Journal of Environmental Quality TECHNICAL REPORTS

VADOSE ZONE PROCESSES AND CHEMICAL TRANSPORT

# Water and Methyl Isothiocyanate Distribution in Soil after Drip Fumigation

Shad D. Nelson, Husein A. Ajwa,* Tom Trout, Mary Stromberger, Scott R. Yates, and Shankar Sharma

Methyl isothiocyanate (MITC) generators, such as metam sodium (Met-Na), are used for soil fumigation of agricultural land. The ban on the fumigant methyl bromide has resulted in greater use of MITC generators. To understand the efficacy of MITC, it is necessary to assess its generation and disappearance kinetics when Met-Na is applied to soil. This study evaluated the movement of water and distribution and dissipation of MITC in soil after application of Met-Na through surface drip irrigation systems. The effects of varying water application volume (25, 50, and 75 mm) and rate (1.9, 5.0, and 7.5 L $h^{-1}$ $m^{-1}$) were evaluated in a sandy loam soil. Good fumigant distribution within the sandy loam soil was observed under medium water application amount (50 mm) with slow to intermediate drip application rates (1.9–5.0 L $h^{-1}$ $m^{-1}$). Low water application amount (25 mm) or high application rate (7.5 L $h^{-1}$ $m^{-1}$) did not provide adequate MITC distribution throughout the soil bed width and rooting depth. Dissipation patterns of MITC in soil in all water application amounts and rates followed first-order kinetics, with a rate constant of 0.025 ± 0.004 $h^{-1}$ and a half-life of 27 ± 3 h. Simulated water distribution through the soil profile using HYDRUS 2D/3D fitted measured field data well, and the model accurately simulated MITC fumigant distribution in the soil.

Methyl bromide (MeBr) has been used as a preplant soil fumigant for over 40 yr due to its wide spectrum of activity against plant pathogens and weeds (Ajwa et al., 2012). Methyl bromide is commonly used for high-value horticulture crops (e.g., tomatoes, strawberries, peppers, melons, grapes, and ornamentals) and in nurseries (Ristaino and Thomas, 1997). The USEPA determined that MeBr is a Class I Stratospheric Ozone Depleting Substance, and under provisions of the U.S. Clean Air Act its manufacture has been phased out except for critical uses (USEPA, 2013; Ristaino and Thomas, 1997). Before 2001, approximately 20,000 t of MeBr were applied annually to soils in the United States, which made it one of the most frequently used pesticides in the country. Intensive research has been conducted to evaluate alternatives to MeBr (Ajwa et al., 2002, 2003, 2012; Gamliel et al., 1998). The majority of effective alternatives to MeBr are volatile and semivolatile compounds that disperse throughout the soil profile to control weeds and plant pathogens. One alternative is metam sodium (Met-Na), formulated as 42% sodium N-methyl dithiocarbamate in water, which degrades rapidly in moist soil to produce the volatile chemical methyl isothiocyanate (MITC) (chemical structure $S{=}C{=}N\text{-}CH_3$), which controls many soil-borne pests (Gerstl et al., 1977; Smelt et al., 1989). The physical properties of MITC in the soil are typically less than a 5 d half-life, Henry's constant of 0.011, vapor pressure of 2.8 kPa, and water solubility of 76 g $L^{-1}$ at 20°C (Ajwa et al., 2003). Metam sodium is used to control agricultural pests such as weeds, nematodes, fungi, and other plant disease pathogens (Ben-Yephet and Frank, 1985; Duniway, 2002; McGovern et al., 1998). Metam sodium is the most widely used soil fumigant in California, with over 7000 t applied to soils in 2011 (Segawa, 2012). Metam sodium is ranked first among all pesticides in total usage for US agricultural production, with an estimated annual use of 25000 metric tons (USEPA, 2007).

Metam sodium has typically been applied to the soil surface through overhead irrigation systems or directly injected into the soil through hollow shanks (Gan et al., 1998, 2000; Nelson et

J. Environ. Qual. 42:1555–1564 (2013)
doi:10.2134/jeq2013.03.0072
Received 1 Mar. 2013.

*Corresponding author (haajwa@ucdavis.edu).

---

S.D. Nelson, Dep. of Agronomy & Resource Sciences, Texas A&M Univ.-Kingsville, MSC 228, Kingsville, TX 78363; H.A. Ajwa and S. Sharma, Dep. of Plant Sciences, Univ. of California-Davis, 1636 E. Alisal St., Salinas, CA 93905; T. Trout, USDA–ARS, Water Management Research Unit, Fort Collins, CO 80526-8119; M. Stromberger, Dep. of Soil and Crop Sciences, Colorado State Univ., C127 Plant Sciences Bldg., Ft. Collins, CO 80523; S.R. Yates, USDA–ARS, U.S. Salinity Lab., Riverside, CA 92507.

Assigned to Associate Editor Garey Fox.

**Abbreviations**: 1,3-D, 1,3-dichloropropene; Met-Na, metam sodium; MITC, methyl isothiocyanate.

al., 2002; Noling and Becker, 1994). These application methods are under scrutiny because it has been shown that typical soil injection or sprinkler application can result in excessive soil fumigant release into the atmosphere (Nelson et al., 2001; Roberts et al., 1988; Saeed et al., 2000; Sullivan et al., 2004). Application of Met-Na through drip irrigation systems can be more economical and environmentally friendly in comparison to conventional shank injection and chemigation (Ajwa and Trout, 2004; Schneider et al., 1995; Shaw and Larson, 1999). Changes in fumigant application methods, such as deeper soil application or surface water sealing, can reduce chemical application rates and lower the amount of fumigant released to the atmosphere (Gao and Trout, 2007; Sullivan et al., 2004). Drip fumigation may not only minimize off-gassing of MITC but may also allow the grower to better distribute the application within the targeted rooting zone of the plant (Ajwa and Trout, 2004; Threadgill, 1995). This could result in lower chemical use and decreased human exposure to potentially toxic volatile compounds.

Drip fumigation is a relatively new soil water and chemical management practice. Its rapid adoption in the industry for some high-value crops has been tremendous: one-half of the strawberry production fields in California were drip fumigated in the past 3 yr. Scattered information is available on the behavior and movement of fumigants, such as MITC, in soil when applied via drip irrigation tubing (Ajwa et al., 2003). Studies have shown that excess amounts of water affect fumigant diffusion in soils (Sullivan et al., 2004). Because the rate of fumigant degradation in the soil is concentration dependent (Ma et al., 2001), it is important to know the drip irrigation rate and the chemical dose concentration in the soil after drip fumigation. Kim et al. (2003) demonstrated the importance of the amount of irrigation water needed to apply fumigants to reduce volatilization losses. They showed that drip application near the soil surface with a relatively low water application rate results in rapid fumigant transport to the soil surface, which can cause large flux shortly after application. Their results suggest that fumigants must be applied at sufficient depths when the application water is low to prevent rapid fumigant volatilization from the soil surface.

Numerical computer simulation models can be an effective method of evaluating optimal drip management strategies (Meshkat et al., 1999; Schmitz et al., 2002). Wang et al. (2000) conducted a modeling study using a two-dimensional finite element code CHAIN_2D (Šimůnek and van Genuchten, 1994) to simulate the distribution of 1,3-dichloropropene (1,3-D) concentration in the soil profile after drip fumigation and shank injection of the fumigant into a sandy loam soil. Their results indicated that computer simulation can be used effectively to describe the transport of 1,3-D in drip fumigation, especially when vapor phase diffusion and liquid phase convection are the dominant transport mechanisms. They also found that the model simulation underpredicted 1,3-D dissipation, possibly due to gas phase convection transport, which may occur immediately after shank application.

