Interactive Effect of Organic Amendment and Environmental Factors on Degradation of 1,3-Dichloropropene and Chloropicrin in Soil

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Soil organic matter is an important factor affecting the fate of soil fumigants; therefore, the addition of organic amendments to surface soils could reduce fumigant emissions by accelerating fumigant degradation. Experiments were conducted to determine the degradation of fumigants [a mixture of *cis*- and *trans*-1,3-dichloropropene (1,3-D) and chloropicrin (CP), a similar composition as in Telone C35] in soils with organic amendment under a range of soil moisture, temperature, sterilization, and texture conditions. Degradation of the fumigants followed availability-adjusted first-order or pseudo-first-order kinetics with slower degradation of 1,3-D than CP. Increasing soil water content from 5 to 17.5% (w/w) slightly increased the degradation of 1,3-D, but not that of CP. Five different organic amendments at 5% (w/w) increased fumigant degradation 1.4−6.3-fold in this study. The degradation of both fumigants was accelerated with increasing amount of organic material (OM). Little interaction between soil moisture and OM was observed. Autoclave sterilization of soils did not reduce degradation of either fumigant; however, increasing the incubation temperature from 10 to 45 °C accelerated fumigant degradation 5−14 times. Soil texture did not affect 1,3-D degradation, but CP degraded more rapidly in finer-textured soil. These results suggest that OM type and rate and soil temperature are the most important factors affecting the degradation of 1,3-D and CP.

KEYWORDS: Fumigant degradation; organic material; soil moisture; temperature; sterilization; soil texture

INTRODUCTION

Methyl bromide (MeBr) has been phased out as a soil fumigant due to its effect on stratospheric ozone. Two promising alternative fumigants, 1,3-dichloropropene (1,3-D) and chloropicrin (CP), have been extensively used to control weeds, nematodes, and soilborne pathogens. However, these fumigants can escape from the soil and contribute to volatile organic compounds (VOCs) in the air, which react with nitrogen oxides to form ground-level ozone, an air pollutant (*1*). When fumigant emission is high, 1,3-D and CP concentrations in the ambient air may endanger workers and bystanders. High fumigant emission losses also require that higher application rates be used to effectively control pests, which leads to increased fumigation cost. Therefore, minimizing fumigant emission losses is important to address environmental safety and economic concerns as well as to maximize pest-control efficacy with preplant soil fumigation.

Organic material (OM) has long been used as a soil amendment to improve soil physiochemical properties and provide nutrients. Research has shown that OM amendment can facilitate fumigant degradation and may be used to reduce emission of MeBr, methyl isothiocyanate (MITC), and both *cis*- and *trans*-1,3-D isomers (*2−5*). Soil column studies revealed that incorporating composted manure in the top 5 cm of soil effectively reduced MeBr, MITC, and 1,3-D emissions (*2*, *3*, *6*). Application of composted steer manure and chicken manure in the top 5 cm of raised soil beds at a rate of 5 or 10% (dry weight, w/w) was found to reduce cumulative 1,3-D emission loss by 48 and 28%, respectively, compared to the unamended soil beds and with no differences between the two application rates (*7*). However, the promising effect of OM amendments on 1,3-D and/or CP emission reduction has not been observed in all field conditions (*8*, *9*). The inconsistent findings may relate to the role of OM amendments on fumigant degradation.

Fumigant degradation can be affected greatly by the type of organic materials. Dungan et al. (*4*) found that composted steer manure degraded 1,3-D most quickly among four tested OM amendments (composted steer manure, biosolids, composted chicken manure, and composted forest products). Gan et al. (*2*, *3*) also reported that fumigants (1,3-D, MeBr, and MITC) degraded at a higher rate in soil amended with composted steer manure compared to soil amended with a less decomposed

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biosolid−manure mixture. Degradation of several fumigants was also found to be more rapid as OM amendment rates were increased (*2−5*).

Fumigant degradation in soil includes both chemical and biological mechanisms. Chemical degradation is mainly via direct substitution reactions between the leaving group of fumigant and various functional groups (e.g., −NH$_2$, −NH, −SH, and −OH) in soil organic matter (*10−12*). Bound residues are formed by chemical interaction between fumigants (MeBr, 1,3-D) and soil organic matter (especially the fulvic acids) (*13*). Biological degradation is due to the activity of microorganisms that are able to metabolize organic pesticides and utilize them (directly or indirectly) as a source of energy and nutrients (*14*). The addition of OM to soil can stimulate microbial activity and some microbial populations to enhance fumigant biodegradation (*5, 14−18*). The contributions of chemical and biological mechanisms on fumigant degradation have been studied by comparing sterilized and unsterilized soils; however, results have been variable. For example, some studies reported that chemical mechanisms accounted for most of the total 1,3-D degradation in mineral soils (*2, 4*), especially in mineral soils without fumigation history (*19*), and 1,3-D hydrolysis in unsterilized soil was greater than that in the sterilized soil only after 10 days of incubation (*12*). Conversely, others have reported the important role of microbial activity on 1,3-D dissipation in soils with/without OM amendment (*4, 18, 20*). Moreover, Gan et al. (*2*) found that the sterilization slightly increased the 1,3-D degradation in the biosolid−manure mix soil, but greatly decreased degradation in composted steer manure amended soil. A few studies reported that CP degraded much more slowly in sterilized soil compared to unsterilized mineral soil (*17, 21−23*).

Soil moisture and temperature are major environmental factors affecting the degradation of some fumigants. Increasing soil moisture was reported to increase 1,3-D degradation (*12, 24*) in some cases, but had little influence on degradation of 1,3-D and CP reported by others (*4, 22*), whereas increasing soil moisture decreased the degradation of MITC (*24*). Increasing soil temperature consistently accelerated the degradation of several fumigants in soil regardless of organic amendment (*4, 5, 20, 22, 24*).

To more effectively use OM for reducing fumigant emission, it is critical to understand the fumigant fate in the OM-amended soils. In this regard, information is mostly available for 1,3-D, and little information is available on CP, which is commonly applied in combination with 1,3-D such as in Telone C35 and InLine. Telone C35 has become an increasingly important product for soil fumigation. It is necessary to obtain information on the effect of organic amendment on fumigant fate, which is particularly important in the San Joaquin Valley soils in California because fumigants are heavily applied in this highly agricultural productive region. This study was designed to investigate the degradation of 1,3-D and CP when applied together in San Joaquin Valley soils from organic amendments under various environmental conditions including soil moisture, temperature, sterilization, and soil texture.

