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Demonstration of an Agricultural Chemical Fate & Transport Model to Determine Biosolids PFAS Screening Level Concentrations Required for Groundwater Protection

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Motivations and Objectives

- Identify a modeling framework could be used to specify adequate management strategies that balance the mass loading rate of PFAS in land applied residuals and drinking water concentration safety limits, without crippling residuals recycling programs and affecting the operations and cost of wastewater treatment.

- Screening level approaches for estimating PFAS concentration limits in agricultural soils have been largely derived from soil contaminated sites, which assume a very different conceptual model than a residuals applications to cropland.

Regulatory chemical fate and transport modeling approaches for screening-level analysis of land applied chemicals in agricultural settings have been used nationally and internationally for registration of pesticides for several decades.

- Can these modeling approaches be adapted to PFAS?
- If so, what do the results tell us regarding establishment of PFAS concentration limits in land applied residuals?
- Does the modeling approach predict groundwater PFAS concentrations supported by measurements from field studies?

Motivations and Objectives

Applied the US EPA's Pesticide Root Zone Model (PRZM) to simulate land applications of residuals to agricultural fields in Maine supported by NEBRA

A Guidance Document was created on how to implement PRZM as a screening-level tool to assess the potential for PFAS leaching to groundwater from land applied residuals (work supported by NCASI).

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

- Use PRZM to develop baseline residuals concentration limits. To ensure adequate protection of groundwater quality their default limits are based on the worst-case scenario.
- PRZM can be used to develop site-specific residual concentrations that are protectives of groundwater. In many sites, this may result in higher initial concentrations while maintaining protection of groundwater quality. At other sites it may indicate that a threat to groundwater quality exists.
- Use PRZM to assess alternative residual application management practices

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

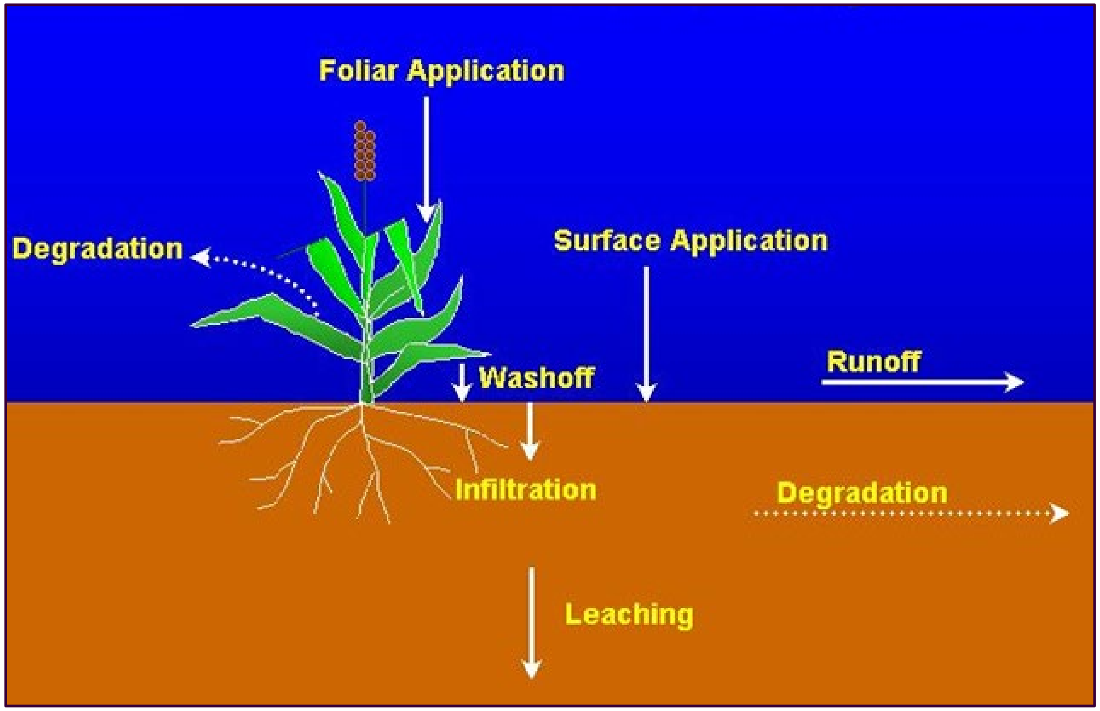
Technical documentation on PRZM and the PWC user manual are included in the PWC installation package.

