminum sheet. The chamber dimensions were chosen to allow for the establishment of half-a-bed and half-a-furrow of nonscaled proportions (i.e., close to field measurements) across the chamber width. The side walls and base of the chambers were made of 9 mm aluminum sheet. In the front wall, a fumigant application port was installed by drilling a hole through the wall 10 cm from the top edge and 17 cm from the left edge and gluing in a brass union with an airtight screw-on cap. Extending radially from this point, arcs of soil gas sampling ports were installed (in the same way as the application port) every 10 cm (for the first 50 cm) and every 20 cm thereafter. The four walls and base of a chamber were joined together using epoxy resin along the seams and bolts inserted (every 10 cm) through the front and rear walls into the side walls and base for mechanical strength. All seams were then further sealed with aluminum tape. Before packing with soil, the absence of leaks was affirmed by pressurizing a sealed chamber and submerging in a water bath.

Soil Packing. Chambers were packed with a sandy loam soil collected from strawberry production beds at Oxnard, CA. The surface (0−15 cm) soil had a pH of 7.9 and an organic matter content of 2.0%. The soil was collected from field beds in depth layers of 0−15, 15−30, 30−45, 45−60, and >60 cm and stored under cool conditions in sealed buckets to preserve field moisture content. The moist, nonsieved soils were packed into the chambers using the same depth increments so as to 'reconstruct' the field soil depth profile and also produce half-a-bed and half-a-furrow across the chamber width (Figure 1). The depth layers were packed vertically in 5 cm increments for which a particular mass of soil was used to give a predetermined (based on field measurements) soil bulk density. The initial moisture content of soil in each depth layer was 16%, 16%, 17%, 17%, and 12%, respectively. The bulk density of each layer, based on field measurements, was 1.3, 1.6, 1.6, 1.5, and 1.5 g cm^{-3}, respectively. Use of these values demonstrates an important aspect of this experimental approach, i.e., maintenance of Oxnard field conditions within the laboratory system. An outward 'bowing' of the chamber walls due to soil packing was prevented by inserting (during the packing process) bolts through the chamber (front to back) via holes drilled at half-chamber width and 14 and 60 cm from the top of the chamber. Both ends of the bolt were then sealed with aluminum tape to prevent leaks. Once packed, the soil bed surface was 50 cm in width and 117 cm above the base of the chamber, leaving a 5 cm headspace above the bed (Figure 1). The sidewall of the bed had a slight slope such that the base of the furrow was 25 cm in width and 87 cm above the base of the chamber (Figure 1). To allow for separate sampling of

the headspace above the bed surface, bed sidewall, and furrow base, the chamber was capped with galvanized sheet metal plates arranged as shown in Figure 1. In this way, the relative contribution of each compartment to the total fumigant loss from the soil surface could be determined. In each of these compartments, three air outlets were created using panel mount instant connectors (6 mm diameter), as shown in Figure 1. On the backside of the chamber and offset from the outlet ports, each compartment also had four air inlets (6 mm diameter). These inlet/outlet ports allowed for air to be drawn across the soil surface within each compartment for the purposes of fumigant emission sampling.

Headspace Air Sampling System. Following soil packing, the headspace air sampling system was established (Figure 1). The three air outlets from a headspace chamber compartment (i.e., bed, sidewall, or furrow) were 'teed' together using equal lengths of Teflon tubing. A single length of Teflon tube was connected from this 'tee' junction to a 1 L min^{-1} vacuum source, allowing clean air to be pulled across the soil surface of each compartment. The 1 L min^{-1} flow rate was required to maintain a suitably low residence time for the headspace air within each compartment. For the largest compartment (sidewall), the air volume was replaced approximately every 4.5 min using this flow rate. However, such a high flow rate was observed, in separate experiments, to result in significant breakthrough from the 120 mg XAD-4 sorbent tubes (SKC Inc., PA) to be used in this study. Therefore, the 1 L min^{-1} flow rate was subsampled at 50 mL min^{-1} by 'teeing' off the higher flow rate line and directing the subsample through the XAD-4 tubes. Over the early part of the experiment (i.e., the first 24 h), a chain of three XAD-4 tubes, connected in series, was used to mitigate the potential for chloropicrin breakthrough. A system of solenoid valves, controlled by a 21X datalogger (Campbell Scientific Inc., UT), allowed for automatic switching between tubes (or chains of tubes) at 6 h intervals. The sampling system was determined to be leak proof. Additionally, it was determined that the three air outlets on a given headspace compartment pulled approximately equal amounts of air, indicating that the compartment was sampled representatively. Finally, it was also determined that no restriction of air flow across the soil surface was evident. This is an important consideration in ensuring that fumigant was not artificially 'pulled' from the soil.

