STONE ENVIRONMENTAL

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August 6, 2019

MEMO

To: Ned Beecher

From: Mike Winchell, Marco Propato

Stone Project No. 19-052
Subject: Status Update on Biosolids PFOA/PFOS Modeling

This memo provides updates on the evaluation of modeling conducted by the Maine Department of Environmental Protection (DEP) to derive concentration limits of PFOA and PFOS in land applied biosolids and on the alternative PFOA/PFOS fate and transport modeling being conducted. The update on the evaluation of Maine DEP modeling focuses on understanding the methods and assumptions followed in arriving at maximum biosolids PFOA/PFOS concentrations of 2.5 ppb and 5.2 ppb respectively. The update on the alternative fate and transport modeling provides an overview of results from screening level leaching scenarios generated using EPA's Pesticide Root Zone Model (PRZM) and results from some initial refinements more representative of Maine conditions, including some comparisons with monitoring data.

Evaluation of Maine DEP PFOA/PFOS Modeling

Maine DEP applied a combination of tools to derive PFOA/PFOS biosolids concentration screening levels under the Maine Solid Waste Management Rules (ME DEP, 2018, chapter 418). The approach included use of the Regional Screening Levels (RSL) calculator (USEPA, 2019) and a leaching to groundwater model used by DEP for petroleum contaminated sites in Maine (ME DEP, 2014).

First, the RSL calculator was used to derive risk-based screening levels for a residential tap water exposure scenario with 0.5 as hazard and $5x10^{-6}$ as target risk (a target risk set to $1x10^{-6}$gives an identical result). Other than adjusting the risk levels to meet the Maine Solid Waste Management Rules risk standard described above, no other default RSL values were modified as the USEPA default exposure factors for a residential tap water scenario are considered representative for tap water exposure in Maine. For both PFOA and PFOS the screening levels determined by the RSL calculator are 0.201 μg/L (ppb).

The final biosolids screening levels for PFOA and PFOS were derived using a leaching model approach, SESOIL and AT123D models, that DEP has previously used to develop leaching to groundwater soil screening levels for their Remedial Action Guidelines (RAG). For consistency with the RSL approach, the DEP used USEPA RSL chemical-specific parameter information, such as K_{oc}, diffusivity in water, and Henry's Law constants in their leaching to groundwater modeling. This leaching to groundwater modeling produced chemical-specific dilution attenuation factors (DAF), 12.50 L/Kg for PFOA and 25.94 L/Kg for

PFOS. The DAF was then multiplied by the RSL-derived residential tap water screening level to calculate the screening level for the leaching to groundwater pathway, resulting in 2.5 ppb for PFOA and 5.2 ppb for PFOS.

One of the main concerns regarding the approach taken by ME DEP is that the leaching model used has been in general applied to study the possible leaching from underground oil storage facilities and other discharges of oil. To our knowledge, it has not been demonstrated that this model is appropriate in a different context. The conceptual model for the SESOIL/AT123D model assumed that a volume of contaminated soils is released immediately above a shallow water table. The chemical then enters the shallow groundwater aquifer through leaching occurring from recharge to the aquifer. The soil matrix into which the chemical is released has properties similar to those found several meters below the soil surface, including a sand and gravel texture and very low organic matter. This conceptual model is very different than how PFOA/PFOS may enter groundwater from land applied biosolids; thus, the results and conclusions from the ME DEP are unlikely to reasonably represent PFOA/PFOS leaching potential from biosolids-applied soils.

Biosolids are most commonly applied to agricultural landscapes to provide necessary nutrients to a crop. When applied to cultivated cropland (e.g., corn) the biosolids are mixed into the surface soil matrix (roughly the top six inches) through tillage operations. The chemicals found in the biosolids have the potential to leave the application site via plant update through transpiration, via surface runoff and erosion during higher intensity rainfall events, or leach through the soil profile during infiltration of rainfall and snowmelt. The primary impediment to off-site transport of PFOA/PFOS in biosolids is sorption to the higher organic matter content of biosolids and soils in the upper layers of the profile. A modeling approach capable of more accurately representing this concept is required to enable a more accurate assessment of maximum biosolids PFOA/PFOS concentrations to meet tap water protection goals.

Alternative PFOA/PFOS Modeling

Modeling Approach

We have conducted initial screening level modeling of PFOA and PFOS leaching to groundwater using US EPA's Pesticide Root Zone Model (Young and Fry, 2016). The 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., 2012). Their 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. Thus, all transport is vertical from the land surface to the water table, making it a conservative screening level conceptual model. The processes that determine the rate and magnitude of chemical leaching to groundwater include sorption to soil, soil aerobic degradation, 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), with no aerobic degradation 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.

The EPA has defined six screening level groundwater exposure scenarios that reflect very high vulnerability leaching conditions and are assumed to be representative of all high vulnerability locations across the U. S. These scenarios 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. 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.