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

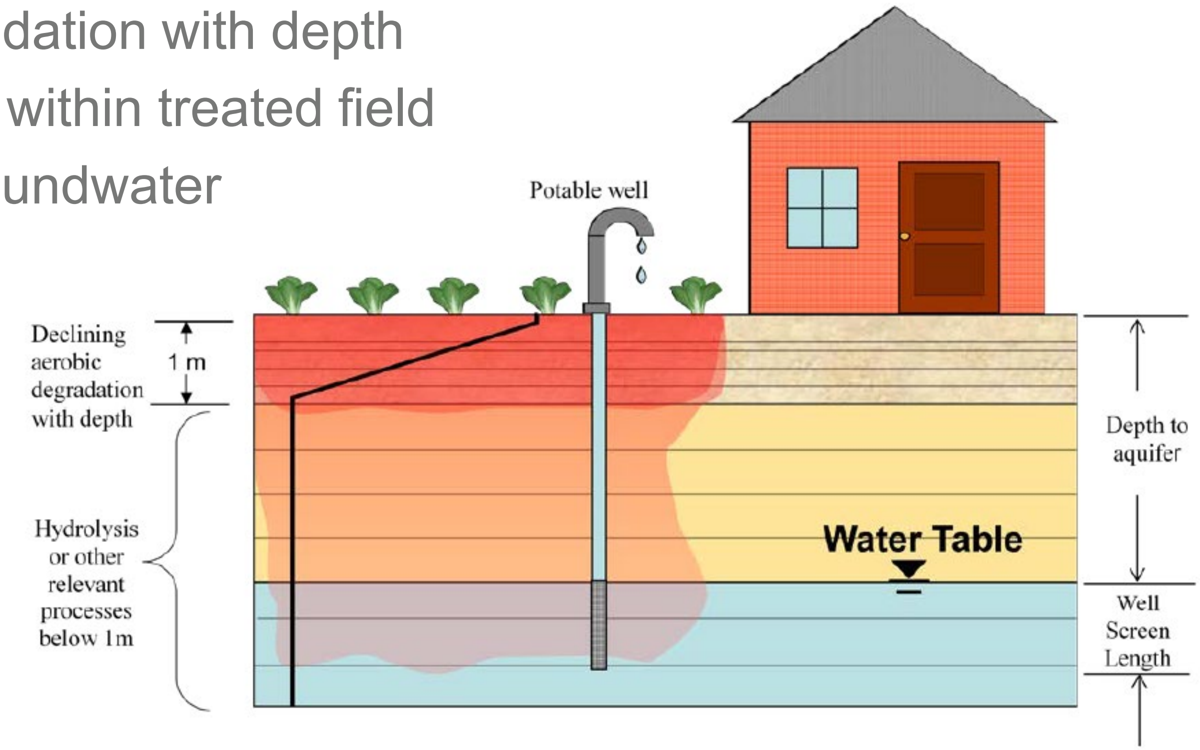
PRZM Groundwater Leaching Conceptual Model

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.



