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Effects of Application Methods and Plastic Covers on Distribution of Cis- and Trans-1,3-Dichloropropene and Chloropicrin in Root Zone[1]

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Abstract: This study examined the effects of three application methods (chisel injection, Avenger coulter injection, and drip irrigation) and two plastic films (polyethylene film [PE] and virtually impermeable film [VIF]) on distribution of cis- and trans-1,3-dichloropropene (1,3-D) and chloropicrin (CP) in a Florida sandy soil after application of Telone C35 or Telone In-Line. Regardless of application method, VIF retained greater amounts of cis- and trans-1,3-D and CP in the root zone with longer residential time than PE. There was better retention of the three compounds in the root zone when applied with the Avenger coulter injection rig than chisel injection, especially in combination with VIF. Distribution of the three compounds in the root zone was less predictable when applied by drip irrigation. Following drip irrigation, more than 50% of the three compounds in the PE and VIF-covered beds was found near the end of the drip tapes in one experiment, whereas the distribution was much more uniform in the root zone in a second experiment. Among the three biologically active compounds, CP disappeared from the root zone more rapidly than cis- and trans-1,3-D, especially in the PE-covered beds.

Key words: 1,3-dichloropropene, chloropicrin, distribution, fumigant, fumigation, methyl bromide alternative, polyethylene mulch, root zone, virtually impermeable film.

The registration of methyl bromide (MBr) as a soil fumigant is being phased out in 2005 under the Montreal protocol (Noling and Becker, 1994; UNEP, 1995). However, MBr still can be used in agriculture through crop use exemption on a yearly basis. Three currently registered liquid volatile fumigants, 1,3-dichloropropene (1,3-D), chloropicrin (CP), and metam sodium, are possible alternatives to MBr. Metam sodium is not volatile and does not have pesticidal activity. However, when placed in contact with moist soil, metam sodium is rapidly converted to a biologically active volatile product, methyl isothiocyanate (MITC) (Smelt and Leistra, 1974; Smelt et al., 1989). 1,3-dichloropropene has good nematicidal activity and some fungicidal activity, but it is weak in herbicidal activity (McKenry and Thomason, 1974; Noling and Becker, 1994; Shoemaker and Been, 1999). Chloropicrin is generally mixed with other fumigants to provide control of soilborne fungal pathogens (Noling and Becker, 1994). 1,3-Dichloropropene products in the market include Telone II, Telone C17, Telone C35, and Telone In-Line (emulsified formulation of 1,3-D and CP). The composition of 1,3-D and CP in Telone In-Line is the same as Telone C35, about 65% 1,3-D and 35% CP. 1,3-dichloropropene consists of two isomers, cis and trans. The cis isomer has greater biological activity than the trans isomer (McKenry and Thomason, 1974; Shoemaker and Been, 1999).

Different formulations of Telone are typically applied to field soil by conventional chisel injection or drip delivery via plastic irrigation tapes. For liquid fumigants to have adequate efficacy, they have to volatilize, diffuse to the root zone, and remain there for a sufficient time. 1,3-Dichloropropene rapidly diffused three dimensionally and reached maximum concentrations in soil profiles in less than 1 day in an Arlington fine sandy loam (California soil) and 1 to 4 days in a Wahiawa silty clay (Hawaii soil) (Schneider et al., 1995; Wang and Yates, 1999). These two studies, however, did not report the distribution of the individual isomers. Concentrations of 1,3-D declined rapidly in uncovered beds applied by chisel or in PE-covered beds applied by shallow drip at 2.5-cm depth but declined more slowly in uncovered beds applied by deep drip at 20-cm depth (Wang and Yates, 1999). The main direction of movement of cis- and trans-1,3-D in the subsurface beds (5 to 90-cm depth) of an Arredondo fine sand (Florida soil) when not covered, or covered with PE or VIF, after chisel injection of Telone II to 30-cm depth, was upward diffusion, whereas downward diffusion of the two isomers was minimal (Thomas et al., 2004a, 2004b). The VIF-covered bed retained greater concentrations of 1,3-D in the root zone than the beds covered with PE or not covered, whereas the concentrations of 1,3-D in the PE-covered bed and the uncovered bed were similar. Vapor pressures and water solubilities of cis- and trans-1,3-D and CP are similar (Hornsby et al., 1995), so diffusion patterns of CP in the subsurface soil are likely to be similar to that of cis- and trans-1,3-D.