MATERIALS AND METHODS

Soils and Chemicals. Three common agricultural soils in the San Joaquin Valley, California, were used in this study (**Table 1**). An Atwater loamy sand (coarse-loamy, mixed, active, thermic Typic Haploxeralfs) was obtained from a cultivated field in Atwater, Merced County. A Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) was obtained from the San Joaquin Valley Agricultural Sciences Center (USDA-ARS) in Parlier, Fresno County. A Madera loam

Table 1. Selected Properties of Atwater Loamy Sand, Hanford Sandy Loam, and Madera Loam

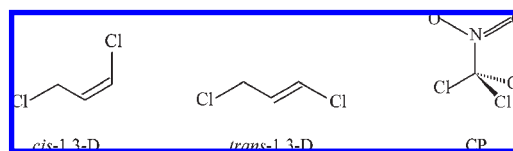| soil property	Atwater loamy sand	Hanford sandy loam	Madera loam
particle size distribution (% sand−silt−clay)	88−5−7	55−40−6	40−34−25
water content at 33 kPa suction (%)	5.4	17.0	23.0
organic matter content (%)	0.7	0.7	1.1
cation exchange capacity (cmol$_c$ kg^{-1})	3.3	6.8	20.0

Figure 1. Chemical structures of 1,3-dichloropropene (1,3-D; *cis*-1,3-D and *trans*-1,3-D) and chloropicrin (CP).

(fine, montmorillonitic, thermic family of Typic Durixeralfs) was obtained from a tree nursery near Le Grand, Merced County. Soils were collected from a 0−30 cm depth, air-dried, and passed through a 2 mm sieve. The prepared soils had water contents (w/w) of 1.1% for the loamy sand, 4.9% for the sandy loam, and 4.3% for the loam soil.

Five composted organic materials were used in the study: composted steer manure, composted chicken manure, One-Earth organic compost, OSH organic compost, and grape pomace. The composted steer manure named Earthgro steer manure blend (major ingredient is composted steer manure) and the composted chicken manure named Earthgro chicken manure (mainly chicken manure) were obtained from Scotts Miracle-Gro (Marysville, OH). One-Earth organic compost and OSH organic compost were obtained from Sun Land Garden Products, Inc. (Watsonville, CA). The ingredients of One-Earth organic compost are composted yard trimmings and mushroom compost (consisting of composted peat moss, rice hulls, forest products, straw, manure, grape pomace, and cocoa hulls). The ingredients of OSH organic compost are redwood and fir products (ground bark and wood fiber), mushroom compost (consisting of one or more of composted peat moss, rice hulls, forest products, straw, manure, grape pomace, sand, cocoa hulls, and vermiculite). Grape pomace was obtained from E&J Gallo Winery (Fresno, CA). The water contents of these materials were 66, 77, 63, 84, and 99% (w/w), respectively.

The chemical 1,3-D (C$_3$H$_4$Cl$_2$) (purity of 99.9%) containing 52.5% *cis*-1,3-D and 47.5% *trans*-1,3-D was provided by Dow AgroSciences (Indianapolis, IN). The chemical CP (Cl$_3$CNO$_2$) (purity of 99.9%) was provided by Niklor Chemical Co., Inc. (Mojave, CA). The chemical structures of *cis*-1,3-D, *trans*-1,3-D, and CP are summarized in **Figure 1**. Ethyl acetate (pesticide grade) and sodium sulfate anhydrous (Na$_2$SO$_4$, 10−60 mesh, ACS grade) were obtained from Fisher Scientific (Fair Lawn, NJ).

Soil Incubation Experiment. Laboratory incubation experiments were conducted to determine the effects of soil water content, OM amendment, temperature, soil sterilization, and soil texture on the degradation of 1,3-D and CP. The soil preparation before fumigant injection in each experiment was as follows:

(1) *Soil water content:* Aliquots of the sandy loam soil were adjusted with water to 5, 7.5, 10, 12.5, 15, and 17.5% (w/w) moisture contents. The 17.5% level was near the field capacity of the soil.

(2) *OM type:* The sandy loam soil with 10% water content (w/w) was amended with the five organic materials (i.e., composted steer manure, composted chicken manure, One-Earth organic compost, OSH organic compost, and grape pomace) at a rate of 5% (w/w, dry weight basis).

(3) *OM rate:* The sandy loam soil at 10% water content (w/w) was amended with composted steer manure at rates of 2, 5, and 10% (w/w, dry weight basis).

(4) *OM effect at various Soil water contents:* The sandy loam soil at 5, 10, and 15% water content (w/w) was amended with composted steer manure at a rate of 5% (w/w, dry weight basis).

(5) *Temperature:* The sandy loam soil at 10% water content (w/w) with or without 5% (w/w, dry weight basis) composted steer manure amendment was incubated at 10, 30, and 45 °C, respectively.

(6) *Microbiology:* The sandy loam soil at 10% water content (w/w) with or without 5% (w/w, dry weight basis) composted steer manure amendment was autoclaved at 121 °C for 60 min. Before autoclaving, the vials were capped with aluminum foil to minimize water loss, and any moisture lost during autoclaving was replaced with distilled water.

(7) *Soil type:* The loamy sand, sandy loam, and loam soils were adjusted to a soil water content of 60% of their individual field capacities [3.2, 10.5, and 13.8% (w/w) for loamy sand, sandy loam, and loam soil, respectively]. Portions of the moisture-adjusted soils were further amended with 5% (w/w, dry weight basis) composted steer manure.

Eight grams of soil (dry weight basis) was placed in a 20 mL glass vial, which was immediately capped with an aluminum cover and a Teflon-faced butyl rubber septum. Five microliters of fumigant solution was injected into each of the vials with a 10 μL microsyringe. The fumigant solution was prepared by dissolving 150 g L^{-1} of 1,3-D and 75 g L^{-1} CP in ethyl acetate. After fumigant application, the treated vials were inverted and immediately placed in incubators. The vials were incubated at 30 °C except those in the temperature experiment, which also included incubation temperatures of 10 and 45 °C. All experiments were conducted simultaneously.