Experimental Conditions. Soil chambers were housed in a controlled temperature room for the duration of the experiment. Surface soil temperature was maintained as close to the field conditions at the Oxnard site as possible by adjusting the temperature within the room to follow a repeating diurnal pattern. Hourly soil temperatures at 5 cm depth ranged from 19.1 °C in the early morning hours to 29.9 °C in the late afternoon hours, representative of the change in temperature over the course of a day (based on average soil temperatures measured at the field site during September 2007). To limit soil temperature fluctuation at depth, the chambers were insulated below 20 cm soil depth. Previous studies have shown that although this does not entirely prevent temperature fluctuation, the amplitude of the fluctuation is markedly reduced, allowing for an improved simulation of field conditions (*8*).

Fumigant Application. Chloropicrin was drip applied to the chambers via the fumigant injection port (5 cm below the bed surface). The fumigant was applied at a rate equivalent to 150 kg ha^{-1} (per treated, or bed, area) over a period of 170 min and in a volume of approximately 1480 mL of water. The chloropicrin (99.9% purity), obtained from TriCal Inc. (Mojave, CA), was dissolved in deionized water in a capped, glass bottle. It was necessary to use mixing and gentle heating (to around 30 °C) to aid and maintain dissolution. After around 1 h of mixing, the solution was pumped at a constant rate into the injection port of the chamber via Teflon tubing. Application was commenced at 08:00 h. Following the 170 min fumigation period, the application port was resealed.

Experimental Treatments. Using triplicate chambers, the approach described above was used to obtain data relating to the soil gas and emission behavior of chloropicrin after drip application to a bed-furrow soil system in the absence of any emission reduction strategy. The usefulness of the chamber approach was thus assessed in relation to the reproducibility of these data. In addition, supplementary studies were carried out to gain an initial understanding of the potential benefits of methods intended to reduce fumigant emissions from the soil surface. Two clear, 30 μm thick, agricultural tarps, designated by their manufacturer as HDPE and SIF, were used in the soil chambers by fitting over the bed and sidewall. A tarp was fixed to the wall of the chamber using aluminum tape to ensure no leakage and, at the base of the sidewall, buried several centimeters into the soil (as would be carried out in the field).

Sampling. Sampling of headspace air from each compartment was commenced at the initiation of fumigant application. Sampled XAD-4 tubes were capped, removed to a freezer (−19 °C), and replaced with new tubes for subsequent sampling periods. On days 0 (day of fumigant application), 1, 2, 3, 6, and 10, samples of soil gas were withdrawn from the chambers at each of the gas sampling ports. From each port, 0.5 mL of soil gas was removed and injected into a 12 mL headspace GC vial that was immediately capped with a Teflon-faced rubber septum and aluminum crimp seal. Gas samples were stored at −70 °C prior to analysis. Soil gas and emission sampling of the chambers continued for 10 days following fumigation, after which time concentrations of chloropicrin within the system were negligible.

Analysis. XAD-4 tubes were extracted by removing the glass wool holding the contents in place and carefully shaking the resin into a 20 mL glass vial. The glass wool and glass tube itself were also placed into the vial. Hexane (3 mL) was then added and the vial immediately capped with a Teflon-faced rubber septum and aluminum crimp seal. Vials were shaken for 30 min, allowed to settle briefly, and the supernatant solution (around 1.5 mL) transferred to a gas chromatography (GC) vial for analysis. The GC analysis was performed using a Hewlett-Packard HP6890 equipped with a microelectron capture detector. The column was a J&W DB-VRX 30.0 m × 0.25 mm × 1.4 μm capillary column (Agilent Technologies) running at a flow rate of 1.4 mL min^{-1} and using He as the carrier gas. The analysis time for each sample was 18.3 min. Over the first minute the GC oven temperature was held at 45 °C. Thereafter, it was increased to 80 °C at a rate of 2.5 °C min^{-1}. During this stage, chloropicrin was eluted with a retention time of 13.2 min. The oven temperature was then increased to 120 °C at a rate of 30 °C min^{-1} and held for 2 min to facilitate column cleanup between samples. Finally, the oven was cooled to 45 °C in preparation for the next sample. The inlet temperature was 240 °C, and the detector temperature was 290 °C. Soil gas samples were analyzed using a Hewlett-Packard HP6890 GC coupled with a G1888 Network Headspace Sampler (Agilent Technologies). Similar GC conditions to those described above were used although the final (120 °C) step was not required between samples, and so total analysis time for each sample was reduced to 15 min. The operating conditions for the headspace sampler were as follows: oven temperature 80 °C, loop temperature 90 °C, transfer line temperature 100 °C, vial equilibration time 5 min, and sample loop volume 0.2 mL. For all analyses, five chloropicrin standards encompassing the range of concentrations observed in the samples were

