EPA
United States
Environmental Protection
Agency

EPA 600/R-25/153 I July 2025 I www.epa.gov/research

Practical Groundwater Science Guides
Per- and Polyfluoroalkyl Substances (PFAS)

Office of Research and Development
Center For Environmental Solutions and Emergency Response

This page is intentionally left blank

EPA 600/R-25/153 I July 2025 I www.epa.gov/research

Practical Groundwater Science Guides
Per- and Polyfluoroalkyl Substances (PFAS)

Michael Brooks[1], Lee Rhea[1], Matt Rovero[1], Richard Wilkin[1], Jingjing Chen[2], Aderonke Adegbule[3], Carolyn Acheson[4], Junqi Huang[1], and Diana Cutt[5]

[1]U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Subsurface Remediation Branch

[2]Formerly, Oak Ridge Institute for Science and Education (ORISE) Postdoctoral Associate, U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Subsurface Remediation Branch

[3]U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Office of Pollution Prevention and Toxics, Existing Chemicals Risk Assessment Division, Risk Assessment Branch

[4]Retired, U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Land Remediation and Technology Division, Contamination Analysis and Innovative Solutions Branch

[5]U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Technical Support Coordination Division

Disclaimers

Table of Contents

List of Tables

List of Figures

Acknowledgments

This document was produced under the U.S. EPA's Superfund and Technology Liaison Research (STLR) Program as part of a project titled *Per- and Polyfluoroalkyl Substances (PFAS): Practical Groundwater Science Guides for Regional Practitioners*. The STLR Program was designed to encourage Office of Research and Development (ORD) scientists and Regional staff to collaborate on contaminated-site-related issues important to the regions and program offices. This STLR project was championed by the EPA Regional staff, the Superfund and Technology Liaisons (STL) for Regions 2 and 3, the Regional Science Liaison (RSL) for Region 9, the programs offices, and the ORD scientists listed below.

Region 2: William Friedmann, Rachel Griffiths, Ula Filipowicz
Region 9: Matthew Small (RSL)
ORD: Michael Brooks, Lee Rhea, Matt Rovero, Rick Wilkin, Diana Cutt (STL), Jingjing Chen, David Gwisdalla, Jonathan Essoka (STL), Charlena Bowling, Mustafa Bob, and Carolyn Acheson
OCSPP: Aderonke Adegbule
OLEM/FFRRO: Caroline Baier-Anderson

Jed Costanza (formerly with the U.S. EPA), Chunming Su, Stephanie Ross, Sandra Halstead, and Erin Gleason with the U.S. EPA are acknowledged for their internal reviews and helpful comments.

Sandra Goodrow, Catherine Jedrzejczyk, and Jennifer Willemsen of the New Jersey Department of Environmental Protection served as external reviewers, and they are likewise acknowledged for their assistance and helpful comments.

Appreciation is expressed to David Gwisdalla for obtaining ORD contract support for preparation of the initial internal science guides on which this report is based.

Abbreviations/Acronyms

AFFF	aqueous film-forming foam
ASTM	American Society for Testing and Materials
CESER	Center for Environmental Solutions and Emergency Response
CMC	critical micelle concentration
EPA	U.S. Environmental Protection Agency
ETFE	ethylene-tetrafluoroethylene
FEP	fluorinated ethylene propylene
FFRRO	U.S. EPA Federal Facilities Restoration and Reuse Office
GPO	Government Printing Office
HDPE	high-density polyethylene
K_d	includes soil-water partition coefficient
K_{OC}	normalized partition coefficient
LDPE	low-density polyethylene
MS	Microsoft
NAPL	nonaqueous phase liquid
NJDEP	New Jersey Department of Environmental Protection
NTU	nephelometric turbidity units

OC	organic carbon
OCSPP	U.S. EPA Office of Chemical Safety and Pollution Prevention
ORD	U.S. EPA Office of Research and Development
PCTFE	polychlorotrifluoroethylene
PFAS	per- and polyfluoroalkyl substances
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PP	polypropylene
PTFE	polytetrafluoroethylene
PVC	polyvinylchloride
PVDF	polyvinylidene fluoride
QA	quality assurance
QAPP	Quality Assurance Project Plan
RSL	regional screening level
SPLP	Synthetic Precipitation Leaching Procedure

Executive Summary

The Center for Environmental Solutions and Emergency Response (CESER) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. CESER develops and provides applied scientific and engineering solutions, technologies, and cutting-edge innovations to protect and remediate our air, land, and water resources. The focus of the Center's research program is on methods and their cost-effectiveness for prevention and control of pollution to land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and groundwater; and restoration of ecosystems.

The intention of this report is to provide easily digestible information for site assessment and remediation practitioners who work on PFAS-contaminated sites. The topics covered include evaluation of site-specific groundwater vulnerability from PFAS-impacted soils, PFAS groundwater sampling, and ways that surface chemistry and surfactant properties of some PFAS may impact their transport and fate. The document compiles information from three technical briefs that were originally released internal to the EPA titled *Per- and Polyfluoroalkyl Substances (PFAS): Practical Groundwater Science Guides for Regional Practitioners*.

The intended audience for this report includes geologists, hydrogeologists, risk assessors, remedial project managers, and others who work on PFAS-contaminated sites. Users of this report should have a basic understanding of PFAS. The information provided in this document will be of use to stakeholders such as state and federal regulators, Native American tribes, consultants, contractors, and other interested parties.

1 Estimating Site-Specific Groundwater Vulnerability from PFAS-Impacted Soils

1.1 Overview

Tools or approaches based on the latest scientific understanding of the behavior of PFAS in the vadose zone are needed to determine PFAS soil screening or cleanup levels that will protect groundwater. EPA's Soil Screening Level Guidance for the migration-to-groundwater pathway uses a simple linear equilibrium soil/water partition equation, which includes soil-water partition coefficients (K_d), or organic carbon (OC) normalized partition coefficients (K_{OC}), to estimate soil leachate concentrations.

Often, predetermined K_d or K_{OC} values are used to calculate migration-to-groundwater soil screening levels (SSLs). Soil concentration levels above calculated SSLs are expected to negatively impact groundwater quality. This approach works in some cases because K_{OC} is fairly constant for many nonpolar compounds, like trichloroethylene, which interact strongly with soil OC but very little with mineral surfaces (Allen-King et al., 1997). As interest in PFAS has grown, the same approach has been used to predict risk from PFAS-contaminated soil to groundwater, but research has shown that this approach may not be the best practice for predicting vulnerability at specific sites (Anderson et al., 2019; Rovero et al., 2021). Unlike nonpolar compounds, PFAS have a polar head group that increases affinity for mineral surfaces (Nguyen et al., 2020) and surfactant behavior that causes the compounds to collect at air-water interfaces (Brusseau et al., 2019).

