Atmospheric Pollutants and Trace Gasses

Degradation and Volatilization of the Fumigant Chloropicrin after Soil Treatment

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ABSTRACT

Chloropicrin (CP) is used in fumigation of soil-borne pests. Because of its high volatility and toxicity, atmospheric emission of CP during soil application may become a source of air pollution. We investigated degradation of CP in three different soils as a function of soil temperature and moisture conditions, and evaluated its volatilization against methyl bromide (MeBr) from packed soil columns. Chloropicrin degraded much faster than MeBr in the same soil, mainly via microbial degradation. Degradation of CP accelerated as soil temperature increased, but was relatively independent of changes in soil moisture. When the soil surface was uncovered, overall volatilization loss of CP was similar to that of MeBr. Covering the soil surface with a polyethylene or high-barrier film was much more effective in reducing volatilization of CP than MeBr. Therefore, surface covers may be used in sensitive areas to reduce human exposure to CP.

CHLOROPICRIN (trichloronitromethane, CCl_3NO_2, CP) fumigation has been used for many decades to control soil-borne pests. It is typically applied together with MeBr as a warning agent or with 1,3-dichloropropene (1,3-D) as a fungicide to achieve broad-spectrum control. For instance, mixtures of MeBr with 2% CP and 1,3-D with 17% CP (i.e., Telone C-17) or 35% CP (i.e., Telone C-35) are used. In 1998, a total of 1.4 million kg of CP was used in California alone, with most application occurring in strawberry cultivation (California Department of Pesticide Regulation, 1999). During the last few years, several chemical fumigants have been tested as alternatives to MeBr, a widely used fumigant that is scheduled for phase-out because of its potential contribution to ozone depletion. Chloropicrin and its combinations with 1,3-D or methyl isothiocyanate (MITC) have been identified as effective replacements for MeBr in many field studies (Moldenke and Thies, 1996; South et al., 1997; Freitas et al., 1999; Porter et al., 1999; Trout and Ajwa, 1999). Therefore, it can be expected that the use of CP will increase.

Chloropicrin is injected mechanically into the subsurface soil at depths >15 cm (Wilhelm et al., 1997). When used with MeBr, the soil surface is often covered with polyethylene films after fumigation, but when used with 1,3-D the soil surface is usually not covered. Because of its high vapor pressure (32 mm Hg, Worthing and Hance, 1991), CP has a high potential to volatilize after injection. Chloropicrin is an acutely toxic chemical (intraperitoneal LD_{50} in mice of 14 mg kg^{-1}) with strong lacrimatory properties (Gehring et al., 1991; Sparks et al., 1997). Laboratory studies have shown that CP may be biologically activated to form metabolites that are moderately potent bacterial mutagens (Schneider et al., 1999). Chloropicrin was also found to be a relatively reactive compound that would promote tropospheric ozone formation if emitted in the presence of other reactive organic compounds (Carter et al., 1997). These characteristics together suggest that volatilization of CP after soil treatment may become a source of air pollution and should be adequately evaluated.

Early studies showed that CP could undergo dehalogenation by soil *Pseudomonas* sp. (Castro et al., 1983) and photohydrolysis (Castro and Belser, 1981). However, relatively little is known about its fate and persistence in soil or its volatilization from soil (Wilhelm et al., 1997). In this study, we determined CP degradation in three soils under different temperature and moisture conditions and evaluated its volatilization against MeBr under different soil surface conditions. This information may be used for assessing environmental risks of current CP fumigation practices and for developing strategies to minimize its atmospheric emission.

MATERIALS AND METHODS

Soils, Chemicals, and Plastic Films

Three soils, an Arlington sandy loam (coarse loamy, mixed, thermic Haplic Durixeralf; Riverside, CA), a Carsitas loamy sand (mixed, hyperthermic Typic Torripsament; Coachella Valley, CA), and a Waukegen silt loam (fine silty over sandy or sandy-skelatal, mixed, mesic Typic Hapludoll; Rosemont, MN) were used in this study. The Waukegen silt loam was sampled from a cold climate where CP had not been used and was included in this study as a reference soil. The Arlington, Carsitas, and Waukegen soils had organic matter contents of 0.92, 0.22, and 3.1%, respectively, and a pH 7.2, 8.0, and 5.5, respectively. Soils were sieved through a 2-mm sieve without air-drying and stored at room temperature before use. Chloropicrin (98.4%) was obtained from Chem Service (Bellefonte, NJ) and MeBr (>99%) from TriCal Co. (Hollister, CA). Polyethylene film was obtained from TriCal and high-barrier film was donated by Klerk's Plastics (Hoogstraten, Belgium).