After incubation for 1, 3, 5, 7, 10, and 15 days, triplicate vials were withdrawn and immediately stored at −80 °C until extraction of the remaining fumigants. Fumigant extraction from the soil samples was conducted using the procedure reported in Guo et al. (*25*), which has an extraction efficiency of >95%. During extraction, anhydrous sodium sulfate at a water/Na$_2$SO$_4$ ratio of 1:7 and 8 mL of ethyl acetate were added to each frozen vial. The vials were resealed and placed in a water bath at 80 °C overnight. Intermittent shaking was conducted to fully extract residual fumigants in the solvent. After settling, approximately 1 mL of the supernatant was transferred into a 2 mL amber glass vial and analyzed using a gas chromatograph with a micro-ECD (GC-μECD) using the procedure reported in Qin et al. (*26*).

Data Analysis and Statistics. The injected amounts of fumigants (i.e., 0.346, 0.317, and 0.326 mg per vial of *cis*-1,3-D, *trans*-1,3-D, and CP, respectively) were treated as the values at time zero. The differences between the residual fumigants in soil and the amount at time zero were attributed to degradation.

To describe the degradation of fumigants in soil over time, data were analyzed initially using several models, including a first-order regression model. Although this model provided a good fit to CP degradation in the OM-amended soils, it did not adequately describe fumigant degradation in all cases. Therefore, further regression analyses were performed using a user-defined availability-adjusted first-order kinetics model, employing the Marquardt−Levenberg algorithm in an iterative process to estimate parameters to best fit fumigant degradation over time (SigmaPlot 10.0):

$$C_t = C_0 \, e^{-k/a(1-e^{-at})} \tag{1}$$

C_t and C_0 are fumigant amounts in soil at time t (days) and time 0, respectively, k is the first-order rate constant (day^{-1}), t is incubation time (days), and a is the unavailability coefficient (dimensionless) (*27*). This model produced a good fit to the data of both 1,3-D isomers and CP in most cases. The model assumes that a portion of fumigant in soil is sorbed by soil, OM, and other media and is not available for direct degradation; equilibrium exists between the adsorbed fumigant and the aqueous phase of fumigant and the ratio of aqueous fumigant to the total parent chemical in soil varies with time (*27*). The higher the first-order rate constant (k), the faster the degradation is. A lower unavailability coefficient (a) means more nonadsorbed fumigant is available for direct degradation; when this coefficient nears zero, the model becomes first-order kinetics. This

equation is invalid once the value of a/k is higher than 1.443. On the basis of eq 1, the half-life of fumigant in soil can be derived as

$$t_{1/2} = -\frac{1}{a} \ln\left(1 - \frac{0.693a}{k}\right) \tag{2}$$

Statistical differences among treatments for k and a were compared using 95% confidence intervals around the estimates. The confidence range of each treatment was calculated as k (or a) $\pm$ (standard error $\times$ 1.96). If the confidence intervals for k or a for two treatments do not overlap, the treatments are significantly different at an α level of 0.05.

RESULTS AND DISCUSSION

Soil Moisture. In the Hanford sandy loam soil with a range of soil water contents, the availability-adjusted first-order kinetics model simulated the degradation of 1,3-D isomers and CP very well, with r^2 values of 0.93−0.98. Although increasing water content tended to reduce the half-lives of both 1,3-D isomers, neither k nor a was statistically different among water content treatments (**Table 2**). Increasing soil water content from 5 to 17.5% decreased the half-life ($t_{1/2}$) for *cis*-1,3-D and *trans*-1,3-D by nearly 50%. In contrast, the kinetic parameters (k, a, or $t_{1/2}$) of CP degradation were not significantly influenced (**Table 2**). Generally, there are two mechanisms (i.e., chemical and biological) in fumigant degradation in soils, and hydrolysis is an important chemical mechanism. Our results suggest that the hydrolysis contributes more to 1,3-D degradation compared to CP degradation. In soil, 1,3-D is initially hydrolyzed to produce 3-chloroallyl alcohols via a mixed Sn1/Sn2 reaction with water or OH$^-$ as nucleophiles, which are further oxidized to carboxylic acid and then to succinic acid, propionic acid, and acetic acid and, finally, to CO$_2$, H$_2$O, and Cl$^-$ (*10, 12, 15*). Earlier studies have demonstrated that CP degradation is through three successive reductive dehalogenations to nitromethane by *Pseudomonas* sp. (*28*) and the final products are CO$_2$, NO^{3-}, and Cl$^-$ (*15*).

The results agreed with some other studies that 1,3-D degraded more rapidly with increased soil moisture (*24*), whereas CP degradation was unaffected by soil moisture (*22*). Guo et al. (*12*) further confirmed that 1,3-D hydrolyzed more rapidly when the soil water content increased from 5 to 15%. However, one study indicated little effect of a soil water content range from 25 to 75% of the water-holding capacity on 1,3-D degradation rate (*4*).

At all soil moisture levels, the degradation rate of CP was significantly higher than those for 1,3-D isomers ($P < 0.05$), suggesting that CP may contribute less to the fumigant emission compared to 1,3-D when they are applied together. The degradation rate of *cis*-1,3-D was slightly lower than that of *trans*-1,3-D (**Table 2**). These data were consistent with other reported values showing slower degradation of 1,3-D than of CP (*29*) and more rapid degradation of *trans*-1,3-D than of *cis*-1,3-D (*12, 30, 31*).

Type of Organic Material. All OM amendments decreased the half-life of fumigants in soil; the half-life in unamended soil was 1.4−3.5 times longer for both 1,3-D isomers and 2.8−6.3 times longer for CP compared to that in the OM-amended soils (**Table 3**), indicating that all sources of OM accelerated fumigant degradation. Studies reported earlier using various organic materials showed similar findings (*2, 4*).

