

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

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Executive Summary

This document provides guidance on how to use the Pesticide Root Zone Model (PRZM) as a screening-level tool to assess the potential for per- and polyfluoroalkyl substances (PFAS) to leach into groundwater from land applied residuals, including industrial solids and municipal wastewater biosolids (collectively referred to as residuals herein). For one individual PFAS compound at time, this modeling framework can be used to identify adequate management strategies that balance the mass loading rate of PFAS in land applied residuals and maintain safe PFAS chemical concentrations in groundwater at levels below drinking water levels of concern.

Descriptions of PRZM inputs and outputs are presented and discussed in the specific context of simulating potential leaching of PFAS from land applied residuals. Step-by-step examples show how to implement PRZM simulations representing the most vulnerable groundwater scenarios developed by U.S. Environmental Protection Agency (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. 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). An example comparison of PRZM modeling simulation results with field data is presented at the end of this guidance document and 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 for assessing potential levels of PFAS chemicals in groundwater resulting from land applied residuals.

Guidelines are provided concerning the more sensitive parameters to be aware of when applying the PRZM modeling approach. Chemical leaching to groundwater is highly dependent upon a chemical's affinity to sorb to soil particles. The chemical sorption coefficient K_d , is one of the most important parameters to estimate for PRZM modeling of PFAS chemical leaching. It is recommended that the selected K_d parameter value be informed by a current literature review specific to the PFAS chemical under investigation. In addition, when reported K_d values vary, multiple simulations should be run to assess the sensitivity of the predicted groundwater concentration to uncertainty/variability in the PFAS chemical sorption behavior. Rainfall and irrigation also heavily influence the downward movement PFAS in soil, so refinements in precipitation inputs to represent local conditions are also recommended. Soil properties also impacts leaching rates and capacity for sorption, thus refinement of these PRZM inputs to reflect local conditions is also recommended as a later refinement step.

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 will 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.

Appendix A of this report examines the suitability of using the SESOIL/AT123D modeling approach to study possible leaching of PFAS into the groundwater from land applied residuals as compared to the use of the PRZM modeling framework. While SESOIL/AT123D may be appropriate for developing site-specific impact

to ground water (IGW) soil remediation standards and baseline soil cleanup objectives for certain pollutants, there are several challenging aspects of this modeling approach that make it much less suitable than PRZM for determining maximum levels of PFAS in land applied residuals that are protective of groundwater. In contrast, PRZM has been found to adequately address many of the issues identified when using the SESOIL/AT123D modeling approach for PFAS from land applied residuals.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of 3,000 or more synthetic chemicals including PFOA, PFOS, GenX, and many other chemical varieties. PFAS have unique, specifically engineered chemical properties that make them enormously effective at resisting heat, water, and oil. The carbon-fluorine bond makes these chemicals extremely strong and stable. Because of these properties, PFAS chemicals are found in everyday commercial products including nonstick cookware, personal care products, and stain resistant textiles. These properties also make PFAS chemicals highly persistent in the environment. PFAS are primarily found near industrial manufacturing sites, some landfills and sewage treatment plants, and certain airports and Department of Defense sites where aqueous film forming foam (AFFF) were used.

While PFAS use has persisted for decades, the scientific understanding of how these chemicals move through the environment is just now beginning to unfold. Since PFAS do not readily degrade, they have the potential to enter into soil and leach into groundwater or surface water, potentially contaminating drinking water resources. One exposure pathway in need of greater understanding is from land applied wastewater treatment solids that may contain PFAS. When wastewater solids, which includes pulp and paper wastewater residuals and municipal biosolids are land applied to agricultural lands, they offer many net environmental benefits from enhancing soil health, recycling nutrients, sequestering carbon, and minimizing fertilizer and pesticide use. However, PFAS has been found in these land applied residuals at varying concentrations depending on the source and may leach into nearby groundwater resources. Understanding the fate and transport pathways of PFAS in land applied residuals is of high importance in order to be protective of groundwater drinking sources.

This document provides guidance on how to use the Pesticide Root Zone Model (PRZM), a screening-level tool, developed by the U.S. Environmental Protection Agency (US EPA) for regulation of pesticide uses in agriculture, to address the potential for PFAS to leach into groundwater from land applied residuals that may contain these chemicals. This modeling framework can be used to identify adequate management strategies that balance the mass loading rate of PFAS in land applied residuals with soil and drinking water levels of concern. After providing information on how to obtain PRZM and its documentation, a general overview of the model is presented. Model input descriptions and how to run PRZM simulations are followed by a step-by-step example of model implementation and results analysis for land applied biosolids containing PFOA and PFOS. Finally, an example of comparing model simulation results to available field data is presented. The modeling approach presented in this guidance document is appropriate for simulating leaching of a single PFAS chemical at a time; the results from one PFAS chemical (e.g., PFOA) are not broadly applicable to all PFAS chemicals as a class.

2. 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 as well as chemical fate and transport processes. It then links PRZM outputs with a receiving surface water model, the Variable Volume Water Model (VWWM).

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> (Accessed on 2/25/2021).

Technical documentation 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.

3. Description of PRZM

PRZM was developed by US EPA and is used by the Agency and other international regulatory bodies in both screening level and refined pesticide exposure risk assessments during the pesticide registration process (Baris et al., 2012a; Young and Fry, 2020). PRZM is included in the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) list of recommended regulatory models for US Pesticide Registration (Williams et al., 2010). The model has gone through several peer review processes, internally by US EPA and by regulatory agencies in Canada and Europe. Publicly available studies conducted by US EPA and Canada's Pest Management Regulatory Agency (PMRA) that compared PRZM to other leaching models concluded that PRZM was the most appropriate regulatory tool for estimating concentrations of pesticides in groundwater (Baris et al., 2012b). A general model overview is provided in the next section, followed by a discussion on model limitations and assumptions.

3.1. Model Overview

PRZM is a one-dimensional finite-difference model that has been developed primarily to describe pesticide fate and transport in agricultural soils. The time step is daily. Although not all processes may be relevant to PFAS fate and transport from land applied residuals, the principal processes modeled by PRZM are briefly described below (for more details see Young and Fry, 2020):

- Hydrology – Processes modeled include precipitation and snowmelt, surface runoff, infiltration/percolation, evapotranspiration, and irrigation. Once in the soil, water movement is always vertical and occurs when a soil horizon is filled to a maximum capacity.
- Crop simulation – Several processes are considered during a crop's growing season: changing root depth, changing plant canopy (both height and areal extent), and crop interception of water. These processes depend on the specific crop grown, weather conditions, and agronomic management. The crop simulation affects water movement and thus the environmental fate and transport of land applied chemicals.
- Erosion – The magnitude of soil erosion resulting from surface runoff is determined daily. Soil erosion is affected by topographic conditions, namely slope and slope length, as well as soil erodibility factors, vegetation, and residue coverage. Chemicals sorbed to soil particles, including PFAS, can be transported to surface water through erosion.
- Chemical application – Several agronomic practices and characteristics can be represented to simulate land application of chemicals. The key characteristics include chemical application rates (mass per unit area), application timing (day of the year), and application method (surface, at depth, incorporated with soil, etc.).
- Chemical transport – Dissolved, sorbed, and vapor-phase concentrations of chemical in the soil are calculated by considering the processes of surface runoff, erosion, microbial and chemical degradation, volatilization, foliar wash off, removal by plant uptake, leaching, dispersion, and sorption. Degradation is typically modeled using a first order degradation rate. Sorption in the equilibrium and non-equilibrium regions is modeled with Freundlich isotherms. Plant uptake is a simple model based on soil concentrations. Some processes may not be relevant to all chemicals.

- Degradation products - Up to two metabolites may be simulated simultaneously with the parent chemical.

Several characteristics of PRZM make it a suitable screening level tool for determining potential PFAS contamination in groundwater following residuals applications: the model is publicly available, it simulates chemical leaching, transport via surface water runoff and erosion, and plant uptake concurrently, and its use has been accepted by US EPA and PMRA to assess potential off-site movement of chemicals applied in agricultural settings. For screening-level regulatory purposes, PRZM represents a balance between complexity, scientific credibility, and the level of effort/cost to run the model as a screening tool that can accommodate a range of environmental conditions. PRZM may be less suitable for characterizing more complex site-specific sub-surface fate and transport problems where more sophisticated three-dimensional models may be needed. These site characterization models typically require the collection of multiple parameters collected from numerous soil, groundwater, and surface water sampling points to adequately delineate the environmental conditions, or plume. However, given the uncertainties in predicting PFAS fate and transport, the physically-based yet simplified PRZM approach, using appropriate parameterization assumptions, represents a suitable screening-level alternative to more complex models.

3.2. Model Assumptions and Limitations

3.2.1. Groundwater Leaching Conceptual Model

US EPA has developed a conceptual model and screening level scenarios for assessing a land-surface-applied chemical's potential to leach to groundwater (Baris et al., 2012a). This conceptual model assumes that a drinking water well is located directly below the location of a chemical application to an agricultural field and that there is no lateral subsurface flow in either the saturated or unsaturated zones, meaning there is no dilution of groundwater concentrations from untreated areas (see Figure 1). Thus, all transport is vertical from the land surface to the water table, making it a conservative screening level conceptual model.

