

Guidance for Using the Volatilization Algorithm in the Pesticide in Water Calculator and Water Exposure Models

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December 8, 2015

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Overview

This document provides guidance for using the volatilization algorithm in the Pesticide in Water Calculator (PWC). The release of the PWC (Version 1.5) includes additional inputs needed to execute the volatilization algorithm. These include the Diffusion in Air Coefficient, Heat of Henry, and Henry's Law Constant. Additional volatilization-related outputs are also now available, including pesticide mass distribution within the soil profile and the amount of pesticide lost due to volatilization.

This document describes these new additions and provides guidance for assessing pre-emergent and bare soil applications in the PWC with the volatilization algorithm.

Applicable Use of the Volatilization Algorithm

The volatilization algorithm calculates the daily pesticide mass flux from soil over the simulation period. It should only be used to evaluate aquatic exposure associated with bare soil and pre-emergent applications of fumigant and conventional pesticides. In addition, the impact of volatilization is not large for aquatic exposure estimates for semi-volatile chemicals with Henry's Law Constants less than 10^{-7} atm•m³/mol. As such, the volatilization algorithm should not be used to evaluate the following at this time:

1. Aquatic exposure associated with foliar applications. The portion of the volatilization algorithm associated with the crop canopy has not been verified at this time. As such, one critical input for crops, the foliar volatilization dissipation rate constant, is not available in the current PWC. This variable parameterizes the contribution of off-gassing of residues from crop surfaces.
2. Aquatic exposure associated with compounds possessing Henry's Law Constants less than 10^{-7} atm•m³/mol. **Figure A-1** in **Appendix A** shows that aquatic exposure does not change for chemicals with the same loading possessing Henry's Law Constants less than 10^{-7} atm•m³/mol.
3. Inhalation exposure or other terrestrial exposure resulting from vapor-phase concentrations resulting from volatilization. Daily volatilization fluxes estimated from the PWC do not provide the precision required for addressing shorter-term inhalation exposure with external air exposure modeling tools. The daily average volatilization flux values potentially underestimate peak flux values, which can spike over short time scales, on the order of hours.¹

The volatilization algorithm can now be executed entirely within the latest version of the PWC interface. Additional inputs required to execute the volatilization algorithm include: Diffusion in

¹ While daily flux rates can under represent peak flux rates which spike over shorter time scales, underestimation of the equivalent daily total mass loss (percent of applied) by the volatilization algorithm is not expected.

Air Coefficient, Heat of Henry, and Henry's Law Constant. The graphical user interface prompts the user for these parameters regardless of the chemical or application method. **For situations which require the volatilization algorithm to be shut off (as described above), the user should specify an input parameter value of 0 for the Diffusion in Air Coefficient and Heat of Henry to effectively eliminate the volatilization dissipation pathway.**

Guidance on Execution of the Volatilization Algorithm

Parameterization guidance is provided below, organized by menu (or tab) in the PWC interface. The ***Chemical Menu*** includes the physical-chemical properties needed to execute the volatilization algorithm. The ***Applications Menu*** specifies bare soil and pre-emergent application input parameters. The ***Crop/Land Menu*** defines the soil, land surface, and soil-air boundary layer parameters, and the ***More Output Parameters Menu*** includes options for generating various output distributions and fluxes throughout the soil profile.

- **Chemical Menu**

In the Chemical Menu, the Henry's Law Constant, Air Diffusion Coefficient, and Heat of Henry are required to execute the volatilization algorithm. These parameters have been added to this menu as shown in **Figure 1** below.