Of particular concern with PFAS are the low concentrations that can contribute to negative health outcomes. Effects of exposure to perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are believed to occur at concentrations below what current methodology can detect; therefore, an understanding of PFAS transport and fate, including sorption mechanisms, is important in protecting human health and the environment. If soil-water K_d partition equations are to be used to reliably predict PFAS behavior, more care is required in selecting an appropriate value for use in calculations to account for the more complex sorption mechanisms exhibited by these compounds.

Given the complications of predicting leaching using default K_d and K_{OC} values for PFAS, a synthetic precipitation leaching procedure (SPLP) modified for PFAS is described for deriving site-specific K_d values. These values can then be used to evaluate groundwater vulnerability more accurately from PFAS-impacted soils.

1.2 Estimating Impacts to Groundwater from Contaminated Soil

Various tools, such as the EPA Regional Screening Level (RSL) calculator (U.S. EPA, 2022) or the New Jersey Department of Environmental Protection's (NJDEP's) soil migration to groundwater exposure pathway calculator (NJDEP, 2023), use regulatory limits and physical, chemical, and toxicological properties of compounds and the associated sites to establish screening levels and to predict impacts to groundwater from contaminants in soil that may leach or migrate. These calculators use a target groundwater concentration to determine a permissible soil leachate concentration, and then an acceptable soil screening level. The conversion from soil to leachate concentration is calculated using sorption parameters of a contaminant (K_d or K_{OC} and Henry's law coefficient), along with soil density and porosity according to the linear adsorption equation (U.S. EPA, 1996a):

$$SSL = C_w * \left(K_d + \frac{\theta_w + \theta_a H'}{\rho_b} \right)$$

SSL = soil screening level (e.g., mg/kg)

C_W = target leachate concentration (e.g., mg/L)

K_d : soil-water partition coefficient (L/kg)

θ_w : water-filled porosity (%)

θ_a : air-filled porosity (%)

H' : Henry's law coefficient (dimensionless)

ρ_b : soil bulk density (kg/L)

In this equation, SSL includes the fraction of contaminant sorbed to soil, dissolved in pore water, and contained within pore gases. A site-specific dilution-attenuation factor (DAF) can be calculated using the following equation (*Figure 1*; U.S. EPA, 1996b):

$$DAF = 1 + \frac{K * i * d}{I * L}$$

DAF: dilution-attenuation factor (dimensionless)

K: hydraulic conductivity (m/yr)

i: hydraulic gradient (m/m)

d: mixing zone depth (m)

I: infiltration rate (m/yr)

L: length of area of concern (m)

The target leachate concentration divided by the DAF is the estimated final groundwater concentration.

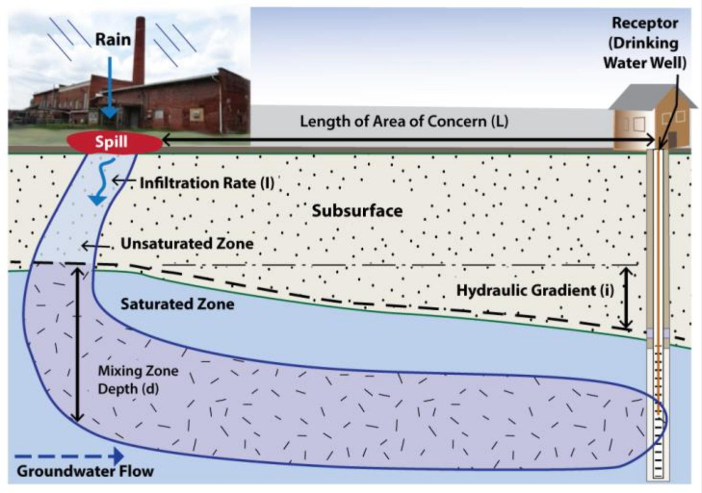

Figure 1.1. Diagram showing factors contributing to dilution-attenuation factor calculation

This process works well when the migration behavior is well defined, but error in the K_d value used in calculations can produce a nearly proportional error in final groundwater concentration or SSL. If site-specific concentrations are needed, it is critical that an appropriate K_d is used for each site in assessing groundwater vulnerability from PFAS-contaminated soil. Because soil properties and PFAS concentration and composition can vary at any given site, it may be necessary to calculate K_d values at multiple locations and at multiple depths to select parameters that accurately represent PFAS migration potential to groundwater. Remedial project managers should work with technical support geologists and hydrogeologists to determine additional sampling locations based on these variables.

1.3 Selecting an Appropriate K_d

Currently, the EPA RSL calculator includes default partition coefficient (i.e., K_d, K_{OC}) values for PFOA, PFOS, perfluorobutane sulfonate, perfluorononanoic acid, and perfluorohexane sulfonate and allows for custom or site-specific values to be used for derivation of screening levels (U.S. EPA, 2022b). Experimentally determined or model-predicted K_d values are also available for many PFAS in the literature, using a wide variety of methodologies. These reported values span several log units even among relatively simple PFAS (Li et al., 2018; Rovero et al., 2021). Reported values of select PFAS are graphically summarized by Rovero et al. (2021) using box and whisker plots in ***Figure 1.2***.

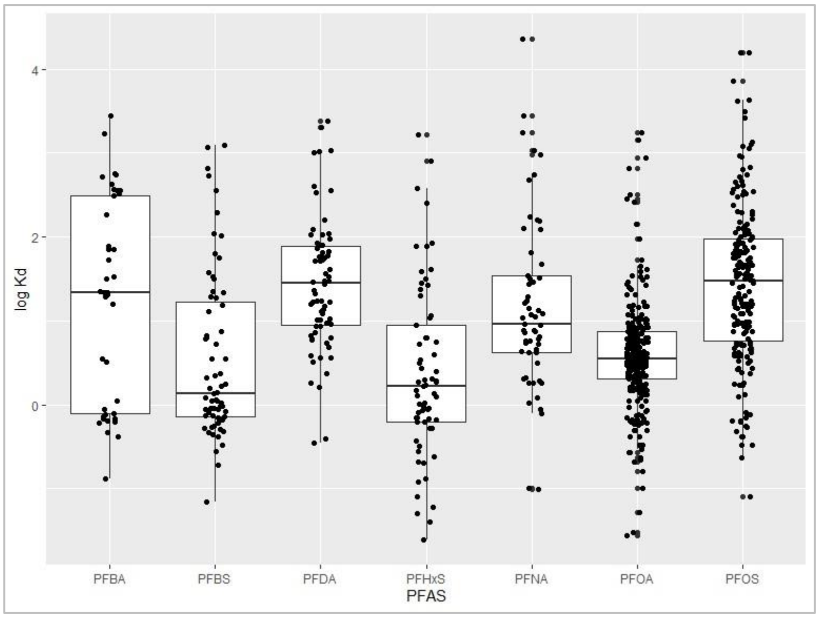

Figure 1.2. Box and whisker plot of log Kd values reported in the literature for seven anionic PFAS, showing values spanning several log units for each compound. The bottom and top of the box indicates the median, and whiskers extending above and below each box mark the extent of non-outlying data. Source: Rovero et al. (2021)

Outlined below are three approaches to determining PFAS K_d values.

