

**PROJECT TITLE**

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## Summary

Per- and polyfluoroalkyl substances (PFAS) are a class of contaminants used in widespread industrial and commercial applications in the past 60 years. PFAS are of particular concern due to their widespread distribution and persistence in the environment, and potential adverse health effects to humans. The research focuses on understanding the impact of historic PFAS releases on the environment by elucidating their fate and transport in the subsurface focusing in the area of Killingworth, Connecticut. In this project, we investigated the mechanisms of retention of PFAS in soil, and we integrated laboratory and field observations to develop a predictive model using HYDRUS. Specifically, Experimental work was conducted to investigate the PFAS partitioning in the solid phase through batch adsorption experiments under various environmental conditions. Field observations and historic data from recent environmental site investigations were utilized to parametrize and calibrate the predictive fate and transport model. Changing environmental conditions including precipitation patterns, PFAS subsurface levels, and pumping rates were assessed in the modeling scenarios to investigate the potential impact of PFAS contamination in the area. The research provided outcomes of scientific merit with respect to PFAS partitioning to soils and critical evaluation of modeling parameter to identify the extent and predict the transport of the PFAS plume in the Killingworth area.

## Introduction

Per- and polyfluoroalkyl substances (PFAS) have been used for decades in industrial applications and consumer goods such as cleaners, stain repellents, fire-fighting foams, cosmetics, and cookware.<sup>1</sup> PFAS are highly persistent in the environment, bioaccumulative, and pose a toxicological risk on living organisms<sup>1</sup> and human health.<sup>2</sup> Although there has been considerable effort to eliminate their use since the 1990s, as of 2016 an estimated population of 5.2 million Americans are exposed to drinking water with detectable levels of the most predominant PFAS compounds, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA).<sup>3,4</sup> According to the 2013-2015 U.S. Environmental Protection Agency's (EPA) third Unregulated Contaminant Monitoring Rule (UCMR3), PFAS are present in drinking water in several areas across the U.S, and, among others in New England, exceeding the EPA advisory level of 70 ppt.<sup>3,5</sup> Recently, EPA released the 2021-2024 PFAS Strategic Roadmap with bolder policies to protect public health and the environment, and hold polluters accountable.<sup>6</sup> Amongst other strategies, the EPA Roadmap suggested setting a national primary drinking water regulation for PFOA and PFOS, and health advisories for GenX and perfluorobutane sulfonic acid (PFBS).<sup>6</sup>

Several accidental releases of aqueous film forming foam (AFFF) related to fire-fighting activities have occurred in several areas across the State of Connecticut. In 2019, two accidental spills of AFFF from Bradley International Airport released more than 60,000 gallons of AFFF and de-icing material into Farmington River, impacting the water systems in the area. Releases resulted in increased concentrations of PFAS in surface water, sediments, soil, and fish.

The research focused on a Connecticut site where the groundwater has been impacted by PFAS, and particularly in the area of Killingworth, where recent investigations revealed that PFAS contamination has reached residential wells.

The impacted area includes Killingworth's Fire Department and the nearby lot where AFFF was used for fire training exercises and extends half a mile east to residential properties where elevated PFAS concentrations were identified. Elevated levels of PFAS have been detected in the tap water of the Town Hall and more than 15 homes in Killingworth, but the extent of the PFAS contamination in the subsurface is currently unknown. There is a mobile home neighborhood less than half-mile to the north that is also impacted. The area is of high priority for the State given the unknown extent of the impacted soil and groundwater, and the public health concerns.

### **Objective(s)**

The project goal was achieved through the following objectives:

#### **O1: Understanding of PFAS retention in vadose zone**

Phase partitioning to soils is one of the major retention mechanisms for all ligands, including PFAS. The major outcome of this objective is the parametrization to describe transport processes including modified sorption coefficients.

#### **O2: Development and parameterization of predictive transport model**

In this objective, a subsurface flow and PFAS transport model was calibrated and validated using water level data and PFAS concentrations recorded in wells within the study area using a modified version of HYDRUS.

#### **O3: Assessment of PFAS impact on Connecticut sites**

The model was used in a predictive mode to assess the impact of PFAS on the Killingworth area and gain insights on potential impacts on other Connecticut sites. In this objective, several scenarios were simulated using the calibrated model to assess the impact on the extent of PFAS contamination and provide insights into PFAS fate and transport in CT.

### **Results/Discussion**

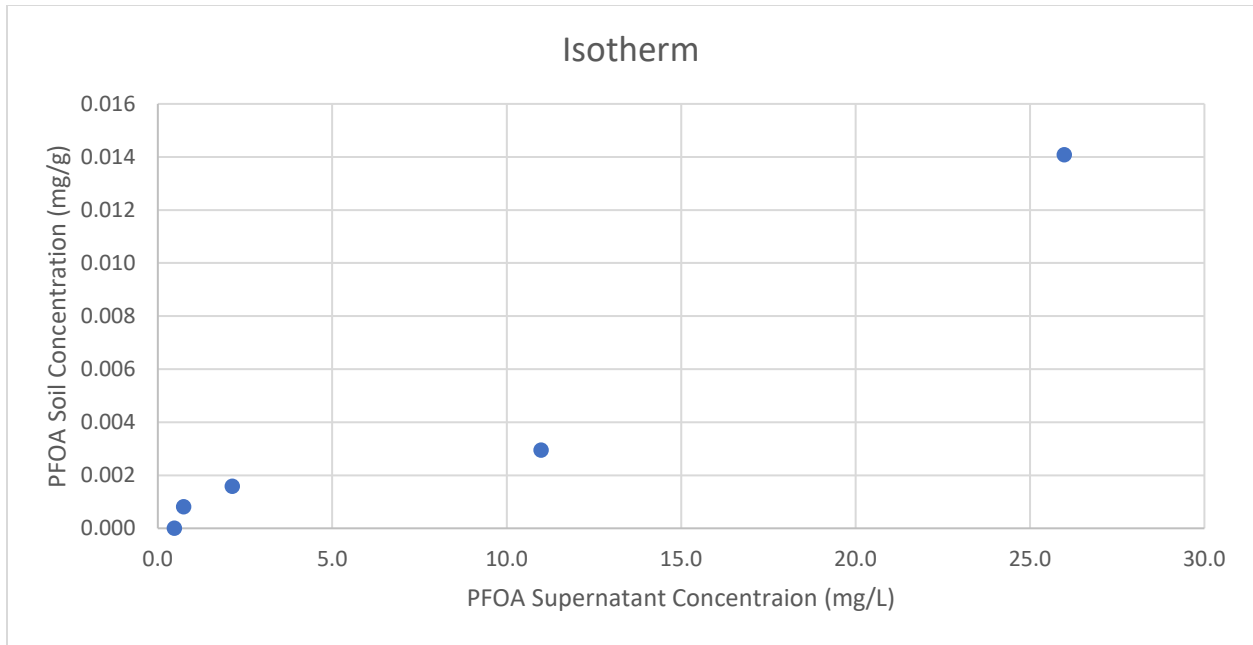
#### **Site Characterization**

A series of characterization methods were utilized to characterize soil samples including measurement of pH, hydraulic conductivity, and soil particle analysis.