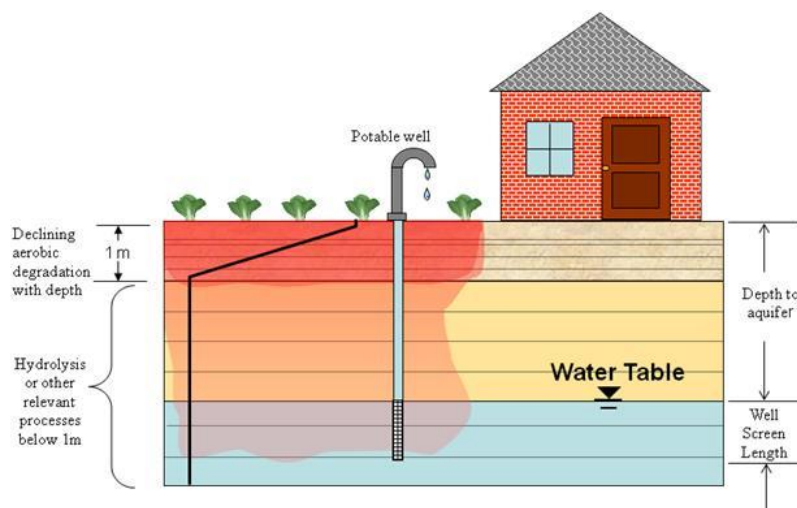


Figure 1. PRZM Groundwater Exposure Conceptual Model (source: Baris et al., 2012a)

The processes that determine the rate and magnitude of chemical leaching to groundwater include sorption to soil, soil aerobic degradation, chemical hydrolysis, potential plant uptake, and infiltration rates. The conceptual model assumes that aerobic degradation decreases with depth in the soil and is also a function of temperature (lower degradation rates with lower temperature). No aerobic degradation is assumed below a

depth of 1 meter. The timing, rate, and method of a chemical applied to the land surface can all be defined to match actual agronomic practices.

When assessing potential ecological and drinking water risks associated with pesticide applications, US EPA also estimates chemical concentrations in surface water, including ecological water bodies (the US EPA farm pond) and high vulnerability surface drinking water sources (the US EPA Index Reservoir). These chemical concentrations in surface water are determined based on transport via surface runoff and erosion from the applied fields. Because PRZM considers surface and sub-surface hydrologic transport processes concurrently, chemical leaching potential to groundwater (including PFAS leaching) is impacted by the magnitude of chemical loss via surface transport processes. In addition to groundwater, PFAS concentrations in surface receiving waters resulting from residuals applications could be examined using PRZM and VVWM (both contained in PWC).

3.2.2. Background Concentrations and Other PFAS Sources

Land applied residuals are assumed to be the sole source of PFAS in the PRZM simulation approach described in this guidance document. However, PFAS have been found in “uncontaminated” soil and water as a results of atmospheric deposition. If better characterized, these “background” concentrations and atmospheric deposition rates could be accounted for as additive sources of PFAS chemicals applied to the soil outside of the land application process.

3.2.3. Plant Uptake

PFAS has the potential to accumulate in agricultural plants through uptake from soil (see Ghisi et al., 2019 for a review). While the PRZM model 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. A conservative approach for screening-level analyses of potential groundwater contamination is to not consider this process. If plant uptake is accounted for, then less chemical would be available for leaching and lower potential groundwater concentrations. As more data become available regarding plant uptake of PFAS, modeling approaches with PRZM may be refined to account for this.

4. Model Inputs for PFAS Simulation

Several PRZM input parameters need to be provided by the user to model a PFAS leaching scenario. The focus here is to provide guidance on how to identify the processes, the physical and chemical properties, and other PRZM input parameters that are relevant to predict PFAS fate in the soil matrix and potential leaching to groundwater resulting from land-applied residuals. As the chemical fate processes are sensitive to the choice of input parameters, it is also important to investigate the possible range of realistic values and their implications on predictions. In addition to the chemical properties, the residuals application method and the site characteristics (soil type, depth of groundwater, precipitation rates, etc.) are also important in determining the potential for PFAS leaching to groundwater. A description of each of the primary PRZM model inputs relevant to the simulation of PFAS are provided in the sections below. Lengthier discussions are provided for the more important parameters to consider. The PWC user manual contains a more thorough description of each input parameter.

4.1. Chemical/Physical Inputs

The current PWC interface tab to enter chemical and physical inputs is shown in Figure 2 below.

Pesticide Water Calculator (PWC), Version 2.001

File Scenario Help

Chemical Applications Land Crop Runoff Watershed Batch Runs More Options Out: Pond Out: Reservoir

Chemical ID (optional)

Parent Daughter Granddaughter

☒ K_{oc} ☐ K_d Sorption Coeff (mL/g)

Water Column Metabolism Half-life (day)

Water Reference Temperature (°C)

Benthic Metabolism Half-life (day)

Benthic Reference Temperature (°C)

Aqueous Photolysis Half-life (day)

Photolysis Reference Latitude (°N)

Hydrolysis Half-life (day)

Soil Half-life (day)

Soil Reference Temperature (°C)

Foliar Half-life (day)

Molecular Weight (g/mol)

Vapor Pressure (torr)

Solubility (mg/L)

Henry's Coefficient

Air Diffusion Coefficient (cm²/day)

Heat of Henry (J/mol)

Estimate & Overwrite Henry's Coefficient

Molar Formation: Decline Ratio

Water Column Metabolism

Benthic Metabolism

Photolysis

Hydrolysis

Soil

Foliar

Figure 2. PWC Tab for Chemical and Physical Inputs

- **Sorption coefficient (K_{oc}/K_d).** A key process affecting PFAS fate in soil following residuals applications is the adsorption to soil. The propensity of the chemical substance to stay sorbed onto soil or dissolved in water is quantified by the soil sorption coefficient K_d : the lower the coefficient, the less strongly bound to soil particles, and the higher the risk of chemical migration to the groundwater. K_d is often normalized to the organic content of the soil matrix, to obtain the organic carbon-water partition coefficient, K_{oc} , which is also an input option in PRZM. The Interstate Technology and Regulatory Council (ITRC) provides the following background on PFAS behavior in soil, “PFCAs and PFSAAs are present as organic anions at relevant environmental pH values, and are therefore relatively mobile in groundwater, but will also tend to associate with the organic carbon fraction of soil or sediment in the saturated zone. Sorption to organic carbon generally increases with increasing perfluoroalkyl tail length, indicating that the short-chain PFSAAs (for example, PFBS) and PFCAs (for example, PFHxA) are less retarded than their long-chain counterparts (PFOS and PFOA, respectively). In addition, PFSAAs tend to sorb more strongly than PFCAs of equal chain length, and branched isomers are less sorptive than linear isomers” (ITRC, 2020, section 5.2.3). Published data about the sorption of PFAS provides a wide range of measured sorption values as well as a mixed understanding of the correlations with organic carbon content, pH, and other soil properties. There is evidence that for certain PFAS chemicals, desorption occurs more slowly than sorption, indicating that for the more strongly sorbing compounds like PFOS, their presence in the soil matrix is more persistent and likely less bioavailable and less subject to migration. In general, sorption coefficient values based on laboratory samples (derived using sorption isotherms) underestimate the impact of sorption during fate and transport modeling most probably due to the spatiotemporal concentration

variabilities in soil, and interactions with organic carbon alone are insufficient to reliably predict PFAS partitioning coefficients (Li et al, 2018). Thus, field values may be more appropriate for characterizing PFAS transport. Review and ranges of published K_d values for PFOA and PFOS were recently compiled by Li et al. (2018). Li et al. also reports percentiles of the available published data as well as the different lab and field-based values. For some of the other PFAS, published sorption coefficients have been summarized and kept up-to-date by ITRC (2020) and can be found in the Physical and Chemical Properties Table provided as a separate Excel file (Table 4-1).

- **Water column metabolism half-life and reference temperature, benthic metabolism half-life and reference temperature, aqueous photolysis half-life and reference latitude.** These processes are not considered in groundwater modeling, and the respective PRZM inputs do not need to be populated.
- **Hydrolysis half-life, soil half-life, and soil reference temperature.** Biotic and abiotic transformations have been observed in some polyfluorinated PFAS. Polyfluorinated PFAS that degrade are referred to as ‘precursors’ and typically form perfluoroalkyl acids (PFAAs), such as PFOA and PFOS. PFAAs have not been shown to degrade or otherwise transform under ambient environmental conditions. PFAAs are sometimes referred to as ‘terminal PFAS’ or ‘terminal degradation products’. PFAAs are strong acids and are anionic in the environmentally relevant pH range of 5.5 to 8.5. They are extremely persistent in the environment and do not degrade or transform under typical environmental conditions. “The fundamental differences between polyfluorinated precursors and perfluorinated chemicals that affect transformation potential are the presence, location, and number of carbon-hydrogen (C-H) bonds and potentially carbon-oxygen (C-O) bonds throughout the alkyl carbon chain. Specifically, PFAS with C-H bonds are subject to a variety of biotic and abiotic reactions that ultimately result in the formation of shorter chain PFAAs.” (ITRC, 2020 chapter 5). 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. For PRZM modeling, this means a half-life of zero.
- **Foliar half-life.** This input parameter is not relevant when land applied residuals are considered.
- **Molecular weight.** This model input is used directly in the degradate production routines if degradates are simulated. It is also used indirectly to calculate the Henry’s Law coefficient.
- **Vapor pressure (at 25°C).** The higher the vapor pressure, the greater the volatility of the chemical. It is also used indirectly to calculate the Henry’s law coefficient. Very little data on measured vapor pressure values for PFAS exist, and much of the data on PFAS is extrapolated or modeled. Therefore, care must be taken when providing this information. If volatilization is not a process that affects the PFAS being considered, this input parameter is not important for leaching simulations.
- **Solubility (at 25°C).** Solubility quantifies the ability of a given substance to dissolve in a solvent. For a given temperature and pressure, the higher the solubility the less volatile the compound is. Solubility is also used indirectly to calculate the Henry’s law coefficient. Reported values for solubility of individual PFAS chemicals may vary depending upon the method used to determine solubility, the form of the analyte (acid or salt), pH, salinity, and whether the value is empirical or obtained through modeling.
- **Henry’s Constant (dimensionless).** This chemical specific constant K_h characterizes the propensity of the compound to remain dissolved in water versus volatilizing into the gas phase. For most organic

compounds with moderate or low solubility, Henry's Law Constant can be derived from the chemical vapor pressure and solubility (the PWC graphical user interface enables the user to calculate K_h automatically from input vapor pressure and solubility values by clicking the "Push to Estimate Henry" button). K_h is directly proportional to vapor pressure and inversely proportional to solubility. The PWC K_h estimation routine assumes that the user entered vapor pressure and solubility relevant to 25°C (for a thorough understanding of the volatilization algorithm, the PWC documentation provides specific guidance). The user has also the option to manually enter a K_h value. Vapor pressures of PFAS compounds are generally low while water solubilities are high, thus indicating a preference to be in the water phase.