Experimentally Determined K_d

These values are determined by measuring the partitioning behavior of PFAS between the soil and aqueous phases. Several factors should be considered if selecting one of these values for use in screening level calculations:

How similar are the soil conditions between the experiment and the applicable site?

There are conflicting data regarding the influence of various soil properties on PFAS sorption, and the effect of these properties differ among PFAS compounds. The conflicting data make it challenging to assess whether two soil sites are similar. OC and clay-silt content are often cited as important factors (e.g., Fabregat-Palau et al., 2021) but will not guarantee similar sorption behavior.

Did the experiment measure adsorption or desorption?

Partition coefficients calculated by measuring adsorption of PFAS onto soil are typically lower than those calculated by measuring desorption from soil back into solution (Chen et al., 2016; Rovero et al., 2021). Evidence suggests some level of irreversible sorption to soil may also occur (Chen et al., 2016).

Were PFAS introduced to the soil during the experiment?

K_d values calculated when PFAS are introduced to the soil in laboratory conditions are generally lower than values determined using contaminated soil from field sites, even when considering only desorption experiments (Rovero et al., 2021; Zareitalabad et al., 2013). The mechanism behind this difference is unclear.

Each of these considerations requires an understanding of the source of each K_d value used. Practitioners may be able to curate a selection of values suitable for the types of sites they frequently encounter, but any predetermined value should be used with caution.

Model-Predicted K_d

Modeling software (e.g., EPI Suite™, SPARC, COSMOtherm) can predict some properties of chemicals based on their structural compositions. Although experimental values are preferred, this software can be useful for compounds that are difficult to measure due to reactivity, volatility, hazards associated with use, or other considerations. These models can produce octanol-water partitioning (K_{OW}) and K_{OC} values for several common PFAS. EPI Suite™ can predict two values of log K_{OC} using different methods; for PFOS, as an example, they are 3.409 (K_{OW} method) and 4.855 (molecular connectivity index method). Log K_{OC} values for PFOS collected from literature cited in Rovero et al. (2021) have first, median, and third quartile values of 2.67, 3.03, and 3.53, respectively. This places the first model-predicted value near the third quartile, whereas the second predicted value is among the outlying values. Neither value predicted by EPI Suite™ is suitable for all sites, and no site-specific parameters are used in their calculation. Therefore, the use of this type of sorption coefficient is not recommended.

Some studies (e.g., Fabregat-Palau et al., 2021) have reported success in constructing models of K_d or K_{OC} by breaking a database of experimental values into a “training” set for model creation and a “validation” set for confirming that the model parameters selected accurately predict sorption behavior. The scope of application for these models would depend on the data used for model construction and validation. In Fabregat-Palau et al. (2021), for example, all data used in model generation are from laboratory batch studies, yet authors note “K_d values obtained from *in situ* experiments have been shown to be significantly higher”, which suggests the model is inappropriate for use in a risk assessment scenario.

Site-Specific K_d

The technical recommendation for determining groundwater vulnerability from PFAS-impacted soils is the use of site-specific K_d values. These values are determined by analysis of contaminated material from the site under investigation. This approach eliminates or reduces many of the concerns regarding data applicability, although large or geologically complex sites may require multiple K_d measurements.

There is currently no recommended method for determination of site-specific K_d values: however, guidelines for adsorption/desorption testing are provided by the EPA Office of Prevention, Pesticides, and Toxic Substances (U.S. EPA, 2008). Two approaches receiving attention are measuring concentrations through lysimeters installed on site or performing extractions using a modified SPLP.

A lysimeter generally consists of a porous material through which soil pore water is pulled by an applied vacuum into an underground container. When positive pressure is applied via the vacuum line, liquid in the container is forced through a second line to a collection vessel on the surface. Lysimeter installation requires boring a hole to the appropriate depth of the unsaturated zone, packing the area around the device to ensure hydraulic connectivity with the surrounding soil and prevent infiltration from above, and maintaining the vacuum pump on the surface for the duration of sample collection.

Soil core collection (source: EPA 2021)

SPLP is comparatively simple, involving the collection of soil samples from the site, combining a known mass of soil with a known volume of the appropriate extraction fluid, tumbling for 18 hours on an end-over-end mixer, and collecting the resulting solution. Analysis of lysimeter pore water and SPLP solution for PFAS concentration would follow the same procedure after these collection and extraction steps.

Lysimeters have the advantage of measuring the actual condition of pore water at the site, including temporal variability, whereas SPLP leachates are indicative of long-term leaching potential. The installation, operation, and interpretation of results to carry out a lysimeter study are more complex than the steps to perform an analogous SPLP study. Furthermore, it is unclear whether the silica flour commonly used to pack lysimeters will adsorb PFAS and thus reduce PFAS concentration in collected pore water, and it may not be possible to collect pore water in all conditions, particularly in shallow installations or extreme climates. Additional information on the use of lysimeters for PFAS migration is available in Costanza et al. (2025).

Because of the simplicity of implementation for field and laboratory personnel, several states have adopted SPLP for screening risk to groundwater from PFAS. Some technical recommendations for adapting the procedure to be more suitable for PFAS are provided as follows.

1.4 Deriving Site-Specific K_d Values for PFAS Using a Modified SPLP

The SPLP (EPA Method 1312) is designed to determine the mobility of organic and inorganic analytes present in liquids, soils, and wastes. A mass of sample is mixed with extraction fluid and shaken for 18 hours, after which the fluid is filtered and analyzed. The extraction fluid is a simple composition of reagent water adjusted with a mixture of sulfuric and nitric acids to a pH of 4.2 (for soils from east of the Mississippi River) or 5.0 (for soils from west of the Mississippi River). This process simulates natural leaching in the environment. The EPA SSL Guidance recommends the SPLP as an alternative to using the soil-water partitioning equation, although it may not be appropriate for all sites (U.S. EPA, 1996b).

SPLP Modifications for PFAS

Early analysis suggests that the SPLP is suitable for PFAS with minimal modifications. Containers and equipment in contact with samples should avoid polytetrafluoroethylene (PTFE) (Teflon®) and low-density polyethylene (LDPE) in favor of high-density polyethylene (HDPE). Glass fiber filters can adsorb PFAS from solution (Lath et al., 2019), so replacing filtration with centrifugation may improve data quality, but the impact of this change is still under investigation.