Metam sodium is a water-soluble liquid and differs from other fumigants such as 1,3-D, chloropicrin, or MeBr, which are volatile and semivolatile compounds. The generation of the volatile MITC in soil starts immediately after application of Met-Na (Smelt and Leistra, 1974), and the distribution of the generated MITC in the soil depends largely on the application method and environmental conditions (Ajwa et al., 2003). Therefore, the efficacy of drip-applied Met-Na depends on the movement (distribution) and residence time of the generated MITC in soil. To strategize effective application of Met-Na and best utilization of MITC, it is necessary to understand its fate in soil under various drip fumigation conditions. Our studies were conducted (i) to evaluate the effect of the amount and rate of water application on water and MITC distribution in the soil profile after drip fumigation with Met-Na, (ii) to determine MITC dissipation kinetics in soil, and (iii) to compare HYDRUS 2D/3D model simulations of water and MITC distribution in soil to field measurements. The simulation was conducted only for MITC. No attempt was made to simulate Met-Na transformation because it efficiently (e.g., >92%) and quickly converts to MITC (tens of minutes) under the study conditions (Zheng et al., 2006).

## Materials and Methods

### Field Experiments

Drip fumigation studies were conducted on a Hanford sandy loam soil (coarse-loamy, mixed, thermic Typic Durizeralfs) at the San Joaquin Valley Agricultural Sciences Center, a USDA-ARS research station located at Parlier, California. This soil (620, 270, 110, and <10 g kg$^{-1}$ sand, silt, clay, and organic matter, respectively) was selected to represent sandy loam soils that are dominant in drip-irrigated fields in the California Central Valley. The soil was slip plowed to 1.5 m to eliminate compacted layers, chiseled to 0.3 m, and disked. Soil beds were formed (height 0.15 m), and one drip tube (RO-DRIP Tape, Roberts Irrigation Products, Inc.) with 16 mm inside diameter and 0.2 mm wall thickness was placed approximately 0.03 m below the soil surface at the center of a 0.9-m-wide and 30.5-m-long bed. The beds were covered with a 0.025-mm-thick, high-density polyethylene mulch.

Two studies were conducted to evaluate the effects of varying drip irrigation amount and application rate on water and MITC distribution in the soil profile. Drip application parameters and time required for each application are shown in Table 1. In all tests, 0.93 kg of Vapam HL (42% Met-Na, AMVAC) was applied uniformly throughout the application period to each 30.5-m-long bed (equivalent to 356 L ha$^{-1}$ Vapam [150 L Met-Na ha$^{-1}$]). In the first set of tests, Met-Na was applied with 22.5, 45, and 67.5 L m$^{-1}$ water (equivalent to 25, 50, or 75 mm of water applied to the 0.9-m-wide beds) at a constant water application rate using a 3.0 L h$^{-1}$ m$^{-1}$ drip tape with 0.30-m emitter spacing. The actual concentrations of Vapam in water were 1433, 717, and 478 mg L$^{-1}$ for the 25-, 50-, or 75-mm water treatments, respectively (Table 1). In the second set of tests, the Vapam was applied in 50 mm water (717 mg Vapam L$^{-1}$) through drip tapes of varying flow rates (1.9, 5.0, and 7.5 L h$^{-1}$ m$^{-1}$ with 0.30, 0.20, and 0.10 m drip emitter spacing, respectively).

Soil-water content and soil-air MITC concentration was monitored for 5 d after drip fumigation. Soil water content at various depths was measured every 5 min using calibrated Sentek EnviroSCAN RT6 capacitance-type water sensors (SENTEK Sensor Technologies). Figure 1 shows water content under

**Table 1. Drip fumigation treatments.**

| Application treatment† | Drip tape rate | Emitter spacing | Water amount‡ | Application duration | MITC§ concentration |
|---|---|---|---|---|---|
| | L h$^{-1}$ m$^{-1}$ | cm | mm | h | mg L$^{-1}$ |
| Amount | | | | | |
| Low | 3.0 | 30 | 25 | 3.79 | 1433 |
| Medium | 3.0 | 30 | 50 | 7.59 | 717 |
| High | 3.0 | 30 | 75 | 11.38 | 478 |
| Rate | | | | | |
| Slow | 1.9 | 30 | 50 | 12.00 | 717 |
| Intermediate | 5.0 | 20 | 50 | 4.55 | 717 |
| Fast | 7.5 | 10 | 50 | 3.03 | 717 |

† Each treatment received 473 g a.i. of metam sodium.

‡ Fifty millimeters water corresponds to 0.66 m$^3$.

§ Methyl isothiocyanate.

the drip tape (bed center) before and after drip application of 75 mm water. Data collected with SENTEK sensors were used to calculate the change in volumetric soil water content immediately before drip application, at the end of each application and before drip application, and at 24 h after starting any application. Soil-air MITC concentrations were measured by collecting 50 mL of soil air through stainless steel soil-air sampling probes (1.0 mm inner diameter) spaced 0.05 m apart and inserted to various depths (0.0, 0.1, 0.2, 0.3, 0.4, and 0.6 m from the soil surface), with equivalent sets of sampling probes located at bed center, half way to the bed edge (0.2 m), and at the edge of the bed. Duplicate sets of probes were placed near the tape emitters and between emitters along the bed. Soil-air samples were taken at the end of each application and at 24, 48, 72, and 96 h after the start of drip fumigation.

Soil-air MITC gas samples were taken by drawing 50 mL of air through ORBO-32 charcoal cartridges (Sigma-Aldrich) using a 50-mL air-tight syringe. The cartridges were immediately sealed and stored on dry ice until placed in a −20°C freezer. The MITC was extracted from the cartridges by emptying charcoal into 11.2-mL glass vials, adding 5 mL ethyl acetate, and crimp sealing with aluminum seals with grey Teflon–coated butyl septa. The vials were shaken for 1 h and allowed to settle for 1 h, and then the solvent supernatant (1 mL) was pipette transferred into 2-mL amber glass gas chromatography vials and cap sealed. Analysis of MITC was performed using a split/splitless Agilent 6890 series gas chromatograph system equipped with an Agilent 5973N mass selective detector and a Zebron ZB-624 column (30-m × 0.25 mm inner diameter × 1.4 μm film thickness) for volatile compound separation. The total gas chromatography flow rate was 56.7 mL min$^{-1}$ using He carrier gas and $N_2$ makeup gas. The injector temperature was 140°C, and the oven temperature program was 45°C for 2 min, increased 15°C min$^{-1}$ to 140°C, and held for 0.5 min.