Degradation Experiments

Degradation of CP was first determined at 20°C in sterile and nonsterile soils to distinguish chemical and microbial transformations. Soil (10.0 g oven-dry weight) with 10% water content was placed in 21-mL glass vials. Sterile soil samples

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Abbreviations: CP, chloropicrin; GC, gas chromatograph; HBF, high-barrier film; MeBr, methyl bromide; MITC, methyl isothiocyanate; PEF, polyethylene film; UT, untarped.

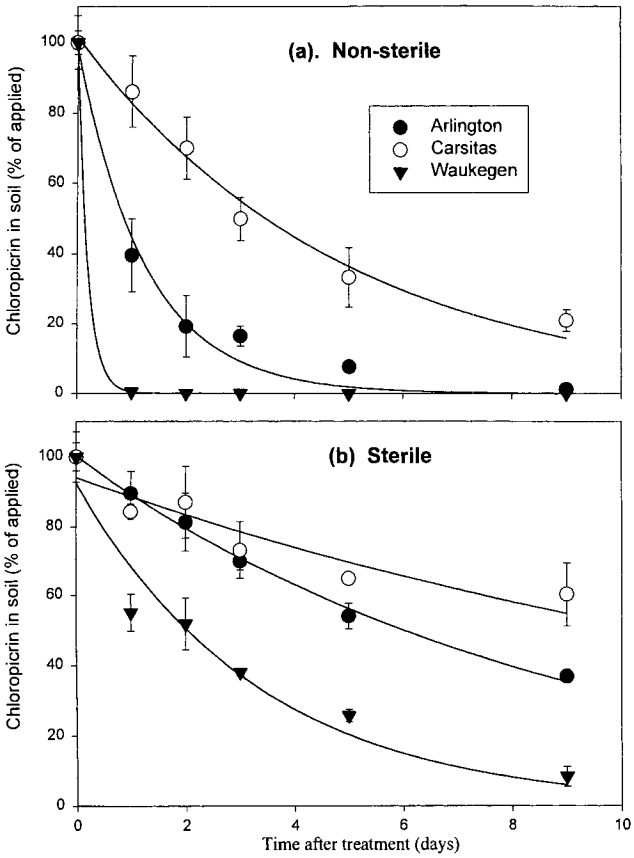

Fig. 1. Degradation of chloropicrin in soils before and after sterilization. Symbols are measured data with standard deviations and lines are fitted with the first-order decay model.

were obtained by autoclaving soil vials twice at 121°C for 60 min, with a 24-h interval between the first and second autoclaving. Each sample was spiked with 100 μl of CP solution (5 g L^{-1}) to give an initial concentration of 50 mg kg^{-1}, and the treated sample vials were immediately capped with Teflon-faced septa and aluminum seals. Fumigant addition for sterile soil samples was carried out under aseptic conditions. The closed soil vials were incubated in the dark at 20 ± 0.5°C.

At 1, 2, 3, 5, and 9 d after the treatment, triplicate vials were removed from each treatment and immediately stored at −21°C to stop the degradation. For extraction, the sample vials were decapped while the soil was still frozen and 10 g of anhydrous sodium sulfate and 10 mL of ethyl acetate were added into each vial, followed by immediate recapping of the vial. After the soil was thawed at room temperature, sample vials were vortexed at a high speed for 2 min and a portion of the supernatant was transferred into a gas chromatograph (GC) vial. Preliminary experiments indicated a near 100% recovery of CP for this extraction method. Quantification of CP in the ethyl acetate extract was made on a Hewlett–Packard (Palo Alto, CA) 6890 GC with electron capture detector (ECD). The conditions were 30 m × 0.25 mm × 1.4 μm Rtx-624 capillary column (Restek Co., Bellefonte, NJ), 1.4 mL min^{-1} column flow (helium), 110°C isothermal oven temperature, 240°C inlet temperature, and 300°C detector temperature.

