Modeling volatilization emissions of soil-applied pesticides under agricultural field conditions

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Abstract

Pesticides can volatilize from treated soil to the atmosphere causing increased environmental pollution and human exposure. Exposure assessment to airborne pesticides requires reasonable predictions of pesticide emissions. Understanding the volatilization behavior due to changes in environmental conditions can help in assessing the risk uncertainty and designing better mitigation strategies. In this study, we developed a mechanistic model that can be used to predict the hourly volatilization emissions from pesticide-treated soil at different environmental conditions. Pesticide properties and local environmental conditions drive the transport processes at the soil-air interface within the model. The numerical model simultaneously calculates the soil fluxes of heat, moisture, and pesticide at the soil-air interface with inputs of hourly meteorological data. The initial condition of pesticide concentration in soil is obtained from the applied mass during treatment. The numerical model was compared with an analytical model and with field observations for a soil injected fumigant and two surface applied pesticides.

The model performance of 14 pesticides under stagnant conditions against the Jury's analytical model showed reasonable agreement with values for the coefficient of determination ($R^2$) ranging from 0.76 to 0.99. The model was a good predictor of the field-scale volatilization of a fumigant (1,3-dichloropropene) application when compared to observations ($R^2 = 0.8$). Both the timing of the peak and the temporal variability of the measured volatilization of the fumigant were captured by the model when the fumigant was incorporated at a depth of 46 cm in the soil column. The model also showed reasonable agreement with the measured volatilization of two surface-treated pesticides, though site-specific meteorological data was unavailable for these observations.
1. Introduction

Pesticides are widely used in agriculture and are critical to maintaining the food supply for a growing world population. About 1.2 billion pounds of pesticides were used in the agricultural application within the United States (Donley, 2019). Pesticides applied to agricultural fields can volatilize and travel in the atmosphere to off-target areas (Bedos et al., 2002; Figueiredo et al., 2021) causing unintentional exposure to agricultural workers and nearby residential populations (Moon et al., 2013), and destroying nearby sensitive crops (Unsworth et al., 2002). Volatilization ranging from 5 to 63% of herbicide application was noted in a 13-year field study (Prueger et al., 2017). Similar field studies found volatilization of 16 to 36% of fumigant applications (Yates et al., 2015; Ashworth et al., 2018). Volatilization of a certain pesticide may vary across different locations and times of application due to the influence of local meteorology and surface soil conditions (Prueger et al., 2005). Sometimes, cumulative exposure via volatilization can be higher than exposure from drift (Figueiredo et al., 2022).

Field measurements of pesticide volatilization are expensive and time-consuming, requiring vertical measurements of wind, temperature, and air concentration. It is also difficult to extrapolate information from limited field studies to evaluate all combinations of environmental conditions that may be required for risk assessment (Yates, 2009). Computer models are convenient to evaluate multiple scenarios with various environmental conditions and physicochemical properties (Yates and Ashworth, 2019).

Predictive models describing volatilization range in complexity from simple empirical models considering vapor pressure only (Hsieh et al., 1995; Woodrow et al., 1997) to complex vadose zone transport models (Brown et al., 2019). Simple screening tools are often used by regulatory agencies that are based on empirical correlation with vapor pressure (USEPA, 2010, 2014; CDPR, 2021). These simple empirical methods provide fast results to identify pesticides with significant potential emissions that require more rigorous testing. However, the empirical methods using vapor pressure alone do not indicate the variability due to environmental factors or the timing of peak emissions. It is imperative to use a mechanistic model for better evaluation of the transport processes under different soil and meteorological conditions. A mechanistic model solves the time-dependent flow of water, heat, and chemical species within the soil column to simulate soil fluxes of the chemical species. There are regulatory tools in Europe such as Pesticide Emission Assessment at Regional and Local scales (PEARL) (Leistra et al., 2001; Leistra and Van Den Berg, 2007; Van den Berg et al., 2016) that solves the coupled equations of heat, moisture, and pesticide in the soil-plant-atmosphere interface. PEARL requires daily averaged inputs of temperature and moisture for the upper soil boundary. The diurnal fluctuation within a day is not considered. Moreover, the stagnant atmospheric boundary is also not applicable to turbulent conditions where high wind speeds may significantly drive volatilization (Bish et al., 2021).

There is no mechanistic model available in the United States for specific assessment of pesticide emissions (USEPA, 2010) and only a few studies have been performed to measure and predict volatilization fluxes. In the United States, groundwater models such as HYDRUS (Brown et al., 2019) and PRZM (USEPA, 2020) have been modified and implemented to calculate pesticide volatilization. These models were originally developed to calculate the chemical movement in the entire vadose zone with a later addition of the volatilization component. In their implementation, these models also calculated the atmospheric mass transfer of a chemical species using Fick’s law assuming a stagnant boundary layer based on Jury et al. (1983). Such an assumption of a fixed atmospheric boundary layer may not be realistic in turbulent field conditions. The atmospheric boundary layer is dynamic, and the mass transfer coefficients can significantly vary diurnally and seasonally depending on the atmospheric stability and local wind speed. Scholtz et al. (2002) demonstrated the coupling of the soil transport processes in a one-dimensional (1-D) soil column with a dynamic atmospheric boundary layer. Moreover, the groundwater models are complex with the requirement of many inputs necessary for assessing vadose zone transport. Emissions modeling from an agricultural application can be accomplished by solving the predominant transport processes at the soil surface and adjoining air interface. Such a 1-D numerical model at the soil surface is appropriate to predict hourly volatilization at a field scale with minimum input data and technical requirements.

In this work, we demonstrate the development of a comprehensive fate and transport model for predicting the post-application volatilization of pesticides from bare soil. The model solves the transient flow of heat, moisture, and pesticide in the soil with a dynamic atmospheric boundary layer. Model simulations were validated both with an analytical solution at stagnant environmental conditions and with field observations. The model assessment shows the applicability of the model for both conventional surface-treated pesticides and soil-incorporated fumigants.