- **Air diffusion coefficient.** The air diffusion coefficient is related to the kinetic energy associated with molecular motion and is dependent on the molecular weight of the compound. An input of zero for the air diffusion coefficient effectively shuts off dissipation of the chemical due to volatilization. A conservative approach for assessing PFAS leaching potential into the groundwater is to set this value to zero.
- **Heat of Henry.** This input is the enthalpy of phase change from aqueous solution to air solution. The conservative approach with respect to the PFAS leaching would suggest this be set to zero.
- **Daughter/granddaughter check box columns and molar conversion factors.** Checking these boxes allows for the simulation of a daughter and granddaughter degradates of the parent. Chemical properties of the degradates should be entered as described above for the parent. The user should also enter the ratios of moles of degradates produced to moles of parent degraded for each of the processes.

A thorough technical and regulatory guidance document that also provides an up-to-date assessment of the physical and chemical properties and environmental fate and transport processes of PFAS, already referenced several times in this document, was published by the Interstate Technology and Regulatory Council (ITRC) in April 2020 (ITRC website also has fact sheets, explainer videos, training module videos, and external tables of data and information about PFAS, <https://pfas-1.itrcweb.org/>). This publication is also a helpful resource for parameterizing PFAS physical/chemical properties required for PRZM simulations.

4.2. Application Inputs

This set of inputs focuses on describing the application characteristics of the chemical to the soil and is entered in the PWC application tab shown in Figure 3.

Figure 3. PWC Tab for Chemical Applications Inputs

- **Number of applications.** This is the number of chemical applications per year. For residuals, this typically is once per year, however it is also possible to apply more or less frequently.
- **Absolute/relative application dates.** Application dates can be entered as absolute dates, e.g. specific month and day of the year, or as relative to crop emergence dates, e.g. 10 days before crop emergence. If the timing of residuals applications is well understood, then entering specific dates (e.g., April 30th) is the recommended approach.
- **Application amount.** This is the mass of chemical that is applied per unit area (kg/ha). When residuals are considered, usually the initial information available is the concentration c (ppb=ng/g) of chemical content in the residuals dry sample, the fraction f of dry mass in the wet residuals applied, and its mass rate of application per unit area M_b (kg/ha). With the units in parenthesis, the mass m_c (kg/ha) of chemical applied per unit area is: $m_c = c \cdot 10^{-9} \cdot f \cdot M_b$
- **Application method.** Several application methods can be specified depending on how the land applied residuals are integrated into the soil. These different methods impact the availability of the chemical for surface transport via runoff and erosion.
 - Below crop: this option is not relevant for land applied residuals.
 - Above crop: this method would be appropriate if residuals were applied to the land surface without incorporation, typical of a hay field application.

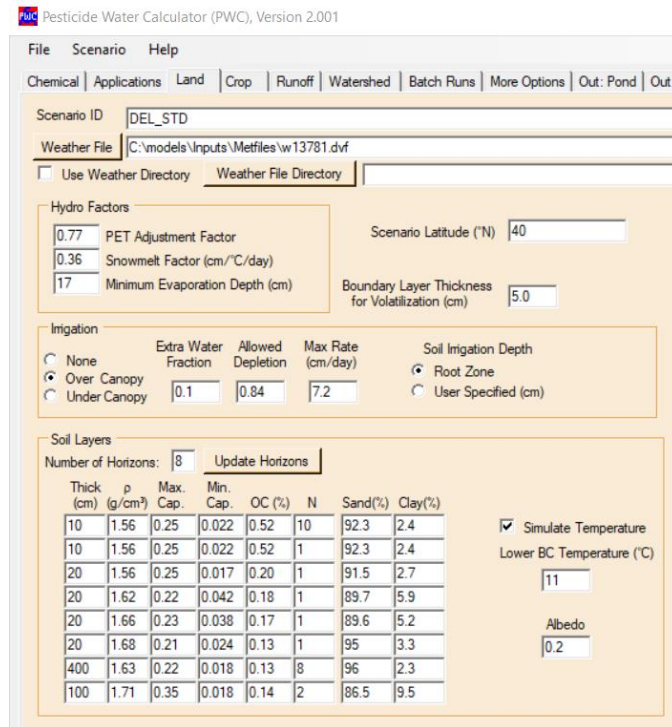
-
- Uniform below: using this application method, the chemical is applied uniformly to a user-specified depth. This method could be applicable if a residuals application is immediately followed by uniform tillage to a certain depth (the user can specify the depth).
 - At depth: the chemical is placed entirely at a specific depth. This is generally not applicable to land applied residuals.
 - T-band: the chemical is distributed to a depth specified by the incorporation depth, with a specified fraction placed into the top 2 cm. In the case of residuals containing PFAS, other application methods are generally more suitable in describing the initial chemical distribution.
 - Linearly increasing (Δ) / decreasing (∇): chemical mass is distributed in the soil linearly, increasing or decreasing with depth down to the depth specified by the user. Land applied residuals could be modeled as linearly decreasing to a certain depth. Linearly increasing with depth would be a less appropriate choice of application method for most residuals applications. The linearly decreasing with depth option, along with the uniform distribution option, represent the most appropriate application methods for incorporated residuals.
- **Custom, reservoir or pond.** If evaluating potential surface water contamination is an objective of the study, the user can select which water body receives the runoff from the field. This is not applicable for chemical leaching into the groundwater.
 - **Efficiency/drift.** These parameters have utility when considering spray drift applications to account for chemical loss due to spray and drift loading into surface water body. These are not applicable to land applied residuals. A value of 0 for spray drift and a value of 1.0 for efficiency should be entered for biosolid applications.
 - **Application refinements.** The user can further tailor application timing characteristics by specifying:
 - Applications occur every [] year, or
 - Applications occur from year [] to year []

When assessing screening levels of PFAS in land applied residuals, a conservative approach sometimes used is to have applications occurring every [1] year from year [1] to year [last]. However, in many real case scenarios, residuals are not (or cannot be) applied every year because of other requirements such as nutrient limitations. As an example, to characterize applications occurring every 5 years in a 20 year period, one can enter “Applications occur every [5] years” and “From year [1] to year [20]”. Note that PZRM simulations run with PWC typically extend from 30 to 100 years. The correct characterization of chemical application patterns is quite important since the predictions of chemical concentrations in the groundwater are greatly influenced by these choices.

- **Application window batch analysis.** These options allow the user to analyze the impact of different application day on the simulation. Generally, this type of analysis is not relevant for determining screening level groundwater PFAS concentrations resulting from land applied residuals.

4.3.Land Inputs

The user is required to enter the proper land scenario for assessing PFAS leaching potential to groundwater. An example associated with the Delmarva Corn groundwater scenario is shown in Figure 4. The scenario should represent the residuals application area of interest and including climatic and soil conditions. Irrigation practices are also specified here.