Degradation of CP was further determined in soil at 30, 40, and 50°C to evaluate temperature effects. Similar treatment procedures as given above were followed and only nonsterile soils were used. The initial fumigant concentration in soil was 50 mg kg^{-1} and the soil moisture content 10% (w/w). The

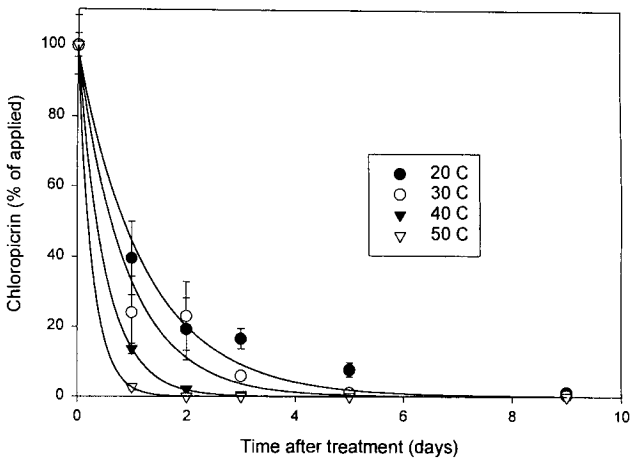

Fig. 2. Degradation of chloropicrin in Arlington sandy loam at different soil temperatures. Symbols are measured data with standard deviations and lines are fitted with the first-order decay model.

treated vials were immediately transferred to and kept in incubators with set temperatures. At different time intervals, triplicate samples were removed from each treatment and analyzed for residual CP concentration following the same sample preparation and analytical procedures as given above.

Degradation of CP was also determined at 20°C in soils with different moisture contents to evaluate the effect of soil moisture. Only Arlington sandy loam and Carsitas loamy sand were used in this experiment. Soils were preadjusted to four different moisture levels by either air-drying or water addition. The soil mass in each vial was 10.0 g as oven-dry weight. The samples were spiked with CP at 50 mg kg^{-1}. The final soil moisture contents (w/w) were 1.8, 6.0, 11.0, and 16.0% for both soils. At different time intervals, triplicate samples were extracted and analyzed for residual CP concentration.

Column Volatilization Experiment

Volatilization of CP and MeBr was simultaneously determined from large columns packed with the Arlington soil at room temperature (20 ± 1°C). Three soil surface conditions were created: (i) untarped (UT) surface, (ii) surface covered with 0.035-mm high-density polyethylene film (PEF), and (iii) surface covered with a high-barrier film (HBF). The schematics of the column system were given in detail elsewhere (Gan et al., 2000). The columns were made of stainless steel and had a dimension of 70 cm (length) × 12 cm (i.d.). Columns were packed with soil at a bulk density of 1500 kg m^{-3} and a moisture content of 6% (w/w). Chloropicrin (350 mg) and MeBr (350 mg) were injected at the same time into the columns at the 30-cm depth via a side sampling port. A sampling chamber of 4 cm (length) × 12 cm (i.d.) was immediately sealed onto the top of the soil column and a vacuum was used to continuously sweep the column headspace at 120 mL min^{-1}

Table 1. First-order degradation rate constants (k, d^{-1}) of chloropicrin in soil at different temperatures (numbers in parentheses are correlation coefficient r).

