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Predicting Regional Emissions and Near-Field Air Concentrations of Soil Fumigants Using Modest Numerical Algorithms: A Case Study Using 1,3-Dichloropropene

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Soil fumigants, used to control nematodes and crop disease, can volatilize from the soil application zone and into the atmosphere to create the potential for human inhalation exposure. An objective for this work is to illustrate the ability of simple numerical models to correctly predict pesticide volatilization rates from agricultural fields and to expand emission predictions to nearby air concentrations for use in the exposure component of a risk assessment. This work focuses on a numerical system using two U.S. EPA models (PRZM3 and ISCST3) to predict regional volatilization and nearby air concentrations for the soil fumigant 1,3-dichloropropene. New approaches deal with links to regional databases, seamless coupling of emission and dispersion models, incorporation of Monte Carlo sampling techniques to account for parametric uncertainty, and model input sensitivity analysis. Predicted volatility flux profiles of 1,3-dichloropropene (1,3-D) from soil for tarped and untarped fields were compared against field data and used as source terms for ISCST3. PRZM3 can successfully estimate correct order of magnitude regional soil volatilization losses of 1,3-D when representative regional input parameters are used (soil, weather, chemical, and management practices). Estimated 1,3-D emission losses and resulting air concentrations were investigated for five geographically diverse regions. Air concentrations (15-day averages) are compared with the current U.S. EPA's criteria for human exposure and risk assessment to determine appropriate setback distances from treated fields. Sensitive input parameters for volatility losses were functions of the region being simulated.

KEYWORDS: 1,3-Dichloropropene; ISCST3; air dispersion modeling; PRZM3, volatilization

INTRODUCTION

1,3-Dichloropropene (1,3-D) is an effective nematicide found in Telone (trademark of Dow AgroSciences) II fumigant, Telone C-17 fumigant, Telone C-35 fumigant, and InLine (trademark of Dow AgroSciences) fumigant. 1,3-D is a mixture of *cis*- and *trans*-1,3-D isomers (approximately 50/50 by weight), both of which have the propensity to volatilize following application to soil. Future uses of 1,3-D will likely increase as a replacement for methyl bromide (a soil fumigant that is being phased out due to stratospheric ozone depletion issues). Therefore, proper characterization of 1,3-D transport and exposure is important for the stewardship and expansion of 1,3-D use in fumigant markets.

Both empirical (*1*) and deterministic (*2*−*7*) numerical models have been used to predict fumigant volatilization from soil. Modeling attempts are typically limited to idealized situations in which variability in soil, weather, and chemical properties is ignored. This work focuses on a method to distinguish correct order of magnitude 1,3-D soil flux predictions on a regional basis when uncertainty in input parameters is accounted for.

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Many factors can affect fumigant volatilization under field conditions. A sensitivity analysis is paramount in pesticide exposure modeling to deduce model inputs that create the largest variance in model predictions (*8*−*10*). Sensitivity analysis addresses parametric uncertainty associated with coefficients found in mathematical expressions but not the potential variability that arises from approximating physical phenomena using these mathematical expressions. Regional predictions for 1,3-D mass volatilization from soil using a robust deterministic model can then be addressed once uncertainty in regional parameters is characterized.

Air concentrations surrounding treated fields are averaged over specific time periods to obtain exposure values for use in human risk assessment when exposure is compared to effect. Air concentrations typically decrease as the distance from a treated field increases. The U.S. Environmental Protection Agency (EPA) assumes that lifetime exposure for residential populations is associated with a series (up to 70) of annual exposure events, each of which has a duration of 15 days. This 15-day period corresponds to the typical maximum length of time for off-gassing of 1,3-D following an application. A 15-day time-weighted multidirectional average air concentration

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Figure 1. Selection of modeling scenarios based upon 1,3-D use information.

of 33.9 μg/m^3 was deemed the appropriate reference concentration by the U.S. EPA for human exposure and risk assessment (*11*).

This work involves multiple major objectives. The first objective was to develop and implement a modeling system that could predict fumigant mass loss and subsequent off-site air concentrations. The second objective was to obtain appropriate regional input parameters (soil, weather, management practices, and physicochemical properties) required by the numerical system. The third objective was to evaluate the modeling system against two field study observations. A fourth objective was to evaluate the sensitivity of the model to uncertainty in input parameters. Ultimately, the modeling tool will be used to assess the impact setback distances from treated fields have on 1,3-D concentrations in air and for comparison to current standards set by the U.S. EPA for 1,3-D.

MATERIALS AND METHODS

Field Studies. Agronomic field-scale studies for quantifying 1,3-D volatility from soil have been performed by Dow AgroSciences in Florida near Immokalee (*12*) and in the Salinas valley of California (*13*). 1,3-D was applied by mechanical shank injection, and the volatility flux was experimentally determined using the aerodynamic flux method (AFM; *14*, *15*). AFM uses atmospheric gradients of wind speed, temperature, and pesticide concentrations above the soil surface to estimate the mass-flux of the chemical. All three of these independent parameters were experimentally measured under field conditions.

Predominant soil series at the study sites in Florida (FL) and California (CA) were Myakka and Metz, respectively. The raised bed, tarped, FL study had 1,3-D injected at ~25 cm below the soil surface. The CA bare soil experiment had 1,3-D shank injected into soil at a depth of 45.7 cm. Cumulative amounts of measured 1,3-D leaving the field for the FL and CA sites were 39.9 and 25%, respectively, following several weeks of monitoring (with trace level emissions detected at the end of the sampling interval).

Scenarios Used For Regional Assessment. Geographic regions were selected on the basis of major 1,3-D sales areas (**Figure 1**). Washington (WA), California (CA), North Carolina (NC), Georgia (GA), and Florida (FL) are representative of >95% of the U.S. market for 1,3-D products. Predominant agricultural soils in these high-use regions were selected using the U.S. EPA PATRIOT database (*16*) with the exception of Washington, where a Quincy loamy sand soil was used. Regional scenarios used in PRZM3 simulations to determine 1,3-D emission losses are summarized in **Table 1**.

Table 1. 1,3-D Scenarios Used in the Stochastic PRZM3 Simulations for Soil Flux Predictions

location	crop	soil type	application period
Tifton, GA	vegetables/tomatoes	Tifton loamy sand	Aug 10
Clayton, NC	tobacco	Appling sandy loam	May 15
Yakima, WA	potatoes	Quincy loamy sand	Aug 10
Gainesville, FL	vegetables/tomatoes	Satellite	Aug 10
Salinas, CA	vegetables	Arroyo Seco sandy loam	Aug 10 Oct 1 (shank only)

Numerical Models Used. *Choice of Modeling Algorithms.* A method to distinguish correct order of magnitude 1,3-D soil flux predictions on a regional basis and to account for uncertainty in input parameters was sought. The pesticide root zone model (PRZM; *17*) is used by the agrochemical industry and the U.S. EPA for predicting pesticide fate and exposure (*18*). PRZM3 is a one-dimensional soil compartment model that addresses hydrology, runoff, erosion, and pesticide dissipation in the soil root zone. PRZM3 has been predominately used to predict pesticide leaching and surface runoff patterns and has been evaluated elsewhere (*19*−*25*). However, few studies using PRZM3 to predict the mass flux of volatile pesticides have been reported (*26*).