Among these OM amendment treatments, the first-order rate constant (k) of both 1,3-D isomers followed the order of composted steer manure > grape pomace > composted chicken manure > One-Earth organic compost > OSH organic compost. This parameter was significantly larger in composted steer manure or grape pomace amended soils than in the other three OM-amended soils ($P < 0.05$, **Table 3**). A similar order was also

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Table 2. Effects of Soil Water Content on 1,3-Dichloropropene (1,3-D) and Chloropicrin (CP) Degradation in Hanford Sandy Loam Using an Availability-Adjusted First-Order Decay Model[a]

soil water content (%, w/w)	degradation rate constant, k (day^{-1})	unavailability coefficient, a	half-life, $t_{1/2}$ (days)
		cis-1,3-D	
5.0	0.11 ± 0.01	0.11 ± 0.03	10.7
7.5	0.13 ± 0.02	0.12 ± 0.03	8.2
10.0	0.14 ± 0.02	0.11 ± 0.04	7.0
12.5	0.13 ± 0.02	0.08 ± 0.03	6.7
15.0	0.13 ± 0.01	0.07 ± 0.02	6.2
17.5	0.16 ± 0.03	0.08 ± 0.04	5.5
		trans-1,3-D	
5.0	0.13 ± 0.02	0.12 ± 0.03	8.0
7.5	0.16 ± 0.02	0.13 ± 0.03	6.4
10.0	0.16 ± 0.03	0.11 ± 0.04	5.6
12.5	0.16 ± 0.02	0.08 ± 0.03	5.5
15.0	0.16 ± 0.02	0.08 ± 0.02	5.1
17.5	0.18 ± 0.03	0.09 ± 0.04	4.5
		CP	
5.0	0.34 ± 0.04	0.10 ± 0.03	2.3
7.5	0.35 ± 0.04	0.14 ± 0.04	2.3
10.0	0.33 ± 0.04	0.15 ± 0.04	2.5
12.5	0.30 ± 0.04	0.14 ± 0.04	2.8
15.0	0.30 ± 0.04	0.15 ± 0.04	2.8
17.5	0.41 ± 0.07	0.24 ± 0.06	2.2

[a] The incubation temperature was 30 °C; values of k and a for each compound were not significantly different from one another (using 95% confidence interval around the estimates) ($P < 0.05$); correlation coefficient, r^2, was in a range of 0.93−0.98. The plus/minus value is the standard error ($n = 3$).

found for the unavailability coefficient (a), implying that more fumigant was adsorbed by soil and OM (composted steer manure or grape pomace) and was not available for degradation. This finding indicates that OM can increase both the degradation and adsorption of fumigants. However, the mechanism for fumigant interaction with OM and the reaction products between fumigant and OM require further detailed studies to determine their potential impact on the environment. The calculated half-life for both 1,3-D isomers corresponded to the first-order rate constant, which suggests that this parameter may represent fumigant degradation rather than the unavailability coefficient (**Table 3**).

The degradation rate of CP was significantly different among the OM-amended soils. Calculated half-lives followed the order of composted chicken manure > grape pomace > One-Earth organic compost > composted steer manure > OSH organic compost. These results show that the type of OM had different effects on the degradation of 1,3-D isomers compared to CP. The numbers of microorganisms and functional groups that can contribute to the 1,3-D or CP degradation may vary with the OM type. For example, 1,3-D isomers degraded at the lowest rate in OSH organic compost-amended soil, whereas CP degraded the most rapidly with this OM; both 1,3-D isomers and CP degraded in composted steer manure amended soil at relatively high rates. As a commonly used amendment material, composted steer manure would be considered to be an effective source of OM for accelerating 1,3-D and CP degradation.

Similar to the results in unamended soils, CP degradation was significantly faster than the 1,3-D degradation and *cis*-1,3-D degradation was slightly slower than *trans*-1,3-D in any OM-amended soil (**Table 3**). In the whole incubation study, *cis*-1,3-D degradation was consistently slower than *trans*-1,3-D degrada-

Table 3. Effects of Organic Material (OM) Type on 1,3-Dichloropropene (1,3-D) and Chloropicrin (CP) Degradation in Hanford Sandy Loam[a]

organic material type	degradation rate constant, k (day^{-1})	unavailability coefficient, a	half-life, $t_{1/2}$ (days)
		cis-1,3-D	
no OM	0.14 ± 0.02	0.11 ± 0.04	7.0
composted steer manure	0.45 ± 0.06	0.29 ± 0.05	2.0
composted chicken manure	0.22 ± 0.02	0.12 ± 0.03	3.9
One-Earth organic compost	0.19 ± 0.02	0.06 ± 0.02	4.2
OSH organic compost	0.16 ± 0.01	0.02 ± 0.02	4.5
grape pomace	0.33 ± 0.03	0.21 ± 0.03	2.8
		trans-1,3-D	
no OM	0.16 ± 0.03	0.11 ± 0.04	5.6
composted steer manure	0.60 ± 0.09	0.41 ± 0.07	1.6
composted chicken manure	0.29 ± 0.03	0.17 ± 0.03	3.0
One-Earth organic compost	0.22 ± 0.02	0.07 ± 0.03	3.5
OSH organic compost	0.17 ± 0.01		4.0
grape pomace	0.43 ± 0.03	0.19 ± 0.03	1.9
		CP	
no OM	0.33 ± 0.04	0.15 ± 0.04	2.5
composted steer manure	1.30 ± 0.02		0.5
composted chicken manure	0.80 ± 0.04		0.9
One-Earth organic compost	1.40 ± 0.01		0.5
OSH organic compost	1.79 ± 0.01		0.4
grape pomace	1.11 ± 0.02		0.6

[a] Soil water content was 10% (w/w), and the incubation temperature was 30 °C. Degradation of both fumigants in unamended soil (no OM) and that of 1,3-D in OM-amended soils was simulated using the availability-adjusted first-order decay model, whereas *trans*-1,3-D degradation in OSH organic compost amended soil and CP degradation in OM-amended soils was simulated using first-order kinetics model. The significant difference of values of k and a for each compound was determined using 95% confidence interval around the estimates ($P < 0.05$). The application rate of organic material was 5% (dry weight, w/w); correlation coefficient, r^2, was in a range of 0.96−1.00. The plus/minus value is the standard error ($n = 3$).

tion in any soil; however, the difference was not statistically significant. Thus, data for total 1,3-D (sum of both isomers) were used for further analyses and discussion in the following sections.

Amount of Organic Material. Increasing the amount of composted steer manure amendment accelerated the degradation of 1,3-D and CP (**Figure 2**). Both the first-order rate constant (k) and unavailability coefficient (a) increased significantly with increasing OM amount for 1,3-D ($P < 0.05$). The lowest k and a were 0.15 and 0.11, respectively, in the unamended soil, whereas the highest values were in the 10% OM-amended soil (i.e., 1.07 and 0.74, respectively). Due to the dominant role of increasing OM on degradation rate, the half-life of 1,3-D decreased from 6.3 to 0.9 day, which is similar to that given in previous papers (*2, 4*). The increasing unavailability coefficient (a) with OM amendment suggests that more 1,3-D may be incorporated into OM and not available for direct degradation. The higher adsorption of 1,3-D or higher residual 1,3-D in the soils with higher soil organic matter or OM amendment has been reported in several studies (*6, 8, 30, 32*).