## Numerical Modeling

The computer software package HYDRUS 2D/3D (Šimůnek et al., 2007), which is a Windows-operated software based on the same basic algorithms as CHAIN 2D software, was used to simulate water and MITC movement in two-dimensional, variably saturated porous media. This software was used to numerically solve Richards' equation by using a Galerkin type linear finite element computation for saturated and unsaturated flows considering a vertical grid (2.0 m depth, 0.60 m width; drip emitter located at 0 and 0.03 m) to represent water and fumigant distribution in one half of the soil bed profile. The drip tape application was treated as a line source with the two-dimensional plane oriented perpendicular to the tape. Fitting the model requires specific hydraulic input parameters (saturated water content [$\theta_s$], residual water content [$\theta_r$], saturated hydraulic conductivity [$K_s$], and shape parameters [$\alpha$ and $n$])] and initial volumetric water content ($\theta$) distribution in the soil profile. The initial water distribution within the bed before irrigation was measured with gravimetric soil water content samples (oven dried at 104°C for 24 h) and converted to volumetric water content using a bulk density of 1500 kg m$^{-3}$. The soil properties, boundary conditions, and hydraulic parameters in this study were described earlier by Skaggs et al. (2004) to model water movement from a drip line source on the same soil type at the same research plots. The following hydraulic parameters, estimated using the pedotransfer function software program ROSETTA (Schaap et al., 2001), were used: $\theta_r = 0.021$, $\theta_s = 0.34$, $K_s = 1.6$ cm h$^{-1}$, $n = 1.4$, and $\alpha = 0.023$ cm$^{-1}$. During water and Met-Na application, the drip tubing had a constant water flux ($q$) boundary condition that was calculated based on the measured water application rate of 1.9 L h$^{-1}$ m$^{-1}$ (or 3.0, 5.0, or 7.5 L h$^{-1}$ m$^{-1}$) and a modeled drip tube surface area:

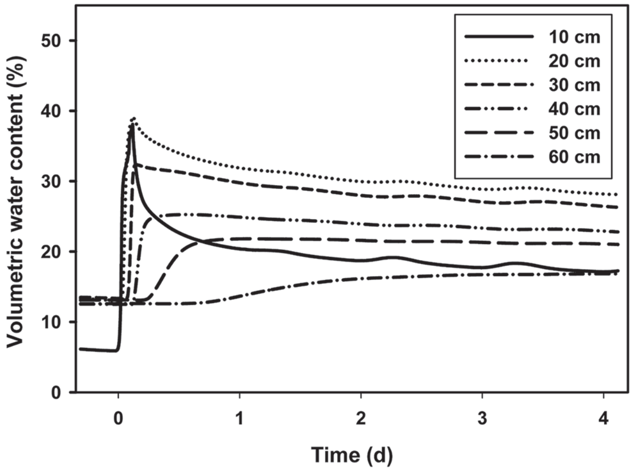

**Fig. 1. Volumetric soil-water content (%) at various depths (10, 20, 30, 40, 50, and 60 cm) under the drip tape as measured by Sentek ENVIROSCAN water sensors.**

$$q = \text{flow rate/surface area} = 1900\ \text{cm}^3\ \text{h}^{-1}/2\pi(1\ \text{cm})(100\ \text{cm}) = 3.025\ \text{cm h}^{-1} \quad [1]$$

The Met-Na was assumed to be uniformly mixed in the water and applied at a constant rate throughout the water application period using a flux boundary condition at the drip tape. At the end of water application, the flux boundary condition at the drip tube became zero, and the MITC concentration was based on 100% conversion of Met-Na. The simulation included a volatilization boundary condition at the soil surface, which used the default value for the boundary layer thickness (0.5 cm) (Jury et al., 1983). A free drainage boundary condition was assumed for the lower boundary at a depth of 2 m, and all other boundaries were assumed to be zero flux conditions due to the effects of symmetry.

# Results

## Varying Water Application Amount

The initial volumetric soil water content at different depths in the profile before irrigation was approximately 6% in the upper 10 cm and ranged between 12 and 14% at all other depths for all studies (Fig. 1). The change in water content and MITC concentrations for one half of the soil bed at the end of each application and 24 h after starting drip fumigation for the various water application amounts (low, medium, and high or 25, 50, and 75 mm water) applied at a constant rate (3.0 L $\text{h}^{-1}$ $\text{m}^{-1}$) are shown in Fig. 2. The contours in the measured profiles were drawn using a kriging interpolation algorithm using Sigmaplot (Sigmaplot ver. 10, Systat Software, Inc.). The low application amount of 25 mm water led to uniform water distribution from the drip line (Fig. 2a). The discrete wetting front was due to the low hydraulic conductivity of the dry soil and is commonly observed during wetting of relatively dry soil. Redistribution of water in the soil profile occurred rapidly within 24 h (Fig. 2b). The low water application amount resulted in high concentrations of MITC (>1100 μg $\text{L}^{-1}$ air) below the drip line, and chemical redistribution followed water distribution contour lines. However, a low concentration (<100 μg $\text{L}^{-1}$ air) of MITC was measured at the edge of the soil bed 24 h after drip fumigation. These results indicate that the generation of MITC was very fast and that most of the MITC was generated within the application period.

The application of the medium water amount (50 mm) showed a greater distribution of water throughout the soil profile at the end of application (Fig. 2c) and after 24 h from starting the application (Fig. 2d). Although the highest concentration of the MITC (1200 μg $\text{L}^{-1}$ air) was generated directly beneath the drip tape, much of the soil profile was subjected to at least 100 μg MITC $\text{L}^{-1}$ air at the end of application. Large MITC concentrations remained in the soil profile after water redistribution 24 h later.

The high (75 mm) water amount resulted in the greatest distribution of water throughout the soil profile (Fig. 2e and 2f). The measured MITC concentration (1100 μg $\text{L}^{-1}$ air) at the end of application under the drip tape was not as high as that measured for the 50-mm water application amount treatment. Although the concentration of Met-Na in the irrigation water was the least (478 mg MITC $\text{L}^{-1}$) with the largest water application treatment (75 mm) (Table 1), the concentration of the generated MITC in the soil air space at 20 and 40 cm from the drip tape was greatest (300 μg $\text{L}^{-1}$ air) (Fig. 2f). Greater concentrations of fumigants in soil with 50 and 75 mm than with 25 mm water application were possibly due to (i) slower generation of MITC from Met-Na with larger water applications, (ii) slower partitioning of the generated MITC into the soil-air phase, and (iii) slower diffusion of MITC away from the wetted soil zone due to less total air space. These studies indicate that low application water amount may result in large volatilization losses to the atmosphere and poor soil-borne pathogen and weed control across the sandy loam soil beds when using a single drip tape. Although water moved below a 60-cm depth with high (75 mm) water application amount (Fig. 2f), very little MITC was detected below the 40-cm depth. These results suggest that MITC does not move downward as far as the infiltrating water and therefore should not cause groundwater contamination. This also indicates difficulty in treating deep soil layers with water-applied Met-Na.

## Varying Drip Tape Flow Rate

The effect of drip tape flow rate on water transport and MITC dissipation in soil was evaluated using a fixed amount (150 L $\text{ha}^{-1}$) of Met-Na applied in a fixed amount (50 mm) of water (constant concentration, 682 mg Met-Na $\text{L}^{-1}$) through slow (1.9 L $\text{h}^{-1}$ $\text{m}^{-1}$), intermediate (5.0 L $\text{h}^{-1}$ $\text{m}^{-1}$), and fast (7.5 L $\text{h}^{-1}$ $\text{m}^{-1}$) flow rate drip tapes (Table 1). In this soil, water flow rate through the slow (0.30 m emitter spacing) and intermediate rate (0.20 m emitter spacing) tapes did not exceed soil hydraulic conductivity and resulted in a nonsaturated soil profile and in relatively uniform water distribution patterns within the bed (Fig. 3a–3d). In these treatments, gravitational and matric potential (capillary) forces resulted in uniform water distribution in the soil profile. Although water distribution was similar between the slow and intermediate rate applications, the MITC was more widely distributed with the slow flow drip tape than with the intermediate flow tape (Fig. 3a and 3c), possibly due to slower MITC generation over a longer application time (Table 1).

