Degradation of Methyl Iodide in Soil: Effects of Environmental Factors

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Methyl iodide (MeI) is a promising alternative to the phased-out fumigant methyl bromide (MeBr); however, there are concerns about its environmental fate following soil fumigation. Laboratory experiments were conducted to investigate the effect of various environmental factors on the rate of MeI degradation in soil. The chemical was added to soil at 48.6 mg kg\(^{-1}\) and incubated under different conditions. The MeI degradation rate in soil was determined by extracting and measuring residual concentrations over a 15 d incubation period. In soil, MeI degradation followed availability-adjusted first-order kinetics. At 20°C MeI had a calculated half-life of 32 d in a sandy loam containing 4.3 g kg\(^{-1}\) of organic carbon. It degraded more rapidly as temperature increased, exhibiting a half-life of 23 d at 30°C. Amendment with 10% cattle manure shortened the half-life to 4 d at 20°C. In both unamended and manure-amended soils, the half-life of MeI greatly increased as the organic matter (OM) was removed and it only slightly increased in soils that were sterilized, indicating predominance of chemical reactions in MeI degradation. Soil texture, mineralogy, and moderate moisture content had little influence on MeI degradation. The degradation slowed as the chemical application rate increased. The results suggest that environmental factors, especially soil temperature and organic amendments, should be considered in combination with the minimum effective MeI application rate for achieving satisfactory pest-control efficacy, reducing atmospheric volatilization, and minimizing groundwater contamination.

As the commonly used soil fumigant MeBr was phased out in the United States, substantial efforts have been made to identify practical alternatives. Several studies have demonstrated that MeI is effective in controlling a broad spectrum of soil-borne pathogens (Becker et al., 1998; Waggoner et al., 2000) and has the potential to replace MeBr in soil fumigation (USEPA, 2004). In fact, the USEPA has issued a temporary approval of registering MeI as a soil fumigant (USEPA, 2007). Unlike MeBr, MeI degrades rapidly in the atmosphere via photolysis (half-life 3–7 h), and does not promote ozone depletion in the stratosphere (Solomon et al., 1994).

Methyl iodide is carcinogenic and exhibits moderate to high acute toxicity for inhalation and ingestion (NIOSH, 2008). Therefore, its environmental fate will be of great concern as a fumigant. Potential pathways for MeI to dissipate following field application include degradation in soil, diffusion/leaching to groundwater, and volatilization to the atmosphere. To reduce atmospheric emission of fumigants, treated fields are generally covered with polyethylene films for 7 to 14 d after chemical application. However, the polyethylene film is not effective in preventing MeI volatilization losses and up to 75% of applied MeI can still volatilize to the atmosphere (Gan et al., 1997). There is concern, however, that if surface sealing is sufficient, downward migration of MeI in the soil profile may be significant. In a field trial, Gan et al. (1997) observed that MeI migrated to a depth of 180 cm from the surface within 72 h when applied at 30 cm depth in a sandy loam plot covered with 0.1-mm polyethylene film. Under certain conditions such as a shallow water table or heavy rain events shortly after soil fumigation, MeI may reach groundwater via diffusion/leaching. To diminish the risk of groundwater contamination by MeI and its residual emission to the atmosphere, it would be beneficial if degradation of the applied chemical can be enhanced in soils after pest control is achieved.

At 20°C, MeI is a colorless liquid with a vapor pressure of 398 mm Hg and an aqueous solubility of 14 g L\(^{-1}\). In fresh water at 20°C, degradation of MeI is mainly via hydrolysis (Eq. [1]), with a half-life (\(t_{1/2}\)) of 100 to 251 d (Zheng et al., 2003; Speclab, 2008). In the presence of short-wavelength photoradiation, the hydrolysis will be greatly accelerated (Gan and Yates, 1996):

\[
\text{CH}_3\text{I} + \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{CH}_3\text{OH} + \text{I} + \text{H}^+ \]

[1]

