Temperature and Moisture Effects on Fumigant Degradation in Soil

J. Gan,* S. K. Papiernik, S. R. Yates, and W. A. Jury

ABSTRACT

Recent discovery of the contribution of methyl bromide fumigation to stratospheric ozone depletion has revealed our limited understanding of the environmental processes of fumigants. For instance, little is known about fumigant degradation in soil under high temperature or low moisture conditions that prevail near the soil surface during fumigation. In this study we determined the interaction of soil temperature and moisture with degradation of 1,3-dichloropropene (1,3-D) and methyl isothiocyanate (MITC) for extended soil temperature and moisture ranges. Fumigant degradation increased 5 to 12 times when temperature increased from 20 to 50°C. It was further shown that chemical transformation of fumigants always increased with increasing temperature, but temperature effects on microbial degradation were fumigant dependent. The relative contribution of microbial degradation to the overall fumigant degradation was highest for the soil with highest organic matter content, and was greater for MITC than for 1,3-D isomers. When the temperature was >30°C, microbial degradation of 1,3-D was substantially suppressed, while that of MITC was greatly stimulated. As soil moisture content increased, 1,3-D degradation accelerated, but that of MITC decreased. The specific responses of fumigant degradation to temperature and moisture variations should be considered when describing their transport in the environment, and also may be used for designing fumigation practices that allow reduced atmospheric emissions.

During the last few decades, soil fumigation has been the most widely used method for soilborne pest control (Noling and Becker, 1994; UNEP, 1995). Many fumigants, however, owing to their negative attributes such as high volatility, toxicity or carcinogenicity, have caused various environmental concerns (UNEP, 1995; Baker et al., 1996). The problem culminated recently as the emission of methyl bromide (MeBr) was found to contribute to stratospheric ozone depletion (UNEP, 1995; Yagi et al., 1995; Majewski et al., 1995; Yates et al., 1998). This and the frequent detection of fumigants in ambient air (van den Berg et al., 1994; Baker et al., 1996) mandate that the processes and factors that affect fumigant fate in the environment be better understood.

Degradation in soil is one of the most important processes that counteract a fumigant's upward diffusion and subsequent atmospheric emission. Pesticide degradation in soil is known to be dependent on soil temperature and sometimes on soil moisture content (Walker, 1978; Helweg, 1987; Choi et al., 1988; Walker et al., 1992; Parkin and Shelton, 1994). The effect of these two variables should have even greater significance for fumigant degradation because of the extreme conditions prevailing near the soil surface during fumigation. First, fumigation is usually conducted under warm conditions, when temperature near the soil surface can be very high but moisture content can be very low. Second, fumigated fields are sometimes covered with plastic sheets, which can result in drastically elevated surface temperatures. For instance, temperatures as high as 60 to 70°C were recorded under plastic sheeting in the field (Yates et al., 1996). Thirdly, integration of nonchemical alternatives for pest control with fumigation is under development (Katan and DeVay, 1991; Lazarovits et al., 1991; Chellemi et al., 1994), and some of the nonchemical methods, such as solarization and surface irrigation, greatly alter soil temperature and moisture regimes. For instance, under optimal conditions, soil solarization can raise surface soil temperature up to 60°C (Katan and DeVay, 1991).

In previous studies, fumigant degradation has been determined only at a single temperature (e.g., 20°C) or moisture content (Smelt and Leistra, 1974; Roberts and Stoydin, 1976; Smelt et al., 1989; Gan et al., 1994, 1998; Ou et al., 1995), and little is known about their behavior under other conditions. The main purpose of the present study was to determine degradation of 1,3-dichloropropene (1,3-D) and methyl isothiocyanate (MITC) across a range of soil temperature (20–50°C) and moisture (1.6–16%) conditions. These fumigants are the most important alternatives to MeBr, and therefore their use is expected to increase. Because of their toxicity–carcinogenicity and reported high emission potential (Leistra and Crum, 1992; van den Berg et al., 1994; Chen et al., 1995; Baker et al., 1996; Gan et al., 1998), a better understanding of their environmental behavior and the underlying mechanisms of degradation is important.

Pesticide degradation in nonsterile soil is often a combination of chemical and microbial reactions. Chemical degradation is commonly measured as the degradation in sterile soils, while the reduction in degradation caused by sterilization is attributed to *inhibition of* microbial degradation. Many studies indicate that pesticide degradation in nonsterile soils accelerates with increasing temperature (Walker, 1978; Walker et al., 1992; Parkin and Shelton, 1994). This conclusion, however, has been drawn from observations using temperatures <30°C, and may not be valid for higher temperatures because of the potential inhibition of microbial activity at high temperature. Thus, another objective of this study was to measure the effect of temperature on chemical and microbial transformations, and to quantify the relative contribution of microbial and chemical processes to the total degradation of fumigants as a function of temperature.