A suggested modified SPLP (summarized in ***Table 1.1***) reduces sample sizes by a factor of 10, using 10 grams of soil with 200 milliliters of extraction fluid, to minimize waste and simplify centrifugation. At least two parallel extractions should be performed for each sample using two extraction fluids: one to measure partitioning, such as the standard SPLP fluid or a groundwater analog, and a second to determine total extractable PFAS. A suggested fluid consists of 1% ammonium hydroxide (30% solution) in 99% methanol. Samples are shaken for 18 hours, then centrifuged at 10,000 revolutions per minute (15,000 *g*) for 10 minutes. The required volume of extract is decanted into an HDPE container for analysis.

The K_d for the soil is calculated as:

$$K_d = \frac{[Total] - [Extract]}{[Extract]}$$

where *[Extract]* is the concentration of PFAS in the selected extraction fluid, and *[Total]* is the concentration of total extractable PFAS in the methanol solution, assuming partitioning to air is negligible, and is equivalent to calculating K_d by dividing the soil partition by the aqueous partition. The concentrations of the extractants can be substituted for C_w and SSL in the adsorption equation presented previously when partitioning to the vapor phase is of interest.

Further Considerations for PFAS SPLP

Until an official method is available, those using the SPLP to evaluate PFAS mobility should evaluate their process recovery and method detection limits using laboratory control samples or internal standards. Other leaching methods may also be appropriate, such as those explored in Rayner et al. (2022). Negative bias in PFAS concentration from adsorption to container walls is expected and can be quantified with analysis of spiked control samples.

Table 1.1. Summary of recommended modifications to the SPLP for PFAS analysis

Modification	Explanation
Use only PFAS-free containers and equipment	PFAS contamination may result from common laboratory materials. Use HDPE bottles and avoid sample contact with PTFE (Teflon®) or LDPE whenever possible.
Reduce sample sizes	Reducing the mass of the sample from 100 grams to 10 grams and the volume of the extraction fluid from 2 liters to 200 milliliters reduces waste and simplifies centrifugation.
Use alternate extraction fluids	Use a methanol solution for total extraction in addition to the standard SPLP extraction fluid.

Modification	Explanation
Eliminate filtration steps and replace with centrifugation	PFAS will adsorb on filter surfaces; avoiding filtration may improve data quality, particularly for long-chain and uncharged PFAS. Centrifuge and decant or pipet sample. Conduct extraction in a centrifuge bottle to avoid transferring sample when feasible.

1.5 Contacts

Matt Rovero (rovero.matthew@epa.gov)
Rick Wilkin (wilkin.rick@epa.gov)
U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Subsurface Remediation Branch

1.6 References

Allen-King, R. M., McKay, L. D., & Trudell, M. R. (1997). Organic carbon dominated trichloroethene sorption in a clay-rich glacial deposit. *Groundwater, 35*(1), 124–130. https://doi.org/10.1111/j.1745-6584.1997.tb00067.x

Anderson, R. H., Adamson, D. T., & Stroo, H. F. (2019). Partitioning of poly- and perfluoroalkyl substances from soil to groundwater within aqueous film-forming foam source zones. *Journal of Contaminant Hydrology, 220*, 59–65. https://doi.org/10.1016/j.jconhyd.2018.11.011

Brusseau, M. L., Yan, N., Van Glubt, S., Wang, Y., Chen, W., Lyu, Y., Dungan, B., Carroll, K. C., & Holguin, F. O. (2019). Comprehensive retention model for PFAS transport in subsurface systems. *Water Research, 148*, 41–50. https://doi.org/10.1016/j.watres.2018.10.035

Chen, H., Reinhard, M., Nguyen, V. T., & Gin, K. Y. (2016). Reversible and irreversible sorption of perfluorinated compounds (PFCs) by sediments of an urban reservoir. *Chemosphere, 144*, 1747–1753. https://doi.org/10.1016/j.chemosphere.2015.10.055

Costanza, J., Clabaugh, C. D., Leibli, C., Ferreira, J., Wilkin, R. T. (2025). Using suction lysimeters for determining the potential of per- and polyfluoroalkyl substances to leach from soil to groundwater: A review. *Environmental Science & Technology, 59*(9), 4215-4229. https://doi.org/10.1021/acs.est.4c10246

Fabregat-Palau, J., Vidal, M., & Rigol, A. (2021). Modelling the sorption behaviour of perfluoroalkyl carboxylates and perfluoroalkane sulfonates in soils. *Science of The Total Environment, 801,* 149343. https://doi.org/10.1016/j.scitotenv.2021.149343

Lath, S., Knight, E. R., Navarro, D. A., Kookana, R. S., & McLaughlin, M. J. (2019). Sorption of PFOA onto different laboratory materials: Filter membranes and centrifuge tubes. *Chemosphere, 222*, 671–678. https://doi.org/10.1016/j.chemosphere.2019.01.096

Li, Y., Oliver, D. P., & Kookana, R. S. (2018). A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). *Science of the Total Environment, 628–629*, 110–120. https://doi.org/10.1016/j.scitotenv.2018.01.167

New Jersey Department of Environmental Protection. (2023, June). *Soil and soil leachate migration to ground water exposure pathway calculator* (Version 1.2). https://www.nj.gov/dep/srp/guidance/rs/soil_migration_pathway_calculator.xlsm

Nguyen, T. M. H., J. Bräunig, K. Thompson, J. Thompson, S. Kabiri, D. A. Navarro, R. S. Kookana, C. Grimison, C. M. Barnes, C. P. Higgins, M. J. McLaughlin and J. F. Mueller (2020). Influences of chemical properties, soil properties, and solution pH on soil–water partitioning coefficients of per- and polyfluoroalkyl substances (PFASs). *Environmental Science & Technology*, *54*(24), 15883-15892. https://doi.org/10.1021/acs.est.0c05705

Rayner, J. L., Slee, D., Falvey, S., Kookana, R., Bekele, E., Stevenson, G., Lee, A., & Davis, G. B. (2022). Laboratory batch representation of PFAS leaching from aged field soils: Intercomparison across new and standard approaches. *Science of the Total Environment, 838,* 156562. https://doi.org/10.1016/j.scitotenv.2022.156562

Rovero, M., Cutt, D., Griffiths, R., Filipowicz, U., Mishkin, K., White, B., Goodrow, S., & Wilkin, R. T. (2021). Limitations of current approaches for predicting groundwater vulnerability from PFAS contamination in the vadose zone. *Groundwater Monitoring & Remediation, 41*(4), 62–75. https://doi.org/10.1111/gwmr.12485

U.S. Environmental Protection Agency. (1996a). *Soil screening guidance: Technical background document*. https://www.epa.gov/superfund/superfund-soil-screening-guidance#technical