In this current PFOA/PFOS modeling effort, refinement of the EPA's standard groundwater scenarios was conducted to better represent Maine soils and weather, as well as regulatory and typical groundwater depths. 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 1) 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 1). The crop for these simulations was parameterized to represent corn, which typically has higher biosolids application rates than grassland. The EPA's SAMSON weather dataset for Portland, Maine was used in each of the scenarios. Two different depths to groundwater were simulated. A 1-m depth was conservatively chosen to reflect EPA's regulatory depth based on the Part 503 rules. In addition, a second depth of 4.57 m was chosen 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.

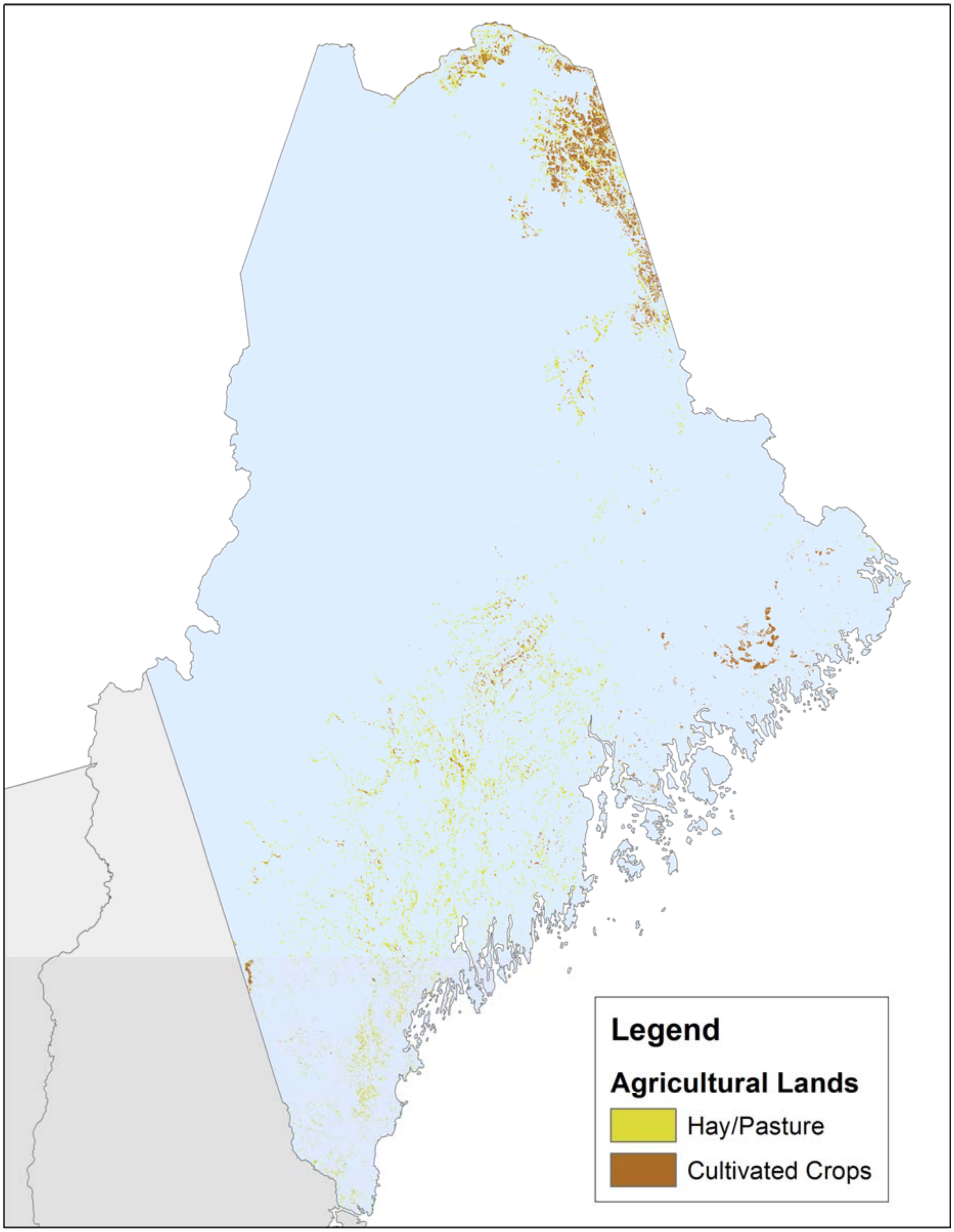

Figure 1. Agricultural lands in Maine from 2016 NLCD. Soils underlaying these areas were used to represent typical soils for purpose of leaching modeling.

Soil Name	Hydrologic Group	Top Depth (cm)	Bottom Depth (cm)	Thickness (cm)	OM (%)	Bulk Density (g/cm3)	Field Capacity (%)	Wilting Point (%)
Adams	A	0	18	18	3.5	1.15	14.8	5.7
Adams		18	54	36	2	1.25	10.3	3.9
Adams		54	69	15	1	1.35	8.2	2.3
Adams		69	165	96	0.25	1.4	5.2	0.9
Caribou	B	0	18	18	5.5	1.13	27.6	8.3
Caribou		18	48	30	3.25	1.25	36.7	11.8
Caribou		48	152	104	0.5	1.48	21.8	9.3
Plaisted	C	0	18	18	5.5	1	20.7	7.2
Plaisted		18	41	23	2.5	1.1	17	4.6
Plaisted		41	64	23	1	1.25	15.5	3.7
Plaisted		64	165	101	0.25	1.7	15.5	3.9
Scantic	D	0	23	23	6	1.17	30.6	16.8
Scantic		23	41	18	2.25	1.44	32	19.1
Scantic		41	74	33	1.5	1.54	31.5	24.2
Scantic		74	165	91	0.25	1.57	34.1	25.9

Table 1. Soil properties for Maine agricultural soils selected for modeling.