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In the ocean MeI reacts with chloride to form methyl chloride with reaction half-lives at 10.8 and 19.2°C of 58 and 20 d, respectively (Speclab, 2008). Sorption of MeI on soil solids is insignificant, as indicated by its small partition coefficient (Kd) of 0.08 to 0.13 mL g⁻¹ (Gan and Yates, 1996). In moist soils, MeI degrades principally through chemical processes such as nucleophilic substitution reactions with H₂O (hydrolysis, Eq. [1]) or soil organic matter (methylation, Eq. [2]):

\[
\text{CH}_3\text{I}+\text{OM}-\text{XH} \rightarrow \text{CH}_3\cdot\text{X} - \text{OM} + \text{I} + \text{H}^+
\]

where -XH represents nucleophilic functional groups (e.g., -NH₂, -NH, -SH, -OH, -COOH) of soil organic matter (Gan and Yates, 1996; Avila-Zárraga and Martínez, 2001). The reported half-life of MeI in mineral soils ranges from 11 to 43 d, (Gan and Yates, 1996; Zheng et al., 2003), greater than that of other soil fumigants including 1,3-dichloropropene (1,3-D), chloropicrin, and methyl isothiocyanate (t½ < 10 d). The relative persistence of MeI in soil may pose contamination risks to shallow groundwater and may induce substantial atmospheric emissions after tarp removal. Considering that soil disinfestation is normally achieved within the first 72 h after fumigation (Waggoner et al., 2000; Guo et al., 2004a), an ideal situation would be containment of MeI in the soil and rapid degradation to nontoxic compounds after this time. Although manipulation of the soil environment at the time of fumigation can significantly affect MeI persistence, little is known about the environmental conditions that facilitate MeI degradation. The objectives of this study were to examine the effects of various environmental factors and soil characteristics, including temperature, moisture, soil texture, organic matter content, clay mineralogy, and microorganisms, on the rate of MeI degradation, and to propose application strategies for promoting MeI effectiveness on soil pest control while minimizing environmental risks.

Materials and Methods

Chemicals and Soil Materials

The chemical MeI (iodomethane, 99.5% purity) was purchased from Sigma-Aldrich (Milwaukee, WI). Soils used in the study include a Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Xeric Dystrodystric Tb Haploxeralfs), a Madera loam (fine, smectitic, thermic Abruptic Torriorthents), and an Atwater loamy sand (coarse-loamy, mixed, active, thermic Typic Acrudox, coarse-loamy, mixed, active, thermic Typic Haploxeralfs) collected from surface layers of agricultural fields in the San Joaquin Valley of California. The Hanford soil was sampled from the San Joaquin Valley Agricultural Sciences Center, USDA-ARS, Parlier, CA. The soil is widely distributed in the San Joaquin Valley and in the valleys of central and southern California (National Cooperative Soil Survey, 1999). Orchards and vineyards on this soil type often require preplant soil fumigation for successful establishment. The Madera soil was gathered from a nursery at Le Grand, CA. The Atwater loamy sand was obtained from an orchard at Atwater, CA. The soils collected were never treated with MeI or other fumigants in the field. All soils were air-dried, sieved to <2 mm, and stored at 20°C before use. Selected physical and chemical properties of the soils are given in Table 1. Composted cattle manure (moisture content 52.1%; OC 192 g kg⁻¹; pH 8.4) obtained from a local garden center was used as an organic amendment.

Incubation Experiments

The rate of MeI degradation in soils under different conditions was determined based on the residual amounts of the spiked chemical after incubation. Briefly, air-dried soils were adjusted to preset gravitational moisture contents with deionized water. After passing through a 2-mm sieve for uniformity, subsamples (10.0 g oven dry mass) of the moist soils were weighed into 20-mL glass vials. The vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa. Five microliters of 97.3 g L⁻¹ MeI ethyl acetate stock solution were injected into each of the vials with a 10-μL syringe puncturing the rubber septa. Preliminary studies indicated that the puncture in the septa resulting from MeI addition did not promote fumigant volatilization. The MeI application rate was 48.6 mg kg⁻¹ soil, appropriate for sterilizing the top 40 cm of soil in fumigation practice (Guo et al., 2004a). The vials were then placed upside down and incubated at a controlled temperature (20°C if not specified). At 0, 1, 3, 5, 7, 10, and 15 d after injection, triplicate vials were withdrawn and stored in a –40°C freezer to retard any further chemical and biological reactions. Vials transferred into the freezer instantly after MeI spiking were treated as “time zero” and used as controls to index degradation of MeI during soil incubation. Once the incubation timecourse was finished, MeI was extracted from the soil with ethyl acetate following a standard extraction method (Gan et al., 1998; Zheng et al., 2003) that minimizes volatilization of fumigants during extraction. The concentration of MeI in the ethyl acetate extracts was analyzed using gas chromatographic (GC) techniques detailed below. Differences of extractable MeI in the control (time zero) vials and the incubated vials were attributed to degradation of the chemical.