Pesticide Water Calculator (PWC), Version 2.001

File Scenario Help

Chemical Applications Land Crop Runoff Watershed Batch Runs More Options Out: Pond Out: f

Scenario ID: DEL_STD

Weather File: C:\models\Inputs\Metfiles\w13781.dvf

☐ Use Weather Directory ☒ Weather File Directory

Hydro Factors

PET Adjustment Factor: 0.77

Snowmelt Factor (cm/°C/day): 0.36

Minimum Evaporation Depth (cm): 17

Scenario Latitude (°N): 40

Boundary Layer Thickness for Volatilization (cm): 5.0

Irrigation

☐ None ☒ Over Canopy ☐ Under Canopy

Extra Water Fraction: 0.1

Allowed Depletion: 0.84

Max Rate (cm/day): 7.2

Soil Irrigation Depth: ☒ Root Zone ☐ User Specified (cm)

Soil Layers

Number of Horizons: 8 Update Horizons

Thick (cm)	ρ (g/cm ³)	Max. Cap.	Min. Cap.	OC (%)	N	Sand (%)	Clay (%)
10	1.56	0.25	0.022	0.52	10	92.3	2.4
10	1.56	0.25	0.022	0.52	1	92.3	2.4
20	1.56	0.25	0.017	0.20	1	91.5	2.7
20	1.62	0.22	0.042	0.18	1	89.7	5.9
20	1.66	0.23	0.038	0.17	1	89.6	5.2
20	1.68	0.21	0.024	0.13	1	95	3.3
400	1.63	0.22	0.018	0.13	8	96	2.3
100	1.71	0.35	0.018	0.14	2	86.5	9.5

☒ Simulate Temperature

Lower BC Temperature (°C): 11

Albedo: 0.2

Figure 4. PWC Tab for Land Inputs

As discussed in more detail below, US EPA has developed several high vulnerability groundwater leaching scenarios (and additional relevant surface water scenarios that reflect conditions less vulnerable for groundwater leaching) that can be downloaded and will fully populate this tab, as shown above. However, to better represent local conditions, the user can refine scenarios tailored to specific residuals application areas. The following aspects of the “Land” inputs that a user should focus on to refine a scenario are as follows:

- **Scenario ID.** Starting from an existing US EPA groundwater or surface water scenario is a good approach to building a custom scenario. See the PWC documentation for loading US EPA “standard” scenarios.
- **Weather time series.** The weather file button opens a file browser to allow for selection of weather files. The weather information must contain daily precipitation, pan evaporation, temperature, wind speed, and solar radiation and must be in the same format as PRZM weather files (see PRZM manual). Weather files formatted for PRZM, both 30-year and 100-year time series, are available for download in association with the PWC model from EPA. Choosing a weather file associated with a station near the residuals application region of interest is recommended.
- **Hydro factors.** These are inputs that generally affect the hydrology near the surface. These parameters vary geographically and are not crop or soil dependent.

- **Irrigation.** The user can enter information regarding local irrigation practices. Irrigation may affect the overall leaching process and potential for PFAS to reach groundwater.
- **Soil layers.** These are the parameters describing different properties of the soil horizons: horizon thickness and porosity, maximum capacity (or also referred as field capacity), minimum capacity (or also referred as wilting point), and organic carbon content. In addition, temperature related soil properties can be activated and specified. PFAS leaching predictions will be sensitive to soil parameters. The PRZM soil properties can be customized to reflect local conditions and derived from soil surveys or from a farm's technical service provider. The soil properties associated with EPA's screening level groundwater scenarios are designed to be conservative and represent "worst case" leaching potential.

4.4. Crop Inputs

Inputs related to the simulated crop/s are provided in the PWC Crop tab shown in Figure 5. Example inputs shown here are directly from the US EPA Delmarva Corn groundwater scenario file, but can be modified directly by the user. Version 2.001 of PWC provides the capability to parameterize more complex cropping cycles and rotations. However, 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.

Pesticide Water Calculator (PWC), Version 2.001

File Scenario Help

Chemical Applications Land Crop Runoff Watershed Batch Runs More Options Out: Pond Out: Reservoir Out: Custom Out:GW Advanced

☐ Simple Crop Schedule ☒ More Complex Crop Schedules

☒ Crop Cycles < 1 year

Crop Cycles Per Year: 1 [Update]

Emergence			Mature			Removal			Root Depth (cm)	Canopy			Post-Removal Foliage			Planting Periodicity (years)	Lag From Start (years)
Day	Mon	Day	Mon	Day	Mon	Cover (%)	Height (cm)	Holdup (cm)		Surface Applied	Removed	Left on Plant					
10	4	30	5	15	6	98	300	0.27	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	1	0				

☐ Evergreen ☐ Crop Cycle > 1 year

Figure 5. PWC Tab for Crop Inputs

4.5. Runoff Inputs.

As mentioned above, PRZM also estimates contaminant mass transport from surface runoff. 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. PRZM requires inputs to parameterize both the runoff and erosion processes. These inputs, with values from US EPA's Delmarva Corn groundwater scenario, are shown in Figure 6. The runoff curve numbers are an important input for both surface water transport of chemicals and groundwater leaching potential. US EPA's screening level groundwater scenarios are designed to be highly conservative, and thus, assume a runoff curve number of 10, essentially resulting in no runoff and the maximization of leaching. While acceptable for a highly conservative screening level assessment, more realistic runoff curve numbers can

be applied based on US EPA's surface water scenarios or based on standard Natural Resources Conservation Service guidance on curve number selection (NRCS, 1986).

Pesticide Water Calculator (PWC), Version 2.001

File Scenario Help

Chemical Applications Land Crop Runoff Watershed Batch Runs More Options Out: Pond Out: Reservoir Out: Custom Out:

No. of Time-Varying Factors: 1

☐ Specify year

Day	Mon	CN	USLE-C	N
1	5	10	.638	.014
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				

☒ Use Lag Method for To

0.37 USLE K
1.34 USLE LS
1 USLE P
3 IREG
6 Slope (%)

PRZM5 Runoff & Erosion Extraction

Distribution of Runoff in Surface		Distribution of Eroded Solids	
R-Depth (cm)	2.0	E-Depth (cm)	0.1
R-Denote (1/cm)	1.55	E-Denote (1/cm)	0
Efficiency	0.266	Efficiency	1.0

Figure 6. PWC Tab for Runoff Parameters

4.6.Uncertainty of Input Parameters

Considering that many PFAS are minimally volatile and that they degrade slowly if at all, the most important chemical input parameter that may significantly affect groundwater concentration predications is the sorption coefficient, K_d . As discussed earlier, the current scientific literature reports a range of observed behavior regarding the partitioning of PFAS between dissolved and sorbed phases in soil. Given these uncertainties, an initial set of simulations may consider the lowest sorption coefficient values provided by the literature, typically equal to the laboratory minimum measured values. Under these conditions, the propensity for the chemicals to be mobile is maximized, simulating the worst-case leaching potential conditions. 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 laboratory- or field-derived expected sorption values, the former of which are generally considered to underestimate field sorption. This approach may provide a better understanding of PFAS leaching potential and expected groundwater concentrations reflective of typical conditions in agricultural settings. From the perspective of determining the limits of initial PFAS content in residuals that are protective of groundwater, the findings under the most conservative sorption assumption should be considered as a first screening step: biosolid applications with initial PFAS content below this initial level may be considered protective of groundwater. If initial PFAS content is higher, then the more typical sorption behavior derived from available literature values can be considered to further investigate potential PFAS leaching.

Other input parameters that the user should consider when trying to determine acceptable PFAS screening levels are the effects of crop and land inputs (such as irrigation) and the effects of weather time series, soil characteristics, and aquifer depths.

5. 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 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. These scenarios can be downloaded from the PWC download link provided in Section 2 and are characterized by very sandy soils, low organic matter, and shallow depth to groundwater. They 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. As shown in the previous sections, the US EPA scenarios provide all of the necessary environmental and climate characteristics to conduct a simulation, requiring only the chemical and application information from the user. 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 of these scenarios 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. As described above, the user can specify all necessary PRZM input parameters to tailor the scenario to specific local conditions. These include crop characteristics, weather, irrigation practices, other hydrologic factors, and soil horizon properties that best represent fields of residuals application in the region of interest. In addition, one can study the effect of alternative application practices, e.g., application of residuals that occur only for a certain number of years or every other year.

It is also worth mentioning that US EPA has developed numerous PRZM screening level scenarios tailored to surface water exposure (drinking water and ecological assessments). These do not necessarily represent “worst case” leaching scenarios, but they can be used to estimate PFAS surface water concentrations following land application of residuals containing PFAS. In addition, these scenarios can also be used as the basis for a groundwater leaching scenario characterization of a particular geographic region. The user can then modify some of the relevant input parameters, for example different soil properties or crop characteristics. A practical example with customized scenario is provided in Section 7.

6. Model Simulations and Results

Once model inputs and scenarios are selected, PRZM is run through the PWC interface to predict potential PFAS concentration in groundwater. This section provides a description of the available outputs and how results can be analyzed.

6.1. Running PRZM Groundwater Scenarios

The screening level estimated PFAS concentrations in groundwater and/or associated maximum allowable concentrations in residuals can be determined through simulation of EPA groundwater scenarios and/or user specified scenarios representative of the local settings. Several outputs are available from these PWC simulations to characterize chemical concentrations in groundwater. An example of these outputs based on the Delmarva Corn groundwater scenario are shown in Figure 7 below.

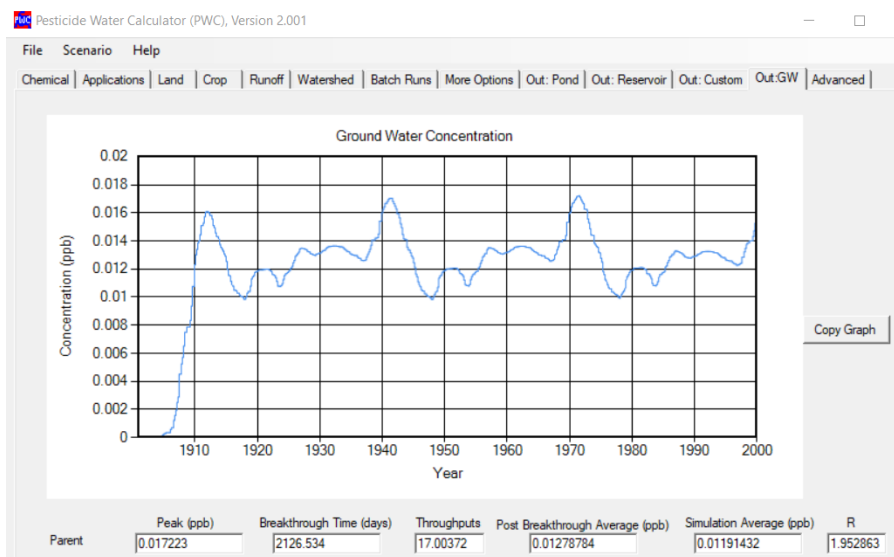


Figure 7. PWC Tab for Groundwater Outputs

Standard PRZM outputs available through the PWC interface include:

- **Peak concentration.** This is the highest predicted concentration, averaged over the top 1 m of the simulated aquifer.
- **Breakthrough time.** The average time that it takes a molecule of chemical to move from the soil surface to the aquifer. This is also the approximate time necessary to reach near steady state concentration in the top 1 m aquifer.
- **Throughputs.** A throughput of one is required to expel the center of mass of the chemical pulse input. Near complete breakthrough will require several throughputs. A throughput is calculated based on the infiltration volume reaching the aquifer, the pore volume of the soil media, and a “retardation factor” describing how fast/slowly the chemical moves. If the “throughputs” value for a model run is less than one, modeling should be repeated with the appropriate extended weather file (i.e., greater than the 30-year standard weather file) in order to observe breakthrough.
- **Post breakthrough average.** Represents the approximate steady state average concentration of the applied chemical within the top 1 m of the simulated aquifer after breakthrough has occurred.
- **Simulation average value.** The temporal average concentration over the entire simulation period of the vertical-averaged top 1 m of the simulated aquifer.