Dow AgroSciences has created many GIS-based numerical tools (that incorporate PRZM3) to predict surface runoff and leaching of pesticides (*27*, *28*). Thus, the use of PRZM3 to predict volatilization losses of soil fumigants is a natural extension of previous research. PRZM3 does have limitations when dealing with water and solute transport, especially considering the simplistic approach to water movement. When a soil layer in PRZM3 exceeds the water-holding capacity, water is moved downward to the next soil layer in a "tipping bucket" fashion. More rigorous models use gravity and matric suction gradients (Richards equation and/or forms thereof; *29*) to approximate water movement at the expense of increased input parameters and computer-processing times required to derive a solution from a discritized solution domain. Increased computer run times can make stochastic methods such as Monte Carlo sampling prohibitively long, and thus PRZM3 is a logical choice for Monte Carlo implementation across a wide spectrum of computer processors. The ability of PRZM3 to mimic Florida and California field observations is addressed under Results.

PRZM3 Modifications. (a) Accounting for Tarped Surfaces. PRZM3 accounts for the volatility of pesticides from soil through a zero-concentration boundary condition for a stagnant air boundary layer at the soil surface. The volatilization rate is a function of the rate of movement of the pesticide to the soil surface and varies as the concentration of a pesticide at the soil surface changes (*30*). The boundary layer thickness (d) of this stagnant air layer is estimated using a water vapor approach (*31*) and is on the order of several millimeters. PRZM3 follows the approach of Wagenet et al. (*32*) who assumed a constant value of 0.5 cm for d. The mass flux loss across the boundary

Table 2. 1,3-D Mass Transfer Coefficient and Activation Energy for a Reference Temperature of 20 °C[a]

parameter	cis	trans
polyethylene film ($\xi_p = +1$)		
h_r^{Tr} (μm s^{-1})	3.034	2.33
E_a^{hr} (J mol^{-1})	26.282	17.22
Hytibar film ($\xi_p = -1$)		
h_r^{Tr} (μm s^{-1})	1.157×10^{-2}	2.005×10^{-2}
E_a^{hr} (J mol^{-1})	222.193	243.86

[a] Values given by Wang et al. (*33*) are the mean values assumed for the normal distribution. Standard deviation for the normal distribution assumed 10% of the mean value.

layer at the soil surface is expressed as

$$J_v = (D_a A/d)(C_g - C_{gs}) = hA(C_g - C_{gs}) \tag{1}$$

where J_v = volatilization flux of pesticide from soil (g/day), D_a = molecular diffusivity of pesticide in air (cm^2/day), A = area of the compartment (cm^2), C_g = vapor-phase concentration in the surface soil layer (g/cm^3), C_{gs} = vapor-phase concentration above the stagnant air boundary layer (g/cm^3), d = stagnant air boundary layer thickness (cm), and h = mass transfer coefficient (cm^3 day^{-1}).

The value of C_{gs} at the top of the stagnant air boundary layer is typically zero for a bare soil surface as the wind can easily transport pesticide mass away from the surface. The term D_a/d in eq 1 represents the mass transfer coefficient (h) for diffusion transport across the boundary layer, and the reciprocal defines the resistance to mass transfer. Resistance to mass transfer at the soil surface will increase if a tarp is present. Thus, the boundary condition (eq 1) can remain the same, but the boundary layer thickness requires adjustment as the mass transfer resistance increases when a tarp is added. This approach has been used by others within the USDA soil model CHAIN_2D (*2*, *4*, *5*). Laboratory-determined, temperature-dependent, mass transfer coefficients for 1,3-D have been reported for a polyethylene-based high-barrier film (HBF) and a virtually impermeable film (VIF) (*33*) and is represented by eq 2.

$$\frac{h}{A} = h_r^{Tr} \exp\left(\frac{T_r - T_a}{RT_a T_r} \xi_p E_a^{hr}\right) \tag{2}$$

h_r^{Tr} = reference mass transfer coefficient at a reference temperature (T_r), E_a^{hr} = activation energy for the reference mass transfer coefficient (J mol^{-1}), ξ_p = empirical phase adjustment factor accounting for any phase mismatch, T_a = air or plastic film temperature (K), T_r = reference temperature (K), and R = universal gas constant (8.314 J mol^{-1} K^{-1}).

PRZM3 was modified to incorporate changes in the mass transfer coefficient across the stagnant boundary layer when either a HBF or VIF tarp was used. New PRZM3 input parameters h_r^{Tr} and E_a^{hr} are now required when a plastic tarp covers the field. The mass transfer coefficient (eq 2) is updated daily (time step of model) based upon the daily PRZM3 simulated surface soil temperature. Mass transfer coefficients and activation energy probability density functions used in the analysis (when a tarp is present) are summarized in **Table 2**.

(b) Converting Daily Mass Flux Predictions into Hourly Rates. PRZM3 produces results on a daily time step, whereas many regulatory air dispersion models operate on an hourly time step. The following assumptions were used in transforming PRZM3 daily values to hourly entries. The sum of the hourly emission losses per day total the cumulative daily loss as predicted by PRZM3. The pesticide application was always made at 8:00 a.m., and a 4-h delay occurred between the application and when the first 1,3-D mass left the soil. Delay intervals of this order are seen in shank injection field trials when injection knife traces are adequately sealed. The simulated daily pesticide loss via volatilization (percent of applied) was scaled by the pesticide application rate, field size, and a sinusoidal weighting function to obtain an hourly mass flux rate loss as required by Gaussian air dispersion models. Volatility mass loss was assumed to be twice as high at noon (i.e., the hottest part of the day) when compared to midnight and varied

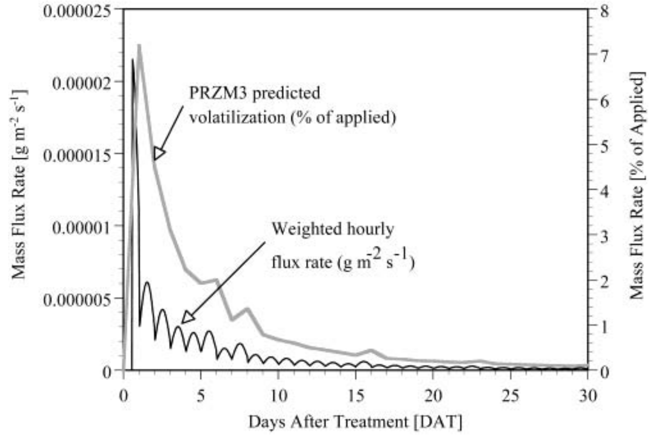

Figure 2. PRZM3 daily flux profile (percent of applied) converted to hourly flux (application rate = 94 kg/ha). Cumulative mass loss via the weighted hourly flux rate equals that predicted by PRZM3.

in a sinusoidal fashion. Sinusoidal weighting for volatility losses indirectly accounts for temperature dependence on physicochemical properties that control the volatility loss of 1,3-D from soil. The sum of the hourly flux rate over a 24-h interval equals the daily loss generated by PRZM3. Characteristic results of this approach are given in **Figure 2**. Assumptions about the time of day when an application is made and the sinusoidal weighting of emission losses should not significantly alter the subchronic air concentration predictions (i.e., 15-day averages) required for a risk assessment. These assumptions would obviously be extremely sensitive if the endpoint air concentration was an instantaneous value or some minor interval (i.e., 1-h average) instead of the 15-day averages used in this analysis.