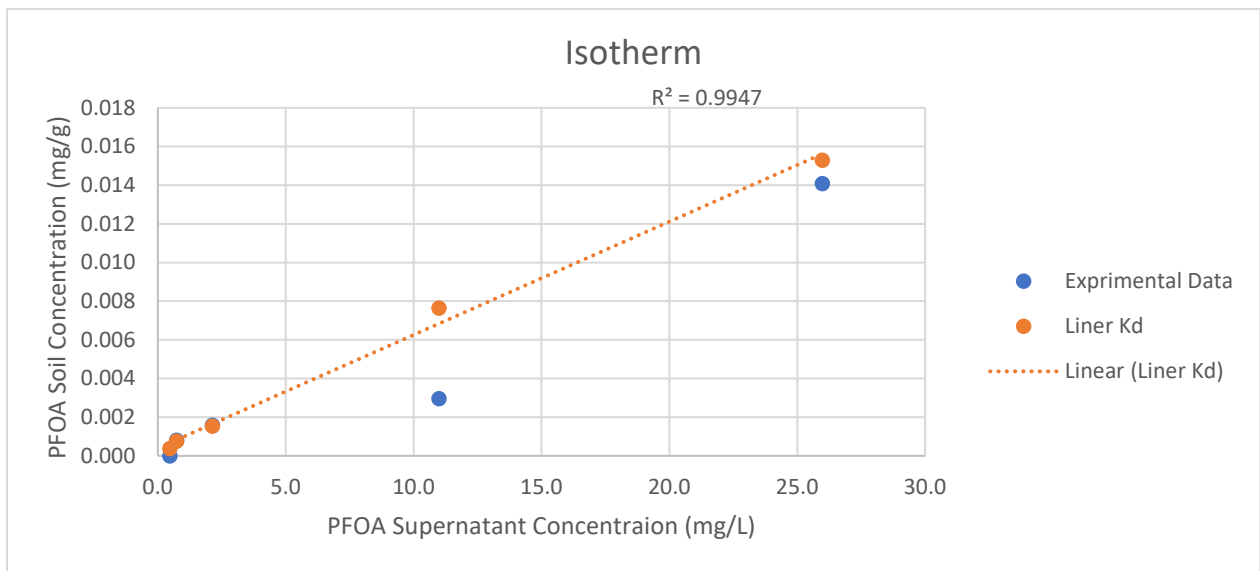
PFAS levels in the field were utilizing previous investigation results conducted by Ensafe in 2022 and previous data collected in nearby wells.

#### **Sorption Experimental Results**

Batch sorption experiments were conducted utilizing Connecticut soils. The soil was pretreated to remove any organic material using hydrogen peroxide. The experiments were conducted without altering the pH conditions of the soil samples and kept constant ~6.5 throughout the duration of the experiment. The ionic strength of the batches was 0.01 M NaNO<sub>3</sub>. The measurement method included direct measurement of PFOA in the solid matrix.



Liner Kd for site-specific conditions



A linear sorption partitioning coefficient was calculated to fit the adsorption data which was estimated at  $K_d = 0.0015 \text{ L/g}$  or  $1.52 \text{ L/Kg}$ . The  $K_d$  calculated for the CT soils is of the lowest reported in the literature. A wide range of parameters have been emerged in the literature ( $0-1769 \text{ L/Kg}$ , with the median value of  $K_d = 3.49 \text{ L/Kg}$ ). The estimated  $K_d$  is ranked in the 1<sup>st</sup> quartile of  $K_d$  values. The variability of those parameters is a well-documented issue in the field, and more investigation is needed to further understand the influence of physicochemical parameters in sorption behavior.

Modeling Results

In this objective, a subsurface flow and PFAS transport model was calibrated and validated using water level data and PFAS concentrations recorded in wells within the study area. To simulate the unsaturated zone flow and transport we developed a 2D HYDRUS 5.2 model, and to simulate the saturated zone a MODFLOW/MT3D-USGS model was created. HYDRUS 5.2 was chosen because it is one of few models capable of simulating PFAS sorption to the air-water interface. Subsurface flow was simulated given site-specific parameters derived by the experiments described previously. Sensitivity analysis was performed to assess the model's sensitivity to parameter uncertainty.

