ACCELERATED DEGRADATION OF METHYL ISOTHIOCYANATE IN SOIL

ROBERT S. DUNGAN, JIANYING GAN and SCOTT R. YATES*
Soil Physics and Pesticides Research Unit, George E. Brown Jr. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Riverside, California, U.S.A.
(author for correspondence, e-mail: syates@ussl.ars.usda.gov, fax: (909) 342 4964)*

(Received 31 July 2001; accepted 14 May 2002)

Abstract. Methyl isothiocyanate (MITC, CH_3NCS) is the primary breakdown product of metam-sodium, and a potential replacement fumigant pesticide for methyl bromide. Methyl isothiocyanate is toxic and has a high potential for volatilization, therefore, minimizing its atmospheric emission is of the utmost importance. One method to reduce fumigant emissions is to enhance their degradation by incorporating organic amendments into the soil surface. In this study we determined the combined effect of temperature and chicken manure application rate on the degradation of MITC. The degradation of MITC was significantly accelerated by both increasing temperature and amendment rate. Differences between sterile and nonsterile degradation kinetics in unamended and organically amended soil indicate that MITC degradation is equally controlled by chemical and biological processes. The amelioration of soil with organic amendments should be further considered when designing fumigation practices that allow for reduced emissions.

Keywords: chicken manure, degradation, fumigant, metam-sodium, methyl isothiocyanate, organic amendment, pesticide, volatilization

1. Introduction

Metam-sodium (sodium-*N*-methyldithiocarbamate) is used in crop production to control soilborne pathogens including nematodes, fungi, and insects. The primary breakdown product of metam-sodium is methyl isothiocyanate (MITC), which has pesticidal activity as a fumigant (Smelt and Leistra, 1974). Fumigants are volatile chemicals and, as a result, a large percentage of the applied material is transferred to the atmosphere. In California's San Joaquin Valley, high levels of MITC were detected in the air near metam-sodium application sites (Baker *et al*., 1996). Methyl isothiocyanate is a skin and mucous membrane irritant (Anonymous, 1990), and little information is currently available on its genotoxic effects (Kassie *et al*., 2001). During 1999, over 7.7 million kg of metam-sodium were used in the production of agricultural crops in California (Trout, 2001). In all likeliness, use of metam-sodium in California will dramatically increase as the scheduled phase-out of MeBr in the United States nears completion in 2005. Therefore, it is of extreme importance to develop strategies that enable reduced MITC emissions to minimize potentially negative impacts on human health and the environment.

Water, Air, and Soil Pollution **142:** 299–310, 2003.

The emission of fumigants from the soil surface is controlled by its rate of diffusion (gas-phase and liquid-phase) and degradation, with gas-phase diffusion being the dominant rate controlling process. Degradation of most fumigants is fairly slow, and in the case of MITC, degradation half-lives ranged from a few days to weeks (Smelt and Leistra, 1974; Gerstle *et al*., 1977; Smelt *et al*., 1989; Boesten *et al*., 1991). Thus, it can be expected that a significant fraction of MITC in soil will be volatilized to the atmosphere. It has been reported that as much as 10–34% of the soil-applied metam-sodium is volatilized as MITC (Van den Berg, 1992; Van den Berg *et al*., 1999). Conceivably, atmospheric emissions of MITC can be reduced if it is degraded near the soil surface before volatilization occurs. Recent studies have shown that the application of organic amendments to soil can significantly reduce fumigant pesticide emissions by enhancing their degradation (Gan *et al*., 1998a, b).

The degradation of MITC is influenced by soil temperature, moisture content, texture, and organic C content (Smelt and Leistra, 1974; Gerstle *et al*., 1977; Smelt *et al*., 1989; Boesten *et al*., 1991), however, temperature and organic amendments often have the largest influence on MITC degradation. The primary objective of this study was to determine the combined effect of temperature and organic amendment rate on the degradation of MITC in soil. The organic amendment selected for use in this study was composted chicken manure. Chicken manure is a rich C and N source, and its incorporation into soil is known to improve the properties of agricultural soils (O'Hallorans *et al*., 1993, 1997). Additional considerations were also given to understanding the effect of soil-moisture content on MITC degradation and quantifying the relative contribution of microbial and chemical processes. Information obtained from this study will be useful for evaluating the potential of using organic amendments to reduce MITC emissions, as well as the conditions needed to achieve optimal degradation.