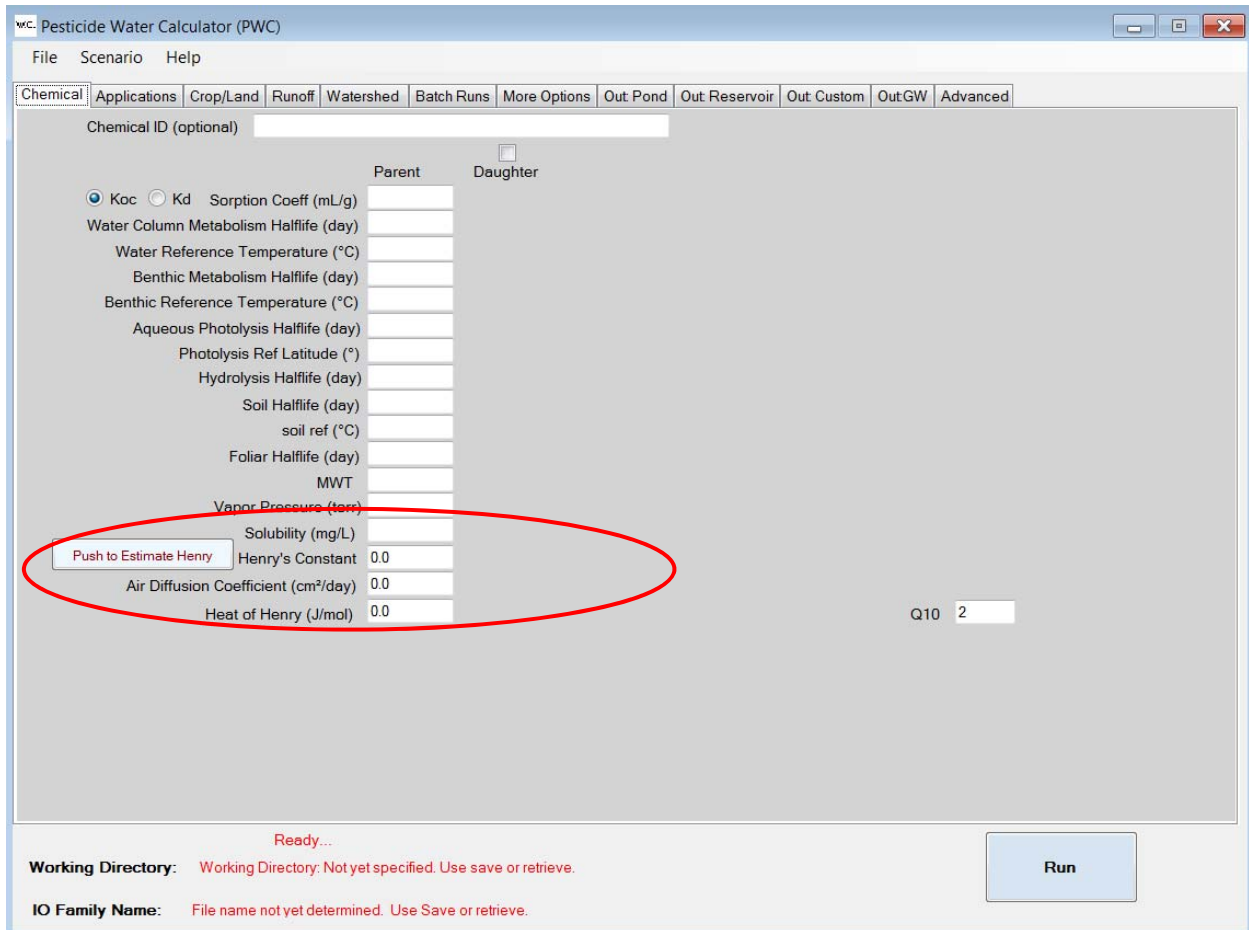


Figure 1. Chemical menu and parameters of interest relevant for volatilization algorithm.

Henry's Constant (dimensionless): The dimensionless Henry's Law Constant (K_h) is the partitioning coefficient of a chemical between air and moist soil. The graphical user interface enables the user to calculate K_h automatically from input vapor pressure and solubility values by clicking the “**Estimate It!**” button. In order to obtain the proper value, the chemical's vapor pressure value at 25°C should be used. The PWC calculates K_h according to the set of equations below:

$$K_h = \frac{HLC \left(\frac{\text{atm} \cdot \text{m}^3}{\text{mol}} \right)}{\text{Universal Gas Constant} \left(\frac{\text{atm} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \right) \times \text{Temperature (K)}}$$

where:

$$\text{Universal Gas Constant } R = 8.21 \times 10^{-5} \frac{\text{atm} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}$$

$$\text{Temperature} = 298 \text{ K}$$

$$\text{HLC} \left(\frac{\text{atm} \cdot \text{m}^3}{\text{mol}} \right) = \frac{\text{Vapor Pressure at } 25^\circ\text{C} \text{ (torr)} \times \frac{\text{atm}}{760 \text{ torr}}}{\text{Solubility} \left(\frac{\text{mg}}{\text{L}} \right) \times \frac{1}{\text{MWT}} \left(\frac{\text{mol}}{\text{g}} \right) \times \frac{\text{g}}{1,000 \text{ mg}} \times \frac{1,000 \text{ L}}{\text{m}^3}}$$

It is important to note that the Henry's Constant input is referenced to 25°C. However, the Henry's Constant for the chemical will vary throughout the simulation based on soil temperature variation, and the Heat of Henry value for the chemical (see description of input parameter above this section). Soil temperature is simulated along with volatilization and varies based on albedo and soil properties. The input of related parameters is discussed within the Crop/Land menu.

Air Diffusion Coefficient (cm²/day): The air diffusion coefficient is related to the kinetic energy associated with molecular motion and is dependent on the molecular weight of the compound. The air diffusion coefficient for a specific compound is calculated as (ACS, 1982):

$$D_{\text{air}} \left(\frac{\text{cm}^2}{\text{day}} \right) = \frac{0.001 T^{1.75} M_r^{1/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \times \frac{3,600 \text{ seconds}}{\text{hour}} \times \frac{24 \text{ hours}}{\text{day}}$$

where:

T is the temperature in K (default of 298 K)

$$M_r = \frac{(M_A + M_B)}{M_A M_B}$$

M_A is the molecular weight of air (approximately 29 g/mol)

M_B is the molecular weight of the chemical (g/mol)