Processes Unaccounted for in Screening Level Modeling

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

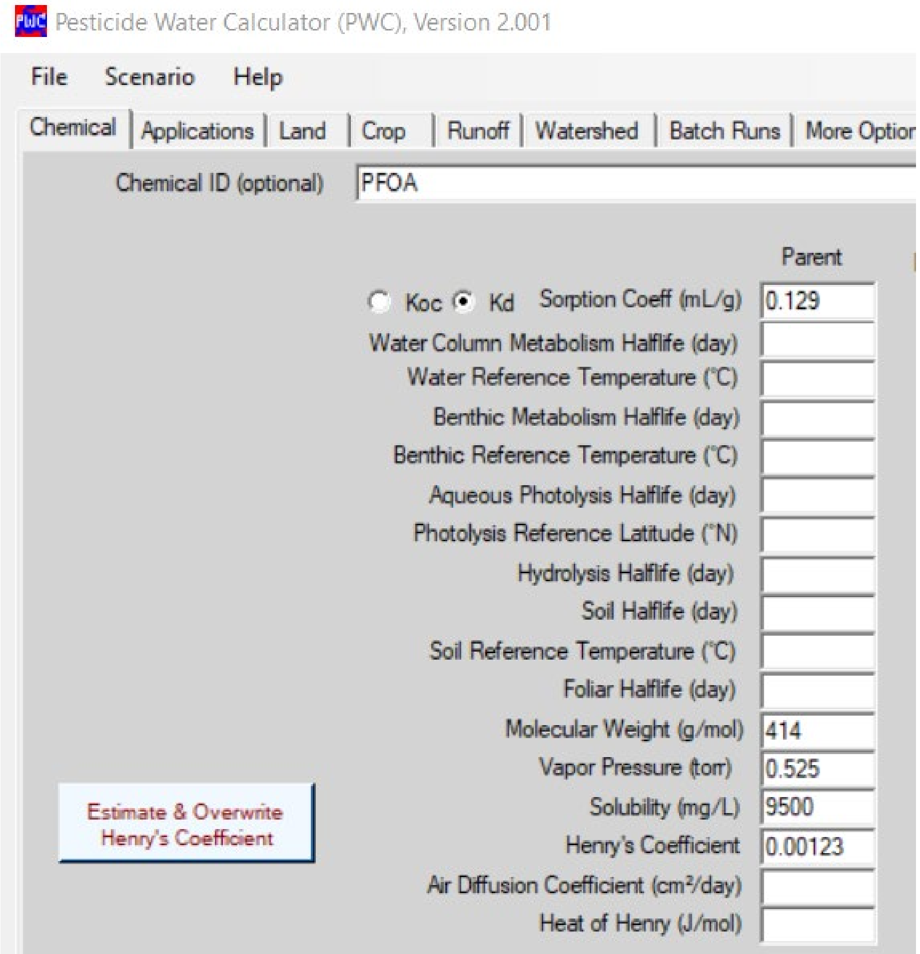
- If well-understood, these background concentrations could be accounted for as additive sources of PFAS chemicals applied to the soil outside of the land application process.

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.