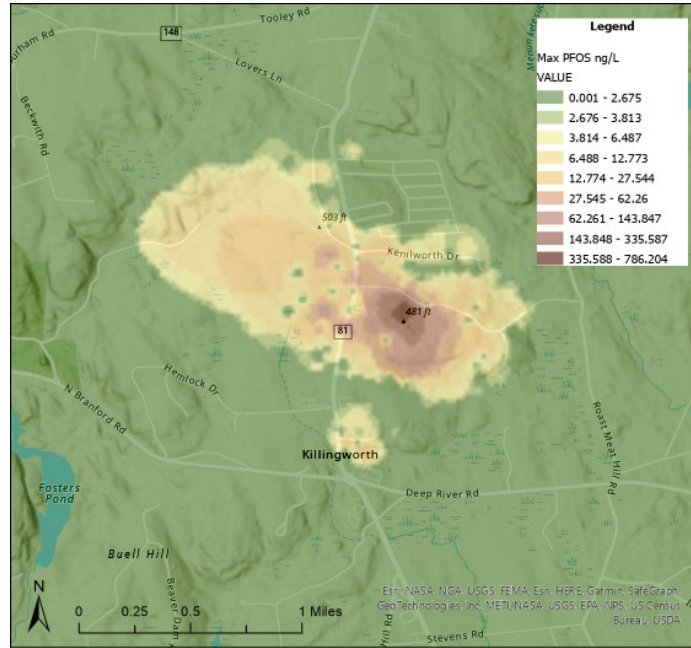


**Figure 1: Killingworth, Connecticut Aerial View**

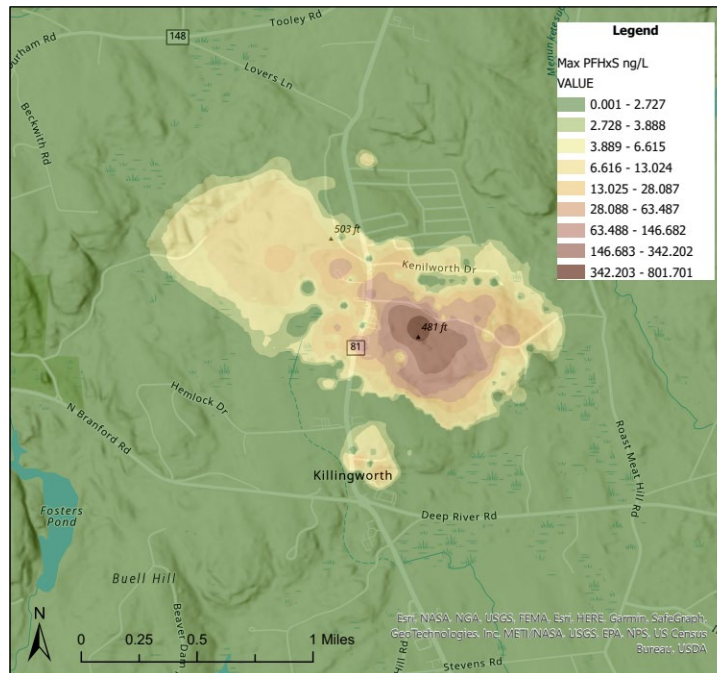
The modeling outlined in this work is designed to simulate the conditions of the firefighting training site found in Killingworth, Connecticut. In the past, firefighters in Killingworth conducted a series of FTAs in an open field located near the cities townhall. These past firefighting training exercises left considerable quantities of AFFF on the top of the soil, providing an ample source of PFOS, PFHxA, and other PFASs leaching. This site is highlighted in figure 1. In addition to the training related contamination shown above, the Connecticut Department of Energy and Environmental Protection (DEEP) has concerns over a potential second contamination source at potential second site shown in figure 1.

In order to better understand the extent of the contamination from the firefighting training site and to confirm the existence of a second source, DEEP carried out a groundwater sampling campaign from April 2021 through December 2021. This campaign collected groundwater samples from 80 different sampling well locations and analyzed these samples for 18 different types of PFAS. Of the PFAS types tested for, only 9 types of PFAS were detected. Of those detected, only 6 PFAS types were found at values above the advisory threshold of 70 ppt (ng/L). These types were PFOA, PFOS, PFHxS, 9Cl-PF3ONS (F-53B Major), PFBS, or PFHxA.

Of particular interest were the spatial results for PFOS, PFHxS, and PFOA. PFOS and PFHxS, being the two biggest PFAS components of legacy AFFFs, were expected to be found at their greatest concentrations under the firefighting training site. The data matches this expectation, as shown in the PFOS and PFHxS plumes in figures 2 and 3.

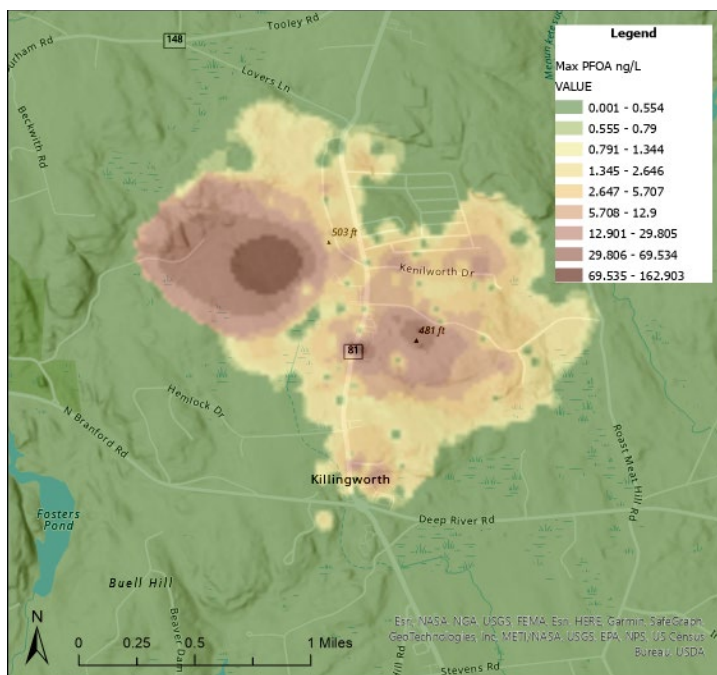


**Figure 2: PFOS Plume**



**Figure 3: PFHxS Plume**

The PFHxS plume largely mirrors the shape of the PFOS plume, which aligns with AFFF as the source. However, the PFOA plume does not follow the same spatial distribution, instead seeing its highest detected concentration at the suspected second source. This is shown in figure 4.



**Figure 4: PFOA Plume**

This difference in plume locations reinforces the hypothesis that there are two different sources of PFAS contamination in Killingworth, Connecticut, and that those sources are situated in the presumed locations. On a smaller geographical scale, testing well results from near the firefighting training site prepared by Leggette, Brashears & Graham, Inc. in 1988 give the depth from the top of the soil to water table as 6 meters.<sup>8</sup> This same report gives the soil type as silty sand, a type of sand categorized most frequently in the USDA NRCS National Engineering Handbook as sandy loam.<sup>9</sup> This categorization was further verified by soil analysis of samples from the site, which also provided a hydraulic conductivity  $K_s = 1.42E-04$  cm/s.

