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

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Presentation Overview

Motivation and Objectives

Modeling Approach

Modeling Agriculturally Applied Biosolids in Maine

Analysis of PFAS Biosolids Application Rates and Concentrations

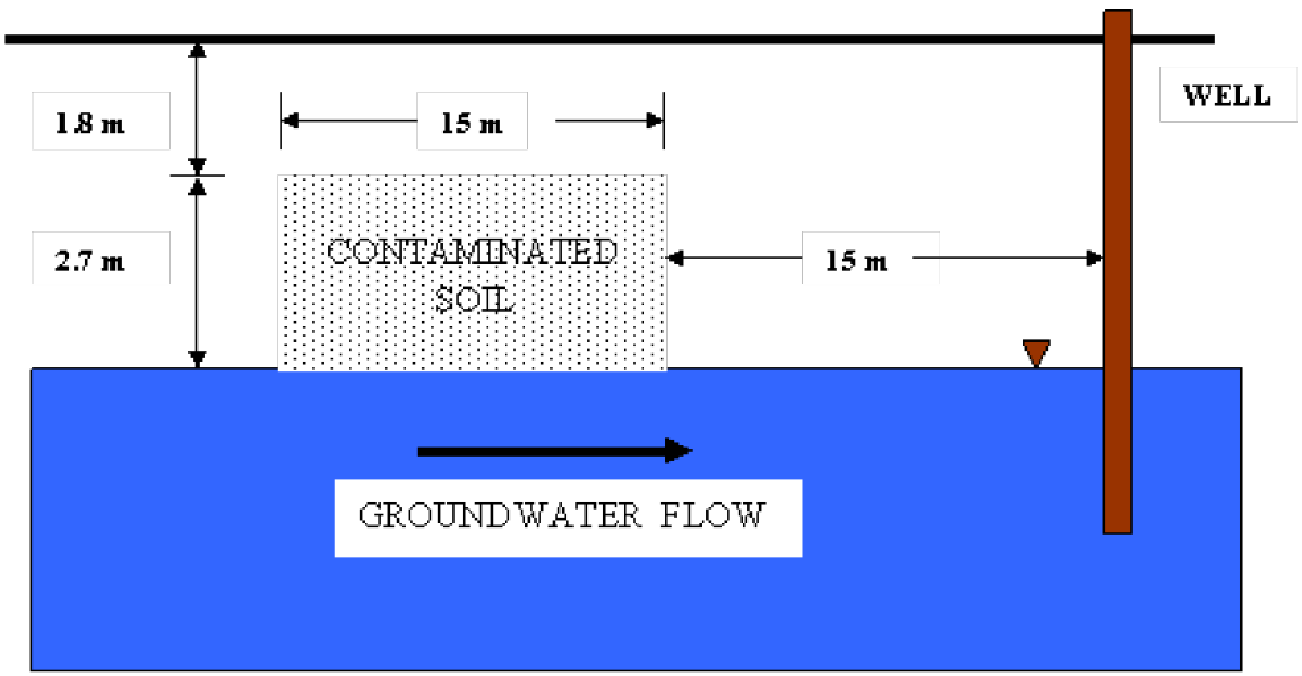
Preliminary Comparisons with Observed Field Data

Summary and Conclusions

Motivation and Objectives

The current biosolids screening level concentrations for PFOA and PFOS (in Maine) of 2.5 ppb and 5.2 ppb were derived from a conceptual model (SESOIL/AT123D) designed for Underground Storage Tank chemical releases and does not realistically reflect land applied biosolids.

- Input of chemical occurs well below soil surface
- Chemical release point is directly above the water table
- Soil properties are not reflective of near surface conditions



SESOIL Conceptual Model

Motivation and Objectives

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 biosolids?
- Does the modeling approach predict groundwater PFOA/PFOS concentrations supported by measurements from field studies?