Chemical/Physical Inputs



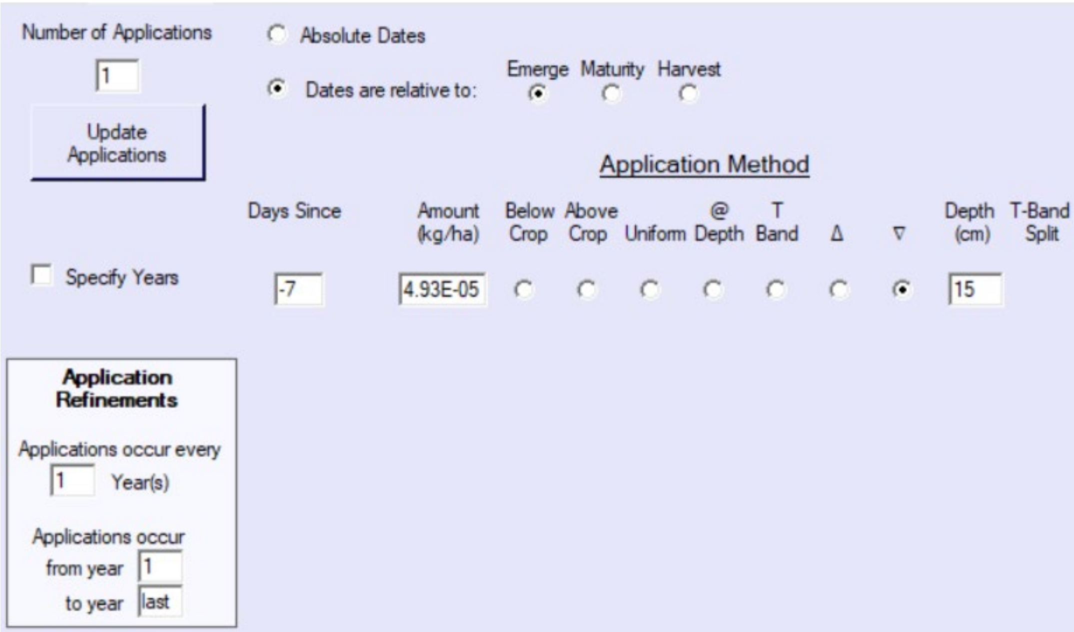
K_d (L/kg)						
	Field/Lab	Min	25th	Median	75th	Max
PFOS	Field	10.0	38.0	83.2	257	3,311
	Lab	1.95	7.76	15.8	24.5	229
PFOA	Field	0.708	4.47	14.5	57.5	724
	Lab	0.129	0.676	2.00	4.90	89.1

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

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).

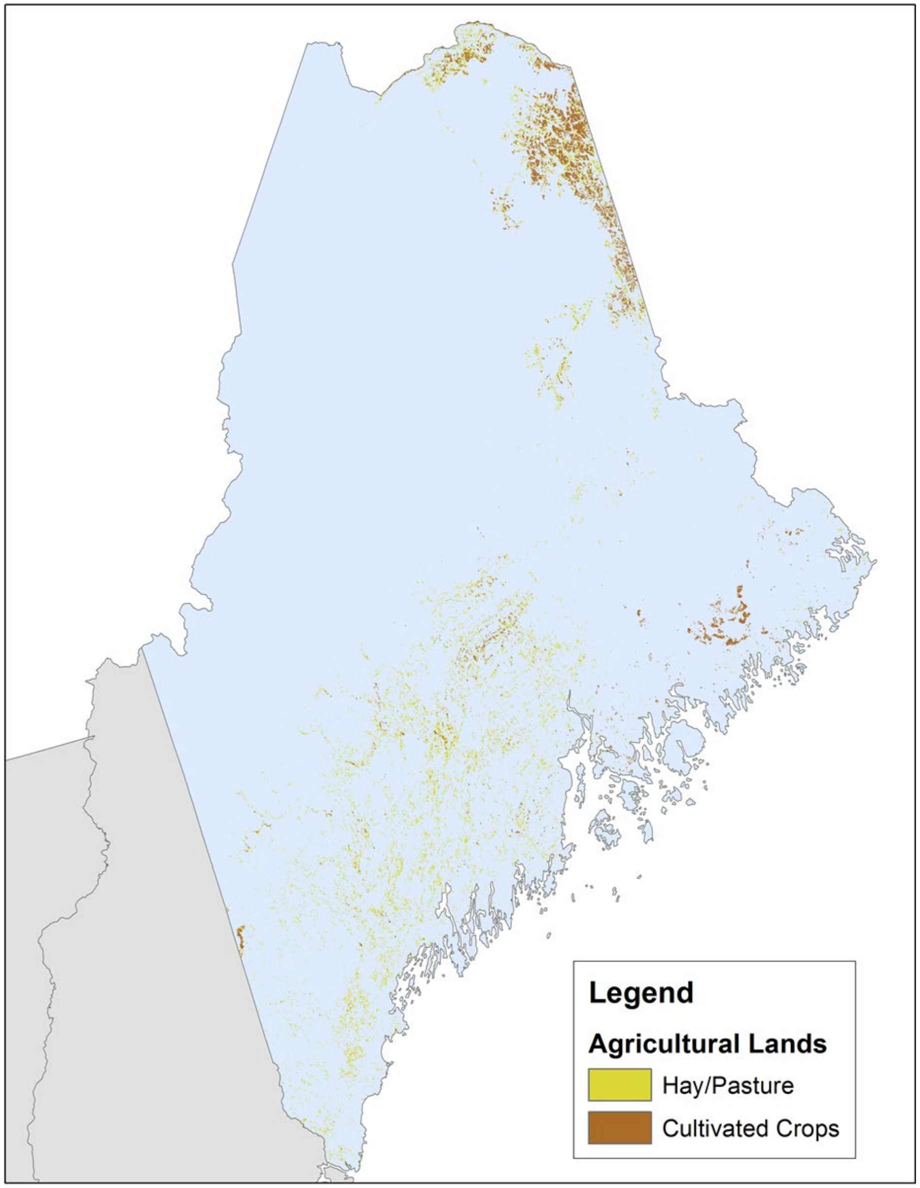
- Characterized by very sandy soils, low organic matter, and shallow depth to groundwater.
- Include two locations in Florida, and one each in Georgia, North Carolina, the Delmarva region, and Wisconsin.
- The depths to groundwater range from 3 meters in Florida to 9 meters in Wisconsin.
- These scenarios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