The first-order rate constant of CP also significantly increased from 0.33 to 2.96 ($P < 0.05$) as the OM amendment increased, whereas the half-life of CP decreased from 2.5 to 0.2 day. Increasing the OM amendment accelerated CP degradation more than it did 1,3-D degradation, suggesting that CP degradation is more strongly influenced by OM. Consistent with our results, Thomas et al. (*33*) reported that increased OM resulted in a more rapid decrease of CP concentration in soil gas phase compared to 1,3-D.

Article

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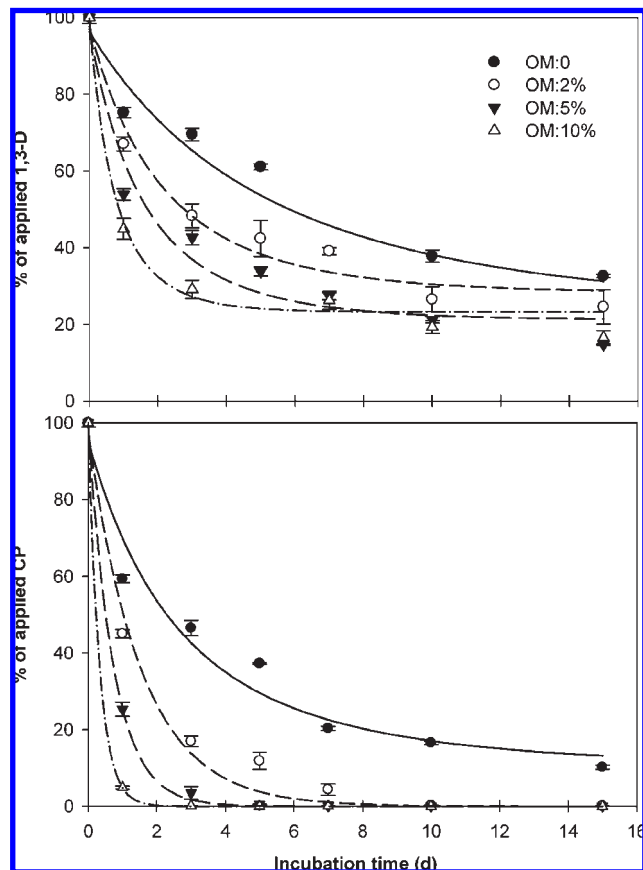

Figure 2. Degradation of 1,3-dichloropropene (1,3-D; sum of *cis*-1,3-D and *trans*-1,3-D) and chloropicrin (CP) in Hanford sandy loam amended with composted steer manure. Symbols represent the mean of triplicate measurements, and error bars indicate the standard deviation. Regression curves were generated using first-order kinetics for the data of CP in organic material (OM) amended soils and the availability-adjusted first-order decay model for the other data; correlation coefficient, r^2, was in the range of 0.93−1.00. The incubation temperature was 30 °C, the tested soil was at 10% water content (w/w), and the application rates of organic material were 0, 2, 5, and 10% (dry weight, w/w), respectively.

Table 4. Effect of Soil Sterilization on 1,3-Dichloropropene (1,3-D; Sum of *cis*-1,3-D and *trans*-1,3-D) and Chloropicrin (CP) Degradation for both Amended and Unamended Sandy Loam Soil[a]

soil treatment	degradation rate constant, k (day^{-1})	unavailability coefficient, a	half-life, $t_{1/2}$ (days)
	1,3-D		
unsterilized	0.15 ± 0.02	0.11 ± 0.04	6.3
sterilized	0.12 ± 0.01	0.05 ± 0.02	6.8
unsterilized OM	0.51 ± 0.07	0.34 ± 0.06	1.8
sterilized OM	0.45 ± 0.04	0.30 ± 0.04	2.0
	CP		
unsterilized	0.33 ± 0.04	0.15 ± 0.04	2.5
sterilized	0.68 ± 0.06	0.24 ± 0.04	1.2
unsterilized OM	1.30 ± 0.02		0.5
sterilized OM	2.42 ± 0.02		0.3

[a] The incubation temperature was 30 °C; fumigant degradation was modeled using the availability-adjusted first-order decay model, except CP degradation in organic material (OM) amended soils, which used a first-order kinetics model; the significant difference of values of k and a for each compound was determined using 95% confidence interval around the estimates ($P < 0.05$); correlation coefficient, r^2, was in the range of 0.94−1.00. The plus/minus value is the standard error ($n = 3$). The tested soil was at 10% water content (w/w) with or without 5% (w/w, dry weight basis) composted steer manure amendment. The sterilized soils were autoclaved at 121 °C for 60 min.

to this result. Different from our study, fresh soils were used in the other studies. Sterilization of soil by autoclaving was reported to accelerate the chemical degradation of MeBr as more chemical reaction sites were formed (*3*, *34*), which might also result in the accelerating degradation of CP in the sterilized soil. The co-application of 1,3-D might play a role in the degradation of CP in this study, but their interactions are still not very clear. Our results imply that the degradation of CP in this study is via chemical rather than microbiological transformation. There might be many microorganisms in the composted steer manure, but they did not affect fumigant degradation significantly, suggesting that the effect of OM on fumigant degradation was primarily via chemical reactions. Apparently, more studies should be conducted to elucidate the role of chemical degradation and biodegradation of fumigants in mineral- and organic-amended soils.