1,3-Dichloropropene is toxic to humans and animals (Anonymous, 1996). As a result, the US Environmental Protection Agency imposes a 30-m buffer zone from any occupied structure. Polyethylene film was a poor barrier to 1,3-D volatilization from the soil surface of soil columns into the atmosphere (Gan et al., 1998) and to cis- and trans-1,3-D volatilization from surfaces of the Arredondo soil in field beds (Thomas et al., 2004b). Use of VIF greatly reduced volatilization losses of cis- and trans-1,3-D from the Arredondo soil in microplots and field beds when compared to the volatilization

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losses from microplots without plastic cover (Thomas et al., 2004a), and from field beds with PE cover or no cover (Thomas et al., 2004b). Chemical and microbial degradation also contribute to the disappearance of cis- and trans-1,3-D and CP in soil (Chung et al., 1999; Gan et al., 1999, 2000; Ou et al., 1995). In this research, the influence of three application methods and two plastic covers on retention of cis- and trans-1,3-D, and CP in the root zone of field plots in a Florida sandy soil, was examined.

Materials and Methods

Chemicals and materials: Analytical grade cis- and trans-1,3-D (99.1% to 99.4% purity) and commercial Telone C35 and Telone In-Line were provided by Dow AgroSciences (Indianapolis, IN). Analytical-grade CP (99.6% purity) was purchased from Chem Service (West Chester, PA). All other chemicals were analytical grade, GC grade, or the highest grade commercially available and used without further purification. Resin sampling tubes (XAD-4, SKC South, Eighty Four, PA) were used to trap vapors of cis- and trans-1,3-D and CP from soil-pore air. Two types of plastic films were used to cover field beds: 0.025-mm-thick polyethylene film (PE) (Sonoco Products, Harksville, SC) and 0.035-mm-thick virtually impermeable film (VIF) (Hytibar, Klerk's Plastics, Hoogstraten, Belgium). Both films had white top sides and black bottom sides.

Field site, plots, and fumigant treatments: This study was carried out at the Plant Science Research and Education Unit (PSREU), University of Florida, in Citra. The slightly acidic (pH 6.5) soil type at this location to a depth of 1 to 2 m is an Arredondo fine sand (loamy, siliceous, hyperthermic, Grossarenic Paleudult with 950, 30, 20, and 15 g/kg sand, silt, clay, and organic matter, respectively). Fumigants were applied to two types of field plots, raised beds and flat soil surface. The dimensions of the beds were 0.9 m wide and 20 m long.

Treatments included (i) Telone C35 applied to raised beds by conventional chisels (three chisels/bed spaced 30 cm apart and 30 cm deep) injected at 327 liters/ha (33 ml/chisel/m row); (ii) Telone C35 applied to a flat soil surface by an Avenger coulter (Yetter, Colchester, IL) injection rig (Anonymous, 2001a, 2001b) with 3 coulters/bed spaced 30 cm apart and 30 cm deep, injected at 243 liters/ha (24 ml/chisel/m row), and immediately bedded; (iii) Telone C35 applied to a flat soil surface by an Avenger coulter broadcast rig (6 coulters/bed spaced 15 cm apart and 30 cm deep) injected at 243 liters/ha (12 ml/chisel/m row); and (iv) Telone In-Line applied to raised beds through a drip-tape placed near the bed center 5 cm beneath the soil surface at 327 liters/ha (75 ml/m row). The drip treatment was applied over a period of 5 hours. Following chemical application, except for Telone In-Line and broadcast, the beds were covered immediately with PE or VIF. The flat plot treated with Avenger coulter broadcast rig was not covered with a plastic film. For drip-application, beds were built simultaneously with placement of PE or VIF and drip-tape. The drip-tape consisted of 16-mm-inside-diam. tubing with emitters spaced 20 cm apart. Two identical drip-application experiments were carried out 2 months apart.

