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A framework for determining site-specific soil screening levels for PFAS

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ABSTRACT

This study illustrates the application of a framework for determining site-specific soil screening levels (SSLs) for PFAS. The framework was used at four sites at which multiple source zones have been impacted by aqueous film forming foam (AFFF). Soil and porewater samples were collected for determination of PFAS concentrations and for measurements of multiple physical and geochemical properties. PFAS-LEACH, a comprehensive modeling platform developed specifically for PFAS was used to conduct detailed mathematical modeling and to determine site-specific SSLs for the three most prevalent PFAS, perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorohexanesulfonic acid (PFHxS). Model simulations successfully predicted measured water contents and PFAS porewater concentrations, delineating the relevant transport processes and determining the most representative input parameters. This information was used to apply a simplified analytical-solution-based screening model and a revised dilution-attenuation factor (DAF) equation implemented in PFAS-LEACH to determine site-specific SSLs. The SSLs determined with the site-specific approach were a factor of three to more than two orders-of-magnitude larger than generic EPA screening values. The disparities were shown to result from the consideration of PFAS retention and attenuation in the vadose zone and in particular the impact of air-water interfacial adsorption. The SSLs determined for PFOS were larger than those for PFOA and PFHxS due to the greater retention properties of PFOS. The influence of input-parameter uncertainty was assessed, producing a factor of four range in SSLs. SPLP leaching-test measurements and soil/porewater concentrations from paired field samples were tested as alternative methods to parameterize the DAF equation.

1. Introduction

It is now well documented that per and polyfluoroalkyl substances (PFAS) are present in soil at innumerable sites in the U.S. and elsewhere (e.g., [1,2]). One of the primary concerns for such PFAS-impacted sites is the potential leaching of PFAS from soil to groundwater. A common means used to assess the risk of groundwater contamination from leaching is to determine soil screening levels (SSLs). The U.S. Environmental Protection Agency (EPA) has established guidance for the determination of SSLs, including for the soil-to-groundwater exposure pathway [3–5]. The application of SSL calculations has since become a standard approach for characterizing the risk posed to groundwater by contaminated soil. Detailed discussions of the basis of the approach and their application are provided in the EPA guidance documents [3–5].

The EPA guidance provides three alternative approaches for determining SSLs. The first is to use generic (i.e., "look-up") values generated by a regulatory agency. For example, the EPA has generated reference SSLs, which are considered to be relatively conservative [3,5]. The second approach is to determine site-specific SSLs by using one or more site-specific input parameters in the EPA dilution-attenuation factor (DAF) equation. The third approach is to conduct detailed mathematical modeling for the site. Due to the consideration of site-specific conditions, approaches two and three may produce more representative and less stringent SSLs [3,5].

The standard methods used currently for determining SSLs do not account for some of the unique properties of PFAS and how these properties impact retention and leaching in the vadose zone. For example, the standard DAF approach is based on the assumption that sorption is controlled by the organic-carbon fraction of the soil. Several studies have shown that PFAS sorption can be influenced by inorganic

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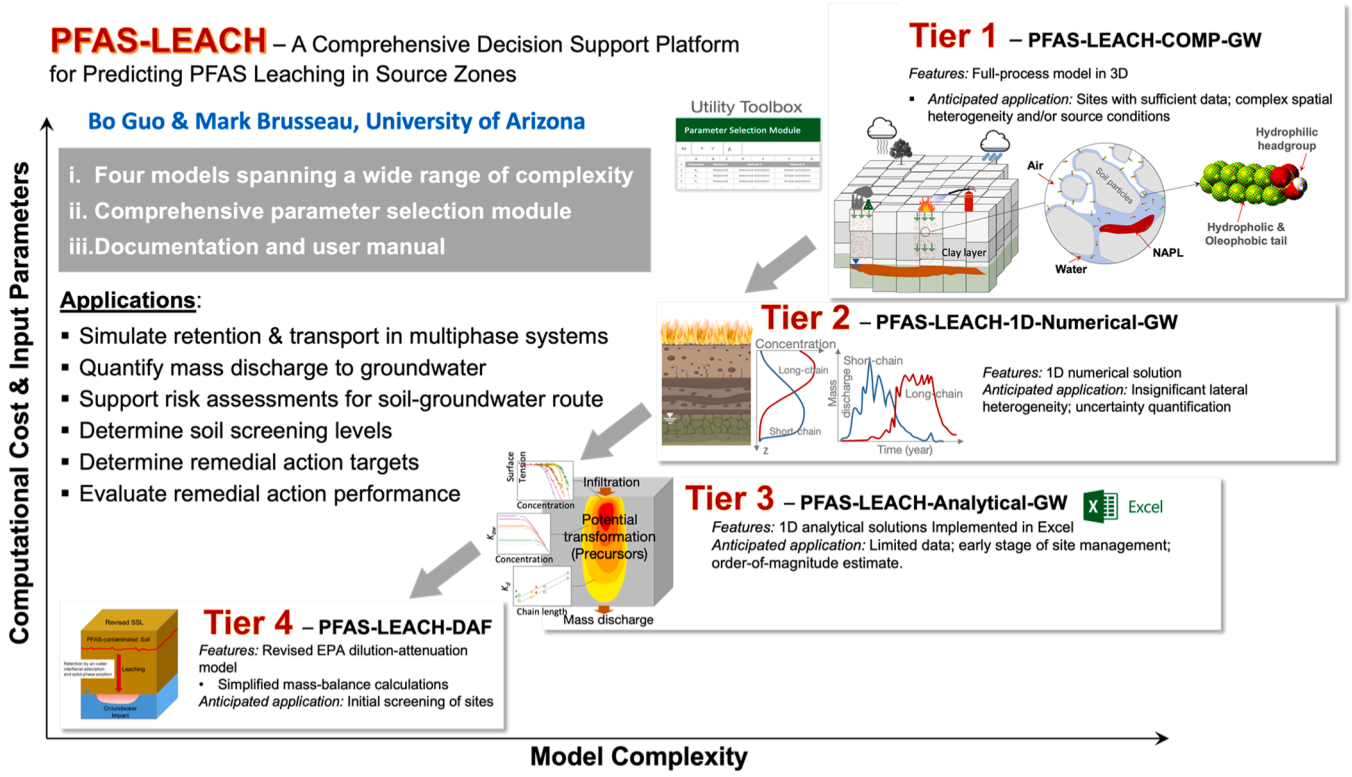

Fig. 1. Conceptual diagram of the PFAS-LEACH modeling platform.

components of the soil, as discussed in recent meta-analyses and reviews [6,7]. Furthermore, it has been demonstrated that many PFAS adsorb at air-water and other fluid-fluid interfaces in unsaturated soil (e.g., [8,9]). Fluid-fluid interfacial adsorption processes are not considered in the standard EPA approach. As such, it is important to consider these and other factors when determining SSLs for PFAS. For example, Brusseau and Guo [10] recently revised the EPA DAF equation to account for air-water interfacial adsorption in the porewater-to-soil conversion term.

A critical element in the determination of representative site-specific SSLs is the robustness of the input parameters used in the calculations, which will depend upon the data source. Methods exist for the determination of the input parameters needed to implement site-specific DAF calculations. However, some of the required parameters are not commonly measured during standard site investigations. In addition, some parameters require specialized measurement methods. Field-measured soil and porewater concentrations have the potential to serve as an alternative source for certain SSL-related parameters. Soil concentrations are routinely measured for PFAS-impacted sites, and the use of lysimetry to collect soil porewater samples is becoming increasingly common. Another alternative that has been proposed is the use of leaching tests such as the EPA synthetic precipitation leaching protocol (SPLP) test [3,5]. The efficacy of these alternative data sources for determining SSLs has not been examined to date for PFAS-impacted sites.

The objective of this study is to illustrate a framework we have developed for the determination of site-specific SSLs for PFAS. The framework is demonstrated through application to four U.S. Department of Defense installations that have been impacted by aqueous film forming foam (AFFF). Extensive site characterization is conducted at the AFFF-impacted source areas, including the collection of soil and lysimeter porewater samples for determination of PFAS concentrations. In addition, soil and porewater samples are characterized for multiple physical and geochemical properties. PFAS-LEACH, a comprehensive modeling platform developed specifically for PFAS [11–16], is used in this project. This effort represents the first such application of PFAS-LEACH for the determination of site-specific SSLS. The demonstration is conducted in two parts. The first consists of a comprehensive approach focused on one source area of the first installation. Detailed mathematical modeling was conducted to delineate the relevant transport processes and determine the most representative input parameters in support of the use of simpler methods for determining SSLs. The second part of the demonstration comprises application to all four installations, employing two input-parameter data sources: EPA default values and alternatively soil, porewater, and SPLP measurements. A simplified analytical-solution based screening model and a revised DAF approach that are available as a user-friendly Excel tool within PFAS-LEACH are used to determine site-specific SSLs. These values are compared to generic SSL values for the soil-to-groundwater exposure pathway.

2. Materials and methods

2.1. Overview of approach

The framework consists of a tiered approach for the application of methods to determine SSLs and a corresponding tiered approach for the determination of input parameters. The methods available for determining site-specific SSLs include (1) advanced numerical modeling using a PFAS-focused transport model, (2) use of a simplified PFAS-focused transport and fate model based on analytical solutions, and (3) application of a revised DAF equation that accounts for PFAS adsorption at the air-water interface. The tiered data sources range from empirical estimates based on standard soil measurements, to laboratory measurements including SPLP tests, to the application of field-measured porewater and soil data sets. The framework employs the PFAS-LEACH platform, illustrated in Fig. 1. Details of PFAS-LEACH are provided in SI-1 of the Supplemental Information. We will employ the Tier 2, 3, and 4 modules of PFAS-LEACH for this study. These three tiers correspond to an advanced numerical model (Tier 2), a simplified analytical model

(Tier 3), and the revised DAF equation (Tier 4).

Advanced mathematical modeling can be used in multiple ways. One is to use modeling to directly determine SSLs. However, this can be a time and resource intensive endeavor, especially when multiple PFAS, multiple source zones at a single site, or multiple sites are the subject of the project. In such cases, an alternative is to employ advanced modeling to support the application of simpler methods for determining SSLs. For example, the modeling can be conducted for a few select PFAS and a single location at a site to conserve time and resources. This modeling can delineate the relevant processes and factors influencing PFAS retention and transport at the site, from which it can be determined which are critical (and which are not) to incorporate into the simpler methods. It can also be used to assess the robustness and representativeness of the input parameters. This is based on the operating assumption that a satisfactory prediction of the target field data, such as field-measured PFAS porewater concentrations, is an indication that all processes and factors significantly influencing transport and retention are represented in the model. And furthermore, that a successful prediction indicates that the parameter values are sufficiently robust. The validated parameter values can then be used as input for simpler models in the determination of SSLs. This is the approach employed in the present study.