2. Materials and Methods

2.1. Soil, organic amendment, and chemical

The soil used in this study was an Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf), obtained from a field in the University of California-Riverside, Agricultural Experiment Station. The field-soil was removed from the Ap horizon, passed through a 2-mm sieve and stored at 5 °C until used. The soil has a pH of 7.2 and contains 0.92% organic matter. The composted chicken manure (CKM) was obtained from Kellogg Supply Inc., Carson, CA and had a moisture content of 36% (w/w). The CKM was stored at room temperature and passed through a 2-mm sieve prior to soil incorporation. The MITC standard (99% pure) was purchased from Sigma Chemical, St. Louis, MO.

2.2. Influence of soil moisture content

To determine if soil moisture content had an effect upon MITC degradation, Arlington sandy loam was adjusted to 25, 50, and 75% of the soil's maximum water holding capacity (WHC_{max}). The Arlington soil has a WHC_{max} of 0.2 kg kg^{-1}; the soil-water potential at 25, 50, and 75% of the soil's WHC_{max} in kPa is 5600, 1200, and 260, respectively. After adjusting the soil moisture content, 10 g (dry wt.) of soil were weighed into 21-mL glass headspace vials. The soil vials were spiked with 100 μL of a 5 g L^{-1} MITC solution in water. The treated vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa (Supelco, Bellefonte, PA), and then incubated at 20 °C. Triplicate samples were removed at specific intervals and frozen at –20 °C until analyzed.

2.3. Influence of amendment rate and temperature

To determine the combined effect of amendment rate and temperature on MITC degradation, soil was amended with 1.0, 2.5, and 5.0% CKM (w/w, dry wt. basis) and incubated at 20, 30, and 40 °C. All soil mixtures were adjusted to a final moisture content of 50% of the soil's WHC_{max} with deionized water. To distinguish between microbial and chemical degradation, a separate set of unamended and CKM-amended soils were sterilized by autoclaving twice (1.0 hr at 121 °C each time), with a 48 hr interval between the first and second autoclaving. The sterilized soil treatment was only conducted at 20 °C. Differences between rate constants of the sterile and nonsterile soils was assumed to be attributable to microbial degradation. The soil vials were each filled with 10 g (dry wt.) of soil, spiked with 100 μL of the standard MITC solution, capped with septa, and incubated. At specific time intervals, samples were removed and frozen at –20 °C until analyzed.

2.4. Sample analysis

To extract the MITC residue from the soil samples, vials were uncapped while the soil was still frozen, and 10 mL of ethyl acetate and 10 g of anhydrous sodium sulfate were added to each vial, followed by immediate recapping. Once the soils thawed, the vials were shaken for 1 hr on a horizontal shaker (200 oscillations min^{-1}), vortexed for 30 s, and then a 1 mL aliquot of the soil extract (i.e., supernatant) was transferred to a GC vial. The supernatant was analyzed for MITC on a Hewlett-Packard 5890 gas chromatograph, equipped with a RTX-624 capillary column (30 m, 0.25 mm × 1.4 μm, Restek Corp., Bellefonte, PA) and connected to a micro-electron capture detector. The operating conditions were as follows: carrier gas, He, 1.3 mL min^{-1}; inlet temperature, 230 °C; detector temperature, 280 °C; column temperature, 100 °C rising to 140 °C at 15 °C min^{-1} after 1 min. The extraction efficiency of MITC residues was >92%, with an average recovery of 97%. All data were subject to first-order fitting to obtain a degradation rate constant k (d^{-1}). Error bars represent the standard error of the data.

