Applying the Pesticide Root Zone Model in Screening-Level PFAS Leaching Assessments

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Benefits of Land Applying Residuals

- Nutrients
- Improved soil properties
- Alternative to landfill disposal

PFAS in Residuals

- Land applied residuals are a potential source of PFAS into the environment

Evaluating PFAS in Land Applied Residuals

- Modeling to estimate PFAS transport and establish limits

- March 2020 - NCASI and Arcadis released report reviewing models for evaluating PFAS in land applied residuals
  - Critical modeling parameters
  - Top-tier, advanced models for estimating potential impactsttps://www.ncasi.org/resource/review-of-models-for-evaluating-per-and-polyfluoroalkyl-substances-in-land-applied-residuals-and-biosolids/
- Feedback received indicated some would prefer to start with a screening-level model as first step
  - Start simple, then progress to advanced models if needed
- PRZM is a prime candidate for this approach
- Resource needed on using PRZM for modeling unique PFAS fate and transport properties after land application, allowing users to make more informed choices during setup and execution

NCASI, in collaboration with NACWA and AF&PA, contracted Stone Environmental to develop a guidance document for applying PRZM in screening-level PFAS leaching assessments

Presentation Overview

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Executive Summary

A Guidance Document was created on how to use EPA's Pesticide Root Zone Model (PRZM) as a screening-level tool to assess the potential for PFAS leaching to groundwater from land applied residuals.

https://www.ncasi.org/resource/guidance-document-for-applying-the-pesticide-root-zone-model-in-screening-level-pfas-leaching-assessments/

The Guidance Document provides a methodology and road-map for regulators and scientists to cost-effectively evaluate potential PFAS leaching to groundwater using EPA-supported models.

The guidance includes:

- ✓ Detailed descriptions of PRZM inputs and outputs in the specific context of simulating potential leaching of PFAS from land applied residuals
- ✓ Guidelines concerning the more sensitive parameters to be aware of when applying the PRZM modeling approach and how to handle uncertainty/variability
- ✓ A procedure for calculating a *dilution attenuation factor* (ratio of chemical mass applied over its concentration in the groundwater) is described which can be used to determine a maximum allowable PFAS application mass rate (per unit area) for any specified drinking water level of concern (DWLOC)

Executive Summary

- ✓ Step-by-step examples that show how to implement PRZM simulations representing the most vulnerable groundwater scenarios developed by US EPA, as well as customized scenarios that may better reflect local conditions (climate, soil, and groundwater conditions). These examples demonstrate how to assess leaching to groundwater based on conservative assumptions of PFAS chemical and physical properties as well as more typical properties and environmental conditions.
- ✓ An example comparison of PRZM modeling simulation results with field data demonstrates the reasonable accuracy of the modeling approach and the level of conservatism compared to measured groundwater concentrations. This provides confidence that the PRZM modeling approach is appropriate as a screening level tool.

How to Obtain PRZM

US EPA developed the Pesticide Water Calculator (PWC) to simulate pesticide applications to land surfaces and the pesticide's subsequent transport to and fate in water bodies, including surface water bodies as well as simple groundwater aquifers.

PWC uses PRZM to model the landscape hydrology and chemical fate and transport processes. It then links PRZM outputs with a receiving surface water model, the Variable Volume Water Model (VVWM).

The current version of the PWC model, PWC version 2.001, can be downloaded from US EPA's Models for Pesticide Risk Assessment (2021) website, https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment#PWC

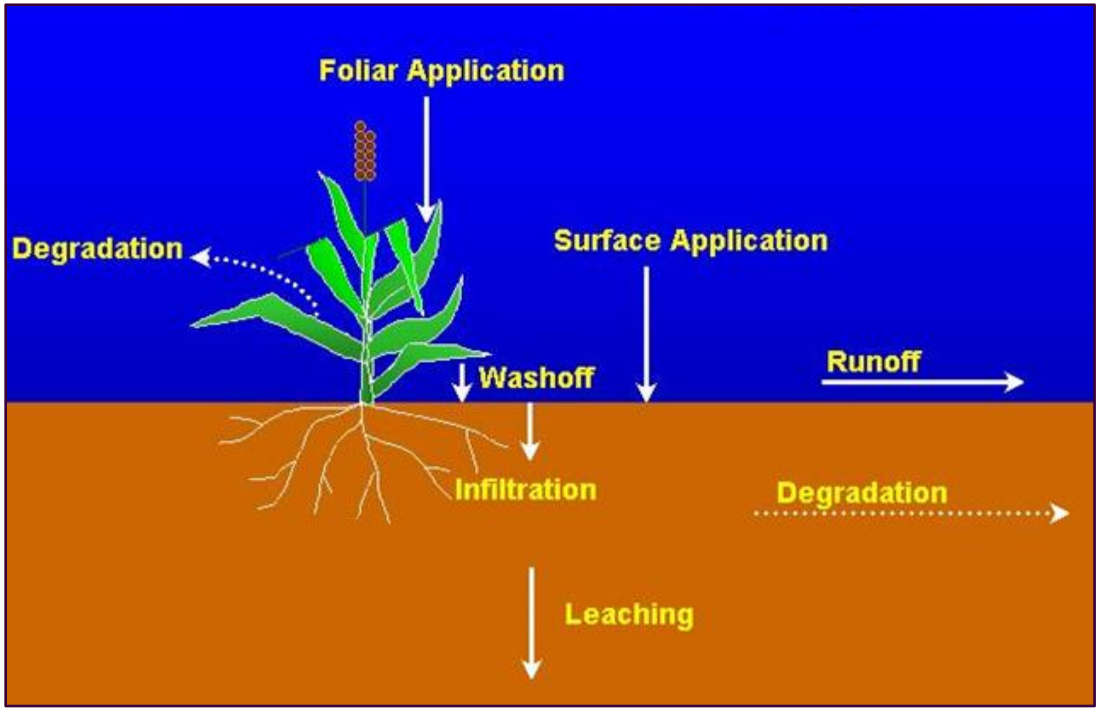
Technical documentation on PRZM and the PWC user manual are included in the PWC installation package.

The PWC website has links to the associated scenarios and weather files that EPA has created for standard drinking water, ecological, and groundwater exposure assessments.

EPA's Pesticide Root Zone Model (PRZM)

The Pesticide Root Zone Model (PRZM) simulates:

- Chemical applications:
  - Rate and timing
  - Method (surface, at depth, integrated with soil)
- Hydrology (daily timestep):
  - Precipitation and temperature
  - Evapotranspiration
  - Surface runoff/erosion
  - Infiltration
- Plant growth:
  - Transpiration
  - Canopy cover
- Chemical fate
  - Degradation (foliar, soil aerobic, hydrolysis)
  - Sorption/desorption
  - Movement via surface runoff, erosion, leaching, plant uptake