P is the pressure in atm (default of 1 atm)

V_A is the molar volume of air (approximately 20.1 cm³/mol)

V_B is the molar volume of compound of interest calculated from the following expression (cm³/mol):

$$V_B = \frac{M_B \left(\frac{\text{g}}{\text{mol}} \right)}{\text{Density of Chemical} \left(\frac{\text{g}}{\text{cm}^3} \right)}$$

The air diffusion coefficient also may be retrieved from sources such as chemical information reports, MSDS documents, or physical chemical property databases, or it can be calculated interactively from EPA's Tools for Site Assessment website, available at: <http://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion.html>. It should be noted that the air diffusion coefficient is adjusted for soil porosity and tortuosity based on Millington and Quirk (1960). The air diffusion coefficient is also more directly used as part of the Jury et al. (1983) equation to determine the volatile flux across the soil-atmosphere boundary.

An input of zero for the air diffusion coefficient effectively shuts off dissipation of the chemical due to volatilization. This value is recommended at this time for simulating foliar applications.

Heat of Henry (J/mol): This parameter is defined as the energy required for the phase change of a chemical from aqueous solution to air solution. The Heat of Henry can be calculated from the Clausius-Clapeyron equation if Henry's Constants at two different temperatures are available (Staudinger and Roberts, 2001). For further instructions, see **Appendix B**. Otherwise, the Heat of Henry can be approximated by the enthalpy of vaporization, which is more commonly available from product chemistry literature, chemical information reports, MSDS documents, or physical chemical property databases. The enthalpy of vaporization is used along with the temperature of the soil to determine the Henry's Law Constant at a specific time. Measured or estimated values (with the cited method description) of the Heat of Henry should be used as much as possible in the PWC input parameterization. Generic default values previously recommended in water model documentation should be avoided.

- **Applications Menu**

In the Applications Menu, the Δ initial chemical soil distribution under the options for application methods to address shank injection applications has been added. This chemical distribution initializes the distribution of the chemical mass in the soil in a linearly increasing fashion from the surface to the specified depth of incorporation. This initial chemical distribution associated with the Δ option is illustrated in **Figure 2** below. **Figure 3** provided below shows the unique application methods associated with bare soil applications (e.g., surface applications and incorporated applications). Input parameter guidance related to the selection of the appropriate application method is provided in **Table 1** below.

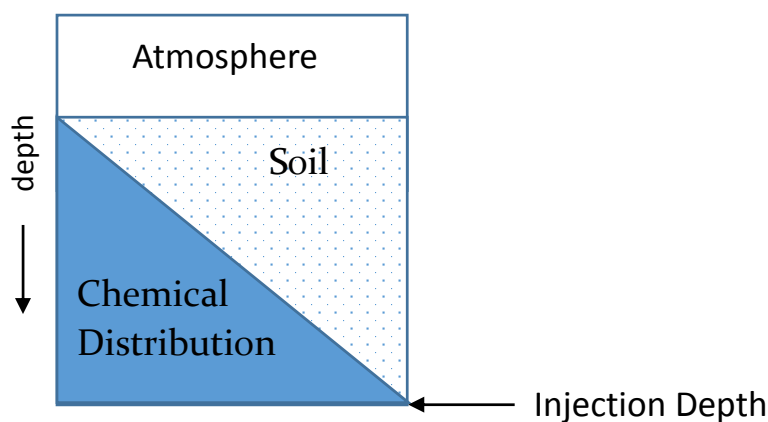


Figure 2. Illustration of the new Δ initial chemical distribution developed in the PWC.

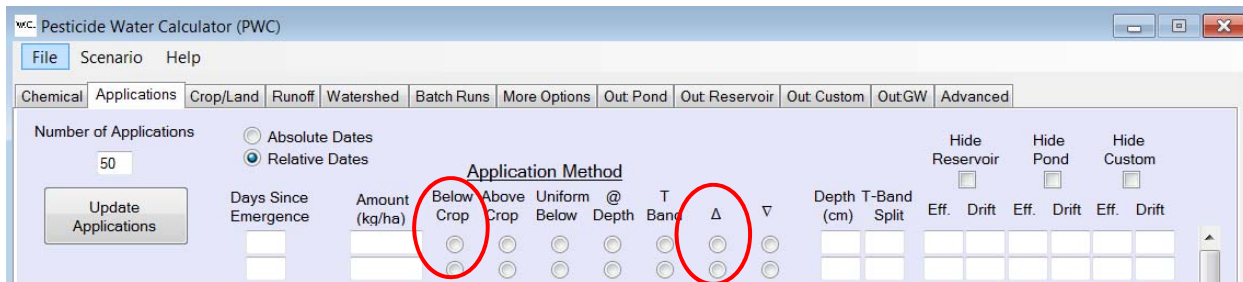


Figure 3. Application menu and parameters of interest relevant for volatilization algorithm.

