Sensitivity Analysis of Soil Fumigant Transport and Volatilization to the Atmosphere

Interest in the use of vadose zone transport models for fumigant risk assessment is increasing. Good modeling practice includes an assessment of model sensitivity and output uncertainty. This computational study evaluated the sensitivity of HYDRUS-1D- and HYDRUS 2D/3D-simulated fumigant cumulative flux, maximum 6-h period mean flux density, and soil gas concentrations to 15 model input variables using Monte Carlo Latin hypercube analysis. The input variables included fumigant physicochemical properties, agricultural film (tarp) properties, and soil properties. Three different application scenarios were investigated: tarped broadcast, tarped bedded shank injection, and a tarped drip line-source application. Model sensitivity to initial water content ($θ_i$), saturated water content ($θ_s$), and tarp permeability varied among scenarios depending on the relative importance of soil gas diffusive resistance and tarp mass transfer resistance to fumigant volatilization. Model outputs were sensitive to fumigant air–water partition and gas-phase diffusion coefficients, two parameters that probably have a small contribution to overall modeling uncertainty because accurate estimation methods for these parameters are available. Sensitivities to the fumigant degradation rate were high in all scenarios, and sensitivity to tarp permeability was high only when substantial volatilization occurred from the tared portion of soil surfaces. Existing literature data for both degradation and tarp permeability are highly variable; parameterizing these processes using literature estimates may contribute substantially to model uncertainty. In several cases, the highest output sensitivities were to $θ_i$. For model comparisons to site-specific field data, soil texture-based estimates of $θ_i$ are potentially large contributors to model uncertainty; direct measurement is recommended.

Soil fumigants accounted for >20% of the 65 million kg of pesticide active ingredients applied in 2009 California production agriculture. Application rates are on the order of 100 kg ha$^{-1}$ and methods vary, including broadcast subsurface shank injection at 25- to 60-cm depths, bedded shank injection, and chemigation applications through surface and subsurface drip irrigation systems. Agricultural plastic films ("tarps") are usually used to cover the soil surface, either partially or completely, to reduce fumigant volatilization into the atmosphere.

Volatile organic compound emissions, including those from fumigants, are regulated in areas of California that do not meet ozone air quality standards because they are ozone precursors (Marty et al., 2010). Post-application emissions vary by fumigant and application method, and are quantified by the cumulative flux or emission ratio (cumulative flux/fumigant applied). Peak emissions are used to estimate off-site air concentrations, which in turn serve as the basis for buffer zones to limit bystander exposure (Sullivan et al., 2004). Agronomists concerned with efficacy typically evaluate soil gas concentrations and their persistence in the soil profile (Ha et al., 2009).

Field studies to estimate fumigant flux are expensive and generally yield uncertain flux estimates (Majewski, 1997; Ross et al., 1996; Wang et al., 2006; Sullivan et al., 2004). Interest in fumigant transport modeling is increasing, and several models have been used to estimate laboratory- and field-scale fumigant transport and volatilization from soils, including CHAIN-2D (Šimůnek and van Genuchten, 1994), HYDRUS-1D (Šimůnek et al., 2008a), HYDRUS 2D/3D (Šimůnek et al., 2011), and HWC-MODEL (Ha et al., 2009). The governing equations and associated boundary conditions for simultaneous solution of transient water flow and convective–dispersive transport of heat and solute are quite similar among most vadose zone transport models. Critical aspects of simulating fumigant transport in the vadose zone, however, also include the strong temperature dependence of tarp permeabilities (Papiernik et al., 2011), post-application tarp perforation and subsequent removal,
and the requirement for two volatilization boundary conditions in situations where only a portion of the field is covered by a tarp. Both HYDRUS-1D (Šimůnek et al., 2008a) and HYDRUS 2D/3D (Šimůnek et al., 2011) simulate tarp dynamics, while HYDRUS 2D/3D also simulates dual surface volatilization boundary conditions and complex field geometries in two or three dimensions. Several recent studies have used the HYDRUS models or their legacy DOS-based precursor CHAIN-2D to describe fumigant transport (Luo et al., 2012; Yates et al., 2012; Luo et al., 2011; Yates, 2009; Cryer and van Wesenbeeck, 2009, 2010).

Sensitivity analysis is a basic component of model evaluation (Crout et al., 2008; Warren-Hicks et al., 2002; van den Berg et al., 2008). Ha et al. (2009) evaluated the sensitivity of 1- and 2-d methyl isothiocyanate soil gas concentrations to temperature-dependent partitioning and degradation parameters in a study of tarped raised beds. The degradation rate was more important than Henry’s Law constant or the gas-phase diffusion coefficient in that study. Cryer and van Wesenbeeck (2010) evaluated the sensitivity of cumulative flux to various parameter groups using the legacy model CHAIN-2D for a single application scenario. They concluded that soil water content and tarp properties were among the most important parameters controlling cumulative flux based on rank correlations between inputs and outputs. Neither study provided detailed sensitivities of multiple output variables in multiple application scenarios.

The objectives of this study were to: (i) determine quantitative sensitivities of HYDRUS-1D- and HYDRUS 2D/3D-simulated fumigant cumulative flux, period mean flux densities, and soil gas concentrations to 15 key model inputs in three application scenarios, (ii) interpret those sensitivities from a mechanistic standpoint, and (iii) qualitatively evaluate potential sources of uncertainty in the model output based on the sensitivity analysis. These results will inform sampling strategies for designed studies to compare field-based and model-simulated flux estimates and facilitate interpretation of simulation results.

Methods Overview

Two analyses were conducted in this computational study. A preliminary analysis evaluated the sensitivity of the fumigant effective gas-phase diffusion coefficient in soil \( D_{\text{eff}} \) (Eq. [6] below) and the effective soil–air surface boundary layer mass transfer coefficient \( K_{\text{MTC}} \) (Eq. [8] below) to seven variables (Table 1) using a Monte Carlo Latin hypercube sensitivity analysis method. This preliminary analysis aided interpretation of the relative importance of diffusive resistance vs. surface mass transfer resistance to post-application fumigant volatilization in the second full sensitivity analysis.