Application of water through a fast flow rate tape with small spacing (0.10 m) between emitters resulted in a saturated zone below the drip tape. This resulted in an increase in gravitational water flow, leading to the least amount of lateral soil water and Met-Na movement in the bed soil profile (Fig. 3e). The fast application rate also resulted in lower MITC concentrations in the soil profile 24 h after irrigation (500 μg MITC $\text{L}^{-1}$ air) (Fig. 3f), in comparison to slow and medium rates (900 and 700 μg MITC $\text{L}^{-1}$ air) (Fig. 3b and 3d, respectively). The generation of MITC may have occurred in this saturated zone, which resulted in faster MITC volatilization losses because high water content under the drip line acted as a barrier to downward MITC movement. The physicochemical properties and environmental fate of Met-Na have been summarized previously (CDPR, 2002, 2004). Although the hydrolysis of Met-Na and MITC in water depends largely on pH and temperature (CDPR, 2004), the conversion rate of Met-Na to MITC is very rapid in moist soil and is usually completed within 1 to 7 h after application (Smelt and Leistra, 1974; Gerstl et al., 1977).

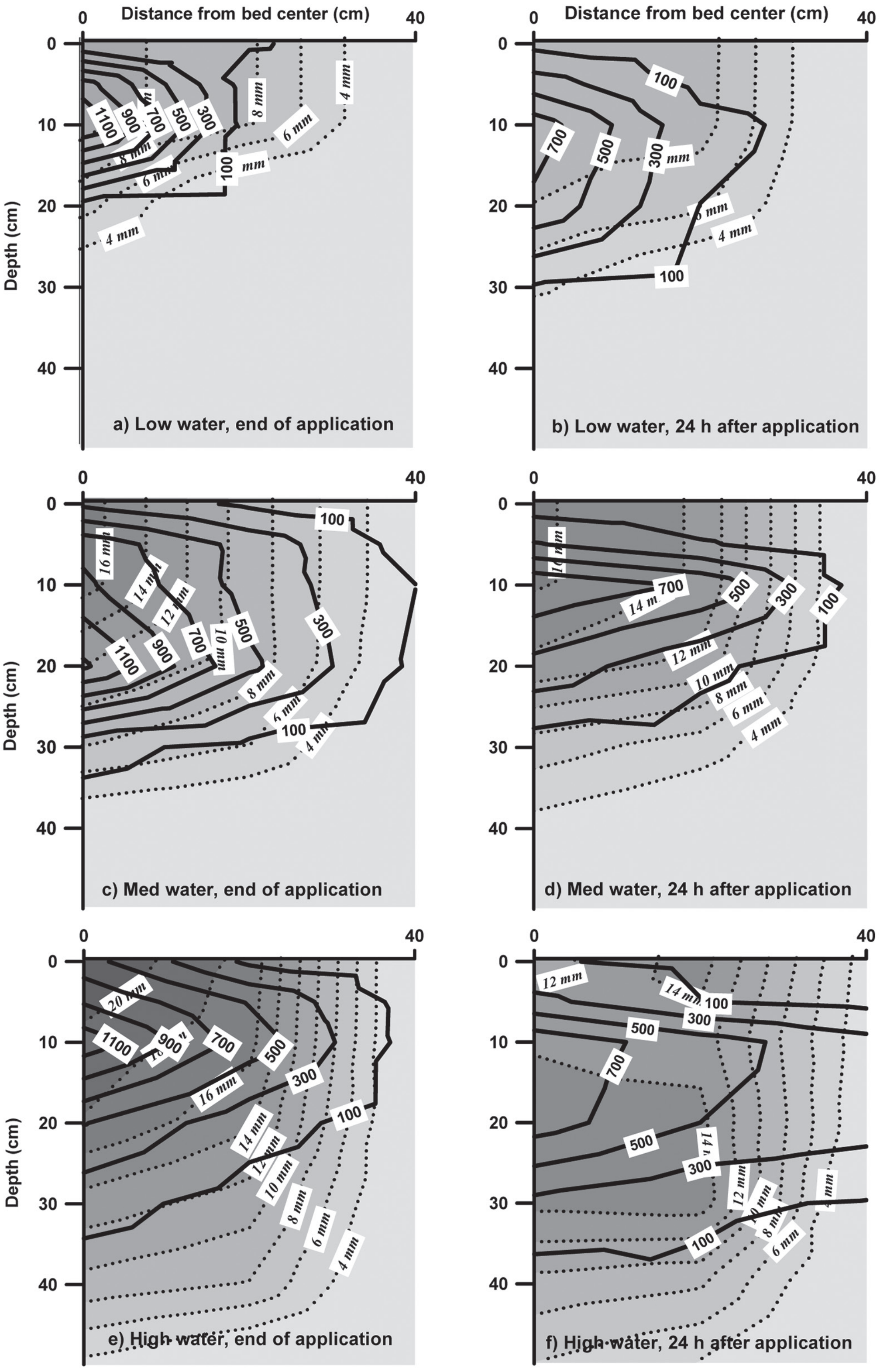

Fig. 2. Change in volumetric soil-water content (%) and concentration distribution of methyl isothiocyanate (µg L$^{-1}$ air) at the end of application and 24 h after starting metam sodium application to soil beds through a 3.0 L h$^{-1}$ m$^{-1}$ drip tape using various water application amounts: 25 mm (a and b), 50 mm (c and d), and 75 mm (e and f). Solid lines represent methyl isothiocyanate concentration (µg L$^{-1}$ air); dotted lines represent change in soil water content (mm).

## Kinetics of Methyl Isothiocyanate Dissipation

To better compare the various treatments in terms of total MITC resident in the soil and potential volatilization losses, MITC concentrations were numerically integrated across a soil bed width of 90 cm to a soil depth of 60 cm. The effects of varying water application amount and rate on the total amount of MITC in the soil-air are shown in Fig. 4a and 4b, respectively. The low irrigation amount resulted in the least total amount