TABLE I

First-order degradation rate constants (k), half-lives ($t_{1/2}$), and correlation coefficients of fitting (r^2) for MITC degradation in unamended Arlington sandy loam at 20 °C at different water holding capacities (WHC)

% of WHC	k (d^{-1})	$t_{1/2}$ (d)	r^2
25	0.16±0.01[a]	4.3	0.95
50	0.12±0.01	5.8	0.92
75	0.13±0.01	5.3	0.97

[a] Mean ± the standard error of k.

3. Results and Discussion

The effect of soil moisture content on the pesticide degradation is well documented. It is commonly believed that pesticides in the dissolved phase are readily accessible for soil microorganisms (Ogram *et al.*, 1985; Speitel *et al.*, 1988). In general, pesticide degradation has been found to increase with increasing soil moisture content (Shelton and Parkin, 1991; Walker *et al.*, 1992; Garciá-Valcárcel and Tadeo, 1999). In this study a slight decrease in degradation occurred at soil moisture levels >25% of the WHC_{max} (Table I). The degradation of MITC at 25% of the WHC_{max} was 1.3 and 1.2 times greater than at 50 and 75% of the WHC_{max}, respectively. Using the same soil, Gan *et al.* (1999) conducted a similar experiment at 30 °C and found that MITC degradation at 80% of the WHC_{max} was 2.6 times slower than at 9% of the WHC_{max}. In Carsitas loamy sand (mixed, hyperthermic Typic Torrpsamments), MITC degradation also steadily decreased as the soil moisture content increased. Differences in our results, compared to that of other pesticide degradation studies, may be attributable to the soil type, microbial community, and or degradation mechanism. Additionally, MITC is quite soluble in water, with a solubility of 7.6 g L^{-1} at 20 °C (Ottnad *et al.*, 1978). Therefore, increasing the water content may not substantially increase the fraction of MITC in the soil aqueous phase or the availability of MITC to the soil microorganisms.

In a fumigated field, the soil water content can change significantly, both spatially and temporally, especially under management practices such as irrigation and tarping. It must be noted that because soil water content can exert effects on both transport and degradation of MITC, the overall effect may be more complicated. In wet soil, MITC diffusion via the gas phase is greatly inhibited, which results in prolonged contact time between soil and the fumigant, allowing more time for degradation to occur. This should be considered while evaluating the overall impact of soil water regimes on the fate of MITC during fumigant treatments.