The second analysis used the Latin hypercube method to evaluate the relative sensitivity of 50-d cumulative flux, maximum 6-h average flux density (\( \mu g \text{ cm}^2 \text{ d}^{-1} \)), and maximum shallow soil gas concentration (\( \mu g \text{ cm}^{-3} \)) to 15 input variables. The input variables included fumigant physicochemical properties, properties of the tarp, soil properties, and amplitude of soil surface diurnal temperature fluctuations (Table 1). Each application was simulated to occur at 0600 h. Maximum 6-h mean flux densities were determined for post-application periods of 0600 to 1200 h, 1200 to 1800 h, 1800 to 2400 h, etc., such as would be reported for a typical field flux experiment. Three fumigant application scenarios were considered: a fully tarped broadcast application simulated with a one-dimensional modeling domain (broadcast scenario, Fig. 1a), a tarp bedded shank application with untarped furrows simulated with a two-dimensional modeling domain (bed scenario, Fig. 1b), and an under-tarp bedded drip application simulated using a line source representation in a two-dimensional modeling domain (drip scenario) (Fig. 2).

Simulation of Water, Solute, and Heat Transport

Both HYDRUS programs simultaneously solve the Richards equation for variably saturated water flow and the advection–dispersion equations for heat and solute transport. Solutions to those flow and transport equations are solved numerically subject to specified

<table>
<thead>
<tr>
<th>Variable†</th>
<th>Description</th>
<th>Median</th>
<th>Range (min.–max.)</th>
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<tbody>
<tr>
<td>( d )</td>
<td>boundary layer thickness</td>
<td>425</td>
<td>50–800</td>
</tr>
<tr>
<td>( d E_{x} )</td>
<td>boundary layer activation energy</td>
<td>–40,000</td>
<td>–60,000 to –20,000</td>
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<td>( \Delta T )</td>
<td>daily temperature amplitude</td>
<td>12.5</td>
<td>5–20</td>
</tr>
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<td>( D_{g} )</td>
<td>gas-phase diffusion coefficient</td>
<td>8.25</td>
<td>6,500–10,000</td>
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<tr>
<td>( D_{g} E_{x} )</td>
<td>( D_{g} ) activation energy</td>
<td>4,650</td>
<td>4,500–4,800</td>
</tr>
<tr>
<td>( \lambda_{w} )</td>
<td>longitudinal dispersivity</td>
<td>10.5</td>
<td>1–20</td>
</tr>
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<td>( D_{w} )</td>
<td>aqueous-phase diffusion coefficient</td>
<td>0.85</td>
<td>0.7–1.0</td>
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<tr>
<td>( k_{1} )</td>
<td>degradation rate constant</td>
<td>0.36</td>
<td>0.03–0.69</td>
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<tr>
<td>( k_{1} E_{x} )</td>
<td>( k_{1} ) activation energy</td>
<td>52.5</td>
<td>40,000–65,000</td>
</tr>
<tr>
<td>( K_{h} )</td>
<td>air–water partition coefficient</td>
<td>0.15</td>
<td>0.05–0.25</td>
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<tr>
<td>( K_{s} E_{x} )</td>
<td>( K_{s} ) activation energy</td>
<td>30,000</td>
<td>20,000–40,000</td>
</tr>
<tr>
<td>( K_{s} )</td>
<td>( K_{s} ) soil–water partition coefficient</td>
<td>0.206</td>
<td>0.0375–0.375</td>
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<td>( \rho_{v} )</td>
<td>soil bulk density</td>
<td>1.54</td>
<td>1.28–1.80</td>
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<td>( \theta_{i} )</td>
<td>initial soil water content</td>
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<td>0.06–0.20</td>
</tr>
<tr>
<td>( \theta_{s} )</td>
<td>saturated soil water content</td>
<td>0.42</td>
<td>0.30–0.54</td>
</tr>
</tbody>
</table>

† Included in both preliminary sensitivity analyses of effective diffusion coefficient \( D_{\text{eff}} \) and surface mass transfer coefficient \( K_{\text{MTC}} \) and main sensitivity analysis. All others used in main sensitivity analysis only.
boundary conditions using Galerkin-type linear finite elements in one (HYDRUS-1D), two, or three dimensions (HYDRUS 2D/3D) depending on the problem (Šimůnek et al., 2008b). The heat transport equation considers conduction and convection with flowing water, while the solute transport equations consider advective and diffusive–dispersive transport in the liquid phase and diffusion in the gas phase.

For all simulations, the relationship between soil water content ($\theta$) and pressure head ($b$) was

$$
\theta(b) = \theta_s - \frac{\theta_s - \theta_r}{(1 + |\alpha b|^n)^{-1/n}} b < 0
$$

$$
= \theta_s + \alpha b \quad b \geq 0
$$

where $\theta_r$ is the residual water content (cm$^3$ water cm$^{-3}$ bulk soil), $\theta_s$ is the saturated water content, and $\alpha$ (cm$^{-1}$) and $n$ are empirical constants (van Genuchten, 1980).

The Water Linear Reduction gas-phase tortuosity model (Moldrup et al., 2000) was used to describe gas-phase tortuosity, $\tau_g$, in all simulations:

$$
\tau_g = \frac{\theta^2}{\theta_s^2}
$$

where $\theta_s$ in this case represents total porosity and $\alpha_v$ is the air-filled porosity (cm$^3$ air cm$^{-3}$ bulk soil). Tortuosity reduces the effective gas-phase diffusion of a fumigant in soil relative to that in air. Fumigant gas-phase diffusive flux density in the soil is proportional to the spatial concentration gradient:

$$
J = -\alpha_v \tau_g D_g \frac{\partial C_g}{\partial x}
$$

where $J$ is flux density ($\mu$g cm$^{-2}$ d$^{-1}$) in the $x$ direction, $D_g$ is the fumigant diffusion coefficient in air (cm$^2$ d$^{-1}$), and $C_g$ is the fumigant gas-phase concentration ($\mu$g cm$^{-3}$ air), which is related to the total soil fumigant concentration $C_T$ (aqueous + sorbed + gas, $\mu$g cm$^{-3}$ soil) through an equilibrium partition coefficient $R_g$:

$$
C_g = \frac{C_T}{R_g}
$$

$$
R_g = \frac{\rho_b K_d}{K_h} + \frac{\theta_s}{K_h} + \alpha_v
$$

where $K_d$ (mL g$^{-1}$) is the linear equilibrium soil water distribution coefficient, $\rho_b$ is soil bulk density (g cm$^{-3}$), and $K_h$ is the dimensionless air–water partition coefficient. When the spatial gradient in $C_T$ is used in Eq. [3], the corresponding effective fumigant gas-phase diffusion coefficient $D_{eff}$ in bulk soil is obtained by combining Eq. [2–5]:

$$
D_{eff} = \frac{K_h D_g (\theta_s - \theta)^{2.5}}{(\theta_s - \theta^2)^{1.5} \rho_b K_d + \theta_s K_h}
$$

where $\theta$ is soil water content and $\alpha_v$ is assumed equal to $\theta_s - \theta$. The effective diffusion coefficient $D_{eff}$ is applicable to total fumigant concentration and accounts for tortuosity of the air-filled soil pore space, the reduction in cross-sectional area due to the presence of...
the soil solid phase, and fumigant partitioning among the solid, aqueous, and gas phases.

**Boundary Conditions**

Atmospheric water flow boundary conditions (BCs) were applied at the top surface of all modeling domains. The potential flux in that BC is controlled by external specified time-variable precipitation and potential evaporation fluxes (Šimůnek et al., 2011). No precipitation was simulated in any of the scenarios. The potential evaporative flux was set to zero for the tarped portion of each modeling domain, while daily potential evaporation of 6.8 mm was used for the un tarped portion of the soil surfaces. This potential evaporation corresponds to early summer reference evapotranspiration rates in California’s San Joaquin Valley and was simulated between 0700 and 1700 h daily, with the maximum rate between 1000 and 1600 h. For atmospheric BCs, actual evaporation is also determined by a limiting critical pressure head at the soil surface. Below that critical pressure head, actual evaporation is less than potential evaporation. That critical pressure head was defined as the HYDRUS default of −15,000 cm based on preliminary simulations that showed minimal effect of that parameter. At the lower boundary, a unit hydraulic gradient (free drainage) BC was applied in all scenarios.

A stagnant layer volatile solute BC was applied at the top of all modeling domains. That BC describes fumigant surface volatilization flux density, \(J(\mu g \text{ cm}^{-2} \text{ d}^{-1})\) through a boundary of thickness \(d\) (cm) as:

\[
J = \frac{D_g}{d}[C_g(0) - C_g(d)] = k_{\text{MTC}}[C_g(0) - C_g(d)] \tag{7}
\]

where \(C_g(0)\) and \(C_g(d)\) are the solute gas-phase concentrations at the soil surface and at the top of the equivalent boundary layer of thickness \(d\), respectively, and \(k_{\text{MTC}}\) (cm d\(^{-1}\)) is a first-order mass transfer coefficient (Jury et al., 1983). The value of \(C_g(d)\) was assumed equal to zero in all cases. The equivalent boundary layer thickness \(d\) has no physical meaning but represents a mass transfer resistance at the soil surface. Appropriate \(d\) values may be estimated for any fumigant–tarp combination from standard tarp \(k_{\text{MTC}}\) measurements (Papiernik et al., 2011). For un tarped bare soil areas, \(d = 0.5\) cm was assumed (Jury et al., 1983), while \(d\) values ranging up to 800 cm were used to simulate mass transfer resistance in tarped regions based on polyethylene tarp fumigant permeability data (Papiernik et al., 2011). At the bottom of each modeling domain, the solute BC was a Cauchy (third-type) BC, where fumigant flux out of the domain is the product of the fumigant aqueous concentration and water flux.

Combining Eq. [5] and [7] give s the effective mass transfer coefficient \(K_{\text{MTC}}\) applicable to the total fumigant concentration \(C_T\) (Jury et al., 1983):

\[
K_{\text{MTC}} = \frac{k_{\text{MTC}}}{R_g} = \frac{K_g D_g}{d[\rho_b K_d + \theta + (\theta_s - \theta)K_h]} \tag{8}
\]

Soil surface temperature was assumed to vary sinusodially with time:

\[
T(t) = T_0 + \Delta T \sin\left[\pi \left(\frac{2r - 7}{12}\right)\right] \tag{9}
\]

where \(t\) is time (d), \(T_0\) is the average temperature, assumed here to be 25°C, and \(\Delta T\) is the amplitude of the daily fluctuation. Default volumetric heat capacities for soil constituents and default thermal conductivity parameters for sands (Chung and Horton, 1987) were used. The volume fraction of soil mineral components for each simulation was specified as \((1 - \theta_s)\).

The temperature dependence of the diffusion coefficients, air–water distribution constant, degradation rate constant, and boundary layer depth \(d\) were simulated using an Arrhenius-type relationship (Šimůnek et al., 2011):

\[
x_{i,T} = x_{i,T_0} \exp\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \tag{10}
\]

where \(x_{i,T}\) is the value of the desired coefficient at temperature \(T\) (K), \(x_{i,T_0}\) is the value at the reference temperature \(T_0 = 293\) K, \(R\) is the universal gas constant = 8.314 J mol\(^{-1}\) K\(^{-1}\), and \(E_a\) (the “activation energy,” J mol\(^{-1}\)) is the proportionality constant between \(\ln(x_i)\) and the reciprocal temperature. While the various \(E_a\) values in Table 1 are not true activation energies in a chemical thermodynamic sense, the “activation energy” terminology is retained here to maintain consistency with the historical Arrhenius relationship.