2. Model description

The numerical model consists of a set of partial differential equations that describes the one-dimensional (vertical) flow of the heat, moisture, and pesticide at the soil-atmosphere interface. The model requires minimum inputs of application rate, pesticide properties, and standard hourly data of meteorological parameters. After soil application, the pesticides are assumed to penetrate the surface soil layer and are distributed among the three phases. Based on their mobility characteristics, pesticides thereafter desorb to the soil water and move to the surface by diffusion and convection from where it diffuses to the air near the soil surface. Past studies (Mayer et al., 1974; Jury et al., 1983) developed governing equation for pesticide transport with assumptions of constant environmental conditions and linear equilibrium distribution of pesticides between air, water, and soil media. In the current work, mass conservation is coupled with transport equations of heat and water flow in the soil to simulate varying environmental conditions. The sections below describe the governing equations and relevant parameters used to simulate the dynamic volatilization of pesticides from soil to the atmosphere.

2.1. Mass conservation of pesticides

A one-dimensional upward transport of the pesticide in the soil layer is based on the following mass-conservation equation:

\[
\frac{\partial C_T}{\partial t} + \frac{\partial J_z}{\partial z} + \mu C_T = 0
\]

(1)

where \( C_T \) is the total pesticide concentration in soil, \( J_z \) is the mass flux of pesticide, \( \mu \) is the decay or soil degradation rate, \( t \) is time and \( z \) is soil depth (Jury et al., 1983).

The total soil concentration (\( C_T \)) is assumed to be distributed in equilibrium among the three different phases

\[
C_T = \rho_x C_S + \theta C_L + u C_G
\]

(2)

where \( C_S \), \( C_L \), \( C_G \) are pesticide concentrations in solid, liquid, and gas phases respectively; \( \rho_x \) is the soil density, \( \theta \) is the volumetric water content and \( u \) is the volumetric air fraction in the soil.
The gas-liquid equilibrium is assumed to follow Henry’s law and linear adsorption is assumed for the soil-liquid partitioning of pesticide

\[ C_G = K_H C_L; \quad C_S = K_d C_L = f_w K_w C_L \]  \hspace{1cm} (3)

where \( K_H \) is the dimensionless Henry’s constant of the pesticide and \( K_d \) primarily represents pesticide adsorption to the organic matter within the soil. Thus, \( K_H \) is computed from the \( f_{GC} \), the soil organic carbon fraction, and \( K_w \), the organic carbon partition coefficient. The equilibrium relationships in equation (3) can be used to rewrite equation (2) as shown in equation (4) below:

\[ C_T = (\rho_d K_d + \theta + a K_H) C_L = f C_L. \]  \hspace{1cm} (4)

Similar expressions can be derived to compute total pesticide mass from soil-gas and soil adsorbed concentrations as shown in equation (5) below:

\[ C_T = f C_G / K_H; \quad C_T = f C_S / K_d \]  \hspace{1cm} (5)

where \( f \) is a partitioning factor used to convert phase concentrations to total soil concentration \( (C_T) \). This factor \( f \) will be very useful in combining all the governing equations as a function of \( C_T \) and eventually developing a solution.

The pesticide mass flux \( (J_L) \) within the soil column includes both diffusion and convective movement as described in equation (6). Equation (6) ignores hydrodynamic dispersion.

\[ J_L = -D_L \frac{dC_L}{dz} - D_t \frac{dC_T}{dz} + J_w C_L \]  \hspace{1cm} (6)

where the first and second terms characterize the gaseous and liquid diffusion respectively, and the third term describes the convective movement due to steady-state water flow. \( D_L \) and \( D_t \) are diffusion coefficients of pesticides in pure air and water. \( J_w \) is the water flux in the soil due to upward evaporation.

Using the “partitioning factor” \( f \), the mass flux \( J_L \) is rewritten as shown in equation (7):

\[ J_L = -D_L \frac{dC_T}{dz} + V_E C_T \]  \hspace{1cm} (7)

where \( D_L \) is the effective diffusion coefficient derived from combination of gaseous and liquid phase diffusion coefficients as shown in equation (6).

\[ D_E = (K_H D_G + D_L) / f \]  \hspace{1cm} (8)

and \( V_E \) is the effective convective velocity as described in equation (9) below:

\[ V_E = J_w / f \]  \hspace{1cm} (9)

The diffusion coefficients in the soil are related to the binary diffusion coefficients through a tortuosity factor (shown in equation (10)). This tortuosity factor accounts for the reduced cross-sectional area and increased path length of the diffusing solute in soil

\[ D_G = \xi_G D_G^{air}; \quad D_L = \xi_L D_L^{water} \]  \hspace{1cm} (10)

where \( \xi_G \) and \( \xi_L \) are the binary gas and liquid tortuosity factors; \( D_G^{air} \) and \( D_L^{water} \) are the binary diffusion coefficients of the pesticide in air and water respectively.

The tortuosity factor is a function of the soil geometry and Jury et al. (1983) employed Millington and Quirk (1961) formula to obtain this factor. These formulas are shown in equation (11):

\[ \xi_G = \frac{a^{10/3}}{(\theta + a)^{10/3}}; \quad \xi_L = \frac{a^{10/3}}{(\theta + a)^{10/3}} \]  \hspace{1cm} (11)

where \( \theta \) is the volumetric water content and \( a \) is the volumetric air content. The combination of \( \theta \) and \( a \) in the denominator term denotes the soil porosity \( (\phi) \).