To investigate the effect of temperature on the degradation rate of MeI, batches of vials containing 11.0 g of moist Hanford sandy loam (10% moisture content) 48.6 g kg⁻¹ MeI were incubated at 10, 20, and 30°C, respectively. Procedures for sampling, extraction, and analysis were followed as described above.

To determine the effect of soil moisture, air-dry Hanford soil was adjusted with deionized water to gravimetric moisture contents of 5, 10, and 15%, and incubated with MeI as described above.

To examine the effect of organic amendments on MeI degradation, air-dry Hanford soil was amended with (10% dry mass basis) cattle manure, adjusted to 10% moisture content, and incubated with MeI. The effect of soil OM was also explored by heating the Hanford soil at 375°C for 12 h to remove the indigenous OM, adjusting to 10% moisture content, and incubating with MeI following the procedure described above.

The effect of microorganisms on MeI degradation was evaluated by autoclaving nonamended and manure-amended Hanford soils (10% moisture content) at 121°C for 60 min, and conducting the MeI incubation as described above. The degradation rates of MeI were compared with those of nonsterilized corresponding soils.
Aliquots of the three tested soils (Hanford sandy loam, Madera loam, and Atwater loamy sand) with varied mineralogy and texture were further heated at 375°C for 12 h to remove OM and microorganisms. The treated soils were then adjusted with deionized water to 50% of their individual water holding capacities (Atwater 5%; Hanford 17%; and Madera 23%) and incubated with MeI at 20°C. Degradation rates of MeI in these three different soils were compared to evaluate the effect of soil texture and mineralogy.

The effect of initial application rate on degradation of MeI in soil was studied by spiking MeI into 10% moisture Hanford sandy loam at 7, 22, 49, and 74 mg kg⁻¹ and determining amounts of the remaining chemical after incubation at 20°C.

Chemical Analysis

Concentrations of MeI in ethyl acetate extracts were analyzed with an Agilent 6890N gas chromatograph (GC) equipped with a micro electron capture detector (μECD) (Agilent Technologies, Palo Alto, CA). A DB-VRX capillary column (30 m length × 0.25 mm i.d. × 1.4 μm film thickness, Agilent Technologies, Palo Alto, CA) was used for separation of fumigants. The GC carrier gas (He) flow rate, inlet temperature, and detector temperature were set at 2.0 mL min⁻¹, 150 and 300°C, respectively. The oven temperature program was as follows: initially 45°C, increasing at 2.5°C min⁻¹ to 75°C, then at 99°C min⁻¹ to 110°C and held for 7 min. The retention time for MeI was 2.7 min and the method detection limit was 0.001 mg L⁻¹ when a volume of 1 μL solution was injected using a split ratio of 100:1.

Data Analysis

The amount of MeI extracted from the control vials at time zero was treated as 100%. The remaining MeI recovered from the incubated soils was converted to percentage (%) relative to the controls. Final data are reported as means of triplicate measurements. To illustrate the degradation kinetics of MeI in soil under different conditions, the data were further fitted against incubation time using user-defined computational models (SigmaPlot 10.0, Jandel Scientific, San Rafael, CA), employing the Marquardt-Levenberg algorithm in an iterative manner.

Results and Discussion

Degradation of Methyl Iodide in Soils

As sorption of MeI on soil materials is insignificant (Gan and Yates, 1996), degradation becomes the predominant process determining the relative portion of the applied chemical available for atmospheric volatilization and groundwater contamination. Degradation of MeI over time in the Hanford sandy loam (OC 4.3 g kg⁻¹) is shown in Fig. 1. In unsterilized, sterilized, and OM-removed soils incubated at 20°C, degradation of MeI followed an availability-adjusted first-order kinetics model:

\[
 C_t = C_0 e^{-\lambda t} \left(1 - e^{-\alpha t}\right) 
\]

where \( C_t \) and \( C_0 \) are relative amounts of MeI in soil at time \( t \) (d) and time \( 0 \), respectively, \( k \) is the first-order rate constant (d⁻¹), \( t \) is incubation time (d), and \( a \) is the pseudo unavailability coefficient (dimensionless; Wang et al., 2006). This model considers that the sorbed and gaseous phase MeI in soil is not readily available for direct degradation; an equilibrium exists between the sorbed/gaseous phase and the aqueous phase of MeI; and the ratio \( \lambda \) of aqueous MeI to the total parent chemical in soil varies with time: \( \lambda(t) = \varphi e^{-at} \), where \( \varphi \) is the fraction of aqueous MeI relative to the total amount at \( t = 0 \). Based on Eq. [3], the half-life of MeI in soil can be derived:

\[
 t_{1/2} = \frac{-1}{a} \ln\left(1 - 0.6934a/k\right) 
\]