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Published in J. Environ. Qual. 28:1436–1441 (1999).

Abbreviations: 1,3-D, 1,3-dichloropropene; MITC, methyl isothiocyanate; OM, organic matter; GC, gas chromatography; μECD, microelectron capture detector; E_a, activation energy.

MATERIALS AND METHODS

Soils and Chemicals

Two Californian soils, an Arlington sandy loam (coarse loamy, mixed, thermic, hapllic Durixeralf) and a Carsitas loamy sand (mixed, hyperthermic Typic Torrpsamments), and a Minnesotan soil, a Waukegen silt loam (fine silty, over sandy or sandy-skeletal, mixed, mesic Typic Hapludoll), were used in this study. The two Californian soils were both taken from the southern California region, and the Waukegen silt loam was included as a reference soil from a cooler climate region where the soil is normally not treated with fumigants. The Arlington sandy loam contained 0.92% organic matter (OM) and had a pH of 7.2. The Carsitas loamy sand contained 0.22% OM and had a pH value of 8.0. The Waukegen silt loam contained 3.1% OM and had a pH of 5.5. Soils were sieved through a 2-mm mesh without air-drying, and stored at room temperature before use. 1,3-D (48% *cis* isomer and 50% *trans* isomer) and MITC (99%) standards were purchased from Chem Service (Bellefonte, NJ). Telone EC formulation provided by Dow AgroSciences LLC (Indianapolis, IN) contained 89.3% 1,3-D.

Incubation Experiments for Temperature Effects

In the first incubation experiment, degradation of 1,3-D and MITC was determined in nonsterile soils at 20, 30, 40, and 50°C. Before fumigant treatment, soils were adjusted to 12% (w/w) moisture content, and 10 g of soil (oven dry wt.) were weighed into 21-mL glass headspace vials. Solutions of fumigants in water (5 $\mu g\ \mu L^{-1}$) were prepared in closed serum bottles. To overcome solubility limitation, 1,3-D solution was prepared by mixing Telone EC formulation with water. One hundred microliters of fumigant solution was added to the headspace vials using a gas-tight syringe, and the treated samples were capped with aluminum seals and Teflon-faced butyl rubber septa. The closed soil vials were then kept at the specified temperatures in incubators, with temperature variation <0.5°C.

At different times, triplicate vials were removed from each treatment and immediately stored at −20°C. For extraction, the sample vials were decapped while still frozen, and after addition of 10 mL ethyl acetate and 10 g anhydrous sodium sulfate, the vials were immediately recapped. After the samples were thawed at room temperature, they were vortexed at a high speed for 2 min, and the supernatant was transferred into a gas chromatography (GC) vial. Preliminary studies indicated that the recovery of fumigant residues was >95% using the above procedure. Analysis of fumigant residues was done using a HP 6890 GC equipped with a micro-electron capture detector (μECD). The GC conditions were 30 m × 0.25 mm × 1.4 μm RTX-624 capillary column (Restek Co., Bellefonte, PA), 1.0 mL min^{-1} column flow, 110°C isothermal oven temperature, 240°C inlet temperature, and 300°C detector temperature.

To differentiate between chemical and microbial transformations, fumigant degradation at the different temperatures also was measured using sterilized soils. Soil with 12% water content was weighed into headspace vials at 10 g per vial, and then autoclaved twice at 121°C for 60 min, with a 24-h interval between the first and second autoclaving. Soil samples were aseptically spiked with fumigants at the same rates as above. The treated soil vials also were incubated in the dark at 20, 30, 40 or 50°C. At different times, triplicate samples were removed, extracted, and analyzed using the procedures described above. In addition to autoclaving, mercuric chloride poisoning at 1000 mg kg^{-1} was used as an alternative sterilization method in the preliminary experiment. The impact on fumigant degradation was found to be similar between the two sterilization techniques.

The changes in residual concentrations over time for each treatment were fitted to a first-order kinetic model to obtain the degradation rate constant k (d^{-1}). Fumigant degradation in sterile soils was assumed to be chemical degradation and that in nonsterile soils to be total degradation. The difference in rate constant between nonsterile and sterile treatments was assumed to be due to microbial degradation.

Incubation Experiments for Moisture Effects

In a separate experiment, the effect of soil moisture content on fumigant degradation was measured at 30°C. Only Arlington sandy loam and Carsitas loamy sand were used in the moisture experiment. Soils were adjusted to four different moisture contents and weighed into headspace vials at 10 g (dry wt.) per vial. The soil vials were then spiked with 100 μL fumigant solutions. The final moisture contents were 1.8, 6, 11, and 16% (w/w) for both soils. Triplicate samples were removed after different time intervals and analyzed on GC following solvent extraction. Disappearance of fumigants in soil was fitted to the first-order kinetic model, and the estimated rate constants were subjected to analysis of variance at $\alpha = 0.05$ for different moisture levels.