Temperature. Increasing temperature accelerated the degradation of all fumigants in both unamended and amended sandy loam soil (**Figure 3**). At 10 °C, the degradation of 1,3-D in the soil was very slow. The availability-adjusted first-order kinetics was unable to produce a half-life value because the ratio of a/k was much higher than 1.443. By using the first-order kinetics model (r^2 and k were 0.77 and 0.021, respectively), a half-life of 32.5 days was predicted. The first-order kinetics model was further used for describing degradation data at other temperatures, in order to have a consistent comparison. The half-life of CP at 10 °C was 8.9 days. When the incubation temperature was increased, the degradations of 1,3-D and CP accelerated significantly. The half-life of 1,3-D at 10 °C was about 4.2 times that at 30 °C and 13.9 times that at 45 °C. The half-life of CP at 10 °C was 2.6 times that at 30 °C and 5.4 times that at 45 °C. Similarly, the increase of 1,3-D and CP degradation with increasing temperature was shown in other studies with a temperature range of 20−40 or 50 °C (*4*, *20*, *22*, *24*). Our results support that the soil temperature is a critical factor affecting fumigant degradation. When fumigants are applied during cool season or in a region with low temperature, the residual fumigants may persist for a
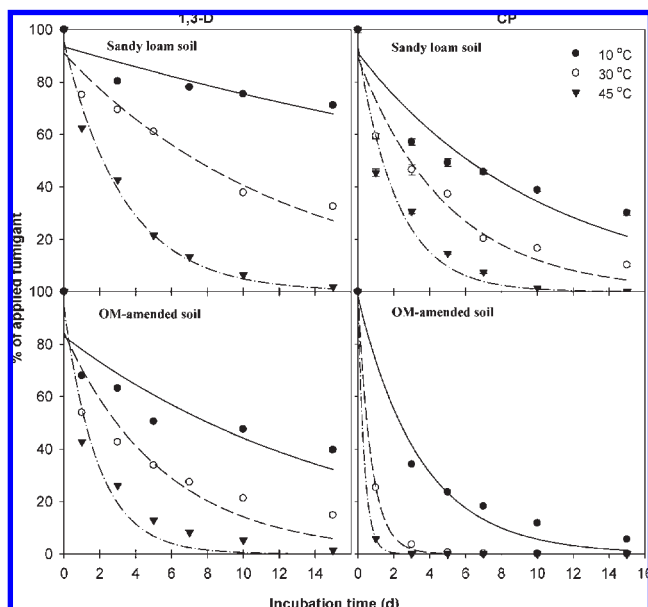
Moreover, our study showed that the degradations of all fumigant compounds in the OM-amended soil with 5, 10, and 15% water contents were similar to one another (data not shown), suggesting that there is little or no direct interaction between organic amendment and soil water content. However, increasing soil water content may reduce soil air pores and the diffusion of fumigants to soil surface that can lead to reduced emissions and increased degradation time in soil.

Biological Degradation. After autoclaving, the microorganisms in soil were assumed to be killed completely and the biological effect on fumigant degradation was minimal. Our results showed that sterilization did not affect 1,3-D degradation in the soils (regardless of OM amendment) (**Table 4**), implying that chemical processes are the dominant factor in 1,3-D degradation, which is corroborated by other studies (*2*, *4*, *12*, *19*). The soils used in this study were air-dried, ground, and stored, which may have reduced soil microbial diversity, population levels, and activity and thus reduced the potential impact of biodegradation (*23*). The primary role of biodegradation of CP has been shown in several previous studies (*17*, *21*−*23*, *28*). Contrary to these reports in the literature, CP degraded more quickly in sterilized soil than in unsterilized soil regardless of OM amendment in our study (**Table 4**). The fewer microorganisms in our soils may contribute

Figure 3. Degradation of 1,3-dichloropropene (1,3-D; sum of *cis*-1,3-D and *trans*-1,3-D) and chloropicrin (CP) in both amended and unamended sandy loam at three incubation temperatures. Symbols represent the mean of triplicate measurements, and error bars indicate the standard deviation. Regression curves were generated using first-order kinetics for all of the data; correlation coefficient, r^2, was in the range of 0.76–0.98. The incubation temperatures were 10, 30, and 45 °C. The tested soil was at 10% water content (w/w) with or without 5% (w/w, dry weight basis) composted steer manure amendment.

relatively long time; therefore, the waiting time for planting the next crop may need to be prolonged to avoid phytotoxicity.

For both 1,3-D and CP in mineral soil, the relationship between degradation rate constant, k, and absolute temperature, T (K), was described by the Arrhenius equation very well ($r^2 > 0.99$):

$$\ln k = \ln A - \frac{E_a}{RT} \tag{3}$$

A is the frequency factor, R is the gas constant ($8.31 \, \text{J mol}^{-1} \text{K}^{-1}$), and E_a is the activation energy (kJ mol^{-1}). The E_a was 55.6 for 1,3-D and 35.9 kJ mol^{-1} for CP. The lower E_a value for CP than for 1,3-D suggests that the degradation of 1,3-D is more sensitive to the temperature change than is that of CP in mineral soil. The calculated E_a of 1,3-D was in the range reported for other studies in sandy loam soil (*20, 24*).

Organic material amendment accelerated fumigant degradation at all incubation temperatures (**Figure 3**). At 10 °C for the OM-amended soils, the calculated half-lives of 1,3-D and CP were 10.6 and 2.5 days, respectively. When incubation temperature was increased to 30 or 45 °C, the half-life of 1,3-D decreased to 3.9 and 1.3 days, respectively; the half-life of CP decreased to 0.5 and 0.2 day, respectively. Dungan et al. (*4*) also found that OM amendment greatly accelerated 1,3-D degradation with an even lower half-life at a similar temperature (e.g., 0.8 day at 30 °C). The Arrhenius equation also described the relationship between the degradation rate constant of 1,3-D or CP and the absolute temperature, T° (K) in the OM-amended soil very well ($r^2 > 0.98$). The calculated E_a values were 44.0 kJ mol^{-1} for 1,3-D and 49.8 kJ mol^{-1} for CP; these values imply that the degradations of 1,3-D and CP had similar responses to the temperature change in OM-amended soil. A similar E_a (53.4 kJ mol^{-1}) for 1,3-D

degradation was observed in 5% (w/w, dry mass) steer manure amended sandy loam soil in another study (*4*).

On the basis of the degradation rate values, Q_{10} values were calculated using van't Hoff's equation

$$Q_{10} = \frac{k_{T+10}}{k_T} \tag{4}$$

where k_T is the degradation rate constant at temperature T (°C) and k_{T+10} is the degradation rate constant at a temperature 10 °C higher. The Q_{10} values varied between the temperature ranges of 10−30 and 30−45 °C, but the difference was small. The average Q_{10} values (from 10 to 45 °C) in the mineral soil and OM-amended soil were 2.1 and 1.8 for 1,3-D and 1.6 and 1.9 for CP. Consistently, a few studies reported a Q_{10} value of 2 in a temperature range of 20−40 °C for 1,3-D (*4, 20*); in addition, the degradation rate constant of CP increased 1.4, 2.9, and 2.0 times, respectively, with every 10 °C increase from 20 to 50 °C (*22*).