Model Inputs

Several input parameters need to be determined to model the potential fate and transport of PFOA/PFOS from land-applied biosolids to groundwater via leaching from the soil surface. As these processes may be sensitive to the choice of these parameters, it is also important to investigate the possible range of realistic values that characterize the chemical-physical properties of PFOA and PFOS.

A key parameter affecting this process is the soil adsorption coefficient K_d that measures the propensity of the chemical substance to stay sorbed onto soil or dissolved in water. Published data about the sorption of PFAS provides a wide range of measured values for K_d as well as significant differences between analyzed data from laboratory and field samples. The variability of published K_d values for PFOA and PFOS compiled in a recent publication (Li et al., 2018) and a few percentiles for the available published data are reported in Table 2 below.

log K_d (log L/kg)						
	Field/Lab	**Min**	**25th**	**Median**	**75th**	**Max**
PFOS	Field	1	1.58	1.92	2.41	3.52
	Lab	0.29	0.89	1.2	1.39	2.36
PFOA	Field	-0.15	0.65	1.16	1.76	2.86
	Lab	-0.89	-0.17	0.30	0.69	1.95

Table 2. PFOS and PFOA sorption distributions (logKd).

In order to be conservative, the initial simulations considered were run with K_d values set equal to the laboratory minimum measured values provided by the literature. Under this condition, the propensity for the chemicals to be mobile is maximized, therefore the use of these values represents the worst possible cases. In order to understand better the effects of different K_d on expected groundwater concentrations, some results presented below assumed field median K_d values, which may be more reflective of actual conditions in Maine agricultural settings. We will note that the PRZM model can also parameterize the sorption processes using a K_{oc} value, in which case the sorption throughout the soil is dependent upon the organic carbon content. 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, and presented their sorption summary statistics in terms of K_d. In choosing the use of the minimum laboratory K_d for this modeling exercise, we have captured the worst-case leaching potential conditions, and groundwater concentration simulations based on a preliminary review of published K_{oc} sorption fall within the groundwater concentration range simulated using the K_d.

In general, PFAS are very persistent with limited degradation expected. Venkatesan and Halden (2014) measured soil half-life of about 500 days for PFOA and more than 1,000 days for PFOS. However, they noticed that "the term half-life used here does not imply degradation of PFAS (…) but the loss of these compounds observed in their study most likely may include potential leaching, plant uptake, volatilization from soil, or a combination of these". Due to this uncertainty in soil aerobic degradation, a conservative assumption of zero degradation was assumed for the screening level simulations conducted in this analysis.

The other chemical physical parameters used for these simulations running the PRZM model through EPA's PWC interface (Young, 2016) are from USEPA (USEPA 2106a, and USEPA 2016b) and summarized in the Table 3 below (note that half-life values of "0" indicate no degradation via that process):

Parameter		PFOS	PFOA
K_d (L/Kg)	Lab minimum	1.95	0.13
	Field median	83.18	14.45
Hydrolysis Half-life (days)		0	0
Surface Soil Half-life (days)		0	0
Soil Reference Temperature (°C)		25	25
Foliar Degradation Half-life (days)		0	0
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

Table 3. Environmental fate properties for PFOS and PFOA used in current modeling.

To mimic a typical biosolids application, these simulations consider applications with the following characteristics (a) once per year one week before planting, (b) a high rate of biosolids application rate - 20 wet tons/acre, solid content 22%, (c) median content of chemicals - 5 ng/g (ppb) for PFOA and 11 ng/g (ppb) for PFOS on a dry weight basis, and (d) biosolids assumed deposited on the surface and integrated into the first 6 inches of soil (linearly decreasing concentration with depth). These inputs are representative of typical biosolids characteristics reported by NEBRA based upon practices commonly utilized in Maine and biosolids produced in Maine. With these application rate characteristics, typical annual PFOA/PFOS applications rates are 49 mg/ha for PFOA and 110 mg/ha for PFOS.

Model Scenarios

We chose to initially model PFOA and PFOS 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). For both PFOA and PFOS, we ran simulations assuming the most conservative sorption coefficients (K_d) based on the minimum lab measured value. The model simulations were run for 100 consecutive years and assumed biosolids applications occurred every year. This is a very conservative assumption because, in order to meet crop nitrogen requirements, real world biosolids application rates generally decrease over the first few years after implementation of a land application program and PFOA and PFOS concentrations in biosolids have been slowly decreasing over the last decade. Ten screening level scenarios were run in total (five scenarios, two chemicals, one K_d assumption).