PRZM Chemical Processes

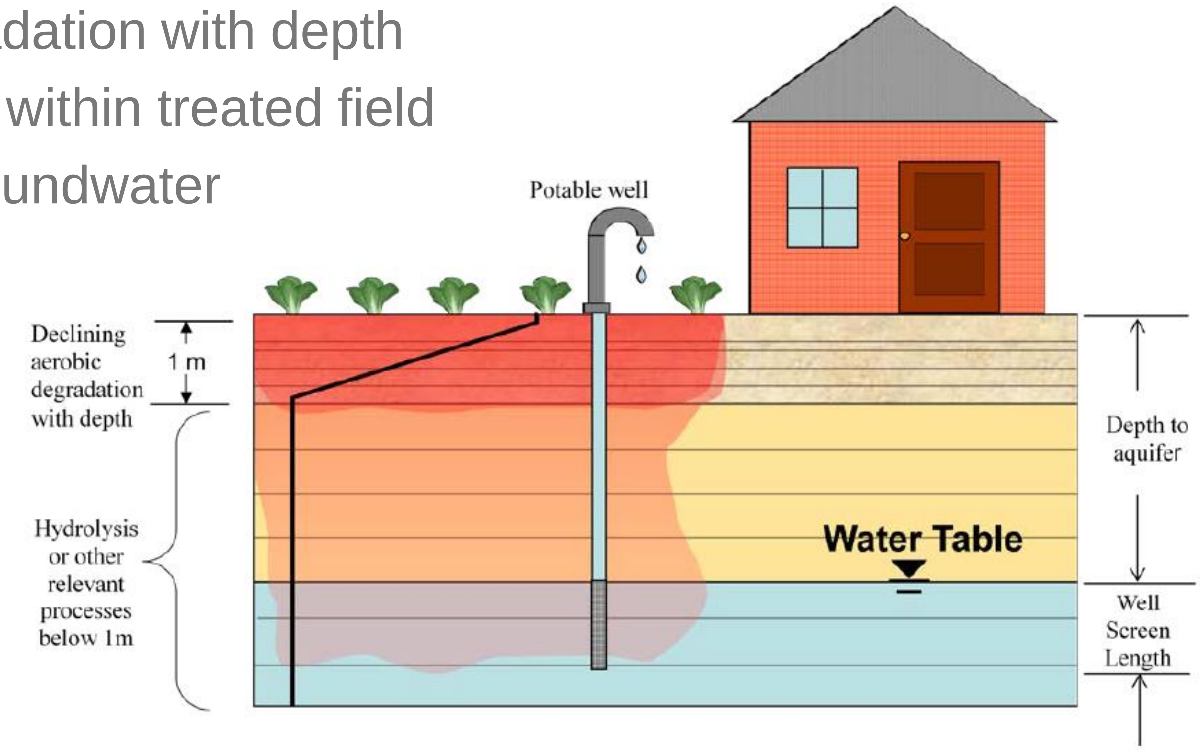
PRZM Groundwater Leaching Conceptual Model

The US EPA and Canada's Pest Management Regulatory Agency completed a research study in 2012 (Baris et al., 2012) that established a groundwater exposure conceptual model and scenarios for use in screening level modeling to evaluate pesticide registrations.

The conceptual model makes conservative assumptions that include:

- Maximizing infiltration by reducing runoff processes
- Reducing aerobic soil degradation with depth
- Setting groundwater source within treated field
- Ignoring potential lateral groundwater transport and dilution

PRZM serves as the physically based model applied to this regulatory modeling approach.



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Processes Unaccounted for in Screening Level Modeling

Background concentrations and other PFAS sources such as from atmospheric deposition.

- If well-understood, these background concentrations could be accounted for as additive sources of PFAS chemicals applied to the soil outside of the land application process.

No plant uptake from soil.

- While PRZM has the capability of simulating chemical uptake by plants, there is high uncertainty in the magnitude of this process regarding PFAS chemicals, and the modeling of this component in PRZM is relatively simplistic.
- Conservative approach → More chemical is available for leaching

Potential macro-pore or rock-fracture flow is not simulated in PRZM.

Model Scenarios

For a screening level assessment, a sound approach is to first assess the impact of known residuals application patterns under the most vulnerable groundwater scenarios.

US EPA has defined six screening level PRZM groundwater exposure scenarios that represent various regions and reflect very high vulnerability leaching conditions and are assumed to be representative of all high vulnerability locations across the US (downloadable from PWC link).

- Characterized by very sandy soils, low organic matter, and shallow depth to groundwater.
- Include two locations in Florida, and one each in Georgia, North Carolina, the Delmarva region, and Wisconsin.
- The depths to groundwater range from 3 meters in Florida to 9 meters in Wisconsin.
- These scenarios are also linked to specific weather files that characterize each simulated area.

Model Scenarios

For a PFAS leaching assessment, evaluating all six US EPA screening level scenarios would cover a range of "worst case" scenarios expected across the US.

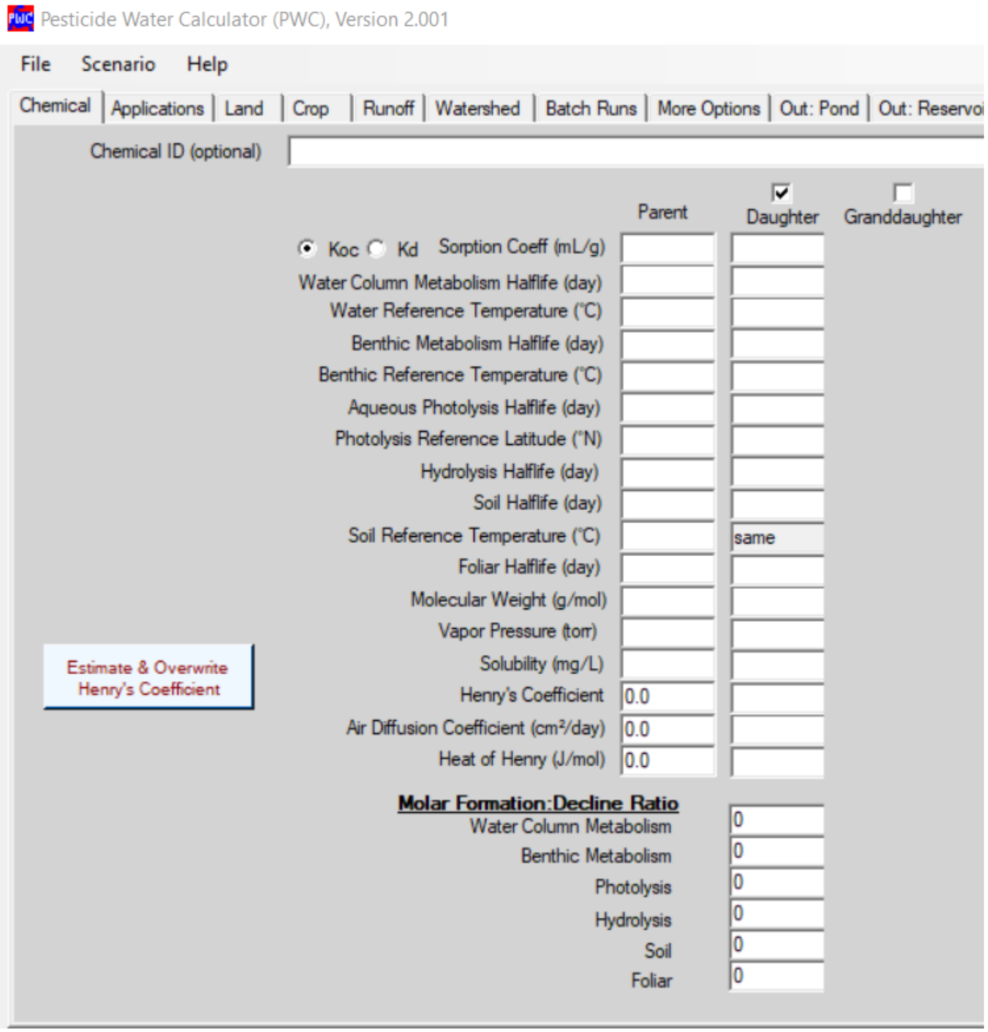
Refinement to reflect more geographically specific conditions is typically conducted if a chemical exceeds a maximum concentration level in one or more of the screening level scenarios.