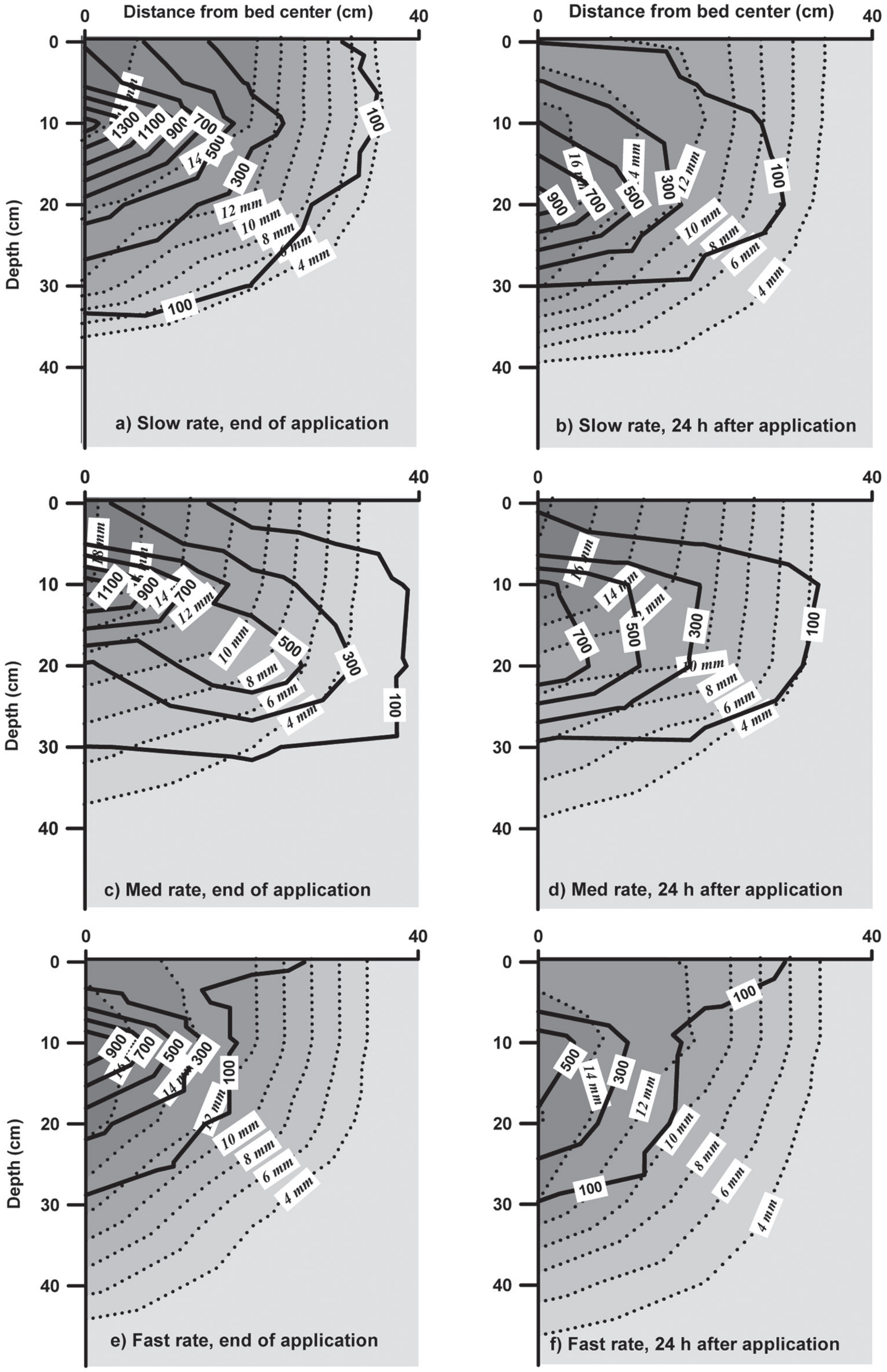

**Fig. 3. Change in volumetric soil-water content (%) and concentration distribution of methyl isothiocyanate (μg L$^{-1}$ air) at the end of application and 24 h after starting Met-Na application in 50 mm water to soil beds at various water application rates: 1.9 L h$^{-1}$ m$^{-1}$ drip rate (a and b), 5.0 L h$^{-1}$ m$^{-1}$ drip rate (c and d), and 7.5 L h$^{-1}$ m$^{-1}$ drip rate (e and f). Solid lines represent methyl isothiocyanate concentration (μg L$^{-1}$ air); dotted lines represent change in soil water content (mm).**

of MITC in the soil, suggesting that this amount of water was not sufficient to prevent rapid MITC volatilization losses through the soil surface (Fig. 4a). The medium and high water application amounts resulted in higher MITC concentrations (nearly twice that observed from low water amount) within the soil profile, with the highest weighted average MITC concentrations occurring from the 75 mm water application treatment. Although this amount of MITC would most likely control soil-borne pathogens, residual MITC levels in the soil could also delay crop planting due to potential phytotoxicity effects to desired plants.

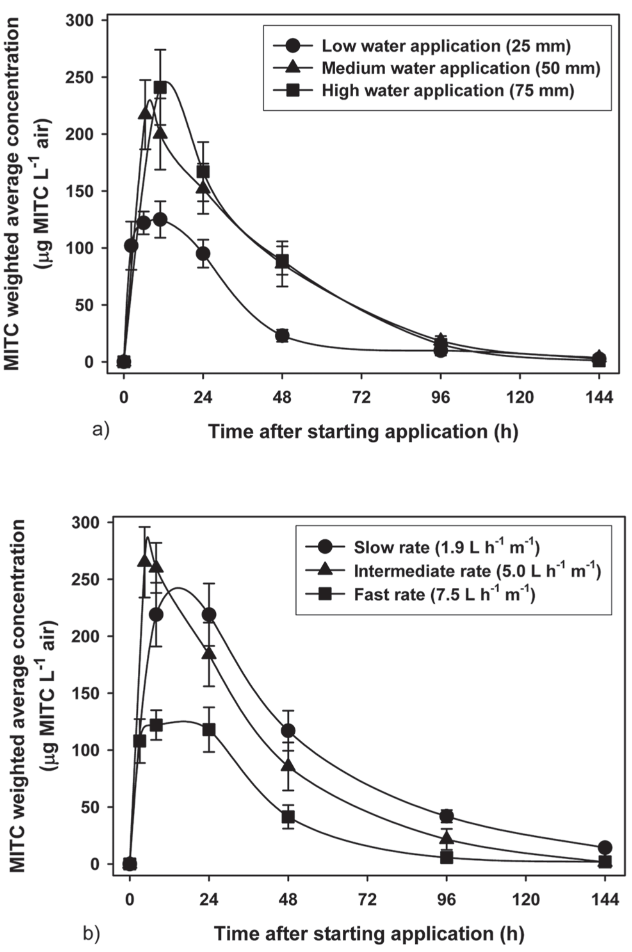

**Fig. 4. Weighted average concentrations of methyl isothiocyanate (MITC) in the soil-air phase for varying water application amounts (25, 50, and 75 mm) and drip fumigation rates (1.9, 5.0, and 7.5 L h$^{-1}$ m$^{-1}$).**

In the varying drip application rate experiment, the fast rate resulted in approximately one half the soil gas MITC amount found in the slow and intermediate water application rates (Fig. 4b). This suggests higher volatilization loss of MITC, potentially increased bystander and worker exposure, and decreased soil pest control with fast application rates. Our studies estimated that volatilization losses of MITC from the fast rate or low amount of application water is greater than 40% relative to the amount applied (~60% of Met-Na is converted to MITC). These results indicate that fast rate or low application water amount may result in large volatilization losses to the atmosphere and poor efficacy to control soil pests and weeds when using a single drip tape and standard polyethylene tarp. The effective dose, ΣConcentration × Time (ΣC × T), was estimated by integrating the area under the curve for the various treatments in Fig. 4. Assuming Henry's constant of 0.011, the effective MITC dose for Met-Na application in the fast rate or high amount is not sufficient to reduce major soil pest viability (except for nematodes) by 90% when compared with values obtained by other studies (Klose et al., 2008). However, the calculated dose for the other treatments was sufficiently high to control many of the soil pests reported by Klose et al. (2008). The concentrations in Fig. 4 are averages over the soil profile and may not reflect the actual dose at each depth.