We subsequently ran several additional PRZM scenarios that were modified to represent Maine soils, weather, and relevant groundwater depths. These scenarios were derived from the EPA's Maine Potato standard surface water PRZM scenarios. The weather station utilized was changed from Caribou to Portland Maine and the crop parameters used were changed from potato to corn. Runoff curve numbers were set to a very low value (10) to maximize leaching as is done for EPA's standard groundwater scenarios. Four different scenarios were developed, one for each soil hydrologic group. Scenarios were run assuming both a very shallow groundwater table of 1 meter and a more typical depth to groundwater of 4.57 meters. In addition to the most conservative assumption for sorption based on the minimum laboratory K_d, we ran simulations assuming more typical sorption based on the median of field-derived values.

PRZM scenarios were also created to better understand the broader sensitivity of estimated PFOA/PFOS concentration limits in biosolids to sorption variability (K_d) in order to keep groundwater concentrations below regulatory maximums. Additional simulations were conducted to understand how biosolids application rates and biosolids concentrations of PFOA/PFOS combine to allow groundwater concentration limits to be met.

Results and Discussion

Groundwater Scenario Simulation Results

Of the five standard EPA groundwater scenarios considered, the Delmarva corn field, the North Carolina cotton field, and the Wisconsin corn field are the most vulnerable to chemical leaching into the groundwater. However, under minimum laboratory measured sorption coefficients and the modeled biosolids application rates, the predicted concentrations in groundwater are always well below 70 ppt (0.07 ppb), the current recommendation proposed by EPA for groundwater that is a current or potential source of drinking water (see Table 4). For the other 2 screening level scenarios (Florida and Georgia), the levels of PFOA/PFOS in groundwater are lower. Note that in these simulations, the application rate of PFOS (110 mg/ha) is more than twice the application rate of PFOA (49 mg/ha).

PRZM-Scenario	ChemID	Kd (L/Kg)		Peak (ppt)	Breakthrough Time (years)	Post Breakthrough Average (ppt)
Delmarva	PFOS	Lab-Minimum	1.95	26	45.8	21
FL potato	PFOS	Lab-Minimum	1.95	17	17.5	15
GA peanuts	PFOS	Lab-Minimum	1.95	11	34.0	10
NC_cotton	PFOS	Lab-Minimum	1.95	30	66.4	23
WI_corn	PFOS	Lab-Minimum	1.95	17	91.7	15
Delmarva	PFOA	Lab-Minimum	0.13	15	5.9	11
FL potato	PFOA	Lab-Minimum	0.13	10	2.3	7
GA peanuts	PFOA	Lab-Minimum	0.13	7	5.1	5
NC_cotton	PFOA	Lab-Minimum	0.13	20	9.5	15
WI_corn	PFOA	Lab-Minimum	0.13	16	12.0	13

Table 4. PRZM modeling results for PFOS/PFOA for EPA standard groundwater scenarios.

For the simulations with Maine specific soils, a corn crop, and a shallow 1 m groundwater table depth, simulation results are reported for the same laboratory minimum K_d values (Table 5). In addition, a set of simulations were run to study the differences in groundwater concentration when K_d values were set to the literature field median for soils. These scenarios produce the "worst" and "typical" case groundwater PFOA/PFOS concentrations identified with K_d minimum; and when, in addition to K_d equal to field median, the groundwater table was lowered to 4.57 m, the median water table depth in Maine.

For this series of Maine-specific simulations, peak ground-water concentrations are well below 70 ppt for all scenarios considered (see Table 5). 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 is very low and never reaches complete breakthrough with 100 years of annual biosolids applications, regardless of the groundwater table depth. PFOA only reaches complete breakthrough when the water table depth is a shallow 1m but with lower concentrations (5 ppt to 6 ppt for the post-breakthrough average).

PRZM-Scenario	ChemID	Kd (L/Kg)		Peak (ppt)	Breakthrough Time (years)	Post Breakthrough Average (ppt)
ME_Corn_Adams	PFOS	Lab-Minimum	1.95	21	5.0	17
ME_Corn_Caribou	PFOS	Lab-Minimum	1.95	27	6.7	22
ME_Corn_Plaisted	PFOS	Lab-Minimum	1.95	23	5.4	20
ME_Corn_Scantic	PFOS	Lab-Minimum	1.95	23	5.8	19
ME_Corn_Caribou	PFOS	Field-Median	83.18	< 0.1	> 100	N/A
ME_Corn_Scantic	PFOS	Field-Median	83.18	< 0.1	> 100	N/A
ME_Corn_Caribou – 4.57 m	PFOS	Field-Median	83.18	< 0.1	> 100	N/A
ME_Corn_Scantic – 4.57 m	PFOS	Field-Median	83.18	< 0.1	> 100	N/A
ME_Corn_Adams	PFOA	Lab-Minimum	0.13	16	0.5	7
ME_Corn_Caribou	PFOA	Lab-Minimum	0.13	18	1.0	11
ME_Corn_Plaisted	PFOA	Lab-Minimum	0.13	16	0.7	9
ME_Corn_Scantic	PFOA	Lab-Minimum	0.13	14	0.9	9
ME_Corn_Caribou	PFOA	Field-Median	14.45	9	45.6	6
ME_Corn_Scantic	PFOA	Field-Median	14.45	8	39.4	5
ME_Corn_Caribou – 4.57 m	PFOA	Field-Median	14.45	< 0.1	> 100	N/A
ME_Corn_Scantic – 4.57 m	PFOA	Field-Median	14.45	< 0.1	> 100	N/A