Air Dispersion Modeling. The industrial source complex short-term (ISCST3) (*34*) model was developed by the U.S. EPA as a regulatory tool for air dispersion modeling. ISCST3 is a Gaussian plume model used for estimating air quality surrounding contaminant release sites. Examples of use include vehicle exhausts in urban areas (*35*), industrial sulfur dioxide emissions (*36*), methyl bromide concentrations resulting from soil fumigation in rural areas (*37*), and 1,3-D township-wide air concentrations for multiple transient agricultural sources within a California township (*38*). Meteorological data inputs required by ISCST3 include hourly air stability class, wind speed, air temperature, wind direction, and mixing and ceiling height for the airshed. Thus, the hourly emission flux patterns derived from PRZM3 simulations are appropriately transported throughout an airshed via the Gaussian plume analysis that utilizes hourly values for regional meteorological conditions.

Air dispersion models such as ISCST3 are based upon wind-driven convection and dispersion. Wind direction exhibits considerable temporal variability in many agricultural areas of the United States. An example wind direction pattern (wind rose) is given in **Figure 3** for Waycross, GA, for a single year of historical data (EPA SCRAM website). A wind rose allows the temporal variability to be displayed in a two-dimensional graphic (polar coordinates). Each petal in **Figure 3** represents the percentage of time the wind blew from a particular direction (in 22.5° gradations) for a range of wind speeds (shades along a petal) over the 1-year time interval. Wind direction is nearly random (equal probability of occurring from any direction) for Waycross and many other regions of the country, although proximity to some geographic features (e.g., mountains and oceans) may result in preferential wind directions.

Selecting a specific receptor location near a treated field for air concentration calculations is not appropriate because air concentrations will differ depending on temporal variability. Thus, a more accurate portrayal of air concentrations resulting from soil fumigant treated fields is a directional average around the entire field. Directional averaging eliminates problems associated with single-point receptors such as potentially "missing" the contaminant plume or unecessarily high bias should receptors be placed downwind over a short time frame sampling interval. Directional averaging provides a mechanism for comparison

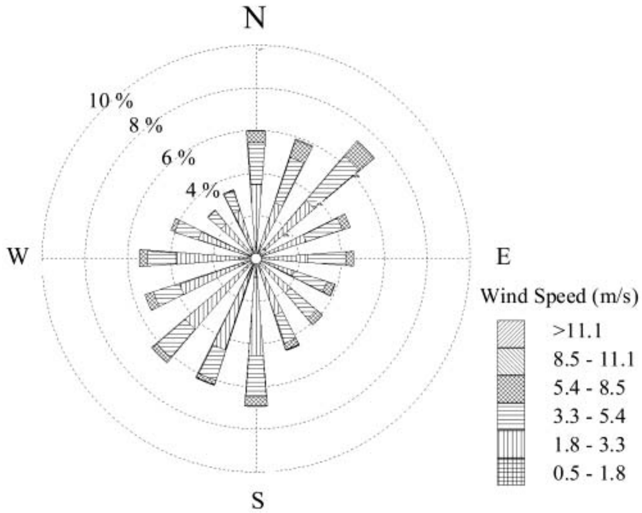

Figure 3. Wind rose pattern at Waycross, GA (1984 historical data from SCRAM).

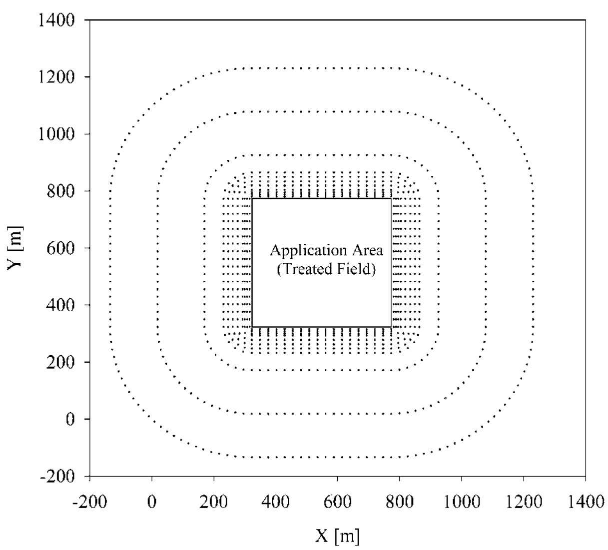

Figure 4. Example for the relationship of field size to receptor placement for a 50-acre field.

of various management practices when the temporal nature of wind speed and direction is accounted for.

Receptor locations for air concentration calculations with directional averaging were selected such that the distances for all receptor nodes fall exactly at the setback distance of interest. Distances of 7.6, 15.2, 22.9, 30.5, 45.7, 61.0, 76.2, 91.4, 152.4, 304.8, and 457.2 m (25, 50, 75, 100, 150, 200, 250, 300, 500, 1000, and 1500 ft) are generated, with the spacing between each neighboring receptor being 25 m (**Figure 4**). All receptors were placed at 1.5 m above the ground to mimic the breathing height for adults. Each receptor node along one of the perimeters, seen in **Figure 4**, is exactly the same distance from the closest field edge as all other receptors along the perimeter. The multidirectional 1,3-D air concentration is simply the average of all receptors falling along one of the equidistant (from field) perimeters over a specific time interval. The receptor density in this exercise is adequate to capture a contaminant plume that initiated over the field boundaries and travels in any direction.

Stochastic Implementation. The stochastic implementation of PRZM3 and ISCST3, with random weather, was obtained using Monte Carlo (MC) and Latin hypercube sampling methods (*39*, *40*) via visual basic application (VBA) programming with Microsoft Excel (MS) and the MS Excel add-in software package Crystal Ball (trademark of Decisioneering, Inc.). In this way, the source code for either model did NOT require modification for stochastic implementation and every input parameter for each model can be assigned uncertainty (if desired). The use of Crystal Ball with VBA provides an easier and more general approach to incorporate MC techniques than reported elsewhere where only a subset of PRZM3 inputs could be varied (*41*). Probability density functions (PDFs) for input parameters were sampled for each simulation year, spreadsheets were updated, a random weather file was chosen from a weather library for a region of interest, input files were created, PRZM3 or ISCST3 was executed, and results were imported and summarized back into Excel. Thus, uncertainty in soil and physicochemical properties, random weather years, management practices, and so forth were described stochastically through definition and sampling of user-supplied PDFs for model input parameters.