Modeling results are given in Table 2. The model fits the MeI degradation kinetics data well, with regression coefficients >0.99; fitting the data with the simple first-order decay model \((C = C_0 e^{-kt})\), however, yielded poor trend lines and lower regression coefficients (<0.95, data not shown). In general, MeI degraded slowly in the unsterilized Hanford soil, with a calculated \( t_{1/2} \) of 31.9 d (Table 2). Reported half-lives of MeI in a Greenfield

\[
\text{Table 1. Selected properties of the soil materials.}
\]

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Hanford</th>
<th>Madera</th>
<th>Atwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taxonomic name</td>
<td>Xerorthents</td>
<td>Durixeralfs</td>
<td>Haploxeralfs</td>
</tr>
<tr>
<td>Particle sizes†</td>
<td>Sand, g kg⁻¹</td>
<td>880</td>
<td>548</td>
</tr>
<tr>
<td>Silt, g kg⁻¹</td>
<td>50</td>
<td>396</td>
<td>344</td>
</tr>
<tr>
<td>Clay, g kg⁻¹</td>
<td>70</td>
<td>56</td>
<td>252</td>
</tr>
<tr>
<td>pH†</td>
<td>7.2</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>TOC§, g kg⁻¹</td>
<td>4.3</td>
<td>6.4</td>
<td>4.2</td>
</tr>
<tr>
<td>CEC¶, cmol kg⁻¹</td>
<td>3.3</td>
<td>6.8</td>
<td>20</td>
</tr>
</tbody>
</table>

† Measured by sodium hexametaphosphate dispersion and hydrometer methods. § Total organic carbon (TOC) obtained from organic matter content multiplying a coefficient 0.58. Organic matter content was measured by combustion method. ¶ Cation exchange capacity (CEC) determined by the barium acetate saturation and calcium replacement method (Ribble and Quick, 1960).
sandy loam (pH 7.4, OC 4.7 g kg⁻¹, and clay 95 g kg⁻¹), a Carsetas loamy sand (pH 7.3, OC 12.8 g kg⁻¹, and clay 110 g kg⁻¹), and an Arlington sandy loam (pH 7.2, OC 9.2 g kg⁻¹, and clay 74 g kg⁻¹) are 43, 11, and 13 d, respectively (Gan and Yates, 1996; Zheng et al., 2003). The MeI degradation may be the result of hydrolysis, chemical reactions with soil OM and clay minerals, and microbial degradation. The half-life of MeI via hydrolysis in water at 20°C is 108 d (Zheng et al., 2003), suggesting that direct hydrolysis is not a major pathway for MeI dissipation in soil. The outstanding differences between half-lives of MeI in soil and water entail the catalytic effect of soil surfaces/constituents on fumigant degradation. Sterilization slowly reduced the degradation of MeI in soil (Fig. 1) and increased its half-life to 33.6 d (Table 2). Fumigation with MeI presumably inhibited soil microbial activity, and therefore, autoclaving did not significantly increase the sterilization effect. Removal of OM substantially reduced the degradation rate of MeI in soil (Fig. 1), indicating the importance of OM in eliminating the applied fumigant. The half-life of MeI in OM-removed Hanford soil was 52.8 d (Table 2), greater than those in the OM-containing soils.

The Effect of Temperature

Temperature is a critical factor controlling the rate of most chemical reactions and microbial processes. In a range of 10 to 30°C, degradation of MeI in the Hanford sandy loam (10% moisture content) accelerated as temperature increased (Fig. 2). At 10°C, MeI degraded fairly slowly: around 85% of the applied parent chemical remained in soil after 15 d of incubation and its calculated half-life was 67.9 d (Table 3). In contrast, the half-life was reduced to 31.9 d at 20°C (Table 2). When the incubation temperature was elevated to 30°C, the half-life of MeI further decreased to 23.0 d (Table 3). Viewing Fig. 2 it is clear that the degradation rate of MeI in soil can be manipulated by controlling the temperature. On warm days the soil surface, especially when covered by transparent plastic films, usually is much warmer than underlying soils. Enhancing degradation of MeI will mitigate atmospheric volatilization and reduce downward migration of the chemical.