Jury et al. (1984a) combined the soil geometry, water content, and pesticide properties to rewrite effective diffusion as provided in equation (12):

\[ D_E = \frac{[\theta - \theta^10/3 K_d D_G^{air} + \theta^10/3 D_L^{water}]}{[\rho_d K_d + \theta + (\theta - K_H) B]} \]  \hspace{1cm} (12)

The boundary layer provides greater resistance to the diffusion of pesticides across the soil-air interface with a low Henry’s law constant \( K_H \) value \((\approx 2.5 \times 10^{-5})\) due to low vapor density in soil. Evaporation moves the pesticide upward to the surface where the pesticide accumulates, and the vapor density increases at the surface thus volatilization increases with time (Jury et al., 1984a). Pesticides with large \( K_H \) \((\approx 2.5 \times 10^{-5})\) values have higher vapor density in soil and therefore the boundary layer provided little resistance. This category of pesticides diffuses rapidly as soon as it is transported to the surface, and therefore it does not accumulate at the surface over time.

Jury et al. (1983) assumed that the pesticide at the surfacediffuses through a stagnant air boundary layer before entering the well-mixed bulk atmosphere. The pesticide flux through this layer of thickness \( d \) is described using Fick’s law

\[ J_L \bigg|_{z=a} = -\frac{D^{air}}{d} (C_G \bigg|_{z=a} - C^{air}_{G}) \]  \hspace{1cm} (13)

where \( C_G \bigg|_{z=a} \) is the gas concentration at the soil surface and \( C^{air}_{G} \) is the concentration in the bulk atmosphere. Jury et al. (1983) computed the value of \( d \) as 5 mm based on 50% humidity. Bulk air concentration \( (C^{air}_{G}) \) is assumed zero. Henry’s law constant \( K_H \) provides the equilibrium partitioning between pesticide concentrations in air and soil water.

Combining with equation (7), the upper boundary condition can be written as

\[ -D_E \frac{dC_T}{dz} + V_E C_T = -H_E C_T \]  \hspace{1cm} (14)

\[ H_E = -\frac{D^{air}}{d} \times \frac{K_H}{f} \]  \hspace{1cm} (15)

The one-dimensional chemical transport problem in equation (1) was analytically solved by Jury et al. (1983) and the volatilization flux at the soil surface was computed as provided in equation (16):

\[ J_L \bigg|_{z=a} = \frac{1}{2} C_0 \cdot \exp(-\mu t) \left[ V_E \left[ erf \frac{(V_E t)}{\sqrt{4D_E t}} \right] - erf \frac{(L + V_E t)}{\sqrt{4D_E t}} \right] + (2H_E + V_E) \exp[H_E (H_E + V_E) / D_E] \left[ erf \frac{(V_E t)}{\sqrt{4D_E t}} \right] \right] - erf \left[ \frac{(2H_E + V_E) t}{\sqrt{4D_E t}} \right] \]  \hspace{1cm} (16)

where erf(x) is the complementary error function.

2.2. Soil transport of heat and moisture

Environmental conditions, specifically evaporation rate, can drive pesticide volatilization. The degree of partitioning in soil, transport, and volatility of a pesticide strongly depends on the moisture and temperature within the soil column. Therefore, a non-isothermal model is needed to solve simultaneously the transport of heat, moisture, and pesticide mass in the soil-air continuum. The surface fluxes of heat and moisture are driven by diurnal solar radiation that serves as the boundary conditions in these models.

A multilayer soil model consists of two equations for the temperature and moisture profiles within the soil column. Equation (17) provides the one-dimensional heat flow within the soil which is based on Fourier’s law.
\[
\frac{\partial T_s}{\partial t} = \frac{\partial}{\partial z} \left( \kappa_s \frac{\partial T_s}{\partial z} \right)
\]  
(17)

where \( T_s \) is the soil temperature at height \( z \), \( C_{p,\text{soil}} \) is the specific heat of soil, \( \rho_s \) is the bulk density of moist soil, and \( \kappa_s \) is the thermal conductivity of the soil. The expression \( D_T = \kappa_s / \rho_s C_{p,\text{soil}} \) is called the thermal diffusivity and describes the rate of heat penetration into the soil column as a function of the diurnal cycle. The thermal conductivity, \( \kappa_s \), depends on many factors including porosity, particle density, and moisture content of the soil. The model sets a value of \( \kappa_s \) at 0.172 J/s/mK from McCumber and Pielke (1981). The volumetric heat capacity of the soil (\( C_{p,\text{soil}} \)) is calculated using the weighted contribution of dry soil and water content as shown in equation (18):

\[
\rho_s C_{p,\text{soil}} = (1 - \theta) \rho_s C_{p,\text{drysoil}} + \theta \rho_w C_{p,w}
\]  
(18)

where \( \theta \) is the volumetric soil water content; \( \rho_w \) is the dry bulk density; \( C_{p,\text{drysoil}} \) is the specific heat of solid soil, \( \rho_w \) is the water density, and \( C_{p,w} \) is the specific heat of liquid water.

The water transport in the soil is defined by Richard's equation

\[
\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left( D_h \frac{\partial \psi}{\partial z} + K_h \right)
\]  
(19)

where \( D_h \) is the soil water diffusivity and \( K_h \) is the hydraulic conductivity. These parameters are derived from relationships in Clapp and Hornberger (1978) as a function of soil moisture (\( \theta \)) (Jacobson, 2005). Equations (20) and (21) provide the empirical equations for calculating \( K_h \) and \( D_h \) using relations from Clapp and Hornberger (1978).

\[
K_h = K_{sat} \left( \frac{\theta}{\theta_{sat}} \right)^{b+3}
\]  
(20)

\[
D_h = -\frac{b K_{sat} \psi_{sat}}{\theta_{sat}} \left( \frac{\theta}{\theta_{sat}} \right)^{2b+2}
\]  
(21)

where \( \psi_{sat}, \theta_{sat} \), and \( K_{sat} \) are saturation soil properties and \( b \) is the retention curve fitting parameter depending on soil type.