U.S. Environmental Protection Agency. (1996b). *Soil screening guidance: User's guide* (Publication 9355.4-23). https://semspub.epa.gov/work/HQ/175238.pdf

U.S. Environmental Protection Agency. (2008). *Fate, Transport, and Transformation Test Guidelines: OPPTS 835.1230 Adsorption/Desorption (Batch Equilibrium)*. https://www.regulations.gov/document/EPA-HQ-OPPT-2009-0152-0006

U.S. Environmental Protection Agency. (2022). *Regional screening levels (RSLs)*. https://www.epa.gov/risk/regional-screening-levels-rsls

Zareitalabad, P., Siemens, J., Hamer, M., & Amelung, W. (2013). Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater—A review on concentrations and distribution coefficients. *Chemosphere, 91*(6), 725–732. https://doi.org/10.1016/j.chemosphere.2013.02.024

2 Groundwater Sampling for PFAS

2.1 Overview

The technical guidelines suggested here are based on PFAS sampling recommendations developed by many organizations, in addition to field experience, current sampling practices, and accumulated data and research. Field et al. (2021) summarized current guidelines. Early guidance related to sampling groundwater for PFAS has been mostly consistent with occasional updated findings (Field et al., 2021; Kidd et al., 2022; NJDEP, 2024). Some older guidelines relying on the precautionary principle have specified excluding from field mobilizations all materials and equipment that might be coated with or that might contain PFAS or fluorinated materials.

Newer guidelines are increasingly based on laboratory testing of sampling equipment and materials, and consideration of potential exposure pathways for the sample. They are less restrictive and conditionally allow the use of more materials. Field et al. (2021) provided recommendations for sampling equipment and consumables based on materials testing and the potential for complete sample exposure pathways. Wanzek et al. (2024) recommends that older guidance be updated to continue to restrict materials that come in direct contact with water samples, specifies industry best practices for sampling, and emphasizes equipment decontamination procedures and collection of QA/QC samples. All sampling methodologies must be documented in approved Quality Assurance Project Plans (QAPPs).

The discussion of potential sources of PFAS that may contaminate field samples in this document should not be considered definitive. Much like the current understanding of the science of PFAS, the recommendations related to groundwater sampling is expected to evolve.

2.2 Existing Site Data

Site data should be reviewed to help plan PFAS sampling events and to evaluate if there are concerns with any PFAS-associated materials at the site. Drilling and monitoring well construction logs can be checked to determine what materials were used for drilling (e.g., drill rods, auger lubricants, drilling mud) and what materials were used for well construction (e.g., filter sand, bentonite, and concrete). Some sites might have legacy wells constructed with materials such as fluorinated polymers that could preclude sampling for PFAS. Measurements of depth to water and total well depth from previous sampling logs can be used to estimate reasonable purge volumes. These estimates can be used to plan for adequate container capacity for PFAS purge water (Investigation Derived Waste, IDW).

If available, PFAS data from past sampling events should be referenced, so that wells can be sampled in order from lowest to highest anticipated concentrations of expected contaminants. Otherwise, sampling should progress from locations expected to have the lowest concentrations (typically distal or side gradient to the source area) to locations expected to have the highest concentrations (typically proximal to the source area). PFAS samples should be gathered prior to those for other analytes, particularly if materials needed for sampling other analytes include fluorinated materials such as Teflon® bottle septa.

2.3 Sample Turbidity

Turbidity in water samples collected for PFAS analysis can skew analytical results by binding to the PFAS, removing it from solution. This effect is a particular concern for longer-chain PFAS. Filtering samples is problematic because some PFAS may adsorb to filter materials that are currently used for field sampling. For these reasons, it is recommended that groundwater sampling be conducted using a low-flow method and no filtering be performed.

Minimal disturbance to the water column is advised because of the high propensity for PFAS to partition to air-water interfaces, such as those that could develop due to drawdown of the water level around a well. The pump intake should preferably be no deeper than the depth of the middle of the submerged section of the well screen and the sampling depth and purge volume should be consistent across sampling events.

Until there is scientific consensus on a suitable limit for turbidity in PFAS samples, this document offers an interim recommendation of no greater than 10 Nephelometric Turbidity Units (NTU) which is consistent with recommendations and requirements by others (e.g., Puls and Barcelona, 1996; Yeskis and Zavala, 2002; NJ DEP, 2024). If the turbidity during sampling exceeds 10 NTU then adjustments may be tried, such as reducing the depth of the pump intake or reducing the flow rate. If the turbidity remains above 10 NTU then the well should be redeveloped before another sampling attempt. In some cases, it may be necessary to replace the well using a smaller well screen slot size and compatible sand pack particle size.

2.4 Sampling Equipment and Supplies

All supplies and equipment that will be used for sampling groundwater to be analyzed for PFAS or related analytes, must be vetted before use. Equipment and supplies can be broadly categorized by whether it will come in direct contact with the PFAS samples. It must be verified that all materials that will come in direct contact with samples, or have a reasonable possibility of doing so, do not have a realistic potential to significantly bias analytical results. However, some items may be permissible without documentation of risk. For example, pumps with plastic or elastic parts may not pose a practical problem due to very short contact times. Other items may not be reasonably expected to come in direct contact with the samples.

In addition to equipment and supplies, air and rainwater may be a concern when sampling. Although studies have found that concentrations of PFAS particles in the air and in rainwater contacting groundwater samples are unlikely to reach the detection limits for PFAS analyses (e.g., Wanzek et al., 2024), others have documented measurable concentrations of PFAS in rainwater (e.g., Cousins et al., 2022). Consequently, samples should be shielded from rainwater when collected.

The potential to bias results high (e.g., leaching from fluorinated tubing) and the potential to bias results low (e.g., adsorption on sampling materials) should be assessed. Fluoropolymers are often present in equipment used to sample for PFAS (Wanzek et al., 2024) whereas materials such as glass can sorb PFAS. High-Density Polyethylene (HDPE) is a commonly recommended piping and container material and is specified for sample containers in the current EPA-approved PFAS analysis methods for groundwater, U.S. EPA 8327 and U.S. EPA 1633. However, loss of long-chain PFAS (greater than six carbons along the carbon backbone) have been reported when samples were stored in this material for one week prior to analysis (Folorunsho et al., 2024). The alternative material polypropylene (PP) was also tested and performed similarly to HDPE.

Several methods can be used to determine whether equipment or supplies are suitable for use when sampling PFAS. A literature search may be adequate to determine whether a material may contain or be contaminated with PFAS. The potential for sampling bias has been documented by Field et al. (2021) and includes the results of soak tests for many types of equipment. Alternatively, laboratory analyses of PFAS-free water exposed to the equipment can be used. Field, equipment, and trip blanks should be comprehensive enough to determine whether any of the sampling equipment, or the surrounding environment, could contribute PFAS contamination to the sample. PFAS-free water, typically supplied by the laboratory, should be used for all blank collection as well as final decontamination rinses of reusable equipment before each sample is collected. Note that whether equipment or water is "PFAS-free" may depend on the detection limit of the analysis method selected. As methods achieve lower detection limits, the applicability of literature values may change.