As discussed above, it is recommended that several scenarios representative of the most vulnerable conditions to chemical leaching to groundwater be considered. For screening level studies, the scenario resulting in the highest predicted concentrations in groundwater, from the ensemble of scenarios considered, are identified for use in the risk assessment. The most significant groundwater concentration metric considered in human health risk assessment is the post breakthrough average concentration, representing long-term average exposure.

It is also possible to select other PRZM output parameters that may be helpful in better understanding the chemical and water mass balance. The PWC tab used for specifying additional output options is shown in Figure 8.

Pesticide Water Calculator (PWC), Version 2.001

File Scenario Help

Chemical Applications Land Crop Runoff Watershed Batch Runs More Options

Optional Output to the PRZM5 Time Series (zts) File

- ☐ Daily volatilization from field (kg/ha)
- ☐ Cumulative volatilization from field (kg/ha)
- ☐ Daily pesticide leached (kg/ha)
- ☐ Cumulative pesticide leached (kg/ha)
- ☐ Pesticide decayed in field (kg/ha): from: cm to: cm
- ☐ Pesticide mass in entire soil profile (kg/ha)
- ☐ Pesticide mass in part of soil profile (kg/ha): from: cm to: cm
- ☐ Pesticide mass on foliage (kg/ha)
- ☐ Pesticide Mass in Equilibrium Region
- ☐ Pesticide Mass in Nonequilibrium Region

☐ Precipitation (cm)

☐ Evapotranspiration (cm)

☐ Soil water in entire profile (cm)

☐ Irrigation (cm)

☐ Infiltration (cm) at a depth of cm

Optional Waterbody Output Files

- ☐ Create HED Files
- ☐ Additional Frequency of Return (years): 15

Figure 8. PWC Tab for More Output Options

The most significant ones with respect to PFAS in residuals applications are:

- Daily and cumulative chemical mass leached per unit area, and
- Chemical mass per unit area in the entire/part soil profile.

6.2.Simulation Results Evaluation

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. There are several general methods to investigate sensitivity of results with respect of model inputs. A detailed summary of these methods goes beyond the scope of this guidance, but ample literature is available. A general discussion in the context of PFAS leaching potential to groundwater is provided here.

In addition to more tailored weather/soil/crop scenarios that may better characterize local conditions, the two main parameters that can greatly affect predicted chemical concentrations are the sorption coefficient and the depth of the water table. Additional scenarios can be run by varying these parameters and studying how estimated groundwater concentrations change. The main focus is to investigate how chemical concentrations may increase/decrease with respect to the primary analysis results, for example if the water table depth is decreased or PFAS has a higher tendency to be adsorbed to soil (a higher K_d or K_{oc}). Application frequency is

also another factor that greatly affects results. The worst-case application scenario, where applications occur every year, is a good starting point, but more realistic application frequencies should also be considered.

For screening level assessments, the highest concentrations from the ensemble of the sensitivity analysis study case scenarios should be determined. Another, more sophisticated, method could weigh the different predicted concentrations by the likelihood of the scenario (if known), or alternatively one can just include results with their estimated variability.

Once the worst case/highest concentration of chemical in the groundwater, c_w (ng/l=ppt), is identified for a given PFAS application rate, 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 and 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. For example, if the mass of chemical applied per unit area is initially above this set screening level m_s , residuals can be diluted or applied at a lower rate to cover more area, reducing the amount of chemical mass applied per unit area. Similarly, alternative residuals application schedules can be investigated to determine the appropriate application frequency to meet groundwater concentration limits. A complete example of this output analysis is provided in the “Step-by-Step Example” section that follows.

7. Step-by-Step Example

This section walks through an example of 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. The most relevant aspects of the study are summarized in the following sections to provide a complete case study on how to use PRZM in a screening level PFAS leaching assessment.

7.1. Chemical/Physical Inputs

As discussed previously, the key process affecting chemical potential leaching to groundwater is its propensity to stay sorbed onto soil or dissolved in water. This property is described by the sorption coefficient K_d . The variability of published K_d values for PFOA and PFOS was compiled in a recent publication (Li et al., 2018); percentiles for the published data are reported in Table 1.

Table 1. PFOS and PFOA Sorption Distributions (K_d)

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

To be conservative, the initial PFOS and PFOA leaching simulations considered K_d values set equal to the laboratory minimum measured values provided by the literature (1.95 and 0.129 for PFOS and PFOA, respectively). Under this condition, the propensity for the chemicals to be mobile is maximized, therefore the use of these values represents the worst possible leaching potential from a chemical property standpoint. To better understand the effects of different K_d values on expected groundwater concentrations, some results were also generated using field median K_d values, which may be more reflective of actual Maine agricultural conditions. Users can also parameterize the PRZM model sorption processes using a K_{oc} value, in which case the sorption throughout the soil is dependent on the organic carbon content. The higher the organic content, the more the chemical is sorbed to soil. However, in the literature review publication by Li et al. (2018), they did not find a strong correlation between sorption of PFOA and PFOS with organic matter. By using the minimum laboratory K_d , sorption capacity becomes minimal and does not change across the soil horizons because of different organic matter content, capturing the worst-case leaching potential conditions.

The other relevant PRZM chemical physical parameters used for these simulations are summarized in Table 2 below. Note that all half-life values were set to “0” indicating no degradation processes. Other PRZM chemical inputs not listed below are also irrelevant for PFOA and PFOS (and thus left empty or zero).

Table 2. Environmental Fate Properties for PFOS and PFOA Used in Current Modeling

Parameter		PFOS	PFOA
K_d (L/Kg)	Lab minimum	1.95	0.129
	Field median	83.18	14.45
Molecular Weight - MWT (g/mol)		538	414
Vapor Pressure (torr) at 25 °C		0.002	0.525
Solubility (mg/L) at 25 °C		680	9500
Henry's Constant (dimensionless)		8.51E-05	0.00123

7.2. Application Inputs

Applications of PFOA and PFOS were modeled to be representative of typical biosolids characteristics reported by NEBRA based upon practices commonly utilized in Maine and biosolids produced in the Northeast. To mimic typical biosolids application schedules, these simulations considered applications occurring once every year for the entire simulation period with the timing defined as one week before corn planting and with biosolids always containing the same amount of PFOA and PFOS. As discussed above, this is a conservative assumption 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. In addition, PFOA and PFOS concentrations in biosolids have been slowly decreasing over the last decade.

As shown in Figure 9, a biosolids application was assumed to occur one week before crop emergence and integrated into the first 15 cm (6 in) of soil, modeled in PRZM as linearly decreasing concentration with depth (▽). NEBRA provided data showing that the median chemical concentrations in biosolids is 5 ng/g (ppb) for PFOA and 11 ng/g (ppb) for PFOS on a dry weight basis. Biosolids applied in the field were assumed to have a 22% solid content and were applied at a rate of $44.83 \cdot 10^3$ wet kg/ha (20 wet us tons/acre). This resulted in annual application rates of 49.3 mg/ha for PFOA and 108 mg/ha for PFOS (e.g., the mass rate of PFOA applied is $m_c = 5 \cdot 10^{-9} \times 0.22 \times 44.83 \cdot 10^3 = 4.93 \cdot 10^{-5}$ kg/ha = 49.3 mg/ha). If interested in determining the proper chemical application rate that does not lead to exceedance of a given DWLOC, then

one can set the simulations with any arbitrary chemical mass rate m_c to calculate the dilution attenuation factor $d = m_c/c_w$ (which is independent of the initial chemical mass applied rate).

The screenshot shows a software interface for PWC Application Inputs for PFOA. It includes several input fields and buttons. At the top, there's a 'Number of Applications' field set to '1' and an 'Update Applications' button. Below this, there are radio buttons for 'Absolute Dates' and 'Dates are relative to:' with options 'Emerge', 'Maturity', and 'Harvest'. The 'Application Method' section has a row of radio buttons for 'Days Since', 'Amount (kg/ha)', 'Below Crop', 'Above Crop', 'Uniform', '@ Depth', 'T Band', 'Δ', 'T', and 'Depth (cm)'. The 'Specify Years' checkbox is unchecked. The 'Application Refinements' section has 'Applications occur every' set to '1' Year(s), 'Applications occur from year' set to '1', and 'to year' set to 'last'.