Table 1. PWC crop management input parameter guidance for consideration using the volatilization algorithm with bare soil pesticide applications.		
PWC Input Parameter	Input Value and Unit	Comment
Crop Scenarios and Application Date	<p>While bare soil and pre-emergent applications are being simulated, existing crop scenarios in the PWC should be used, relevant to the registered or proposed crop use, to account for representative variations in soil and meteorological conditions.</p> <p>Select the relative date button and enter the days prior to emergence (using a negative sign (e.g., -7) days or any number of days since emergence) considering the plant back interval, if specified on the label.)</p>	Exposure from runoff and leaching will be determined from the occurrence of rainfall, relative to the application date on a field with bare soil.
Application Rate (kg/ha)	Maximum broadcast or area-treated application rate for each crop use.	The maximum broadcast application rate usually applies. However, the application rate may be adjusted to account for banded applications (such as T-Band, injected ¹ , or bedded applications) provided an area-treated normalized application rate is specified on the label.

Table 1. PWC crop management input parameter guidance for consideration using the volatilization algorithm with bare soil pesticide applications.

PWC Input Parameter	Input Value and Unit	Comment
Application Method and Incorporation Depth (cm) ³	<p><u>Surface Applications:</u> (Including Overhead Sprinkler, Overhead Chemigation, Drip Chemigation, Flooded Applications, and Drench Applications):</p> <p><u>Application Method:</u> select Below Crop button (soil applied, uniform chemical mass distribution to 4 cm default depth)</p>	In this case, no depth is specified because the model will use a uniform chemical mass distribution to a default depth of 4 cm.
	<p><u>Soil Incorporated (e.g., shank injection or knifed-in):</u></p> <ul style="list-style-type: none"> ➤ <u>Application Method:</u> select Δ button (soil applied, chemical mass linearly increasing from the surface to the incorporation depth). ➤ <u>Depth:</u> Use the most shallow incorporation depth specified on the label. 	The most shallow injection depth is the most protective assumption for surface water exposure estimates.
Application Efficiency and Spray Drift Fraction	<p><u>Surface (Overhead Chemigation) and Incorporated Applications:</u></p> <p>Eff = 1.0 Drift = 0.0</p>	No spray drift is assumed to accompany overhead chemigation, drip chemigation, or knifed-in/shank injection applications.

Table 1. PWC crop management input parameter guidance for consideration using the volatilization algorithm with bare soil pesticide applications.		
PWC Input Parameter	Input Value and Unit	Comment
	<u>Surface</u> (Overhead Sprinkler) Applications ² ; Follow standard guidance from Off-Site Transport Guidance (USEPA, 2013)	Overhead sprinkler applications with semi-volatile compounds are generally subject to spray drift deposition to water bodies.

Notes:

- ¹ For flat fume knifed or shank injection applications, the broadcast application rate will generally apply as opposed to bedded shank injection applications.
- ² For fumigant applications through an overhead sprinkler, a drift of zero and application efficiency of one may be specified, since the spray material remaining in air is expected to volatilize sufficiently in air to prevent spray drift deposition to water bodies.
- ³ Generic guidance is presented here for surface and incorporated applications. Based on other specific applications on the label, the user may decide to use Uniform below, @Depth, T-Band, or the ∇ options. Please refer to the PWC Manual for further explanation.

- **Crop/Land Menu**

The Crop/Land Menu includes various inputs that are critical to the execution of the volatilization algorithm and dynamic soil temperature routine. The dynamic soil temperature routine should be executed to account for variations in the phase-change resulting from changes in temperature in the soil. The dynamic soil temperature routine can be activated by clicking the checkbox beside “**Simulate Temperature**”. While the standard PWC crop scenarios are used with the volatilization algorithm, several additional parameters are needed to execute the volatilization algorithm and dynamic soil temperature routine. These parameters, their physical significance, and the related input parameter guidance are provided below.