- The user can specify all necessary PRZM input parameters to tailor the scenario to specific local conditions - crop characteristics, weather, irrigation practices, other hydrologic factors, and soil horizon properties.
- Effects of alternative application practices, e.g., application of residuals that occur only for a certain number of years or every other year can be assessed.

US EPA has developed numerous PRZM screening level scenarios tailored to surface water exposure (drinking water and ecological assessments).

- Used to estimate PFAS surface water concentrations following land application of residuals containing PFAS.
- Can also be used as the basis for a groundwater leaching scenario characterization of a particular geographic region.

Chemical/Physical Inputs



A key process affect PFAS fate in soil following residuals applications is the adsorption to soil.

Some inputs are not considered in groundwater modeling, e.g. water column metabolism.

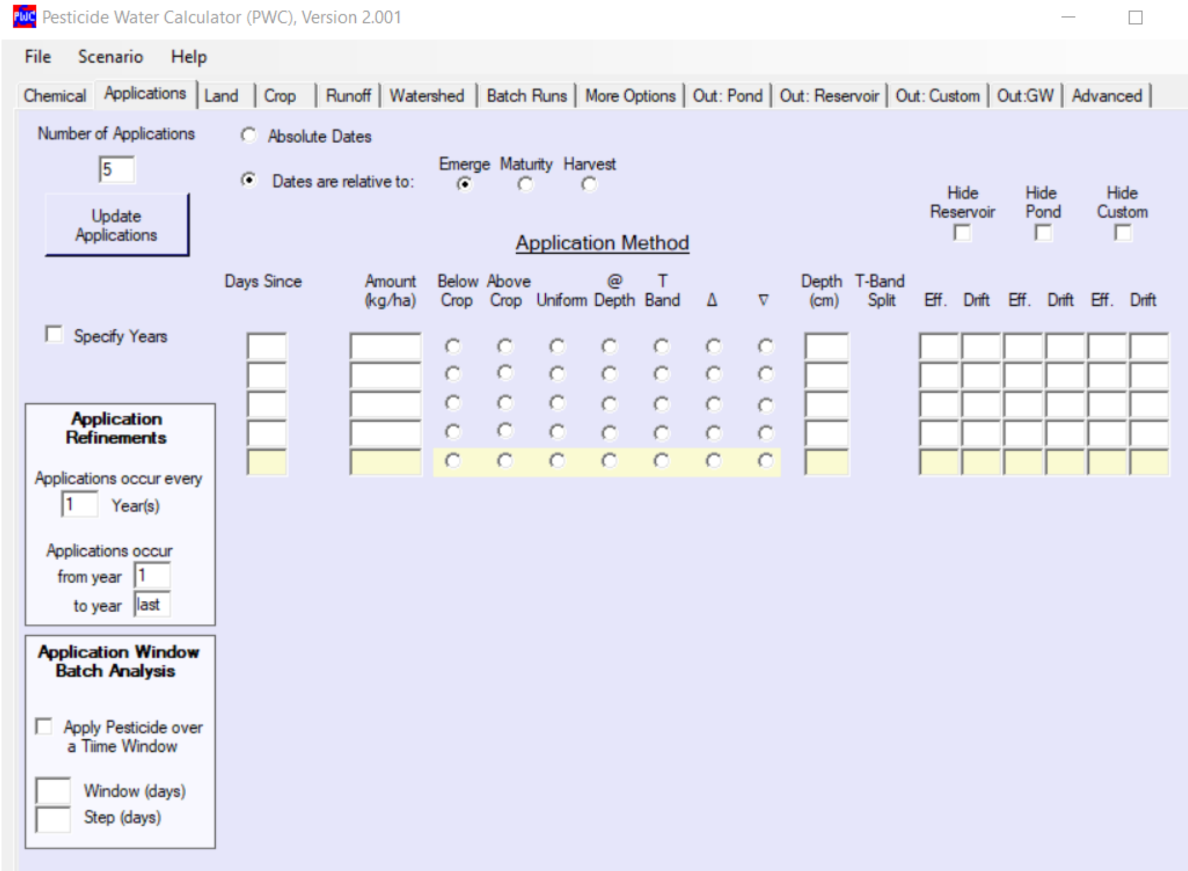
Some PRZM inputs are irrelevant when applied to land applied residuals, e.g. foliar half-life

Biotic and abiotic transformation: Thoughtful specification of these PRZM input parameters will be important for some PFAS chemicals as they may greatly affect overall fate and transport. If data are unavailable to characterize degradation rates of a specific PFAS chemical, then an assumption that the chemical is stable is most appropriate.

Up-to-date assessment of the physical/chemical properties at

Interstate Technology and Regulatory Council (ITRC) - https://pfas-1.itrcweb.org/

Application Inputs

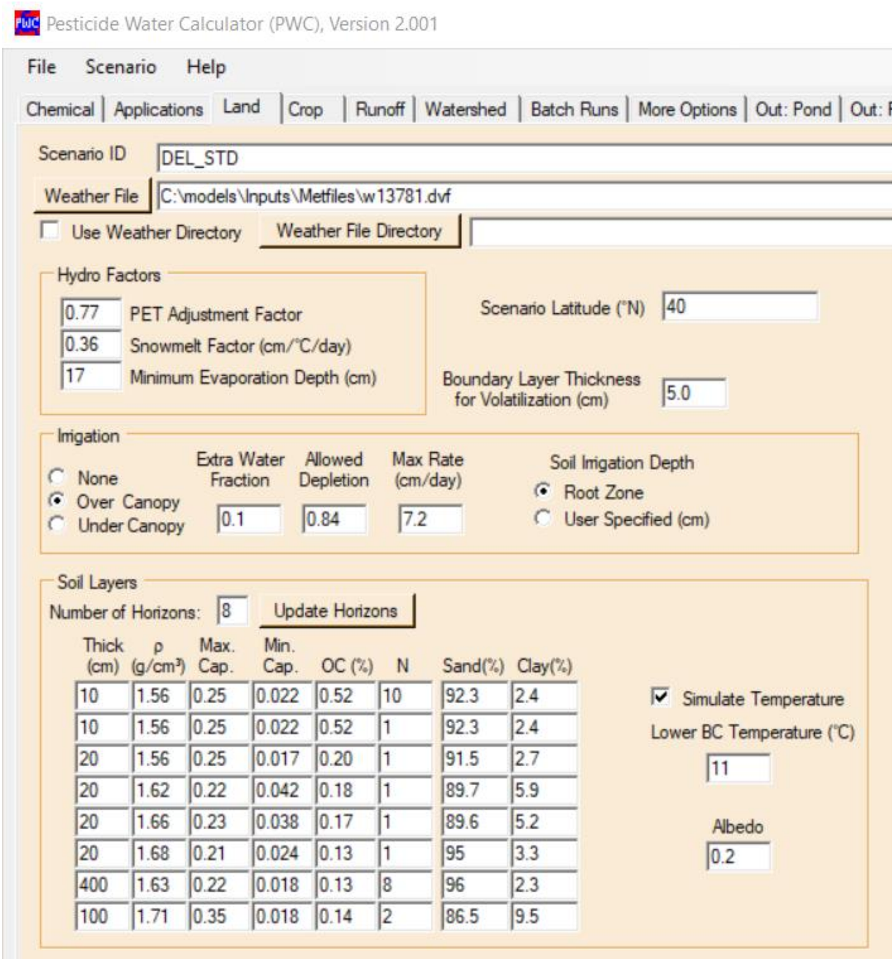


Application characteristics of the chemical to the soil:

- Amount (chemical mass/unit area)
- Date
- Frequency
- How it is integrated in soil

When surface water contamination is evaluated, then receiving water body is specified

Land Inputs



The land scenario should represent the residuals application area of interest and including:

- Climate
- Soil conditions
- Irrigation practices

US EPA has developed several high vulnerability groundwater leaching scenarios (and surface water scenarios) that can be downloaded and will fully populate this tab.