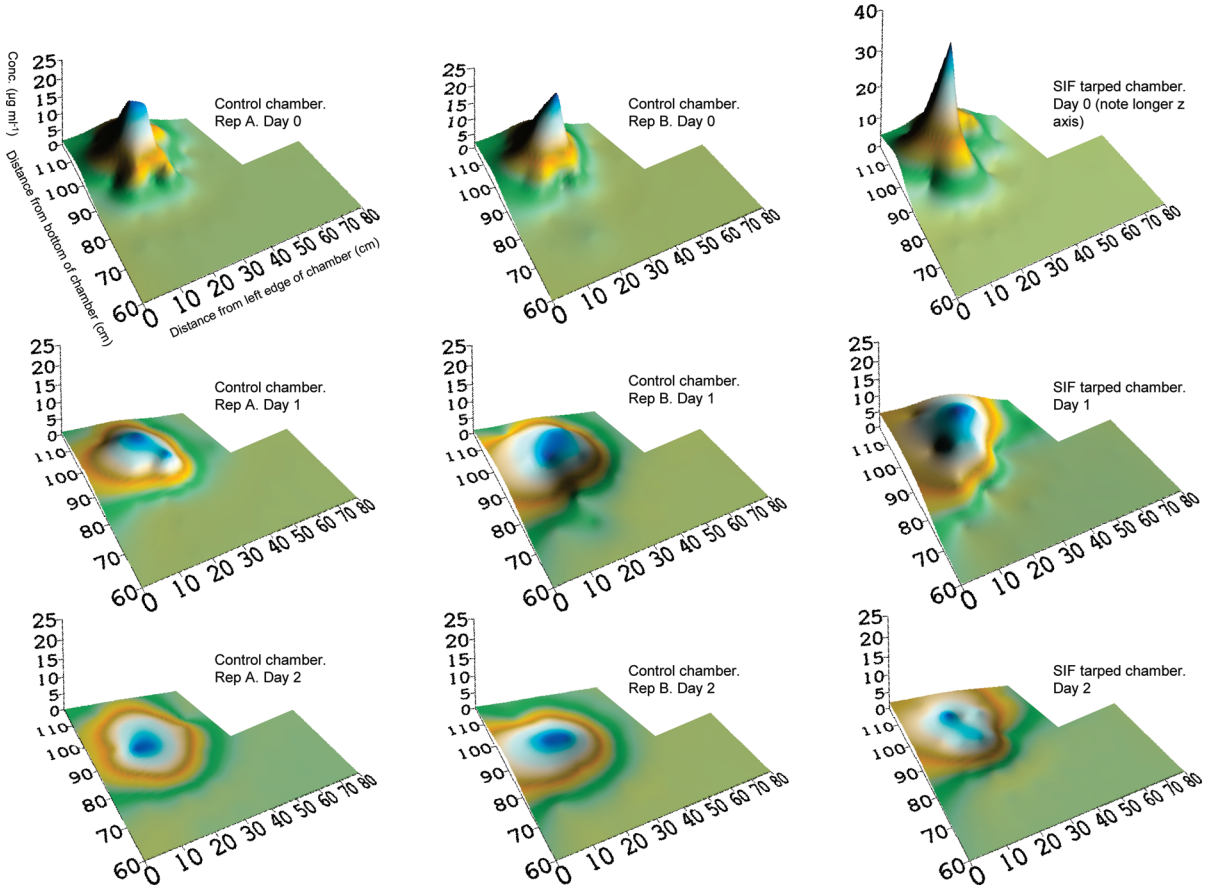

FIGURE 2. Soil gas concentrations of chloropicrin in two replicate control chambers (left and center columns of graphs) and the SIF-tarped chamber (right column of graphs) over the initial period of the experiment. Axes labels shown in upper left graph also apply to all other graphs. Concentrations in the area of the chamber not shown (i.e., 0−60 cm from the base of the chamber) were nondetectable.