## Numerical Modeling

Water infiltration and redistribution and MITC formation, distribution, loss, and degradation of MITC in the soil air space within one-half of the soil bed were simulated using HYDRUS 2D/3D. Skaggs et al. (2004) found good prediction of water distribution in a Hanford sandy loam using HYDRUS, but its performance at predicting fumigant distribution were not evaluated. The model predicted that the generation of MITC was rapid and reached the concentration maxima within 6 h, followed by a slow exponential decay (dissipation). The field data generally agreed with this trend (Fig. 4a and 4b). Kinetic parameters for MITC dissipation in a sandy loam soil used in computer simulation assessments are shown in Table 2. The MITC dissipation values shown in this table that are not in parentheses were generated using the field measured data (Fig. 4) based on first-order kinetics of MITC dissipation from the soil over time using the following equation:

$$C = C_o \times \exp(-kt) \qquad [2]$$

where $C$ is the MITC concentration (μg L$^{-1}$ air) at time (h), $C_o$ is the predicted potential MITC concentration (μg L$^{-1}$air), and $k$ is the rate constant (h$^{-1}$). The kinetic parameters in parentheses in Table 2 are computer-generated values. The MITC degradation pattern for all irrigation application amounts and rates followed first-order kinetics having a rate constant ($k$) of 0.025 ± 0.005 h$^{-1}$ and a half-life of 27 ± 3 h. There was close conformity between experimental data and the predicted model parameters ($P$ = 0.01), with high $R^2$ values ranging from 0.88 to 0.99.

To evaluate HYDRUS 2D/3D in fitting distribution data of water content and MITC in the gas phase across the soil profile,

**Table 2. Kinetic parameters† for methyl isothiocyanate dissipation in soil.**

| Application treatment | $C_o$ | k | $t_{1/2}$ | $R^2$ |
|---|---|---|---|---|
| | μg L$^{-1}$ | h$^{-1}$ | h | |
| Amount | | | | |
| Low | 160 (207) | 0.029 (0.028) | 24 (25) | 0.94 (0.99) |
| Medium | 258 (305) | 0.024 (0.028) | 29 (25) | 0.99 (0.99) |
| High | 331 (550) | 0.029 (0.028) | 24 (29) | 0.99 (0.99) |
| Rate | | | | |
| Slow | 276 (213) | 0.023 (0.026) | 30 (26) | 0.95 (0.99) |
| Intermediate | 305 (429) | 0.025 (0.027) | 28 (25) | 0.99 (0.99) |
| Fast | 137 (420) | 0.021 (0.030) | 29 (23) | 0.88 (0.99) |

† Values in parentheses were calculated from the predicted concentrations by the HYDRUS 2D/3D model. All other values were calculated from actual field measurements shown in Fig. 4.

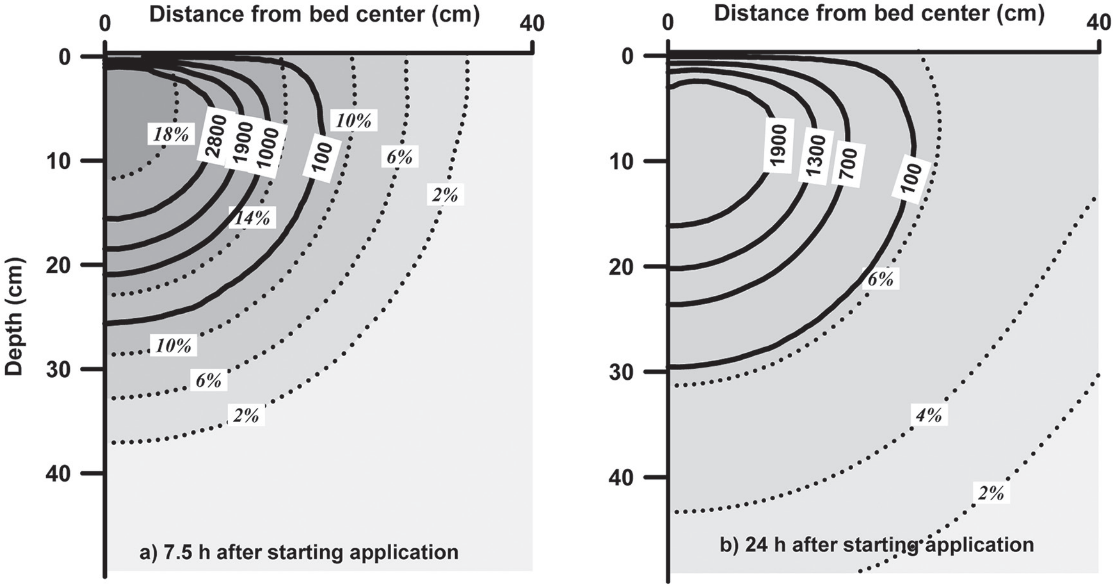

**Fig. 5. Computer-simulated water and fumigant distribution in soil after applying 50 mm water using HYDRUS 2D/3D. Solid lines represent methyl isothiocyanate concentration (μg L$^{-1}$ air); dotted lines represent change in soil water content (mm).**

simulations of each irrigation treatment were run. As a case example, simulated contour graphs for the intermediate water application rate (5.0 L h$^{-1}$ m$^{-1}$) are shown in Fig. 5. Our studies found that HYDRUS 2D/3D was able to simulate water and MITC movement reasonably well (data not shown).

## Discussion

Variability in pest control when using Met-Na is believed to result from inadequate distribution of MITC within the soil profile, especially for sandy soils (Nelson et al., 2004; Candole et al., 2007). A better understanding of how Met-Na moves in the soil water phase when applied by drip irrigation lines is necessary to predict MITC distribution within the soil bed at concentrations required to provide adequate pest control throughout the growing season. The distribution of volatile chemicals in the soil profile after application through drip irrigation lines is influenced by many factors, such as chemical properties (e.g., solubility, effective vapor pressure, and degradation rate), temperature, soil water content, and soil texture and porosity (Ajwa et al., 2002; Frick et al., 1998). Although Met-Na has a higher solubility than other soil fumigants, its distribution in soil is also dependent on its ability to move through the soil matrix (Gerstl et al., 1977) and how rapidly it converts to MITC. The soil type and application method affect how well it is distributed.

Our results indicate that the water application amount must exceed 25 mm in sandy loam soils to get sufficient lateral movement of the water and chemical to treat a typical planting bed. Even though high water application amounts result in a lower concentration of Met-Na in the irrigation water, the better distribution of water seems to improve MITC distribution. High water amounts may require long irrigation periods to prevent soil sloughing off the sides of the raised bed (Ajwa and Trout, 2004). High water amounts in the soil may also lead to a longer delay before planting to avoid phytotoxicity problems.

The fast application rate (7.5 L h$^{-1}$ m$^{-1}$) of water resulted in high soil water contents near the drip tape, which appeared to increase downward gravitational water flow such that lateral water movement and MITC distribution across the width of the bed was reduced. Moderate to slow water application rates allowed capillarity to induce greater lateral movement. Although water percolated past 60 cm under the fast application rate, MITC did not penetrate beyond the 30-cm depth, suggesting that Met-Na does not completely move with the water front or that Met-Na converts rapidly to MITC under high soil water content. Reduced vertical distribution reduces the risk of groundwater contamination but also reduces soil treatment in the lower soil profile. The concentration of MITC also decreased more rapidly within the treated zone, indicative of the high water-filled pore space restricting downward chemical movement and increased chemical flux into the atmosphere.