RESULTS AND DISCUSSION

Temperature Effect on Total Fumigant Degradation

Degradation of fumigants in nonsterile soils, or total degradation, is well described by first-order reaction kinetics ($r > 0.90$). Degradation of all fumigants in all three soils consistently accelerated as the temperature increased (Fig. 1, 2, 3). For instance, in the Arlington sandy loam, the half-life of *cis*-1,3-D at 20, 30, 40, and 50°C was 5.2, 3.0, 1.9, and 1.0 d, respectively. In the same soil at the corresponding temperatures, the half-life of *trans*-1,3-D was 4.7, 2.0, 1.4, and 0.7 d, respectively, and that of MITC was 5.3, 3.5, 1.3, and 1.1 d, respectively. Thus, degradation of *cis*-1,3-D, *trans*-1,3-D, and MITC increased by 5.2, 7.1, and 5.1 times, respectively, as temperature increased from 20 to 50°C. The respective increases were 8.8, 11.9, and 10.6 times for Carsitas loamy sand, and 6.9, 5.6, and 4.8 times for Waukegen silt loam. The positive association of fumigant degradation with soil temperature implies that under typical fumigation conditions, fumigants may degrade considerably faster in the surface layer than in the subsurface soil. This effect should be especially significant when the air temperature is high, or when a surface cover is used. For instance, if the temperature were elevated to 50°C, the half-life of 1,3-D and MITC would be <1 d for both Arlington and Carsitas soils.

The temperature dependence of fumigant degradation can have implications both for the description of fumigant behavior after injection into the soil, and for the development of practices that may prevent excessive emissions. For instance, to simulate fumigant transport in soil more accurately, different degradation rates may need to be allocated for different soil depths in transport models. In practice, as surface soil temperature is greatly enhanced when surface tarps are used, tarping may result in reduced fumigant emissions because of increased degradation at elevated temperatures. On the other

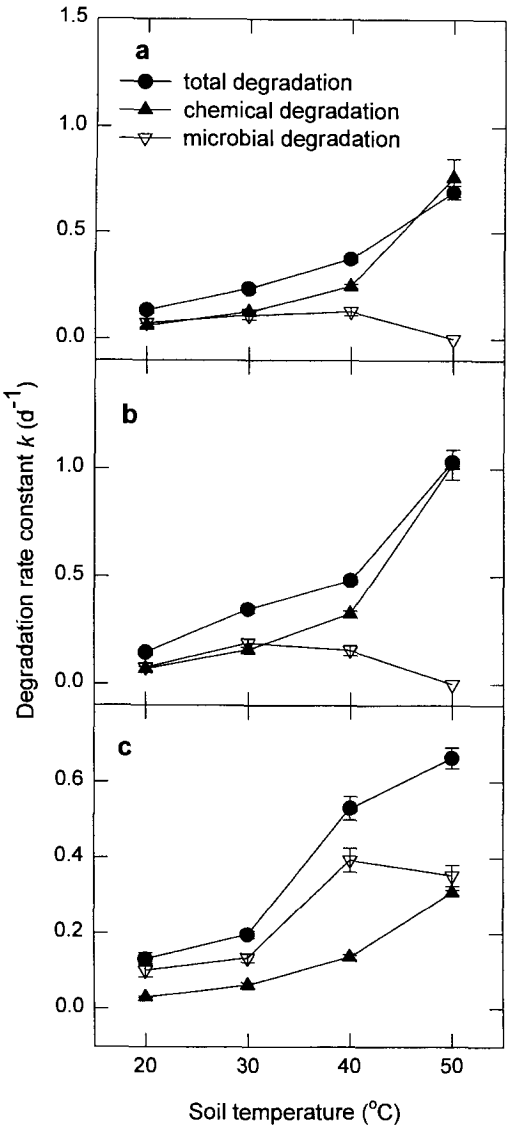

Fig. 1. First-order rate constants (k, d^{-1}) for total, chemical and microbial degradation of fumigants in Arlington sandy loam at different soil temperatures. (*a*) *cis*-1,3-D; (*b*) *trans*-1,3-D; and (*c*) MITC. Vertical bars are the standard error of k.