The Effect of Soil Moisture

Moisture plays an important role in determining fumigant diffusion and degradation. Increasing soil moisture will decrease the pores available for fumigant vapor diffusion. As such, surface water sealing has been demonstrated to be effective in reducing fumigant emission losses (Gao and Trout, 2006, 2007). Meanwhile, higher moisture contents favor more fumigant partitioning in the aqueous phase, which is readily subject to chemical and biological degradation. Guo et al. (2004b) reported that hydrolysis of 1,3-D in a sandy loam soil was promoted as the moisture content increased from 5 to 15%. However, when MeI was incubated at 20°C in the Hanford soil at various moisture contents (i.e., 5, 10, and 15%), no significant differences in the chemical degradation kinetics were observed (Fig. 3; Paired t test $P > 0.20$), confirming that hydrolysis is not a major pathway for MeI degradation in soil, since MeI hydrolyzes in water at a rather low rate, with $t_{1/2} > 100$ d (Zheng et al., 2003; Speclab, 2008). Although moisture content does not impact MeI degradation, it does influence distribution and gas-phase diffusion of the chemical in soil following subsurface application (Guo et al., 2004a).

The Effect of Organic Amendment

Degradation of MeI was significantly enhanced when the Hanford sandy loam soil was amended with 10% cattle manure, ($P < 0.001$, Fig. 4). Within 15 d, only 13% of the applied MeI remained in the manure-amended soil, while in the unamended soil more than 70% persisted (Fig. 4). The manure amendment reduced the half-life of MeI from 31.9 to 3.5 d (Table 3). Reaction with OM is a major mechanism for MeI degradation in soil (Gan and Yates, 1996). In nature, MeI is subject to $S_N$2 substitution reactions. As illustrated in Eq. [2], the sterical structure of MeI favors attack by nucleophiles, and iodide is a readily leaving group. Naturally decayed organic materials possess nucleophilic functional groups such as carboxylic (-COOH), phenolic (aromatic C-OH), alcoholic (-OH), and amine (-NH$_2$) groups. In soil, OM reacts rapidly with MeI via nucleophilic substitution, resulting in methylated organic molecules (Eq. [2]). This explains the persistence of MeI in the Hanford sandy loam after OM removal (Fig. 1). Accelerated degradation in soil by organic amendments has been observed for other fumigants including 1,3-D, MeBr, and chloropicrin (Gan and Yates, 1996; Gan et al., 1998; Xu et al., 2003; Guo et al., 2004b). The accelerated degradation suggests the feasibility of 1,3-D and MeBr in soil following subsurface application (Guo et al., 2004a).

### Table 2. Fitting results of methyl iodide (MeI) degradation in Hanford sandy loam using the availability-adjusted first-order decay model.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Degradation rate constant, $k$ (d⁻¹)</th>
<th>Unavailability coefficient, $a$</th>
<th>Correlation coefficient, $r^2$</th>
<th>Half-life, $t_{1/2}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsterilized</td>
<td>0.0233 ± 0.0011</td>
<td>0.0044 ± 0.0008</td>
<td>0.997</td>
<td>31.9</td>
</tr>
<tr>
<td>Sterilized</td>
<td>0.0224 ± 0.0006</td>
<td>0.0049 ± 0.0005</td>
<td>0.998</td>
<td>33.6</td>
</tr>
<tr>
<td>Organic matter removed</td>
<td>0.0146 ± 0.0029</td>
<td>0.0041 ± 0.0010</td>
<td>0.991</td>
<td>52.8</td>
</tr>
</tbody>
</table>
of employing surface application of organic residues (e.g., manure and compost) to reduce MeI atmospheric emissions and groundwater contamination.