With the known relationship of \( \psi, \theta, \) and \( K \) from a soil characteristic curve, this equation can be solved numerically with the boundary conditions at the surface. The surface boundary conditions of temperature and moisture are provided by evaporation, heat fluxes, and precipitation.

### 2.3. Surface energy balance

Energy fluxes at the soil-atmosphere interface can be summed to zero since the soil surface has no storage capacity for energy. The resulting energy balance (see equation (22) below) is the basis for the estimation of evaporation from the soil and the rate of heating that influences the surface temperature and moisture. The water balance at the soil surface is implicit within such an energy balance

\[
R_n - H - \lambda E - G = 0
\]  
(22)

Here, \( R_n \) is the net radiation into the surface; \( H \) is the sensible heat flux, the heating of the atmosphere by surface energy loss; \( E \) is the evaporation rate with \( \lambda \) is the latent heat of vaporization of water with a value of 2.26×10^6 J/kg, and \( G \) is the ground heat flux due to conduction from the soil surface to depth beneath i.e. heat penetration into the soil surface. Net radiation (\( R_n \)) includes absorption and reflection of shortwave radiation and emission and reception of longwave radiation. Net radiation is calculated from Campbell (1985) as shown in equation (23) below:

\[
R_n = R_s (1 - a) + \varepsilon_s \sigma_s T^4 - \varepsilon_s \sigma_s T^4
\]  
(23)

The first term is net shortwave radiation after being reflected by surfaces. The second term is the incoming longwave radiation emitted by the atmosphere and the third term is outgoing longwave radiation emitted by the surface. \( R_s \) is the incoming solar radiation; \( a \) is the surface albedo (reflectivity); \( \varepsilon_s \) and \( \varepsilon_s \) are emissivities of atmosphere and surface; \( \sigma \) is the Stefan-Boltzmann constant; \( T_{air} \) is the air temperature at a reference measurement height (\( z_{ref} \)) and \( T_s \) is the soil surface temperature.

Albedo can be calculated from soil surface moisture (\( \theta_{surface} \)) using the following relationship (van Bavel and Hillel, 1976) in equation (24):

\[
\varepsilon_s = 0.1 + (0.25 - \theta_{surface})
\]  
(24)

The emissivity of the soil surface also strongly depends on the water content as given by van Bavel and Hillel (1976) as shown in equation (25)

\[
\varepsilon_s = 0.9 + 0.18 \theta_{surface}
\]  
(25)

Longwave emission from the atmosphere occurs mostly due to water vapor and carbon dioxide. Therefore, atmospheric emissivity primarily depends on air temperature and humidity. Swinbank’s (1963) derived an empirical model based on air temperature near the surface as given in equation (26):

\[
\varepsilon_s = (0.92 \times 10^{-5}) \frac{T_{air}^2}{100}
\]  
(26)

The sensible and latent heat fluxes in equation (22) are calculated using the flux-gradient method as provided in equations (27) and (28) (Scholz et al., 2002).

\[
H = -\rho_{air} C_{p,air} \left( T_{air} - T_{surface} \right) / R_s
\]  
(27)

\[
E = -\left( \frac{q_v - q_s}{R_s + R_d} \right)
\]  
(28)

where \( \rho_{air}, C_{p,air} \) are density and specific heat properties of air. \( T_{air} \) is the ambient temperature at a measurement height \( z_{ref} \). \( T_{surface} \) is the soil surface temperature. \( R_s \) is the aerodynamic mass transfer resistance that provides resistance to the flow of heat and water vapor from the soil surface to the atmosphere. \( R_d \) is the soil surface resistance to the water vapor flow in soil pores and is a function of saturated and actual soil moisture at the surface. \( q_v \) and \( q_s \) are water vapor densities of air at reference ambient height and at immediately above the surface.

Evaporation is related to the vapor deficit that depends strongly on the temperature. Atmospheric vapor density at a measurement height \( z_{ref} \) is obtained from relative humidity (RH) and saturated vapor density \( (q_{sat}) \) as shown in equation (29):

\[
q_v = \frac{RH}{100} \times q_{sat} \left( T_{air} \right)
\]  
(29)

The water vapor density at the soil surface is strongly dependent on soil moisture. It is generally estimated from relative humidity at the surface using equation (30).

\[
q_v = a \times q_{sat} \left( T_{surface} \right)
\]  
(30)

where \( a \) is a coefficient that represents the moisture-dependent relative humidity near the surface. Barton (1979) developed an empirical model based on moisture content for \( a \) as shown in equation (31).

\[
a = \frac{1.8 \theta_{surface}}{\theta_{surface} + 0.3}
\]  
(31)

The ground heat flux at the soil-atmosphere boundary is calculated from the heat flux gradient in the topsoil layer using equation (32).

\[
G = \frac{\partial T}{\partial z} \bigg|_{z=0}
\]  
(32)

The aerodynamic resistance \( R_a \) was determined using equation (33) with the assumption of neutral atmospheric stability.

\[
R_a = \frac{1}{k^2 \nu_{ref}} \ln \left( \frac{z_{ref}}{z_0} \right)
\]  
(33)
where, \( z_{\text{ref}} \) is the measurement height of temperature (\( T_{\text{an}} \)) and wind speed (\( u_{\text{ref}} \)), \( z_0 \) is the surface roughness length, and \( \kappa \) is the von Karman constant with a value of 0.4.

Wind speed plays a critical role in generating a mechanical turbulent mixing and achieving a neutral atmospheric surface layer. The aerodynamic resistance \( R_e \) in equation (33) can be modified for unstable and stable atmospheric conditions using corrections with stability functions. It was though noted that the iterative calculations of the hourly stability did not significantly affect the surface energy balance and the final flux estimates. Also, the hourly stability calculations sometimes caused convergence issues in the surface energy solver and generated unreasonable outcomes. Therefore, neutral stability was only used to provide reasonable estimates. More detailed work in future is warranted to understand the impact of stability conditions on volatilization.