Table 5. PRZM modeling results for PFOS/PFOA for Maine groundwater scenarios

Groundwater Simulation Sensitivity Analysis

The sensitivity of the predicted groundwater concentration results with respect to model inputs is an important aspect to consider. In addition to soil/crop characteristics, the two main parameters that affect predicted chemical concentrations in the groundwater are the sorption coefficient and the depth of the water table. Therefore, a series of simulations were run to investigate these dependencies using the worst-case Maine soil/crop scenario, the Maine corn with Caribou soil, as test case. Figure 2 and Figure 3 show the variation of PFOA and PFOS concentration in applied biosolids as a function of different sorption coefficients when maximum PFAS concentration in groundwater was set to 70 ppt (results would scale linearly if this limit was different) and assuming the yearly biosolids application rate is the same as other simulations (20 wet tons/acre).

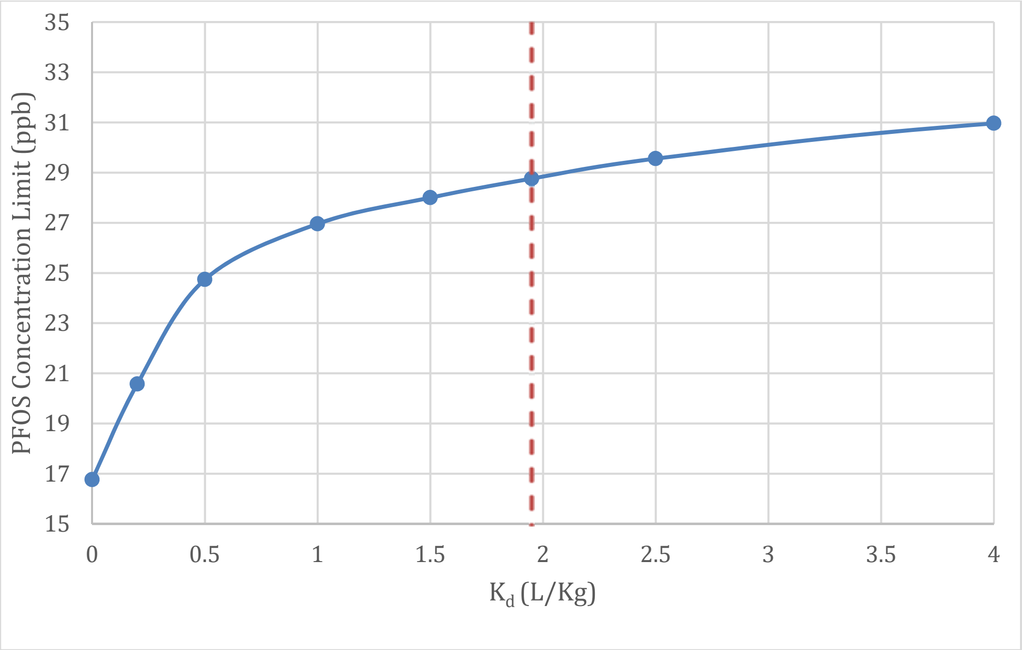

Figure 2. Biosolids PFOS concentration limits as a function of the sorption coefficient K_d when biosolids are applied once every year at a rate of 20 wet tons/acre with a dry matter content of 22% and a PFOS concentration limit in the groundwater of 70 ppt. The model simulation of PFOS leaching is based on a worst case Maine-specific soil (Caribou) and water table at 1 m depth below ground surface. The dotted red vertical line is the minimum K_d value available from the literature (laboratory measurement), K_d=1.95 (L/kg).

With the most conservative K_d of $1.95\ L/Kg$, the PFOS concentration limit in the biosolids would be 29 ppb in order to not exceed 70 ppt in the groundwater when biosolids is applied once a year at a rate of 20 wet ton/acre and 22% dry solids content. For lower application rates, PFOS biosolids concentrations could be higher (see Table 6). Notice also that around the minimum K_d of 1.95 L/Kg, a 50% change of K_d corresponds to an approximately 5% change (~2 ppb) in the biosolids PFOS concentration limit. Less sensitivity is observed for higher sorption values. Therefore, the choice of K_d is important but biosolids concentration limits are not highly sensitive to its choice.