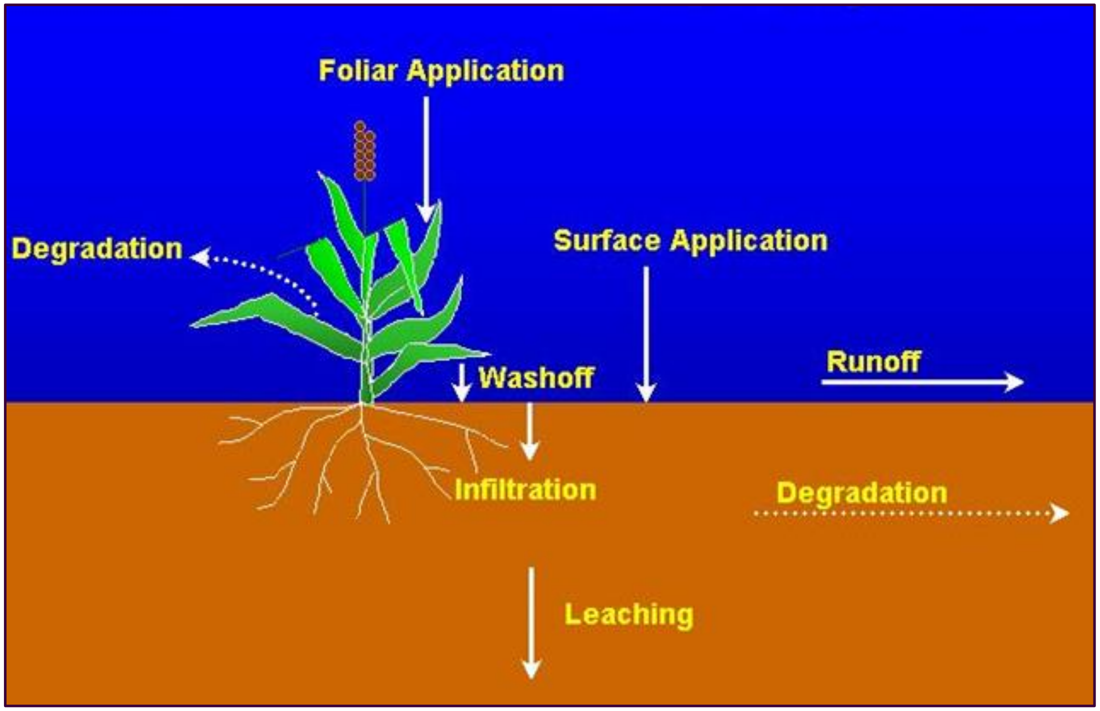
Objectives:

- Apply the US EPA's Pesticide Root Zone Model (PRZM) to simulate land applications of biosolids to agricultural fields in Maine
- Predict PFOA/PFOS concentrations in shallow groundwater based on a range of published sorption properties (K_{oc}/K_d)
- Based on conservative screening level assumptions, determine biosolids concentration/application rate limits to achieve groundwater protection goals
- Determine if the modeling approach warrants further development and application in PFAS regulatory modeling