The soil surface resistance \( R_s \) depends on soil texture and soil moisture. Camillo and Gurney (1986) provided an empirical formula (as given in equation (34)) to estimate this resistance as a function of soil moisture at the surface

\[
R_s = 3.5 \left( \frac{\theta_{\text{sat}}}{\theta_{\text{surf,ave}}} \right)^{2.3} + 33.5
\]

(34)

2.4. Dynamic simulation of pesticide transport

The hourly simulations of moisture content (\( \theta \)) and convective water flow (\( J_w \)) from equation (19) feed into the pesticide mass flux calculations in equation (1). Thus, the three governing equations for the transport of heat, moisture, and pesticide mass are combined within the soil column to reflect the dynamic variability of the field conditions. While Jury’s analytical solution used Fick’s law for a stagnant boundary layer in equation (13); the soil-atmosphere boundary condition was modified to account for the effect of wind speed and turbulence. Effective diffusivity (\( H_E \)) in equation (15) was modified based on the turbulent boundary layer as shown in equation (35) below:

\[
H_E = \left( \frac{1}{R_e} \right) \left( \frac{K_f L}{f} \right)
\]

(35)

where \( R_e \) is the aerodynamic mass resistance representing the resistance to the mass transfer at the boundary layer and is based on the logarithmic profile of wind speed as shown in equation (33). The “partitioning factor” \( f \) is used to convert the liquid phase concentration to the total soil concentration as shown in equation (5). \( K_f \) is the dimensionless Henry’s law constant for a pesticide.

2.5. Numerical simulation setup

The one-dimensional transport equations of heat, moisture, and pesticide in the soil were numerically solved using the Crank-Nicolson finite difference method. This semi-implicit second-order numerical scheme is unconditionally stable and faster compared to explicit forward Euler’s finite difference scheme used in similar models such as PEARL (Van den Berg et al. 2016) and PRZM (USEPA, 2020). Implicit numerical schemes have been proven to provide better accuracy for solving non-linear Richard’s equation in unsaturated soils (Chávez-Negrete et al., 2018). Appendix A provides the general numerical solution with the finite difference method that was applied in the three transport equations. To solve the three differential equations, a certain soil depth was spatially discretized with each soil layer of height (\( \Delta z \)) and time steps of 1 hr (\( \Delta t \)). The dynamic model solves the heat and water flow in the soil in tandem with the energy balance every hour. Inputs of measured hourly climate data for air temperature, relative humidity, solar radiation, and wind speed drive the surface energy balance within the model that serves as upper boundary conditions for the soil profile of temperature and moisture. At each time step (1 hr), the surface heat fluxes were repetitively computed until the sum of all heat fluxes converged to a minimum criterion of <0.001 W/m² from a range of soil surface temperatures. The soil temperature profile was determined when this criterion is met. The combination of resulting evaporation flux (\( E \)) and precipitation input (\( P \)) was consequently utilized as an upper boundary condition to compute the soil moisture profile. At the lower soil boundary, a no-flux boundary condition was used for both temperature and moisture.

The solutions of the soil moisture and the convective water flux (\( J_w \)) feed into the pesticide transport equation. The pesticide mass within the soil column was computed along with the volatilization flux at the upper soil-atmosphere boundary. The pesticide mass is homogeneously distributed in the soil depth \( L \) with initial concentration calculated from an application rate (\( AR \)) as shown in equation (36) below.

\[
C_0 = AR/L
\]

(36)

The derivative in equation (14) (\( \partial C/\partial t \)) was discretized using a 2nd order backward difference method to solve the upper boundary condition for the pesticide transport in both cases of stagnant and dynamic soil-atmosphere boundaries. Equation (37) below provides the numerical discretization of \( \partial C/\partial t \) at the surface layer.

\[
\frac{\partial C_T}{\partial z} \bigg|_{z=0} = \frac{5}{2\Delta z} [C_T|_{z=0} - 4 C_T|_{z=1} + C_T|_{z=2}]
\]

(37)

Equation (37) can be rewritten to compute the surface pesticide concentration at the upper boundary as shown in equation (38) below:

\[
C_T|_{z=0} = \frac{D_E (4 C_T|_{z=1} - C_T|_{z=2})}{3D_E - (V_E + H_E) \times 2\Delta z}
\]

(38)

The volatilization flux could then be calculated from the product of soil surface concentration and the effective diffusivity (\( H_E \)). The pesticide concentration was assumed zero at the lower boundary.

2.5.1. Model evaluation at stagnant environmental conditions

The numerical model was initially tested at stagnant boundary conditions similar to Jury et al. (1983). These simulations were performed to evaluate the numerical algorithm that solves the pesticide transport in the one-dimensional soil column and demonstrate the numerical accuracy of the model at three distinct evaporation rates. Simulations were performed for three scenarios of water flux: (i) no evaporation (\( E=0 \)); (ii) with evaporation (\( E=5 \) cm/day); and (iii) with downward infiltration (\( E=-5 \) cm/d). Thus, these simulations did not account for the dynamic variability due to meteorological conditions.

A 10-day simulation was performed for 14 pesticides with both Jury’s analytical solution and the current numerical model every hour after application. An application rate of 1 kg/ha and a depth of penetration (\( L \)) of 10 cm were assumed as used in Jury’s calculations (Jury et al., 1983, 1984a). The initial soil concentration of the pesticides (\( C_0 \)) was therefore calculated as 1 g/m³. Environmental parameters (Table S1) and pesticide properties (Table S2) were also derived from Jury et al. (1983) for these simulations (shown in Supplementary Data). The model simulation of these 14 pesticides was performed to evaluate the model performance with varying pesticide properties.