The detailed modeling component of this study is focused on one of several characterized source areas of Installation 1, which is referred to herein as Site 1. It is also focused on three specific PFAS, perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and perfluorohexane sulfonic acid (PFHxS). These three PFAS represent the great majority of PFAS quantified in soil at the study site, comprising approximately 90 % of the total quantified PFAS mass.

A tiered approach for parameter determination has also been developed [16,17]. In this study, the use of parameter values obtained from different sources was tested for select parameters. For the advanced numerical modeling (Tier 2) and analytical modeling (Tier 3), this included testing two sets of parameters: (1) the use of hydraulic soil parameters determined from empirical soil-texture based correlations versus laboratory measurements, and (2) the use of literature-sourced organic-carbon normalized sorption coefficients and measured organic-carbon contents versus measured sorption coefficients. For the determination of SSLs by the revised DAF equation (Tier 4), this included comparing the use of literature-derived estimates, laboratory sorption measurements, SPLP measurements, and the use of field-measured soil-porewater data to parameterize the distribution-conversion term in the DAF equation.

A high-resolution field study was conducted to characterize PFAS concentrations in soil and porewater. Soil samples were also characterized for multiple physical, hydraulic, and geochemical properties. The soil and porewater data served two purposes. The first was to support validation testing of the advanced transport model. The second was to serve as an alternative approach for determining SSLs. The site-specific SSLs determined with the various approaches are compared to SSLs calculated using the standard EPA DAF equation and to generic SSLs reported by the EPA.

2.2. Field Sites

The field component of the study was conducted at four U.S. Department of Defense installations. Installation 1, the focus of the comprehensive application, is located in a semi-arid continental climactic zone. The other three installations are in semi-arid highlands, semi-arid continental, and semi-arid highlands climatic zones, respectively. General information about the four installations is provided in Table SI-1 in the SI.

Source area delineation efforts conducted at the four sites have identified multiple PFAS source areas where AFFF was deployed for firefighter training, emergency response, systems testing, or from hangar fire suppression systems. The source area that is the focus of the first phase of the study (Site 1) is located within 300 m of three current or former fire training areas, including one of the largest identified PFAS source areas within the installation. The fieldwork consisted of subsurface soil sampling, lysimeter installation, and porewater sampling.

Similar methods were used at all four sites, with the following differences. The number of lysimeters installed at each installation varied. The number of porewater sampling events also varied, from 2 to 5. Specific lysimeter-sampling procedures such as pressures applied and collection period varied as a function of site conditions. Soil moisture sensors were installed only at Installation 1. Details of instrument installation and sampling are provided in SI-2.The soils samples used in the SPLP tests for Installations 2–4 were collected from the same boreholes in which the lysimeters were installed, and at the specific depth interval corresponding to the lysimeter placement. The SPLP soil samples for Installation 1 were collected approximately two years prior to the lysimeter installation. The use of paired samples provided the opportunity to directly compare SPLP and in-situ porewater concentrations for multiple paired data sets. The SPLP tests were performed by a commercial laboratory (ELLE) using USEPA Method 1312.

2.3. Detailed Mathematical Modeling (Tier 2 model)

The first step in the application of the SSL framework at Installation 1 involved mathematical modeling simulations of flow and transport with the advanced numerical (Tier 2) model as noted above. The model was first tested for its ability to reasonably simulate water flow by comparing predicted results to soil-moisture data measured for the site. The model was then validated against measured PFAS porewater concentrations determined for samples collected from the installed lysimeters.

The governing equations for the Tier 2 model are provided in the cited works [11,13]. Each of the models has a set of required input parameters related to soil properties, site conditions, and PFAS properties. The number of input parameters are greater for the Tier 2 model compared to the Tier 3 and 4 modules. These parameters can be obtained from multiple sources, including field measurements, laboratory measurements, or via estimation based on specific properties and conditions. The parameters needed for the Tier 2 model are listed in Table SI-2, with data sources for Site 1 listed in the last column.

The ability of the Tier 2 model to simulate water flow was evaluated by testing against measured soil-moisture data collected for the field site. The simulation period started one year prior to the first sampling period and was carried forward to match the timeframe of the field sampling (430 days). Two sources of soil-hydraulic parameter values were tested. First, the measured soil texture data were used as input to the Rosetta program to estimate hydraulic properties [18,19], which were then used for the simulations. Second, measured hydraulic properties were used to attempt to improve the simulations, as discussed below.

After the model was deemed to produce representative simulations of the measured soil-moisture data, the model was validated against the measured PFAS porewater concentrations. In this case, the gravimetric measured water-content profile was used as the initial condition and the simulation lasted for 430 days. There are multiple approaches available for developing validation metrics. We employed an approach focused on quantifying and comparing uncertainties for both the model simulations and the measured data. Additional discussion of model validation is provided in SI-5.

The model domain encompassed the approximate volume of the characterized source area. The vadose zone was split into nine horizontal layers based on the borehole logs and measured soil textures. Hydraulic properties varied from layer to layer based on the values determined for the relevant input parameters. The lower boundary condition for water flow was set as a time-variant specified head boundary. One advantage of conducting detailed modeling is the ability to account for time-dependent infiltration and nonuniform distributions of soil concentrations. The latter was represented using the PFAS soil

concentrations measured for each interval.

Information on precipitation, including rainfall and snow melt, were used to set water input. Precipitation was classified as snow for the continuously frozen period and water inputs were set to zero. During the melt period the daily difference in snowpack was converted to available water using a snow water equivalent ratio of 0.264, measured at the nearest National Water and Climate Center Snow Telemetry station [20]. Precipitation was set equal to water inputs for the remainder of the study period. Evapotranspiration was determined by latent heat flux measurements, corrected for local ground cover using the crop coefficient for grass (0.62, AmeriFlux Network).

Additional parameters were determined, including air–water interfacial adsorption coefficients, air-water interfacial areas, solid–phase adsorption coefficients, and a dispersivity coefficient. The Langmuir isotherm was used to represent air-water interfacial adsorption, based on the results of two recent studies. The first involved a comprehensive meta-analysis of air-water interfacial adsorption measurements obtained with surface-science methods, molecular modeling, and multiple physical methods [9]. The measurements reported in 70 out of 74 studies were fully consistent with Langmuir adsorption and inconsistent with the Freundlich isotherm, the other isotherm that has been used to date in some studies. The other study involved detailed mathematical modeling of spatially and temporally variable porewater concentrations measured at a heavily instrumented vadose-zone site [21]. The results of the simulations indicated that the Langmuir isotherm was sufficient to represent air-water interfacial adsorption. Langmuir parameters were obtained from a compilation of measured data [16,22]. Ionic strength exhibited minimal variability across Site 1 and therefore was treated as spatially constant. Air-water interfacial areas were estimated using the thermodynamic approach, which involves integration of the soil-water characteristic curve [23]. A scaling factor was applied to account for the impact of solid-surface roughness on A_{aw}. The empirical regression equation employed is reported in [23]. Soil texture does not vary greatly across Site 1, and thus a single scaling factor was used.

Solid-phase adsorption was assumed to be linear. The solid–phase adsorption coefficients (K_d) were determined based on the relationship $K_d = f_{oc}K_{oc}$, where f_{oc} is the organic carbon content, K_{oc} is the organic-carbon normalized adsorption coefficient, and K_{oc} values were measured for the soil from the site. The use of this approach allowed K_d in the model input to vary as a function of f_{oc}, which was measured for the soil intervals. It is recognized that the standard K_{oc} approach may not be valid for PFAS in some cases, such as when other soil constituents beyond organic carbon and other mechanisms beyond hydrophobic interaction significantly contribute to adsorption. However, the empirical data set used to determine estimated values is based on measured apparent K_{oc} values that implicitly incorporate the contribution of inorganic soil constituents to adsorption [6]. The vertical dispersivity was estimated using: $\alpha_L = 0.82[\log (Z_w/100)]^{2.446}$ where α_L is longitudinal (vertical) dispersivity for the vadose zone and Z_w (cm) is the depth to groundwater [24,25].

2.4. SSL Determination (Tier 3 & 4 models)

The second step in the SSL-determination process involved application of the analytical model (Tier 3) and the revised DAF equation (Tier 4) modules of the PFAS-LEACH Excel tool to determine SSLs. The equations comprising the Tier 3 model are presented in detail in Guo et al. [14], Smith et al. [15], and the PFAS-LEACH Tiers 3 and 4 User Guide [16]. The Tier 4 model employs the revised DAF equation that accounts for PFAS-specific retention [10]. It is presented herein in the same format as the original EPA equation:

$$SSL^{Rev} = C_{gw}^{T} DAF[K_d + (K_{aw}A_{aw} + \theta_w + \theta_a H)\frac{1}{\rho_b}] \quad (1)$$

where C_{gw}^{T} is the targeted protective groundwater concentration, DAF is the dilution-attenuation factor, H is Henry's coefficient, θ_w is volumetric water content, θ_a is volumetric air content, ρ_b is soil bulk density, and the other parameters are defined in Table 1. Note that the PFAS selected for the focus of this study have very low vapor pressures, and therefore the $\theta_a H$ term is ignored. Eq. (1) can be rewritten as follows [10]:

$$SSL = C_{gw}^{T} DAF \frac{\theta_w}{\rho_b} R_d \quad (2)$$

where R_d is the nondimensional distribution coefficient defined as:

$$R_d = \left(1 + K_d\frac{\rho_b}{\theta_w} + K_{aw}\frac{A_{aw}}{\theta_w} + H\frac{\theta_a}{\theta_w}\right) \quad (3)$$

As noted previously, the DAF equation comprises two sets of terms that are used to translate from the defined protective groundwater concentration to the associated SSL. The DAF term accounts for dilution and attenuation during migration from soil to a groundwater receptor

Table 1
Parameter Values for SSL Determination for Site 1: Averaged parameter values.