Modeling Approach: EPA's Pesticide Root Zone Model

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

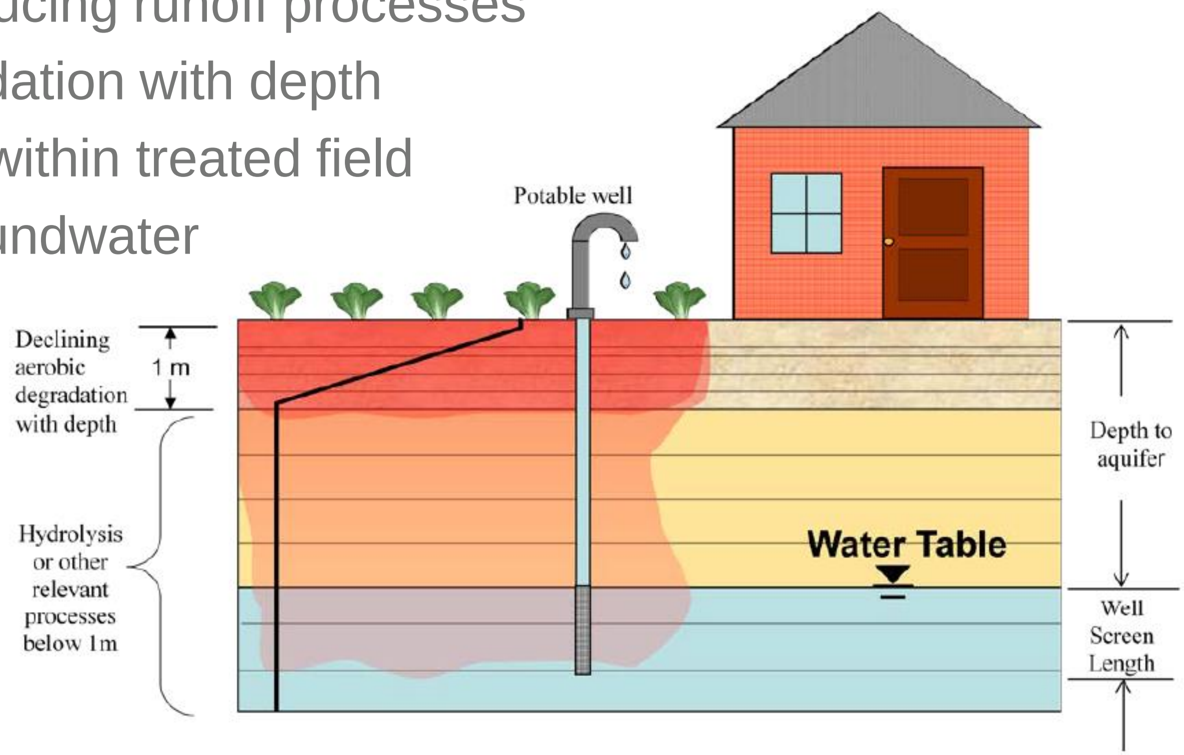
Modeling Approach: PRZM Groundwater Exposure Scenarios

The US EPA and Canada's PMRA (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.



Modeling Approach: Application of PRZM Groundwater Scenarios for PFAS Biosolids Applications

Biosolids applications containing PFAS chemicals to agricultural fields are analogous to pesticide applications to agricultural fields.

Information required for each PFAS chemical includes:

- Application rate (mass/unit area)
  - Tons/acre of biosolids
  - Concentration of PFAS in biosolids
- Application timing (date)
- Application frequency (once per year, twice per year, once every other year)
- Application method (surface, incorporated, incorporation depth)
- Degradation rates
- Sorption (K_d or K_{oc})

Hydrology and crop-related inputs for a PFAS leaching simulation are the same as pesticide leaching simulation.

Modeling Approach: PFOA and PFOS Model Inputs

Chemical Applications:

- Annual biosolids application rate of 10 to 20 wet tons/acre
- Dry matter content of 22%
- PFOA biosolids concentration of 5 ng/g (ppb)
- PFOS biosolids concentration of 11 ng/g (ppb)
- Incorporated 6 inches within the soil
- Applied before corn planting in spring, applied every year

Environmental Fate:

- Soil aerobic degradation: STABLE
- Hydrolysis: STABLE
- Sorption: Based on recent literature review (Li et al. (2018)), looked at lower end of published values (laboratory minimum to field median)
  - PFOA: 0.13 to 14.45 L/kg
  - PFOS: 1.95 to 83.18 L/kg

Modeling Results: EPA "Standard" Groundwater Leaching Scenarios

Scenarios represent high vulnerability leaching sites nationally and are used for national regulatory decisions:

- Sites in Delmarva, FL, GA, NC, WI
- Depth to water table ranging from 3 to 9 meters