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

Local Land Inputs - Maine Leaching Scenarios

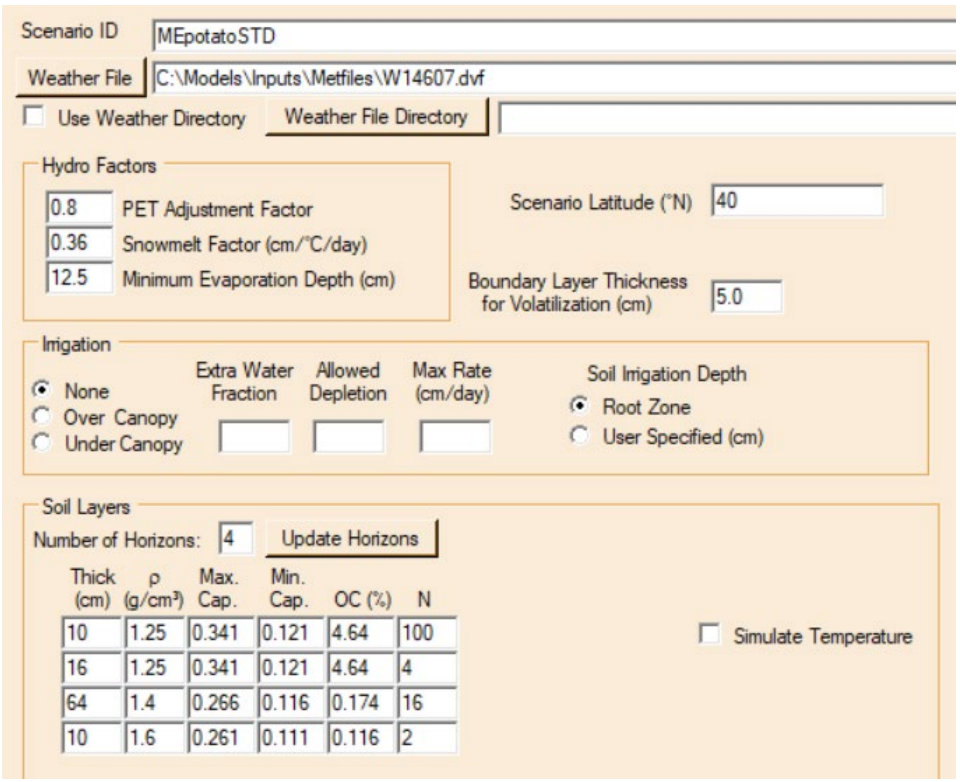
Maine-specific scenarios were developed to better represent:

- 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

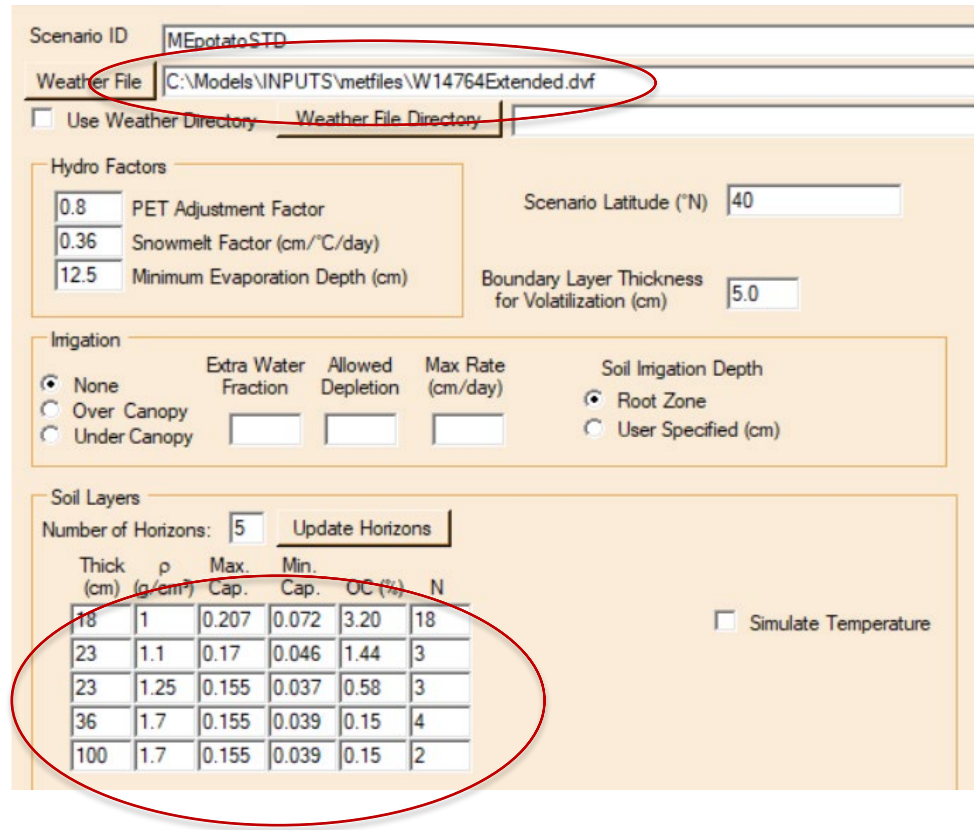


Local Land Inputs – Maine soil and weather

Original Maine potato scenario weather and soils:

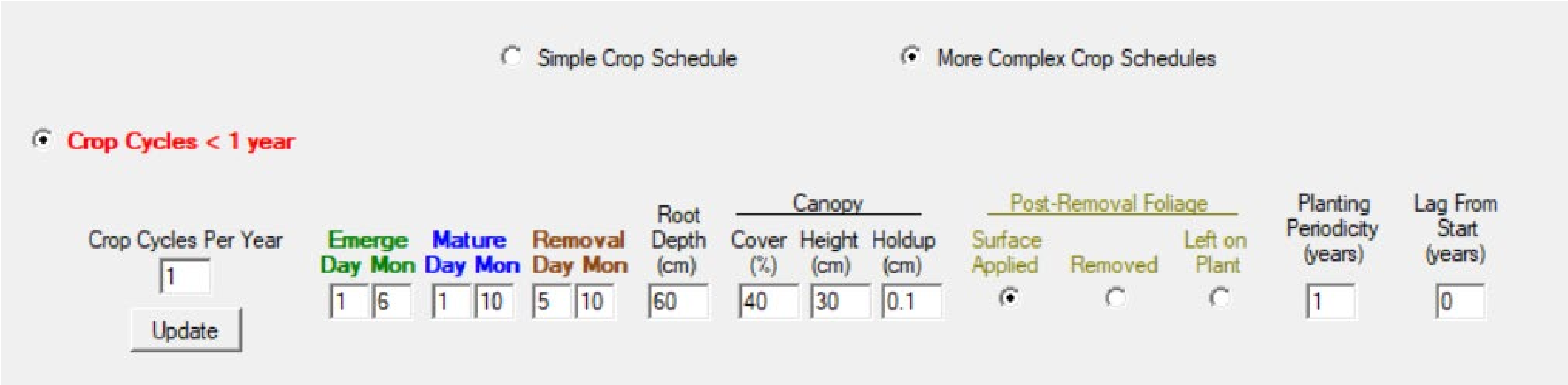


Modified Maine corn scenario weather and soils:

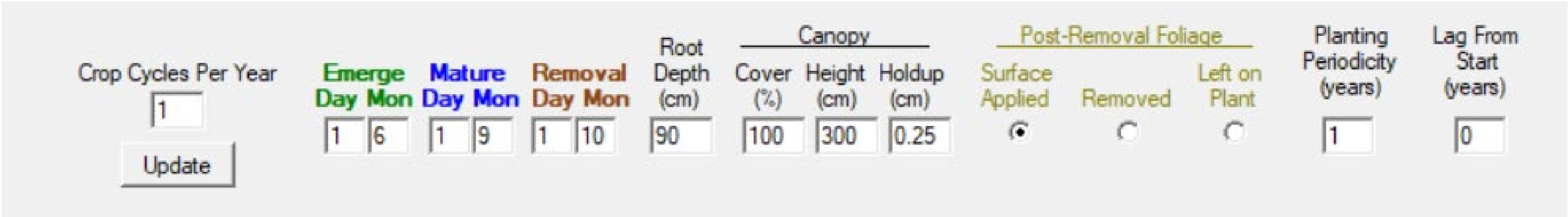


Crop Inputs

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

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.

Maximum PFAS Application Rates

	PWC Simulation Results		Screening Level Calculations for DWLOC = 20 ppt				
	Annual Applied Mass Rate (mg/ha)	Worst Case Post Breakthrough Conc. (ppt)	Attenuation Dilution Factor (mg/ha/ppt)	Maximum Annual Mass Rate (mg/ha)	Biosolids Mass Annual Application Rate (t/ha)	Biosolids Solid Content (%)	Maximum Initial Conc. in Biosolids (ppb)
PFOA	49.3	11	4.48	**90**	44.83 (20 us ton/acre)	22	**9**
PFOS	108	22	4.91	**98**			**10**