**Fumigant Application Scenarios and Initial Conditions**

The geometric configuration of the one-dimensional broadcast, two-dimensional bed, and two-dimensional drip applications, discretization, and initial fumigant concentration conditions are shown in Fig. 1 and 2. Soil profiles were uniform, and the vertical modeling domain depths were arbitrarily chosen as 100 cm based on preliminary simulations that demonstrated little effect of depth on fumigant volatilization flux beyond that value. The initial profile soil temperature in each scenario was taken as the final temperature distribution obtained in 5.25-d preliminary simulations using an average soil temperature of 25°C and an amplitude of 12.5°C (Eq. [9]). In all scenarios, 100 kg ha\(^{-1}\) applications were simulated at 0600 h on Day 1. All simulations were conducted for an arbitrary “long” period of 50 d to ensure complete fumigant volatilization or degradation. Observation nodes were defined in each modeling
domain to obtain simulated soil gas concentrations at the end of each 6-h interval (Fig. 1 and 2). The observation nodes were situated approximately 50 cm away from the region where the fumigant was applied (Fig. 1 and 2). For the bed and broadcast applications, these nodes were near the tarp surface; in the drip scenario, the nodes were below the drip line source. The end-of-simulation fumigant mass balance errors for 1200 simulations in each scenario, expressed as percentage of the initial application, were 0.2, 0.4, and 0.7% (broadcast), 0.7, 1.0, and 1.5% (bed), and 0.7, 1.0, and 1.5% (drip) for the 10th, 50th, and 90th percentile, respectively.

A majority of California fumigant applications occur in sandy loam soils (Johnson and Spurlock, 2009), and average values for the sandy loam texture for residual water content $\theta_r\, (0.039)$, $\alpha\, (0.029\text{ cm}^{-1})$, $n\, (1.45)$ (Schaap et al., 2001), and saturated hydraulic conductivity $K_s\, (106\text{ cm d}^{-1})$ (Carsel and Parrish, 1988) were used in all simulations. Saturated water content $\theta_s$ was varied to determine the model output sensitivity to that variable (Table 1).

In the drip scenario, the fumigant chemigation was simulated with a water application of 288 cm$^2$ during 13.2 h, corresponding to a drip-line water application rate of 4.4 L m$^{-1}$ h$^{-1}$. The application was simulated through a 2.5-cm-diameter line source 1 cm below the soil surface (Fig. 2). The fumigant concentration was 373 μg L$^{-1}$ and the water temperature was 12°C.

**Latin Hypercube Sensitivity Analysis**

Latin hypercube sampling is efficient in obtaining representative samples across the entire input parameter space (McKay et al., 1979). The Latin hypercube sensitivity analysis method used in this study was similar to that reported by van Griensven et al. (2006), originally adapted from the basic method of Morris (1991). For a model output $M$ that is a function of $N$ input parameters $(x_1, ..., x_N)$, a sensitivity index $S_i$ is defined that describes the effect of a perturbation $\Delta x_i$ of model input $x_i$ with the remaining parameters $x_{j \neq i}$ constant:

$$S_i = \frac{M(x_1, ..., x_i + \Delta x_i, ..., x_N) - M(x_1, ..., x_i, ..., x_N)}{M(x_1, ..., x_i + \Delta x_i, ..., x_N) + M(x_1, ..., x_i, ..., x_N)}/2$$  \[11\]

The individual $S_i$s are point estimates of the normalized partial derivative of $M$ with respect to $x_i$, so are local measures of sensitivity. Latin hypercube sampling was used to estimate the mean $S_i$ (denoted here as $\mu_i$) across the entire $N$-dimensional parameter hyperspace. The standard deviation of $S_i\, (= \sigma_i)$ across that same parameter space provides a measure of the interaction between $x_i$ and the other inputs and of the nonlinear effect of $x_i$ on the dependent variable $M$ (Morris, 1991; Saltelli et al., 2005).

The procedure for estimating $\mu_i$ and $\sigma_i$ was to (i) randomly select a single value from each decile of each of the $N$ assumed uniform $x_i$ distributions, (ii) form 10 vectors of input parameters $(x_1, ..., x_N)$ by randomly selecting one $x_i$ without replacement from each sample drawn in the first step, (iii) run the model using each of those 10 $(x_1, ..., x_N)$ input vectors, and (iv) again run the model using each of the 10 input vectors but with the perturbed value $x_i + \Delta x_i$ substituted for $x_i$. Thus, for each $x_i$, 20 model runs were conducted, yielding 10 estimates of $S_i\,$. The perturbations $\Delta x_i$ were taken as ±10% of the base $x_i$ with the sign of the perturbation randomly selected.

For both the preliminary and full sensitivity analyses, a single trial consisted of estimating 10 $S_i$s for each of the input variables (Table 1). Results from four trials were then used to calculate the mean sensitivities $\mu_i$ and standard deviation $\sigma_i$ for each input variable–dependent output variable combination. In the preliminary sensitivity analysis, $D_{\text{eff}}$ (Eq. [6], six input variables) and $K_{\text{MTC}}$ (Eq. [8], seven input variables) were the dependent variables ($M$, Eq. [11]), and that analysis was conducted using a spreadsheet.

In the second main sensitivity analysis, there were 15 input variables $\times$ 20 simulations per variable $\times 300$ HYDRUS simulations per trial for each modeling scenario (broadcast, bed, and drip). The dependent variables were cumulative flux, maximum 6-h flux density, and soil gas concentration.