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

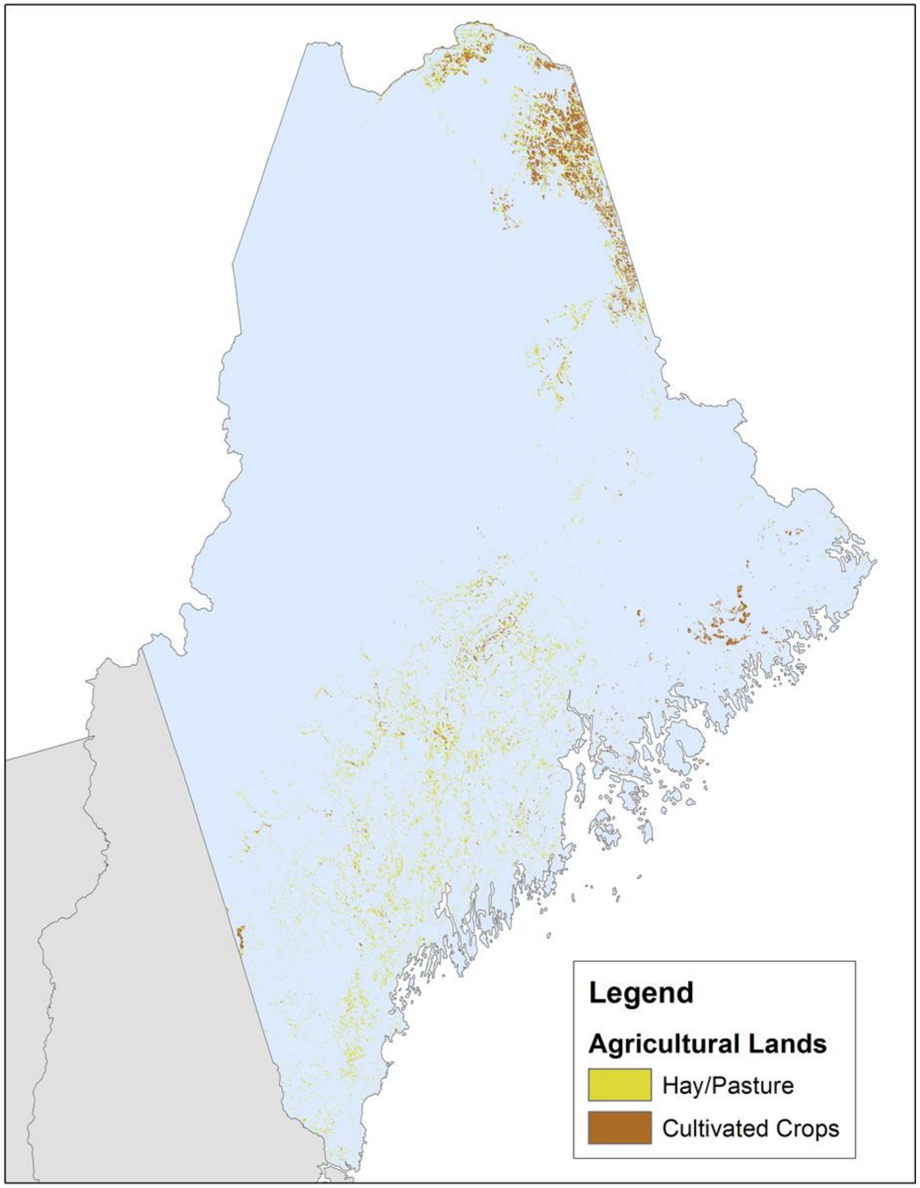
	Peak Conc. (ppt)		Post-Breakthrough Avg. Conc. (ppt)	
Chemical	**Min**	**Max**	**Min**	**Max**
PFOA	7	20	5	15
PFOS	11	30	10	23