prepared in hexane. Chromatogram analysis was performed using Chemstation Rev.A.10.02 (Agilent Technologies).

Results and Discussion

Soil Gas Concentrations. Figure 2 shows concentrations of chloropicrin in the soil gas for duplicate control chambers on days 0, 1, and 2 of the experiment. It is noticeable that concentrations in Chamber A were consistently slightly lower than in Chamber B. Overall, however, the strong similarity observed in the distribution of chloropicrin gas between the replicate chambers demonstrates a good level of reproducibility. Also shown in Figure 2 are the concentrations of chloropicrin in the soil gas of the SIF-tarped treatment. In each case, peak concentrations in the soil gas were observed around the point of fumigant addition on the day of fumigant application (day 0), reaching a maximum of 23.1 (±2.3) μg mL^{-1} in the control and 39.2 μg mL^{-1} in the SIF-tarped treatment. Concentrations of chloropicrin in the soil gas declined rapidly in response to both increasing distance from the application point and time. In drip fumigation, movement of the fumigant through the soil is initially controlled by the movement of the applied water (*13*) and evidently provided a distribution of chloropicrin within the expected rooting zone of strawberry plants, i.e., the top 30 cm (*14*). Maxima of 6.4 (±1.1) and 2.1 (±0.9) μg mL^{-1} were observed on days 1 and 2, respectively, for the control. In the SIF-tarped treatment, maxima of 12.5 and 4.7 μg mL^{-1} were observed on days 1 and 2, respectively.

The greater maximum concentrations of chloropicrin gas in the SIF treatment (and HDPE treatment; data not shown) when compared to the control indicate that tarping maintained the chloropicrin within the soil. This is further demonstrated by the relatively high concentrations of the gas observed at the bed surface in the SIF treatment, particularly on days 0 and 1 (Figure 2). Indeed, in the control chambers gas concentrations across the bed surface ranged from 0.5 to 4.1 μg mL^{-1} (mean 2.7 μg mL^{-1}), while in the SIF treatment they ranged from 2.1 to 8.4 μg mL^{-1} (mean 5.7 μg mL^{-1}). Clearly, over the initial period an accumulation of gas below the tarp occurred, caused by the tarp physically limiting chloropicrin transfer across the soil−air boundary. By day 2, soil gas concentrations were relatively low, although they remained slightly higher at the soil surface of the SIF treatment compared to the control. Reduction in fumigant gas concentrations over time are considered to have been primarily due to emission losses from the soil surface and degradation within the soil. Due to the presence of the tarp, the latter of these two processes is thought to have been more important in the SIF (and HDPE) treatments than in the control because of an increased contact time between the fumigant and the soil.

Cumulative Emissions. Cumulative emissions of chloropicrin from the entire soil surface (bed + sidewall + furrow) in the control and tarped soil chambers are shown in Figure 3. The total emission loss from the control averaged around 60% and for the two tarped treatments around 40%. As in a previous study (*1*), the significance of the bed compartment (as compared to the sidewall and furrow) was marked across all treatments. On average, 93.9% of the total chloropicrin emissions occurred from the bed, 6.0% from the sidewall, and 0.1% from the furrow. In the control chambers, the replicate measurements of cumulative emissions showed a very good level of agreement. These emissions increased rapidly during and immediately following fumigant applica-