Parameters Utilized. Specific PRZM3 and ISCST3 input parameters were assumed to be normally or log-normally distributed with the mean value given by the single-valued magnitude (nominal value) obtained from respective databases, user manuals, and/or expert judgment. The distribution standard deviation was assumed to be 10% of the mean unless actual field or laboratory data were available. It is assumed variances of this magnitude are adequate to capture the parametric sensitivities in model input, although actual field variability can be greater. 1,3-D soil degradation rates in the water and solid phases for each horizon were assumed to be equal, and degradation in the soil gas phase was assumed to be negligible. Subsurface soil layers were assigned 1,3-D degradation rates one-third of the surface horizon. For a soil horizon having two to three soil layers, the total number of varied PRZM3 input parameters was 26 or 31, respectively (**Table 3**).

PRZM3 weather was randomly sampled from the regional weather library (containing 100 years of meteorological data for each weather station). Regional weather patterns were generated using the U.S. Department of Agriculture CLImate GENerator program CLIGEN (*42*). Physicochemical parameters for 1,3-D used in this analysis are summarized in **Table 4**. Shank injection depths were uniformly distributed between 30.5 and 61 cm (12−24 in.).

ISCST3 dispersion parameters were fixed at regulatory default values (*34*), but other stochastic parameters included weather year, field size, application date, application rate, and the 1,3-D air degradation coefficient (**Table 5**). Management information for WA, NC, GA, and FL were obtained from >500 grower interviews and records. This grower survey information resulted in ∼1580 records of field sizes and corresponding application rates for all crops treated in these regions between 1990 and 2000. Similar information for CA for 1999 was obtained from California Data Management System, Inc. A log-normal distribution was fitted to the field size and application rate data with the exception of WA. WA had many fields exceeding 300 acres. The maximum number of acres treated by conventional practices is ∼5 acres per hour or ∼120 acres per day assuming "around the clock" application (Ryan Roslak, DAS Telone Specialist, personal communication). Thus, larger WA fields were divided by 120 acres to arrive at the total number of "subfields" treated within the region on consecutive days as dictated by commercial equipment constraints.

Meteorological Data and Regions Simulated. Hourly meteorological data required by ISCST3 were obtained from the EPA Support Center for Regulatory Air Models (SCRAM). SCRAM weather station locations were selected on the basis of proximity to high-use regions for 1,3-D (**Figure 1**). SCRAM information contains U.S. EPA quality checked and approved weather files specifically for the purposes of regulatory air quality modeling. Meteorological stability class was estimated using the program PCRAMMET (*43*) using measured data from the closest weather station where mixing height data were recorded.

Sensitivity Analysis. The integrity of transport modeling results often depends on the expert judgment of model users to identify input data requirements (*8*). A statistically sound sensitivity analysis is vital in determining which model inputs create the greatest variance on model output(s), especially if some input parameters are not measured, but rather empirically estimated. Both principal component analysis (PCA) and ANOVA methods were used with MC simulation results to deduce sensitive model input parameters.

Table 3. Soil and Management Properties Stochastically Varied in PRZM3 Simulations (Subscript Denotes Soil Layer *i*)[a]

parameter	CA	FL	GA	NC	WA
weather location	Salinas	Gainesville	Tifton	Clayton	Yakima
soil type	Arroyo Seco sandy loam	Satellite	Tifton loamy sand	Appling sandy loam	Quincy loamy sand
crop type	vegetables	vegetables/tomatoes	vegetables/tomatoes	tobacco	potatoes
appl type	shank, drip	shank, drip	shank, drip	shank, drip	shank
appl period	Aug 10, Oct 1	Aug 10	Aug 10	May 15	Aug 10
appl rate (kg/ha)	99.4–614.5 U	112.7 ($\sigma = 6$, N)	112.7 ($\sigma = 6$, N)	99.4–614.5 U	112.7 ($\sigma = 6$, N)
CN2	72 ($\sigma = 2$, N)	72 ($\sigma = 2$, N)	78 ($\sigma = 2$, N)	78 ($\sigma = 2$, N)	77 ($\sigma = 2$, N)
DOI (cm)	40.7 (30.5–50.8 U)	30 N	(30.5–50.8 U)	(30.5–50.8 U)	(30.5–50.8 U)
QFAC	4.0 N	4.0 N	4.0 N	4.0 N	4.0 N
soil reflectivity	0.97 N	0.97 N	0.95–0.98 U	0.95–0.98 U	0.95–0.98 U
BD_i	1.25, 1.53, 1.55 N	1.27, 1.27 N	1.42, 1.55 N	1.52, 1.35, 1.35 N	1.35, 1.45 N
$ISWC_i$	0.255, 0.231, 0.190 N	0.114, 0.085 N	0.156, 0.257 N	0.194, 0.437, 0.447 N	0.118, 0.049 N
T_{bottom} (°C)	22.0 N	23.0 N	22.0 N	22.0 N	22.0 N
soil albedo	0.18 N	0.40 N	0.40 N	0.18 N	0.40 N
FC_i	0.255, 0.231, 0.190 N	0.114, 0.085 N	0.156, 0.257 N	0.194, 0.437, 0.447 N	0.118, 0.049 N
WP_i	0.139, 0.133, 0.117 N	0.045, 0.030 N	0.084, 0.159 N	0.134, 0.391, 0.318 N	0.052, 0.031 N
OC_i	1.16, 0.10, 0.10 N	1.30, 0.10 N	0.291, 0.436 N	0.727, 0.145, 0.145 N	1.00, 0.30 N

[a] Mean values represented in table with PDF assumed (N = normal, U = uniform).

Table 4. Physicochemical Stochastic Properties Used in PRZM3 Analysis

parameter	μ/σ or range	distribution
Henry's coefficient, cis (cm^3 cm^{-3}), at 25 °C	0.0599/0.0060	normal
Henry's coefficient, trans (cm^3 cm^{-3}) at 25 °C	0.0349/0.0035	normal
enthalpy of vaporization (cis = trans) (kcal mol^{-1})	9.60/0.96	normal
surface soil degradation rate constant (water phase) (day^{-1})	0.082/0.078	log-normal
surface soil degradation rate constant (solid phase) (day^{-1})	0.082/0.078	log-normal
soil/water equilibration partition coefficient (K_D) (cis = trans) (cm^3 g^{-1})	0.658/0.459	log-normal
diffusion coefficient in air (cis = trans) (cm^2 day^{-1})	7499/750	normal

Table 5. Stochastic Properties Used in ISCST3 Analysis

parameter	μ/σ or range	distribution type
CA field size (acre)	40.2/73.3	log-normal
CA appl rate (kg/ha)	$10 \le$ rate ≤ 380	custom
CA appl date (Julian)	Jan–Dec	uniform
FL field size (acre)	80.3/106.7	log-normal
FL appl rate (kg/ha)	94.1/25.3	log-normal
FL appl date (Julian)	Jan–March Aug–Nov	uniform
GA field size (acre)	58.3/87.0	log-normal
GA appl rate (kg/ha)	79.7/32.6	log-normal
GA appl date (Julian)	Feb–April	uniform
NC field size (acre)	13.9/12.2	log-normal
NC appl rate (kg/ha)	90.6/28.9	log-normal
NC application date (Julian)	Feb–April	uniform
WA field size (acre)	$5 \le$ acre ≤ 120	custom
WA appl rate (kg/ha)	$40 \le$ rate ≤ 340	custom
WA appl date (Julian)	Aug–Oct	uniform
1,3-D deg rate constant in air (s^{-1})	1.60×10^{-5}/ 3.20×10^{-6}	normal
weather year	1984–1991 (or 1992)	uniform