Parameter	Symbol	Value	Units	Source
Net infiltration	I	13.8	cm/yr	Estimated from measurements
Temperature	T	12.5	°C	Measurement
Median grain size	d_{50}	0.010	cm	
Water content	θ_w	0.337	cm^3/cm^3	
Water saturation	S_w	0.80	(-)	
Air-water interfacial area scaling factor	SF	4.0	(-)	Estimated from d50 and θ
Air-water interfacial area	A_{aw}	267	cm^{-1}	Scaled thermodynamic method
Soil bulk density	ρ_b	1.44	g/cm^3	Measurement
Saturated hydraulic conductivity for vadose zone	K_{sat}	29.5	cm/day	Measurement and estimated, mean for soil profile
Residual water content	θ_r	0.038	(-)	
Saturated water content	θ_s	0.420	(-)	
van Genuchten parameter	α	0.009	cm^{-1}	
van Genuchten parameter	n	2.32	(-)	
Longitudinal dispersivity for vadose zone	α_L	13.4	cm	Empirical equation
Solid–phase adsorption coefficient	K_d	PFAS specific	cm^3/g	Measurement
Air–water interfacial adsorption coefficient	K_{aw}	PFAS specific	cm^3/cm^2	Empirical equation
Groundwater darcy flux	q	27.9	m/yr	Site characterization
Longitudinal source length	L	50	m	
Saturated zone thickness	b_{sat}	91	m	
Vertical dispersivity for aquifer	α_v	0.28	m	Computed by EPA equations
Mixing zone thickness	d_m	5.5	m	
Dilution factor	DF	23.4	(-)	
Depth to groundwater	Z_w	300	cm	Measurement
Attenuation factor	AF	PFAS specific	(-)	Tier 3 simulations

Note: Tier 4 SSL calculations use a subset of the above parameters
K_d values are 7.5, 0.52, and 1.1 cm^3/g for PFOS, PFHxS, and PFOA, respectively
K_{aw} values are 0.075, 0.0010, and 0.0038 cm^3/cm^2 for PFOS, PFHxS, and PFOA, respectively
AF values are 8.4, 1.0, and 1.0 for PFOS, PFHxS, and PFOA, respectively

well. It consists of two components, the dilution factor (DF) and the attenuation factor (AF). A site-specific DF is employed in both the Tier 3 and Tier 4 models for the application to Site 1 of Installation 1. It is defined as:

$$DF = 1 + \frac{q}{I}\frac{d_m}{L} \quad (4)$$

where the terms are defined in Table 1, along with the values used to calculate the site-specific DF.

The AF is assumed to be 1 in the standard and revised EPA approaches. Conversely, the Tier 3 model explicitly calculates an AF based on the ratio of the highest simulated porewater concentration within the soil profile and the highest simulated concentration in the porewater leachate entering groundwater. It was demonstrated that the AF obtained by this approach derives an SSL that is equivalent to that determined with a more rigorous method that determines the SSL by incrementally decreasing the soil concentration until the simulated receptor groundwater concentration reaches the selected protective groundwater concentration [15].

The second term in the DAF equation is the distribution-conversion term, represented by the term in brackets in Eq. (1) and the $\frac{\theta_w}{\rho_b} \quad R_d$ term in Eq. (2). The term is used to convert from a porewater concentration to a soil concentration. The distribution of a specific PFAS within a soil sample is represented by [26]:

$$\frac{C_t}{C_{pw}} = \frac{\theta_w}{\rho_b}R_d \quad (5)$$

where C_t is total soil concentration and C_{pw} is porewater concentration. Inspection of Eq. (5) reveals that R_d represents the ratio of total mass present in the soil sample to the mass present as dissolved solute in porewater. The $\frac{\theta_w}{\rho_b}$ term represents the ratio of porewater volume to soil-solids mass and can be considered a unit conversion term, wherein the $\frac{C_t}{C_{pw}}$ term has units such as L/kg. Notably, inspection of Eqs. (2) and (5) reveals that the $\frac{\theta_w}{\rho_b}R_d$ term in Eq. (5) is identical to the distribution-conversion term in the SSL equation. This serves as the basis for employing measured soil and porewater concentrations to determine the distribution-conversion term.

The Tier 3, Tier 4, standard EPA DAF, and other DAF-based approaches are based on the assumption of a homogeneous vadose zone, in contrast to the simulations conducted with the Tier 2 model that incorporated layered heterogeneity. They also assume temporally constant parameter values. Therefore, some method must be used to account for spatial and temporal variability. A common approach, used herein, is the use of temporally or spatially averaged values. Net infiltration was estimated from cumulative measured precipitation minus estimated evapotranspiration for the study period, normalized to one year. Net infiltration was estimated to be 13.8 cm/yr, representing 45 % of total precipitation. A mean saturated-zone hydraulic conductivity was obtained from statistical analysis of slug-test measurements conducted in the vicinity of Site 1. Measurements corresponding only to the interval from the top of the saturated zone to 6 m below were included to match the estimated mixing-zone depth. The measurements from different depths within this interval were grouped into four discrete layers. An ensemble of depth-weighted averages was then computed by random sampling of the Ksat values from each layer. A final mean value was extracted from this ensemble assuming a lognormal distribution. The longitudinal source length (L) was determined from the distance between soil borings with the highest PFAS concentrations at Site 1. The mixing-zone depth (d_m) was calculated using the equation provided in the EPA guidance.

The mean values of the layer-specific van Genuchten parameters from Tier 2 were used to represent the effective hydraulic properties of the entire soil column for the Tier 3 model. These parameters are not required for the Tier 4 model. Similarly, single depth-weighted mean values were used for θ_w, A_{aw}, and K_d for both Tier 3 and Tier 4 models. The volumetric water content was determined by converting the mean of the gravimetric measurements of the field soil samples. The A_{aw} was determined for the selected mean water content by applying a scaling factor to the interfacial area determined with the thermodynamic method, which is based on integration of the soil-water characteristic curve [23]. The K_d was determined from the mean of the measured organic-carbon contents and either the literature-based or laboratory measured K_{oc}. Values for all parameters and their associated sources are provided in Table 1.

It is recognized that the approach described above may impart some level of uncertainty to the calculated SSLs. In addition, the impact of parameter uncertainty is generally not uniform across the different parameters. For example, parameters such as hydraulic conductivity exhibit much greater spatial variability than bulk density or porosity. Similarly, precipitation and water saturation are likely to exhibit greater temporal variability compared to subsurface temperature. The impact of input-parameter variability on calculated SSLs can be addressed using specified ranges of values for each parameter or a statistical approach based on Monte Carlo analysis. Both approaches are available in the PFAS-LEACH Excel tool, and the latter approach was used herein in addition to the use of averaged values. Specific details of the Monte Carlo analysis are provided in SI-6.

The field-measured soil and porewater data were used in two ways to parameterize the DAF equation. For the first, the measured soil and porewater concentrations were tabulated and C_t/C_{pw} ratios were calculated for each sample set for each PFAS. Mean C_t/C_{pw} ratios were then determined for each PFAS and used for the site. This method was used for the focused study Site 1 for which the number of paired data sets were limited. The second method was used for the installation-wide application to the four installations. The paired concentration data were log-transformed and plotted to obtain regressions as follows:

$$\log C_t = \log C_{pw} + \log\left(\frac{\theta_w}{\rho_b}R_d\right) \quad (6)$$

$$\log C_{pw} = \log C_t - \log\left(\frac{\theta_w}{\rho_b}R_d\right) \quad (7)$$

The regressions should yield a slope of 1 for conditions of linear equilibrium adsorption, where the antilog of the intercept in both cases represents the distribution-conversion term ($\frac{\theta_w}{\rho_b}R_d$). Each data set for each PFAS was plotted using both regressions, and the one with the slope closest to 1 and lower normalized root-mean square error (NRMSE) was used. As will be discussed, the porewater concentrations exhibited comparatively minimal temporal variability, apart from the first sampling round for some PFAS. Therefore, temporally averaged mean porewater concentrations were used for both methods, with extreme outliers excluded.

The EPA guidance discussed the use of SPLP data as an optional approach for determining the distribution-conversion term to calculate SSLs. One concern with their use is the 20:1 dilution used in the test and the likelihood that the measured aqueous concentrations will not be representative of in-situ conditions. Another critical issue is that the SPLP test is conducted under saturated conditions, which is not representative of typical soil conditions. Based on these factors, we employ the SPLP data as a means to determine a K_d value, which is then used in the parameterization of the distribution-conversion term. This approach eliminates the preceding issues. However, other potential issues persist, such as the possibility that the specified 18-hour contact period may be insufficient to attain equilibrium conditions.

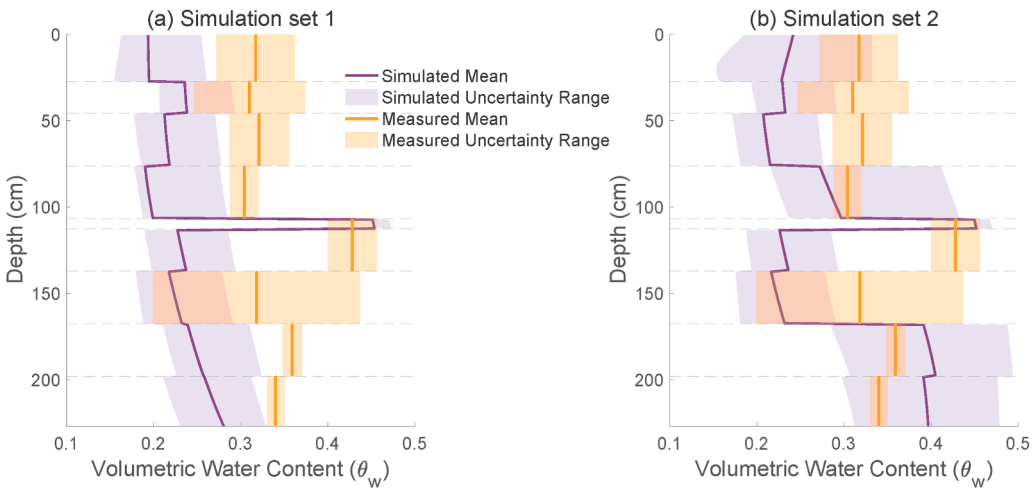

Fig. 2. Measured and simulated soil water content profiles. Left: Simulation set 1, with hydraulic parameters for all layers determined from texture-based empirical correlations; Right: Simulation set 2, with hydraulic parameters for some layers determined from laboratory measurement. The bold orange line and the orange shaded bands represent the measured mean and corresponding uncertainty ranges (+/- standard deviation) of the independent water-content measurements. The bold purple line represents the simulated mean water content, with the purple shaded region indicating the associated uncertainty range (+/- standard deviation) resulting from parameter variability.