	Soil		
Temperature	Arlington	Carsitas	Waukegen
°C			
20	0.45 (0.97)	0.16 (0.93)	3.25 (0.94)
30	0.62 (0.95)	0.49 (0.96)	8.37 (0.99)
40	1.78 (0.99)	0.95 (0.96)	13.99 (0.99)
50	3.65 (0.99)	1.77 (0.98)	23.66 (0.98)

into a HP 5890 GC. A computerized relay system was used to automate the introduction of a sample from the headspace from each column into the GC at an 11-min interval. After 9 d, films in PEF and HBF columns were torn to simulate removal of surface cover that is typically done in field practices. Volatilization from these columns was further monitored until the headspace concentration fell below detection. The GC conditions used for on-line monitoring were as follows: 100-μl gas sampling valve, 60 m × 0.53 mm × 3.0 μm AT-624 capillary column (Alltech, Deerfield, IL), 20 mL min^{-1} column flow (nitrogen), 100°C isothermal oven temperature, and 280°C detector temperature. Volatilization fluxes were calculated as μg m^{-2} s^{-1} and cumulative volatilization losses as percentage of applied fumigants.

To compare the movement of CP and MeBr in soil after fumigant injection, soil air (0.5 mL) was withdrawn from the columns at different depths along the column using a gas-tight syringe. The soil air was directly transferred into empty headspace vials (8.7 mL) and immediately capped. Fumigant concentration was determined on a HP 5890 GC in tandem with an automated headspace sampler. The GC conditions were similar to those used in the degradation experiments.

RESULTS AND DISCUSSION

Chloropicrin Degradation in Different Soils

Degradation of CP followed the first-order kinetics in all soils with the correlation coefficient $r \geq 0.93$ (Fig. 1). The first-order degradation rate constant (k) at 20°C was 0.45, 0.16, and 3.25 d^{-1} for Arlington sandy loam, Carsitas loamy sand, and Waukegen silt loam, respectively. This translates into half-lives ($t_{1/2}$) of only 1.5, 4.3, and 0.2 d. These values were in general agreement with Wilhelm et al. (1997), who reported a $t_{1/2}$ of 4.5 d in a sandy loam and 1.3 h in an alfalfa-amended anaerobic soil. Compared with the other fumigants, CP degradation appears to be very rapid. For instance, $t_{1/2}$ in the Arlington soil was 38 d for MeBr (Papiernik et al., 2000) and ≥5 d for 1,3-D isomers and MITC. In the Carsitas loamy sand, $t_{1/2}$ was 11 d for MeBr and 9 to 13 d for 1,3-D isomers and MITC (Gan et al., 1999). Degradation of CP in the sterile soils, however, was significantly inhibited (Fig. 1b), suggesting an important role of soil microorganisms in CP degradation. After sterilization, $t_{1/2}$ increased to 6.3, 13.9, and 2.7 d in the Arlington, Carsitas, and Waukegen soils, respectively. Based on the difference in degradation between nonsterile and sterile soils, it was estimated that microbial degradation accounted for 68 to 92% of the overall CP degradation. Contribution of microorganisms in CP degradation was more predominant than either MeBr or 1,3-D, and was similar to that in MITC degradation (Gan et al., 1999).

Table 2. First-order degradation rate constants (k, d^{-1}) of chloropicrin in soil with different water contents (numbers in parentheses are correlation coefficient r).

Moisture content	Water potential	Arlington sandy loam	Carsitas loamy sand
%, w/w	kPa		
1.8	∞	0.28 (0.98)	0.21 (0.89)
6.0	832	0.48 (0.99)	0.26 (0.97)
11.0	6.3	0.54 (0.99)	0.23 (0.99)
16.0	1.1	0.57 (0.99)	0.17 (0.98)