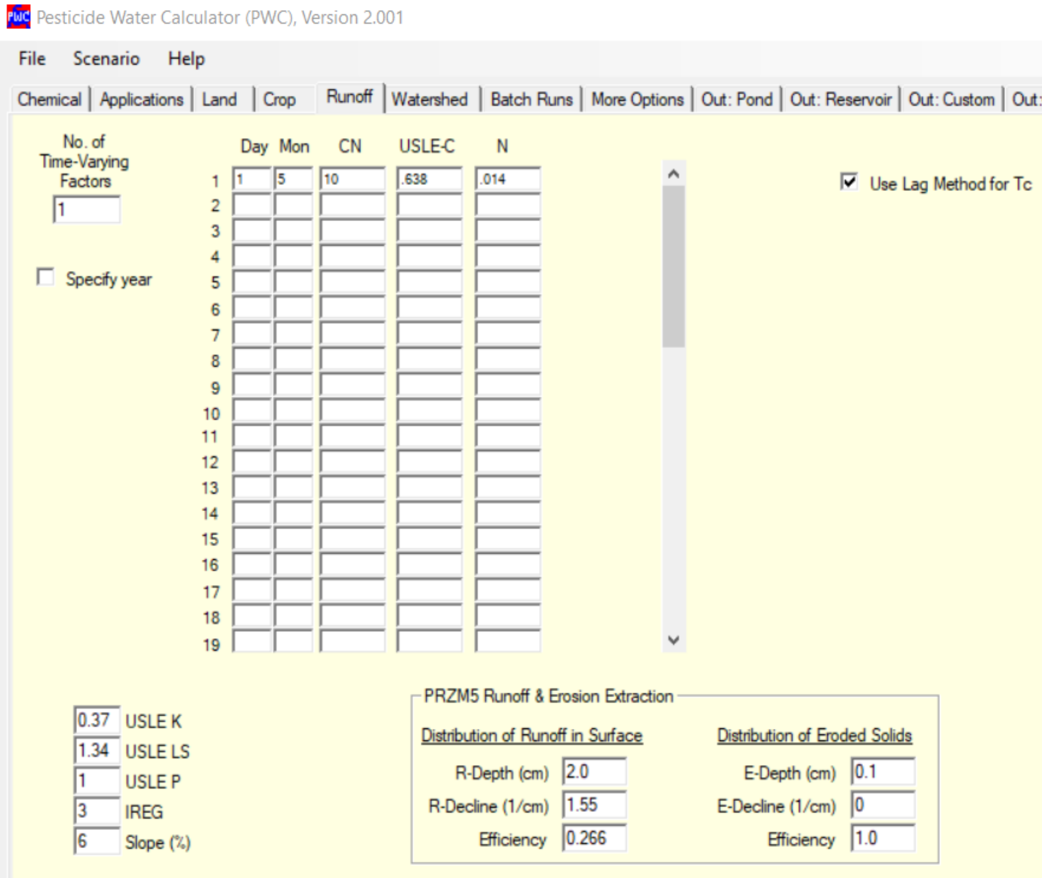
To better represent local conditions, the user can refine scenarios tailored to specific residuals application areas.

Crop Inputs

Most US EPA standard scenarios assume a single crop cycle per year.

For the purposes of PFAS screening level leaching simulations, a simple single crop cycle derived from one of EPA's standard scenarios is most common but other cropping cycle scenarios may be appropriate.

Runoff and Erosion Inputs



This is particularly important when the interest is to assess potential contamination of surface water. However, this pathway is also important to properly account for contaminant that leaves the site and does not leach to groundwater.

For groundwater modeling, assume a runoff curve number CN=10 for screening level, essentially resulting in no runoff and the maximization of leaching. This can be modified as a refinement to account for runoff loses.

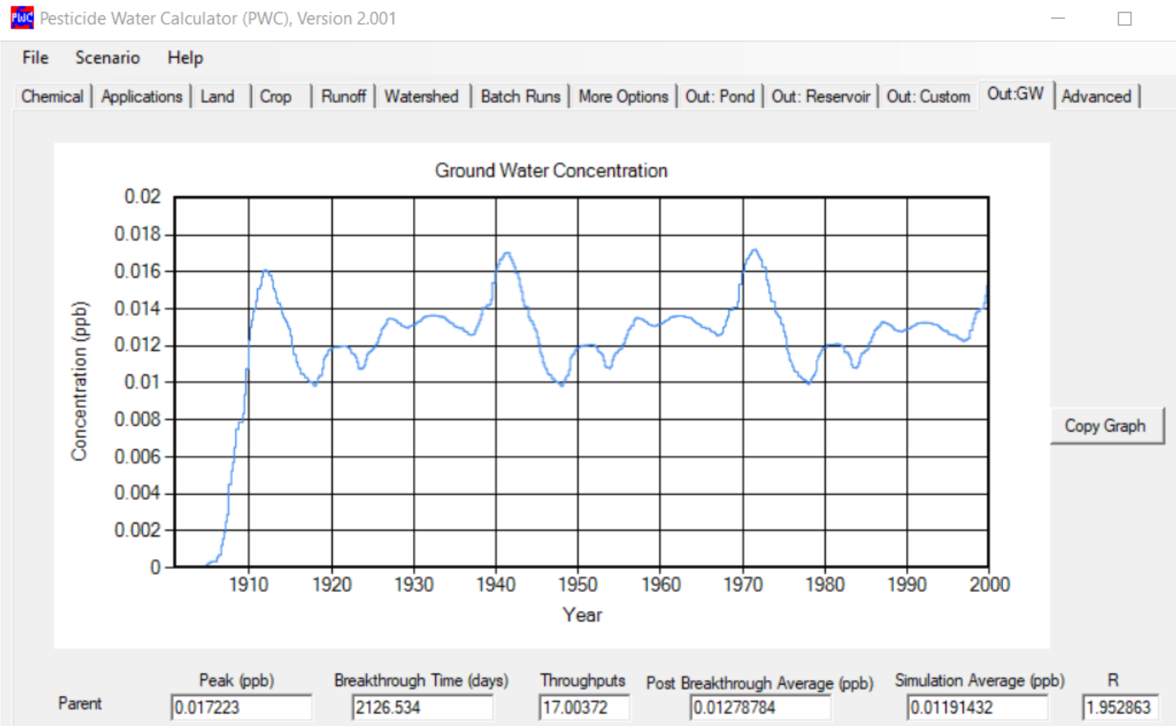
Uncertainty and Variability of Input Parameters

Considering that most PFAS are non-volatile and that they degrade slowly if at all, the most important chemical input parameter that may significantly affect groundwater concentration predications in PRZM is the sorption coefficient, K_d.