Candole et al. (2007) measured MITC concentrations in the soil gaseous phase after application of Met-Na through one drip tape into raised sandy loam soil. They found that the greatest MITC concentration (400–500 μg MITC L$^{-1}$ air) was at 10 to 20 cm below the drip tape, and a very small amount (20 μg MITC L$^{-1}$ air) was detected at 20 cm away from the drip tape. In their study, however, the amount of water (34 mm) used to apply Met-Na was insufficient for lateral movement of water and Met-Na in a 0.8-m-wide soil bed. In addition, water moves more vertically than laterally in sandy and loamy sand soils, and multiple drip tapes are needed for good distribution of fumigants in wide soil beds. The findings in our study showed that, for a sandy loam soil, a moderate water application amount (50 mm) and rate (3.0–5.0 L h$^{-1}$ m$^{-1}$) of irrigation through a single drip tape placed at the center of the bed should be adequate for water and MITC to permeate an 0.8-m-wide planting bed to a depth of 0.4 m. Greater MITC concentrations in the soil profile with higher water application amount (50 and 75 mm) or with slow to intermediate (1.9–5.0 L h$^{-1}$ m$^{-1}$) application rates may be due to (i) slower generation rate of MITC from Met-Na, (ii) slower release of MITC from water, and (iii) slower diffusion of MITC away from the wetted soil zone.

The $C_o$ values at $t = 0$ differed between the model prediction and field measurements, especially at low amount of water or fast application rate. Except for the slow application rate, $C_o$ values calculated from the modeled data were greater than values obtained from the actual measurements. In another study, Ma et al. (2001) reported that first- and half-order kinetics described the MITC degradation ($R^2 > 0.78$), and the rate constant ($k$) varied with variation in $C_o$. In their study, the concentration effect was ignored. In our study, the discrepancy in $C_o$ values between the model prediction and field measurements could be due to the fact that the plastic polyethylene film used in this study to cover the soil surface was permeable, and a portion of generated MITC may have escaped into the atmosphere before sampling. This would lead to lower measured $C_o$ values. The model prediction does not account for such volatilization losses that contribute to the soil dissipation process. When the modeled initial concentrations were excluded, the modeled data accurately predicted the soil degradation rate constant.

Computer modeling can be a valuable tool to predict how well drip-applied fumigants move in soil systems and if fumigant distribution is adequate to provide the necessary dose and time needed for pest control. Wang et al. (2000) used the two-dimensional finite model CHAIN_2D (Šimůnek and van Genuchten, 1994), which is based on the same algorithms as HYDRUS 2D software, to simulate 1,3-D concentration and distribution in the soil profile after subsurface drip application and its subsequent release into the atmosphere. They observed that this model simulated 1,3-D behavior well when applied via drip irrigation lines but underpredicted 1,3-D emissions when applied by shank injection, possibly due to gas flow through the chisel traces. Our attempt to simulate water movement and volatile chemical phase movement of MITC in the soil profile using HYDRUS 2D/3D led to reasonable agreement between computer simulation and field measurements.

Our study showed that water application rate and the amount of water applied during drip fumigation influence the distribution of Met-Na, its subsequent degradation and release of the soil fumigant MITC, and the distribution of MITC in the soil. Drip tapes with high application rate ($7.5\ \mathrm{L\ h^{-1}\ m^{-1}}$) or low water application amounts (25 mm) provided the poorest MITC distribution throughout the soil bed width and rooting depth in Hanford sandy loam soil.

## References

Ajwa, H.A., and T. Trout. 2004. Preplant drip application of alternative fumigants to methyl bromide for strawberry production. HortScience 39:1707–1715.

Ajwa, H.A., T. Trout, J. Mueller, S. Wilhelm, S.D. Nelson, R. Soppe, and D. Shatley. 2002. Application of alternative fumigants through drip irrigation systems. Phytopathology 92:1349–1355. doi:10.1094/PHYTO.2002.92.12.1349

Ajwa, H.A., S. Klose, S.D. Nelson, A. Minuto, M.L. Gullino, F. Lamberti, and J.M. Lopez-Aranda. 2003. Alternatives to methyl bromide in strawberry production in the United States of America and in the Mediterranean region. Phytopathol. Mediterr. 42:220–244.

Ajwa, H.A., W. Ntow, R. Qin, and S. Gao. 2012. Properties of soil fumigants and their fate in the environment. In: R. Krieger, editor, Hayes handbook of pesticide toxicology. Vol. 1. 3rd ed. Elsevier, New York.

Ben-Yephet, Y., and Z.R. Frank. 1985. Effect of soil structure on penetration by metam-sodium and of temperature on concentrations required to kill soilborne pathogens. Phytopathology 75:403–406. doi:10.1094/Phyto-75-403

California Department of Pesticide Regulation (CDPR). 2002. Evaluation of methyl isothiocyanate (MITC) as a toxic air contaminant: Part A. Environmental fate. Environmental monitoring and pest management branch. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/mitc/augfinl02/augparta.pdf (accessed 23 July 2013).

California Department of Pesticide Regulation (CDPR). 2004. Metam sodium (sodium N-methyldithiocarbamate), risk characterization document. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA. http://www.cdpr.ca.gov/docs/risk/rcd/metam.pdf (accessed 23 July 2013).

Candole, B.L., A.S. Csinos, and D. Wang. 2007. Distribution and efficacy of drip-applied metam-sodium against the survival of Rhizoctonia solani and yellow nutsedge in plastic-mulched sandy soil beds. Pest Manag. Sci. 63:468–475. doi:10.1002/ps.1363

Duniway, J.M. 2002. Status of chemical alternatives to methyl bromide for pre-plant fumigation of soil. Phytopathology 92:1337–1343. doi:10.1094/PHYTO.2002.92.12.1337

Frick, A., B.J. Zebarth, and S.Y. Szeto. 1998. Behavior of the soil fumigant methyl isothiocyanate in repacked soil columns. J. Environ. Qual. 27:1158–1169. doi:10.2134/jeq1998.00472425002700050022x

Gamliel, A., A. Grinstein, L. Klien, Y. Cohen, and J. Katan. 1998. Permeability of plastic films to methyl bromide: Field study. Crop Prot. 17:241–248. doi:10.1016/S0261-2194(98)00004-0

Gan, J., S.R. Yates, D. Wang, and F.F. Ernst. 1998. Effect of application methods on 1,3-dichloropropene volatilization from soil under controlled conditions. J. Environ. Qual. 27:432–438. doi:10.2134/jeq1998.00472425002700020026x

Gan, J., S.R. Yates, F.F. Ernst, and W.A. Jury. 2000. Degradation and volatilization of the fumigant chloropicrin after soil treatment. J. Environ. Qual. 29:1391–1397. doi:10.2134/jeq2000.00472425002900050004x

Gao, S., and T.J. Trout. 2007. Surface seals reduce 1,3-dichloropropene and chloropicrin emissions in field tests. J. Environ. Qual. 36:110–119. doi:10.2134/jeq2006.0107