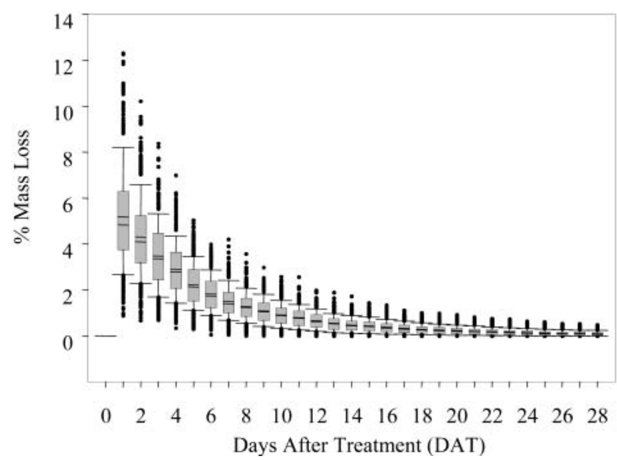

Figure 5. Discrete mass loss distribution for FL simulations using PRZM3 (shank, 10-in. incorporations, Satellite soil, Avon Park, FL, weather).

RESULTS

Stochastic Volatilization Predictions. Variability in model output for 500-year PRZM3 stochastic iterations is graphically illustrated in **Figure 5** for a representative South Florida simulation (shank injection), where daily mass loss is given as a percentage of applied. The boxes in **Figure 5** define the 25th–75th percentile, whiskers representing the 5th and 95th percentiles, and symbols representing outlier points. Variability in fumigant mass losses from soil for this scenario is high, ranging from 1 to 13% of applied for the 24-h interval immediately following the application.

PRZM3 Comparison against Field Observations. Comparison between field observations and the best-fit PRZM3 predictions is given in **Figure 6** for simulated percentile values of 84.4 and 89.6 for Florida and California, respectively. Results from the two-dimensional finite element model for water and solute transport (CHAIN_2D; *2*) are also provided for the Florida scenario. Correct order of magnitudes for cumulative volatilization losses are recovered by PRZM3 when compared to both experimental observations and rigorous model predictions (CHAIN_2D). PRZM3 predictions at ~85% percentile do a reasonable job of mimicking field observations for these field studies. Thus, the 85th percentile was empirically chosen as a reasonable exceedence percentile for PRZM3 modeling for geographic regions lacking field observations. This would be

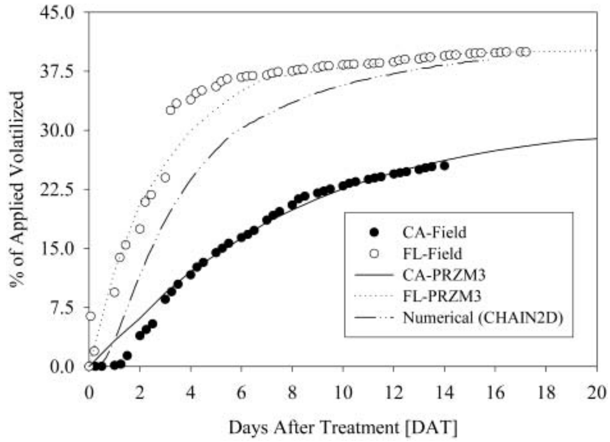

Figure 6. Comparison of PRZM3 predictions at the 84.5 and 89.6 percentile values for FL (10-in. shank bed) and CA (18-in. shank), respectively, to field observations (shank injection). FL simulation results using CHAIN_2D are also provided.

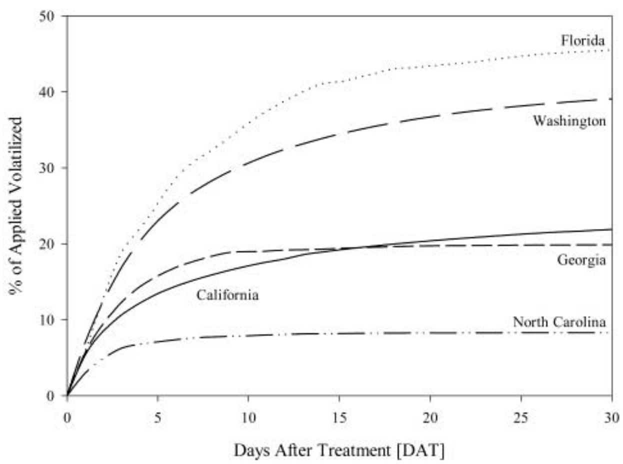

Figure 7. PRZM3 predicted cumulative mass loss of 1,3-D for various geographically different regions [shank injection (12–24 in.), bare soil].

an indication that PRZM3 underpredicts shank injection mass losses and therefore percentiles >50% would have to be used for median predictions (assuming these field trials represent median behavior for their appropriate regions). If a polyethylene tarp is used, then cumulative results are reduced by ~49%.

Selection of Regional Flux Distribution. The empirical best-fit percentile value of 85% for cumulative 1,3-D volatilization loss following shank injection was used with all other regions (CA, FL, GA, NC, and WA) when representative, regionally specific, 1,3-D volatility profiles were selected (**Figure 7**). Regions having the highest predicted 1,3-D mass loss include FL and WA. Elevated daily temperatures and higher soil porosity contribute to the increased mass loss over other scenarios. The predicted PRZM3 cumulative volatilization loss for shank-injected 1,3-D ranged from 8.3 to 45.5% of applied (for PRZM3 predictions at the 85th exceedence percentile and the five regions investigated).

PRZM3 Sensitivity Analysis. Cubic equation R^2 and P values for the linear term, squared, and cubic terms for each parameter in a linear analysis were documented. ANOVA results for individual parameters were sorted by R^2. ANOVA results indicate parameters affecting soil temperature are routinely sensitive for both cumulative and daily maximum volatility losses for 1,3-D. Temperature parameters include soil reflectivity, albedo, temperature of the bottom soil horizon, and QFAC (factor for the rate increase in physicochemical properties when the soil temperature increased by 10 °C). Sensitive soil properties were bulk density, field capacity, wilting point, organic carbon, and initial soil water content at application (for various layers within the soil). Sensitive physicochemical properties included diffusion coefficients in air and Henry's coefficients for both isomers, soil−water partition coefficient for the trans isomer, and soil degradation coefficients (both isomers, shank injection only). Other sensitive parameters for several regions include the SCS curve number and pesticide incorporation depth. All parameters having a P value of ≤0.05 were assumed to be sensitive. Representative sensitivity analysis results are illustrated for the FL simulation in **Table 6** for shank (bare soil). Percent of explainable variance is calculated using ANOVA techniques. Parameter nomenclature and descriptions are found in the Glossary.