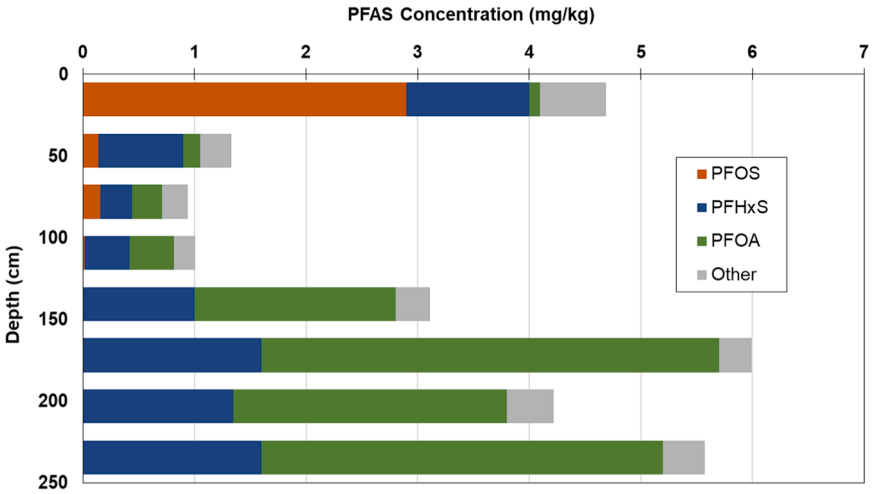

Fig. 3. PFAS soil concentration profiles for Site 1. PFOS, PFHxS, and PFOA together represent the vast majority of quantified PFAS. Other PFAS category includes short and very long-chain carboxylates and sulfonates, sulfonamides, fluorotelomers, and ether compounds (n = 37).

3. Results and discussion

3.1. Field data for Site 1 at Installation 1

The soils at Site 1 range from loamy sand to sandy loam, with median grain diameters (d50) ranging from 0.005 to 0.033 cm. Organic-carbon contents (OC) range from 0.18 to ~0.9 % across the characterized interval, except for the uppermost soil layer and an isolated 5-cm layer at approximately 110 cm depth for which OCs are 1.2 and 2.6 %, respectively. The depth-interval weighted mean of the organic carbon content is 0.65 %. The sum of aluminum, iron, and manganese oxide concentrations range from approximately 38–56 mg/g. Soil pH is near-neutral (7.5–8.5). The following lysimeter porewater properties were measured over multiple sampling events: specific conductivity (1700–2400 μmho/cm), pH (7.3–7.9), and total dissolved solids (220–1500 mg/L).

Water contents did not change significantly over the sampling period, especially for the lower depth intervals. Moisture probe B, placed at approximately 170 cm below ground surface, changed 10 % over the summer season and 15 % over the entire study period. Probe C, placed at approximately 330 cm below ground surface, changed less than 10 % over the study period. Gravimetric water-content measurements collected during lysimeter installation are therefore deemed sufficiently representative for the duration of the study period. Mean and variance of measured water contents obtained from the three independent gravimetric measurement datasets conducted at the start of the study are converted to volumetric water content and presented in Fig. 2. It is noted that the water saturations are relatively high, ranging from approximately 0.7 to close to saturation.

Soil concentrations were quantified for 40 PFAS. PFOS, PFHxS, and PFOA comprised approximately 90 % of the total quantified mass in soil. Mean concentrations for Site 1 were 0.4 mg/kg for PFOS, 1.0 mg/kg for PFHxS, and 1.6 mg/kg for PFOA across the entire sampled depth. As shown in Fig. 3, PFOS is concentrated in the uppermost section approximately 75 cm below ground surface, while PFHxS and PFOA concentrations are highest in the deeper sample intervals.

Mean porewater concentrations were 0.26 μg/L for PFOS, 1070 μg/L for PFHxS, and 1205 μg/L for PFOA across all sampling events and lysimeter depths (Fig. 4). Concentrations were higher at the lower sampling intervals for PFHxS and PFOA, whereas they were higher near the surface for PFOS. This is consistent with the soil-concentration

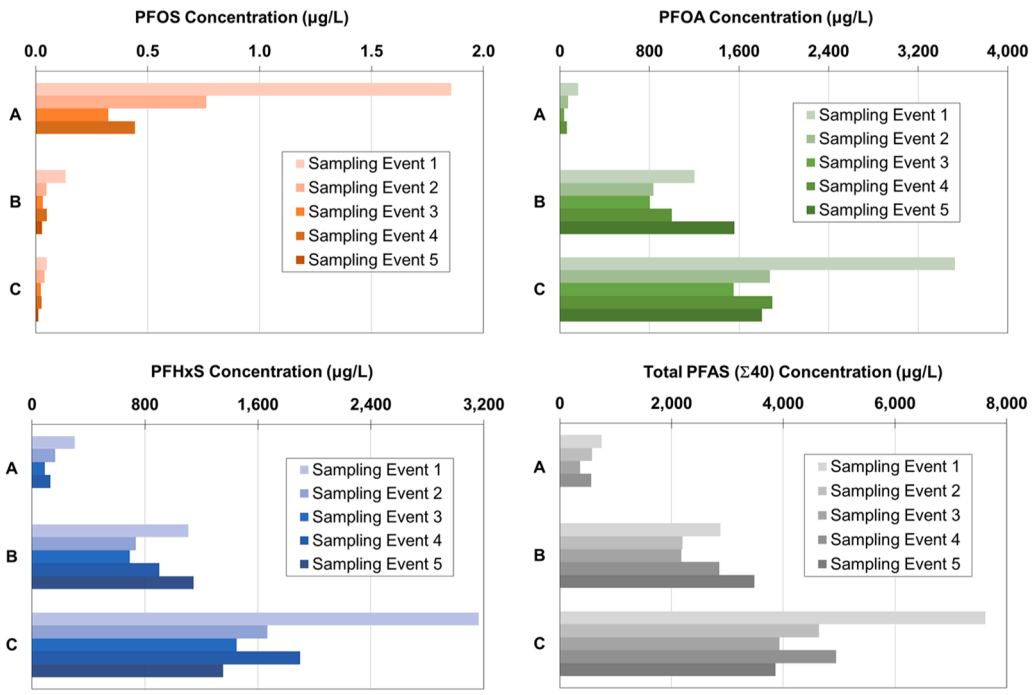

Fig. 4. Lysimeter PFAS Concentrations for Site 1. Installation depths were approximately 90 cm for suction lysimeter A, 170 cm for lysimeter B, and 230 cm for lysimeter C.

Table 2
Soil-to-Porewater Ratios (C_t/C_{pw}) for Site 1.

Parameter	Lysimeter A	Lysimeter B	Lysimeter C	Mean
PFOS	21	–	–	–
PFHxS	2.3	1.7	0.8	1.6
PFOA	4.8	3.8	1.7	3.4

– Concentrations too low to determine PFOS ratio
Ratios determined using average of multiple lysimeter porewater sampling events (n = 4–5) and co-located soil from same depth interval as each lysimeter.

distributions. Average PFOS concentrations in lysimeter A were 14–28 times higher than in lysimeters B and C. These field data indicate there is considerable attenuation of PFOS within the vadose zone.

The porewater concentrations remained relatively constant over the project period for most analytes, including PFOS, PFHxS, and PFOA as illustrated in Fig. 4. The first sampling event is an exception to the stable trend wherein PFOS in lysimeter A and PFHxS and PFOA in lysimeter C differ significantly from the other time periods. The samples comprising the first sampling event were collected shortly after installation and may have been impacted by the installation actions. Thus, it is possible that they may not reflect long-term conditions.

Ratios of co-located soil and porewater concentrations were calculated for each lysimeter. For example, soil collected from approximately 75–110 cm below ground surface in boring A was paired with shallow lysimeter A installed at approximately 90 cm. The ratios could not be determined for PFOS for the deeper two intervals due to extremely low porewater concentrations. As shown in Table 2, the soil-to-porewater ratio for PFOS is an order of magnitude larger than those for PFHxS and PFOA. This is consistent with the greater magnitudes of solid-phase and air-water interfacial adsorption that have been measured for PFOS in prior studies. The magnitudes of the ratios for all three PFAS are consistent with values reported in a prior study [27].

3.2. Advanced Numerical Modeling (Tier 2) Results for Site 1

Simulated water contents produced with the Tier 2 model are compared to measured values in Fig. 2. For the first simulation set, the simulations were performed using a set of hydraulic input parameters that were estimated based on measured soil texture data. The Rosetta 3 program was used for the estimations [18,19]. These parameters include the saturated hydraulic conductivity and van Genuchten soil-water characteristic parameters [28].

Overall, the initial simulation results do not adequately capture the observed moisture profile. Significant discrepancies are observed throughout much of the profile, with limited overlap between the simulated and measured uncertainty bounds. The model underestimates measured water contents, and the simulated ranges do not intersect with the measured intervals over the great majority of the domain. Thus, the simulated water contents are consistently lower than observed values, failing to replicate the relatively high moisture retention evident in the measurements. A notable match occurs at ~100 cm, where the model predicts an abrupt change in water content that is reflected in the field data. One region of moderate agreement is found near 130 – 160 cm depth, where the simulated and measured intervals show some overlap. However, below 160 cm, the model again underestimates the water content relative to observations. These results suggest that the initial parameter set may not be representative of the site's actual retention characteristics and highlight the need to explore alternative parameter combinations for improved model performance.