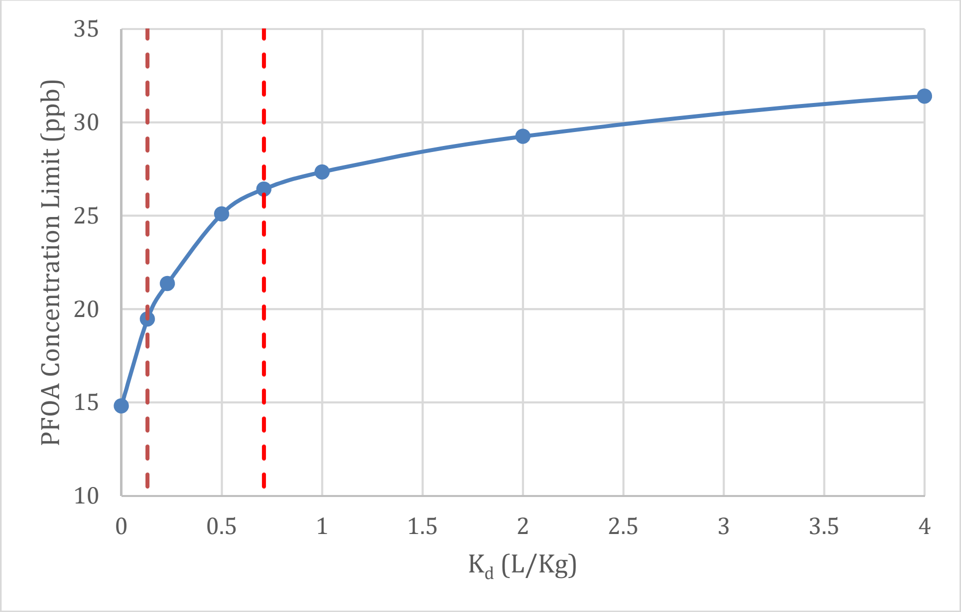

Figure 3. Biosolids PFOA concentration limits as a function of the sorption coefficient K_d when biosolids are applied once every year at a rate of 20 wet tons/acre with a dry matter content of 22% and a PFOA concentration limit in the groundwater of 70 ppt. The model simulation of PFOA leaching is based on a worst case Maine-specific soil (Caribou) and water table at 1 m depth below ground surface. The dotted red vertical lines are the minimum K_d values available from the literature K_d=0.13 laboratory and K_d=0.71 field.

With the laboratory minimum K_d of 0.13, the PFOA concentration limit in the biosolids would have to be no more than 19 ppb in order to not exceed 70 ppt in the groundwater when biosolids are applied once a year at a rate of 20 wet ton/acre and 22% dry solids. For lower biosolids application rates, initial PFOA concentration in the soil could be higher (see Table 6). Notice also that around the minimum K_d, a 55% change of K_d corresponds to approximately 9% change (~2 ppb) in the PFOA concentration limit. Compared to PFOS, maximum concentrations are more sensitive to the sorption coefficient. However, K_d variation between 0.13-0.71 (minimum values measured in laboratory and field) results in a maximum concentration of PFOA in applied biosolids that ranges between 19-26 ppb for the assumed biosolids application rate of 20 wet tons/acre per year.

Figure 4 below shows how the groundwater table depth can influence the PFOA concentration limit in applied biosolids. The worst case scenario is obtained when the water table is 0.5 m deep (green line). In this case, with the lowest K_d of 0.13, PFOA concentrations in biosolids should not exceed 18 ppb. With a deeper groundwater table, PFOA concentration limits could be higher. For example, the limit would be a little over 25 ppb when the water table is 4.57 m deep (purple line) and assuming $K_d = 0.13$.