The Effect of Soil Microorganisms

Figure 1 illustrates that additional sterilization had little influence on MeI degradation in the Hanford sandy loam at 20°C. In both unsterilized and sterilized soils, the degradation kinetics of MeI were nearly identical (Paired $t$ test, $P > 0.18$). The results do not imply, however, that microorganisms are not important for MeI degradation. It is speculated that even in unsterilized soils, fumigation with MeI at 48.6 mg kg$^{-1}$ had already generated sterilization effects similar to that of autoclaving, and the activity of most microbes was inhibited. Dungan et al. (2003) observed that soil microbial activity was inhibited on application of 1,3-D or propargyl bromide at recommended rates. Heterotrophic microbial activity can be severely suppressed in the first week after treating soils with MeBr and other available fumigants. Microbial diversity recovered to 73% of its original level 12 wk after the MeBr treatment (Ibekwe et al., 2001). Tests with Hanford soil amended with cattle manure showed that additional sterilization did not affect initial degradation of MeI (Fig. 5). The degradation kinetics of MeI in the unsterilized and sterilized soils were similar (Paired $t$ test, $P > 0.26$) for the first 5 d following fumigant addition (Fig. 5); however, significantly less MeI (Paired $t$ test, $P < 0.03$) was recovered from the unsterilized soil with continued incubation (Fig. 5). The more rapid degradation of MeI in the unsterilized soil was possibly due to the recovery of microbial activity over time. Gan and Yates (1996) also observed considerable suppression of MeI degradation in a potting mix after sterilizing the material. Indeed, reactivation and re-establishment of soil microorganisms starts shortly after fumigant application (Dungan et al., 2003). It can be concluded that biological degradation of MeI and other fumigants by soil microbes may be significant, but not in the first 1 to 2 wk following application.

The Effect of Soil Mineralogy and Texture

Organic matter was removed from an Atwater loamy sand, a Hanford sandy loam, and a Madera loam to test the effect of mineralogy and texture on MeI degradation at 20°C. As illustrated in Fig. 6, degradation of MeI in the three OM-removed soils showed similar patterns, although the soils differed substantially in texture and clay mineralogy. In the current study, soil texture and mineralogy do not appear to be important.

Table 3. Kinetic parameters for methyl iodide (MeI) degradation in soil under different conditions. Values are obtained by fitting measured data with the availability-adjusted first-order decay model.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Temperature</th>
<th>Moisture content</th>
<th>Degradation rate constant, $k$ (d$^{-1}$)</th>
<th>Unavailability coefficient, $a$</th>
<th>Half-life, $t_{1/2}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hanford sandy loam</td>
<td>10°C</td>
<td>10%</td>
<td>0.0102 ± 0.0003</td>
<td>0.0006 ± 0.0002</td>
<td>67.9</td>
</tr>
<tr>
<td>Hanford sandy loam</td>
<td>30°C</td>
<td>10%</td>
<td>0.0346 ± 0.0023</td>
<td>0.0124 ± 0.0026</td>
<td>23.0</td>
</tr>
<tr>
<td>Hanford sandy loam</td>
<td>20°C</td>
<td>5%</td>
<td>0.0230 ± 0.0022</td>
<td>0.0043 ± 0.0008</td>
<td>32.2</td>
</tr>
<tr>
<td>Hanford sandy loam</td>
<td>20°C</td>
<td>15%</td>
<td>0.0237 ± 0.0017</td>
<td>0.0040 ± 0.0009</td>
<td>31.1</td>
</tr>
<tr>
<td>Hanford, manure amended</td>
<td>20°C</td>
<td>10%</td>
<td>0.2219 ± 0.0077</td>
<td>0.0712 ± 0.0086</td>
<td>3.5</td>
</tr>
<tr>
<td>Hanford, manure amended, sterilized</td>
<td>20°C</td>
<td>10%</td>
<td>0.2066 ± 0.0124</td>
<td>0.1072 ± 0.0168</td>
<td>4.2</td>
</tr>
<tr>
<td>Atwater loamy sand, organic matter removed</td>
<td>20°C</td>
<td>10%</td>
<td>0.0151 ± 0.0015</td>
<td>0.0048 ± 0.0013</td>
<td>51.7</td>
</tr>
<tr>
<td>Madera loam, organic matter removed</td>
<td>20°C</td>
<td>10%</td>
<td>0.0155 ± 0.0033</td>
<td>0.0051 ± 0.0009</td>
<td>50.6</td>
</tr>
<tr>
<td>Hanford sandy loam, 7 mg kg$^{-1}$†</td>
<td>20°C</td>
<td>10%</td>
<td>0.0944 ± 0.0091</td>
<td>0.0019 ± 0.0005</td>
<td>7.4</td>
</tr>
<tr>
<td>Hanford sandy loam, 22 mg kg$^{-1}$†</td>
<td>20°C</td>
<td>10%</td>
<td>0.0375 ± 0.0047</td>
<td>0.0031 ± 0.0007</td>
<td>19.0</td>
</tr>
<tr>
<td>Hanford sandy loam, 74 mg kg$^{-1}$†</td>
<td>20°C</td>
<td>10%</td>
<td>0.0198 ± 0.0029</td>
<td>0.0081 ± 0.0010</td>
<td>41.1</td>
</tr>
</tbody>
</table>