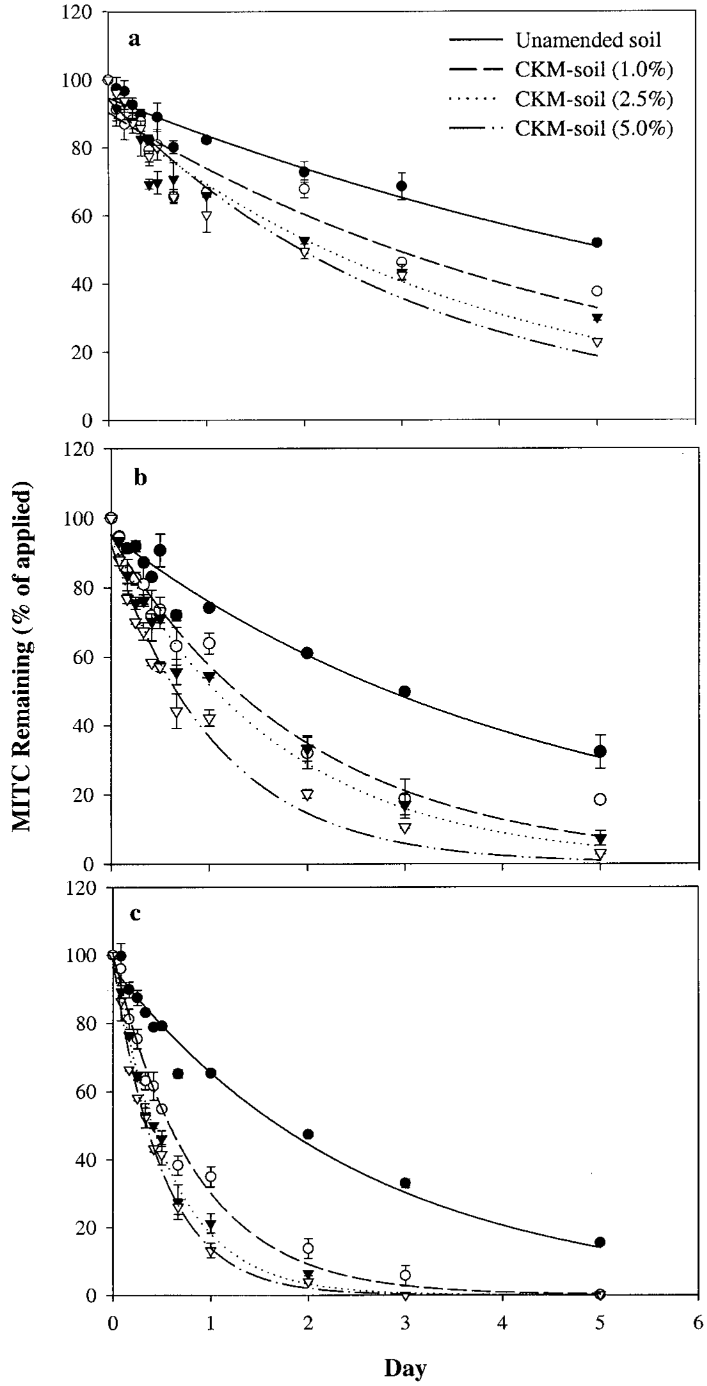

Figure 1. Disappearance of methyl isothiocyanate in Arlington sandy loam amended with 1.0, 2.5, and 5.0% chicken manure (w/w) and incubated at (a) 20 °C, (b) 30 °C, and (c) 40 °C.

TABLE II

First-order degradation rate constants (k), half-lives ($t_{1/2}$), and correlation coefficients of fitting (r^2) for MITC degradation in Arlington sandy loam with different CKM amendment rates and incubation temperatures

Temp (°C)	Matrix	k (d^{-1})	$t_{1/2}$ (d)	r^2
20	Unamended soil	0.12±0.01[a]	5.8	0.92
	CKM-soil (1.0%)	0.20±0.03	3.5	0.89
	CKM-soil (2.5%)	0.28±0.01	2.5	0.91
	CKM-soil (5.0%)	0.32±0.04	2.2	0.95
30	Unamended soil	0.23±0.02	3.0	0.96
	CKM-soil (1.0%)	0.50±0.01	1.4	0.97
	CKM-soil (2.5%)	0.59±0.05	1.2	0.98
	CKM-soil (5.0%)	0.92±0.08	0.8	0.98
40	Unamended soil	0.39±0.03	1.8	0.98
	CKM-soil (1.0%)	1.20±0.08	0.6	0.99
	CKM-soil (2.5%)	1.70±0.08	0.4	0.99
	CKM-soil (5.0%)	2.00±0.08	0.3	0.99

[a] Mean ± the standard error of k.

The disappearance of MITC in unamended and CKM-amended soil is well described by first-order degradation kinetics ($r^2 > 0.89$) (Table II). The degradation of MITC in soil was accelerated as the temperature and CKM application rate increased (Figures 1a–c), and follows the empirical equation:

$$\ln k = a + bx^c + d \cdot T^{-1} \tag{1}$$

where

k = the degradation rate constant (d^{-1});
x = the amendment rate (%);
T = the temperature (°C);
a, b, c, and d are the constants 0.79, 0.81, 0.31, and –63.8, respectively.