To improve the model's predictive performance, a revised parameter set was developed by incorporating measured values for hydraulic properties at four discrete depth intervals. Notable improvements are observed across multiple depth intervals (Fig. 2, right). In particular, the simulated water contents are in much better agreement with measurements at 0 – 30 cm, 70 – 100 cm, and below 160 cm, where the predicted values now fall well within the uncertainty intervals of the measured values. The overlap between simulated and measured uncertainty ranges has increased, and the overall water-content profile more closely resembles the observed trend. Despite these improvements, some mismatch persists between 50 – 70 cm and 110 – 130 cm, where the model underpredicts the water content. Nonetheless, this revised parameter combination demonstrates a clear enhancement in model representation and highlights the benefit of incorporating even limited

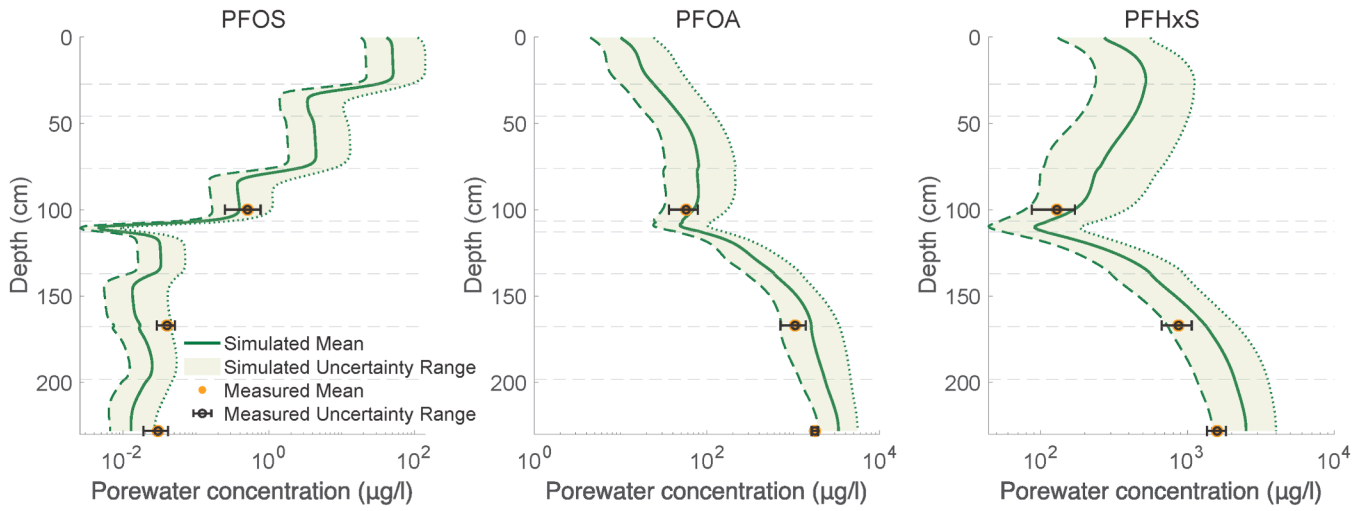

Fig. 5. Measured and simulated PFAS porewater concentration profiles. The solid green line represents the mean simulated concentration across all parameter realizations. The green shaded area indicates the uncertainty range derived from lower and upper bounds of key input parameters for the simulations. In each plot, the dashed and dotted green lines represent the range between the higher and lower retention scenarios. Measured PFAS concentrations are shown as orange circles, with horizontal black error bars representing the 95 % uncertainty ranges based on the range of porewater concentrations measured across multiple sampling events.

laboratory measurements of hydraulic parameters into parameter determination.

The model could have been directly calibrated to the measured values to possibly further improve the match between simulated and measured water contents. This however was not done as it was desired to base the simulations as much as possible on parameter input values obtained from measurements, be that from estimates based on soil texture or from direct laboratory measurement of soil properties. This approach was considered to be most compatible with the objective of the modeling, which was to support the use of the simpler methods for SSL determination, recognizing that the simpler methods make use of estimated/measured input parameters for site-specific application and the fact that it is not possible to calibrate these parameters in such applications.

Following the improved agreement between simulated and measured water contents using parameter combination 2, the second parameter set was adopted for simulating PFAS porewater concentrations. Input parameter uncertainty was accounted for in the simulations through the use of lower and upper bounds for key parameters. Three sets of predictive simulations were thus conducted. One set used mean values of the input parameters. The second and third sets shifted the PFAS soil concentrations by + /- 25 % and other parameters + /- one standard deviation to represent lower and higher retention scenarios that account for measurement uncertainty.

The measured and simulated PFAS porewater concentrations are presented in Fig. 5. Overall, the model captures the general magnitude and vertical distribution of PFAS porewater concentrations at the three measurement depths. For all three compounds, the simulated mean concentrations (solid green lines) fall within the range of measured data (orange markers with uncertainty intervals). In addition, the green shaded region, which represents the uncertainty range associated with input parameter variability, encompasses the observed concentrations.

These results indicate that the model is capturing the relevant processes influencing the distribution of the three PFAS between porewater and soil. Notably, the simulations are based on linear solid-phase adsorption. The successful simulations therefore suggest that nonlinear adsorption is not a significant factor for this system. In addition, air-water interfacial adsorption is represented with the Langmuir isotherm, which produces linear adsorption at lower concentrations (e.g., below the critical reference concentration) [9]. Thus, the simulation results indicate that air-water interfacial adsorption is effectively linear over the concentration ranges encountered at the site. The results also indicate that both solid-phase and air-water interfacial adsorption are not significantly rate limited. Preferential flow and other nonideal flow phenomena were not included in the simulations, which suggests that they do not materially impact flow and transport at Site 1 under the extant conditions of the study period. The apparent insignificance of these nonideal processes is consistent with the results of a recent study wherein detailed mathematical modeling was conducted to simulate field-measured PFAS porewater concentrations [21]. They are also consistent with the results of a study that investigated soil-porewater ratios for field-measured data sets [27]. The successful simulations also indicate that the input parameters are sufficiently robust.

3.3. SSL Determination for Site 1 of Installation 1

The second phase of this study focused on the determination of site-specific SSLs for the three PFAS, reflecting the unique behavior of these compounds under the site's climatic and hydrogeologic conditions. SSLs were calculated using the analytical model (Tier 3) and revised DAF equation (Tier 4) approaches. The key hydraulic and transport parameters used in these calculations were informed by the advanced

Table 3
Calculated site-specific soil screening levels by different approaches for Site 1.

PFAS	Tier 3 Site 1	Tier 4 Site 1	Soil:Porewater Site 1	Soil:Porewater Installation-wide	Standard EPA Approach Site 1	EPA Regional Screening Levels[a]
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
PFOS	17	2.0	2.0	1.5	0.73	0.031
PFOA	0.19	0.19	0.3	0.2	0.12	0.061
PFHxS	0.22	0.22	0.4	0.5	0.18	0.0042

[a] from https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables (accessed November 2024)

numerical model simulations and are summarized in Table 1. The laboratory measured K_{oc} values were similar to the selected literature values. Therefore, there was minimal difference in calculated SSLs for the two data sources. Target protective groundwater concentrations used in the SSL determinations are 4 ng/L PFOS, 10 ng/L PFHxS, and 4 ng/L PFOA. This first set of calculations employs Module 0 of the PFAS-LEACH Excel tool, which does not consider SSL uncertainty. The calculated SSLs are presented in Table 3.

Both the Tier 3 and Tier 4 SSLs are significantly larger for PFOS compared to PFOA and PFHxS. This reflects the greater retention of PFOS from both solid-phase and air-water interfacial adsorption. The Tier 4 SSL is considerably lower than the Tier 3 SSL for PFOS. This is a result of the Tier 3 model accounting for attenuation within the vadose zone due to site-specific retention processes as well as the impact of air-water interfacial adsorption on converting porewater concentrations to soil concentrations. In contrast, the Tier 4 module includes air-water interfacial adsorption in the distribution-conversion term but omits vadose-zone attenuation. The standard EPA approach—excluding air-water interfacial adsorption and vadose-zone attenuation—results in substantially lower SSLs. This stepwise reduction illustrates the cumulative impact of omitting PFAS-specific retention mechanisms.

The AF reflects the overall attenuation that PFAS experience while migrating through the vadose zone due to adsorption and retention processes. A larger AF indicates stronger retention of PFAS in the soil and correspondingly lower concentrations reaching groundwater. The magnitude of AF depends upon the specific PFAS, soil properties, the vertical PFAS soil-concentration profile, and the distance between the contaminated soil interval and groundwater. The AF values are reported in Table 1 for the three target PFAS.

The value for PFOS is significantly larger than for the other two PFAS, as would be expected. Notably, the AF values are 1 for both PFOA and PFHxS. This indicates that attenuation in the vadose zone is minimal for both PFAS for this system, in contrast to PFOS. This difference reflects the impact of two primary factors. The first is the greater retention of PFOS due to greater magnitudes of solid-phase and air-water interfacial adsorption compared to the other two. The second factor is the difference in soil-concentration distributions illustrated in Fig. 3. Whereas the highest PFOS concentrations occur near the surface, the highest concentrations for PFOA and PFHxS occur at depth. As a result, the distance between the high-concentration interval and groundwater is significantly shorter for PFOA and PFHxS.

The SSLs determined with the Tier 3 and 4 modules are the same for PFOA and PFHxS because of the AF = 1 values. These results illustrate that the simplest, Tier 4 approach may in some cases be sufficient, especially for the shortest-chain PFAS given that they typically experience comparatively low magnitudes of adsorption and retention. Concomitantly, the results also indicate that it may often be important to account for vadose-zone attenuation for longer-chain PFAS to determine representative SSLs. This can be done using the Tier 3 model.

The field-measured soil and porewater data were also used for SSL calculations. Specifically, the mean C_t/C_{pw} ratios reported in Table 2 for Site 1 were used to determine the distribution-conversion term ($\frac{\theta_w}{\rho_b}R_d$) in the revised SSL DAF equation (Tier 4). The distribution-conversion term determined in this manner was then multiplied by the same target groundwater concentration and DF used above. The SSLs determined by this approach are presented in Table 3. Inspection of the values shows that they are in the same range as those determined with the Tier 3 and 4 models for PFOA and PFHxS, and to the SSL determined with the Tier 4 model for PFOS. This analysis illustrates the utility of employing field-measured data for supporting SSL determinations.

The collection of porewater with the suction lysimeter is a dynamic process and the resultant concentrations may be influenced by a number of factors [29–31]. Uncertainty remains regarding the robustness of porewater-concentration data collected with the suction lysimeter. The results in Table 3 can be used to evaluate the representativeness of the soil and porewater data. Recall that the Tier 4 approach employs a distribution-conversion term that was calculated for each PFAS using measured values for multiple input parameters (Eqs. 2 and 3), including PFAS-specific parameters K_{oc} and K_{aw} as well as a soil-specific parameter (A_{aw}). The similarity of the SSLs obtained from the field-measured C_t/C_{pw} ratios to the SSL values calculated with Tier 4 indicates that the distribution-conversion terms determined with the two approaches are similar. This suggests that the soil-porewater data provided a robust characterization of PFAS distribution in the soil for this site. And, given that the Tier 4 calculations are based on assumptions of linear, equilibrium adsorption, the similarity suggests that the porewater samples represent equilibrium concentrations. This result illustrates that field measured soil and porewater data can be used as an alternative for determining the distribution-conversion term.