Groundwater sampling (source: EPA 2024)

Blanks are useful for detecting and identifying the causes of high bias in PFAS sample analytical results but are generally not helpful for detecting low bias. Low bias can result from sample collection and handling in the field due to potential adsorption onto equipment, to the material of some field filters, and to fine particulates suspended in groundwater samples. The potential to cause low bias may, in part, be evaluated by using matrix spike samples.

The PFAS sampling supplies and equipment identified as acceptable in ***Table 2.1*** must be verified against all applicable requirements of government agencies and stakeholders. In general, it is acceptable to use materials that are coated with PFAS-free wax or made of HDPE, PP, polyvinylchloride (PVC), silicone, polyurethane, or acetate. It is unacceptable to use glass or fluorinated materials such as polytetrafluoroethylene (PTFE) (e.g., Teflon®, Hostaflon®), polyvinylidene fluoride (PVDF) (e.g., Kynar®), polychlorotrifluoroethylene (PCTFE) (e.g., Neoflon®), ethylene-tetrafluoroethylene (ETFE) (e.g., Tefzel®), or fluorinated ethylene propylene (FEP) (e.g., Teflon®, Hostaflon®, Neoflon®). Aluminum foil should also be avoided unless it can be determined that it is PFAS free. Tests for the presence of PFAS on materials such as aluminum foil should not be generalized across brands because results across studies have varied.

Many commonly used groundwater pumps and tooling have grips, fittings, seals, and other components made of plastic materials that can contain PFAS or could have been exposed to PFAS. These tools include dedicated submersible pumps permanently installed in monitoring wells. Although the potential impact of sampling devices is not well understood, site practitioners should be aware of the potential for different types of groundwater sampling equipment to contaminate PFAS samples or reduce detected concentrations.

When using a peristaltic pump, all tubing, including that used in the pump roller head, should be PFAS free. HDPE tubing should be used for well purging, except for the flexible tubing section used between the rollers in a peristaltic pump to draw water by suction. This flexible tubing must also be PFAS free, such as Tygon® silicone tubing. Dedicated tubing should be used for each well. Various pumps might contain O-Rings that contact the flow-through water. These rings do not present a significant risk of PFAS contamination given their small surface area and the short contact time, and purging before sampling should mitigate any effect from these rings. Submersible PFAS-free bladder or centrifugal pumps are an option for sampling at sites with groundwater depths greater than about 25 feet. No-purge samplers (i.e., bailers) are generally not recommended for collecting samples from groundwater monitoring wells for evaluating contaminant concentrations. The use of passive samplers deployed in monitoring wells is an area of active research and is not covered in this guide.

The manufacturing process for LDPE can contaminate it with PFAS. However, unless performing work where LDPE is specifically disallowed for a particular site, it is acceptable to use LDPE materials for sample organization and temporary storage. Some projects may allow use of LDPE materials if it is verified that the LDPE is not contaminated with PFAS. Nonetheless, HDPE is a preferable alternative. New powder-free nitrile gloves should be donned between handling any LDPE and collecting additional PFAS samples. LDPE bags such as Ziploc® can be used for sample organization, bottle protection, ice containment, and chain of custody (COC) protection. LDPE sheeting can also be used to cover the ground of the sampling work area. Samples collected from each location should be placed together into sealed waterproof bags and maintained in laboratory-supplied coolers containing ice made from PFAS-free water in bags made of waterproof material. If any samples shipped with PFAS samples have analytical methods that specify glass bottles, they should be wrapped in bubble wrap (typically made of LDPE) to prevent breakage. COCs should also be maintained in waterproof bags. The coolers should be sent overnight to the appropriate laboratory with COC forms and a custody seal.

Disposal of PFAS-contaminated investigation-derived waste (IDW) is described by ASTM E3274-21 and U.S. EPA (2024). Currently, thermal destruction or landfilling are listed as acceptable methods that could be used for disposal of sampling consumables. The receiving facility should be contacted prior to disposal to verify they accept PFAS-contaminated materials.

Table 2.1. Acceptable PFAS sampling equipment and supplies

Field Documentation Supplies
PFAS-free site map, sampling documentation forms, chain of custody forms, field book
Plastic-free clipboards
Fine-point Sharpie® unless specified otherwise. Note that some permanent markers contain PFAS (Rodowa et al., 2020.)
Personal Protective Equipment and Supplies
PFAS-free personal protective equipment (e.g., uncoated Tyvek®)
PFAS-free clothing not exposed to fabric softener; not waterproofed with Gore-Tex™ or Teflon®; and not treated to be stain resistant, insect repellant, or ultraviolet protection
Powder-free nitrile gloves (or other suitable materials but not latex)
PFAS-free insect repellant, sunscreen, and any other personal care products. Lists of PFAS-free products of these types are readily available.
Purging, Sampling, and Decontamination Equipment
PFAS-free water level indicator
PFAS-free graduated cylinders for alkalinity and turbidity screening
Tygon® silicone tubing or other elastic PFAS-free tubing if using a peristaltic pump

HDPE tubing to extend down the well
Two 250-milliliter HDPE sample bottles with HDPE caps for US EPA analytical methods 1633 and 8327; containers unspecified for EPA prep method 3512.
PFAS-free water from the laboratory. Herein, for practical purposes, water will be considered PFAS-free if PFAS are not quantified above the method detection limit for any PFAS analytes. PFAS-free water is used for field, equipment, and trip blanks.
PFAS-free spray bottles
Alconox® or Liquinox® detergent for decontamination
Polyethylene or PVC brush to scrub sampling equipment during decontamination
Sample Packaging and Shipping Supplies
PFAS-free sample labels
Sample and quality assurance/quality control bottles from the laboratory in cooler(s) (Igloo® or Coleman®)
Ziploc® or equivalent bags (if low-density polyethylene [LDPE] is acceptable). HDPE containers or bags are preferable.
Bubble wrap for glass containers (if LDPE is acceptable or HDPE is available)
PFAS-free tape to secure chain of custody forms inside the top of the cooler and to seal the cooler for shipment
Ice made from PFAS-free water (avoid chemical “blue” ice)

2.5 Contacts

Lee Rhea (rhea.lee@epa.gov)
Rick Wilkin (wilkin.rick@epa.gov)
U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division

2.6 References

ASTM. (2021). E3274-21 - Standard Guide for Management of Investigation-Derived Waste Associated with PFAS.