In unamended soil at 20, 30, and 40 °C, the k values varied from 0.12, 0.23, and 0.39 d^{-1}, respectively, which corresponds to half-lives of 5.8, 3.0, and 1.8 d. Thus, degradation of MITC in unamended soil increased approximately 1.9 and 3.3 times per 10 °C increase in temperature. A half-life of 5.8 d for MITC is close to results obtained by other researchers (Smelt and Leistra, 1974; Taylor *et al.*, 1996). At these degradation rates it would be expected that a significant portion of applied MITC would volatilize as a result of rapid gas-phase diffusion. The incorporation of CKM into soil at 1.0, 2.5, and 5.0% significantly increased the degradation of MITC at all temperatures tested (Table II). The half-life values of soil amended with 5.0% CKM at 20, 30, and 40 °C were 2.2, 0.8, and 0.3 d, respectively. Compared to unamended soil at 20 °C, the MITC degradation rate increased 17 times when soil was amended with 5.0% CKM at 40 °C.

In CKM-amended soils, the impact of temperature was similar between like treatments. Methyl isothiocyanate degradation increased about 2 to 6 times as the temperature increased from 20 to 40 °C. Overall, the impact of amendment rate upon degradation was not similar at each temperature tested. For example, the rate of MITC degradation in CKM-amended (5.0%) soil at 20, 30, and 40 °C increased 2.7, 4.0, and 5.1 times, respectively, when compared to unamended soil at the corresponding temperature. Based upon these results, the combination of temperature and amendment appear to magnify the degradation of MITC. This maybe is the result of the influence of temperature on both biological and chemical reaction rates.

A relationship between temperature, CKM application rate, and degradation rate constants, k, was determined by fitting the data in Table II to the Arrhenius equation:

$$\ln k = \ln A - \frac{Ea}{RT} \tag{2}$$

where

k	=	the rate constant;
T	=	the temperature (°K);
A	=	the frequency factor;
R	=	the gas constant (8.31 J mol^{-1} K^{-1});
E_a	=	the activation energy (kJ mol^{-1}).

For each amendment rate, the data closely followed the empirical equation ($r^2 = 0.99$). As shown by the plot of ln k vs. $1/T$ (Figure 2), the degradation of MITC clearly increases with increasing temperature at all amendment levels. The difference of the slope between the amended soils and unamended soil suggests that there is a synergistic effect from the amendment. Activation energies (E_a) were calculated from the slope of the line. The E_a values for unamended soil and amended soil at 1.0, 2.5, and 5.0% CKM were 47.7, 72.1, 73.0, and 74.0 kJ mol^{-1}, respectively.

From the degradation rate constant values, Q_{10} values were calculated using Van't Hoff's equation:

$$Q_{10} = \frac{k_{t+10}}{k_t} \tag{3}$$

where k_t is the degradation rate at temperature t and k_{t+10} is the degradation rate at a temperature 10 °C higher. The average Q_{10} values for unamended soil and