2.5.2. Model evaluation in the dynamic field environment

The second set of evaluations was performed with model simulations for three pesticides with volatilization flux data from other studies in the literature. These simulations were performed with the dynamic calculations of soil temperature and moisture from the local meteorological data. Model predictions of the surface soil moisture and temperature have been tested against observations in Ohio and Iowa and showed reasonably good agreement (Ghosh, 2020). All simulations were performed with soil properties of sandy loam soil. The model was simulated for a highly volatile fumigant application – 1,3-dichloropropene (Anderson et al., 2019), a volatile herbicide – triallate (Yates, 2006a), and a semi-volatile herbicide (Prueger et al., 2017). Table 1 lists the physicochemical properties of these three pesticides. Details about the measurement data collection and relevant model inputs (such as application time and
Table 1. Pesticide properties and application rates used in dynamic environmental simulations.

| Pesticide   | Type       | Application Type | Application Rate (kg/ha) | $K_D$ (dimensionless) | $K_{SC}$ (m/kg) | Soil half-life (days) |
|-------------|------------|------------------|--------------------------|-----------------------|----------------|----------------------|
| Metolachlor | Herbicide  | Surface treatment| 1.5                      | $3.2 \times 10^{-4}$  | 0.2            | 15                   |
| Triallate   | Herbicide  | Surface treatment| 8.75                     | $7.9 \times 10^{-4}$  | 3.6            | 100                  |
| 1,3-D       | Fumigant   | Soil incorporated| 66.5                     | 0.144                 | 0.02           | 2.5                  |

Table 2. 10-d cumulative volatilization (% of application) of 14 pesticides simulated with both Jury’s analytical model and current numerical model for three scenarios of soil water flux (E).

| Pesticide   | $E=0$ mm/d | $E=5$ mm/d | $E=15$ mm/d |
|-------------|------------|------------|-------------|
|             | Current Model | Jury | Current Model | Jury | Current Model | Jury |
| Atrazine    | 0.06       | 1.00      | 1.41        | 0.00 | 0.00          |      |
| Bromacil    | 0.02       | 0.47      | 0.92        | 0.00 | 0.00          |      |
| 2,4-D       | 0.01       | 0.21      | 0.68        | 0.00 | 0.00          |      |
| DDT         | 0.27       | 0.28      | 0.27        | 0.27 | 0.27          |      |
| Lindane     | 2.02       | 2.97      | 2.83        | 1.34 | 1.13          |      |
| Phorate     | 5.99       | 7.98      | 6.79        | 4.45 | 3.18          |      |
| Diazinon    | 6.93       | 24.24     | 24.17       | 1.85 | 0.71          |      |
| Dieldrin    | 1.28       | 1.36      | 1.29        | 1.20 | 1.11          |      |
| Methyl-Parathion | 0.03 | 0.06      | 0.06        | 0.01 | 0.01          |      |
| Parathion   | 0.02       | 0.02      | 0.03        | 0.03 | 0.01          |      |
| Simazine    | 0.01       | 0.18      | 0.26        | 0.00 | 0.00          |      |
| Triallate   | 3.46       | 2.95      | 3.79        | 3.29 | 3.15          | 2.64 |
| Trifluralin | 9.72       | 7.03      | 9.89        | 7.21 | 9.56          | 6.86 |
| Napropamide | 0.11       | 0.11      | 1.12        | 1.33 | 0.01          | 0.01 |

rates, initial moisture conditions, and depth of incorporation) are discussed in the Supplementary Data.

2.5.3. Model performance statistics

Model performance statistics were computed for all the simulations including coefficient of determination ($R^2$), mean bias (MB) and error (ME), normalized mean bias (NMB) and error (NME), and root mean squared error (RMSE). Since $R^2$ only indicates the linear relationship between the model and observations, other “goodness of fit” indicators such as coefficient of efficiency (COA) and index of agreement (IOA) were also computed. The statistical formulae of these performance statistics are provided in the Table S3 of Supplementary Data.

3. Results and discussion

3.1. Validation against Jury’s analytical solution at stagnant environmental conditions

The cumulative volatilization during 10 days after an application for each scenario of water flux is provided in Table 2. The model evaluation metrics and the hourly flux plots are provided in Table S4 of the Supplementary data.

The numerical model showed close agreement with the analytical model for all the pesticides in the three scenarios. The coefficient of determination ($R^2$) ranged from 0.76 to 0.99 for 14 pesticides. The coefficient of efficiency (COE) ranged from -0.04 to 0.95 and the index of agreement (IOA) ranged from 0.43 to 0.98. The normalized mean error (NME) was close to zero for most pesticides with some high values above 1 for a few pesticides. Overall, all the performance indicators demonstrated a satisfactory agreement of the numerical model with the analytical solution.

Volatilization rates of high volatile pesticides, such as Lindane, and trichloroethylene, were highest immediately after application and then decreased with time. The volatilization for such pesticides was slightly enhanced with evaporation ($E=5$ mm/d) and decreased with downward water flux ($E=5$ mm/d). In contrast, volatilization of low volatile pesticides, such as atrazine and napropamide, significantly increased with time when evaporation occurred and decreased swiftly with downward water flux. Volatilization of these low volatile pesticides declined very slowly at zero water flux. The low volatile pesticides tend to accumulate near the surface and cannot easily overcome the boundary layer resistance and emit into the atmosphere.

Volatilization rates for immobile pesticides (large $K_{SC}$ value), such as DDT and Dieldrin, were nearly constant across all three scenarios. The water fluxes did not have much effect on these classes of pesticides, since they tend to bind to the soil for a long time and only the freely available mass soluble in water diffuses to the atmosphere.

The model generally agreed with Jury’s analytical solution of volatilization at stagnant boundary conditions considering pesticides with different ranks of volatility. The model comparison with the analytical solution validates the numerical algorithm’s robustness that is required for predictions under non-steady variable atmospheric boundary conditions.