Gerstl, Z., U. Mingelgrin, and B. Yaron. 1977. Behavior of vapam and methylisothiocyanate in soils. Soil Sci. Soc. Am. J. 41:545–548. doi:10.2136/sssaj1977.03615995004100030024x

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: 1. Model description. J. Environ. Qual. 12:558–564. doi:10.2134/jeq1983.00472425001200040025x

Kim, J.-H., S.K. Papiernik, W.J. Farmer, J. Gan, and S.R. Yates. 2003. Effect of formulation on the behavior of 1,3-dichloropropene in soil. J. Environ. Qual. 32:2223–2229. doi:10.2134/jeq2003.2223

Klose, S., H.A. Ajwa, G.T. Browne, K.V. Subbarao, F.N. Martin, S.A. Fennimore, and B.B. Westerdahl. 2008. Dose response of weed seeds, plant-parasitic nematodes, and pathogens to twelve rates of metam sodium in a California soil. Plant Dis. 92:1537–1546. doi:10.1094/PDIS-92-11-1537

Ma, Q.L., J. Gan, S.K. Papiernik, J.O. Becker, and S.R. Yates. 2001. Degradation of soil fumigants as affected by initial concentration and temperature. J. Environ. Qual. 30:1278–1286. doi:10.2134/jeq2001.3041278x

McGovern, R.J., C.S. Vavrina, J.W. Noling, L.A. Datnoff, and H.D. Yonce. 1998. Evaluation of application methods of metam sodium for management of fusarium crown and root rot in tomato is southwest Florida. Plant Dis. 82:919–923. doi:10.1094/PDIS.1998.82.8.919

Meshkat, M., R.C. Warner, and S.R. Workman. 1999. Modeling of evaporation reduction in drip irrigation system. J. Irrig. Drain. Eng. 125:315–323. doi:10.1061/(ASCE)0733-9437(1999)125:6(315)

Nelson, S.D., C. Riegel, L.H. Allen, Jr., D.W. Dickson, J. Gan, S.J. Locascio, and D.J. Mitchell. 2001. Volatilization of 1,3-dichloropropene in Florida plasticulture and effects on fall squash production. J. Am. Soc. Hortic. Sci. 126:496–502.

Nelson, S.D., S.J. Locascio, L.H. Allen, Jr., D.W. Dickson, and D.J. Mitchell. 2002. Soil flooding and fumigant alternatives to methyl bromide in tomato and eggplant production. HortScience 37:1057–1060.

Nelson, S.D., D.W. Dickson, H.A. Ajwa, and D.A. Sullivan. 2004. Efficacy of metam sodium under drip and surface spray application in Florida tomato production. Subtropical Plant Sci. 56:16–20.

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

Ristaino, J.B., and M.W. Thomas. 1997. Agriculture, methyl bromide, and the ozone hole: Can we fill the gaps? Plant Dis. 81:964–977. doi:10.1094/PDIS.1997.81.9.964

Roberts, P.A., A.C. Magyuarosy, W.C. Matthews, and D.M. May. 1988. Effects of metam-sodium applied by drip irrigation on root-knot nematodes, *Pythium ultimum* and *Fusarium* spp. in soil and on carrot and tomato roots. Plant Dis. 72:213–221. doi:10.1094/PD-72-0213

Saeed, I.A.M., D.I. Rouse, and J.M. Harkin. 2000. Methyl isothiocyanate volatilization from fields treated with metam-sodium. Pest Manag. Sci. 56:813–817. doi:10.1002/1526-4998(200009)56:9<813::AID-PS205>3.0.CO;2-M

Schaap, M.G., F.J. Leij, and M.Th. van Genuchten. 2001. ROSETTA: A computer program for estimating soil hydraulic properties with hierarchical pedotransfer functions. J. Hydrol. 251:163–176. doi:10.1016/S0022-1694(01)00466-8

Schmitz, G.H., N. Schutze, and U. Petersohn. 2002. New strategy for optimizing water application under trickle irrigation. J. Irrig. Drain. Eng. 128:287–297. doi:10.1061/(ASCE)0733-9437(2002)128:5(287)

Schneider, R.C., R.E. Green, J.D. Wolt, R.K.H. Loh, D.P. Schmitt, and B.S. Sipes. 1995. 1,3-dichloropropene distribution in soil when applied by drip irrigation or injection in pineapple culture. Pestic. Sci. 43:97–105. doi:10.1002/ps.2780430202

Segawa, R. 2012. California regulatory update for fumigants. California EPA, Department of Pesticide Regulation. http://mbao.org/2012/Segawa.pdf (accessed 23 July 2013).

Shaw, D.V., and K.D. Larson. 1999. A meta-analysis of strawberry yield response to preplant soil fumigation with combination of methyl bromide-chloropicrin and four alternative systems. HortScience 34:839–845.

Šimůnek, J., and M.Th. van Genuchten. 1994. The CHAIN_2D code for simulating the two-dimensional movement of water, heat, and multiple solutes in variably-saturated porous media. Research Rep. 136, Version 1.1. U.S. Salinity Laboratory, USDA–ARS, Riverside, CA.

Šimůnek, J., M. Šejna, and M.Th. van Genuchten. 2007. The HYDRUS software package for simulating the two- and three-dimensional movement of water, heat and multiple solutes in variably-saturated media. User Manual, Version 1.02. PC Progress, Prague, Czech Republic.

Skaggs, T.H., T.J. Trout, J. Šimůnek, and P.J. Shouse. 2004. Comparison of HYDRUS-2D simulations of drip irrigation with experimental observations. J. Irrig. Drain. Eng. 130:304–310. doi:10.1061/(ASCE)0733-9437(2004)130:4(304)

Smelt, J.H., and M. Leistra. 1974. Soil fumigation with dichloropropene and metham-sodium: Effect of soil cultivations on dose patterns. Pestic. Sci. 5:419–428. doi:10.1002/ps.2780050407

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

Sullivan, D.A., M.T. Holdsworth, and D.J. Hlinka. 2004. Control of off-gassing rates of methyl isothiocyanate from the application of metam-sodium by chemigation and shank injection. Atmos. Environ. 38:2457–2470. doi:10.1016/j.atmosenv.2004.02.002

Threadgill, E.D. 1995. Safe use and calibration of irrigation systems for chemigation. In: K.D. Hickey, editor, Methods for evaluating pesticides for control of plant pathogens. The American Phytopathological Society, St. Paul, MN. p. 45–49.

USEPA. 2007. Pesticide industry sales and usage: 2006–2007 Pesticide market estimates. http://www.epa.gov/pesticides/pestsales/07pestsales/usage2007_2.htm (accessed 23 July 2013).

USEPA. 2013. US Environmental Protection Agency. 2013. The phaseout of methyl bromide: Critical use exemption. http://www.epa.gov/ozone/mbr/cueinfo.html (accessed 23 July 2013).

Wang, D., J.A. Knuteson, and S.R. Yates. 2000. Two-dimensional model simulation of 1,3-dichloropropene volatilization and transport in a field soil. J. Environ. Qual. 29:639–644. doi:10.2134/jeq2000.00472425002900020035x

Zheng, W., S.R. Yates, S.K. Papiernik, and J. Nunez. 2006. Conversion of metam sodium and emission of fumigant from soil columns. Atmos. Environ. 40:7046–7056. doi:10.1016/j.atmosenv.2006.06.009