Soil Texture. Among the three soil types with moisture adjusted to 60% field capacity, differences in the first-order rate constant (k) and the unavailability coefficient (a) of 1,3-D were not statistically significant (**Table 5**). The half-life of 1,3-D was within a range of 5.5−7.2 days among these soil types.

The first-order rate constant (k) of CP in the loam soil was significantly higher than in the other two soils ($P < 0.05$), whereas the unavailability coefficient (a) was similar (**Table 5**), resulting in a faster degradation of CP in loam soil. The higher amount of clay and soil organic matter in the loam (**Table 1**) might be responsible for the faster CP degradation; however, their combined effect on 1,3-D degradation appears to be limited.

The degradation of 1,3-D and CP was accelerated by OM amendment for all soils (**Table 5**). The half-life of fumigant degradation in unamended soil was 3−5 times that in OM amended soil, indicating that OM plays a prevailing role in fumigant degradation.

When our study was compared to some other studies that had similar amount of fumigants and similar experimental conditions [sandy loam, soil water content of 5 or 12% (w/w), temperature of 30 °C, and soil organic matter content of 0.92% (w/w)] (*20, 22, 24*), the half-lives of *cis*-1,3-D, *trans*-1,3-D, and CP in our study were found 2.3−4.0 times others. This could be attributed to the different microorganism levels between the soils (dry vs fresh) and also possible competitions between the fumigant compounds as the 1,3-D isomers and CP were applied together in our study but individually tested in the other studies.

Management Implications of Soil Amendment with Organic Material To Reduce Fumigant Emissions. Emission and degradation are two major processes affecting the fate of soil fumigants. Fumigant degradation is affected by a number of environmental factors. Soil water content slightly increased 1,3-D degradation but had no effect on CP degradation in this study. Increasing soil temperature accelerated degradation of both 1,3-D and CP; therefore, creating higher temperature conditions at the soil surface may promote fumigant degradation. Degradation of CP was faster in finer-textured soil, whereas degradation of 1,3-D was less affected by soil texture.

Greater fumigant degradation in surface soil with OM amendment leads directly to reduced emissions, which is beneficial from an environmental standpoint. This study confirmed the significant effect of OM on fumigant degradation (and adsorption) under various soil conditions. Different types of OM showed varied effects on the degradation of 1,3-D and CP; therefore, further research is needed to determine the effectiveness, characteristics, and kinetics of the reactions between fumigants and

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Table 5. Effect of Soil Type on 1,3-Dichloropropene (1,3-D; Sum of *cis*-1,3-D and *trans*-1,3-D) and Chloropicrin (CP) Degradation for both Amended and Unamended Soils[a]

treated soil	degradation rate constant, k (day^{-1})	unavailability coefficient, a	half-life, $t_{1/2}$ (days)
		1,3-D	
loamy sand	0.13 ± 0.01	0.08 ± 0.02	7.2
sandy loam	0.15 ± 0.02	0.11 ± 0.04	6.3
loam	0.14 ± 0.01	0.04 ± 0.02	5.5
loamy sand + OM	0.66 ± 0.08	0.49 ± 0.07	1.5
sandy loam + OM	0.51 ± 0.07	0.34 ± 0.06	1.8
loam + OM	0.57 ± 0.07	0.39 ± 0.06	1.7
		CP	
loamy sand	0.36 ± 0.04	0.16 ± 0.03	2.3
sandy loam	0.33 ± 0.04	0.15 ± 0.04	2.5
loam	0.61 ± 0.06	0.13 ± 0.05	1.2
loamy sand + OM	1.51 ± 0.01		0.5
sandy loam + OM	1.30 ± 0.02		0.5
loam + OM	1.79 ± 0.02		0.4

[a] The incubation temperature was 30 °C; fumigant degradation was modeled using the availability-adjusted first-order decay model, except CP degradation in organic material (OM) amended soils, which used a first-order kinetics model; the significant difference of values of k and a for each compound was determined using 95% confidence interval around the estimates ($P < 0.05$); correlation coefficient, r^2, was in the range of 0.94−1.00. The plus/minus value is the standard error ($n = 3$). The tested soils were adjusted to water content levels of 60% of their individual field capacity with or without 5% (w/w, dry weight basis) composted steer manure amendment.

organic materials to identify the most effective OM that can be used in the field to minimize fumigant emissions. That the degradation of both 1,3-D and CP increased with OM amendment rates suggests that applying high amounts of OM would achieve the greatest effect on fumigant emission control. However, the choice of OM type and amount will largely depend on the availability of suitable OM, its cost, and relevant soil environmental factors in order to achieve the maximum effect of OM amendment on fumigant emission control. In addition to the potential benefits of OM on fumigant emission management, the agronomic benefits of this practice on improving soil physicochemical properties and providing nutrients for subsequently planted crops should also be considered.

In addition to monitoring the effectiveness of OM amendments on emission management, it is also critical to determine fumigation efficacy to ensure that rapid degradation of fumigants does not negatively affect pest control. To minimize impacts on pest control, OM amendments should be restricted to surface soils (e.g., 0−5 cm). Additional treatment of surface soils may be required to ensure control of weeds and other pests.

LITERATURE CITED

(1) Segawa, R. Volatile organic compound (VOC) emissions from pesticides. *California Department of Pesticide Regulation*, **2005**; www.cdpr.ca.gov/docs/pur/vocproj/vocmenu.htm.

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

(3) Gan, J.; Yates, S. R.; Papiernik, S.; Crowley, D. Application of organic amendments to reduce volatile pesticide emission from soil. *Environ. Sci. Technol.* **1998**, *32*, 3094–3098.

(4) Dungan, R. S.; Gan, J.; Yates, S. R. Effect of temperature, organic amendment rate and moisture content on the degradation of 1,3-dichloropropene in soil. *Pest Manage. Sci.* **2001**, *57*, 1107–1113.

(5) Dungan, R. S.; Gan, J.; Yates, S. R. Accelerated degradation of methyl isothiocyanate in soil. *Water, Air Soil Pollut.* **2003**, *142*, 299–310.