Table 6. Regional PRZM3 Sensitivity Analysis (P Value ≤ 0.05) for 1,3-D Flux to Atmosphere for Shank Injection Applications (Bare Soil), FL Scenario

FL cumulative shank	% variance explained (sensitive parameters only)
inc depth	19.2
QFAC	16.2
Henry's coefficient, trans	15.4
soil reflectivity	14.6
wsID	10.8
WP-2	8.5
FC-2	7.7
deg, cis	7.7

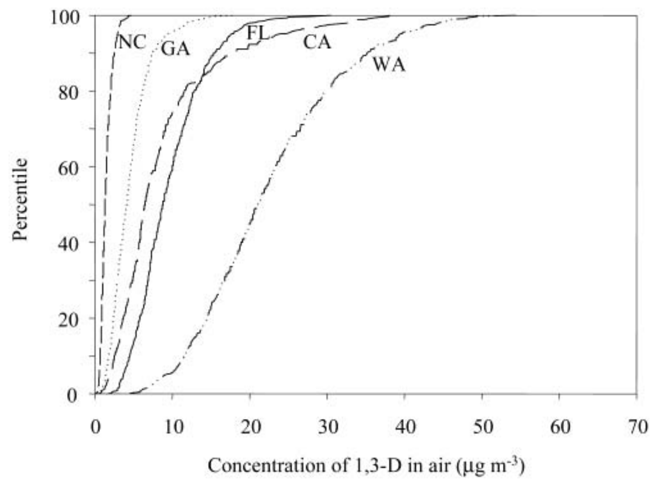

Figure 8. Simulated subacute (15 day average) concentrations of 1,3-D in air at the 100-ft buffer distance for WA, NC, GA, FL, and CA represented as an exceedence percentile function.

Regional Air Concentration Predictions. Figure 8 represents exceedence percentile functions for 1,3-D concentrations in air (15-day average) at a 100-ft buffer zone surrounding the treated field for each of the five regions investigated. A buffer zone is defined as the minimal distance from the edge of a treated field to structures where individuals may reside. Results were obtained via 500 ISCST3 Monte Carlo iterations in which the volatilization mass loss functions given in **Figure 7** were used. The highest concentrations at the higher percentiles were found in WA, where field sizes and application rates (mainly for potatoes) tended to be greater. The lowest concentrations, even at the higher percentiles, are found in NC, where field sizes and 1,3-D application rates (typically tobacco) tend to be smaller.

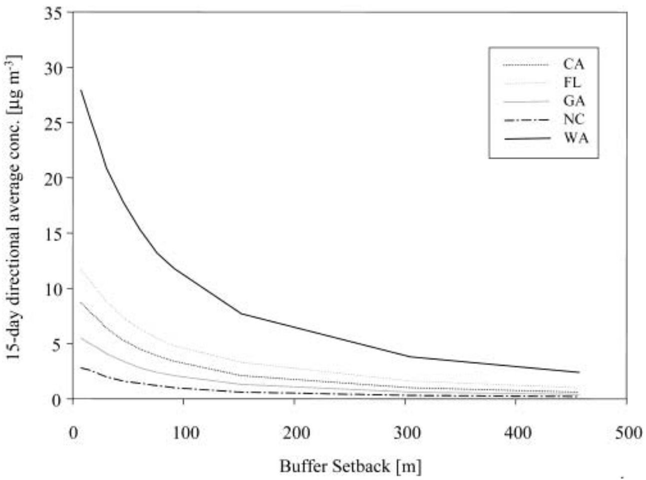

Figure 9. Multidirectional 15-day average air concentration predictions at the 50th percentile for various buffer setback distances.

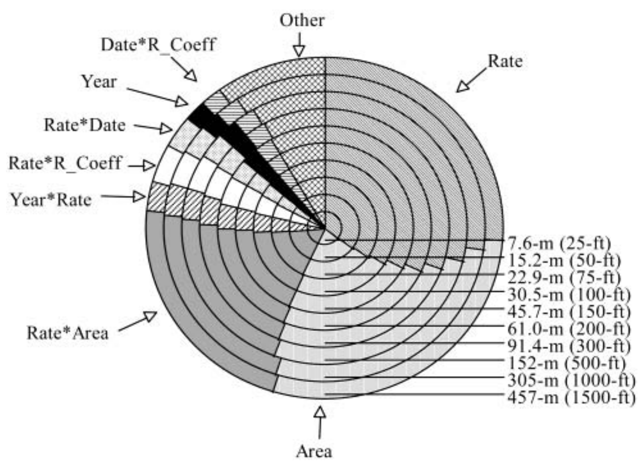

Figure 10. Percent explainable variance for GA simulation data set as a function of buffer setback.

Predicted 50th percentile air concentrations (15-day multidirectional) surrounding treated fields are presented in **Figure 9** for five regions with various buffer setback distances. Air concentrations are below what the U.S. EPA considers to be acceptable (33.9 μg m^{-3}; *11*) for all regions, suggesting 30.5 m (100-ft) buffers will offer a conservative measure for mitigating air exposure values. In many cases, a much smaller buffer surrounding a treated field may be acceptable.

ISCST3 Sensitivity Analysis. ANOVA results indicate a multiparametric linear equation using primary and cross terms does a reasonable job of approximating the ISCST3 exposure data. R^2 values ranged from 0.70 to 0.90 for all regions and buffer distances analyzed in this assessment. Application rate and field size were consistently the most sensitive parameters for all of the regions simulated. The relative sensitivities for the application rate and field size decreased and increased, respectively, as the buffer setback distance increased. Thus, for near-field buffers [<61 m (200 ft)], the application rate is the most sensitive parameter for a 15-day multidirectional air concentration. For far-field buffers [>61 m (200 ft)], the field size becomes the most sensitive parameter (**Figure 10**). **Figure 10** represents ANOVA explainable variances as a percent attributable to the parameters investigated for the GA data set. All other regional data sets exhibited similar behavior. The parameters in the legend are the weather year (Year), application date (Date), field size (Area), 1,3-D degradation coefficient in air (R_Coeff), and appropriate cross terms.

Rate, area, and the combination of (rate × area) account for ~75% of the variance in the simulation data represented by **Figure 10**. The "other" column represents a combination of the other seven parameters or cross-term parameter combinations not listed in the legend. Typically, the sensitivities of these parameters in the "other" category had individual percent explainable variances between 0 and 2%.

Conclusions. A numerical system was constructed to provide a seamless integration of Monte Carlo methods, PRZM3, ISCST3, database relationships, and analysis of results for both emission losses of soil fumigants and resulting near-field air concentrations. Comparison between field observations for 1,3-D emissions and PRZM3 numerical predictions illustrates correct order of magnitude predictions are attainable (for both the initial 24-h and cumulative totals for 1,3-D volatilization). The empirically determined 85th percentile of the PRZM3 model 1,3-D flux predictions leads to comparable estimates of field trial observations for shank injection studies (FL, CA). PRZM3 was then used to extrapolate 1,3-D volatilization loss patterns to different geographically diverse regions making up the 1,3-D marketplace where experimental field information was unavailable. In general, the total cumulative mass losses occurred in the following order: FL > WA > CA > GA > NC for shank injection. Representative cumulative losses of 1,3-D from shank injection ranged from 8 to 46% of applied (bare soil). Simulation results indicate tarped fields reduce predicted volatility losses from shank injection applications by approximately 49% when compared to the untarped counterpart.