The model was set to run for 14,610 days, or 40 years, to capture the multi-decade nature of the PFAS transport in the site and to simulate the period from 1981 to 2020. Output for the model was set to print every 500 days and on the final 14,610th day. Solute transport used the Crank-Nicholson scheme for time weighting and the Galerkin finite elements space weighting scheme. Millington & Quirk tortuosity was used. The mesh was initialized as a vertical XZ plane with a height of 6 meters and a width of 30 meters. 6 meters was chosen as it is the empirical depth to the water table at the site, while 30 meters was chosen to provide sufficient length to observe any lateral phenomena while remaining within the length of the firefighting training site. The

location of the cross-section being modeled is shown below in figure 5, with the Killingworth town hall also highlighted for reference.



**Figure 5: Model Cross-Section Location**

The mesh was discretized to have the distance between each pair of nodes be 20 centimeters both in the horizontal and vertical directions. The top boundary layer was set to be an atmospheric boundary, while the bottom boundary layer was set to be a free drainage layer. The vertical boundary layers were both set to be no flux boundaries. To appropriately model a partially saturated zone, the pressure heads in the model were initialized to linearly increase from the soil surface downward to the water table. The model parameters are summarized in Table 1.

<b>Soil Hydraulic Parameters [Units]</b>	<b>Parameter Definition</b>	<b>Values</b>
$\theta_r$ [-]	Residual soil water content	0.065
$\theta_s$ [-]	Saturated soil water content	0.41
$\alpha$ [1/m]	$\alpha$ for soil water retention curve	7.5
$n$ [-]	$n$ for soil water retention curve	1.89
$K_s$ [m/day]	Saturated hydraulic conductivity	0.123
$I$ [-]	Tortuosity parameter for conductivity	0.5
<b>Disp. L. [m]</b>	Longitudinal dispersivity	0.453
<b>Disp. T. [m]</b>	Transverse dispersivity	0.0453



### Table 1: Base Model Soil Hydraulic Parameters

Three different PFAS constituents (PFOA, PFOS and PFBS) were simulated, along with a tracer. A set of models was run that only included soil sorption and another set that included both soil and air-water interface sorption. The soil sorption coefficients for PFOS were taken from Silva et al.<sup>10</sup> while air-water interface sorption coefficients were sourced from Brusseau et al 2022.<sup>11</sup> For PFOA, PFOS and PFBS they are 0.003, 0.05 and 0.00017 m respectively. The fourth solute is a tracer.

The homogenous model for the Killingworth site for PFOA is shown in Figure 5-7. It takes 12.88 years for 4 ppt to reach the water table without AWI sorption and 21.23 years to reach the water table with AWI sorption included.