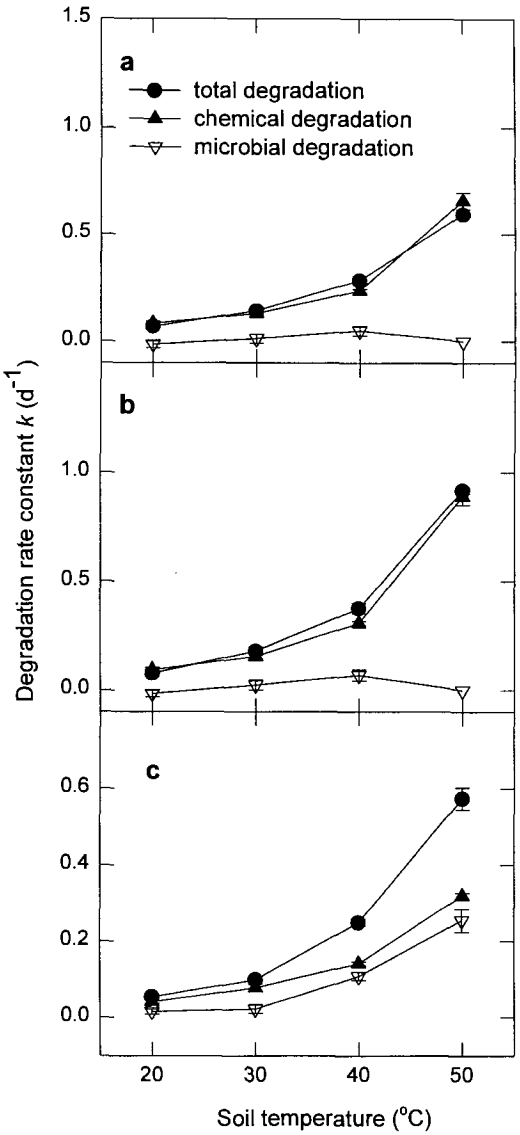

Fig. 2. First-order rate constants (k, d^{-1}) for total, chemical and microbial degradation of fumigants in Carsitas loamy sand at different soil temperatures. (*a*) *cis*-1,3-D; (*b*) *trans*-1,3-D; and (*c*) MITC. Vertical bars are the standard error of k.

hand, if fumigation occurs in cold, nontarped soil, the fumigants may degrade more slowly in soil, leaving more of the applied material available for volatilization.

Temperature Effect on Chemical and Microbial Transformations

Degradation rates of fumigants in sterile soils were different from those in nonsterile soils, which indicates that both chemical and microbial mechanisms were involved (Fig. 1, 2, 3). Chemical degradation of each fumigant consistently increased with increasing temperature in all soils, and the relationship closely followed the empirical Arrhenius equation ($r > 0.97$). Activation energy (E_a) calculated by fitting the estimated k values to the Arrhenius equation ranged from 61.2 to 74.9 kJ $mole^{-1}$ for the Arlington sandy loam, 53.5 to 76.4 kJ $mole^{-1}$ for the Carsitas loamy sand, and 67.9 to 82.9 kJ $mole^{-1}$ for the Waukegen silt loam. These activation energies indicate an average increase in degradation rate per 10°C increase in temperature of between 2.0 and 3.2 times. It also was observed that in the same soil at the same temperature, chemical degradation of 1,3-D isomers was 1.7 to 5.9 times greater than that of MITC. In a previous study, it was shown that 1,3-D can undergo chemical transformation via nucleophilic substitution with soil organic matter (Gan et al., 1998). These results together suggest the importance of chemical transformation of 1,3-D in soil.

The effects of temperature on microbial degradation of fumigants were different from those on chemical degradation, and the relative effects appeared to be independent of soil type. In both Arlington and Carsitas soils, microbial degradation of 1,3-D remained essentially unchanged across the range from 20 to 40°C. When temperature increased further to >40°C, microbial degradation of 1,3-D was inhibited completely (Fig. 1 and