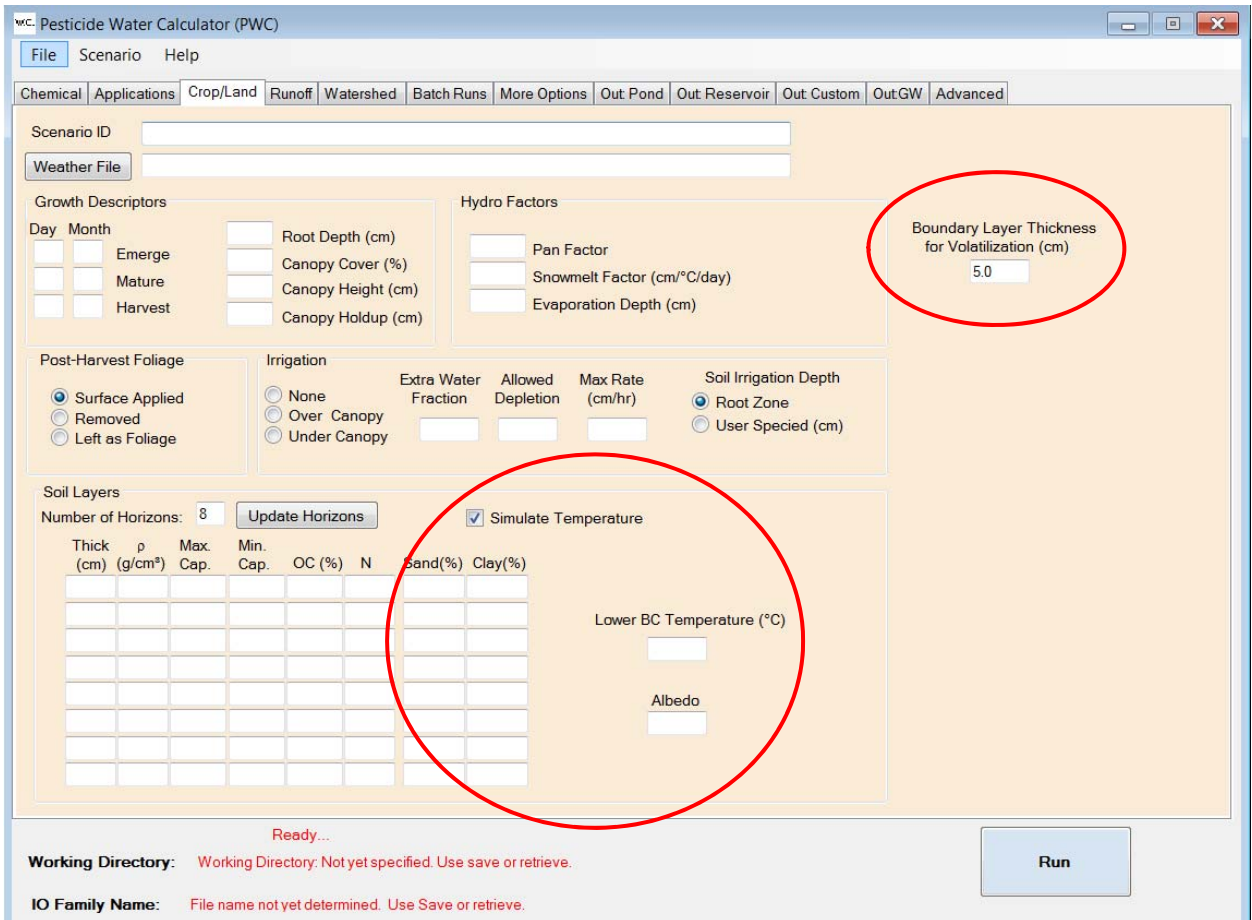


Figure 4. Crop/Land menu and parameters of interest relevant for volatilization algorithm.

Boundary Layer Thickness (cm): This is the depth of the stagnant boundary layer. The Jury et al. (1983) equation for the determination of volatile flux across the soil-atmosphere boundary constrains the atmospheric compartment to this depth. Since the Jury model for flux is based on diffusion factors only, it does not consider dispersion resulting from wind speed and turbulence above this stagnant boundary layer. By definition, the stagnant boundary layer height is analogous to the aerodynamic roughness length, given that there is essentially no wind below this height (due to frictional drag being completely dependent on the underlying bare soil surface²). For bare soil, the surface roughness length is very low considering its relatively smooth surface compared to more complex landscapes containing more significant obstacles to wind flow, such as trees or terrain. **A default boundary layer thickness depth of 5.0 cm is recommended** corresponding to the appropriate surface roughness length for bare soil specified in several sources (Stull, 1988; USEPA, 2004). However, the user may decide to use a different value to evaluate situations involving hillier terrain.

² Roughness length is constant within discrete land surface types. It does not vary with wind speed or temperature.

Lower Boundary Condition (BC) Temperature (°C): This parameter is specified as the constant temperature occurring at a specific depth below the surface. At this depth, heating and cooling cycles (often observed in top soil resulting from air mass temperature changes, diurnal and annual insolation cycles, and changes to land cover over the course of the year) no longer occur. The ground water temperature is roughly equivalent to this temperature. The national distribution of the lower boundary condition can be derived referencing the contour map in **Figure 5**.