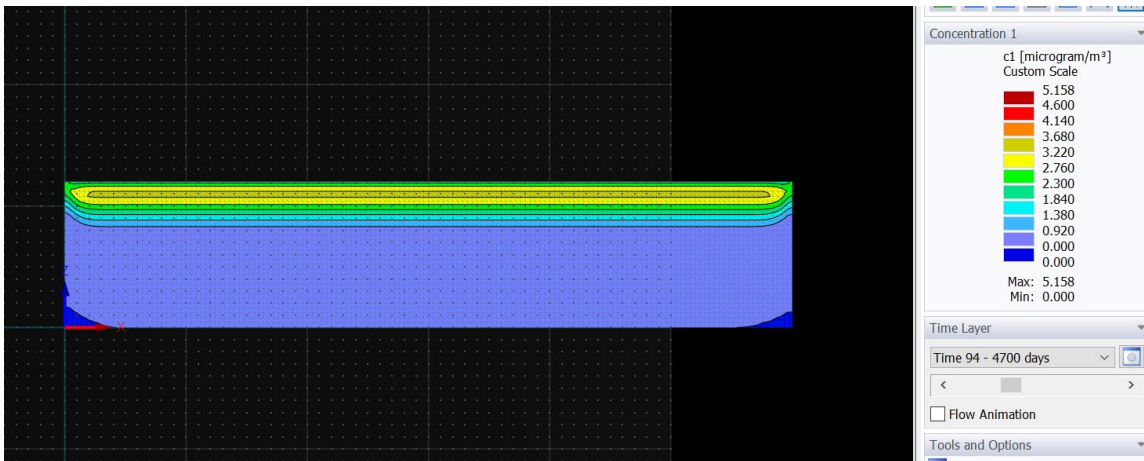


Figure 5: PFOA without AWI sorption, homogenous model

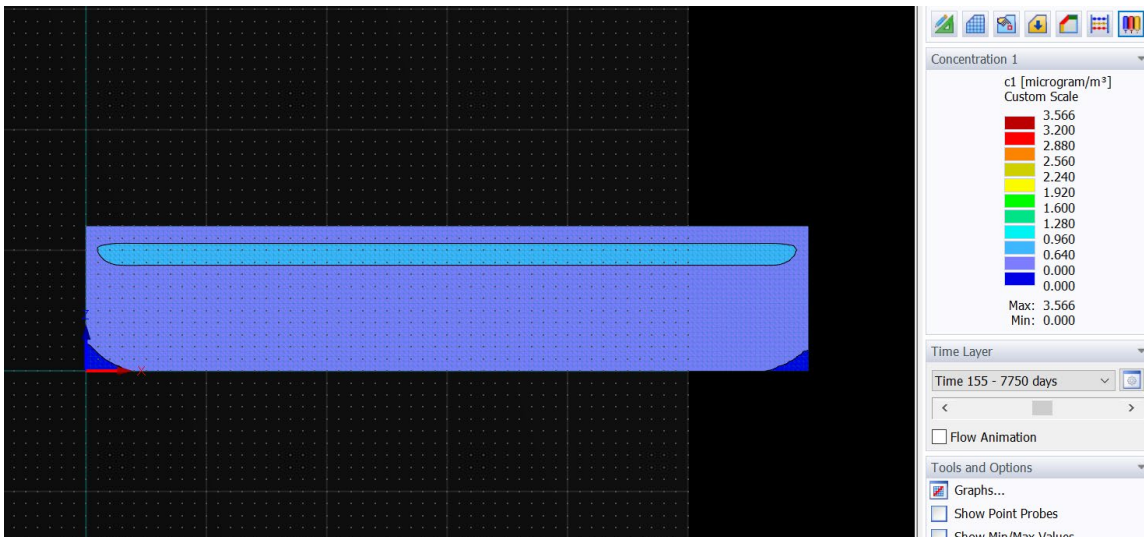
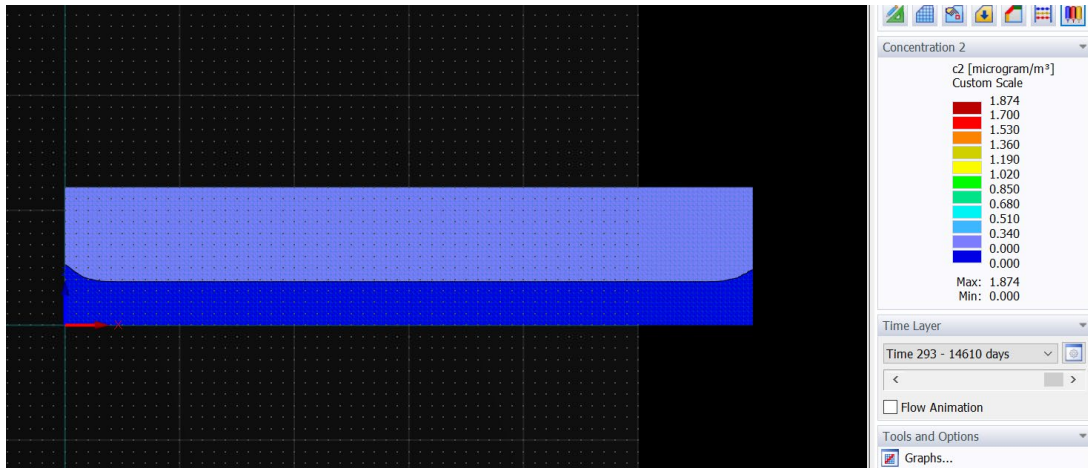
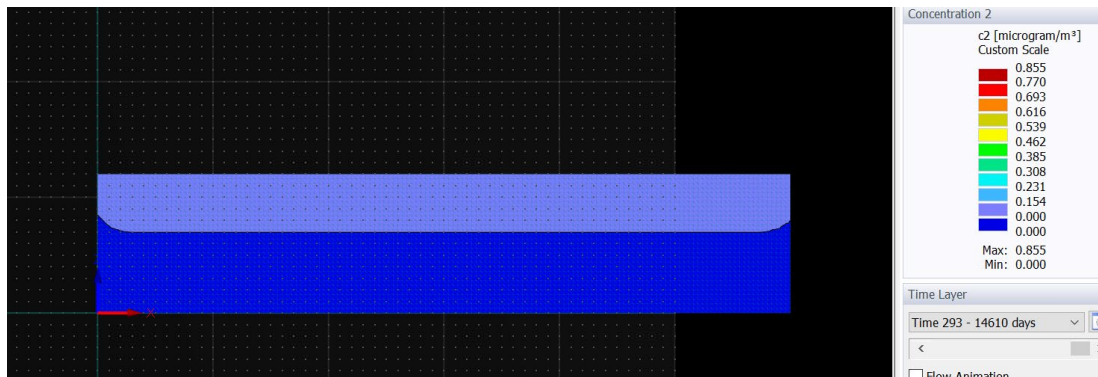


Figure 6: PFOA with AWI sorption, homogenous model

As shown in Figure 7 and 8 PFOS without and with AWI sorption respectively, does not reach the water table over the 40 year period.

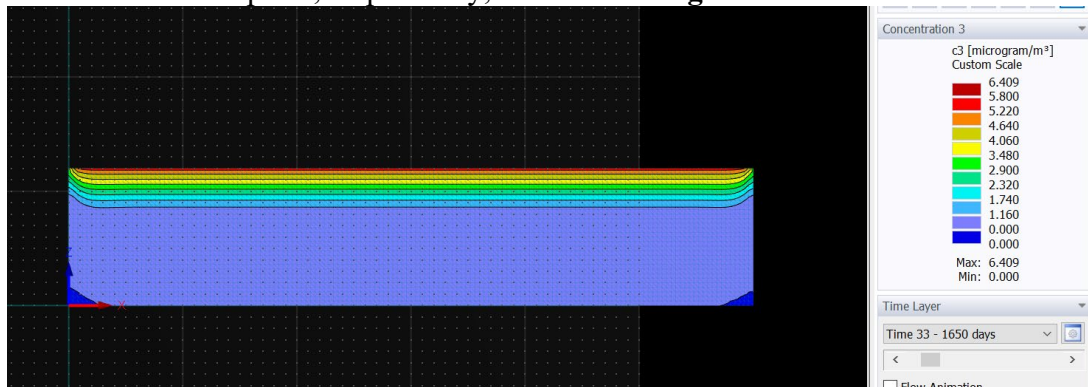


**Figure 7: PFOS without AWI sorption, homogenous model**

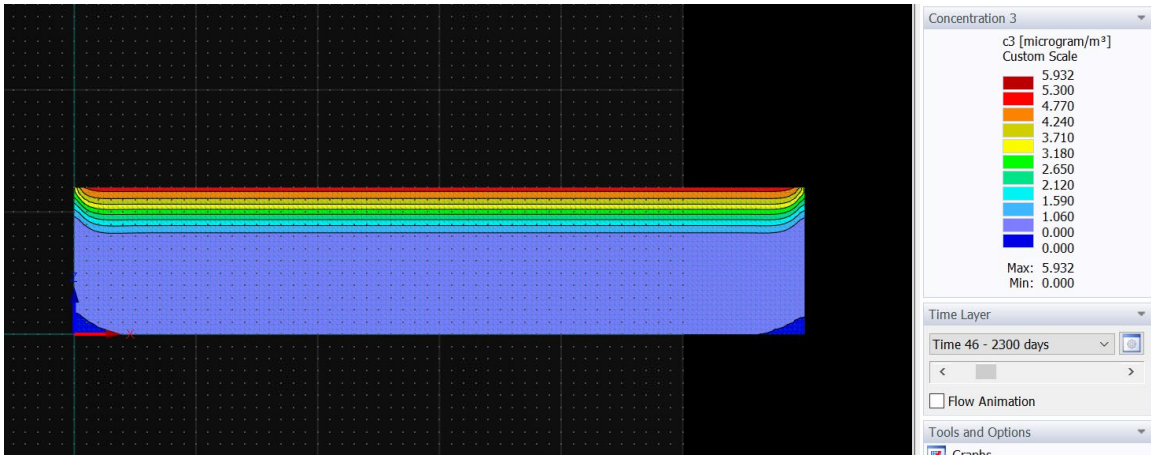


**Figure 8: PFOS with AWI sorption, homogenous model**

PFBS reaches the water table in 4.52 years, and 6.3 years when modeled without and with AWI sorption, respectively, as shown in Figures 9 and 10.