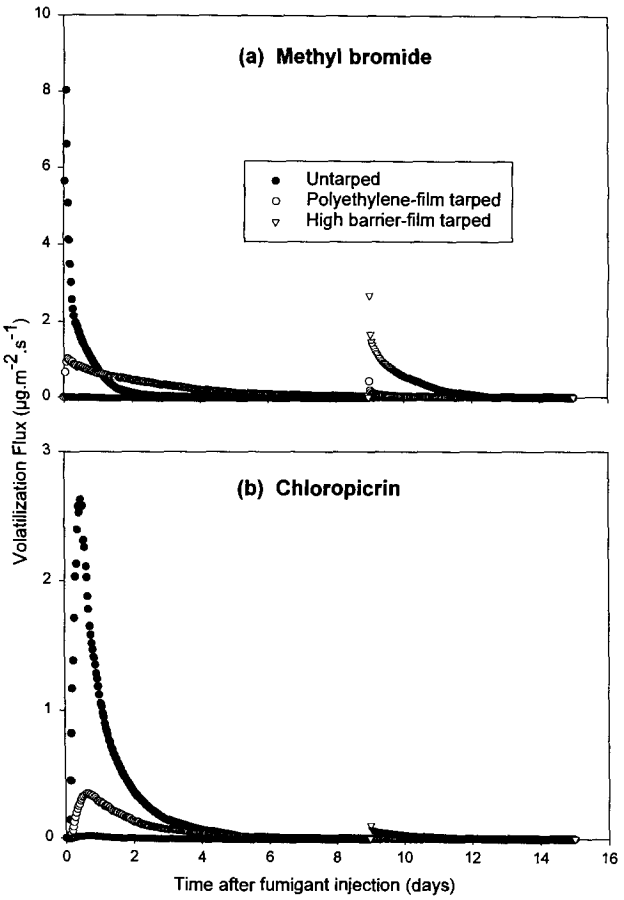

Fig. 3. Volatilization fluxes of methyl bromide (MeBr) and chloropicrin (CP) from columns packed with Arlington sandy loam at different surface conditions.

Castro et al. (1983) showed that four species of soil *Pseudomonas* were able to sequentially dechlorinate CP to $CHCl_2NO_2$, CH_2ClNO_2, and CH_3NO_2 within 1 h. The significant contribution of microbial transformation to the rapid CP degradation observed in this study for all soils, including the Waukegen soil from a cold climate, further suggests that CP degrading microorganisms may be abundantly present in the soil environment.

Temperature and Moisture Effects on Degradation

Degradation of CP accelerated as soil temperature increased (Fig. 2 and Table 1). The acceleration occurred in all three soils. For instance, when soil temperature increased from 20°C to 50°C, CP degradation was enhanced by 8, 11, and 7 times in Arlington sandy loam, Carsitas loamy sand, and Waukegen silt loam, respectively. At 40°C or above, CP became extremely labile, and $t_{1/2}$ was less than 0.4, 0.7, and 0.05 d in Arlington, Carsitas, and Waukegen soils, respectively (Table 1). Similar temperature dependence was also observed for 1,3-D and MITC in these soils (Gan et al., 1999). However, at the same temperature, CP appeared to be more degradable than the other fumigants. For instance, at 40°C in Arlington soil, $t_{1/2}$ was 1.8, 1.4, and 1.3 d for *cis*-1,3-D, *trans*-1,3-D, and MITC, respectively, but was only