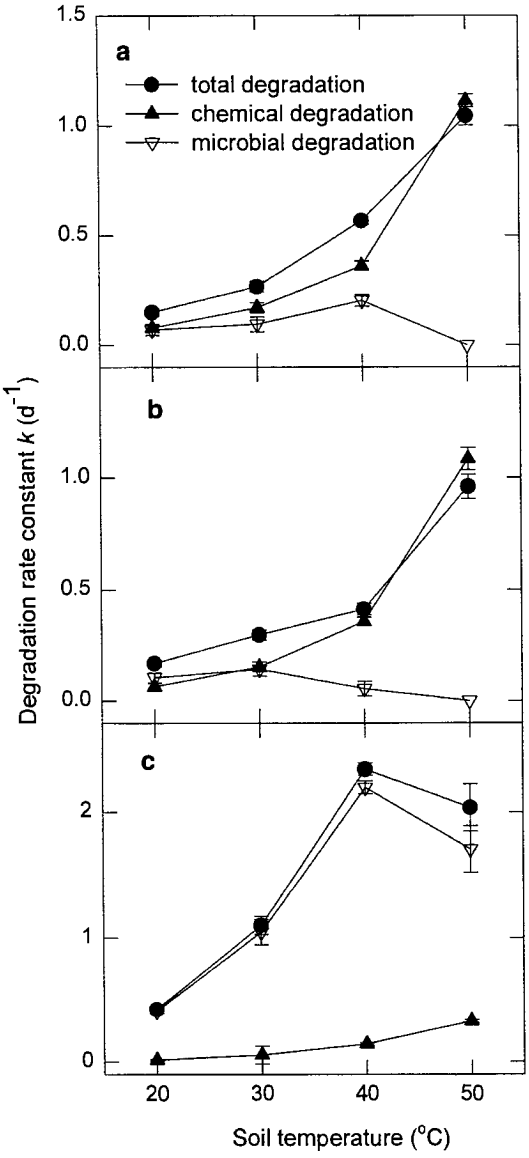

Fig. 3. First-order rate constants (k, d^{-1}) for total, chemical and microbial degradation of fumigants in Waukegen silt loam at different soil temperatures. (*a*) *cis*-1,3-D; (*b*) *trans*-1,3-D; and (*c*) MITC. Vertical bars are the standard error of k.

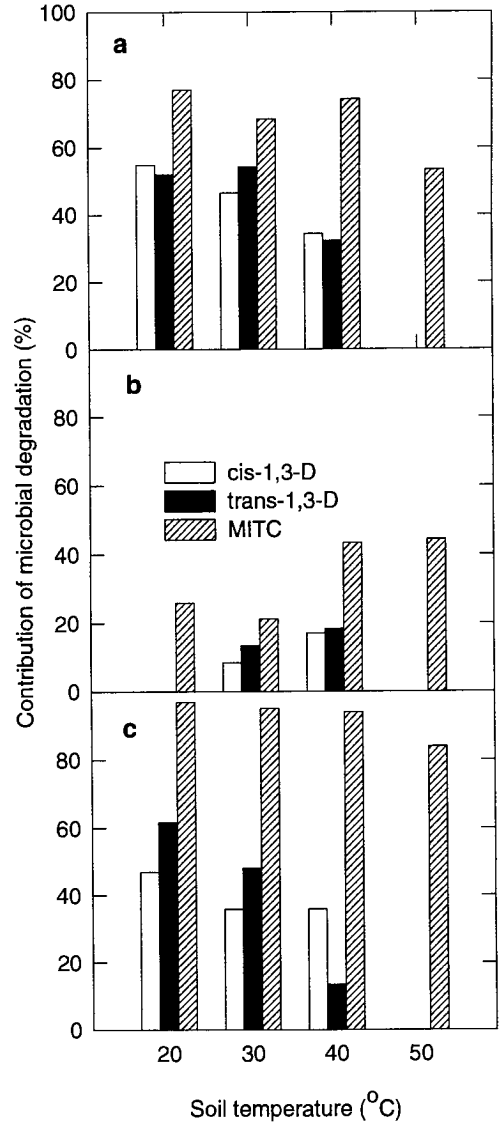

Fig. 4. Relative contribution of microbial degradation to total fumigant degradation as a function of soil temperature. (*a*) Arlington sandy loam; (*b*) Carsitas loamy sand; and (*c*) Waukegen silt loam.

2). Microbial degradation of MITC in Arlington sandy loam, however, increased rapidly when temperature increased from 20 to 40°C, and then decreased slightly when temperature increased further to 50°C (Fig. 1c). In Carsitas loamy sand, microbial degradation of MITC increased consistently as temperature increased (Fig. 2c), and microbial degradation at 50°C increased by 18 times compared with that at 20°C. A similar pattern also was observed for the cold climate Waukegen soil, in which microbial degradation of 1,3-D isomers was inhibited at high temperatures, while significant microbial degradation of MITC occurred at 40 or 50°C (Fig. 3).

The difference in temperature effects on chemical and microbial degradation also was reflected by the relative contribution of these two mechanisms to total fumigant degradation (Fig. 4). For 1,3-D isomers in Arlington and Waukegen soils, microbial degradation accounted for about 50% of the total degradation at 20 and 30°C. This contribution, however, diminished as temperature increased further, and became negligible at temperatures above 40°C. Microbial degradation of 1,3-D isomers in Carsitas loamy sand contributed significantly less to the total degradation than in the other two soils at the same temperatures (Fig. 4b). Again, total suppression of microbial degradation was observed at >40°C. Microbial degradation apparently played a much greater role in MITC degradation. In both Arlington and Waukegen soils, microbial degradation was the predominant pathway of MITC degradation, contributing 51 to 77% to the total degradation in Arlington sandy loam (Fig. 4a), and 84 to 97% in Waukegen silt loam (Fig. 4c). In Carsitas LS, although microbial degradation of MITC was less predominant than in the Arlington soil, its relative contribution increased with increasing temperature, reaching 44% at 50°C (Fig. 4b).