Figure 9. PWC Application Inputs for PFOA

7.3. Land Inputs

Initially PFOA and PFOS leaching potential were simulated using five of the six EPA screening level leaching scenarios, including one from Florida (Florida Potato) and four from other regions (Georgia Peanuts, North Carolina Cotton, Delmarva Sweet Corn, and Wisconsin Corn). The sixth was excluded because Florida was already represented. To assess long term leaching potential, extended weather files were used to simulate 100 consecutive years instead of the standard 30 years (these extended weather files are also available from the PWC download link provided in Section 2 and are comprised of the standard 30 year meteorological data repeated over 100 years). A total of ten screening level scenarios were run in this stage of the project: five scenarios and two chemicals (PFOA and PFOS), using the minimum laboratory K_d values.

Additional PRZM simulations were run by considering scenarios that better represent Maine soils, weather, and relevant groundwater depths. These scenarios were derived by modifying the EPA's Maine Potato standard surface water PRZM scenario (MEpotatoSTD).

A soils analysis was conducted in GIS by overlaying agricultural land from the 2016 National Land Cover Dataset (cultivated cropland and pasture/hay, see Figure 10) with soil map units from the NRCS SSURGO database. From the selected agricultural soils, the acreage of each soil series (by soil component name) was calculated and the most common soil within each hydrologic soil group (A, B, C, and D) was identified. These soils were Adams, Caribou, Plaisted, and Scantic for hydrologic groups A, B, C, and D respectively. The soil parameters necessary for modeling with PRZM were then extracted, resulting in four Maine-specific leaching scenarios (see Table 3).

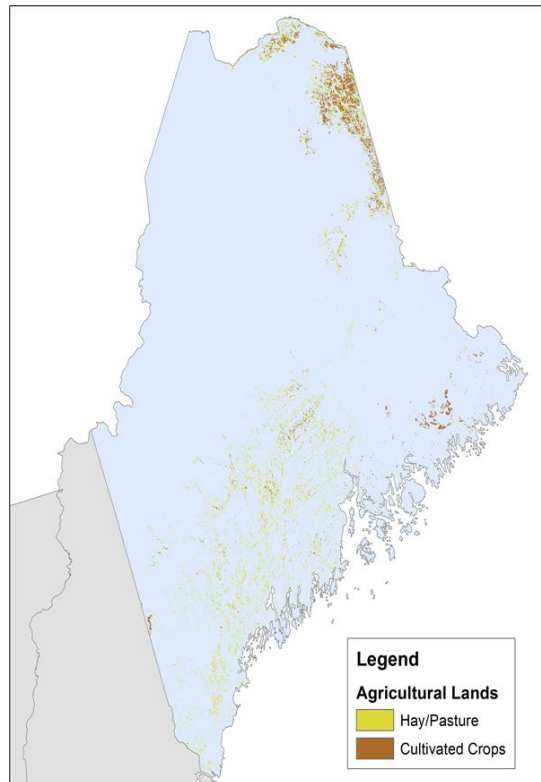


Figure 10. Agricultural lands in Maine from 2016 NLCD. Soils underlying these areas were used to represent typical soils for purpose of leaching modeling.

Table 3. Soil Properties for Maine Agricultural Soils Selected for Modeling

Soil Name	Hydrologic Group	Top Depth (cm)	Bottom Depth (cm)	Thickness (cm)	OC (%)	Bulk Density ρ (g/cm ³)	Max Capacity (Field) (%)	Min Capacity (Wilting Point) (%)
Adams	A	0	18	18	3.5	1.15	14.8	5.7
		18	54	36	2	1.25	10.3	3.9
		54	69	15	1	1.35	8.2	2.3
		69	165	96	0.25	1.4	5.2	0.9
Caribou	B	0	18	18	5.5	1.13	27.6	8.3
		18	48	30	3.25	1.25	36.7	11.8
		48	152	104	0.5	1.48	21.8	9.3
Plaisted	C	0	18	18	5.5	1	20.7	7.2
		18	41	23	2.5	1.1	17	4.6
		41	64	23	1	1.25	15.5	3.7
		64	165	101	0.25	1.7	15.5	3.9
Scantic	D	0	23	23	6	1.17	30.6	16.8
		23	41	18	2.25	1.44	32	19.1
		41	74	33	1.5	1.54	31.5	24.2
		74	165	91	0.25	1.57	34.1	25.9

The weather station utilized was changed from Caribou to the EPA's SAMSON weather extended dataset for Portland, Maine (for a comprehensive list of available US meteorological data assembled by EPA to support predictive exposure modeling see Burns et al., 2007). Two different depths to groundwater were simulated. A 1-m depth was chosen to reflect a highly conservative assumption, matching what is assumed by some regulatory agencies. In addition, simulations were run using a second aquifer water table depth of 4.57 m based on an evaluation of groundwater depths from the Maine Geological Survey Water Well Database groundwater database (Maine DACF, 2019). The depth of 4.57 m represents the median of 7,924 measurements taken across the state. Figure 11 shows on the left the standard Maine potato scenario PWC land inputs and the modified ones on the right. Notice the different weather file and the soil layer characteristics that in this example are mimicking Plaisted soil with groundwater table depth of 1 m. When the water table depth was increased to 4.57 m, the only modification was to increase the fourth soil horizon thickness to 3.93 m (0.36 m + 3.57 m).

Scenario ID: MEpotatoSTD

Weather File: C:\Models\Inputs\Metfiles\W14607.dvf

☐ Use Weather Directory ☐ Weather File Directory

Hydro Factors

0.8 PET Adjustment Factor Scenario Latitude (°N) 40

0.36 Snowmelt Factor (cm/°C/day)

12.5 Minimum Evaporation Depth (cm) Boundary Layer Thickness for Volatilization (cm) 5.0

Irrigation

☒ None Extra Water Fraction Allowed Depletion Max Rate (cm/day) Soil Irrigation Depth

☐ Over Canopy ☐ Root Zone

☐ Under Canopy ☐ User Specified (cm)

Soil Layers

Number of Horizons: 4 Update Horizons

Thick (cm)	ρ (g/cm³)	Max. Cap.	Min. Cap.	OC (%)	N
10	1.25	0.341	0.121	4.64	100
16	1.25	0.341	0.121	4.64	4
64	1.4	0.266	0.116	0.174	16
10	1.6	0.261	0.111	0.116	2

☐ Simulate Temperature

Scenario ID: MEpotatoSTD

Weather File: C:\Models\INPUTS\metfiles\W14764Extended.dvf

☐ Use Weather Directory ☐ Weather File Directory

Hydro Factors

0.8 PET Adjustment Factor Scenario Latitude (°N) 40

0.36 Snowmelt Factor (cm/°C/day)

12.5 Minimum Evaporation Depth (cm) Boundary Layer Thickness for Volatilization (cm) 5.0

Irrigation

☒ None Extra Water Fraction Allowed Depletion Max Rate (cm/day) Soil Irrigation Depth

☐ Over Canopy ☐ Root Zone

☐ Under Canopy ☐ User Specified (cm)

Soil Layers

Number of Horizons: 5 Update Horizons

Thick (cm)	ρ (g/cm³)	Max. Cap.	Min. Cap.	OC (%)	N
18	1	0.207	0.072	3.20	18
23	1.1	0.17	0.046	1.44	3
23	1.25	0.155	0.037	0.58	3
36	1.7	0.155	0.039	0.15	4
100	1.7	0.155	0.039	0.15	2

☐ Simulate Temperature

Figure 11. Modifications of PWC Land Inputs of the Maine Potato Surface Water Standard Scenario.

7.4. Crop inputs

Crop parameters were changed from potato to corn since this crop is most grown on Maine fields where biosolids are applied. PWC crop input modifications are shown in Figure 12. These corn-specific crop parameters were adopted from an EPA corn standard scenario used in surface water exposure assessments (PAcornSTD).

The screenshot displays the 'PWC Crop Inputs' interface, comparing parameters for a Potato scenario (top) and a Corn scenario (bottom). The interface is divided into two sections: 'Simple Crop Schedule' and 'More Complex Crop Schedules'. The 'More Complex Crop Schedules' section is active, indicated by a radio button. The 'Crop Cycles < 1 year' section is also active. The parameters are organized into columns: 'Crop Cycles Per Year', 'Emergence', 'Mature', 'Removal', 'Root Depth', 'Canopy' (Cover, Height, Holdup), 'Post-Removal Foliage' (Surface Applied, Removed, Left on Plant), 'Planting Periodicity', and 'Lag From Start'. The 'Update' button is visible below the 'Crop Cycles Per Year' input.

Crop Cycles Per Year	Emergence		Mature		Removal		Root Depth (cm)	Canopy			Post-Removal Foliage			Planting Periodicity (years)	Lag From Start (years)
	Day	Mon	Day	Mon	Day	Mon		Cover (%)	Height (cm)	Holdup (cm)	Surface Applied	Removed	Left on Plant		
1	1	6	1	10	5	10	60	40	30	0.1	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	1	0
1	1	6	1	9	1	10	90	100	300	0.25	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	1	0

Figure 12. Modifications of PWC Crop Inputs of Maine Potato Scenario from Potato (Top) to Corn (Bottom)

7.5. Runoff Inputs

For the refined Maine simulations, runoff curve numbers from the EPA Main Potato surface water scenario were modified and set to a very low NRCS curve number CN equal to 10. This runoff input modification maximizes leaching as is done for EPA's standard groundwater scenarios while all other parameters were left the same as those in the standard Maine potato surface water scenario.