**Input Variables Evaluated in Sensitivity Analyses**

The preliminary analysis estimated sensitivities $S_i$ of $D_{\text{eff}}$ (Eq. [6]) and $K_{\text{MTC}}$ (Eq. [8]) with respect to $D_{\text{g}}, K_{\text{gt}}, \theta_{\text{br}}, K_{\text{d}}$, $d$, $\theta_s$, and $\theta_{\text{eff}}$ (Table 1), while the second analysis evaluated the sensitivity of HYDRUS outputs to all 15 variables listed in Table 1. Each chemical property input was assigned a uniform distribution based on the approximate ranges of published or estimated data for 1,3-dichloropropene, chloropicrin (trichloronitromethane), methyl bromide, and methyl iodide (Table 1). Ranges for aqueous and gas-phase fumigant diffusion coefficients (Table 1) were based on estimates from the on-line SPARC calculator (http://archemcalc.com/sparc.php, Hilal et al., 2003a, 2003b), while the gas-phase diffusion activation energy was calculated from SPARC $D_{\text{g}}$ estimates as a function of temperature. The range of dimensionless Henry’s Law constants were obtained from the literature (Kim et al., 2003; Glew and Moelwyn-Hughes, 1953; Ruzo, 2006). Henry’s Law activation energies were measured or estimated from enthalpy of vaporization data (USEPA, 2001; Kim et al., 2003; Chickos and Acree, 2003; Glew and Moelwyn-Hughes, 1953). The range of fumigant soil degradation rates were based on the compilation of Dungan and Yates (2003), and the range of degradation activation energies were based on the variation in aerobic degradation rates with temperature reported by Dungan and Yates (2003), Gan et al. (2000), and Guo and Gao (2009). The range for soil water partition coefficients was calculated using organic C normalized soil partition $K_{\text{OC}}$ data from the California Department of Pesticide Regulation pesticide chemistry database of registrant data submisions and the EU FOOTPRINT database (http://sitem.herts.ac.uk/aeru/
footprint/en/), assuming a soil mass fraction organic C of 0.005. While enhanced vapor sorption coefficients have been reported for very dry soil conditions, we assumed this mechanism to be of minor importance in our scenarios due to (i) fumigant label preapplication requirements that specify soil water contents at the 20-cm depth of at least 50% of the available water content, (ii) the presence of a tarp fully or partially covering the soil surface, which minimizes evaporation, (iii) low clay contents of sandy loam soils (<20%), and (iv) the small and nonpolar nature of fumigant molecules, especially methyl bromide, 1,3-dichloropropene, and methyl iodide. These factors reduce sorption enhancement effects (Petersen et al., 1996).

The uniform initial soil water content \( \theta_i \) spanned the approximate range of 50 to 75% of sandy loam water contents at field capacity \( (h = −300 \text{ cm}) \) as calculated from data in the UNSODA database (Leij et al., 1996). The range of saturated water contents and bulk densities were chosen from UNSODA data for sandy loam soils. In the preliminary analysis, the uniform distribution of \( \theta_i \) (Table 1) was used as the sampling distribution for \( \theta \) in Eq. [6] and [8]. The dispersivity maximum and minimum were based on approximate ranges for soil columns and field soils (Radcliffe and Šimůnek, 2010, p. 249–346). The boundary layer depth and activation energy \( d \) and \( dE \) were calculated from the polyethylene tarp permeability data of Papiernik et al. (2011). The upper bound for the daily temperature amplitude of 20°C was based on reported under-tarp field temperature data (Yates et al., 2002).

**Results**

**Initial Sensitivity Analysis of the Gas-Phase Diffusion and Boundary Layer Mass Transfer Coefficients**

The sensitivity analysis of \( D_{\text{eff}} \) (Eq. [6]) and \( K_{\text{MTC}} \) (Eq. [8]) assumed isothermal conditions, so the resulting \( \mu_i \) are only a general guide to the relative importance of input variables to the simulated processes. As expected from Eq. [6] and [8], the respective sensitivities of \( D_{\text{eff}} \) and \( K_{\text{MTC}} \) to \( \rho_b \), \( K_d \), \( \theta_i \), and \( \theta_s \) were identical (Table 2). Sensitivities to \( \rho_b \) and \( K_d \) were essentially identical because these variables only occur together as a product in both Eq. [6] and [8]. The principal differences between \( D_{\text{eff}} \) and \( K_{\text{MTC}} \) were their sensitivities to \( \theta \) and \( \theta_i \), and to \( d \), which only appears in Eq. [8]. Both \( \theta \) and \( \theta_i \) influence fumigant partitioning through the denominator of both equations, but partitioning effects on \( D_{\text{eff}} \) are overshadowed by their role in determining tortuosity. Hence, diffusive transport is particularly sensitive to both \( \theta \) and \( \theta_i \) (Table 2).

**General Comparison of the Modeling Scenarios**

Across all 1200 simulations for each scenario, median 50-d emission ratios for the broadcast, bed, and drip application scenarios were 0.10 (0.02 and 0.33 for the 10th and 90th percentiles, respectively), 0.21 (0.05 and 0.50) and 0.32 (0.17 and 0.61), respectively (Fig. 3a). In the bed scenario, the majority of fumigant volatilization occurred from the untarped portion of the soil surface; the median fraction of total cumulative volatilization from the untarped soil area was 0.90 (0.83 and 0.94 for the 10th and 90th percentiles, respectively). In contrast, the fraction of total volatilization from untarped soil in the drip scenario was only 0.11 (0.02 and 0.28 for the 10th and 90th percentiles, respectively). Maximum 6-h mean flux densities displayed the same trend among scenarios as the emission ratios, with medians of 56 \( \mu g \text{ cm}^{-2} \text{ d}^{-1} \) for the broadcast scenario, 132 \( \mu g \text{ cm}^{-2} \text{ d}^{-1} \) in the bed scenario, and 286 \( \mu g \text{ cm}^{-2} \text{ d}^{-1} \) in the drip scenario (Fig. 3b). Maximum soil gas concentrations were similar among scenarios, with median concentrations of 1 to 2 \( \mu g \text{ cm}^{-3} \) (Fig. 3c).

General differences in temporal flux dynamics and gas concentrations at the observation points among the three application scenarios are illustrated in Fig. 4. These simulations used the median of each input variable (Table 1). For each scenario, the temporal flux patterns across all 1200 simulations were generally similar to those shown in Fig. 4a. In the drip scenario, the maximum 6-h mean flux density always occurred in the afternoon (1200–1800 h) or evening (1800–2400 h) of the day of application, and those fluxes were generally quite high compared with the bed and broadcast scenarios. In the bed scenario, 25% of maximum period mean flux densities occurred during the second (1200–1800 h) period on the day of application, and those fluxes were generally quite high compared with the bed and broadcast scenarios. In the bed scenario, 25% of maximum period mean flux densities occurred during the second (1200–1800 h) period on the day of application, but the majority (60%) were during 0600 to 1200 or 1200 to 1800 h during Day 2. The timing of the maximum period mean flux density in the broadcast scenario was similar to the bed scenario, but the magnitude of those peak fluxes was generally lower (e.g., Fig. 4a).