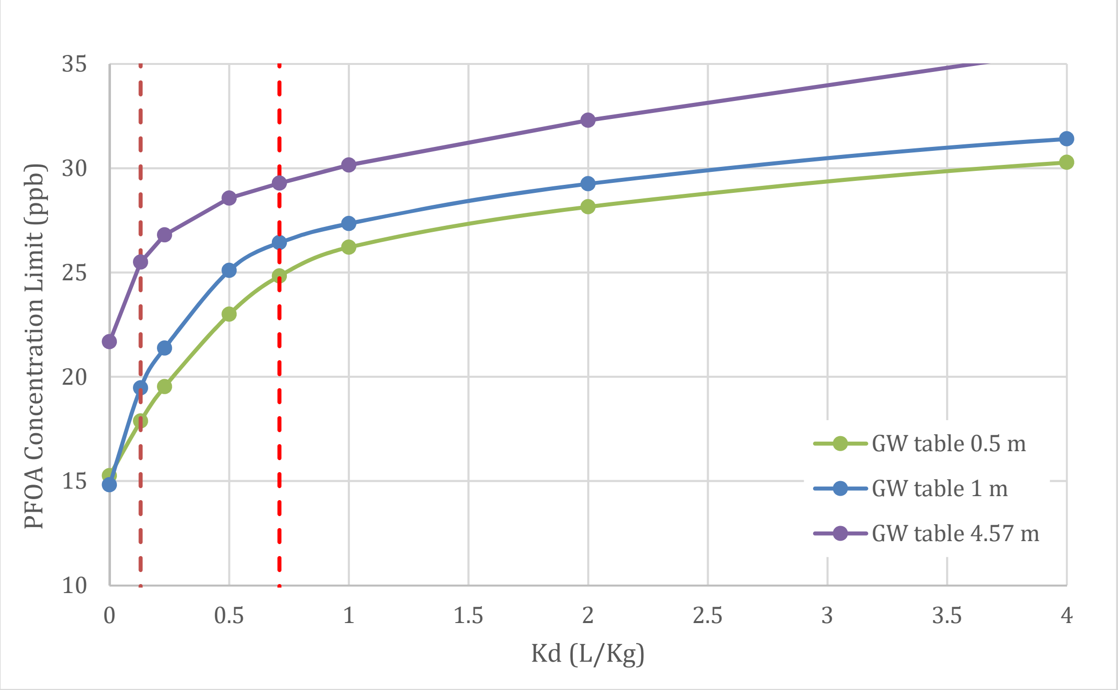

Figure 4. Biosolids PFOA concentration limits as a function of the sorption coefficient Kd when biosolids are applied once every year at a rate of 20 wet tons/acre with a dry matter content of 22% and a PFOA concentration limit in the groundwater of 70 ppt. The model simulation of PFOA leaching is based on a worst-case Maine-specific soil (Caribou) and water table from 0.5 m to 4.57 m depth below ground surface. The dotted red vertical lines are the minimum Kd values available from the literature Kd=0.13 laboratory and Kd=0.71 field.

Table 6 below summarizes the different PFAS concentration limits in applied biosolids to meet different desired groundwater quality limits and for different yearly biosolids application rates. The results are based on the worst-case soil scenario (Caribou), the most conservative sorption assumption (laboratory minimum), and a shallow 1 m water table depth. As expected, by decreasing groundwater limits, the PFAS concentration limits in applied biosolids also decrease. However, by decreasing the biosolids application rate, allowable PFAS concentrations in applied biosolids could be higher. In fact, regardless of the biosolids application rate, it is the yearly PFAS mass rate applied (mg/ha) that affects groundwater concentrations. It is the annual application rate (mass per unit area) of applied biosolids that is most important in assessing the potential impacts of PFAS to groundwater.

		Biosolids Concentration Maximum			
Application Rate (wet ton/acre)	**Groundwater Concentration Limit (ppt)**	**PFOA (ppb)**	**PFOS (ppb)**	**PFOA (mg/ha)**	**PFOS (mg/ha)**
10	201	112	167	551	826
10	70	39	58	192	288
20	201	56	84	551	826
20	70	19	29	192	288

Table 6. Biosolids PFAS concentrations and mass rates limits in applied biosolids for different application rates and groundwater limits. Groundwater concentration limit sources are: 201 ppt screening level from the RSL calculator used by ME DEP to determine soil limits from PFOA and PFOS; 70 ppt from the current recommended limit proposed by US EPA.

Lastly, when water quality groundwater limits are set to the combined PFOS+PFOA concentration (as is the case in Maine), Figure 5 below shows examples of how to determine if the combined PFAS concentration in applied biosolids is in compliance with these limits: if PFAS concentrations are below the line, the resulting groundwater concentration would be below the set groundwater limit (70 ppt in this case). For example, a yearly biosolids application rate with an initial PFOS concentration of 11 ppb and PFOA concentration of 5 ppb should not cause PFAS concentration in groundwater to exceed 70 ppt when biosolids are applied yearly at a rate of 20 wet ton/acre. The results are based on the worst-case soil scenario (Caribou), the most conservative sorption (laboratory minimum K_d), and a shallow 1 m water table depth.

The PFOA/PFOS limits line in Figure 5 moves up or down for different water quality limits, biosolids application rates, and biosolids dry matter content. For example, an application rate of 10 wet tons/acre and 22% dry solids content would move the PFOA/PFOS biosolids concentration limit line upwards. The PFOA/PFOS limits at the Y and X axes intersections respectively would increase to 38 ppb for PFOA and 58 ppb for PFOS (two times higher than the reference values at 20 wet tons/acre) for a groundwater limit of 70 ppt. These limits would be reduced by half if groundwater quality limits were set to 35 ppt.

With higher sorption assumptions, these concentration limits in Figure 5 would also increase. 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. In the case of PFOS, sorption based on the field median results in almost zero leaching to groundwater, so the combined PFAS concentration limit is based solely on PFOA. These example variations on application rates and sorption assumptions are presented in Figure 6. The nearly horizontal lines for the cases of median field sorption indicate that PFOS is not contributing to the total PFAS concentration in groundwater. Although not shown in Figure 6, a greater depth to the water table would also increase the biosolids PFAS limits by approximately 1 ppb for every one-meter increase in the groundwater depth.