7.6. Groundwater Scenario Simulation Results

PRZM was run for the multiple scenarios discussed above for both PFOA and PFOS. The example PRZM output shown in Figure 13 is for a scenario that considered PFOA with a minimum laboratory sorption coefficient, Maine environmental conditions with Plainsted soil and a water table depth of 1 m.

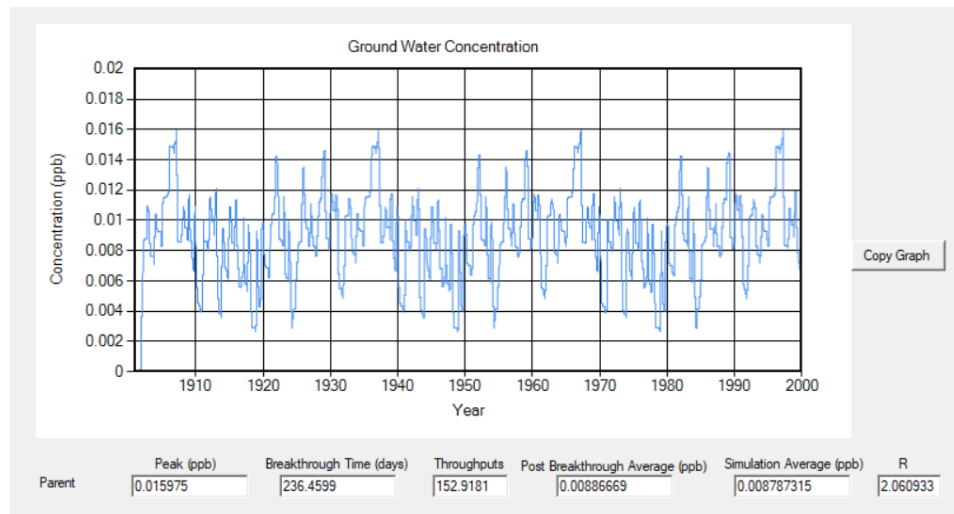


Figure 13. PWC Ground Water Concentration Outputs for PFOA Simulation Under Maine Environmental Conditions and a Groundwater Depth of 1 m

Of the five standard EPA groundwater scenarios considered, the Delmarva corn, the North Carolina cotton, and the Wisconsin corn were the most vulnerable to chemical leaching into the groundwater. For the other two screening level scenarios (Florida and Georgia), the levels of PFOA/PFOS in groundwater were lower. However, even under minimum laboratory measured sorption coefficients and the modeled typical biosolids application rates, the predicted post breakthrough average concentrations in groundwater were always well below 70 ppt (0.07 ppb), a recently used regulatory drinking water level of concern for PFOA and PFOS (see Table 4).

Table 4. PRZM Modeling Results for PFOS/PFOA for EPA Standard Groundwater Scenarios

PRZM-Scenario	ChemID	Kd (L/Kg)		Breakthrough Time (years)	Post Breakthrough Average (ppt)
Delmarva	PFOS	Lab-Minimum	1.95	45.8	21
FL potato	PFOS	Lab-Minimum	1.95	17.5	15
GA peanuts	PFOS	Lab-Minimum	1.95	34.0	10
NC_cotton	PFOS	Lab-Minimum	1.95	66.4	23
WI_corn	PFOS	Lab-Minimum	1.95	91.7	15
Delmarva	PFOA	Lab-Minimum	0.13	5.9	11
FL potato	PFOA	Lab-Minimum	0.13	2.3	7
GA peanuts	PFOA	Lab-Minimum	0.13	5.1	5
NC_cotton	PFOA	Lab-Minimum	0.13	9.5	15
WI_corn	PFOA	Lab-Minimum	0.13	12.0	13

Simulation results with Maine specific scenarios are reported for the same laboratory minimum K_d values (Table 5). Post breakthrough groundwater concentrations were also well below 70 ppt for all scenarios considered. When K_d is set to the field median, the leaching process becomes much slower for both PFOS and PFOA. For these cases, the PFOS groundwater concentration was very low and never reached complete breakthrough with 100 years of annual biosolids applications, regardless of the groundwater table depth. PFOA only reached complete breakthrough when the water table depth was a shallow 1 m but with lower concentrations (5-6 ppt for the post-breakthrough average).

Table 5. PRZM Modeling Results for PFOS/PFOA for Maine Groundwater Scenarios

PRZM-Scenario	Chem ID	Kd (L/Kg)		Breakthrough Time (years)	Post Breakthrough Average (ppt)
ME_Corn_Adams	PFOS	Lab-Minimum	1.95	5.0	17
ME_Corn_Caribou	PFOS	Lab-Minimum	1.95	6.7	22
ME_Corn_Plaisted	PFOS	Lab-Minimum	1.95	5.4	20
ME_Corn_Scantic	PFOS	Lab-Minimum	1.95	5.8	19
ME_Corn_Caribou	PFOS	Field-Median	83.18	> 100	N/A
ME_Corn_Scantic	PFOS	Field-Median	83.18	> 100	N/A
ME_Corn_Caribou – 4.57 m	PFOS	Field-Median	83.18	> 100	N/A
ME_Corn_Scantic – 4.57 m	PFOS	Field-Median	83.18	> 100	N/A
ME_Corn_Adams	PFOA	Lab-Minimum	0.13	0.5	7
ME_Corn_Caribou	PFOA	Lab-Minimum	0.13	1.0	11
ME_Corn_Plaisted	PFOA	Lab-Minimum	0.13	0.7	9
ME_Corn_Scantic	PFOA	Lab-Minimum	0.13	0.9	9
ME_Corn_Caribou	PFOA	Field-Median	14.45	45.6	6
ME_Corn_Scantic	PFOA	Field-Median	14.45	39.4	5
ME_Corn_Caribou – 4.57 m	PFOA	Field-Median	14.45	> 100	N/A
ME_Corn_Scantic – 4.57 m	PFOA	Field-Median	14.45	> 100	N/A

Assuming these simulation results for Maine are representative of the worst case leaching conditions in the State, the maximum application rates of PFAS that would lead to concentrations not exceeding a DWLOC can be calculated (Table 6).

Table 6. Example Calculations to Determine Maximum PFAS Application Rates and Maximum Allowable Initial PFAS Concentrations for a Given Biosolids Application Rate

	PWC Simulation Results		Screening Level Calculations for DWLOC = 70 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	314	44.83 (20 us ton/acre)	22	32
PFOS	108	22	4.91	344			35

The highest post breakthrough groundwater concentrations were from the Maine Caribou soil scenario for both PFOA and PFOS (11 ppt and 22 ppt, respectively). Using the modeled annual chemical application rates, the attenuation dilution factors $d = m_s/c_w$ are 4.48 mg/ha/ppt for PFOA and 4.91 for PFOS. By

multiplying these values by the DWLOC, the maximum chemical application rate is obtained. For example, if the DWLOC=70 ppt, PFOA applications should not exceed an annual applied mass rate m_s of 314 mg/ha (4.48 mg/ha/ppt multiplied by 70 ppt), while PFOS application rate should be below 344 mg/ha. With the modeled biosolids application rates (20 wet us tons/acre with 22% solid content), these mass rate limits correspond to initial maximum concentrations in biosolids of 32 ppt and 35 ppt for PFOA and PFOS, respectively (chemical mass rate/biosolids dry mass rate, e.g. for PFOS $344 \times 10^{-3} / (0.22 \times 44.83 \times 10^6) = 35$ ppb).

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).

With higher sorption assumptions, concentration limits would increase. For example, under sorption conditions based on a median of observed field values, the modeling suggests that higher concentrations of both PFOA and PFOS in biosolids would be possible without exceeding groundwater concentration limits. As expected, a higher portion of the chemicals will be sorbed to soil and thus less bioavailable as well as less dissolved into water available for leaching. In the case of PFOS, sorption based on the field median values resulted in almost zero leaching to groundwater. For PFOA, the dilution attenuation factor could increase up to 8.22 mg/ha/ppt, allowing yearly applications of 575 mg/ha of PFOA for a DWOLC equal to 70 ppt. These results show the importance of considering PFAS sorption property uncertainty when determining the maximum allowable PFAS concentrations in biosolids. The results also show the importance of the water table depth. If the water table depth is equal to the median depth from Maine wells (4.57 m), then no breakthrough was observed for both PFOA and PFOS in 100 years of annual biosolids applications.

As mentioned earlier, land application of biosolids typically do not occur every year because of other constraints, such as limitations on nutrient applications. The application schedule is quite important in estimating possible PFAS concentrations in the groundwater. This modeling framework can be used to assess the effect of alternative biosolids application practices. For example, if the same Maine Caribou scenario under the most conservative leaching assumption and same mass application rates considered above was run with biosolids applied once every 2 years instead of every year, then predicted post breakthrough concentrations of chemicals in groundwater would be reduced by approximately half. Therefore, the PFAS screening level in biosolids could be double the ones calculated previously and still result in concentrations not exceeding the DWOLC.

8. Comparison with Field Data

Several recent publications provide field-measured data that can be compared with the PRZM-simulated PFOA/PFOS groundwater concentrations. 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. The general framework for this comparison is to build PRZM simulations whose inputs describe as close as possible the observed characteristics of the real-world scenario. As discussed in earlier sections, the key PRZM inputs other than the chemical/physical properties of the chemicals in question, are:

- **Applications inputs.** It is important to obtain the PFAS application rates and frequencies as accurately as possible to reflect the field study conditions. Understanding the potential historical applications of residuals containing PFAS or other PFAS sources is also important. Attempting to make model comparisons to sites where the historical sources of PFAS are unknown is difficult.