Gas concentrations at the observation points were “instantaneous” concentrations at the end of each 6-h period. While the drip scenario observation node was located 45 cm below the drip line, these concentrations were generally comparable in magnitude to

<table>
<thead>
<tr>
<th>Variable†</th>
<th>( D_{\text{eff}} )</th>
<th>( K_{\text{MTC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_i )</td>
<td>( \sigma_i )</td>
<td>( \mu_i )</td>
</tr>
<tr>
<td>( d )</td>
<td>−</td>
<td>−0.99</td>
</tr>
<tr>
<td>( \rho_b )</td>
<td>−0.62</td>
<td>0.17</td>
</tr>
<tr>
<td>( K_d )</td>
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<td>0.15</td>
</tr>
<tr>
<td>( \theta_i )</td>
<td>−1.44</td>
<td>0.59</td>
</tr>
<tr>
<td>( \theta_s )</td>
<td>2.62</td>
<td>0.79</td>
</tr>
<tr>
<td>( K_{b} )</td>
<td>0.90</td>
<td>0.09</td>
</tr>
<tr>
<td>( D_{b} )</td>
<td>0.99</td>
<td>0.05</td>
</tr>
</tbody>
</table>

† \( d \), boundary layer thickness; \( \rho_b \), soil bulk density; \( K_d \), soil–water partition coefficient; \( \theta_i \), initial soil water content; \( \theta_s \), saturated soil water content; \( K_{b} \), air–water partition coefficient; \( D_{b} \), gas-phase diffusion coefficient.
the shallow concentrations simulated in the other two scenarios (Fig. 4b). There was a strong diurnal signal in the shallow gas concentrations but much less so in the drip scenario. This was attributable to the lower temperature fluctuations at the deeper depth (Fig. 4c). The simulated concentrations were comparable to shallow gas concentrations measured in field studies when normalized by the application rate (Gao et al., 2008; Gao and Trout, 2007).

Water flow out of the bottom of the profile was generally very low in the broadcast and bed scenarios. In simulations using median input variables, the cumulative water flux at 50 d was 0.035 and 0.038 cm, respectively, the latter being the average flux across the bottom of the bed domain boundary. Deep drainage was higher in the drip scenario, with a cumulative drainage flux of 0.15 cm (average across the bottom domain boundary), and this corresponded to
The importance of diffusion is also indicated by the large negative sensitivities for the drip scenario (Table 3). The mean fraction of eventual total volatilization that occurred in the tarped area. In that scenario, 10% perturbations to either $D_g$ or $K_h$ yielded nearly equivalent percentage changes in cumulative flux for the broadcast and bed scenarios as seen from their respective $\mu_i$ values (Table 3). The high sensitivity of cumulative flux to $\theta_i$ in the broadcast and bed scenarios reflects the importance of diffusive transport in those scenarios. The importance of diffusion is also indicated by the large negative sensitivities of cumulative flux to $\theta_i$ consistent with preliminary sensitivity results for $D_{\text{eff}}$ and $K_{\text{MTC}}$ (Table 2).

Sensitivities for the drip scenario were generally much lower than for the other two scenarios. This was partially attributable to the near-surface application of the drip-applied fumigant directly under the tarp and the corresponding rapid volatilization from the tarped area. The mean fraction of eventual total volatilization that occurred within the first 24 h was 0.54 for the drip application, compared with 0.24 and 0.31 for the broadcast and bed scenarios, respectively. Thus, for the drip scenario, short mean diffusion path lengths and rapid volatilization yielded lower flux sensitivities to diffusion-related variables: $D_g$, $K_h$, $\theta_i$, $\rho_b$, and $K_d$ (Table 3). Initial water content in the drip scenario had only a minor effect on cumulative flux because the post-application water content was dominated by the drip input, similar to the conclusion of Ha et al. (2009). Cumulative flux was sensitive to the degradation rate constant $k_1$ in all scenarios; however, the shorter fumigant soil residence time in the drip scenario noted above contributed to lower $\mu_{d1}$ relative to bed and broadcast applications.

The sensitivity to mass transfer resistance as represented by $d$ (Table 3) varied by application method and was related to the fraction of eventual cumulative volatilization that occurred through the tarping of the profile. In the bedded shank scenario, only a small portion of the volatilization occurred through the tarp. In that scenario, cumulative flux was essentially insensitive to $d$ (Table 3). In contrast, cumulative flux was much more sensitive to $d$ in the drip and broadcast scenarios, where larger fractions of the total cumulative volatilization occurred through tarped surfaces.

<table>
<thead>
<tr>
<th>Input variable†</th>
<th>Broadcast</th>
<th>Bed</th>
<th>Drip</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_i$</td>
<td>$\sigma_i$</td>
<td>$\mu_j$</td>
<td>$\sigma_j$</td>
</tr>
</tbody>
</table>

$g$, gas-phase diffusion coefficient; $k_{i,\text{dry}}$, air–water partition coefficient; $dE_a$, boundary layer activation energy; $D_{E_a}$, $D_g$ activation energy; $K_{i,\text{gas}}$, $K_h$ activation energy; $\Delta T$, daily temperature amplitude; $\lambda_w$, longitudinal dispersivity; $D_w$, aqueous-phase diffusion coefficient; $k_{i,\text{dry}}$, degradation rate constant activation energy; $d$, boundary layer thickness; $\rho_b$, soil bulk density; $K_{i,\text{gas}}$, soil–water partition coefficient; $k_{i,\text{dry}}$, degradation rate constant; $\theta_i$, initial soil water content.
Cumulative flux was relatively insensitive to parameters that control temperature-dependent partitioning and transport (Table 3). This supports previous suggestions that simple isothermal models may be adequate for screening purposes if diurnal flux dynamics are unimportant (Yates et al., 2002). In all scenarios, cumulative flux was insensitive to $D_w$ and $\lambda_w$, variables that describe transport in the aqueous phase.