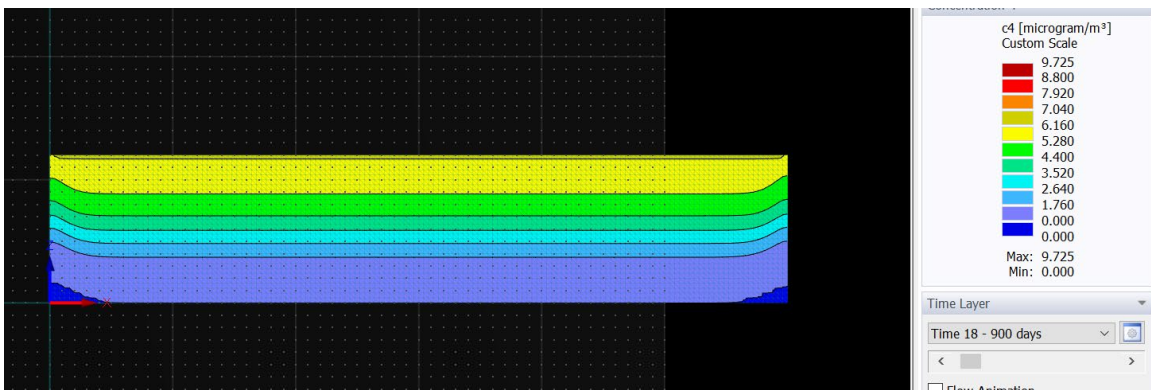


**Figure 9: PFBS without AWI sorption, homogenous model**



**Figure 10: PFBS with AWI sorption, homogenous model**

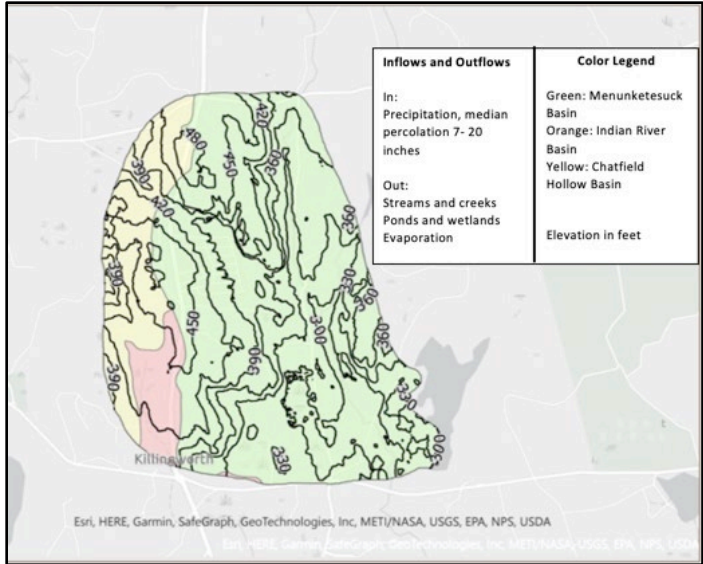
A tracer was also modeled for comparison. It was subject to the same atmospheric conditions and solute concentration, however it was modeled without soil or AWI sorption. As shown in **Figure 11** it reached the water table in 2.47 years.



**Figure 11: Tracer homogenous model**

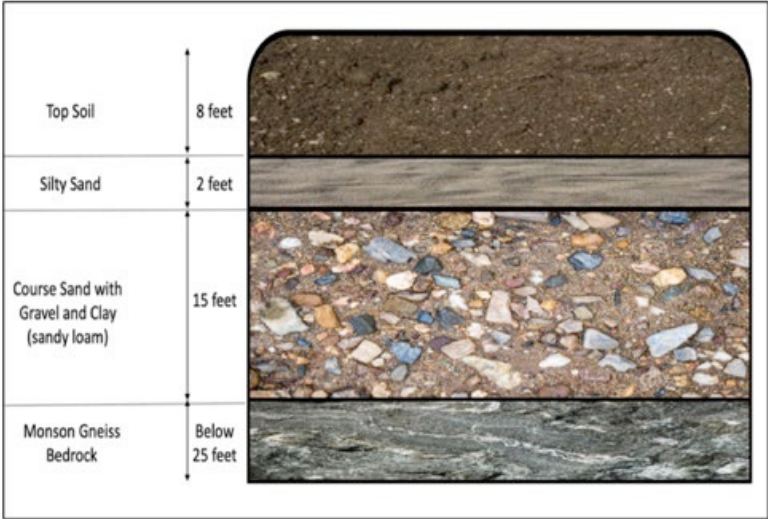
### Three-dimensional Model

A conceptual model of the groundwater system was first created, as seen in Figure 12. The boundaries of the study area were arbitrarily chosen, with the North and South boundaries limited by major roadways. The Killingworth Reservoir lies within the Southeast border of the study area and was chosen as a boundary. One of the purposes of this model was to assess whether the reservoir would be affected by the PFOS plume transport, so this eastern border was of interest.



**Figure 12: Aerial View of Conceptual Model**

In addition to the aerial view, typical cross-section is shown in Figure 13, developed based on information from the Site Investigation Report.<sup>12</sup>



**Figure 13: Cross-sectional View of Conceptual Model**

*MODFLOW Calibration Results*

The values in Table 4 provide a comparison of simulated head values to observed head values provided in the Site Investigation Report and the calibrated RMSE for the hydraulic heads in the base model.

Observation Site	Observed Head (feet)	Simulated Head (feet)	RMSE (feet)
MW1	441	442.77	2.12
MW2	438	440.35	
MW3	438	436.17	
MW4	433	432.67	
MW11	430	435.40	
MW12	436	434.43	
MW13	440	438.02	
MW14	438	437.42	

**Table 4: Calculations for The Regression Model of Simulated and Observed Heads**

*MT3D-USGS Calibration Results*

The results of the calculations can be observed in graphically in Table 5. RMSE calculation value of 0.55 ppb, shown in Table 5, was considerably high for the validity of simulation. Reasoning for this discrepancy can be attributed to the possibility of other PFO source locations. This was deduced because of high observation values in areas that were predicted to have lower concentrations, specifically at the Town Hall and Town Garage. A possible second PFOS source could be occurring south of the FTA site because of these unprecedented observations. When the Town Garage and Hall observations were excluded from the RMSE, a more reasonable value of 0.09 ppb was calculated, shown in the last column of Table 5.