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- **Background or initial PFAS concentrations.** If historical residuals or PFAS applications are unknown, background or initial PFAS concentrations in the soil are helpful when making model comparisons to field data. A low initial PFAS concentration in soil will be most suitable for comparisons with PRZM simulations based upon the screening level approach described in this document.
 - **Climate data.** Using the same or similar local weather of the monitoring site as input to the model will help in achieving a simulation representative of the field study conditions.
 - **Land and crop inputs.** Properly adjusting the soil properties and groundwater table depth to describe local conditions at the field site will improve the model parameterization and field site comparison.

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.

One study conducted by Gottschall et al. (2016) provides enough information to allow a semi-quantitative comparison with the example modeling. Gottschall et al. (2016) monitored groundwater and soil concentrations in an agricultural field after a one-time application of biosolids at a rate of approximately 9.8 dry tons/acre. Concentrations in biosolids were 1.6 ppb for PFOA and 7.2 ppb for PFOS. This is equivalent to 35 mg/ha and 158 mg/ha of PFOA and PFOS, respectively. Maximum observed groundwater concentrations at a 2 m depth during the one-year monitoring period were 1.5-3 ppt and 0-0.8 ppt for PFOA and PFOS, respectively. PFOA/PFOS were not detected at deeper groundwater depths. Weather data and soil information were not available. In an effort to model the Gottschall et al. (2016) field site experiment, a PRZM simulation was constructed by modifying the worst-case Maine Caribou soil and minimum K_d scenario, adjusted to have a 2-m groundwater depth. A one-time application of biosolids was made containing PFOA and PFOS mass according to the study data (35 mg/ha and 158 mg/ha of PFOA and PFOS, respectively). The background concentrations of PFOA and PFOS in the soil were very low (approximately 0.1 ng/g) and not accounted for in the model simulation. The results from these PRZM simulations showed peak concentrations of PFOA and PFOS of 4 ppt and 3 ppt, respectively. Without accounting for background PFOA/PFOS, the model predictions were 2.7 to 1.3 times higher than the monitoring data for PFOA and 3.8 times or greater for PFOS. Despite not having complete information about the Gottschall et al. (2016) field site and no effort made concerning site-specific calibration, the PRZM model scenarios and simulation results showed very reasonable agreement with groundwater concentrations observed in the field and are conservative compared to the field observations. This provides confidence that the results from the PRZM modeling approach presented here would be appropriate in assessing screening levels of PFAS chemicals in land applied biosolids that are protective of groundwater.

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

The SEasonal SOIL (SESOIL) compartment model linked to the Analytical Transient 1-, 2-, and 3-Dimensional Simulation of Waste Transport in the Aquifer System (AT123D) model (ESCI, 2014) 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.

The objective of this document is to provide regulators and modelers with a brief overview comparing the use of the SESOIL/AT123D and PRZM models to determine maximum levels of PFAS in land applied residuals that are protective of groundwater.

A description of the modeling framework of SESOIL/AT123D and its use in regulatory decision-making is provided. A discussion about the suitability of using SESOIL/AT123D to study possible leaching into the groundwater from land applied residuals as compared to the use of the PRZM modeling framework follows.

A.1. Brief Description of SESOIL/AT123D Modeling Approach

SESOIL is a one-dimensional vertical transport and fate model for the unsaturated (vadose) zone and produces a leachate concentration at the base of the modeled unsaturated zone (i.e., the concentration just on top of the aquifer).

Recent versions of SESOIL have been bundled with the AT123D model that simulates contaminant transport under one-dimensional groundwater flow. The bundled software is called SEVIEW (ESCI, 2014) and it includes other capabilities such as linkage between SESOIL parameters and another groundwater flow model, the U.S. Geological Survey modular finite-difference flow model (MODFLOW).

SESOIL input parameters include (a) the physical and chemical properties of the contaminant, (b) soil parameters describing the physical properties of the soil matrix, (c) climate parameters describing monthly air temperature, cloud cover, relative humidity, albedo, and rainfall to model the hydrologic cycle, (d) application parameters to describe the soil profile characteristics and contaminant load in the soil matrix, and (e) the source size parameters to set the dimensions of the contaminant release.

The model simulates the mechanisms of runoff, infiltration, evapotranspiration, and ground water recharge and the contaminant fate accounting for convective transport, volatilization, adsorption-desorption, chemical degradation-decay, biological transformation, hydrolysis, and photolysis. Contaminant transport downward is calculated via advection using the retardation factor.

When linked to SESOIL, the AT123D model takes the predicted contaminant concentration at the base of the vadose zone (just on top of the aquifer) and estimates how the contaminant plume in the groundwater migrates and affects Points of Compliance (Observation Wells).

SESOIL/AT123D has also been used for evaluating soil contamination from PFAS. While the models may be appropriate for developing site-specific IGW soil remediation standards and baseline soil cleanup objectives for certain pollutants, the SESOIL/AT123D modeling approach may not be as suitable for determining maximum levels of PFAS in land applied residuals that are protective of groundwater.

A.2. Comparison of SESOIL/AT123D and PRZM Approaches to Evaluating Potential Groundwater PFAS Contamination from Land Applied Residuals

Several aspects of SESOIL/AT123D make the simulation of soil contaminations from land applied residuals and the assessment of possible groundwater contamination challenging. Some issues are identified below and are compared to the PRZM approach. The objective here is not the characterization of how well the two models behave in predicting PFAS leaching to groundwater from land-applied residuals. Rather, the focus here is more about identifying general model framework features that may affect the modeling of leaching potential of contaminants initially present in land applied residuals:

- **Crop Simulation** - Land applied residuals are typically applied on agricultural land as soil amendment before crop planting. The presence of the crop in part of the year and its management practices such as irrigation may greatly affect the hydrologic cycle from evapotranspiration to infiltration. SESOIL does not consider crops at the surface. It might be possible for the modeler to modify the climate parameters to account for some of these effects, but this approach would not be very accurate or transparent. The PRZM model explicitly simulates specific crops (e.g., corn, hay) and their impact on the hydrology of the applied field, including runoff, infiltrations, evaporation, and erosion. PRZM can also be parameterized to reflect field management practice, including irrigation and conservation tillage, which can further influence the hydrology. Thus, PRZM will better represent the off-site and vertical transport of PFAS from a surface application.
- **Time step** – SESOIL runs on a monthly time step. While the effect on longer term groundwater concentration averages may not be as significant, simulation on a daily time step, such as in PRZM, better accounts for weather dynamics and the time required for contaminant breakthrough to groundwater.
- **Contaminant Load, Placement, and Timing** – As mentioned above, SESOIL is generally employed to develop site-specific IGW soil remediation standards and baseline soil cleanup objectives by assuming an initial soil matrix with a specified contaminant concentration.

Perhaps because of its typical use, efforts that have employed SESOIL to determine maximum allowable initial contaminant concentration in residuals have relied on model frameworks used for developing baseline soil cleanup objectives which are established under worst case conditions with respect to the potential for groundwater contamination. These approaches generally assume a soil profile with an initial contaminated zone that may span several feet of depth. These initial soil contamination conditions may be overly conservative when considering land applied residuals where, under typical application practices (i.e., sprayed liquid slurry at a rate of 10-20 wet ton/acre with 10%-20% dry solid content), the depth of the deposited residuals on the field surface is significantly smaller.

Another conservative assumption used for soil remediation, and in some applications of SESOIL/AT123D for PFAS, is that the initial modeled contaminated soil is assumed to sit just above the aquifer boundary. While some PFAS chemicals have relatively low soil sorption capacity, and a higher propensity to dissolve in water, the soil matrix between the surface and the aquifer can still retain some of the chemicals and make them less subject to migration into the groundwater. PRZM applications of contaminants in land applied residuals are introduced to the soil matrix at the land surface (with options for soils incorporation), as occurs in reality with a land application to an agricultural field. This provides a conceptually more accurate description of how chemicals within the residuals enter the environment.

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. Although not typically used, SESOIL can mimic up to 10 years of successive contaminant loads on the top soil layer with

desired rates and timing. The contaminant loads entered in the final year are used for all subsequent years. Therefore, one can model residual applications occurring every year by entering only one year of contaminant load; the second year uses the inputs of the first year and so on. However, if one is interested in more complicated application patterns, such as often occur with land applied residuals because of other management criteria (e.g., nutrient input targets), for example applications occurring every other year, these can be modeled for the first 10 years and after that the contaminant load is either zero or constant, (i.e., equal to that entered for the last year). In comparison, PRZM is quite flexible in describing the actual application practice and it is straightforward to implement for the entire period of the simulation.

- **Surface water contamination / Plant uptake** – These fate pathways are often conservatively not considered when studying potential groundwater contamination (less chemical would be available for leaching if they were accounted for) and therefore less noteworthy in this context. However, they could be important when one is interested in other possible PFAS exposure pathways. In SESOIL, it is not possible to consider these processes. In contrast, PRZM has the capability of simulating chemical uptake by plants although the modeling of this component in PRZM is relatively simplistic. In addition, PFAS concentrations in surface receiving waters resulting from residuals applications could be examined using PRZM and VVWM (both contained in PWC). Therefore, PRZM could model PFAS fate and transport to the three PFAS potential contamination pathways, leaching, surface water runoff, and plant uptake while automatically accounting for the chemical mass balance in just one consistent modeling framework.

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