Summary of PRZM Standard Scenario Results

Modeling Results: 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



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

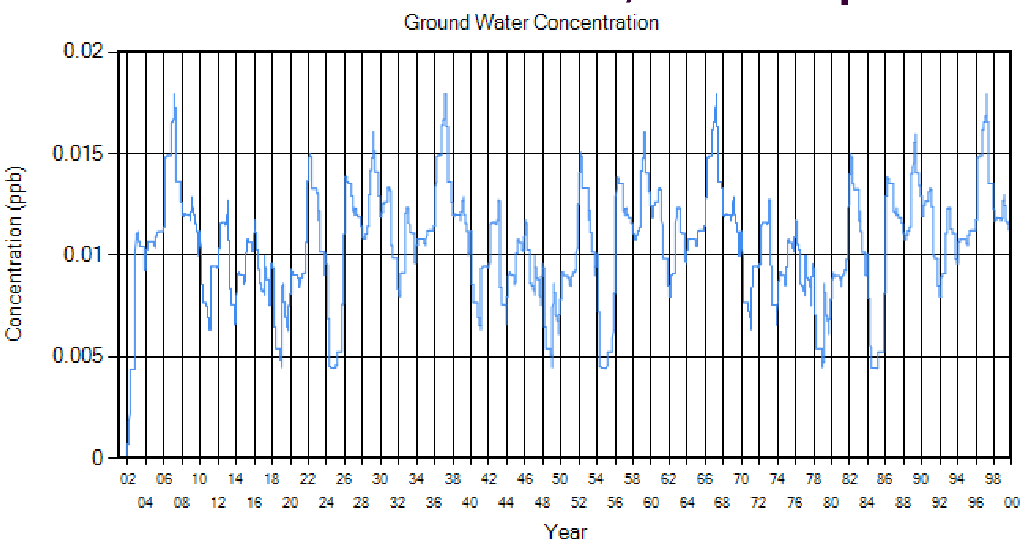
Modeling Results: Maine Leaching Scenarios, Variability Based on Sorption Variability/Uncertainty

Based on the recent Li et al. (2018) publication, reported sorption for PFOA and PFOS has shown relatively high variability.

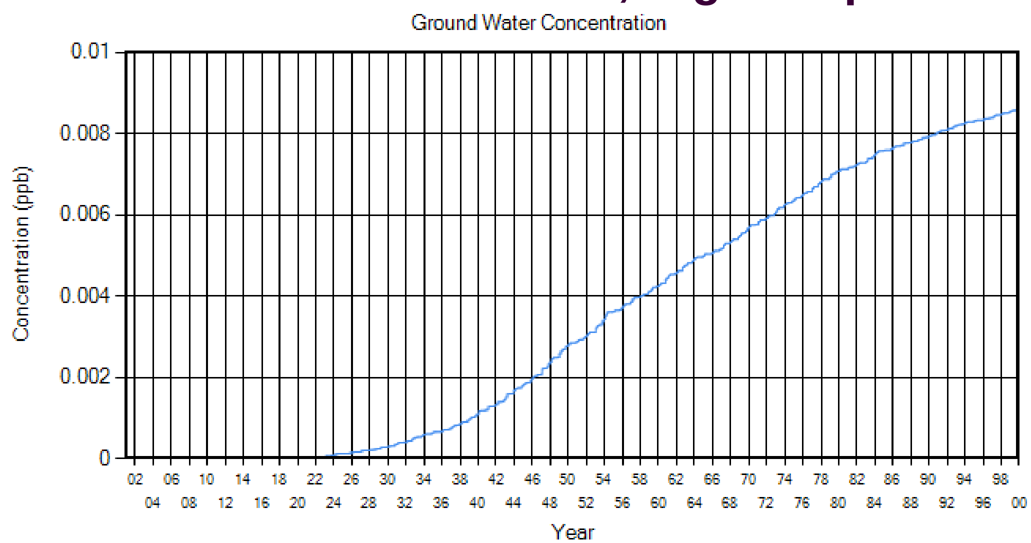
- When sorption is low, retention in the soil is less and leaching to groundwater is increased and is more rapid
- When sorption is high, retention in the soil is high and leaching to groundwater can slow considerably

Given observations of PFOA/PFOS residues in soil, it is expected that sorption greater than laboratory minimum is more realistic.

PFOA Concentration, Low Sorption



PFOA Concentration, High Sorption



Biosolids Application Rate and Concentration Limits: Balancing Mass Loads to Protect Groundwater

The annual and long-term loading rate of PFOA/PFOS from land applied biosolids will determine the potential concentrations in groundwater. This requires management of both:

- Biosolids application rates (tons/acre)
- PFAS concentrations in biosolids

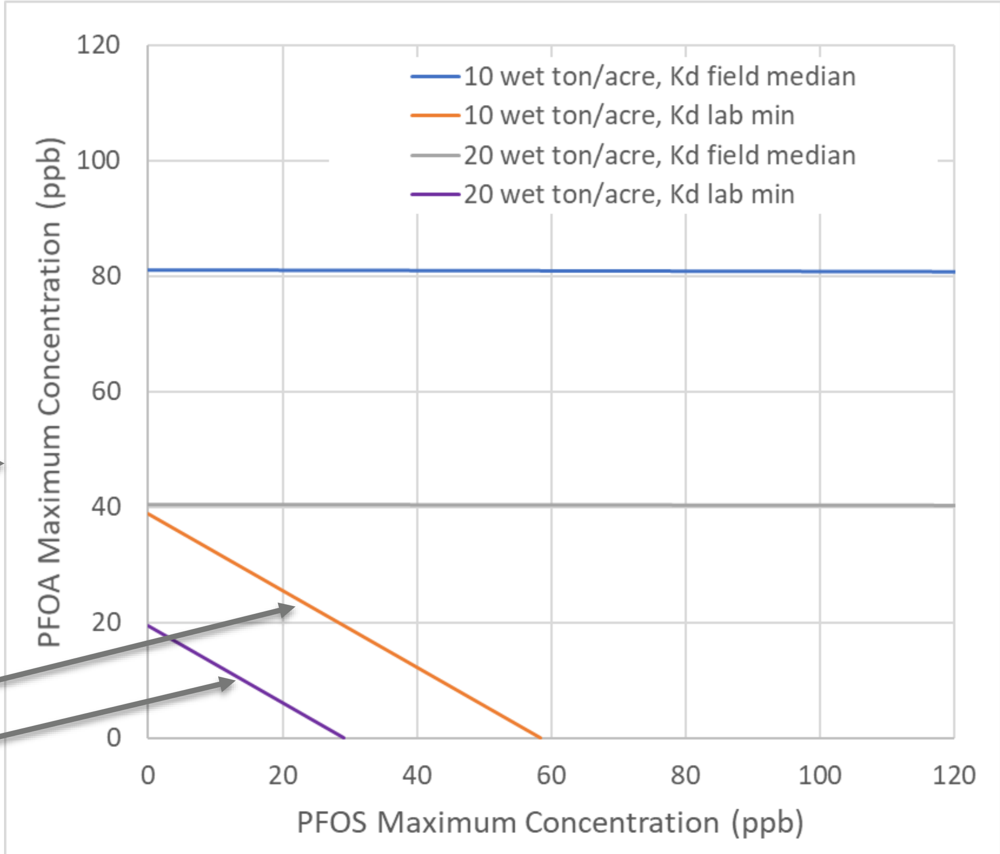
Given a high (20 ton/acre) rate, PFOA+PFOS concentrations below 19 – 29 ppb would limit peak groundwater concentrations to 70 ppt.

PFAS Concentrations and Biosolids Application Rates Required to Keep Peak PFOA+PFOS groundwater conc. below 70 ppt.

Worst case sorption scenarios:

Low biosolids rate

High biosolids rate

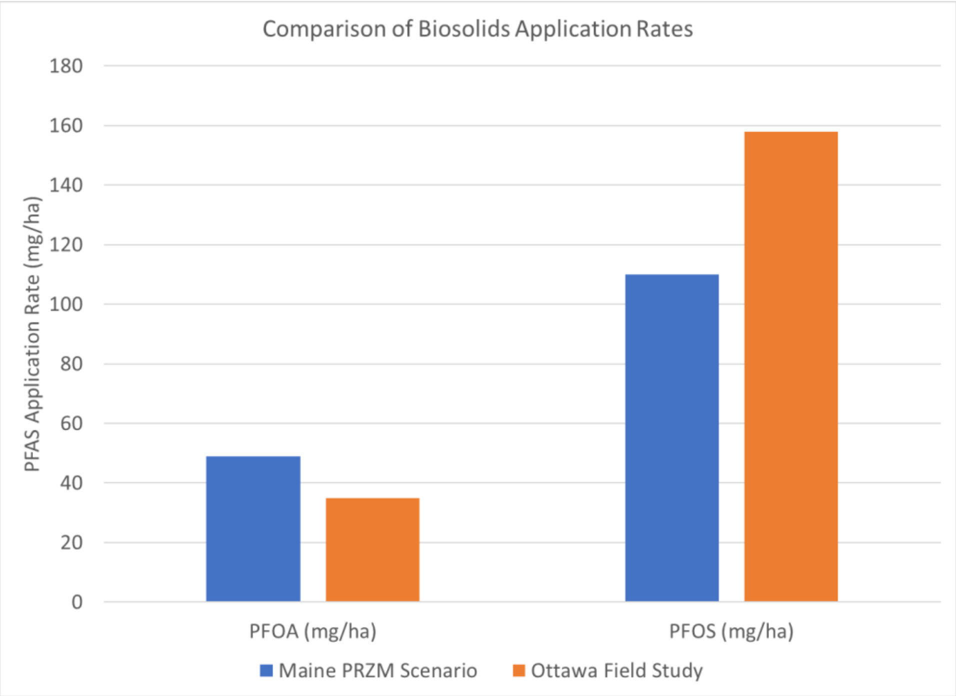


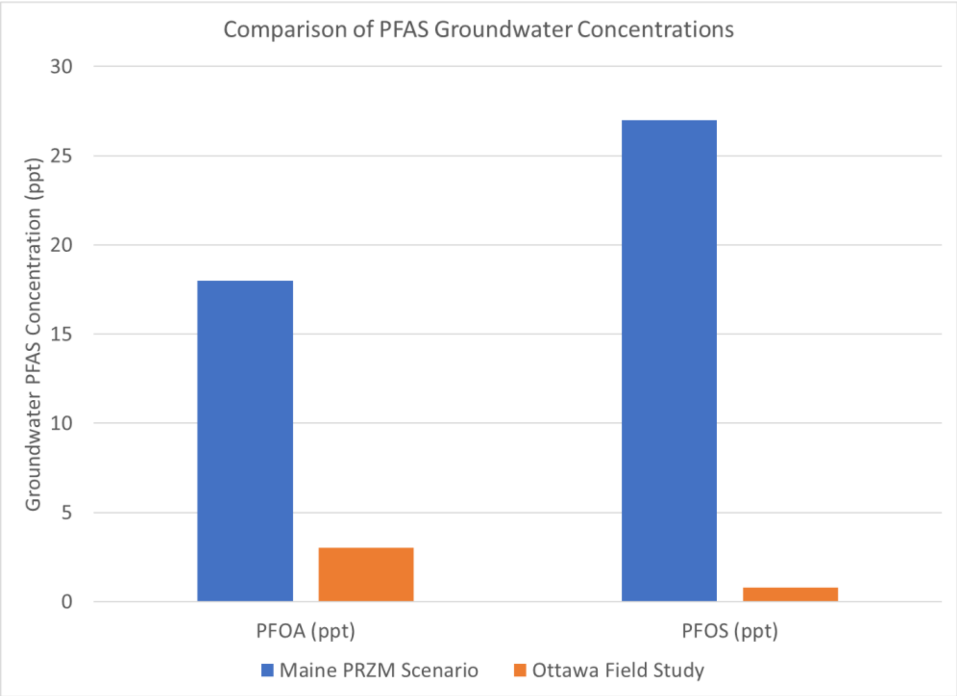
Preliminary Comparisons of PRZM Simulation with Observed Field Data

Gottschall et al (2017) reported on a land application of biosolids made to an agricultural field in Ottawa Ontario (orange bars, 1-year totals).

The biosolids application rate and concentrations of PFOA and PFOS in the biosolids were comparable to typical Maine rates and concentrations.

The Maine PRZM scenario simulation (blue bars, 100-yr. totals) predicted PFAS concentrations in groundwater 6 to 12 times higher than concentrations observed in Ottawa field study. (Not really valid comparison because of time difference.)