Soil-pore air sampling: The vapor concentrations of cis- and trans-1,3-D and CP in soil-pore air at 20-cm depth were measured with ten 20-cm-long stainless steel soil gas probes (Thomas et al., 2004b), arbitrarily distributed within each treated plot. In the second drip-application experiment, 10 additional 10-cm-long gas probes were installed in the PE and VIF-covered beds. Soil-pore air was withdrawn daily from the probes. For some beds, soil-pore air was sampled periodically for up to 21 days. Plastic syringes were used to withdraw 30 ml of soil-pore air from the probes through a XAD-4 resin sampling tube, which absorbed cis- and trans-1,3-D and CP (Thomas et al., 2004b, 2004c). The sampling tubes were stored in an ice chest and transported to the laboratory within 3 hours after collection. These tubes were stored at −80 °C until analysis. Analysis was carried out within 6 weeks after storage. A storage study indicated that the three fumigants in the tubes stored at −80 °C were stable for ≤6 weeks (data not included).

Extraction and GC analysis: XAD-4 Resin in the sampling tubes was transferred to 25-ml glass tubes with Teflon-lined caps. To prevent leakage, the tops of the tubes were wrapped with Teflon tape. After adding 10 ml hexane, the tubes were placed on a reciprocal shaker set to deliver 500 strokes/minute for 15 minutes. After centrifugation at 1000 rpm for 5 minutes, 1 ml of the hexane fraction was transferred to vials for analysis by gas chromatography (Thomas et al., 2004c).

Statistical analysis: Statistical analysis was carried out using the general linear model procedure, and the Waller-Duncan k-ratio *t*-test was used for means separation (SAS Institute, Cary, NC).

Results

Subsurface distribution of cis- and trans-1,3-D and CP: Twenty-two hours after chisel or Avenger coulter injection of Telone C35 in the PE and VIF-covered beds, as well as the uncovered bed, cis- and trans-1,3-D and CP (the biologically active compounds) had diffused upward from 30 cm deep to 20 cm deep in large concentrations, particularly in the VIF-covered beds (Fig. 1). Concentrations of cis- and trans-1,3-D and CP at 20 cm deep in all five beds decreased after 22 hours, but the decreases were more rapid in the PE-covered beds than in the VIF-covered beds. Concentrations of the three compounds of Telone declined more slowly in the Avenger coulter injected beds than in the corresponding chisel injected beds ($P \leq 0.05$). Even though the plot that received Telone C35 by Avenger coulter broadcast application at a rate of 243 liters/ha was not covered with a plastic mulch, the concentrations of cis-