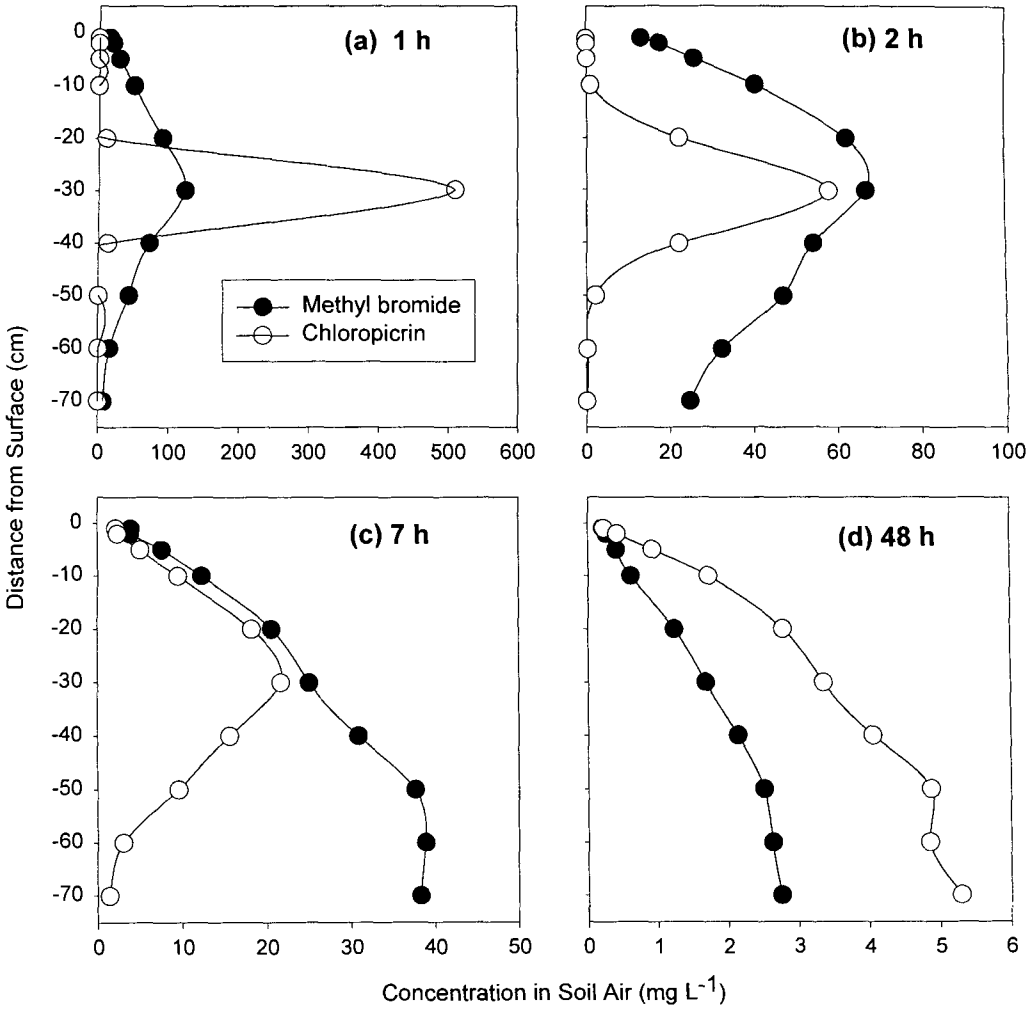

Fig. 4. Distribution of methyl bromide and chloropicrin in the untarped column packed with Arlington sandy loam at different times after fumigant injection.

0.4 d for CP. Rapid CP degradation at temperatures ≥40°C also implies that the activity of CP degrading microorganisms was not inhibited by the high temperature. A previous study showed that MITC degraders were not suppressed by high soil temperatures, but 1,3-D degraders were inhibited at temperatures >40°C (Gan et al., 1999).

The positive dependence of CP degradation on soil temperature can have implications for development of strategies for reducing its atmospheric emissions. For instance, applying CP when soil is relatively warm would stimulate its degradation, which, if combined with the use of a surface barrier, may result in substantially reduced emissions. Surface covers such as plastic mulches are known to enhance soil temperature by trapping solar energy. This has been employed in practices such as soil solarization to raise soil temperature sufficiently (40–60°C) to cause thermal destruction of soilborne nematodes and pathogens (Katan and DeVay, 1991; Lazarovits et al., 1991). Therefore, rapid CP degradation may be expected in solarized soil, while integration of CP fumigation with solarization may lead to less CP emission.

Response of CP degradation to soil moisture content was slightly different between Arlington and Carsitas soils (Table 2). In Arlington sandy loam, CP degradation occurred at a considerably slower rate when the soil was near air-dryness. However, in the same soil with ≥6.0% moisture content, CP degraded at a greater rate, and moisture variation showed no significant effect (Table 2). In Carsitas loamy sand, the CP degradation rate was similar for the entire moisture range (1.8–16.0%). Overall, it may be concluded that under typical field conditions, soil moisture is unlikely to affect CP degradation significantly. Soil moisture, however, may affect the movement of CP in soil, because occupancy of air pores by water reduces diffusion of organic vapor in soil (Jury et al., 1997). Slower diffusion may result in greater CP degradation because of longer contact of the fumigant with the soil.