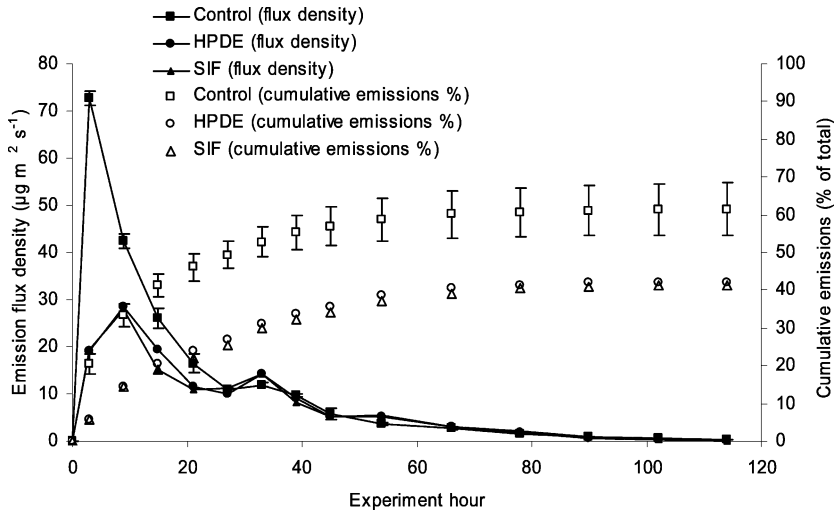

FIGURE 3. Chloropicrin emission flux density (left *y* axis) and cumulative emissions (as percentage of total initially added) (right *y* axis) over the course of the experiment. All values are for the sum of the bed, sidewall, and furrow compartments.

tion, reaching the maximum 'plateau' value of approximately 60% after 3 days. The rapid emission loss and high total loss from the control chambers was likely a result of fumigant application close to the soil surface (5 cm soil depth), although even higher emissions (82% of total added) for shank injection of chloropicrin at 30 cm depth and using cylindrical soil columns have been noted (*2*). Despite the application being closer to the soil surface in the present study (for which higher emissions would be expected), coaddition of water may have caused the lower emissions via transport of the chloropicrin away from the soil surface and formation of a 'water seal' which has been shown previously to reduce fumigant losses from soil (*8, 15*). Nevertheless, the soil gas concentration data (Figure 2) confirm that the chloropicrin was readily lost from the soil pore space (due to emissions) in the control chambers. In the absence of a remediation strategy, therefore, chloropicrin emissions from bed-furrow systems are likely to be very high when applied close to the soil surface (as is common practice). The need for remediation strategies to effectively reduce the level of emissions is clear.

The two tarped treatments showed almost identical timewise trends and absolute cumulative emission values to one another. This suggests that the two tarps, despite being designated as HDPE and SIF, which would be expected to exhibit differing fumigant permeabilities, were in fact not dissimilar. This was further investigated in subsequent experiments using a tarp permeability measurement technique (*16*) in which the mass transfer coefficient, or *h* value, of a tarp is determined. For the two tarps used here, chloropicrin *h* values of 1.22 and 1.15 cm h^{-1} were found for the HDPE and SIF, respectively. This difference is considered small, less than experimental uncertainty, and the two tarps can therefore be considered identical in their ability to limit chloropicrin diffusion. This finding highlights the ambiguity associated with categorizing tarps as HDPE, SIF, VIF, etc. Much more satisfactory in terms of the ability to select a tarp capable of yielding a certain level of emission reduction is to designate a numerical, objectively determined value (e.g., the *h* value) to each tarp. Nevertheless, here, both tarps markedly reduced chloropicrin emissions from the soil surface to around two-thirds of the control value. More marked reductions in chloropicrin emissions when using tarps in laboratory studies have been reported by Gan et al. (*2*). Values of 20% and 1.2% total emissions were reported for HDPE and 'high-barrier' film, respectively, by these workers (compared to 82% total emissions for the control). Under field conditions, differing tarps yielded chloropicrin emission losses as follows: LDPE, 11.2−18.0% (*1*); HDPE, 31.9% (*1*), 45% (*12*), 9.2% (*15*), and 9.5−18.0% (*17*); VIF, 1.2% (*15*) and 3.9% (*1*). No published data for chloropicrin emission losses from soils tarped with SIF were found. Overall, the data available in the literature exhibits a wide range of values for a given tarp category and an absence of reported *h* values for the tarps used. It is considered that differences in *h* value (even for tarps within a particular category, e.g., HDPE) would have been a highly significant factor in influencing the extent of chloropicrin emissions and hence the differences observed. The higher of the values for the HDPE are comparable to those found for tarps in the present study and, in relation to the values for the range of tarps, suggest that emissions from the tarped treatments here, despite being lower than the control, were still relatively high.