3.2. Validation against field-scale measurements

3.2.1. 1,3-dichloropropene

Fig. 1 shows the modeled flux of cis-1,3-D based on three different calculation methods of flux (Ashworth et al., 2018). A peak flux of 43,881 g/m²·h was measured during early morning 7:00-9:00 AM on the day after application (September 9, 2016). Similarly, the model also simulated a peak flux of 45,235 g/m²·h at 8:00 AM the next day after application. The delayed surge in volatilization unlike surface sprayed pesticides is due to the travel time of the injected fumigant 1,3-D from 46 cm below the soil to the soil surface. The model was successful in capturing this delayed surge of volatilization peaks after 24 hr of application like the field study.

The Fresno study found 27.1-36.4% cumulative volatilization of cis-1,3-D based on three different calculation methods of flux (Ashworth et al., 2018). Modeled cumulative volatilization after 14 days was 24.5% of 66.5 kg/ha application of cis-1,3-D. Previous field studies near Buttonwillow, CA (Yates et al., 2008, 2015, 2016) found 16-35% cumulative flux of bare soil 1,3-D application. van Wesenbeek et al. (2007) measured 1,3-D flux of 26.5% at a field site near Douglas, GA. Brown et al. (2019) simulated 10 to 58% volatilization losses of 1,3-D for 17 different application methods using HYDRUS model. The variations of flux values between different studies are primarily due to flux calculation and/or application methods rather than environmental conditions. The model predictions of 1,3-D emissions are reasonably close to the findings from previous studies mentioned above. Moreover, there is little variability between different studies though data were collected at different locations and times. Thus, the high volatility of 1,3-D is not significantly impacted due to local environmental conditions, unlike semi-volatile pesticides as shown for triallate and metolachlor below. The performance indicators (NMB=0.0, R2 = 0.8, COE=0.7, IOA=0.9) demonstrate a very good agreement between the current model predictions and field observations of the fumigant volatilization. Performance indicators including mean bias and error are reported in Table S5 of the Supplementary data.

The total soil mass per unit area depleted from 66.5 kg/ha to 0.55 kg/ha after 14 days primarily due to a very short half-life of 1,3-D in soil. The high concentration of 1,3-D (6650 g/m³) at 46 cm, slowly diffuses to the upper and lower soil layers with the surface concentration reaching a maximum of 0.005 g/m³ after 24 hr of application. This is still a very small fraction of the total fumigant (0.75 ppm) injected beneath the soil.
Fig. 1. Comparison of modeled vs observations of volatilization flux of 1,3-dichloropropene. Average observations of three concurrent field measurements were obtained from Anderson et al. (2019).

3.2.2. Triallate

Modeled volatilization rate of triallate is shown in Fig. 2 along with average flux observations from Yates (2006a). Fig. 2 shows the high volatilization of triallate in the first few hours after application, then significantly decreased to below 3500 μg/m²·hr. Yates (2006a) noted similar trends with volatilization rates dropping to below 5000 μg/m²·hr after a few hours of application.

Peak volatilization of 16800 μg/m²·hr was noted during the first day of measurements as compared to a model peak of about 19000 μg/m²·hr. The model simulated total cumulative volatilization of 23% compared to the measured cumulative loss of 31% after 6 days of sampling by Yates (2006a). A slight difference was expected since the model was simulated with different meteorological conditions than in Yates (2006a). Tabernero et al. (2000) found 14% to 32% cumulative volatilization of triallate using laboratory experiments at different temperature conditions. Different environmental conditions, including soil moisture and heat fluxes, drive this slight variability of triallate emissions.

The flux rates of triallate in the field are significantly higher than estimates with Jury’s analytical model (3.29% at E=5 mm/d as shown in Table 2). High evaporation during daytime drives the large emissions and cannot be captured using Jury’s analytical model which can only simulate constant evaporation rates. And therefore, it is more suitable to use a dynamic mechanistic model with variable heat and moisture flux simulations for evaluation in the field conditions. The normalized mean bias (NMB) was calculated as -0.4 with an R² value of 0.7 and a low COE value of 0.3. These indicate the moderate performance of the model when compared to observations from the literature.

Soil transport to the surface is vapor-dominated for highly volatile pesticides like triallate. The pesticide quickly diffuses into the atmo-

Fig. 2. Comparison of modeled vs observations of volatilization flux of triallate. Average observations of three concurrent field measurements were obtained from Yates (2006b).
sphere, as soon it reaches the surface and thereby depletes immediately after application.

3.2.3. Metolachlor

Fig. 3 shows the post-application volatilization rates of metolachlor from both the model and observations. Peak observation of metolachlor flux was about 1015 μg/m²·hr as compared to modeled peak flux of 749 μg/m²·hr. The model performance statistics were calculated as $R^2 = 0.4$, COE = 0.3 and IOA = 0.7. Such moderate performance of the model could be because the local micro-meteorological conditions were different than the input meteorological dataset from a distant site location.

Total cumulative volatilization was noted to be 16.8% after 10 days during the year 2010 by Prueger et al. (2017). While 11.2% of metolachlor volatilized after the first 5 days and 5.6% volatilized during 6-10 days of the field study. Modeling showed 14.6% cumulative volatilization after 10 days of metolachlor application. While 8.3% cumulative volatilization was modeled after the first 5 days, 6.3% was modeled during 6-10 days after spray application. These results show that the model compared well with the 2010 measurements of volatilization in Prueger et al. (2017). A range of 5 to 63% cumulative loss of metolachlor was measured during 13 years of measurements by Prueger et al. (2017). Prueger et al. (2005) reported metolachlor losses from 5 to 25% after 5 days of application during a five-year field measurements study. Bedos et al. (2017) also measured metolachlor volatilization using an enclosed chamber. This study found peak volatilization of 331 μg/m²·hr and cumulative volatilization of 2.8% after 3 days. Rice et al. (2002) determined 6.5% metolachlor losses due to volatilization after 21 days of application to freshly tilled soil. Prueger et al. (2005) identified that the variation in metolachlor volatilization was associated with soil moisture, local climate conditions, and complex interactions between meteorology, soil conditions, and pesticide properties. Metolachlor is semi-volatile and slightly immobile in soil. High fluxes of metolachlor could occur when wet soil condition increases the soluble concentrations and drives the flux across the boundary layer. Dry soil conditions allow the metolachlor concentrations to accumulate in the soil that cannot overcome the boundary layer resistance in absence of a significant upward evaporation rate. Therefore, the metolachlor emissions widely vary among different measurement studies due to varying soil moisture conditions. Such measurements of different variables in the field can only provide a qualitative understanding of the interacting factors. Sensitivity analyses of the proposed mechanistic model can provide better insight into such interactions.