The current scientific literature reports a range of observed behavior regarding the partitioning of PFAS between dissolved and sorbed phases in soil:

- An initial set of simulations may consider the lowest sorption coefficient values provided by the literature, typically equal to the laboratory minimum measured values:
  - Results in worst-case leaching potential conditions
  - If simulated residuals applications lead to concentrations below the DWLOC, applications of the residuals at the specified PFAS concentration may be considered protective of groundwater.
- As is the standard practice in the US EPA environmental fate parameter input selection guidance used with the PRZM model for pesticide regulation (US EPA, 2009), one can also consider using average sorption values assessed from multiple test systems or experiments. This approach may provide a better understanding of PFAS leaching potential and expected groundwater concentrations reflective of typical conditions in agricultural settings.

Model Simulations and Results



Several groundwater concentration outputs are available.

- The most significant considered in human health risk assessment is the **post breakthrough average concentration**, representing long-term average exposure.

Optional outputs available to better understand chemical and water mass balance in the soil matrix.

The sensitivity of groundwater concentration estimates to input parameter uncertainty is also an important aspect to consider when assessing the robustness of the findings from an analysis of model results.

- Tailored weather/soil/crop scenarios that may better characterize local conditions
- Sorption coefficient (already discussed)
- Depth of water table

For screening level studies, the scenario resulting in the highest predicted concentrations in groundwater, is identified for use in the risk assessment.

PFAS Screening Level Applicable Mass/Area

$\mathbf{c_w}$ (ng/l=ppt) is the worst case/highest concentration of chemical in the groundwater identified for a given PFAS application rate, $\mathbf{m_c}$ (kg/ha)

→ the PFAS screening level applicable mass per unit area, m_s (kg/ha), for a specified drinking water level of concern DWLOC (ppt) can be identified as:

$$m_s = \frac{m_c}{c_w} \times DWLOC$$

The ratio m_c/c_w (kg/ha/ppt) is a **dilution attenuation factor**

Indicates how much chemical mass applied with a given application pattern (e.g., residuals land applied once every 1 year) is necessary to increase the chemical concentration in groundwater by one unit.

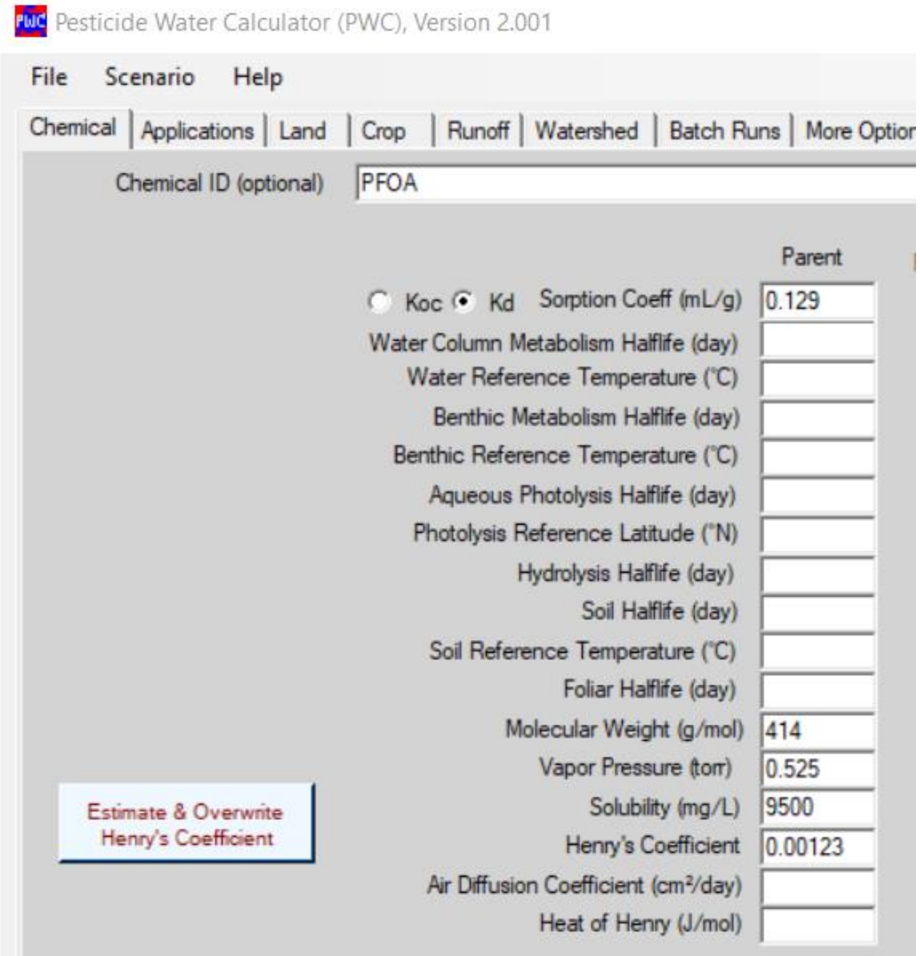
- The best agronomic practices can then be identified that constrain the residuals mass applied to levels required to keep groundwater concentrations below the DWLOC.

Step-by-Step Example

Modeling Land Applied Biosolids in Maine:

- Screening level modeling simulations from a study sponsored by the Northeast Biosolids & Residuals Association (NEBRA).
- This study assessed potential leaching to groundwater of PFOA and PFOS initially present in biosolids applied annually on agricultural fields in Maine.

Chemical/Physical Inputs



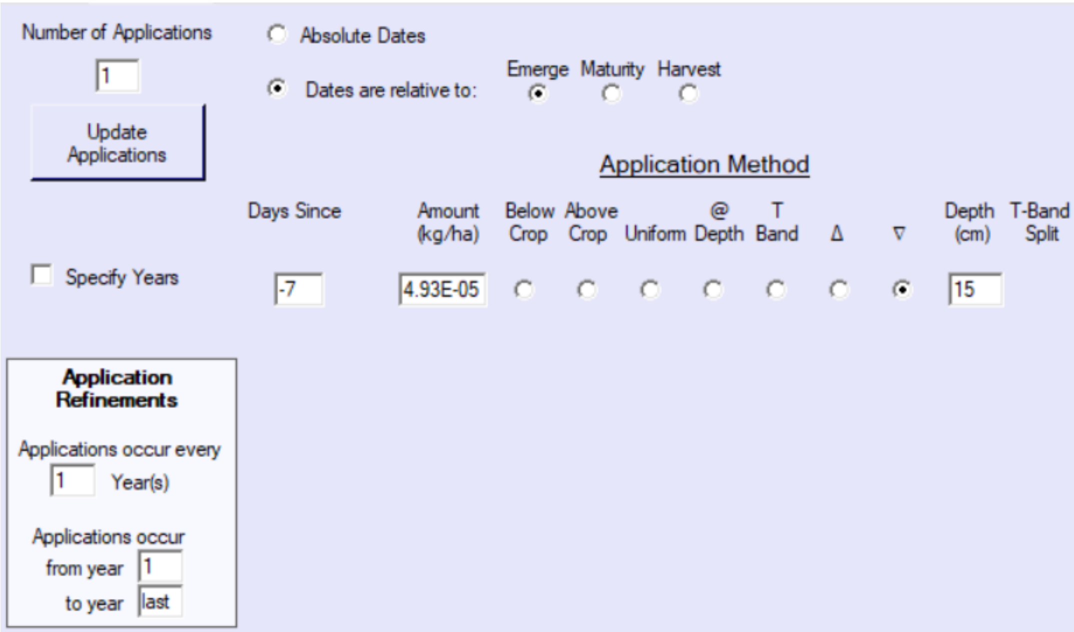
K_d (L/kg)						
	Field/Lab	Min	25th	Median	75th	Max
PFOS	Field	10.0	38.0	83.2	257	3,311
	Lab	1.95	7.76	15.8	24.5	229
PFOA	Field	0.708	4.47	14.5	57.5	724
	Lab	0.129	0.676	2.00	4.90	89.1

Source: Li et al., 2018

Literature identified a range of sorption coefficients.