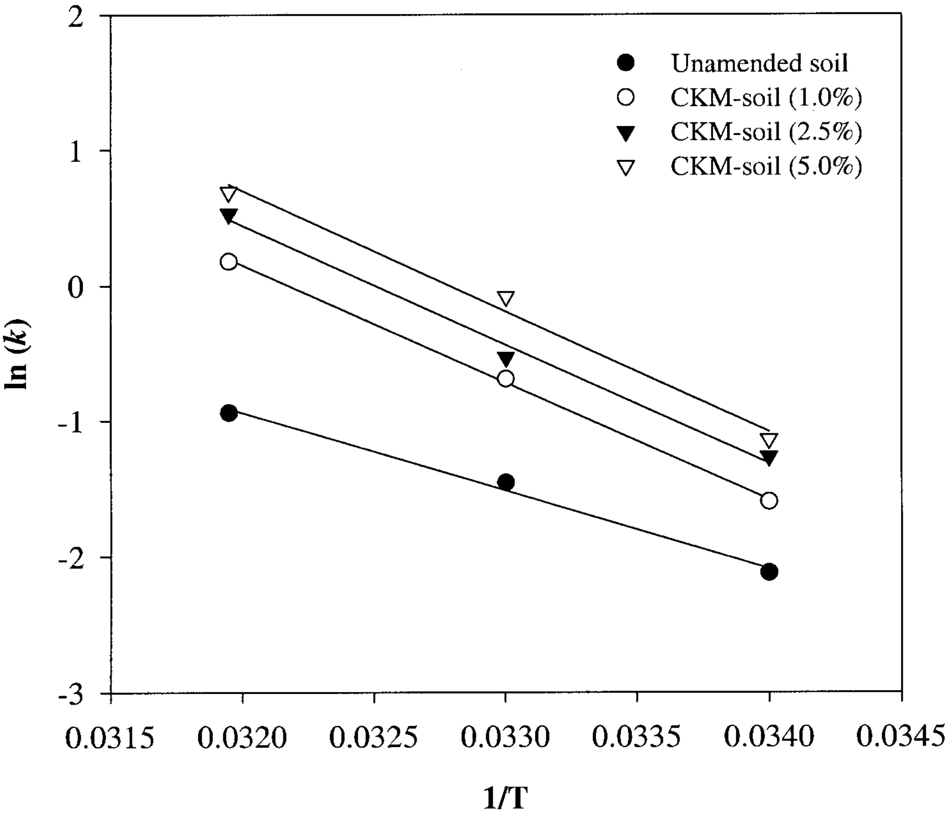

Figure 2. Arrhenius plot for the relationship between log rate of methyl isothiocyanate degradation in unamended and chicken manure-amended Arlington sandy loam and the reciprocal of temperature.

soil with 1.0, 2.5, and 5.0% CKM were 1.8, 2.5, 2.5, and 2.6, respectively. Based upon these values, the Q_{10} predicts that with every 10 °C rise in temperature a 1.8, 2.5, and 2.6-fold in MITC degradation will occur. Since MITC degradation is a function of temperature, considerably more MITC should be degraded in the surface soil layer, which is subject to larger diurnal temperature variations than subsurface layers. Additionally, properties of the individual soil (e.g., bulk density, particle size, particle type, organic matter content, and moisture content) will have a direct influence upon its thermal conductivity and, hence, its capacity to degrade MITC. Therefore, post-fumigation practices such as soil packing, tarping, surface irrigation and amelioration with organic amendments, which can greatly alter a soil's thermal conductivity, will also have a significant impact upon MITC degradation.

Differences between the degradation rate constants (k) in nonsterile and sterile soil (unamended and CKM-amended soil) were significantly different, with biological degradation contributing to the overall MITC degradation in this study

TABLE III

First-order rate constants of MITC degradation in unamended soil and CKM amended Arlington sandy loam at 20 °C, and the relative contribution of biological degradation

Matrix	Nonsterile k (d^{-1})	Sterile k (d^{-1})	Biological degradation %[b]
Unamended soil	0.12±0.01[a]	0.06±0.01[a]	50
CKM-soil (1.0%)	0.20±0.03	0.06±0.01	70
CKM-soil (2.5%)	0.28±0.01	0.12±0.01	57
CKM-soil (5.0%)	0.32±0.04	0.19±0.02	41

[a] Mean ± the standard error of k.
[b] The contribution from biodegradation was calculated from the difference of k between nonsterile and sterile samples divided by the nonsterile k value.

(Table III). Degradation of MITC was two times faster in nonsterilized than in sterilized unamended soil, meaning about 50% of the degradation could be attributed to biological mechanisms. Similar results were obtained by Taylor *et al*. (1996) who found that MITC degradation, on average, was two times greater in a nonsterile soil than in a sterile soil. The addition of CKM to sterile and nonsterile soil considerably increased the rate of degradation over that of the soil only treatment (Table III). In soil amended with 1.0% CKM, as much as 70% of the degradation was attributable to biological mechanisms, while at 5.0% CKM, only 41% of the degradation was biologically associated. Apparently, CKM not only contains microorganisms that contribute to the degradation of MITC, but also chemically catalyzes the degradation of MITC as a significant amount of MITC was degraded even in sterile soil.