PRZM3 sensitivity analysis indicates parameters affecting the soil temperature (soil albedo, reflectivity, and temperature at bottom of soil boundary) and bulk densities are sensitive model input parameters. Thus, the time of year when 1,3-D applications are made can effect the total volatilization losses, along with application equipment that can disturb the soil bulk density. Sensitive physicochemical properties include diffusion and Henry's law coefficients for both isomers and, in several cases, the 1,3-D soil degradation rate constant.

Numerically generated 1,3-D flux profiles from soil, evaluated against field observations, were used with air dispersion modeling to predict region-specific off-site 15-day multidirectional exposure averages for 1,3-D concentrations in air. The air concentration considered to be acceptable by the U.S. EPA in the 1998 RED decision (33.9 μg/m^3) was not exceeded at the 100-ft buffer distance at the 50th percentile for any of the five representative 1,3-D use regions simulated. This suggests the 100-ft buffer zone is a conservative approximation and provides adequate safety for the population of individuals residing near treated fields for all 1,3-D uses in the United States. This statement is based upon current understanding of 1,3-D concentration estimates at 100-ft buffers and U.S. EPA risk assessment methodologies found in the 1,3-D Registration Eligibility Decision (*11*).

GLOSSARY

AE-Tarp-Cis = activation energy for tarp material for determining the temperature dependence of the mass transfer coefficient (cis isomer) (J mol^{-1})

AD = pesticide application date (Julian)

AR = pesticide application rate (kg/ha)

BD_i = bulk density of soil layer i (cm^3 cm^{-3})

CN2 = SCS curve number − crop

CN-Crop = SCS runoff curve number at the time of application

DOI = depth of incorporation (cm)

Deg-Air = first-order degradation coefficient of both isomers in air (day^{-1}) (used only in ISCST3 simulations)

Deg-Cis = first-order degradation coefficient of cis isomer in soil (day^{-1})

Deg-Trans = first-order degradation coefficient of trans isomer in soil (day^{-1})

Diff-Cis = diffusion coefficient of cis isomer in air ($cm^2\ day^{-1}$)

Diff-Trans = diffusion coefficient of trans isomer in air ($cm^2\ day^{-1}$)

enthalpy vapor = enthalpy of vaporization (assumed cis = trans) ($kcal\ mol^{-1}$)

FC_i = field capacity of soil layer i ($cm^3\ cm^{-3}$)

FS = field size (hectares)

Henry-trans = Henry's law coefficient for the trans isomer ($cm^3\ cm^{-3}$)

Henry-cis = Henry's law coefficient for the cis isomer ($cm^3\ cm^{-3}$)

inc. depth = pesticide incorporation depth into soil at time of application (cm)

$ISWC_i$ = initial soil water content of soil layer i ($cm^3\ cm^{-3}$)

Kd-Cis = soil/water equilibrium partition coefficient for the cis isomer (cm^3/g)

Kd-Trans = soil/water equilibrium partition coefficient for the trans isomer (cm^3/g)

OC_i = organic carbon percent of soil layer i

QFAC = factor for rate increase when temperature increases by 10 °C for Henry's coefficient and enthalpy of vaporization estimates

soil albedo = physical parameter controlling the flux of energy at the interface between the soil and atmosphere (function of soil reflectivity)

soil reflectivity = reflectivity of soil surface to longwave radiation (fraction)

T_{bottom} = temperature at the bottom boundary (°C)

WP_i = wilting point of soil layer i ($cm^3\ cm^{-3}$)

wsID = unique weather station ID given to a randomly generated weather file

LITERATURE CITED

(1) Woodrow, J. E.; Seiber, J. N.; Dary, C. Predicting Pesticide Emissions and Downwind Concentrations Using Correlations with Estimated Vapor Pressures. *J. Agric. Food Chem.* **2001**, *49*, 3841−3846.

(2) Simunek, J.; van Genuchten, R. *The CHAIN_2D Code for Simulating the Two-Dimensional Movement of Water, Heat, and Multiple Solutes in Variable-Saturated Porous Media*, version 1.1; Research Report 136; U.S. Salinity Laboratory, USDA-ARS: Riverside, CA, 1994.

(3) Chen, C.; Green, R. E.; Thomas, D. M.; Knuteson, J. A. Modeling 1,3-Dichloropropene Fumigant Volatilization with Vapor-Phase Advection in the Soil Profile. *Environ. Sci. Technol.* **1995**, *29*, 1816−1821.

(4) Wang, D.; Yates, S. R.; Gan, J. Temperature Effect on Methyl Bromide Volatilization in Soil Fumigation. *J. Environ. Qual.* **1997**, *26*, 1072−1079.

(5) Wang, D.; Yates, S. R.; Jury, W. A. Temperature Effect on Methyl Bromide Volatilization: Permeability of Plastic Cover Films. *J. Environ. Qual.* **1998**, *27*, 821−827.

(6) Wang, D.; Knuteson, J. A.; Yates, S. R. Two-Dimensional Model Simulation of 1,3-Dichloropropene Volatilization and Transport in a Field Soil. *J. Environ. Qual.* **2000**, *29*, 639−644.

(7) Yates, S. R.; Wang, D.; Papiernik, S. K.; Gan, J. Predicting pesticide volatilization from soils. *Environmetrics* **2002**, *12*, 569−578.

(8) Wolt, J.; Singh, P.; Cryer, S. A.; Lin, J. Sensitivity Analysis for Validating Expert Opinion as to Ideal Data Set Criteria For Transport Modeling. *Environ. Toxicol. Chem.* **2002**, *21*, 1558−1565.

(9) Fontaine, D. D.; Havens, P. L.; Blau, G. E.; Tillotson, P. M. The Role of Sensitivity Analysis in Groundwater Risk Modeling for Pesticides. *Weed Technol.* **1992**, *6*, 716−724.

(10) Cryer, S. A.; Havens, P. L. Regional Sensitivity Analysis Using a Fractional Factorial Method For The USDA Model GLEAMS. *Environ. Modeling Software* **1999**, *14* (6), 613−624.

(11) U.S. EPA. Reregistration Eligibility Decision (RED) 1,3-Dichloropropene; EPA 738-R-98-016, Dec 1998.

(12) Knuteson, J. A.; Dolder, S. C.; Carver, L. S.; Yoder, R. N. Degradation and Transport of Telone in a Vegetable Production System in South Florida. *Book of Abstracts*, 216th National Meeting of the American Chemical Society, Boston, MA, Aug 23−27, 1998; ACS: Washington, DC, 1998; AGRO-147.

(13) Knuteson, J. A; Petty, D. G. Field Volatility Experiments for 1,3-Dichloropropene. In *Abstracts of Technical Papers*, 210th National Meeting of the American Chemical Society, Aug 20−24, 1995, Chicago, IL; ACS: Washington, DC, 1995.

(14) Parmele, L. H.; Lemon, E. R.; Taylor, A. W. Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. *Water Air Soil Pollut.* **1972**, *1*, 433−451.