Start with minimum laboratory K_d ,capturing the worst-case leaching potential conditions

Application Inputs



Biosolids application occurring once every year. This is very conservative because:

- Nitrogen requirements for many crops may be exceeded in subsequent application years due to a slow build-up of nitrogen from earlier biosolids land applications. Thus, biosolids application rates would need to be downwardly adjusted.
- PFOA and PFOS concentrations in biosolids have been slowly decreasing over the last decade.

Initial concentrations: PFOA: 5 ng/g (ppb) , PFOS 11 (ppb)

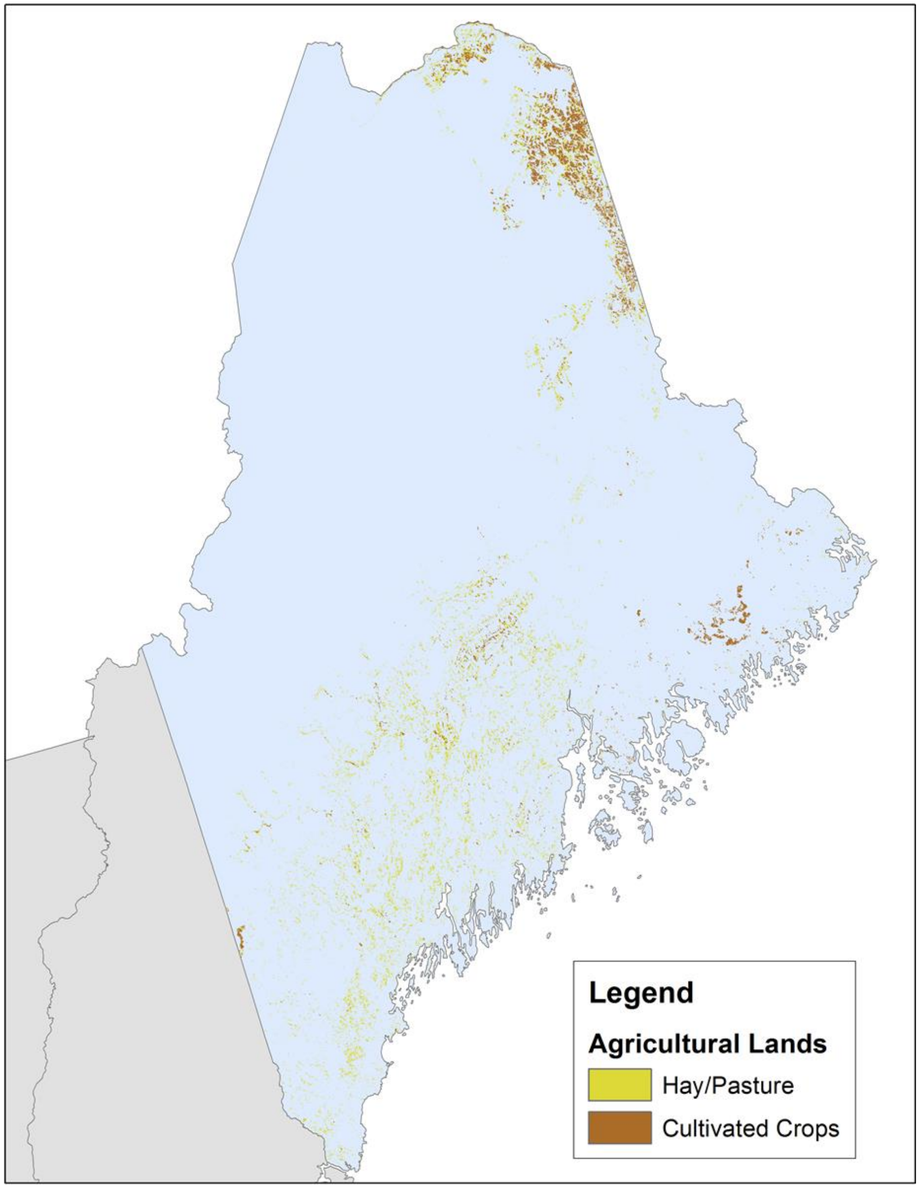
Application characteristics:
- Solid content: 22%
- Rate: 44,830 wet kg/ha (20 wet us tons/acre)

PFOA mass applied: $5*10^{-9}x0.22x44{,}830 = 49.3$ mg/ha

Local Land Inputs - Maine Leaching Scenarios

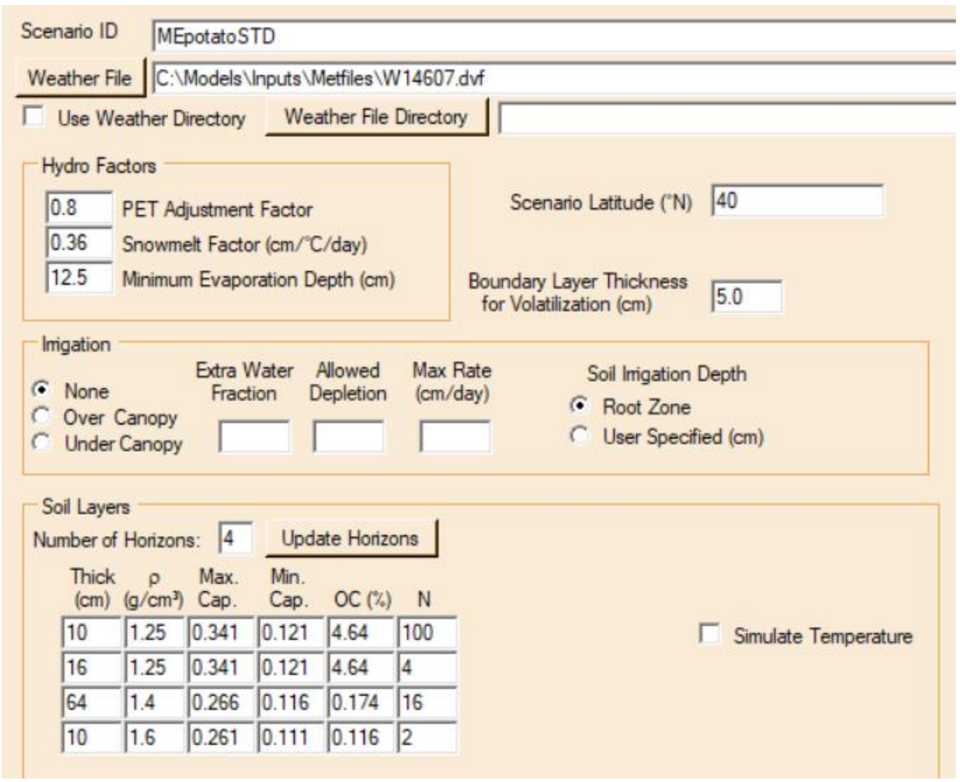
Maine-specific scenarios were developed to better represent:

- Maine weather (Portland, ME)
- Maine depth to water table
  - 1 m conservative regulatory assumption
  - 4.57 m based on average of Maine Geological Survey Water Well Database measurements
- Maine agricultural soils and crop
  - Identify most common agricultural soil in each of 4 hydrologic group
  - Parameterized PRZM soil horizons accordingly
  - Corn crop