Although CKM accelerates the degradation of MITC, there is no clear understanding of the biological and chemical mechanisms that stimulate its degradation. The addition of chicken manure to soil results in a large CO_2 flux (Abdel *et al*., 1993), which suggests that a large population of degrading microorganisms have been added or the introduced nutrients have stimulated indigenous microbial populations. The degradation of MITC by the soil microorganisms may be carried out by catabolism, but a continuous effort to isolate organisms which utilize MITC as a sole C source in our laboratory have failed to date (unpublished observation). Based upon this information, a more likely scenario is that MITC is degraded cometabolically. Cometabolism refers to the transformation of a compound by an organism that does not use it as a sole C source (Horvath, 1972; Dagley, 1984). Specifically, enzymes released during the biodegradation of natural and exogenous C sources (e.g., chicken manure), which are not specific for MITC, maybe fortuitously metabolizing MITC. Based upon the simple molecular structure of MITC, which contains only one carbon atom, and is similar to common substrates such as methanol, one might expect that there are microorganisms capable of using MITC as a sole C source. As of now, little information is available on the mechanism(s) of MITC degradation in soil, which should be an area for further research.

4. Conclusion

Chicken manure, often used to increase soil fertility, significantly enhanced MITC degradation when compared to unamended soil. The degradation in unamended and chicken manure-amended soil is attributable to biological and chemical mechanisms, although an understanding of these mechanisms is currently unknown. The rate of MITC degradation was a function of temperature and amendment rate, both of which influence microbiological and chemical properties of a soil and, hence, the degradation process. With respect to temperature, degradation of MITC closely followed the Arrhenius equation. The soil moisture content also influenced MITC degradation, but only slightly in the opposite direction of temperature and amendment rate. This does appear favorable, since the soil surface is generally hotter and drier than subsurface soil layers, thus, MITC degradation may be further enhanced in the surface layer. However, enhanced degradation under these conditions does not necessarily imply reduced volatilization, since soil moisture often has a large influence on the transport of fumigant pesticides in soil. Soil moisture, therefore, must be considered along with temperature and amendment rate when fumigant emission studies are being investigated. Overall, the incorporation of chicken manure into the soil surface layer should allow for reduced fumigant emissions, and amendment rates used in this study were also low enough to allow for realistic field applications. Emission reduction studies should now be conducted to determine the effectiveness of chicken manure.

Acknowledgement

This study was funded by the USDA-National Research Initiative Grant No. 98-35316-6450.

References

Abdel Magid, H. M., Sabrah, R. E. A., Rabi, R. K., El Nadi, A. R. H. and Abdel Aal, S. I.: 1993, 'Biodegradation of municipal refuse and chicken manure in a winter-wheat ecosystem in Saudi Arabia', *J. Arid Environ.* **25**, 411–419.

Anonymous: 1990, 'Summary of toxicity data on methyl isothiocyanate (MITC)', *J. Pesticide Sci.* **15**, 297–304.

Baker, L. W., Fitzell, D. L., Seiber, J. N., Parker, T. R., Shibamoto, T., Poor, M. W., Longley, K. E., Tomlin, R. P., Propper, R. and Duncan, D. W.: 1996, 'Ambient air concentrations of pesticides in California', *Environ. Sci. Technol.* **30**, 1365–1368.

Boesten, J. J. T. I., Van der Pas, L. J. T., Smelt, J. H. and Leistra, M.: 1991, 'Transformation rate of methyl isothiocyanate and 1,3-dichloropropene in water-saturated sandy subsoils', *Neth. J. Agric. Sci.* **39**, 179–190.

Dagley, S.: 1984, 'Introduction' in D. T. Gibson (ed.), *Microbial Degradation of Organic Compounds*, Marcel Dekker, NY, U.S.A., pp. 1–11.