The active involvement of soil microorganisms in

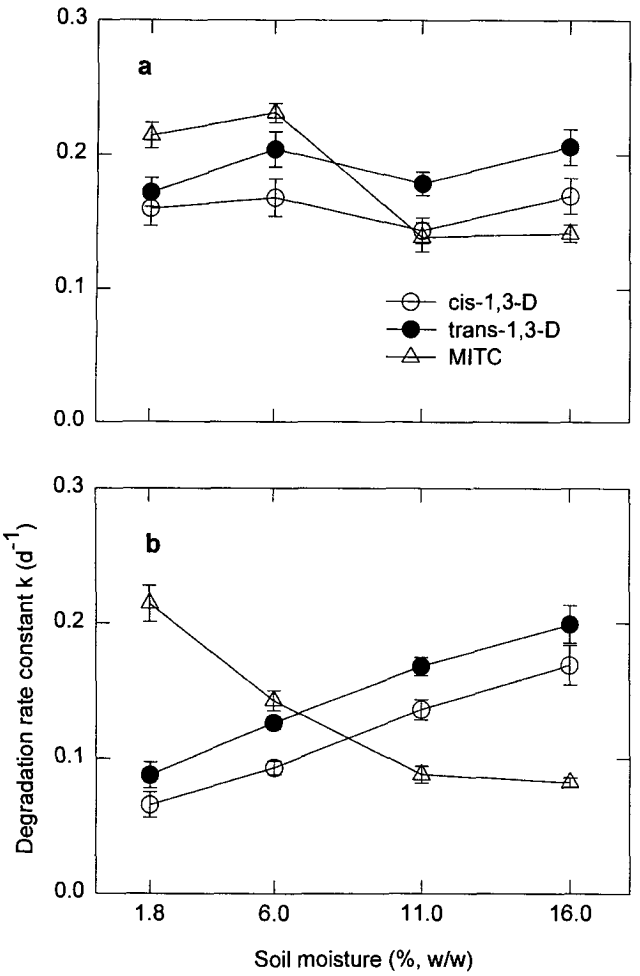

Fig. 5. First-order degradation rate constants (k, d^{-1}) of 1,3-D isomers and MITC in soil at 30°C in soil with different moisture contents. (*a*) Arlington sandy loam; and (*b*) Carsitas loamy sand. Vertical bars are the standard error of k.

MITC degradation suggests that soils, including those from cooler regions without fumigation history, may have indigenous microbial consortia that can degrade MITC metabolically or cometabolically. This is possible because MITC is a single C compound that structurally resembles some simple microbial substrates such as methane. In comparison, the three-C 1,3-dichloropropene is apparently more recalcitrant for microbial degradation. Numerous studies have shown that pesticide-degrading microorganisms in growth media have maximum metabolism activity at 28 to 30°C (e.g., Alexander, 1994; Smith et al., 1994). Our observation suggests that the populations responsible for fumigant degradation may differ in their sensitivity to high temperatures. It appears that 1,3-D degraders were not active at temperatures >40°C. In contrast, MITC degraders, regardless of their soil origination, were relatively insensitive to high temperatures, and generally more microbial degradation occurred at higher temperatures.

Effect of Soil Moisture Content

Response of fumigant degradation to soil moisture variation appeared to be dependent on both the fumigant and soil type (Fig. 5). In Arlington sandy loam, degradation of 1,3-D isomers was not significantly affected by soil moisture content. In Carsitas loamy sand, however, degradation of both isomers increased steadily with increasing moisture content, and the relationship was linear ($r > 0.99$). The increase in k for each incremental moisture increase was significant at $\alpha = 0.05$. Compared with that at 1.8% moisture content, degradation at 16% moisture content was 2.3 to 2.6 times faster. Degradation of MITC showed the opposite trend; as soil moisture water increased, degradation of MITC generally became slower, and this was more evident in Carsitas loamy sand than in Arlington sandy loam (Fig. 5). In Arlington soil, the greatest decrease ($P < 0.05$) occurred when moisture content increased from 6 to 11%. In Carsitas soil, MITC degradation consistently decreased as moisture content increased from 1.8 to 11%, and remained the same as moisture content increased from 11 to 16%. Degradation of MITC at 16% moisture content was 2.6 times slower than at 1.8% moisture content.