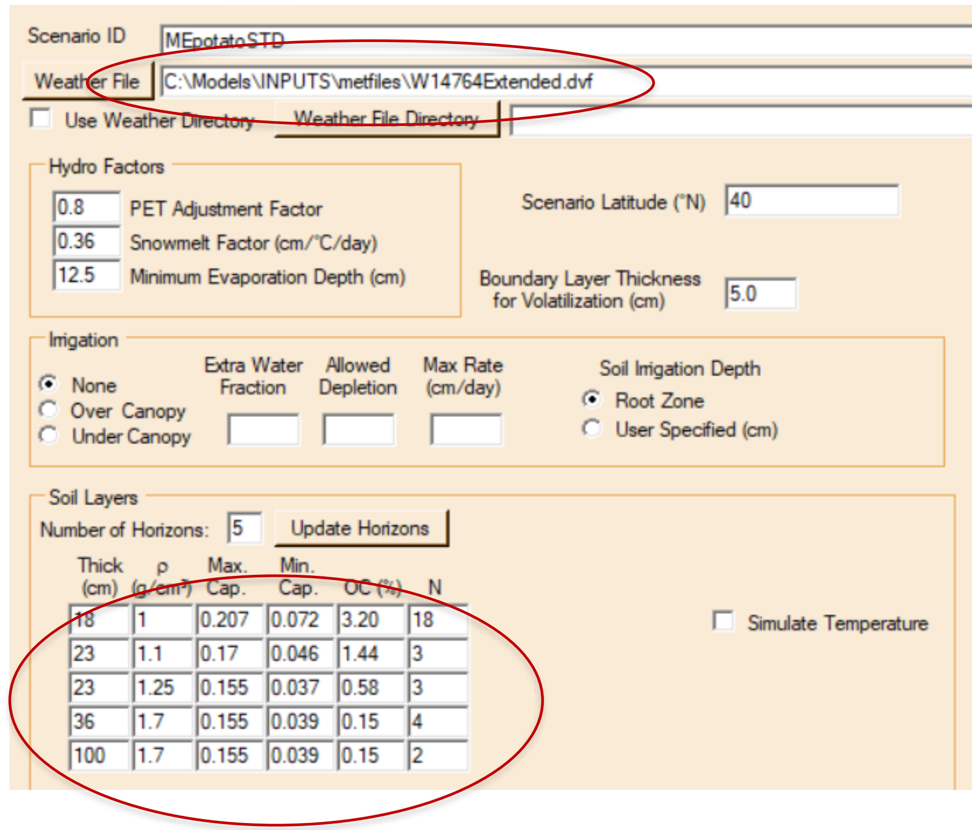


Local Land Inputs – Maine soil and weather

Original Maine potato scenario weather and soils:

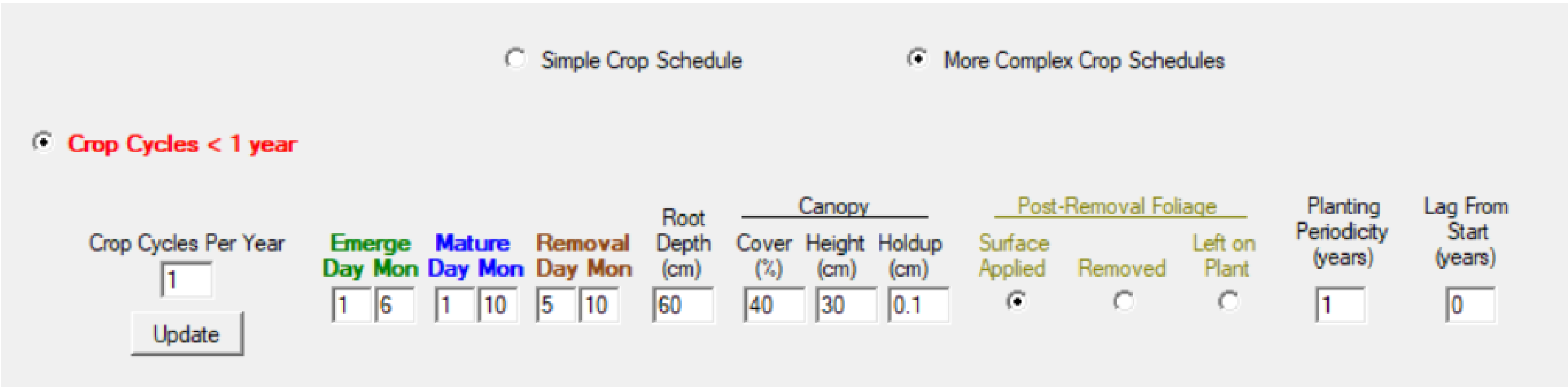


Modified Maine corn scenario weather and soils:

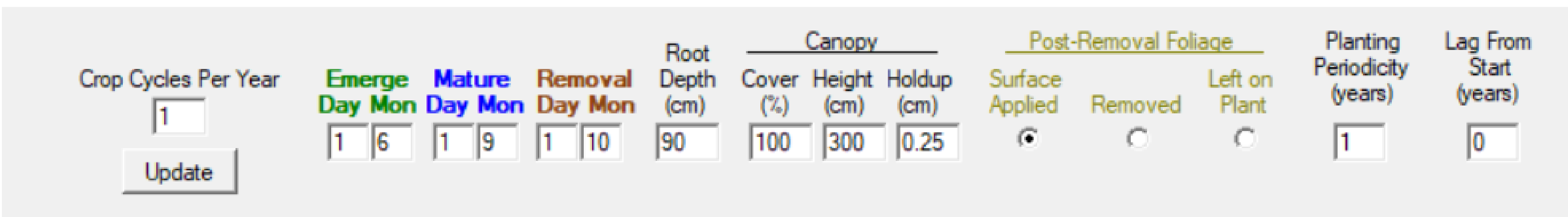


Crop Inputs

Original Maine potato crop cycle info:



Modified Maine corn crop cycle info:



Modeling Results: Maine Leaching Scenarios, Results

Based on the most conservative leaching model parameterization (lowest k_d and shallowest groundwater depth), combined PFOA+PFOS post-breakthrough average groundwater concentrations ranged from 26 ppt – 33 ppt.

Based on more “typical” sorption from field observations, combined PFOA+PFOS post-breakthrough average groundwater concentrations ranged from 5 ppt – 6 ppt (PFOS is retailed in upper 1-m of soil with limited groundwater impact).

			Peak Conc. (ppt)		Post-Breakthrough Avg. Conc. (ppt)	
Chemical	**Kd**	**GW Depth**	**Min**	**Max**	**Min**	**Max**
PFOA	Lab Min	1-m	14	18	7	11
PFOA	Field Median	1-m	8	9	5	6
PFOA	Field Median	4.57-m	< 0.1	< 0.1	< 0.1	< 0.1
PFOS	Lab Min	1-m	21	27	19	22
PFOS	Field Median	1-m	<0.1	< 0.1	<0.1	< 0.1
PFOS	Field Median	4.57-m	< 0.1	< 0.1	< 0.1	< 0.1

Summary of PRZM Maine Scenario Results

Maximum PFAS Application Rates

<table>
<tr><th rowspan="2"></th><th colspan="2">PWC Simulation Results</th><th colspan="5">Screening Level Calculations for DWLOC = 70 ppt</th></tr>
<tr><th>Annual Applied Mass Rate (mg/ha)</th><th>Worst Case Post Breakthrough Conc. (ppt)</th><th>Attenuation Dilution Factor (mg/ha/ppt)</th><th>Maximum Annual Mass Rate (mg/ha)</th><th>Biosolids Mass Annual Application Rate (t/ha)</th><th>Biosolids Solid Content (%)</th><th>Maximum Initial Conc. in Biosolids (ppb)</th></tr>
<tr><td>PFOA</td><td>49.3</td><td>11</td><td>4.48</td><td>314</td><td rowspan="2">44.83 (20 us ton/acre)</td><td rowspan="2">22</td><td>32</td></tr>
<tr><td>PFOS</td><td>108</td><td>22</td><td>4.91</td><td>344</td><td>35</td></tr>
</table>

If the DWLOC were different, the calculations are linearly rescaled.