(15) Majewski, M. S.; Glotfelty, D. E.; Seiber, J. N. A comparison of the aerodynamic and the theoretical-profile-shape methods for measuring pesticide evaporation from soil. *Atmos. Environ.* **1989**, *23*, 929−938.

(16) U.S. EPA. *PATRIOT*, version 1.0; Software Center for Exposure Assessment Modeling, Environmental Research Laboratory, Office of Research and Development: Athens, GA, 1993.

(17) Carsel, R. F.; Mulkey, L. A.; Lorber, M. N.; Baskin, L. B. The Pesticide Root Zone Model (PRZM): A Procedure for Evaluating Pesticide Leaching Threats to Ground Water. *Ecol. Modeling* **1985**, *30*, 49−69.

(18) Jones, R. L.; Mangels, G. Review of the Validation of Models Used in Federal Insecticide, Fungicide, and Rodenticide Act Environmental Exposure Assessments. *Environ. Toxicol. Chem.* **2002**, *21*, 1535−1544.

(19) Mueller, T. C.; Jones, R. E.; Bush, P. B.; Banks, P. A. Comparison of PRZM and GLEAMS Computer Model Predictions with Field Data for Alachlor, Metribuzin and Norflurazon Leaching. *Environ. Toxicol. Chem.* **1992**, *11*, 427−436.

(20) Pennell, K. D.; Hornsby, A. G.; Jessup, R. E.; Rao, P. S. C. Evaluation of Five Simulation Models for Predicting Aldicarb and Bromide Behavior Under Field Conditions. *Water Resour. Res.* **1990**, *26*, 2679−2693.

(21) Russell, M. H.; Jones, R. L. Comparison of Pesticide Root Zone Model 3.12: Leaching Predictions with Field Data. *Environ. Toxicol. Chem.* **2002**, *21*, 1552−1557.

(22) Singh, P.; Jones, R. L. Comparisons of Pesticide Root Zone Model 2.12: Runoff Predictions with Field Data. *Environ. Toxicol. Chem.* **2002**, *21*, 1545−1551.

(23) Smith, M. C.; Bottcher, A. B.; Campbell, K. L.; Thomas, D. L. Field Testing and Comparison of the PRZM and GLEAMS Models. *Trans. ASAE* **1991**, *34*, 838−847.

(24) Walker, A.; Calvet, R.; Del Re, A. A. M.; Pestemer, W.; Hollis, J. M. *Evaluation and Improvement of Mathematical Models of Pesticide Mobility in Soils and Assessment of Their Potential To Predict Contamination of Water Systems*; Blackwell Wissenschafts-Verlag: Berlin, Germany, 1995; p 115.

(25) Zacharias, S.; Heatwole, C. D. Evaluation of GLEAMS and PRZM for Predicting Pesticide Leaching under Field Conditions. *Trans. ASAE* **1994**, *37* (2), 439−451.

(26) Carsel, R. F.; Imhoff, J. C.; Hummel, P. R.; Cheplick, J. M.; Donigan, A. S., Jr. *PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.0*; National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency: Athens, GA, 1995; Cahpter 6.5.

(27) Havens, P. L.; Cryer, S. A.; Rolston, L. J. Tiered Aquatic Risk Refinement: Case Study—At-Plant Applications of Granular Chlorpyrifos to Corn. *Environ. Toxicol. Chem.* **1998**, *10*, 1313−1322.

(28) Cryer, S. A.; Fouch, M. A.; Peacock, A. L.; Havens, P. L. Characterizing Agrochemical Patterns and Effective BMP's for Surface Waters Using Mechanistic Modeling and GIS. *Environ. Modeling Assessment* **2001**, *6*, 195−208.

(29) Swartzendruber, D. The flow of water in unsaturated soils. In *Flow Through Porous Media*; DeWiest, R. J. M., Ed.; Academic Press: New York, 1969; Chapter 6, pp 215−292.

(30) Jury, W. A.; Grover, R.; Spencer, W. F.; Farmer, W. J. Behavior Assessment Model for Trace Organics in Soil: I. Model Description. *J. Environ. Qual*. **1983**, *12*, 558−564.

(31) Jury, W. A.; Grover, R.; Spencer, W. F.; Farmer, W. J. Use of Models for Assessing Relative Volatility, Mobility, and Persistence of Pesticides and Other Trace Organics in Soil Systems. In *Harvard Assessment of Chemicals*; Saxena, J., Ed.; Academic Press: New York, 1983; pp 1−43.

(32) Wagenet, R. J.; Hutson, J. L.; Biggar, J. W. Simulating the Fate of a Volatile Pesticide in Unsaturated Soil: A Case Study with DBCP. *J. Environ. Qual*. **1989**, *18*, 78−84.

(33) Wang, D.; Yates, S. R.; Gan, J.; Knuteson, J. A. Atmospheric volatilization of method bromide, 1,3-dichloropropene, and propargyl bromide through two plastic films: transfer coefficient and temperature effect. *Atmos. Environ.* **1999**, *33*, 401−407.

(34) ISCST3. *Users Guide for the Industrial Source Complex (ISC3) Dispersion Models, Vol. I—User's Instructions*; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards Emissions, Monitoring, and Analysis Division: Research Triangle Park, NC, Sept 1995; EPA-454/B-95-003a.

(35) Hao, J.; He, D.; Wu, Y.; Fu, L.; He, K. A study of the emission and concentration distribution of vehicular pollutants in the urban area of Beijing. *Atmos. Environ*. **1999**, *34* (3), 453−465.

(36) Kumar, A.; Bellam, N. K.; Sud, A. Performance of an industrial source complex model: Predicting long-term concentrations in an urban area. *Environ. Prog*. **1999**, *18* (2), 93−100.

(37) Honaganahalli, P. S.; Seiber, J. N. Measured and predicted airshed concentrations of methyl bromide in an agricultural valley and applications to exposure assessment. *Atmos. Environ.* **2000**, *34*, 3511−3523.

(38) Cryer, S. A.; van Wesenbeeck, I. J. Predicted 1,3-Dichloropropene Air Concentrations Resulting from Tree and Vine Applications in California. *J. Environ. Qual*. **2001**, *30*, 1887−1895.

(39) Rubinstein, R. Y. *Simulation and the Monte Carlo Method*; Wiley: New York, 1981.

(40) Yakowitz, S. J. *Computational Probability and Simulations*; Addison-Wesley Publishing: Reading, MA, 1977.

(41) Havens, P. L.; Carbone, J. P.; Warren-Hicks, W.; Fouch, M. A. Development of a Monte Carlo Sampling Shell for the Pesticide Root Zone Model and its Application by the Federal Insecticide, Fungicide, and Rodenticide Act Environmental Modeling Validation Task Force. *Environ. Toxicol. Chem.* **2002**, *21*, 1566−1569.

(42) Nicks, A. D. *WEPP Climate Generator and Parameter DataBase, CLIGEN*, ver. 1; USDA-ARS Water Quality and Watershed Research Laboratory: Durant, OK, 1989.

(43) U.S. EPA. *PCRAMMET User's Guide*; EPA-454/B-96-001; U.S. EPA Office of Air Quality Planning and Standards Emissions, Monitoring, and Analysis Division: Research Triangle Park, NC, June 1999.

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