Table 4
Calculated site-specific soil screening levels for Site 1 determined by Monte Carlo analysis. All concentrations reported in μg/kg.

Soil Screening Level		Tier 3	Tier 4	Standard EPA Approach
PFOS	Median	16.3	2.0	0.70
	5^{th}-95^{th} percentile	30–8.0	3.6–0.96	1.3–0.32
PFOA	Median	0.19	0.19	0.13
	5^{th}-95^{th} percentile	0.41–0.11	0.41–0.10	0.26–0.06
PFHxS	Median	0.24	0.24	0.19
	5^{th}-95^{th} percentile	0.43–0.10	0.46–0.10	0.36–0.08

The number of paired soil and porewater samples is limited for Site 1. Therefore, the paired data collected for all source areas is also used to determine SSLs. These installation-wide results are discussed in subsection 3.5.

3.4. Impact of Parameter Uncertainty and Parameter Sensitivity on SSLs

As discussed previously, the PFAS-LEACH Excel tool allows for explicit assessment of input-parameter uncertainty via two methods. Ranges for selected parameters were propagated through the model simulations using a Monte Carlo approach (SI-5). The parameter ranges considered are presented in Table SI-3. The ranges for each parameter were determined based on the standard deviation of the aggregated measurements for the individual layers. This approach results in calculated SSLs accompanied by uncertainty intervals.

The SSLs and ranges determined with the Monte Carlo approach are presented in Table 4. The median SSL values reported in Table 4 are very similar to the SSLs presented in Table 3. Inspection of the table reveals that the SSLs range by approximately a factor of 4 for all three PFAS. This represents a relatively narrow range considering the variability of multiple input parameters incorporated in the analysis. This analysis provides a means by which to assess the impact of parameter uncertainty due to spatial/temporal variability and measurement/estimation uncertainty on calculated SSLs. It is important to recognize that conducting such an analysis requires the availability of data sets sufficient to support the determination of means and variances.

Table SI-4 provides a summary of the computed retardation factors, attenuation factors, and dilution factors derived from the Monte Carlo analysis, which can be inspected to assess their comparative impacts on SSL uncertainty. Notably, the DF ranges by a factor of approximately four, which results from variability in both Ksat and recharge. The range in DF contributes significantly to the overall SSL uncertainty. The total retardation factor, which is a primary component of the distribution-conversion term, varies by a factor of two or less and also contributes to SSL uncertainty. Uncertainty in air-water interfacial retardation, due primarily to uncertainty in A_{aw}, is the primary contributor for retardation. The uncertainty in the AF is comparatively small. This assessment

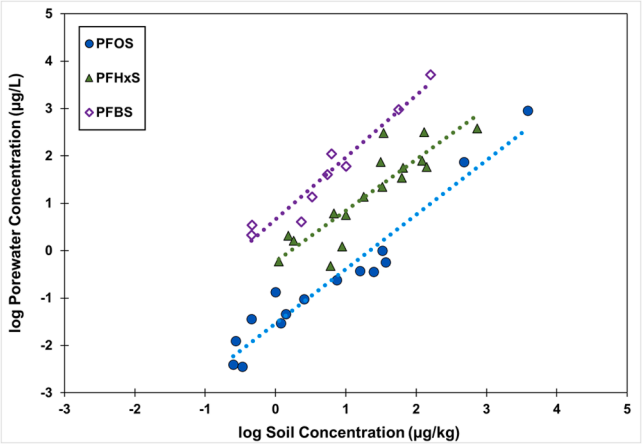

Fig. 6. Field-measured soil and porewater concentrations for PFOS, PFHxS, and PFBS for Installation 4.

highlights which parameters provide the greatest potential contributions to SSL uncertainty and therefore should receive greater focus for characterization.

The SSLs determined with the Tier 3 and 4 methods using both mean parameter values (Table 3) and the Monte Carlo analysis (Table 4) are much greater than the generic EPA Regional Screening levels for all three PFAS. For example, the Tier 3 SSLs for PFOS are approximately 500-times larger than the generic EPA value. Notably, the lowest values in the ranges reported in the Monte Carlo analysis are larger than the generic EPA levels. These results illustrate how the application of site-specific calculations may produce SSLs that are more representative of the site under investigation, and thus provide more robust information for decision making.

In addition to assessing the impact of parameter uncertainty, the Monte Carlo approach can also be used to conduct sensitivity analyses. These can be useful for situations wherein insufficient data are available to establish parameter variability for a given site. They are also useful for evaluating the impact of different site-condition scenarios on SSLs. For an example of the latter case, a site located in a more humid climatic zone may have larger magnitudes of recharge, higher mean water contents, and shallower groundwater compared to an arid site, which would likely result in lower DF and AF values. For another example, soils at a particular site may be finer grained and have large OC and metal-oxide contents, which would likely result in greater retention and correspondingly larger AF and distribution-conversion term values.

A limited analysis was conducted to illustrate the impact of site conditions on SSLs, using PFOS as an example. The analysis focused primarily on DF and the retardation terms, which were shown above to contribute significantly to SSL variability. The magnitudes of infiltration rate and groundwater flux were varied, producing DF values that ranged from close to 1 (minimal dilution) to more than 3-times greater than the EPA default of 20. In addition, parameters mediating the magnitude of air-water interfacial area were varied to produce air-water interfacial retardation factors ranging from close to 1 to almost 200-times larger. These parameter ranges resulted in Tier 3 and Tier 4 SSLs that ranged by more than two orders of magnitude. This highlights the large range over which SSLs can potentially vary, and the benefits of accounting for site-specific conditions when determining SSLs.

3.5. SSL determination for four installations

The final phase of the study involved the determination of SSLs for the four installations, focusing on installation-wide application. Measured data from the paired soil and porewater samples were used to help parameterize the DAF equation. Only paired data for which both soil and porewater concentrations exceeded the detection limit were used for the analysis of the soil-porewater relationship. Data sets with at least 6 paired samples were included in the analysis, resulting in data reported for 11 PFAS. The combined data represent 594 individual paired samples. Extreme outliers, defined by a Z-score $> \sim 2.5$ were not included. These totaled 15 data points, representing 2.5 % of the total. The results of the regressions for all measured data are presented in Table SI-5.

An example of the regression plots is presented in Fig. 6 for PFOS, PFHxS, and PFBS. These results are representative of the measurements obtained for all four installations. The concentrations in general span approximately 3–5 orders of magnitude, providing robust data sets. Inspection of Table SI-5 shows that apart from a few cases for the shorter-chain PFAS, the slopes are close to 1 for all regressions. This indicates that adsorption is generally linear, consistent with the results of the Tier 2 modeling. The NRMSE values are ≤ 0.16 except for the cases with poor r^2. It is observed that the regression (Eqs. 6 or 7) providing the best fit

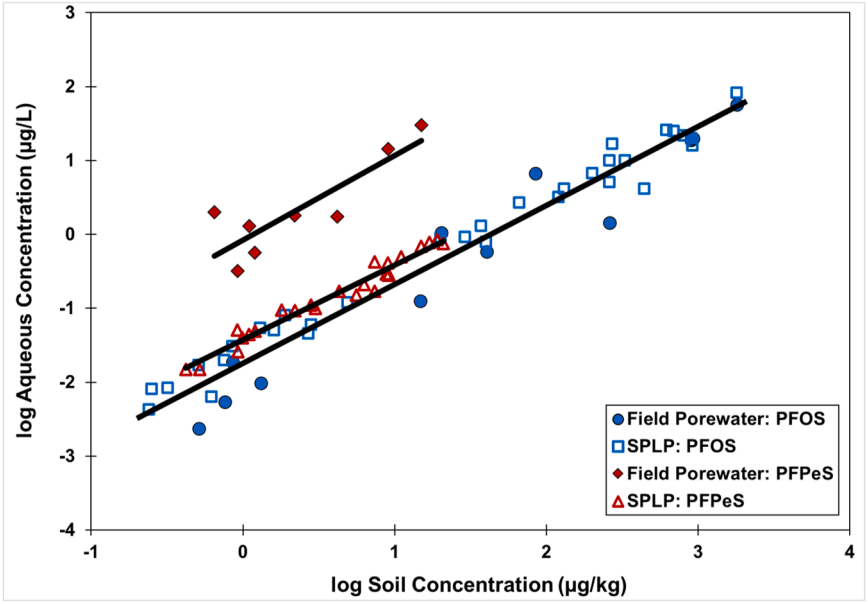

Fig. 7. Comparison of field-measured soil and porewater concentrations to SPLP measured concentrations for PFOS and PFPeS for Installation 2.