Cousins, I. T., Johansson, J. H., Salter, M.E., Sha, B., & Scheringer, M. 2022. Outside the safe operating space of a new planetary boundary for per- and polyfluoroalkyl substances (PFAS). *Environmental Science & Technology*, *56*(16), 11172-11179. https://doi.org/10.1021/acs.est.2c02765

Field, J., Schwichtenberg, T., Deeb, R. A., Hawley, E. L., Sayler, C., Bogdan, D., Shaefer, C. E., Jr., DiGuiseppi, B., & Struse, A. (2021). Assessing the potential for bias in PFAS concentrations during groundwater and surface water sampling. Department of Defense, Strategic Environmental Research and Development Program. https://apps.dtic.mil/sti/pdfs/AD1159282.pdf

Kidd, J., Fabricatore, E., & Jackson, D. (2022). Current and future federal and state sampling guidance for per- and polyfluoroalkyl substances in environmental matrices. *Science of the Total Environment*, *836*, 155523. https://doi.org/10.1016/j.scitotenv.2022.155523

Folorunsho, O., Kizhakkethil, J.P., Bogush, A., & Kourtchev, I. (2024). Effect of short-term sample storage and preparatory conditions on losses of 18 per- and polyfluoroalkyl substances (PFAS) to container materials. *Chemosphere*, *363*, 142814. https://doi.org/10.1016/j.chemosphere.2024.142814

New Jersey Department of Environmental Protection. (2024). Per- and Polyfluoroalkyl Substances (PFAS) Sampling Fact Sheet. https://dep.nj.gov/wp-content/uploads/srp/pfas_sampling_fact_sheet.pdf

Puls, W. & Barcelona, M. (1996). *Low-flow (minimal Drawdown) Ground-water sampling procedures*. U.S. Environmental Protection Agency, Superfund Technology Support Center for Ground Water, National Risk Management Research Laboratory, Subsurface Protection and Remediation Division, Ada OK. https://www.epa.gov/sites/default/files/2015-06/documents/lwflw2a.pdf

Rodowa, A. E., Christie, E., Sedlak, J., Peaslee, G. F., Bogdan, D., DiGuiseppi, B., & Field, J. A. (2020). Field sampling materials unlikely source of contamination for perfluoroalkyl and polyfluoroalkyl substances in field samples. *Environmental Science & Technology Letters*, *7*(3), 156–163. https://doi.org/10.1021/acs.estlett.0c00036

U.S. Environmental Protection Agency Region 4 (2015). Field equipment cleaning and decontamination at the FEC, SESDPROC-206-R3, Science and Ecosystems Support Division, Athens, Georgia. https://19january2017snapshot.epa.gov/sites/production/files/2016-01/documents/field_equipment_cleaning_and_decontamination_at_fec206_af.r3_1.pdf

U.S. Environmental Protection Agency (2024). Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances—Version 2 (2024) https://www.epa.gov/system/files/documents/2024-04/2024-interim-guidance-on-pfas-destruction-and-disposal.pdf.

Wanzek, T., McIntyre, H., Hawley, E., Deeb, R., Bogdan, D., Shaefer, C., DiGuiseppi, B, Struse, A., Schwichtenberg, T., Field, J. (2024). Assessing Potential Bias in PFAS Concentrations in Groundwater and Surface Water Samples. *Groundwater Monitoring & Remediation*, *44*, 28-37. https://doi.org/10.1111/gwmr.12669

Yeskis, D. & Zavala, B. (2002). *Ground-water sampling guidelines for superfund and RCRA project managers*. U.S. Environmental Protection Agency, Technology Innovative Office, Office of Solid Waste and Emergency Response, Washington, D.C. https://www.epa.gov/sites/default/files/2015-06/documents/gw_sampling_guide.pdf

2.7 Additional Information

MassDEP Drinking Water Program. (2021). *Field sampling guidelines for PFAS using EPA Method 537 or 537.1*. Massachusetts Department of Environmental Protection. https://www.mass.gov/doc/field-sampling-guide-for-pfas/download

Michigan Department of Environmental Quality. (2018). *General PFAS sampling guidance*. https://www.michigan.gov/pfasresponse/-/media/Project/Websites/PFAS-Response/Sampling-Guidance/General.pdf

Michigan Department of Environmental Quality. (2018). *Groundwater PFAS sampling guidance*. https://www.michigan.gov/pfasresponse/-/media/Project/Websites/PFAS-Response/Sampling-Guidance/Groundwater.pdf

New York State Department of Environmental Conservation. (2023). *Sampling, analysis, and assessment* *of per- and polyfluoroalkyl substances (PFAS) under NYSDEC's Part 375 remedial programs*. https://www.dec.ny.gov/docs/remediation_hudson_pdf/pfassampanaly.pdf

Puls, R. W. & Barcelona, M. J. (1996). *Ground water issue: Low-flow (minimal drawdown) ground-water sampling procedures* (EPA/540/S-95/504). U.S. Environmental Protection Agency. https://www.epa.gov/sites/default/files/2015-06/documents/lwflw2a.pdf

Quality Assurance Unit. (2017). *Low stress (low flow) purging and sampling procedure for the collection of groundwater samples from monitoring wells*. U.S. Environmental Protection Agency Region 1. https://www.epa.gov/sites/default/files/2017-10/documents/eqasop-gw4.pdf

U.S. Department of the Army. (2018). *Army guidance for addressing releases of per- and polyfluoroalkyl substances (PFAS)*. https://www.fedcenter.gov/ U.S.

Environmental Protection Agency. (2020). *Perfluoroalkyl and polyfluoroalkyl substances (PFAS): Methods and guidance for sampling and analyzing water and other environmental media* (EPA/600/F-17/022h). https://www.epa.gov/sites/default/files/2020-01/documents/pfas_methods-sampling_tech_brief_7jan2020-update.pdf

Wilkin, R. T., Ludwig, R. D., & Ford, R. G. (Eds). (2000). *Workshop on monitoring oxidation-reduction processes for ground-water restoration* (EPA/600/R02/002). U.S. Environmental Protection Agency. https://archive.epa.gov/ada/web/pdf/10003z26.pdf

3 PFAS Surface Chemistry and Surfactant Basics

3.1 Overview

A key distinction between typical organic contaminants and PFAS, at least those currently considered to have notable risk to health and the environment, is that the latter are fluorocarbon surfactants. Surfactants are organic chemicals with a hydrophilic head and a hydrophobic tail. As a result, surfactants partition at fluid/fluid interfaces, such as the interface between air and groundwater in the vadose zone or the interface between a nonaqueous phase liquid (NAPL) and groundwater, if a NAPL is present in the saturated zone. Partitioning at these interfaces is important because it may be an additional retardation mechanism (resulting in subsurface contaminant persistence), and it may alter surface or interfacial tension. In fact, the unsaturated soil horizon could serve as a long-term source of PFAS contamination for both groundwater and surface water (e.g., Wallis et al., 2022). In addition, surfactants may alter contact angles. Alteration of either of these two surface chemistry properties (i.e., surface/interfacial tension or contact angles) may, in turn, alter the distribution of immiscible fluids in the subsurface. For example, source zone–level concentrations of PFAS may lower groundwater saturations in the vadose zone or enhance NAPL transport by lowering the NAPL/groundwater interfacial tension.