It is noted from these comparisons of model results against field measurements, that environmental conditions can have a varied effect on pesticides with different volatility and adsorption properties. Peak fluxes of highly volatile pesticides are not largely affected by varying meteorological conditions as noted for 1,3-D and triallate. However, application times and soil moisture can still affect the initial soil concentrations and consequent peak fluxes for pesticides with large sorption coefficients. The volatilization of semi-volatile pesticides such as metolachlor is largely dependent on local environmental conditions and varies widely for different seasons and geographic locations (Prueger et al., 2017). Currently, the regulatory agencies in the United States rely on micrometeorological measurements for generating emission inputs to exposure assessment models required for pesticide registration (Reiss and Griffin, 2006; Federal Registrar, 2007). It would be laborious and expensive to quantify these varied impacts on volatilization across different time and spatial scales for proper evaluation and therefore mathematical models could prove beneficial for a better understanding of the pesticides’ fate and transport in the soil-atmosphere system (Yates and Ashworth, 2018; Li and Niu, 2021). The proposed model is therefore suitable for such assessment with iterative simulations for different environmental conditions.

4. Conclusions

This work presents the development of a physics-based model for predicting post-application volatilization from soil surfaces. The model is capable of simulating time-dependent volatilization with simple inputs of application rates, pesticide properties, and standard meteorological data that are readily available to engineers and regulatory scientists. Setting up a model for solving the 1-D transport process in the surface soil would require less effort and technical expertise as compared to three-dimensional vadose zone models. Quantitative information could be easily obtained from such a physics-based model about the pesticide’s behavior in a certain region to support field volatility studies and regulatory risk assessments. More testing of the model with field measurements of soil moisture and temperature and volatilization rates will build more confidence for regulatory applications. More recent parameterization of the soil water retention curve such as van
Genuchten model can be tested in future model iterations to improve estimates of soil moisture and latent heat flux that drives the pesticide volatilization.

**Declarations**

**Author contribution statement**

Saikat Ghosh, PhD: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Kevin Crist, PhD: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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**Data availability statement**

Data will be made available on request.

**Declaration of interests statement**

The authors declare the following conflict of interests: The authors have received research support in the past from Syngenta LLC (Award number: 1519757), which is the registrant of S-metolachlor.

**Additional information**

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.heliyon.2022.e11810.

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**Appendix A**

**A.1. Numerical solution with Crank-Nicolson finite difference method**

The general form of one-dimensional diffusion partial differential equation (PDE) can be written as:

$$\frac{\partial \phi}{\partial t} = \alpha \frac{\partial^2 \phi}{\partial z^2} + \beta \frac{\partial \phi}{\partial z} - \mu \phi \tag{A.1}$$

Where $\phi$ is a general variable, $t$ is time and $z$ is the vertical distance within the soil column. The first term is a transient representation of $\phi$ or the rate of change of $\phi$ with time. The second term is the diffusion of $\phi$ within the soil column and the second term is the convective flux of $\phi$ in the soil.

A solution of $\phi$ is numerically calculated on a rectangular grid value of $t$ and $z$. The rectangular domain encompasses I equally spaced intervals ($\Delta t$) at time $t$ indexed by $i = 0, 1, 2...N$ and equal intervals ($\Delta z$) at depth $z$ indexed by $n = 0, 1, 2...N$.

Now each term in equation (A.1) can be implicitly discretized using the finite difference method.

$$\frac{\phi_{n+1} - \phi_n}{\Delta t} = \frac{\alpha}{2} \left[ \frac{\phi_{n+1} - 2 \cdot \phi_n + \phi_{n-1}}{\Delta z^2} \right] + \left( \frac{\alpha}{2} \right) \left[ \frac{\partial \phi}{\partial z} \right] \tag{A.2}$$

$$\frac{\partial \phi}{\partial z} = \frac{1}{\Delta t} \left[ \left( \frac{\phi_{n+1} - \phi_{n-1}}{2 \cdot \Delta z} \right) \right] \tag{A.3}$$

New constants are created to simplify equation (A.1)

$$\lambda = \alpha \frac{\Delta t}{\Delta z^2} \tag{A.4}$$

$$\eta = \frac{\beta \Delta t}{\Delta z} \tag{A.5}$$

Substituting equations (A.2), (A.3), (A.4), and the new constants $\lambda$ and $\eta$ in the PDE (equation (A.1)) and collecting all the terms involving the unknown $\phi^{i+1}$ on the left-hand side, we get

$$\left( \lambda + \eta \right) \phi^{i+1} + 2 \left( 1 - \lambda - \mu \right) \phi^i + \left( \lambda - \eta \right) \phi^{i-1} = 0 \tag{A.6}$$

Introducing the new expressions for coefficients, the system of equations becomes

$$C_n \phi^{i+1} + B_n \phi^i + A_n \phi^{i-1} = D_n \tag{A.7}$$

The above system of simultaneous equations forms a tridiagonal matrix as shown below. It is efficiently solved by the Thomas algorithm based on Gaussian elimination.

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