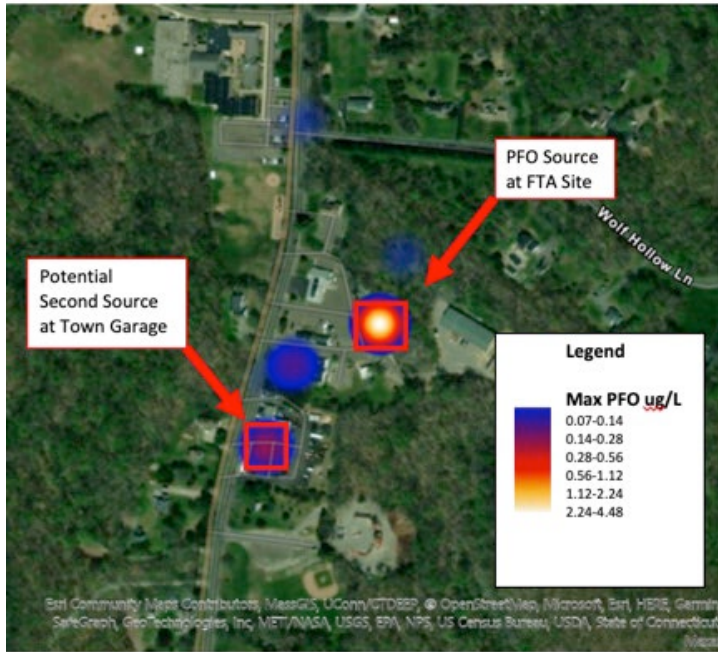
Site	TOB	SSM	Residual	Square Residual	RMSE	RMSE Without Garage and Town Hall
MW11	0.136	0.131	0.005	2.5E-05	0.5523	0.0929
MW14	4.44	4.600	-0.16	2.5E-02		
TW1	0.174	0.293	-0.119	1.4E-02		
MW1	0.133	0.136	-0.003	9E-06		
Fire House	1.009	1.067	-0.058	3.3E-03		
Town Hall	0.918	0.504	0.414	1.7E-1		
Town Garage	1.521	0.135	1.386	1.9		

**Table 5: Regression Calculations Model of Observed and Simulated PFOS Concentrations in ppb**

*Potential Second PFOS Source Analysis*

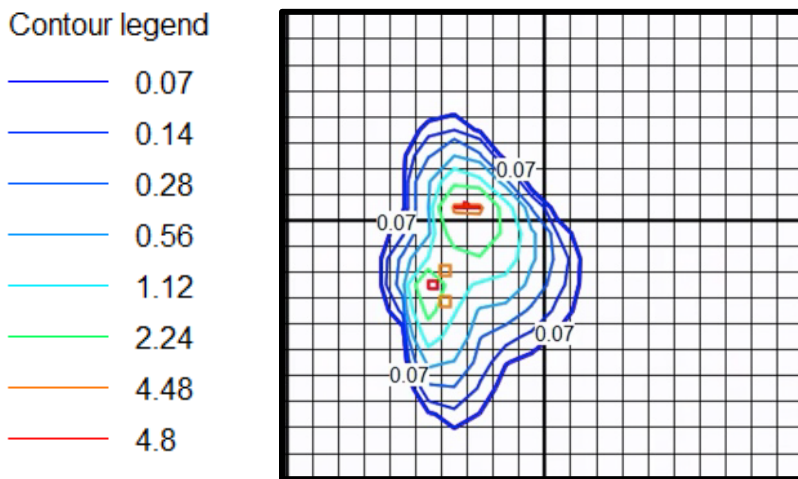
The image in Figure 14 presents a topographic representation of PFOS concentrations recorded in the Site Investigation Report. It provides reasoning to believe a second source may be possible around the Town Garage. However, the data provided only accounts for the source located at the FTA site so potential second source observations, the Town Hall and Town Garage, were

redacted instead of creating a second source. An approximated location of the second source was theorized between the Town Hall and Town Garage, shown in Figures 14 and 15.



**Figure 14: Arial Map Predicting Potential PFOS Second Source**

As demonstrated by the RMSE calculation, adding this second source would allow for all of the concentration observations to be considered. The RMSE calculation for the second source (0.0922  $\mu\text{g/L}$ ) is comparable to the RMSE calculation where the Town Hall and Town Garage observations were omitted, documented in Table 5.