Emission Fluxes. In concurrence with the cumulative emission data (to which they are related), the emission flux rates were markedly reduced from the control levels by tarping (Figure 3). The rapid initial peak emission flux of 70 μg m^{-2} s^{-1} in the control can be contrasted with the smaller and less rapid initial peak of 30 μg m^{-2} s^{-1} in the tarped treatments (which were again similar to each other with regard to emission flux rate values and trend). Clearly, the tarps were effective in reducing and delaying emission fluxes from the soil surface. By maintaining the chloropicrin within the soil, the tarps facilitate increased soil−fumigant contact time (i.e., increased pesticidal efficacy) and, ultimately, degradation of the fumigant by the soil and its microbial biomass. The relatively rapid degradation rate exhibited for chloropicrin in the experimental soil (~0.6 days) exacerbates this process (degradation rate was determined in preliminary studies using a method previously described for 1,3-dichloropropene (*8*)). If the assumption that only the processes of emission and degradation control fumigant fate within the chambers is made, it is clear that tarping increased the percentage of total fumigant lost by degradation from 40% to 60%. In making this assumption it should be noted that soil adsorption, although considered (in common with other soil fumigants) to be relatively insignificant compared to the processes of surface emission and degradation, is also potentially enhanced by tarping due to the increased contact time between the fumigant and the soil. However, Zhang and Wang (*12*) noted that 24 days after addition of chloropicrin to soil columns under tarped conditions only around 2% of the fumigant remained in the soil.

Despite the emission flux rate differences between the control and the tarped treatments over the initial period, after the first day of the experiment the emission flux rates in all treatments were very similar for the remainder of the

experiment. This indicates that the tarps had little effect in controlling emissions after the first day of the experiment. Again, this is somewhat consistent with the soil gas data which suggest that by day 2 the amount of chloropicrin accumulating at the soil surface, i.e., below the tarp, was much reduced. The most likely explanation for this is considered to be differences in the dynamics of fumigant release between the control and tarped treatments. It would appear that the rapid and large loss of chloropicrin, via emission, from the control soil led, after 1 day, to a residual amount of chloropicrin such that the subsequent emissions were equal to those from the tarped treatments. In addition, temperature appeared to exert some control over emission fluxes. Slight increases in emission fluxes were observed across all treatments at 33 and 54 h, corresponding to 'afternoon/early evening' periods of the diurnal temperature regime, i.e., when soil temperatures were relatively high. Under such conditions, elevated emissions of fumigants from soil have been previously noted (*8, 18, 19*) due to the positive relationship between gas diffusion and temperature (*20*).

The ability to study soil fumigant behavior under differing agricultural scenarios within the laboratory is a clear research need due to the high costs of carrying out field experiments. Here, a laboratory soil chamber method has been shown to be useful in assessing the fate and transport of drip-applied fumigants within soil bed-furrow systems. Demonstration that the approach is reproducible, an essential consideration for a new experimental system, comes from the very good agreement between the replicate control chambers in terms of both chloropicrin soil gas concentration and emission measurements (Figures 2 and 3). With the observed potential for very high emissions of chloropicrin when near-surface applied to bed-furrow systems, it is critical that highly effective emission reduction strategies are identified. Although the HDPE and SIF tarps employed in this study markedly reduced emissions, total emissions of around 40% are not considered satisfactorily low for the purposes of mitigating the environmental significance of fumigants. Therefore, tarps with a much lower permeability (low h value) are likely to be required to induce satisfactory reductions in emissions under these conditions. It is considered that relating emissions behavior to tarp h value, rather than a tarp category, would significantly aid the application of future research in this area.

Acknowledgments

This work was funded by the California Strawberry Commission through Agr. 58-5310-6-182. The technical assistance of Q. Zhang and Y. Wang is also gratefully acknowledged.

Literature Cited

(1) Van Wesenbeeck, I. J.; Knuteson, J. A.; Barnekow, D. E.; Philips, A. M. Measuring flux of soil fumigants using the aerodynamic and dynamic flux chamber methods. *J. Environ. Qual.* **2007**, *36*, 613–620.

(2) Gan, J.; Yates, S. R.; Ernst, F. F.; Jury, W. A. Degradation and volatilization of the fumigant chloropicrin after soil treatment. *J. Environ. Qual.* **2000**, *29*, 1391–1397.