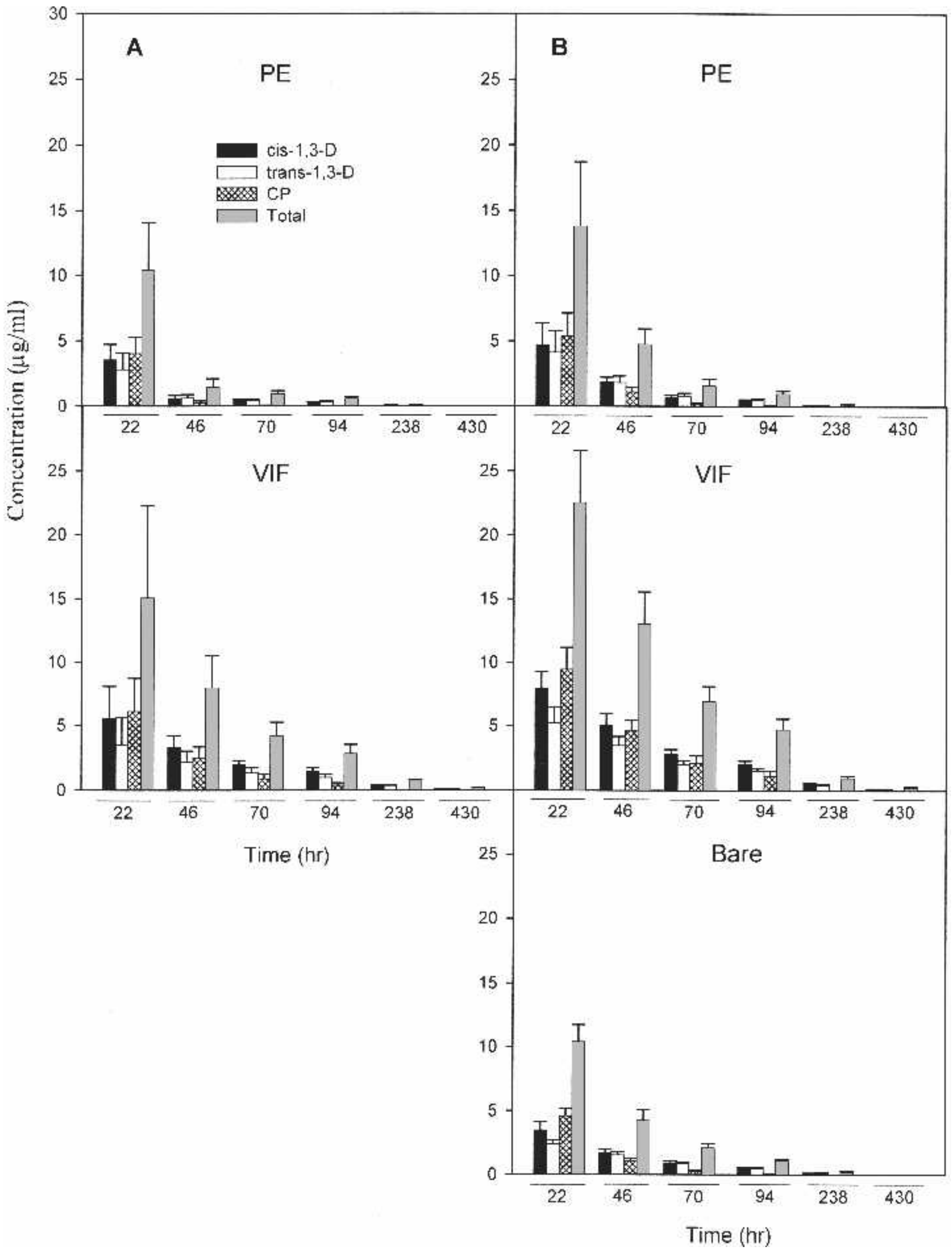

FIG. 1. Average concentrations of cis-1,3-D, trans-1,3-D, CP, and total chemicals (cis-1,3-D + trans-1,3-D + CP) from ten 20-cm-long soil gas probes in the PE or VIF-covered beds at different times after injection of Telone C35 by chisel or Avenger coulters. A) Chisel injection: top panel, PE-covered bed, and bottom panel, VIF-covered bed. B) Avenger coulter injection: top panel, PE-covered bed, middle panel, VIF-covered bed, and bottom panel, uncovered plot applied by broadcast.

and trans-1,3-D and CP at 22 hours after injection were about the same as in the PE-covered bed injected by chisel. Concentrations of the three compounds of Telone declined more slowly after 22 hours in the Avenger coulter broadcast treatment. Among the three compounds, CP concentration declined more rapidly than cis- and trans-1,3-D in all the field plots. Avenger coulter injection provided greater concentrations of cis- and trans-1,3-D and CP in soil-pore air 20 cm deep than chisel injection, and concentrations remained higher for a longer period. In conjunction with VIF cover, the three compounds had greater concentrations 20 cm deep and remained longer than in the beds covered with PE.

Distribution of cis- and trans-1,3-D and CP at the 20-cm depth in the PE and VIF-covered beds treated with Telone In-Line by the first drip-application experiment was highly variable (Fig. 2). More than 50% of the three chemical components was found near the end of drip-tapes in treated beds (data not shown). Similar to the beds applied by chisel and Avenger coulter injection, concentrations of the three compounds applied by drip declined after 22 hours, especially in the PE-covered bed, and concentrations were greater in the VIF-