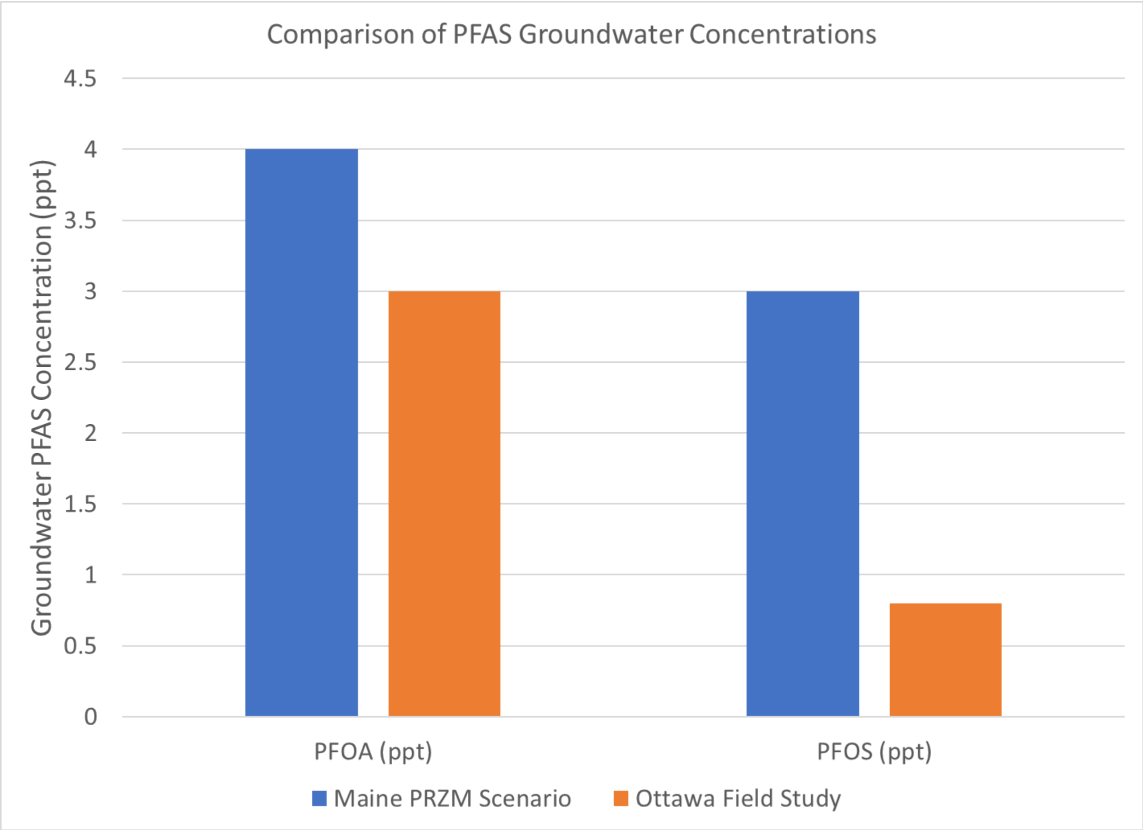
Preliminary Comparisons with Observed Field Data, Modified PRZM Scenario

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

- Only one biosolids application
- Identical PFOA/PFOS application rates
- 2-meter 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.



Uncertainties

Factors Leading to Potentially Lower Groundwater Concentrations:

- The PRZM model scenarios shown are based on maximizing infiltration and recharge. Additional investigation to better account for surface runoff loses may refine predictions in groundwater.
- The screening-level modeling approach shown does not account for lateral groundwater flow or well setbacks from untreated areas.
- Potential plant uptake is not simulated and would reduce chemical available for leaching.
- PFAS concentrations in groundwater vary over time due to dynamics of recharge events. Long-term average PFAS concentration are likely a better end point for chronic exposure concerns than instantaneous peaks.

Factors Leading to Potentially Higher Groundwater Concentrations:

- Potential macro-pore or rock-fracture flow is not simulated in PRZM.
- Other PFAS sources are not accounted for (e.g., deposition)

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 biosolids to groundwater.

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.

Our simulations suggest that, even under "worst-case" leaching conditions, high biosolids applications rates, and every year applications, the combined PFOA/PFOS concentrations in biosolids would need to exceed 19 to 29 ppb to result in peak groundwater concentrations exceeding 70 ppt.

References

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

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

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

Thank You

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