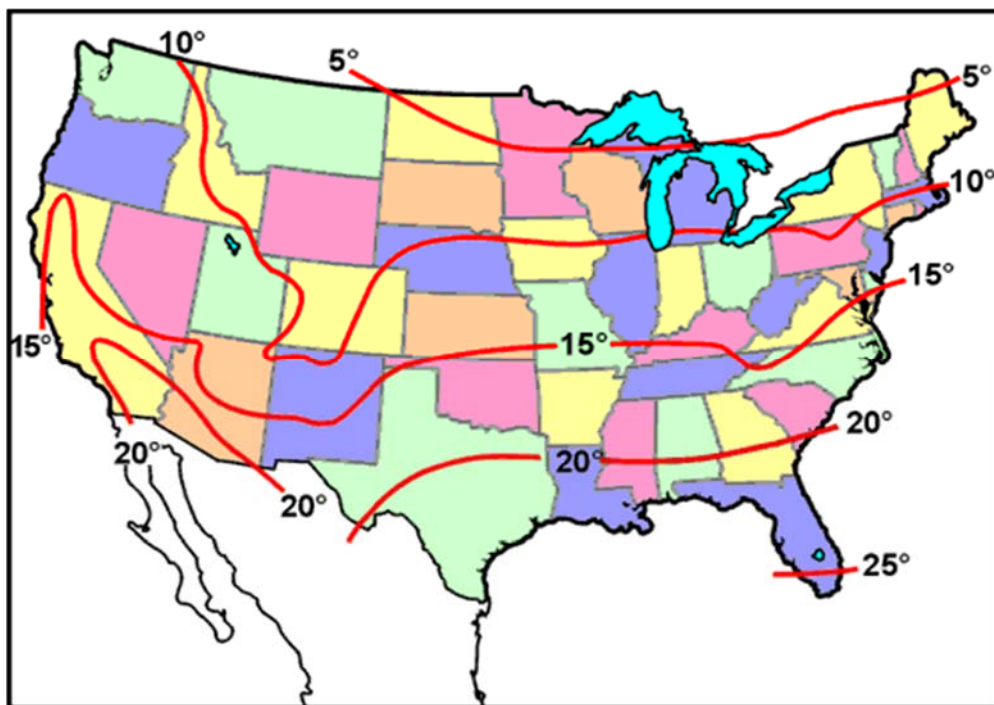


Figure 5. Average shallow groundwater temperatures (°C) in the United States (from <http://www3.epa.gov/ceampubl/learn2model/part-two/onsite/tempmap.html> derived from Collins [1925]).

Albedo: Albedo is the fraction of total incident solar radiation reflected by the surface back to space without absorption. Surface color highly influences albedo values since lighter colors tend to reflect more effectively than darker colors. Albedo is a critical value for the dynamic soil temperature routine, as it dictates the amount of heating through the top soil given air temperature and downward solar radiation from the weather file. Consistent with USEPA (2004), a **daytime albedo value of 0.2 is recommended for bare soil**. This value is representative of conditions associated with the majority of bare soil pesticide applications nationwide.

Sand (%), Clay(%): Soil textural components also need to be specified for the dynamic soil temperature routine. The user will need to retrieve this data from the equivalent soil series of the PWC crop scenario. Consistent with the other soil properties, the percent sand and clay contents need to be included for each soil horizon specified. Soil property data throughout the soil profile

is available from the USGS Soil Survey Geographic Database (SSURGO), and may be retrieved following the steps below:

1. Proceed to the USGS SSURGO Web Soil Survey website at the link provided below:
<http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx>
2. Click on the download soils data tab.
3. Click on the Soil Survey Area (SSURGO) section, and fill in the information with the area of interest.
4. With the results shown below the query area, click on the desired link containing the zip file with the information for the county area of interest.
5. Download the zip file.
6. Extract the directory named (tabular) containing the soil profile data attributes, and save it on a known location on your local computer.
7. Open the Microsoft access database file (.mdb) containing the soil database report template, and enable all macros.
8. In the SSURGO Import Dialogue box which appears, copy the link to the location of the tabular directory, and paste in the field.
9. After waiting several minutes for the soil profile data attributes to load, click on the soil series of interest which appears in the dialogue box. After the soil series is selected, then select the, “Physical Soil Properties”, report name in the drop down menu below the soil series in the dialogue box. After the preceding two entries are selected, click on the, “Generate Report” button at the bottom of the dialogue box.
10. The tabular report of Physical Soil Properties, including the %Sand and %Clay contents specified for each soil horizon, appears on the screen. Parameterize the PWC with the data preserving the horizon-specific data to the existing scenario in the best manner possible.

- **More Output Menu**

The PWC includes an additional menu with options to examine outputs related to the soil profile. Specific functions include (see **Figure 6**):

1. Top left-hand section: Users may select outputs related to the residual pesticide mass distribution retained in the soil as well as specific upward and downward fluxes within the soil profile, including volatilization. These are outputted as daily values to the time series file (.zts) upon running the PWC.
2. Bottom left-hand section: Users may also select daily outputs related to inputs, movement, and removal of soil moisture (e.g., evapotranspiration, irrigation, infiltration, and average soil profile moisture). These are also outputted to the .zts file.
3. Top right-hand section: Users have the option of examining the localities of the soil compartments discretized in the Crop/Land menu, relative to user-specified depths of

interest or to the depth of incorporation specified. After the user enters the depth (in centimeters) of interest in the top box and clicks the “Node Examiner” button, the closest node and the actual simulated depth appear in the text boxes below. While the user should follow the guidance provided in this document on input incorporation depth, the Node Examiner provides the actual incorporation depth simulated, based on the closest soil compartment node.