Gan, J., Yates, S. R., Papiernik, S. and Crowley, D.: 1998a, 'Application of organic amendments to reduce volatile pesticide emissions from soil', *Environ. Sci. Technol.* **32**, 3094–3098.

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

Gan, J., Papiernik, S. K., Yates, S. R. and Jury, W. A. 1999, 'Temperature and moisture effects on fumigant degradation in soil', *J. Environ. Qual.* **28**, 1436–1441.

Garciá-Valcárcel, A. I. and Tadeo, J. L.: 1999, 'Influence of soil moisture on sorption and degradation of hexazinone and simazine in soil', *J. Agric. Food Chem.* **47**, 3895–3900.

Gerstle, Z., Mingelgrin, U. and Yaron, B.: 1977, 'Behavior of vapam and methylisothiocyanate in soils', *Soil Sci. Soc. Am. J.* **41**, 545–548.

Horvath, R. S.: 1972, 'Microbial cometabolism and the degradation of organic compounds in nature', *Bacteriol. Rev.* **36**, 146–155.

Kassie, F., Laky, B., Nobis, E., Kundi, M. and Knasmüller, S.: 2001, 'Genotoxic effects of methyl isothiocyanate', *Mutation Res.* **490**, 1–9.

Ogram, A. V., Jessup, R. E., Ou, L. T. and Rao, P. S. C.: 1985, 'Effects of sorption on biological degradation rates of 2,4-dichlorophenoxyaceitic acid in soils', *Appl. Environ. Microbiol.* **49**, 582–587.

O'Hallorans, J. M., Muñoz, M. A. and Colberg, O.: 1993, 'Effect of chicken manure on chemical properties of a mollisol and tomato production', *J. Agric. Univ. Puerto Rico* **77**, 181–191.

O'Hallorans, J. M., Muñoz, M. A. and Marquez, P. E.: 1997, 'Chicken manure as an amendment to correct soil acidity and fertility', *J. Agric. Univ. Puerto Rico* **81**, 1–8, 900.

Ottnad, M., Jenny, N. A. and Röder, C.-H.: 1978, 'Methyl Isothiocyanate', *Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives*, Vol. 10, Academic Press, NY, U.S.A., pp. 563–573.

Shelton, D. R. and Parkin, B.: 1991, 'Effect of moisture on sorption and biodegradation of carbofuran in soil', *J. Agric. Food Chem.* **39**, 2063–2068.

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

Smelt, J. H., Crum, S. J. H. and Teunissen, W.: 1989, 'Accelerated transformations of the fumigant methyl isothiocyanate in soil after repeated application of metam-sodium', *Environ. Sci. Health B* **24**, 437–455.

Speitel, G. E., Lu, C. J., Turakhia, M. and Sho, X.-J.: 1988, 'Biodegradation of trace concentrations of substituted phenols in granular activated carbon columns', *Environ. Sci. Technol.* **22**, 68–74.

Taylor Jr., G. E., Schaller, K. B., Geddes, J. D., Gustin, M. S., Lorson, G. B. and Miller, G. C.: 1996, 'Microbial ecology, toxicology and chemical fate of methyl isothiocyanate in riparian soils from the upper Sacramento river', *Environ. Tox. Chem.* **13**, 1694–1701.

Trout, T.: 2001, 'California Regulatory Impacts on Adoption of Methyl Bromide Alternative Fumigants', *Methyl Bromide Alternatives*, Vol. 7(3), USDA, Washington, D.C., pp. 4–7.

Van den Berg, F.: 1992, 'Measured and computed concentrations of methyl isothiocyanate in the air around fumigated fields', *Atmos. Environ.* **27A**, 63–71.

Van den Berg, F., Smelt, J. H., Boesten, J. J. T. I. and Teunissen, W.: 1999, 'Volatilization of methyl isothiocyanate from soil after application of metam-sodium with two techniques', *J. Environ. Qual.* **28**, 918–928.

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