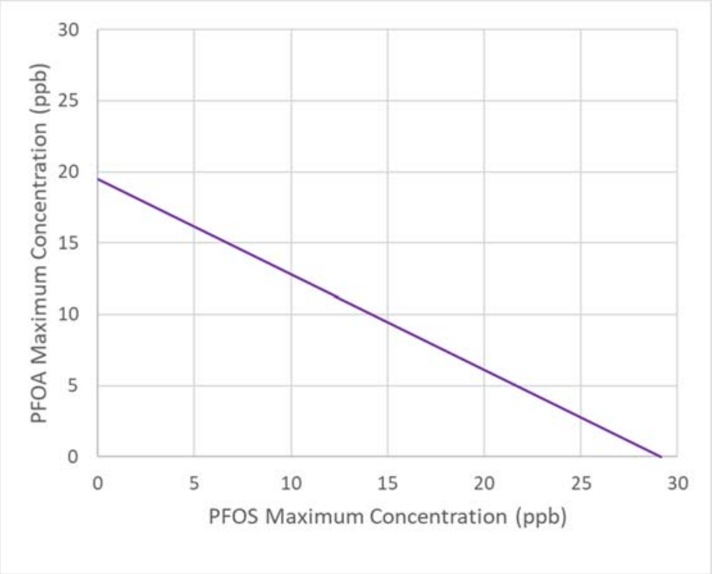

Figure 5. Example graphs to determine if the combined PFOS/PFOA biosolids concentrations result in PFAS concentrations above or below groundwater limit of 70 ppt with yearly biosolids application rate set to 20 wet ton/acre. These results reflect the most conservative PFOS/PFOA leaching scenario.

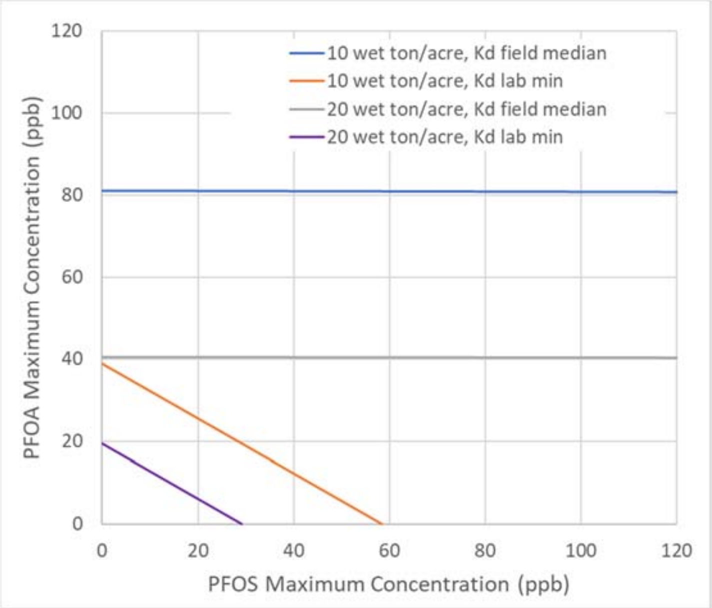

Figure 6. Example graphs to determine if the combined PFOS/PFOA biosolids concentrations result in PFAS concentrations above or below groundwater limit of 70 ppt based on variable yearly biosolids application rates and sorption assumptions. These results reflect a 1 meter depth to groundwater.

Comparison of Simulation Results with Field Data

Several recent publications provide field-measured data that can be compared with the PRZM-simulated PFOA/PFOS groundwater concentrations. While the data available from these studies is not sufficient to generate PRZM model simulations that specifically represent these study sites, the biosolids concentrations reported and the associated measured groundwater concentrations can be compared with the biosolids application rates and groundwater concentrations predicted in this study. Here, we discuss one study that provided enough information to allow a semi-quantitative comparison with the modeling results presented here.

Gottschall et al. (2106) monitored groundwater and soil concentrations in an agricultural field after of a one-time application of biosolids at a rate of approximately 9.8 dry tons/acre. PFOA concentrations in biosolids were 1.6 ppb 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 time period were 1.5-3 ppt and 0-0.8 ppt for PFOA and PFOS respectively. PFOA/PFOS was not detected at deeper groundwater depths. Comparing with the PRZM model simulations of the Maine Caribou soil assuming the lab-minimum K_d and biosolids applications occurring every year (see Table 5), the simulated peak concentrations of PFOA and PFOS were 18 ppt and 27 ppt respectively based on similar application rates of 49 mg/ha and 110 mg/ha for PFOA and PFOS respectively. The conservative Maine leaching exposure scenario predicted PFOA concentrations 6 to 12 times higher than the Gottschall et al. (2016) field site from an application rate that was only 40% higher. For PFOS, the Maine leaching exposure scenario predicted concentrations 34 times higher than the maximum observed concentration at the Gottschall et al. (2016) field site based on an application rate that was 30% lower.

In an effort to better represent the Gottschall et al. (2016) field site experiment, an additional PRZM simulation was run using 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 PFOA mass according to the study data of 35 mg/ha and 158 mg/ha of PFOA and PFOS respectively. The background concentrations of PFOA and PFOS in the soil of approximately 0.1 ng/g were not accounted for in this scenario. 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 more 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 PZRM model scenarios and simulation results show very reasonable agreement with groundwater concentrations observed in the field and are conservative compared to the field observations.

Comparing the Gottschall et al. (2016) field data with the PRZM modeling conducted in this study has demonstrated that the modeling results are generally consistent with observed data, and that the worst-case scenarios simulated (see Table 5) over-predict groundwater concentrations observed in the field given equivalent PFOA/PFOS mass loadings. This provides confidence that the results from the PRZM modeling approach presented here would be protective of groundwater and appropriate for deriving regulatory biosolids screening levels of PFAS chemicals.

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