(3) Qin, R.; Gao, S.; Hanson, B. D.; McDonald, J. A.; Trout, T. J.; Ajwa, H. Effect of drip application of ammonium thiosulfate on fumigant degradation in soil columns. *Agric. Food Chem.* **2007**, *55*, 8193–8199.

(4) California Department of Pesticide Regulations (CDPR) Website, accessed March 4, 2008; http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/vocmenu.htm.

(5) Spokas, K.; Wang, D.; Venterea, R. Greenhouse gas production and emission from a forest nursery soil following fumigation with chloropicrin and methyl isothiocyanate. *Soil Biol. Biochem.* **2005**, *37*, 475–485.

(6) Spokas, K.; Wang, D.; Venterea, R.; Sadowsky, A. Mechanisms of N_2O production following chloropicrin fumigation. *Appl. Soil Ecol.* **2006**, *31*, 101–109.

(7) Yates, S. R.; Gan, J.; Papiernik, S. K.; Dungan, R.; Wang, D. Reducing fumigant emissions after soil application. *Phytopathology* **2002**, *92*, 1344–1348.

(8) Ashworth, D. J.; Yates, S. R. Surface irrigation reduced the emission of volatile 1,3-dichloropropene from agricultural soils. *Environ. Sci. Technol.* **2007**, *41*, 2231–2236.

(9) Gan, J. Y.; Hutchinson, C.; Ernst, F. F.; Becker, J. O.; Yates, S. R. Column system for concurrent assessment of emission potential and pest control of soil fumigants. *J. Environ. Qual.* **2000**, *29*, 657–661.

(10) El Hadiri, N.; Ammati, M.; Chgoura, M.; Mounir, K. Behavior of 1,3-dichloropropene and methyl isothiocyanate in undisturbed soil columns. *Chemosphere* **2003**, *52*, 893–899.

(11) Zheng, W.; Yates, S. R.; Papiernik, S. K.; Wang, Q. Q. Reducing 1,3-dichloropropene emissions from soil columns amended with thiourea. *Environ. Sci. Technol.* **2006**, *40*, 2402–2407.

(12) Zhang, Y.; Wang, D. Emission, distribution and leaching of methyl isothiocyanate and chloropicrin under different surface containments. *Chemosphere* **2007**, *68*, 445–454.

(13) Ajwa, H. A.; Trout, T.; Meuller, J.; Wilhelm, S.; Nelson, S. D.; Soppe, R.; Shatley, D. Application of alternative fumigants through drip irrigation systems. *Phytopathology* **2002**, *92*, 1349–1355.

(14) Pires, R. C. D.; Folegatti, M. V.; Passos, F. A.; Ambrosano, G. M. B.; Minami, K. Effective depth of strawberry radicular system under different soil covers and water levels. *Pesq. Agropec. Bras.* **2000**, *35*, 793–799.

(15) Gao, S. D.; Trout, T. J. Surface seals reduce 1,3-dichloropropene and chloropicrin emissions in field tests. *J. Environ. Qual.* **2007**, *36*, 110–119.

(16) Papiernik, S. K.; Yates, S. R.; Gan, J. An approach for estimating the permeability of agricultural films. *Environ. Sci. Technol.* **2001**, *35*, 1240–1246.

(17) Wang, D.; Juzwik, J.; Fraedrich, S. W.; Spokas, K.; Zhang, Y.; Koskinen, W. C. Atmospheric emissions of methyl isothiocyanate and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries. *Can. J. For. Res.* **2005**, *35*, 1202–1212.

(18) Basile, M.; Senesi, N.; Lamberti, F. A study of some factors affecting volatilization losses of 1,3-dichloropropene (1,3-D) from soil. *Agric. Ecosyst. Environ.* **1986**, *17*, 269–279.

(19) Wang, D.; Yates, S. R.; Gan, J. Temperature effect on methyl bromide volatilization in soil fumigation. *J. Environ. Qual.* **1997**, *26*, 1072–1079.

(20) Wang, D.; Knuteson, J. A.; Yates, S. R. Two-dimensional model simulation of 1,3-dichloropropoene volatilization and transport in field soil. *J. Environ. Qual.* **2000**, *29*, 639–644.

ES800148P