Volatilization from Untarped Soil

Volatilization of MeBr from the UT column started immediately after fumigant injection, while that of CP was delayed (Fig. 3). For instance, maximum volatilization of MeBr occurred at 1.5 h, while that of CP occurred

at 11 h after fumigant injection. The detected maximum flux of MeBr was 8.04 μg m^{-2} s^{-1}, but that of CP was only 2.63 μg m^{-2} s^{-1}. This suggests that the immediate field worker exposure to CP during fumigation is probably smaller than to MeBr in the field. The slower volatilization was apparently a result of the slower movement of CP from the injection point to the soil surface, as illustrated by the distribution patterns of MeBr and CP in the column after treatment (Fig. 4). Distribution of CP at 1 or 2 h was much more focused around the injection point (30 cm) than MeBr, although the difference appeared to diminish as time further increased (Fig. 4). The slower diffusion may be attributed to two reasons. First, CP has a much higher boiling point (112°C) than MeBr (4°C) and time would be needed for the applied liquid CP to completely vaporize in soil. According to Bird et al. (1960), the time needed for the applied liquid CP to vaporize was estimated to be about 75 min. Second, because of a smaller Henry's law constant (0.0001 for CP vs. 0.25 for MeBr), the retardation factor for CP diffusion in the gas phase was calculated to be $>10^3$ greater than that for MeBr (using an equation by Jury et al., 1997). The slower diffusion of CP was also shown in the more gradual decrease of its volatilization flux after reaching a maximum. For instance, volatilization flux of CP surpassed that of MeBr after only 8 h following the injection (Fig. 3). At 24 h after application, the fluxes of CP and MeBr were 1.12 and 0.71 μg m^{-2} s^{-1} respectively. At 48 h after application, the respective fluxes for CP and MeBr were 0.37 and 0.11 μg m^{-2} s^{-1}.

Cumulatively, 88% of the applied MeBr and 82% of the applied CP were lost to volatilization from the UT column by the end of experiment, 15 d after application (Fig. 5). Because volatilization of CP and MeBr was measured from the same column, this result implies that total cumulative emission of CP under field conditions should be similar to that of MeBr. In a field study, Mejewski et al. (1995) showed that when the surface was not covered, 89% of the applied MeBr was lost to volatilization within 5 d. Therefore, assuming that CP is applied as Telone C-17 at 112 L ha^{-1}, it can be estimated that from each hectare of fumigated field, about 21 kg of active ingredient CP may be emitted into the atmosphere. If Telone C-35 is used, as much as 44 kg of CP may enter the ambient air. The implication of such CP emissions can be significant, which mandates that approaches for reducing CP volatilization be investigated.

Volatilization from Covered Soil

Covering the soil surface with a PEF or an HBF greatly changed the volatilization pattern as compared with the UT column (Fig. 3 and 5). When the surface was covered with PEF, volatilization fluxes of MeBr or CP during the initial hours were considerably smaller than from the UT column (Fig. 3). The maximum flux from the PEF column was only about 14% of that from the UT column for both fumigants. However, although the initial fluxes were smaller, MeBr volatilization from

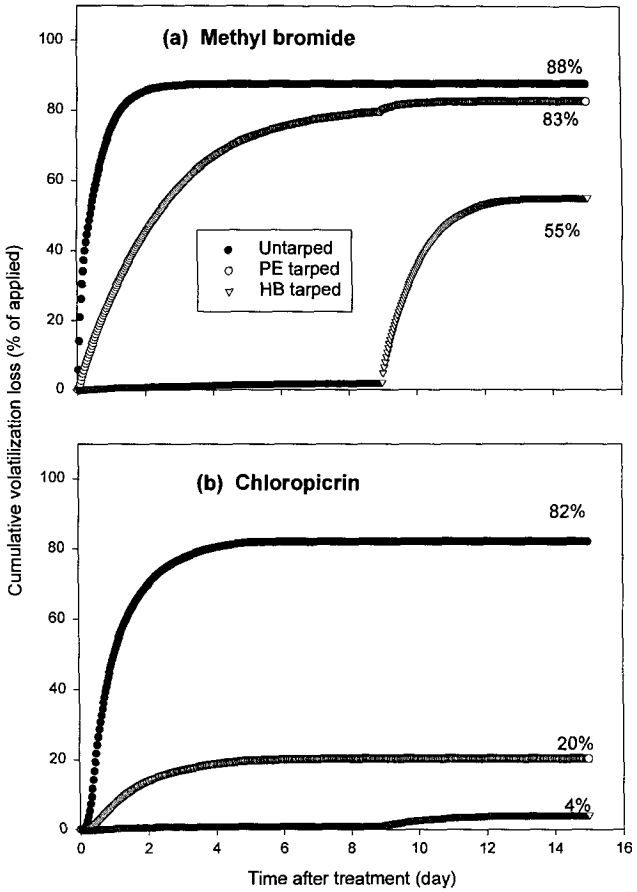

Fig. 5. Cumulative volatilization losses (% of applied) of methyl bromide and chloropicrin from columns packed with Arlington sandy loam at different surface conditions.