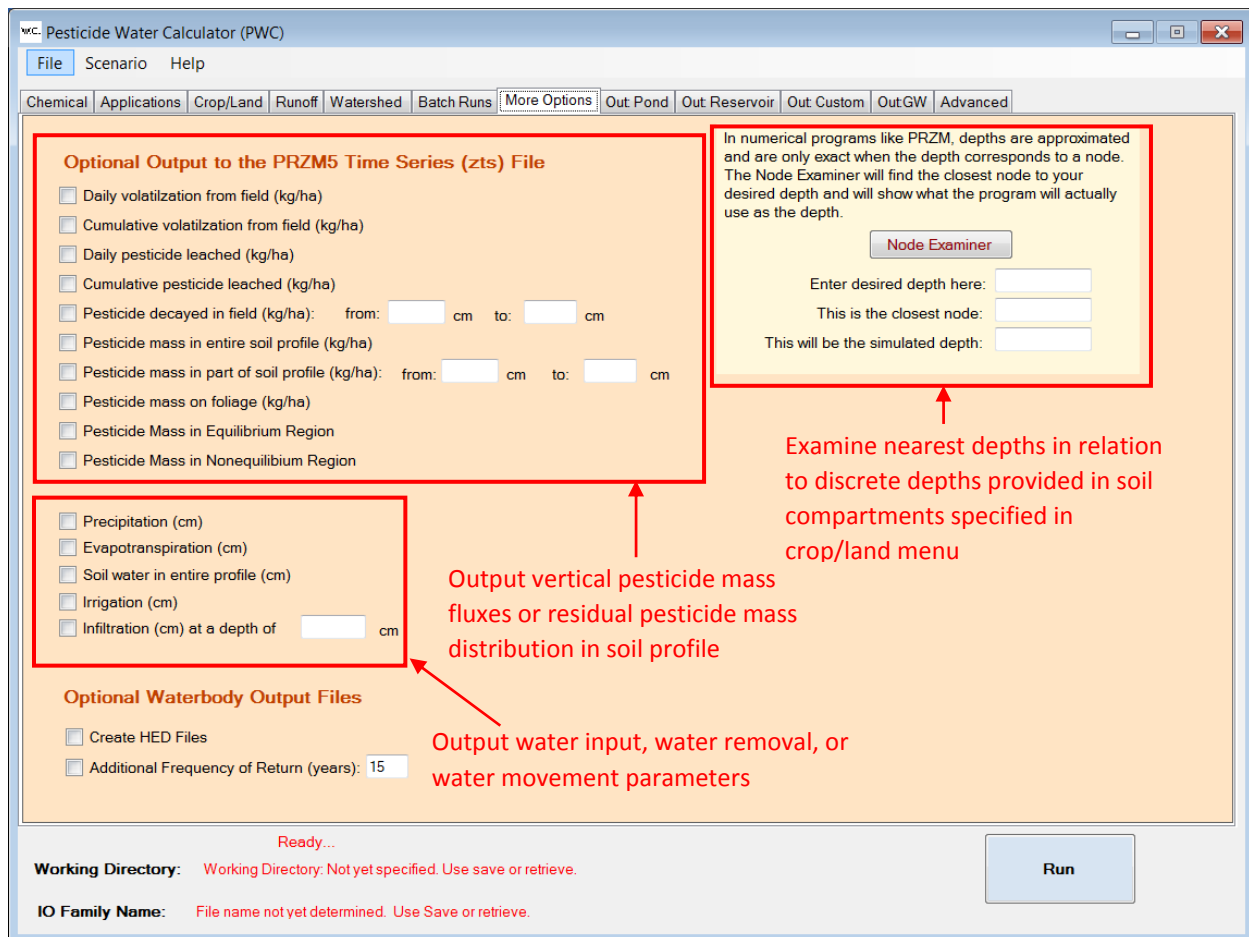


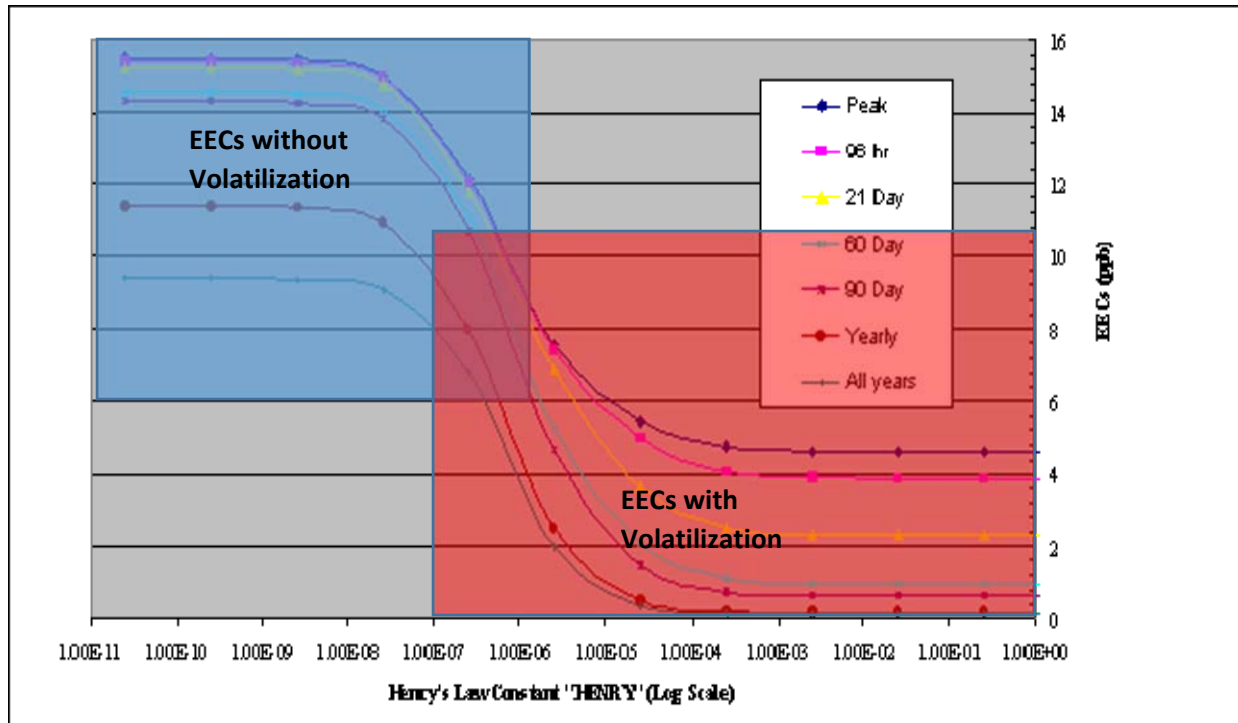
Figure 6. More Output menu and parameters of interest relevant for volatilization algorithm, and movement of chemical and water in the soil.

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Appendix A – Limits of Volatilization Impact on Aquatic Exposure Estimates



Credit: Mohammed Ruhman

Figure A-1. Distribution of estimated exposure concentrations (EECs) in surface water for surface applied compounds of same loading possessing range of Henry's Law Constants.

Appendix B – Calculation of Henry’s Law Constants and Heats of Henry

- Calculation of Unknown Henry’s Law Constant at a Given Temperature:** An unknown Henry’s Law constant can be calculated for one temperature given a known Henry’s Law Constant at another temperature according to a Van’t Hoff relationship derived from the Clausius Clapeyron equation as follows (Staudinger and Roberts, 2001):

$$H(T) = H_{ref} \exp \left[-\frac{\Delta h_{vol}}{R} \left(\frac{1}{T_K} - \frac{1}{T_{Ref}} \right) \right]$$

- where:
- H(T) is the Henry’s Law constant at temperature of interest
 - Δh_{vol} = Heat of Henry or enthalpy of phase change for volatilization of a solute from solution (J/mol)
 - R = universal gas constant = 8.314 J/K/mol
 - H_{ref} = known Henry’s Law constant at T_{ref} (atm-m³/mol)
 - T_K = temperature for H(T) value of interest (K)
 - T_{ref} = temperature at which H_{ref} was measured (K)

- Calculation of Heat of Henry (Δh_{vol}):** Ideally, the Heat of Henry would be calculated from two different Henry’s Law Constants measured at two different temperatures. In these cases, the Heat of Henry would be calculated with the following form of the Van’t Hoff relationship derived from the equation above:

$$-\frac{R}{\left(\frac{1}{T_K} - \frac{1}{T_{Ref}} \right)} \times \ln \left[\frac{H(T)}{H_{ref}} \right] = \Delta h_{vol}$$

Since Henry’s Law Constants at two different temperatures may not be known many times, there are two other different approaches that can be used to calculate or approximate the Heat of Henry.

- Heat of Henry can be estimated by the US EPA EPI Suite software. Open the software, then select the HENRYWIN subprogram on the left of the EPI Suite screen. On the top menu of the HENRYWIN window item, select the Show Options, then select Show Temperature Variation with Results. Enter the chemical name of interest and then push the Calculate button. EPI Suite will give the temperature variation results in the form of an equation: $HLC \text{ (atm-m}^3\text{/mole)} = \exp(A-(B/T)) \{T \text{ in K}\}$. The enthalpy of solvation in Joules/mol is equal to $8.314*B$.
- An alternative approach approximates the Heat of Henry using the chemical-specific enthalpy of vaporization (Δh_{vap}), which may also be calculated from the Van’t Hoff relationship using measured physical chemical properties, including vapor pressure and boiling point according to the following equation:

$$-\frac{R}{\left(\frac{1}{T_{\text{Ref}}} - \frac{1}{T_{\text{BP}}}\right)} \times \ln \left[\frac{\text{VP}}{P} \right] = \Delta h_{\text{vap}}$$

where variables are the same as above except specified below:

T_{ref} = temperature at which vapor pressure was measured (K)

T_{BP} = chemical-specific boiling point, obtained from product chemistry (K)

VP = chemical-specific vapor pressure, obtained from product chemistry (torr)

P = standard atmospheric pressure (= 760 torr).

Note:

¹ If $T_K > T_{\text{Ref}}$ in the above equations, the negative sign from the equations should be removed.