**Sensitivity of Maximum Six-Hour Mean Flux Density**

While the sensitivities of 6-h mean flux densities were generally similar to those of cumulative flux in many cases, there were some differences. First, sensitivities to $K_d$ and $\rho_h$ in the broadcast and bed applications were somewhat greater. The sensitivities of these two variables were essentially equal because their only computational role in HYDRUS is in phase-partitioning calculations (e.g., Eq. [5]). In this role, they only occur together as a product, hence a fixed percentage perturbation to either $K_d$ or $\rho_h$ has an equivalent effect on all model outputs.

Another difference between cumulative flux and maximum 6-h period mean flux densities was for the variables that control the temperature dependence of air–water partitioning and surface mass transfer resistance, $K_h$, $E_a$, $dE_a$, and $\Delta T$. Higher $K_h$, $E_a$, or $\Delta T$ yielded higher $K_h$, enhancing both effective diffusion (Eq. [6]) and the boundary layer mass transfer coefficient (Eq. [8]). Both effects influence period mean maximum flux density to a greater extent than cumulative flux, for which temperature effects tended to average out. Across scenarios, the maximum period mean flux sensitivity $\mu_{DEa}$ reflected the relative fraction of total volatilization associated with the tarped portion of the surface discussed above. In contrast, the 6-h mean flux density generally displayed low sensitivity to $D_w E_a$; this reflects the relatively weak temperature dependence of $D_w$ (Table 1).

**Sensitivity of Soil Gas Concentrations**

Maximum shallow gas concentrations in the broadcast and bed scenarios displayed generally similar $\mu_i$. In these scenarios, gas concentrations were relatively insensitive to variables solely related to volatile mass transfer across the tarped boundary layer (i.e., $d$ and $dE_a$) but were sensitive to those involved in partitioning ($K_h$, $K_a E_a$, $K_d$, and $\rho_h$) and diffusion ($\theta_i$, $\theta_g$, and $D_w$). In all cases, $k_1$ had a negative effect on maximum shallow gas concentrations.

Soil gas concentrations were generally insensitive to $\Delta T$, largely due to the offsetting effect of temperature-dependent factors that decrease the gas-phase concentration ($k_1$ and $d$) and increase fumigant gas concentrations ($K_h$). Temperature was important, however, in determining the 6-h period in which maximum gas concentrations were observed. In the bed scenario, 99% of maximum gas concentrations occurred in the 0600 to 1200 and 1200 to 1800 h time periods when surface soil temperatures were highest, while 66% of the maximum gas concentrations were similarly observed during the two high-temperature periods in the broadcast scenario. While temperature fluctuations at the 45-cm depth were only about 10% of those at the surface (Fig. 4c), maximum gas concentrations at that depth in the drip scenario also occurred at the higher temperature periods. Seventy-seven percent of maximum gas concentrations occurred during the 1800 to 2400 h time period in that scenario. This was the time of higher soil temperatures at that depth due to the phase lag between surface and subsurface soil temperatures (Fig. 4c).

For the drip application, the dominant mechanism for fumigant transport to the 45-cm depth under the line source was convection in moving water as opposed to diffusion in the gas phase. This was evident from simulation results (not shown) where $D_w$ was set to zero. In those simulations, the median of simulated maximum gas concentrations 45 cm below the drip emitter was only 12% less than in corresponding simulations using identical input variables except with nonzero $D_w$. The role of convective transport in the drip scenario was also shown by the relatively high $\mu_{\lambda_w}$ indicating the contribution of convective–dispersive transport as opposed to gaseous diffusion. In contrast to the broadcast and bed scenarios, maximum gas concentrations had a negative sensitivity to $\theta_i$. This was attributable to a greater volume of water, hence fumigant, moving deep into the profile at low $\theta_i$ (Fig. 5).

**Sensitivity Nonlinearity or Interactions**

In several cases, the $\sigma_i$ were large relative to their corresponding $\mu_i$ (Table 3), reflecting nonlinear effects of variables on model output or interactions between variables. An example of nonlinearity was the sensitivity of the maximum 6-h mean flux density to $\theta_i$ in the bed scenario. The individual $S_{\mu_i}$ were significantly correlated with $\theta_i$ (Spearman $r = -0.74$, $P < 0.001$). Because $S_{\mu_i}$ is essentially the derivative of the model output $M$ with respect to $\theta_i$, it is evident that changes in $\theta_i$ lead to much greater changes in the maximum 6-h mean flux density at higher values of $\theta_i$ (Fig. 6). In contrast, $S_{\mu_k}$ values for maximum 6-h flux density in the drip scenario were only weakly dependent on $K_h$ (Spearman $r = -0.31$, $P = 0.052$) but showed a strong interaction with $d$ (Fig. 7).

Two general trends in nonlinearity or interaction were evident. First, there were significant interactions between $\theta_i$ and $\theta_g$ in the bed and broadcast scenarios, where volatilization was substantially mediated by the rate of diffusive transport. The interactive effect of these variables on flux was evident from significant Spearman correlations between $S_{\mu_i}$ and $\theta_g$, ranging from 0.39 to 0.53. Similarly, the correlations between $S_{\mu_i}$ and $\theta_g$ ranged from 0.41 to 0.46. The interaction is attributable to their joint influence on $D_{\text{eff}}$ (Eq. [6]). A second general result was that, while model outputs in all scenarios displayed a negative sensitivity to the fumigant degradation rate constant $k_1$, the effects were nonlinear. In all scenarios, the $S_{\mu_k}$ values of all model outputs were significantly correlated to the $k_1$ values themselves. Spearman correlations between $S_{\mu_k}$ and...
$k_1$ ranged from $-0.36$ to $-0.87$, indicating a greater negative effect on model outputs for shorter degradation half-lives (higher $k_1$).