the PEF column continued at relatively high fluxes for a prolonged time. For instance, in the UT column, MeBr flux decreased to <0.1 μg m^{-2} s^{-1} in 2 d, while this did not occur in the PEF column until 5 d after application. Compared with the UT column (88%), the total loss of MeBr (83%) from the PEF column decreased only slightly. The relatively high emission from the PEF treatment was in agreement with several field studies, in which MeBr emission losses of 34 to 89% were reported (Majewski et al., 1995; Yagi et al., 1995; Yates et al., 1996). The high emission from PEF tarped soil may be attributed to the relatively high permeability of MeBr through the film and its slow degradation in soil. In comparison, emission of CP from the PEF column decreased to only 20%, which was only one-quarter of that from the UT column. Chloropicrin was found to be even slightly more permeable through PEFs than MeBr (Yates et al., 1997). The smaller emission of CP may thus be attributed to its rapid degradation in the soil ($t_{1/2}$ = 1.5 d). The rapid degradation, when coupled with the containment provided by the PEF, may have resulted in extensive degradation that decreased CP available for volatilization.

The HBF was virtually impermeable to both MeBr and CP (Fig. 3 and 5). Cumulatively, only 2.2% of MeBr and 1.2% of CP volatilized from the HBF column up to Day 9, when the film was purposely torn. Rupture

of the film, however, caused a drastic increase in MeBr volatilization, indicating that a large portion of the MeBr in the HBF column was not degraded and still available for volatilization. By the end of the experiment, the overall MeBr emission loss increased to 55%. This suggests that containment alone may be inadequate for reducing volatilization of persistent fumigants, unless the surface is covered for a long time. However, a greater decrease in MeBr emission is likely to occur in the field, because covering with HBF should promote deep penetration of MeBr in soil, a process that was limited by the closed column bottom in this study. As shown in Wang et al. (1997), covering soil with the HBF for 5 d resulted in 36% MeBr emission loss, while covering the soil for 10 or more days decreased the loss to only 1.8 to 3.2%. In comparison with HBF, rupture of PEF only resulted in a limited additional loss (3%) for MeBr. This apparently was attributable to the fact that most MeBr in the PEF column had already volatilized before the film was ruptured. Compared with MeBr, destruction of HBF resulted in relatively small increases in volatilization flux of CP (Fig. 3b). The additional loss of CP from the HBF column after film rupture was less than 3%. Chloropicrin degraded many times more rapidly than MeBr in the Arlington soil. Containment of CP in the soil by the HBF for 9 d was apparently long enough to cause degradation of most CP.

CONCLUSIONS

Chloropicrin degraded rapidly in soil, primarily via microbial degradation by soil microorganisms. Degradation of CP accelerated further as soil temperature increased but was largely independent of soil moisture variation. After injection in subsoil, CP diffused more slowly than MeBr and volatilization of CP during the initial hours was not as rapid as that of MeBr. When there was no barrier at the soil surface, overall loss of CP to volatilization was comparable with MeBr. Covering the soil surface with PEF did not change the overall loss of MeBr, but greatly decreased the emission of CP. Covering the soil surface with HBF further reduced CP emission to a negligible level. These results together suggest that in current practices where CP is applied without surface cover, excessive emissions of this fumigant may occur. To reduce CP volatilization, surface covers may be used. Although PEFs are ineffective for stopping MeBr volatilization, they may be efficient for reducing CP emission. It can be further concluded that surface covers are more effective for reducing volatilization of more degradable fumigants (e.g., CP) than more persistent ones (e.g., MeBr).

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