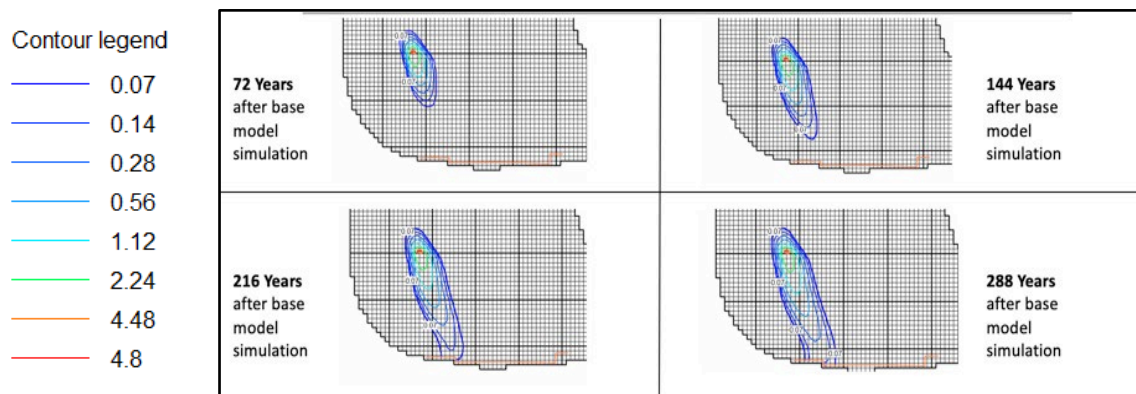


**Figure 15: Model Results Predicting Second Source (concentrations in ppb)**

## Assessment of PFAS impact on Connecticut sites

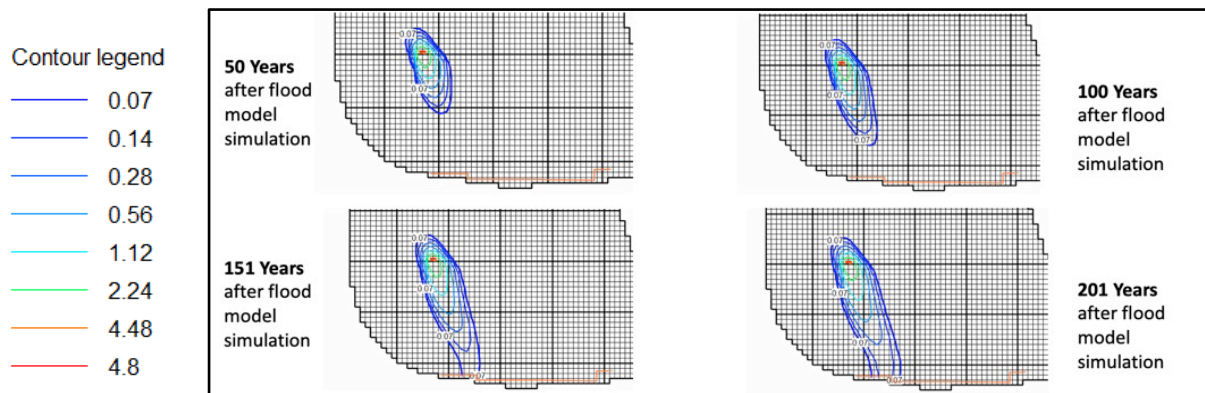
After successful calibration, the model was used in a predictive mode to assess the impact of PFAS on the Killingworth area and assess the effect of varying environmental conditions on the spread of PFAS such as changes in precipitation patterns, and PFAS subsurface levels, and examining if the Killingworth Reservoir is at risk of contamination.

The first predictive simulation conducted assessed the risk of contamination reaching the Killingworth Reservoir, identified as the Southeastern Boundary in the model. The target concentration used in the scenario was 0.07 ppb (70 ppt) detected at the boundary. From model results, it was concluded that there is little risk of the PFOS plume reaching the Killingworth Reservoir. Instead, the contaminant plume moves towards the southern boundary, as shown in Figure 16.



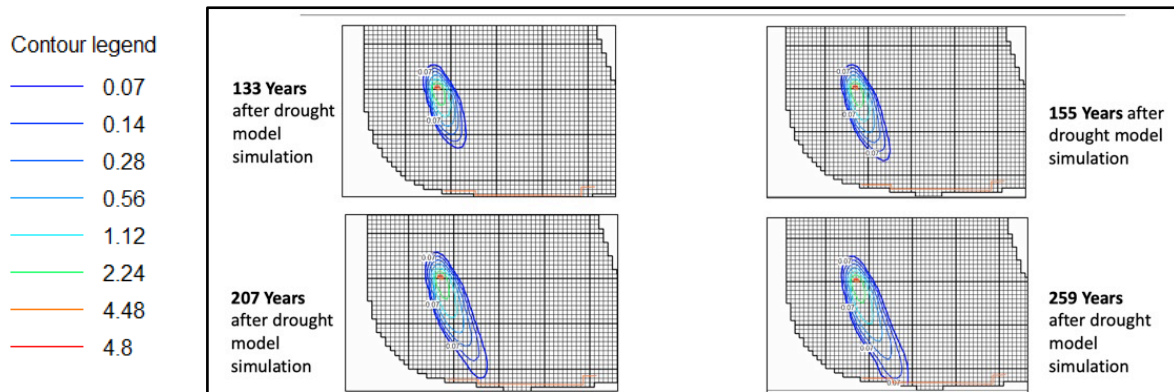
**Figure 16: PFOS Plume Future Projects Occurring in the Base Model**

The groundwater model was also used to simulate outcomes of both drier and wetter conditions. These conditions were simulated by altering the rate of recharge. In order to consider the effects of wet conditions, monthly recharge rates caused by precipitation were increased by both 25% and 50%. The results of increased rates of recharge were visually minor at a 25% increase, but changes to the movement of the plume were observable at a 50% recharge rate increase.



**Figure 17: PFOS Plume Projections Occurring Under 50% Increased Recharge (concentrations in ppb)**

Drought conditions were simulated using similar methods. Instead of increasing the rate of recharge, the recharge rates were decreased from the base model at both 25% and 50%. The future predictions of plume transportation due to a 50% decrease in recharge can be observed in Figure 18.



**Figure 18: PFOS Plume Projections Occurring Under 50% Decreased Recharge (ppb)**

Comparing the future projection results from the base model to the wet and dry conditions models, there is a correlation between aquifer recharge and PFOS plume movement. Under existing hydrological conditions, the plume will exceed the limit of 70 ppt at the southern model border in approximately 216 years. If the region experiences intensified precipitation conditions that resulted in a larger influx of aquifer recharge and higher initial water table levels, the PFOS concentrations would move at a faster rate, reaching the model border after 151 years for 50% recharge change. Alternatively, under dry conditions, where hydrological head levels are lower and groundwater recharge is reduced by 50%, the PFOS plume does not reach the model border until approximately 259 years.

### Conclusions

Mitigating the risks posed by PFAS contamination in soil and groundwater requires accurate prediction of PFAS fate and transport in the subsurface. Despite the fact that PFASs have been widely detected in water bodies globally, their fate and transport in the environment is still not fully understood. An important research priority over the past few years has been to gain a better understanding of the mechanisms of PFAS transport in groundwater, among other pathways. Most of these studies have focused on experimental settings while fewer have studied PFAS transport at field scale. Our research fills this gap by combining experimental studies and flow



and PFAS transport modeling, considering the effects of AWI in the vadose zone, an aspect often neglected in previous studies.

This project developed the first groundwater model to simulate and predict PFAS transport in a Connecticut site and create a framework for future applications in other impacted sites in the state, and the region. An advantage of this model compared to other studies is that it creates an assessment framework that combines field, experimental and numerical methods to enhance the accuracy of PFAS transport modeling.

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