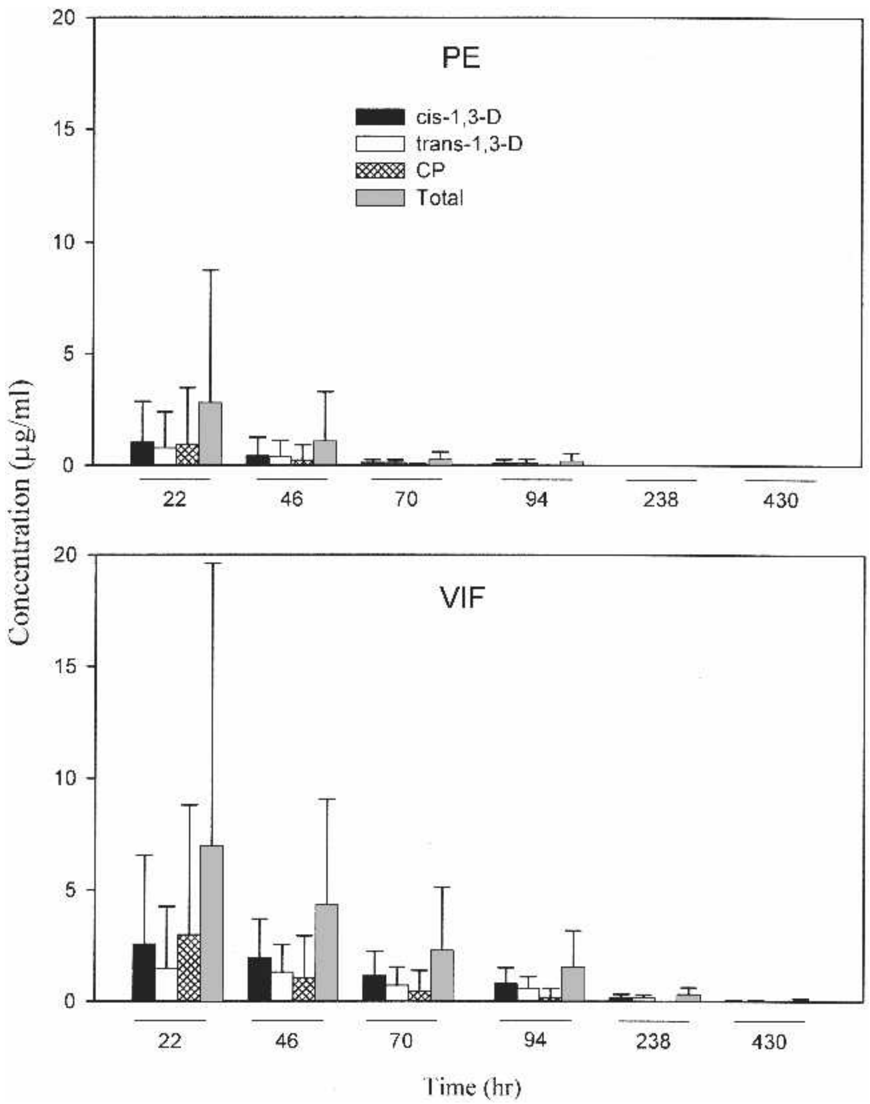

FIG. 2. Average concentrations of cis-1,3-D, trans-1,3-D, CP, and total chemicals (cis-1,3-D + trans-1,3-D + CP) from ten 20-cm-long soil gas probes in the PE or VIF-covered bed in the first drip-application experiment of Telone In-Line.

covered bed than in the PE-covered bed ($P \leq 0.05$). Forty-six hours after the drip-application, average concentrations of cis- and trans-1,3-D and CP in the PE-covered bed declined to 0.44, 0.39, and 0.24 µg/ml, respectively, whereas in the VIF-covered bed they were 1.95, 1.30, and 1.05 µg/ml, respectively.

In the second drip-application experiment (Fig. 3), the distributions of cis- and trans-1,3-D and CP 20 cm deep in the PE and VIF-covered beds were more consistent than in the first drip application, and their concentrations were greater, especially in the PE-covered bed ($P \leq 0.05$). However, concentrations of the three chemicals 20 cm deep in the PE-covered bed in both drip experiments declined more rapidly than in the VIF-covered bed between 17 and 41 hours. Seventeen hours after the second application, the three compounds in the PE and VIF-covered beds had diffused to the 10-cm depth in large concentrations (7.1 ± 2.1, 4.5 ± 1.6, and 7.7 ± 3.7 µg/ml for cis- and trans-1,3-D and CP in the VIF-covered bed, and 3.0 ± 1.3, 2.3 ± 1.2, and 2.7 ± 1.1 µg/ml in the PE-covered bed) and declined thereafter. Average concentrations of the three compounds in ten 10-cm-length gas probes in the VIF-covered bed at 17 hours after the second application were 17% to 39% greater than at the 20-cm depth. In contrast, the three compounds at 17 hours after the application at the 10-cm depth in the PE-covered bed were about one-half as large as at the 20-cm depth. This may have been due to volatilization loss, as PE is permeable to all three of the biologically active compounds of Telone (Gan et al., 1998; Papiernik et al., 2001; Papiernik and Yates, 2002; Thomas et al., 2004b). The disappearance of the three compounds between 17 and 41 hours after application in the PE-covered bed was more rapid at the 10-cm- than at the 20-cm-depth. Patterns of distribution and disappearance of the three chemicals 10 cm deep in the PE and VIF-covered beds were similar to those at 20 cm deep. Similar to the