If the DWLOC is on the combined concentrations, then the screening level of applicable chemical mass cannot exceed the combined

$$m_{PFOA}/d_{PFOA} + m_{PFOS}/d_{PFOS} < DWLOC$$

(a similar constraint is obtained if DWLOC is on the combination of several PFAS compounds).

Comparisons with Field Data

Especially for screening level assessments, one objective of comparing model results to observations is to gauge how conservative model predictions are compared to the range of measured PFAS concentrations under similar conditions.

Build PRZM simulations whose inputs describe as close as possible the observed characteristics of the real-world scenario.

- Applications inputs
- Background or initial PFAS concentrations
- Climate data
- Land and crop inputs

Often not all these data are available, and the modeler has to make some assumptions to fill the missing pieces. When this occurs, the general guidance in this subjective judgement is to be conservative and transparent with selected choices.

Semi-quantitative Comparison with Observed Field Data

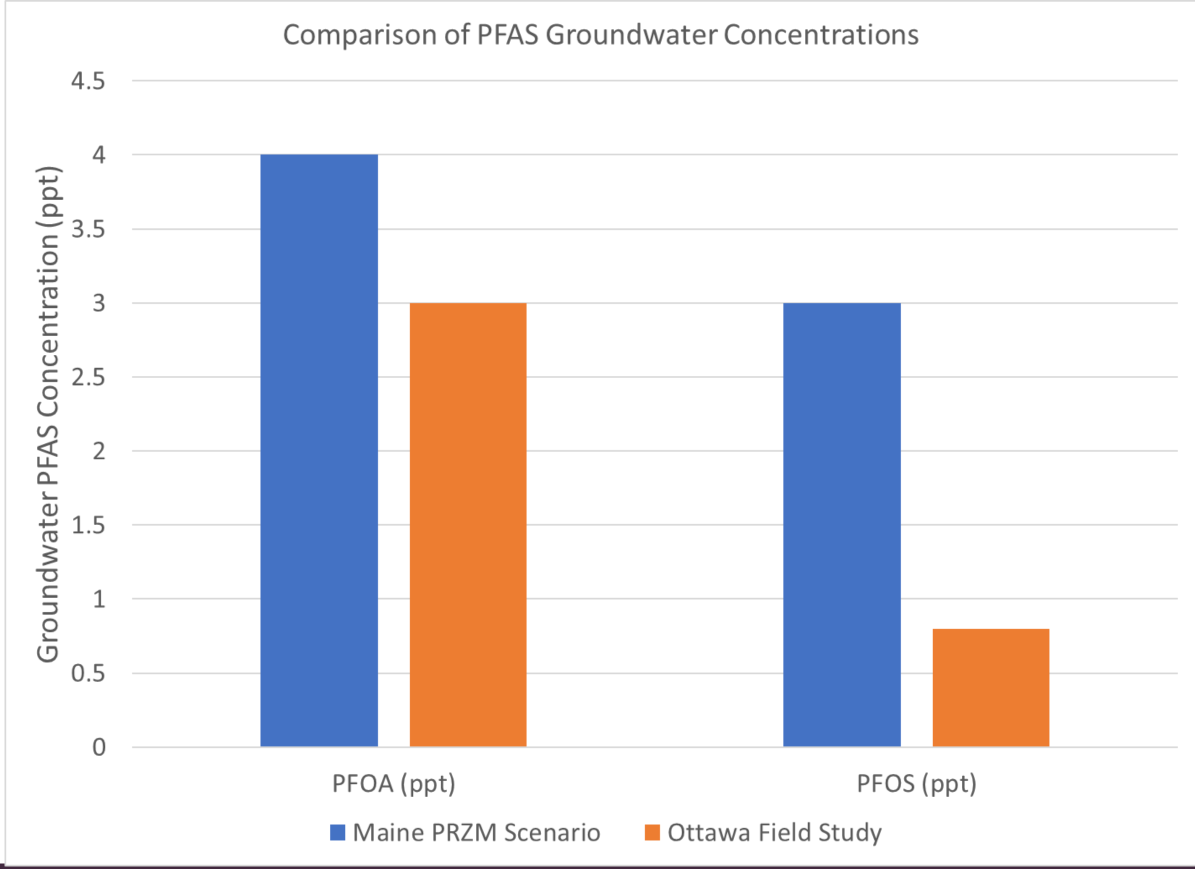
Gottschall et al (2017) reported on a land application of biosolids made to an agricultural field in Ottawa Ontario

The Maine PRZM scenario was modified to represent the Ottawa field study conditions.

- Only one biosolids application
- Identical PFOA/PFOS application rates
- 2 m depth to groundwater

The PRZM scenario predictions are close to the Ottawa field study observations.

Using the low end of sorption data, the PRZM predictions are conservative relative to the field study observations.



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Summary and Conclusions

The screening level modeling approach presented here, as well as the parameter selection guidance and options for refinement to local conditions, are designed to be used in an initial analysis of potential PFAS leaching to groundwater from land applied residuals.

The standard groundwater leaching scenarios from the US EPA are designed to represent "worst-case" conditions nationally relative to potential chemical contamination of groundwater, and thus serve as effective scenarios to conservatively identify whether PFAS leaching to groundwater could be a concern.

Use of this PRZM screening-level modeling approach may allow regulators and other stakeholders to efficiently evaluate PFAS groundwater contamination potential and determine whether a more comprehensive and rigorous modeling and/or field investigation is warranted.

In preparation: Comparison of SESOIL/AT123D with PRZM to assess leaching potential from land applied residuals

SESOIL/AT123D used for development of soil remediation standards in many states, Maine, Oregon, California, Colorado, Wisconsin, Massachusetts, New Hampshire, New Jersey, Hawaii, and others

Review use of the two models in land applied residual context

References

Baris R, Barrett M, Bohaty R, Echeverria M, Kennedy I, Malis G et al. 2012. Final report: Identification of existing models for estimating environmental pesticide transport to groundwater. Health Canada, US Environmental Protection Agency, Washington, DC.

Gottschall N, Topp E, Edwards M, Payne M, Kleywegt S, Lapen DR. 2017. Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field. Sci Total Environ. 574. 1345-1359.

Li Y., Oliver D. and Kookana R. 2018. A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). Science of The Total Environment. 628-629. 110-120.

USEPA (2009). Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides. https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-selecting-input-parameters-modeling

Thank You

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Additional Results

Modeling Results: EPA "Standard" Groundwater Leaching Scenarios

Based on an annual application rate of 20 wet tons/acre, the maximum post-breakthrough average concentrations using the worst-case k_d were 15 ppt and 23 ppt for PFOA and PFOS respectively.

	Peak Conc. (ppt)		Post-Breakthrough Avg. Conc. (ppt)	
Chemical	**Min**	**Max**	**Min**	**Max**
PFOA	7	20	5	15
PFOS	11	30	10	23

Summary of PRZM Standard Scenario Results