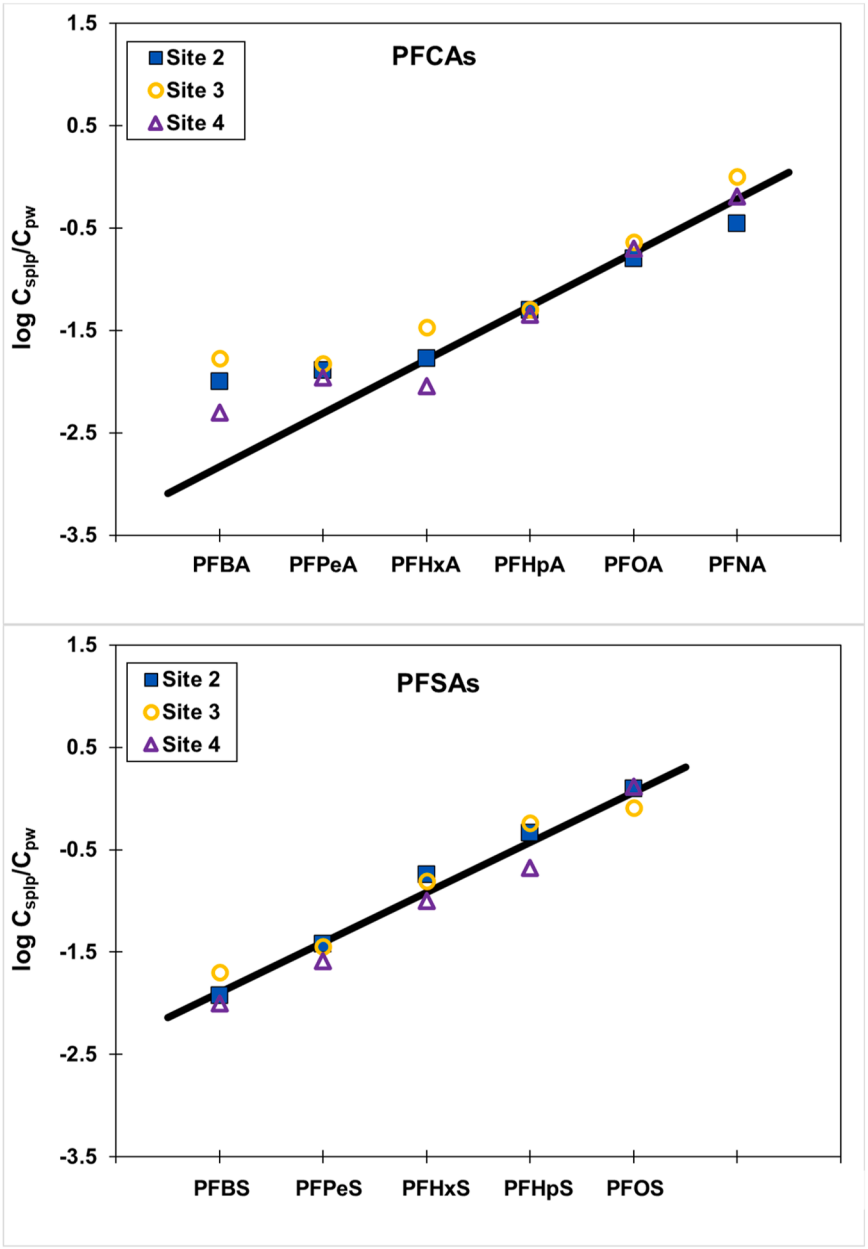

Fig. 8. Comparison of aqueous concentrations measured by SPLP tests (C_{splp}) to those measured for in-situ porewater samples (C_{pw}) for paired samples. (Top) Perfluorocarboxylic acids (PFCAs) [y = 0.52x-3.36, R^2= 0.997], (Bottom) Perfluorosulfonic acids (PFSAs) [y = 0.49x-2.39, R^2= 0.995].

varies among the data. This illustrates the importance of testing both regressions presented in Eqs. (6) and (7).

The regression intercepts represent the log of the distribution-conversion term as discussed above. The intercepts for PFOS are larger than for PFOA, PFHxS, and the other PFAS, which reflects the greater adsorption and retention of PFOS as discussed in Subsection 3.3. The magnitudes of the intercepts range across almost three orders of magnitude as a function of the PFAS. The impact of differences in the magnitudes of retention is observed in Fig. 6. The distribution-conversion terms obtained from the regression intercepts are used to determine SSLs. For Installation 1, they are compared in Table 3 to those determined using the Site 1 soil and porewater data. The two sets of SSLs are similar, indicating consistency between the site and installation-wide measurements.

SPLP tests were also conducted for comparison to the field-measured soil and porewater data. Data are available for the same 11 PFAS as for the soil-porewater data. The combined data represent 742 individual paired samples, with 19 (2.5 %) identified as extreme outliers. Examples of the SPLP data are presented in Fig. 7 for PFOS and PFPeS. The results of the regressions for all measured data are presented in Table SI-6. It is observed that the regression slopes are close to 1 for all but two cases, indicating generally linear solid-phase adsorption. In contrast to the soil-porewater regressions, the SPLP intercepts exhibit minimal differences across PFAS at the two significant-digit level. SPLP data are compared to the field-measured soil-porewater data in Fig. 7. The SPLP concentrations for PFPeS are much lower than the corresponding porewater concentrations for a given soil concentration. Conversely, the SPLP and porewater concentrations are similar for PFOS. This aspect is examined further by direct comparisons of SPLP and porewater concentrations.

The aqueous concentrations measured with SPLP are compared to paired field-measured porewater concentrations in Fig. 8 for three of the installations. Data were not available for the full range of PFAS for Installation 1. The results are quite consistent across the three installations. Significant differences are observed between the two sets of

Table 5
Installation-wide SSLs (all values in μg/kg).

PFAS	EPA RSL[a]	Standard EPA DAF[b]	Revised EPA DAF[c]	*Installation 1*		*Installation 2*		*Installation 3*		*Installation 4*	
				SPLP-DAF[d]	C_t/C_{pw}-DAF[e]	SPLP-DAF[d]	C_t/C_{pw}-DAF[e]	SPLP-DAF[d]	C_t/C_{pw}-DAF[e]	SPLP-DAF[d]	C_t/C_{pw}-DAF[e]
PFOS	0.031	0.23	3.1	1.0	1.2	1.5	4.4	0.73	5.6	0.30	2.7
PFOA	0.061	0.07	0.26	NA	0.14	0.57	0.41	0.42	0.70	NA	0.30

Note: DF set to 20 (EPA default)
Note: target groundwater concentration set to 0.004 μg/L
[a] From https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables for drinking water protection (accessed November 2024)
[b] Koc from literature [6]); foc = EPA default (0.2 %)
[c] Koc from literature ([6]); foc = EPA default (0.2 %); Kaw from literature ([22]); A_{aw} from literature ([23])
[d] Kd measured from SPLP test
[e] porewater-to-soil conversion term determined from field-measured soil and porewater concentration data

measurements, with the magnitude of the difference a function of the specific PFAS. The differences result from the 20–1 dilution and the saturated conditions used in the SPLP test. It is observed that the results for the two shortest-chain PFCAs deviate from the regression fitted to the long chains. This may reflect the impact of solid-phase adsorption, for which similar deviations from long-chain regressions are observed for short-chain PFAS (e.g., [6,32]). These deviations have been attributed to the increased contribution of inorganic soil constituents to adsorption. These results highlight that the use of SPLP data to represent in-situ porewater concentrations is problematic. This supports the alternate use of SPLP data as a means to determine site-specific K_d values as employed herein.

The SSLs calculated for the four installations using the soil-porewater and SPLP data are presented in Table 5. Calculations are presented only for PFOS and PFOA, the two PFAS for which MCLs are currently set. Note that the DF is set to the EPA default of 20 for all four locations to facilitate the comparisons. Similar to the prior results, the SSLs determined with the field-measured soil and porewater data are larger than both the EPA RSL and standard EPA DAF values. Notably, they are similar to the SSLs determined with the revised DAF approach. This latter method accounts for the impact of air-water interfacial adsorption in the distribution-conversion term. The similarity between the two sets of SSLs illustrates an advantage of using soil-porewater measurements as a means to determine the distribution-conversion term, as the measurements implicitly incorporate the impact of all retention processes influencing PFAS distribution in the soil.

The SSL values determined using the SPLP data are also larger than both the EPA RSL and standard EPA DAF values. This suggests that employing a site-specific measured K_d rather than the default impacted the SSL determinations for all four sites. However, it is observed that the SPLP SSLs for PFOS are smaller than the values determined with the revised DAF and soil-porewater methods. This likely reflects the fact that the SPLP measurements do not account for air-water interfacial adsorption. This can be addressed by using the SPLP K_d values in the revised DAF equation. In contrast, the SPLP values are similar to the revised DAF and soil-porewater values for PFOA.

4. Conclusions

A framework for developing SSLs was illustrated in the study, employing the PFAS-LEACH platform and multiple sources of input-parameter determination. Advanced mathematical modeling was employed to characterize and quantify PFAS leaching in the support of developing site-specific SSLs. The model application and validation efforts were demonstrated to be successful. Specifically, the model produced simulations of water contents and PFAS porewater concentrations that were consistent with the measured data sets. This advanced modeling effort supported the application of simpler models to successfully determine site-specific SSLs. The efforts highlighted that the importance of representing relevant retention processes to accurately simulate PFAS transport in the vadose zone carries over to the determination of soil screening criteria. For example, the SSL determined with the Tier 3 model for PFOS was significantly larger than the values determined with the standard EPA DAF approach, reflecting, in particular, the contribution of air-water interface adsorption to attenuation.

One major advantage of the Tier 3 model is that it allows for a nonuniform distribution of initial soil concentrations. In contrast, the standard and revised DAF-based approaches are based on an assumption that soil concentrations are uniform from the ground surface to the bottom of the vadose zone. The Tier 3 model relies on several simplifying assumptions that may limit its applicability in complex field settings. These include the assumptions of one-dimensional, steady-state flow, a homogeneous and uniformly unsaturated vadose zone, and linear adsorption. The Tier 4 model, as a modified version of the EPA DAF method, inherits the strengths and limitations of the original DAF framework. These constraints should be carefully considered when applying the methods to ensure that results are interpreted within the appropriate context of their assumptions. However, the Tier 3 and Tier 4 methods provide site specificity for SSL determinations in contrast to the use of generic SSLs. The methods are also significantly simpler and less costly to apply compared to the Tier 1 and 2 advanced numerical models. Thus, the Tier 3 and Tier 4 methods represent an intermediate approach useful for deriving site-specific SSLs that balances site specificity with the constraints and costs associated with detailed site characterization.

Field-measured paired soil and porewater concentrations were used successfully to determine the distribution-conversion term in the DAF equation. The terms were shown to be a function of the specific PFAS. A major advantage of these data is that they represent the distribution of PFAS within the field soil samples. Concentrations measured with the SPLP test were shown to deviate from the corresponding field-measured porewater concentrations for most PFAS, illustrating their direct use in the DAF equation is problematic. An alternate approach was employed wherein the SPLP measurements were used to determine K_d values.

The SSLs determined with the site-specific methodology were a factor of three to more than two orders of magnitude larger than the generic EPA RSL values, depending upon the PFAS. The conditions employed in the development of the RSLs may often not be representative of the project site. In addition, the RSLs do not account for PFAS-specific transport and retention behavior in the vadose zone. As a result, the RSLs are likely to be overly conservative for many PFAS-impacted sites. This is a particular concern when funding for mitigation and clean-up is limited compared to the inventory of impacted sites. This study illustrates that determining site-specific SSLs that are more representative of site conditions and associated risks can help ensure that funds are directed to the sites that pose the greatest risk. In this regard, the site-specific SSLs obtained with the proposed framework can be used as one means to determine source strength for purposes of assessing the relative risk posed by different source zones present at a facility or across multiple facilities.