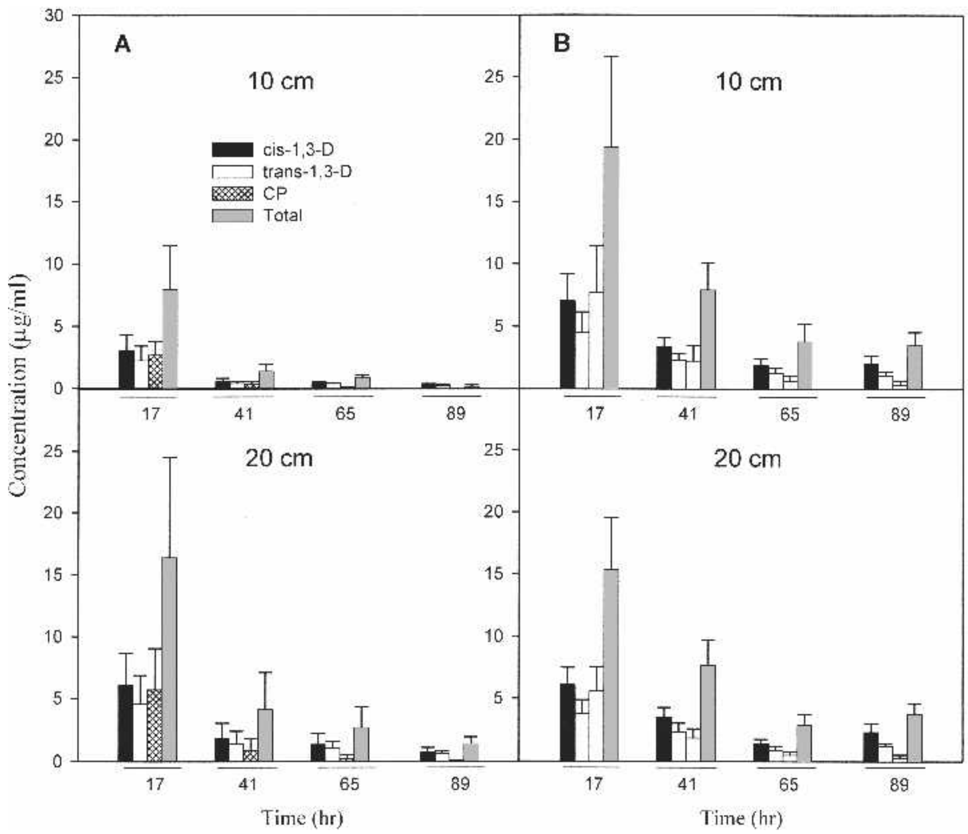

Fig. 3. Average concentrations of cis-1,3-D, trans-1,3-D, CP, and total chemicals (cis-1,3-D + trans-1,3-D + CP) from ten 20-cm- and ten 10-cm-long soil gas probes in the two PE-covered beds (A) and the two VIF-covered beds (B) (two beds were installed with ten 20-cm-long probes and the other two beds with ten 10-cm-long probes) in the second drip-application experiment of Telone In-Line.

chemical behavior found in the chisel or Avenger coulter injected beds, CP in the drip-applied beds also declined more rapidly than cis- and trans-1,3-D.