(6) McDonald, J. A.; Gao, S.; Qin, R.; Trout, T. J.; Hanson, B. D. Thiosulfate and manure amendment with water application and tarp on 1,3-dichloropropene emission reductions. *Environ. Sci. Technol.* **2008**, *42*, 398–402.

(7) Dungan, R. S.; Papiernik, S. K.; Yates, S. R. Use of composted animal manures to reduce 1,3-dichloropropene emissions. *J. Environ. Sci. Health B* **2005**, *40*, 355–362.

(8) Gao, S.; Qin, R.; McDonald, J. A.; Hanson, B. D.; Trout, T. J. Field tests of surface seals and soil treatments to reduce fumigant emissions from shank-injection of Telone C35. *Sci. Total Environ.* **2008**, *405*, 206–214.

(9) Gao, S.; Qin, R.; Tharayil, N.; Hanson, B. D.; Gerik, J.; Wang, D.; Trout, T. J. Emission of 1,3-dichloropropene and chloropicrin from soils with manure amendment and post-fumigation water treatment. In *Proceedings of the Annual International Research Conference on MeBr Alternatives and Emission Reductions*, Orlando, FL, Nov 10−14, 2008; www.mbao.org/2008/034Gao.pdf.

(10) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.

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

(12) Guo, M. X.; Papiernik, S. K.; Zheng, W.; Yates, S. R. Effects of environmental factors on 1,3-dichloropropene hydrolysis in water and soil. *J. Environ. Qual.* **2004**, *33*, 612–618.

(13) Xu, J. M.; Gan, J.; Papiernik, S. K.; Becker, J. O.; Yates, S. R. Incorporation of fumigants into soil organic matter. *Environ. Sci. Technol.* **2003**, *37*, 1288–1291.

(14) Briceno, G.; Palma, G.; Duran, N. Influence of organic amendment on the biodegradation and movement of pesticides. *Crit. Rev. Environ. Sci. Technol.* **2007**, *37*, 233–271.

(15) Dungan, R. S.; Yates, S. R. Degradation of fumigant pesticides: 1,3-dichloropene, methyl isothiocyanate, chloropicrin, and methyl bromide. *Vadose Zone J.* **2003**, *2*, 279–286.

(16) Dungan, R. S.; Ibekwe, A. M.; Yates, S. R. Effect of propargyl bromide and 1,3-dichloropene on microbial communities in an organically amended soil. *FEMS Microbiol. Ecol.* **2003**, *43*, 75–87.

(17) Ibekwe, A. M.; Papiernik, S. K.; Yang, C.-H. Enrichment and molecular characterization of chloropicrin and metam-sodium-degrading microbial communities. *Appl. Microbiol. Biotechnol.* **2004**, *66*, 325–332.

(18) Ibekwe, A. M.; Papiernik, S. K.; Yates, S. R.; Crowley, D. E.; Yang, C.-H. Microcosm enrichment of 1,3-dichloropropene-degrading soil microbial communities in a compost-amended soil. *J. Appl. Microbiol.* **2001**, *91*, 668–676.

(19) Verhagen, C.; Smit, E.; Janssen, D. B.; van Elsas, J. D. Bacterial dichloropropene degradation in soil: Screening of soils and involvement of plasmids carrying the *dhl*A gene. *Soil Biol. Biochem.* **1995**, *27*, 1547–1557.

(20) Ma, Q. L.; Gan, J.; Papiernik, S. K.; Becker, J. O.; Yates, S. R. Degradation of soil fumigants as affected by initial concentration and temperature. *J. Environ. Qual.* **2001**, *30*, 1278–1286.

(21) Zheng, W.; Papiernik, S. K.; Guo, M. X.; Yates, S. R. Competitive degradation between the fumigants chloropicrin and 1,3-dichloropropene in unamended and amended soils. *J. Environ. Qual.* **2003**, *32*, 1735–1742.

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Qin et al.

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

(23) Zhang, Y.; Spokas, K.; Wang, D. Degradation of methyl isothio-cyanate and chloropicrin in forest nursery soils. *J. Environ. Qual.* **2005**, *34*, 1566–1572.

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

(25) Guo, M.; Papiernik, S. K.; Zheng, W.; Yates, S. R. Formation and extraction of persistent fumigant residues in soils. *Environ. Sci. Technol.* **2003**, *37*, 1844–1849.

(26) Qin, R.; Gao, S.; Wang, D.; Hanson, B. D.; Trout, T. J.; Ajwa, H. Relative effect of soil moisture on emissions and distribution of 1,3-dichloropropene and chloropicrin in soil columns. *Atmos. Environ.* **2009**, 2449–2455.

(27) Wang, Q.; Guo, M.; Yates, S. R. Degradation kinetics of manure-derived sulfadimethoxine in amended soil. *J. Agric. Food Chem.* **2006**, *54*, 157–163.

(28) Castro, C. E.; Wade, R. S.; Belser, N. O. Biodehalogenation. The metabolism of chloropicrin by *Pseudomonas* sp. *J. Agric. Food Chem.* **1983**, *31*, 1184–1187.

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

(30) Ou, L. T. Enhanced degradation of the volatile fumigant-nemati-cides 1,3-D and methyl bromide in soil. *J. Nematol.* **1998**, *30*, 56–64.

(31) Chung, K.-Y.; Dickson, D. W.; Ou, L.-T. Differential enhanced degradation of *cis* and *trans*-1,3-D in soil with a history of repeated field applications of 1,3-D. *J. Environ. Sci. Health B* **1999**, *34*, 749–768.

(32) Kim, J.-H.; Gan, J.; Farmer, W. J.; Yates, S. R.; Papiernik, S. K.; Dungan, R. S. Organic matter effects on phase partition of 1,3-dichloropropene in soil. *J. Agric. Food Chem.* **2003**, *51*, 165–169.

(33) Thomas, J. E.; Ou, L. T.; Allen, L. H.; McCormack, L. A.; Vu, J. C.; Dickson, D. W. Persistence, distribution, and emission of Telone C35 injected into a Florida sandy soil as affected by moisture, organic matter, and plastic film cover. *J. Environ. Sci. Health B* **2004**, *39*, 505–516.

(34) Ou, L.-T.; Joy, P. J.; Thomas, J. E.; Hornsby, A. G. Stimulation of microbial degradation of methyl bromide in soil during oxidation of an ammonia fertilizer by nitrifiers. *Environ. Sci. Technol.* **1997**, *31*, 717–722.