Pesticide degradation has generally been found to increase with increasing soil moisture content and the relationship follows the empirical equation:

$$T_{1/2} = a\, M^{-b} \qquad [1]$$

where $T_{1/2}$ is the half-life, M is the soil moisture content, and a and b are constants (Walker, 1978; Walker et al., 1992; Parkin and Shelton, 1994). This model only fitted data for degradation of 1,3-D isomers in Carsitas loamy sand in this study. The reasons for the fumigant- and soil-dependent reactions of fumigant degradation to soil moisture variation are, however, not clear from this study. It is known that pesticide degradation typically occurs in the solution phase, but sometimes catalyzed also by adsorption. It is likely that different moisture conditions influenced the relative distribution of fumigants in the different phases, and thus the degradation.

Soil moisture content in a fumigated field can change drastically both spatially and temporally. In some cases, these changes are brought about through management practices such as surface irrigation or covering. Results from this study suggest that the response of fumigant degradation to variation in soil moisture may vary among the fumigants as well as among soils, and therefore should be evaluated separately. Under field conditions, because fumigant diffusion is reduced in wet soils, the residence time of fumigants in soil increases, which may allow more extensive degradation to occur (Jin and Jury, 1995; Jury et al., 1997). Thus, to better understand the impact of soil moisture on the environmental fate of fumigants, the influences of soil water on fumigant degradation and transport must be considered simultaneously.

CONCLUSIONS

The results from this study demonstrate that fumigant degradation is modified by variations in soil temperature or soil moisture content. The effects of temperature on fumigant degradation result from concurrent influences on chemical and microbial degradation processes.

While temperature dependence of chemical degradation closely followed the Arrhenius equation, a similar dependence for microbial degradation was not always found for the extended temperature range. For 1,3-D isomers, microbial degradation played a relatively small role at 20 to 40°C, and was completely inhibited at temperatures >40°C. For MITC, microbial degradation generally accelerated with increasing temperature up to 50°C. It can be postulated that fumigant degradation at high temperatures will depend on the sensitivity of the pesticide-degrading population of soil microorganisms to high temperatures.

Interacting effects of temperature and moisture on fumigant degradation should be considered in the interpretation of fumigant behavior in the soil–water–air phases. For instance, 1,3-D degradation increased with increases in both temperature and soil moisture content. The effects of soil temperature and moisture content on 1,3-D degradation would tend to be in opposite directions in surface soil, where high temperature and low moisture are expected. On the other hand, MITC degradation decreased with increasing soil moisture content but increased with increasing soil temperature, so its effect would be magnified in the hot, dry surface layer of soil. This knowledge can be useful for designing strategies to minimize the hazardous effects of fumigants on the environment while sustaining their use in production agriculture. For example, several nonchemical approaches, including soil solarization, flooding and steaming, are currently under development as alternatives to MeBr fumigation. Most of these methods, however, are relatively inconsistent in efficacy for pest control when compared with fumigation. Since these techniques can drastically alter soil temperature and moisture regimes, it is conceivable that proper integration of these nonchemical methods with fumigation may not only result in an improvement of pest control effectiveness, but also in reduced fumigant emissions as a result of increased degradation. For example, when surface soil is kept moist due to tarping or irrigation, the surface layer might be both hot and wet, which would maximize 1,3-D degradation near the soil surface, thus reducing its emission into the atmosphere. Studies should be made to explore such integrated pest management practices in more details.

ACKNOWLEDGMENTS

We thank Q. Zhang for her contributions to this project, and Dr. W.C. Koskinen of USDA-ARS, St. Paul, MN, for providing the Waukegen soil used in this study. This study was funded by USDA-National Research Initiatives grant no. 97-35107-4378.

REFERENCES

Alexander, M. 1994. Environmental effects. p. 196–225. *In* M. Alexander (ed.) Biodegradation and bioremediation. Academic Press, San Diego, CA.

Baker, L.W., D.L. Fitzell, J.N. Seiber, T.R. Parker, T. Shibamoto, M.W. Poor, K.E. Longley, R.P. Tomlin, R. Propper, and D.W. Duncan. 1996. Ambient air concentrations of pesticides in California. Environ. Sci. Technol. 30:1365–1368.

Chellemi, D.O., S.M. Olson, and D.J. Mitchell. 1994. Effects of soil solarization and fumigation on survival of soilborne pathogens of tomato in Northern Florida. Plant Dis. 78:1167–1172.

Chen, C., R.E. Green, D.M. Thomas, and J.A. Knuteson. 1995. Modeling 1,3-dichloropropene fumigant volatilization with vapor-phase advection in the soil profile. Environ. Sci. Technol. 29:1816–1821.