**Discussion**

The $\mu_i$ are estimates of the mean normalized partial derivative of model output with respect to each input. While they provide a general indication of variable influence on model output, knowledge of a variable’s uncertainty or variability is also required for a relative assessment of contributions to model output uncertainty. For example, although flux predictions were very sensitive to $D_g$ in some scenarios (Table 3), relatively accurate $D_g$ estimation methods are available (e.g., Hilal et al., 2003a, 2003b; Tucker and Nelken, 1990). Consequently, the overall contribution of $D_g$ to the uncertainty of modeled flux estimates is probably low. Similarly, accurate solubility and vapor pressure measurements should provide relatively accurate $K_h$ estimates, particularly at the milligram per liter aqueous concentration ranges expected in the field (Smith and Harvey, 2007).

Most outputs were very sensitive to $\theta_s$. A common modeling practice is to estimate $\theta_s$ based on soil texture class (Cryer and van Wesenbeeck, 2009; Luo et al., 2012; Yates et al., 2012). Schaap et al. (1998) reported a mean sandy loam $\theta_s$ of 0.389 with a standard deviation of 0.094 ($N = 337$ soils), greater than the 10% perturbation in $\theta_s$ used to estimate sensitivities here. Consequently, uncertainty in $\theta_s$ may contribute substantially to model output uncertainty. In addition to soil-to-soil variations within a texture class, management practices such as cultivation may result in temporal variations in $\theta_s$ within the same soil. Deviations between model predictions obtained using $\theta_s$ estimates may be potentially responsible for large differences between modeled and field-estimated...
fluxes. Alternatively, agreement between model and field-based fluxes may be observed when the model is actually not properly simulating field processes correctly—essentially providing the correct answer for the wrong reasons. In field studies where results are to be used as the basis for modeling, accurate site-specific determination of soil hydraulic properties is strongly preferred.

Model outputs were only moderately sensitive to the equivalent boundary layer $d$ that describes tarp resistance to mass transfer. Tarp mass-transfer coefficients are sometimes highly variable, however, even among similar tarp—chemical combinations. Based on an estimated diffusion coefficient in air of 8899 cm$^2$ d$^{-1}$, we calculated an iodomethane mean $d$ of 1650 cm with a standard deviation of 1450 cm for 22 samples of unused virtually impermeable film (VIF) tarp based on the diffusive resistance data of Papiernik et al. (2011). In addition, the concordance of laboratory-measured permeabilities and actual field permeabilities are poorly understood, particularly given the potential for stretching and tears during application and the potentially high variation of VIF tarp permeability with humidity (Papiernik et al., 2011). Thus, for applications where a large fraction of fumigant volatilization may occur from tarped surfaces (e.g., broadcast or drip), accurate characterization of tarp-specific permeabilities is important. Otherwise uncertainty in $d$ may substantially contribute to uncertainty in model predictions, limiting comparison with field-based flux estimates.

Model outputs were sensitive to degradation rates in all scenarios. Even when measured under well-controlled laboratory conditions, fumigant degradation rates vary substantially with soil type, moisture content, and temperature (Dungan and Yates, 2003). Fumigant degradation is similar to tarp permeability in the sense that the relationship between laboratory and field conditions is poorly understood. Consequently, degradation is potentially a major contributor to simulated estimates of flux in all scenarios.

The output variable sensitivities to the various activation energies that describe temperature dependence were generally low to moderate. For $D_E$ and $K_E$, estimation methods applicable to environmental temperature ranges based on accepted physical chemistry theory are available (Smith and Harvey, 2007; Hilal et al., 2003a, 2003b; Tucker and Nelken, 1990). Obtaining reliable estimates for $K_E$ and $dE_a$ is more difficult. Data for the temperature dependence of lumped degradation coefficients are sparse, although calculations for the limited fumigant aerobic degradation data that are available suggest a relatively narrow range of 40,000 to 65,000 J mol$^{-1}$ for $K_E$ may be reasonable (Dungan and Yates, 2003; Gan et al., 2000; Guo and Gao, 2009). In the case of $dE_a$, the sensitivity of the broadcast maximum 6-h mean flux density was moderate. Data for $dE_a$ are also sparse. Papiernik et al. (2011) measured the temperature dependence of the diffusion resistance across two VIF tarps for several fumigants. Their results showed differences of up to a factor of two. Actual $dE_a$ measurements on the specific tarp–fumigant combination are recommended for site-specific simulations. This is particularly true in cases where a large fraction of volatilization occurs through the tarp (broadcast and drip scenarios) and when period mean flux densities are of primary interest.

Additional factors beyond the 15 variables evaluated here also influence flux and gas concentrations. These include chemical or organic soil amendments (McDonald et al., 2008), water applications (Gao et al., 2008; Gao and Trout, 2007), and the depth of fumigant application (Papiernik et al., 2004). Analysis of these factors was beyond the scope of this study. The sensitivity analysis provides insight into the relative importance of different transport mechanisms under different conditions, however, and will be useful in determining how such mitigation factors can be most efficiently implemented to reduce off-site fumigant air concentrations.

**Conclusion**

Different application scenarios yielded distinctly different sensitivity results. Interpreting the sensitivities from a mechanistic standpoint, we concluded that the $\mu$ are fundamentally related to the dominant transport and volatilization mechanisms in each scenario (i.e., Eq. [6] and [8]). Volatilization in the tarped broadcast scenario was mediated by diffusive transport and tarp mass transfer resistances in series. In that scenario, the cumulative flux sensitivity to boundary layer thickness was greatest, and the maximum 6-h mean fluxes were most sensitive to the boundary layer activation energy. In contrast, the bedded tarp fluxes were less sensitive to tarp parameters; volatilization occurred primarily through the untarped furrow regions. The effect of tarping was intermediate in the drip application, where the magnitude and relative contribution of volatilization through the tarped and untarped surfaces was dependent on both the rates of diffusive transport and soil hydraulic characteristics that influenced post-application fumigant and water penetration into the profile.

Based on this sensitivity analysis, uncertainty in three areas has the greatest potential to contribute to model uncertainty. These are (i) the fumigant degradation rate, (ii) soil water properties—both initial water content and saturated water content (i.e., porosity), and (iii) tarp permeability and permeability temperature dependence. The latter are primarily important in scenarios such as broadcast or near-surface drip application, where most or all volatilization occurs from a tarped soil surface.

**References**