Discussion

Our results indicated that plastic film type and fumigant application methods impact the dispersion and distribution cis- and trans-1,3-D as well as CP in the soil root zone after application of Telone C35 or Telone In-Line. The greater concentrations of the three biologically active compounds in the root zone of the VIF-covered plots than PE-covered plots probably were due to VIF being a better barrier for retarding volatilization loss from soil surface than PE. Wang et al. (1999) used a soil-free apparatus to determine permeability of PE and VIF to cis- and trans-1,3-D and found that PE was about 190 times more permeable to cis- and trans-1,3-D than VIF. In an earlier study, we found that VIF was 2 to 3 times better in reducing cis- and trans-1,3-D volatilization from field beds at the same site used for this study after chisel injection of Telone II than PE, and that volatilization losses of the two chemicals from an uncovered bed and a PE-covered bed were similar to each other (Thomas et al., 2004b). VIF also may be less permeable to CP than PE. The Avenger coulter application was developed recently (Anonymous, 2001a, 2001b) for use in injection of Telone fumigants, and the coulter rig is equipped with devices that provide better sealing of injection traces. Our results showed that concentrations of the three biologically active compounds in the root zone injected by the Avenger coulter rig were consistently greater than those injected by conventional chisels.

Surprisingly, the distributions of cis- and trans-1,3-D and CP at the 20-cm depth were distinctively different in the two drip applications of Telone In-Line carried out 2 months apart. The same delivery tank, pump, drip-tape, and rate of application were used for the two experiments. In the first experiment, more than half of the three chemicals at the 20-cm depth were found near the end of drip-tape in the two plastic-covered beds. In the second experiment, the distribution of the three compounds at the 20-cm depth was markedly more uniform, and average concentrations of the three chemicals in the two plastic-covered beds were greater than in the two beds used for the first drip-experiment. Furthermore, the distribution pattern of the three compounds at the 10-cm depth in the two plastic-covered beds for the second drip-application experiment was similar to that at the 20-cm depth.

The biologically active compounds in Telone C35—1,3-D (especially the cis isomer), and CP—are responsible for killing soil pathogens such as nematodes and fungi in fumigated soil. Greater concentrations of the biologically active compounds in the root zone would be expected to provide greater pathogen control. The VIF-covered bed, injected by Avenger coulters, had a greater average concentration of the fumigant in the root zone; therefore, it was likely that the pathogen density in the root zone of this bed would be low. Because Telone In-Line contains formulation materials that enhanced solubility of cis- and trans-1,3-D and CP in water and during drip-application, large amounts of irrigation water (150 parts water to 1 part Telone In-Line) were used to deliver the fumigant to the subsurface of the field beds. When the fumigant was delivered to the beds, the three compounds should have been predominately in the water phase. Soil microorganisms including bacteria, fungi, protozoa, and nematodes inhabit mainly soil surfaces (Alexander, 1977; Sylvia et al., 1998), and surfaces of moist soil, such as agricultural soil, are coated with a layer of water. Thus, cis- and trans-1,3-D and CP delivered by drip-application would be ready to exert toxicity toward microbial pathogens. On the other hand, when Telone C35 was applied directly to the field beds by chisel or Avenger coulter injection, the three liquid biologically active compounds volatilized and the vapors diffused through soil-pore air space and eventually into the water phase. Therefore, Telone In-Line applied by drip should be more effective in controlling soil pests than Telone C35 applied by injection, even though they have the same biologically active compounds.

In conclusion, this study demonstrated that choice of injection method and plastic cover is important with respect to retention of the biologically active compounds (cis- and trans-1,3-D and CP) of Telone C35 or Telone In-Line in the root zone that may result in good pathogen control. Virtually impermeable film was superior to PE for retaining the three biologically active chemicals in the root zone. Avenger coulter injection provided more uniform distribution and greater levels of the three chemicals in the root zone than chisel injection. The combination of Avenger coulter injection and VIF increased retention of the three chemicals in the root zone.

Literature Cited

Alexander, M. 1977. Introduction to soil microbiology, 2nd ed. New York: John Wiley and Sons.

Anonymous. 1996. 1,3-Dichloropropene—a profile. Indianapolis, IN: DowElanco.

Anonymous. 2001a. Application technology for injecting Telone. Methyl Bromide Alternatives 7:5–6.

Anonymous. 2001b. Yetter's new rig makes Telone application easy. Florida Grower 94:20.

Chung, K.-Y., D. W. Dickson, and L.-T. Ou. 1999. Differential enhanced degradation of cis- and trans-1,3-D in soil with a history of repeated field applications of 1,3-D. Journal of Environmental Science and Health B34:749–768.

Gan, J., S. K. Papiernik, S. R. Yates, and W. A. Jury. 1999. Temperature and moisture effects on fumigant degradation in soil. Journal of Environmental Quality 28:1436–1441.