Choi, J.S., T.W. Fermanian, D.J. Wehner, and L.A. Spomer. 1988. Effect of temperature, moisture, and soil texture on DCPA degradation. Agron. J. 80:108–113.

Gan, J., S.R. Yates, M.A. Anderson, W.F. Spencer, and F.F. Ernst. 1994. Effect of soil properties on degradation and sorption of methyl bromide in soil. Chemosphere 29:2685–2700.

Gan, J., S.R. Yates, D. Crowley, and J.O. Becker. 1998. Acceleration of 1,3-dichloropropene degradation by organic amendments and potential application for emissions reduction. J. Environ. Qual. 27:408–414.

Helweg, A. 1987. Degradation and adsorption of ^{14}C-MCPA in soil — influence of concentration, temperature and moisture content on degradation. Weed Res. 27:287–296.

Jin, Y., and W.A. Jury. 1995. Methyl bromide diffusion and emission through soil under various management techniques. J. Environ. Qual. 24:1002–1009.

Jury, W.A., Y. Jin, J. Gan, and T. Gimmi. 1997. Strategies for reducing fumigant loss to the atmosphere. p. 104–115. *In* J.N. Seiber et al. (ed.) Fumigants: Environmental fate, exposure and analysis. ACS Symp. Series no. 652. Am. Chemical Society, Washington, DC.

Katan, J., and J.E. DeVay. 1991. Soil solarization. CRC Press, Boca Raton, FL.

Lazarovits, G., M.A. Hawke, A.D. Tomlin, Th.H.A. Olthof, and S. Squire. 1991. Soil solarization to control Verticillium dahliae and Pratylenchus penetrans on potatoes in central Ontario. Can. J. Plant Path. 13:116–123.

Leistra, M., and J.H. Crum. 1990. Emissions of methyl isothiocyanate to the air after application of metam-sodium to greenhouse soil. Water Air Soil Pollut. 50:109–121.

Majewski, M.S., M.M. McChesney, J.E. Woodrow, J.H. Prueger, and J.N. Seiber. 1995. Aerodynamic measurements of methyl bromide volatilization from tarped and nontarped fields. J. Environ. Qual. 24:431–444.

Noling, J.W., and J.O. Becker. 1994. The challenge of research and extension to define and implement alternatives to methyl bromide. J. Nematol. 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. J. Nematol. 27: 249–257.

Parkin, T.B., and D.R. Shelton. 1994. Modeling environmental effects on enhanced carbofuran degradation. Pestic. Sci. 40:163–168.

Roberts, T.R., and G. Stoydin. 1976. The degradation of (*Z*) and (*E*)-1,3-dichloropropene and 1,2-dichloropropane in soil. Pestic. Sci. 7:325–335.

Smelt, J.H., and M. Leistra. 1974. Conversion of metam-sodium to methylisothiocyanate and basic data on the behavior of methylisothiocyanate in soil. Pestic. Sci. 5:401–407.

Smelt, J.H., T.W. Teunissen, S.J.H. Crum, and M. Leistra. 1989. Accelerated transformation of 1,3-dichloropropene in loamy soils. Netherlands J. Agric. Sci. 37:173–183.

Smith, A.E., K. Mortensen, A.J. Aubin, and M.M. Molloy. 1994. Degradation of MCPA, 2,4-D, and other phenoxyalkanoic acid herbicides using an isolated soil bacterium. J. Agric. Food Chem. 42:401–405.

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

van den Berg, F., A.H. Ross, L.G.M.Th. Tuinstra, and M. Leistra. 1994. Measured and computed concentrations of 1,3-dichloropropene and methyl isothiocyanate in air in a region with intensive use of soil fumigants. Water Air Soil Pollut. 78:247–264.

Walker, A. 1978. Simulation of the persistence of eight soil-applied herbicides. Weed Res. 18:305–313.

Walker, A., Y-H. Moon, and S.J. Welch. 1992. Influence of temperature, soil moisture and soil characteristics on the persistence of alachlor. Pestic. Sci. 35:109–116.

Yagi, K., J. Williams, N.Y. Wang, and R.J. Cicerone. 1995. Atmospheric methyl bromide (CH_3Br) from agricultural soil fumigations. Science (Washington, DC) 267:1979–1981.

Yates, S.R., J.Y. Gan, F.F. Ernst, A. Mutziger, and M.V. Yates. 1996. Methyl bromide emissions from a covered field. I. Experimental conditions and degradation in soil. J. Environ. Qual. 25:184–192.

Yates, S.R., D. Wang, J. Gan, F.F. Ernst, and W.A. Jury. 1998. Minimizing methyl bromide emissions from soil fumigation. Geophys. Res. Lett. 25:1633–1636.