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

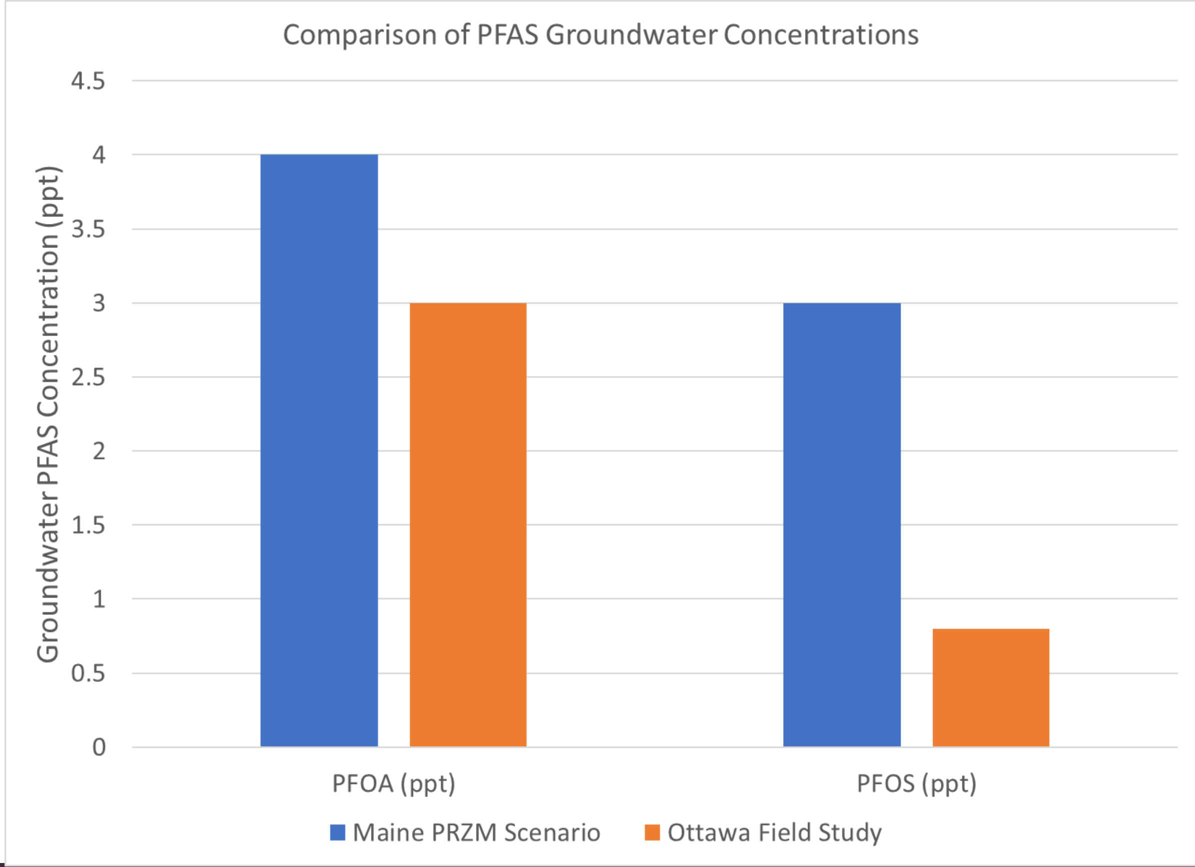
Gottschall et al (2017) reported on a land application of biosolids made to an agricultural field in Ottawa Ontario.

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.



Comparison of SESOIL/AT123D and PRZM in Screening-Level PFAS Leaching Assessments

SESOIL/AT123D has been accepted by several state agencies and the USEPA as the standard modeling tool for the development of site specific impact to ground water (IGW) soil remediation standards and also for establishing baseline soil cleanup objectives.

- Crop Simulation. The presence of the crop in part of the year and its management practices such as irrigation may greatly affect the hydrologic cycle. PRZM can also be parameterized to reflect field management practice, which can further influence the hydrology.
- Time step. Monthly vs daily. Simulation on a daily time step better accounts for weather dynamics and the time required for contaminant breakthrough to groundwater
- Contaminant Load, Placement, and Timing. The correct characterization of contaminant application time patterns is quite important since the predictions of chemical concentrations in the groundwater are influenced by these factors.
- Surface water contamination / Plant uptake. These fate pathways could be important when one is interested in other possible PFAS exposure pathways.

Summary and Conclusions

The US EPA's PRZM model is well-suited to represent the physical processes that determine the potential for PFAS chemicals to leach from land applied residuals to groundwater.

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.

Regulatory agencies in the US, Canada, and elsewhere (EU) have adopted the PRZM model as a screening level tool used in regulatory decision-making.

PRZM model simulations of PFOA and PFOS leaching from agricultural biosolids applications to groundwater were similar but conservative relative to field observations.

This modeling framework could be used to identify adequate management strategies that balance the mass loading rate of PFAS in land applied residuals and drinking water concentration safety limits, without crippling residuals recycling programs and affecting the operations and cost.

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Thank You

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