Gan, J., S. R. Yates, F. F. Ernst, and W. A. Jury. 2000. Degradation and volatilization of the fumigant chloropicrin after soil treatment. Journal of Environmental Quality 29:1391–1397.

Gan, J., S. R. Yates, D. Wang, and F. F. Ernst. 1998. Effect of application methods on 1,3-dichloropropene volatilization from soil under controlled conditions. Journal of Environmental Quality 27:432–438.

Hornsby, A. G., R. D. Wauchope, and A. E. Herner. 1995. Pesticide properties in the environment. New York City: Springer-Verlag.

McKenry, M. V., and I. J. Thomason. 1974. Organism-dosage-response studies in the laboratory with several nematode species. Hilgardia 42:423–437.

Noling, J. W., and J. O. Becker. 1994. The challenge of research and extension to define and implement alternatives to methyl bromide. Journal of Nematology 26:573–586.

Ou, L.-T., K.-Y. Chung, J. E. Thomas, T. A. Obreza, and D. W. Dickson. 1995. Degradation of 1,3-dichloropropene (1,3-D) in soils with different histories of field applications of 1,3-D. Journal of Nematology 27:249–257.

Papiernik, S. K., and S. R. Yates. 2002. Effects of environmental conditions on the permeability of high density of polyethylene film to fumigant vapors. Environmental Science & Technology 36:1833–1838.

Papiernik, S. K., S. R. Yates, and J. Gan. 2001. An approach for estimating the permeability of agricultural films. Environmental Science & Technology 35:1240–1246.

Schneider, R. C., R. E. Green, J. D. Wolt, R. K. H. Loh, D. P. Schmitt, and B. S. Sipes. 1995. 1,3-Dichloropropene distribution in soil when applied by drip irrigation or injection in pineapple culture. Pesticide Science 43:97–105.

Shoemaker, C. H., and T. H. Been. 1999. Compound models describing the relationship between dosage of (Z)- and (E)-1,3-dichloropropene and hatching of *Globodera rostochiensis*. Nematology 1:19–29.

Smelt, J. H., S. J. H. Crum, and W. Teunissen. 1989. Accelerated transformation of the fumigant methyl isothiocyanate in soil after repeated application of metham-sodium. Journal of Environmental Science and Health B24:437–455.

Smelt, J. H., and M. Leistra. 1974. Conversion of metham sodium to methyl isothiocyanate in soil. Pesticide Science 5:401–407.

Sylvia, D. M., J. J. Fuhrmann, P. G. Hartel, and D. A. Zubern. 1998. Principles and applications of soil microbiology. Upper Saddle River, NJ: Prentice Hall.

Thomas, J. E., L. H. Allen, Jr., L. A. McCormack, J. C. Vu, D. W. Dickson, and L.-T. Ou. 2004a. Diffusion and emissions of 1,3-dichloropropene in Florida sandy soil in microplots affected by soil moisture, organic matter, and plastic film. Pest Management Science 60:390–398.

Thomas, J. E., L. H. Allen, Jr., L. A. McCormack, J. C. Vu, D. W. Dickson, and L.-T. Ou. 2004b. Atmospheric volatilization and distribution of (Z)- and (E)-1,3-dichloropropene in field beds with or without plastic covers. Journal of Environmental Science and Health B39:709–723.

Thomas, J. E., L. H. Allen, Jr., L. A. McCormack, J. C. Vu, D. W. Dickson, and L.-T. Ou. 2004c. Persistence, distribution, and emission of Telone C35 injected into a Florida sandy soil as affected by moisture, organic matter, and plastic cover. Journal of Environmental Science and Health B39:505–516.

UNEP. 1995. The Montreal protocol on substances that deplete the ozone layer: 1994 Report of the Methyl Bromide Technical Option Committee. UNEP, Nairobi, Kenya.

Wang, D., and S. R. Yates. 1999. Spatial and temporal distribution of 1,3-dichloropropene in soil under drip and shank application and implications for pest control efficacy using concentration-time index. Pesticide Science 55:154–160.

Wang, D., S. R. Yates, J. Gan, and J. A. Knuteson. 1999. Atmospheric volatilization of methyl bromide, 1,3-dichloropropene, and propargyl bromide through two plastic films: Transfer coefficient and temperature effect. Atmospheric Environment 33:401–407.