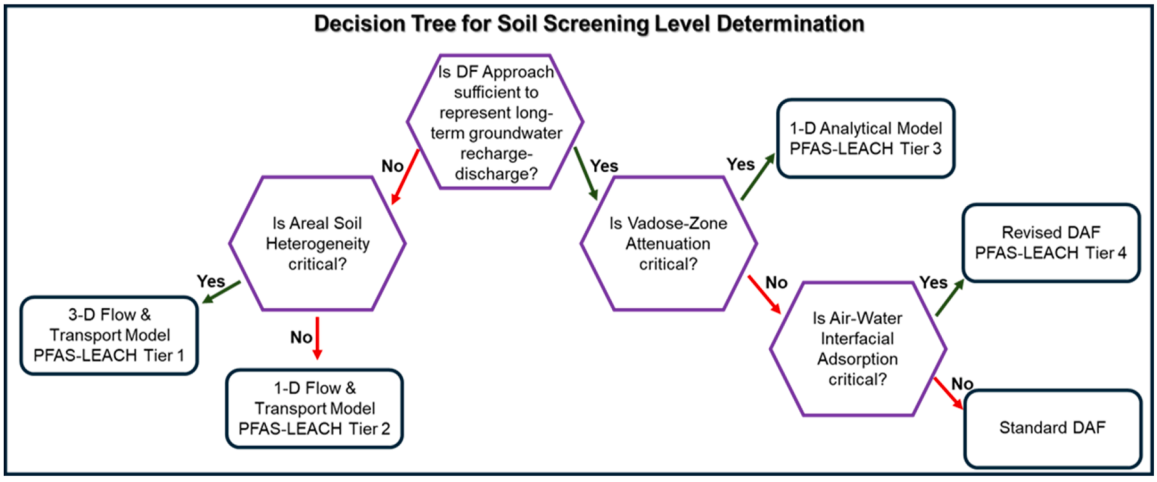

Fig. 9. Transport and fate-based decision tree for selecting methods to use for SSL determination.

The approach and methodology developed herein for determining site-specific PFAS soil screening criteria can be applied to other PFAS-impacted sites. This can be accomplished by one of three means. The first would be to conduct advanced modeling as done herein, to establish a detailed characterization of PFAS distribution within the soil. This approach would include laboratory-determination of key parameters. Recognizing that this approach may not be feasible in many cases, the second approach would entail application of the Tier 3 model along with limited laboratory and/or field-based measurements of key parameters. The final approach would use the Tier 4 method, which requires the least time and effort. The approach used will depend upon several factors, including the project objectives, the amount and type of information available, and the available resources. A decision tree to aid in the selection of the most appropriate method to employ for SSL calculations is presented in Fig. 9. This tree is based on factors relevant to representing PFAS transport and fate, with the complexity of the approach decreasing from left to right. It is recognized that input and resource requirements will generally also decrease from left to right. Finally, this decision tree is specific to the determination of SSLs, which is a metric based on long-term representations of PFAS behavior and site conditions.

CRediT authorship contribution statement

Mark Brusseau: Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Bo Guo:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Marcy Nadel:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation. **Min Ma:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation. **Joseph Quinnan:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis, Data curation. **Dina Drennan:** Data curation, Formal analysis, Investigation, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazmo.2026.100011.

Data availability

The data are presented in the manuscript and are also available upon request.

References

[1] M.L. Brusseau, R.H. Anderson, B. Guo, PFAS concentrations in soils: background levels versus contaminated sites, Sci. Total. Environ. 740 (2020) 140017.
[2] Y. Wang, U. Munir, Q. Huang, Occurrence of per- and polyfluoroalkyl substances (PFAS) in soil: Sources, fate, and remediation, Soil Environ. Health 1 (2023) 100004.
[3] U.S. Environmental Protection Agency (EPA), Soil Screening Guidance: User's Guide, Second Edition, 9355, . Office of Solid Waste and Emergency Response. Publication, 1996, pp. 4–23.
[4] U.S. Environmental Protection Agency (EPA), Soil Screening Guidance: Technical Background Document. Office of Solid Waste and Emergency Response, Second Edition, Publication EPA, 1996.
[5] U.S. Environmental Protection Agency (EPA), *Guidance for Quality Assurance Project Plans for Modeling*. Office of Environmental Information, 2002.
[6] M.L. Brusseau, Field versus laboratory measurements of PFAS sorption by soils and sediments, J. Hazard. Mat. Adv. 16 (2024) 100508.
[7] S.M. Ghaznavi, M. Choudhary, M. Hannan, G.M. Hettiarachchi, O.G. Apul, A critical review of per- and polyfluoroalkyl substances adsorption by soil, J. Hazard. Mat. Org. 1 (2025) 100001.
[8] M.L. Brusseau, Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface, Sci. Total Environ. 613-614 (2018) 176–185.
[9] M.L. Brusseau, Quantifying the adsorption of PFAS and hydrocarbon surfactants at the air–water interface: A systematic review and meta-analysis of surface-science measurements, molecular-modeling simulations, and environmental-application results, Wat. Res. 284 (2025) 123952.
[10] M.L. Brusseau, B. Guo, Revising the USEPA dilution-attenuation soil screening model for PFAS, J. Hazard Mater. Lett. 4 (2023) 100077.
[11] B. Guo, J. Zeng, M.L. Brusseau, A mathematical model for the release, transport, and retention of per-and polyfluoroalkyl substances in the vadose zone, Water Resour. Res. 56 (2) (2020) e2019WR026667.
[12] J. Zeng, B. Guo, Multidimensional simulation of PFAS transport and leaching in the vadose zone: Impact of surfactant-induced flow and subsurface heterogeneities, Adv. Water Resour. 155 (2021) 104015.
[13] J. Zeng, M.L. Brusseau, B. Guo, Model validation and analyses of parameter sensitivity and uncertainty for modeling long-term retention and leaching of PFAS in the vadose zone, J. Hydrol. 603 (2021) 127172.
[14] B. Guo, J. Zeng, M.L. Brusseau, Y. Zhang, A screening model for quantifying PFAS leaching in the vadose zone and mass discharge to groundwater, Adv. Water Resour. 160 (2022) 104102.

[15] J. Smith, M.L. Brusseau, B. Guo, An integrated analytical modeling framework for determining site-specific soil screening levels for PFAS, Water Res. 252 (2024) 121236.
[16] M. Ma, J. Smith, M.L. Brusseau, B. Guo, User guide: Excel tool for Tiers 3 and 4 models of PFAS-LEACH (PFAS-LEACH-Analytical and PFAS-LEACH-DAF), University of Arizona, 2025.
[17] M.L. Brusseau, N. Yan, S. Van Glubt, Y. Wang, W. Chen, Y. Lyu, B. Dungan, K. C. Carroll, F.O. Holguin, Comprehensive retention model for PFAS transport in subsurface systems, Water Res 148 (2019) 41–50.
[18] M.G. Schaap, F.J. Leij, M.T. van Genuchten, Rosetta: A computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions, J. Hydrol. 251 (3-4) (2001) 163–176.
[19] Y. Zhang, M.G. Schaap, Weighted recalibration of the Rosetta pedotransfer model with improved estimates of hydraulic parameter distributions and summary statistics (Rosetta3), J. Hydrol. 547 (2017) 39–53.
[20] U.S. Department of Agriculture (UDSA). Accessed 2024 (September). National Water and Climate Center. Available online at: ⟨www.nrcs.usda.gov/resources/data-and-reports/snow-and-climate-monitoring-predefined-reports-and-maps⟩.
[21] R. Russell, B. Guo, J. Zeng, M. Brusseau, C. Schaefer, S. Shea, C. Higgins, T. Ferre, Combining field datasets and mathematical modeling to quantify PFAS leaching and mass discharge at an AFFF-impacted site, Water Res. (2025) 124063.
[22] M.L. Brusseau, S. Van Glubt, The influence of molecular structure on PFAS adsorption at air-water interfaces in electrolyte solutions, Chemo 281 (2021) 130829.
[23] M.L. Brusseau, Determining air-water interfacial areas for the retention and transport of PFAS and other interfacially active solutes in unsaturated porous media, Sci. Total Environ. 884 (2023) 163730.
[24] M. Xu, Y. Eckstein, Use of weighted least-squares method in evaluation of the relationship between dispersivity and field scale, Groundwater 33 (6) (1995) 905–908.
[25] M.S. Al-Suwayian, Discussion of "use of weighted least-squares method in evaluation of the relationship between dispersivity and field scale, in: M. Xu, Y. Eckstein. (Eds.), Ground Water 34 (1996) 387–388.
[26] M.L. Brusseau, B. Guo, PFAS concentrations in soil versus soil porewater: Mass distributions and the impact of adsorption at air-water interfaces, Chemo 302 (2022) 134938.
[27] M.L. Brusseau, Influence of chain length on field-measured distributions of PFAS in soil and soil porewater, J. Hazard. Mat. Lett. 4 (2023) 100080.
[28] M.Th van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, Soil Sci. Soc. Am. J. 44 (5) (1980) 892–898.
[29] J. Quinnan, M. Rossi, P. Curry, M. Lupo, M. Miller, H. Korb, C. Orth, K. Hasbrouck, Application of PFAS- mobile lab to support adaptive characterization and flux-based conceptual site models at AFFF releases, Remediation 31 (2021) 7–26.
[30] C.E. Schaefer, G.M. Lavorgna, D.R. Lippincott, D. Nguyen, E. Christie, S. Shea, S. O'Hare, M.C. Lemes, C.P. Higgins, J. Field, A field study to assess the role of air–water interfacial sorption on PFAS leaching in an AFFF source area, J. Contam. Hydrol. 248 (2022) 104001.
[31] J. Costanza, C.D. Clabaugh, C. Leibli, J. Ferreira, R.T. Wilkin, Using suction lysimeters for determining the potential of per- and polyfluoroalkyl substances to leach from soil to groundwater: a review, Environ. Sci. Technol. 59 (2025) 4215–4229.
[32] T.M.H. Nguyen, J. Braunig, K. Thompson, J. Thompson, S. Kabiri, D.A. Navarro, R. S. Kookana, C. Grimison, C.M. Barnes, C.P. Higgins, M.J. McLaughlin, J.F. Mueller, Influences of chemical properties, soil properties, and solution pH on soil-water partitioning coefficients of per- and polyfluoroalkyl substances (PFASs), Environ. Sci. Technol. 54 (2020) 15883–15892.