† Application rate of MeI; if not specified, the application rate was 49 mg kg$^{-1}$.
factors influencing Mel degradation (Paired t test, \( P > 0.12 \)), consistent with previous studies evaluating 1,3-D degradation (Guo et al., 2004b). It has been reported, however, that Mel degradation does vary in different types of OM-containing soils. For example, Gan and Yates (1996) studied degradation of Mel in a loamy sand (OM 25.1 g kg\(^{-1}\)), a sandy loam (OM 9.2 g kg\(^{-1}\)), and a clay loam soil (OM 29.9 g kg\(^{-1}\)). In that study, Mel degradation followed pseudo first-order kinetics in all test soils; however, the half-life differed significantly, ranging from 11 to 43 d. However, based on our results, the differences in half-life were probably caused by soil organic components, not by differences in texture and mineralogy.

**The Effect of Chemical Application Rate**

In moist Hanford sandy loam at 20°C, Mel degradation kinetics differed as a function of application rate (Fig. 7). The degradation reactions were well described by the availability-adjusted first-order model (Eq. [3]). However, the degradation rate constant increased, while the unavailability coefficient decreased as the application rate was reduced (Table 3). When the application rate was increased from 7 to 74 mg kg\(^{-1}\), the half-life of Mel rose from 7.4 to 41.1 d (Table 3). It is commonly accepted that organic compounds degrade in water and soil generally following the pseudo first-order kinetics, in which the degradation rate constant is independent of the initial concentration. However, degradation of fumigant chemicals including Mel in soil reflects a combination of microbiological processes, chemical reactions with soil constituents, and hydrolysis (Gan and Yates, 1996; Zheng et al., 2003), as impacted by chemical partitioning to the aqueous, vapor, and sorbed phases. Therefore, fumigant degradation may significantly deviate from the pseudo first-order kinetics, and the initial concentration will influence the overall apparent degradation rate in soil because of shifts in reactant availability, microbial activity, and phase partitioning. Furthermore, the molar ratio of Mel to reactive OM functional groups in a closed soil system will definitely change with application rate. At higher application rates, the microbial activity will be more severely suppressed.

The significant effect of application rate on fumigant degradation in soil has been reported previously. For example, Ma et al. (2001) observed that the 1,3-D degradation rate in soil was highly dependent on the initial concentration. In another example, Wang et al. (2006) reported that degradation of sulfdimethoxine in a silt loam obeyed the availability-adjusted first order kinetics, and both the degradation rate constant and the unavailability coefficient decreased with increasing Mel. Considering that the application rate influences atmospheric emission and soil degradation of fumigants, Mel and other chemicals should be applied at the lowest rate that achieves satisfactory pest control. However, the effective rate of Mel degradation will differ from soil to soil.

**Conclusions**

The effect of various environmental factors on Mel degradation in soil was investigated using laboratory incubation experiments. Reacting with soil OM via nucleophilic substitution was the principal pathway for Mel degradation. The degradation kinetics could be described by the availability-adjusted first-order decay model, while the degradation rate was chiefly con-
trolled by soil OM and temperature. When MeI was applied at 49 mg kg⁻¹ to a Hanford sandy loam containing 0.9 g kg⁻¹ organic carbon, the chemical degraded slowly, demonstrating a half-life of 32 d at 20°C. Decreasing the temperature to 10°C or elevating it to 30°C resulted in shifting the half-life to 68 or 23 d, respectively. Organic matter greatly facilitated MeI degradation. Soil texture, mineralogy, and moderate moisture content had little influence on MeI degradation. Microbial decomposition was suppressed for the first 2 wk following application. However, soil degradation of MeI was application rate-dependent: the overall degradation slowed down as the initial application rate increased. To reduce atmospheric volatilization and groundwater contamination, fumigation should be conducted at a minimum disinfection-effective application rate considering the differences between soil properties, especially OM content and temperature. Furthermore, amendment with organic residues at the soil surface is recommended to minimize atmospheric emissions.

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References