Another characteristic that makes PFAS significantly different from more traditional, nonsurfactant organic contaminants is surfactant self-assembly, driven by the thermodynamic tendency to minimize interactions between hydrophilic and hydrophobic chemical structures. A prime example of this is the formation of micelles. Other organic co-contaminants, if present, may partition into micelles, resulting in an enhanced transport mechanism.

As a class of chemicals, PFAS have been used in a wide variety of industrial and commercial applications since the early 1900s because of their unique chemical properties (e.g., Buck et al., 2011; Glüge et al., 2020; Kissa, 2001; Wang et al., 2017). Unfortunately, their widespread use has resulted in environmental contamination, with potential health risks on a national and global scale.

The general chemical properties that make PFAS useful in commercial and industrial applications include the ability to impact surface properties and resistance to chemical degradation. The latter stems from the strength of the carbon-fluorine chemical bond (Wang et al., 2017). The former is due to the surfactant nature that arises from the molecular structure of the chemicals. Although not all PFAS are surfactants (Buck et al., 2011), many of those of immediate concern are surfactants. For example, perhaps two of the most notable PFAS are the fluorocarbon surfactants perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS).

Surfactant properties may significantly impact environmental transport and fate. Consequently, the purpose of this technical brief is to provide a summary of important surface chemistry concepts and highlight how these concepts impact PFAS transport and fate in the subsurface. Although connections to relevant PFAS references are made, a complete review of all PFAS literature is beyond the scope of this technical brief (more extensive reviews include Interstate Technology Regulatory Council, 2023, and Sharifan et al., 2021). Moreover, this technical brief focuses on transport in the subsurface, but the principles discussed are applicable to the broader environment.

3.2 Surface Chemistry and Surfactant Basics

3.2.1 Surface and Interfacial Tension

When two fluids are sufficiently immiscible, they will remain separate as distinct fluid phases when in contact with one another. Common examples of immiscible fluids are air and groundwater in the vadose zone, or a NAPL (e.g., gasoline, aviation fuel, chlorinated solvents) and groundwater. Molecules at the interface of the two fluids are subject to molecular attractive forces that are different from the molecular attractive forces in the bulk fluids. The disparity between these forces results in tension at the interface. *Surface tension* is the term typically used when one fluid is a gas and the other a liquid (e.g., air-water), whereas *interfacial tension* is the term typically used when both fluids are liquids (e.g., water-oil).

3.2.2 Contact Angles

When two immiscible fluids are in contact with a solid, another important surface chemistry property is the *contact angle*, defined as the angle from the solid surface to the fluid/fluid interface (***Figure 3.1***). The contact angle measures the propensity for one fluid relative to another to be in contact with the solid and is used to characterize fluid wettability. An illustration of contact angles from common experience is water beads on a waxed surface; beads of water are created because air acts as the wetting fluid on the waxed surface. In general, contact angles less than 90° indicate a wetting fluid, whereas contact angles greater than 90° indicate a nonwetting fluid. More precise distinctions may also be made. For example, relative to water, a contact angle of approximately 0° indicates a hydrophilic surface, contact angles between approximately 0° and 90° indicate subcritical water repellency, and a contact angle greater than 90° indicates critical water repellency or a hydrophobic surface. These definitions can likewise be applied to oil to distinguish oleophilic and oleophobic surfaces.

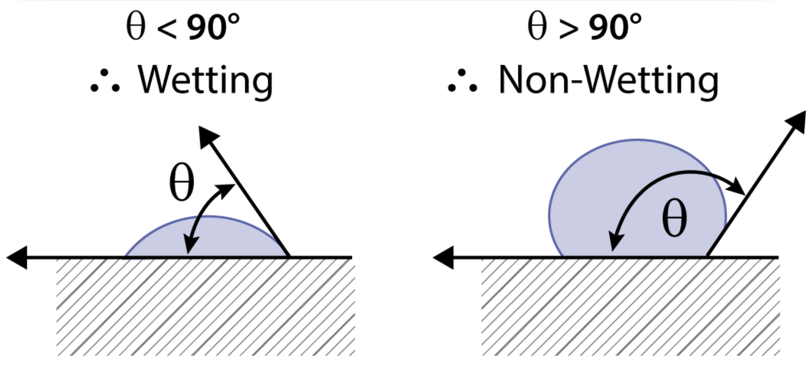

Figure 3.1. Contact angle and fluid wettability. Illustrated is a fluid (white background) in contact with a solid (diagonal line pattern). The solid also supports a drop of a second fluid (blue shading). For example, this may illustrate a water drop resting on a solid, surrounded by air. The contact angle is defined as shown by the intersection of the fluid/fluid interface with the solid.

Why are these properties important?

Relative to contaminants in the subsurface, surface tension, interfacial tension, and contact angles are important to fluid distributions in partially saturated systems, such as the vadose zone, or when a NAPL is present in the saturated zone. In many applications of immiscible fluids, there is no need to explicitly consider these features. These properties are an implicit part of the capillary pressure-saturation-permeability relationships used in immiscible fluid transport modeling. However, when chemicals are introduced into the subsurface that may alter surface chemistry properties, like surfactants, then explicit consideration is necessary.

3.2.3 Surfactants

Surfactants are organic chemicals with a hydrophilic head and a hydrophobic tail. Using PFOA as an example, the perfluorinated alkyl chain is the hydrophobic tail, and the carboxyl functional group is the hydrophilic head. Surfactants can be divided into two broad categories: fluorocarbon and hydrocarbon surfactants (i.e., surfactants without fluorines attached to the carbon chain). Compared with hydrocarbon surfactants, fluorocarbon surfactants repel water and oil more strongly because of the carbon-fluorine bonds within the molecule (e.g., Wang et al., 2017), which helps to explain their advantage in many commercial applications. Mixtures of the two may be an important consideration in some cases, and a prime example may be aqueous film-forming foam (AFFF), which in many formulations is a mixture of hydrocarbon and fluorocarbon surfactants in water.

As a result of the hydrophobic/hydrophilic contrast within the molecule, surfactants partition at fluid/solid and fluid/fluid interfaces. Although solid partitioning is well recognized as an important transport and fate process, partitioning at fluid/fluid interfaces is less known because historically, it has not been relevant to typical organic contaminants. If surfactants are present at sufficiently low

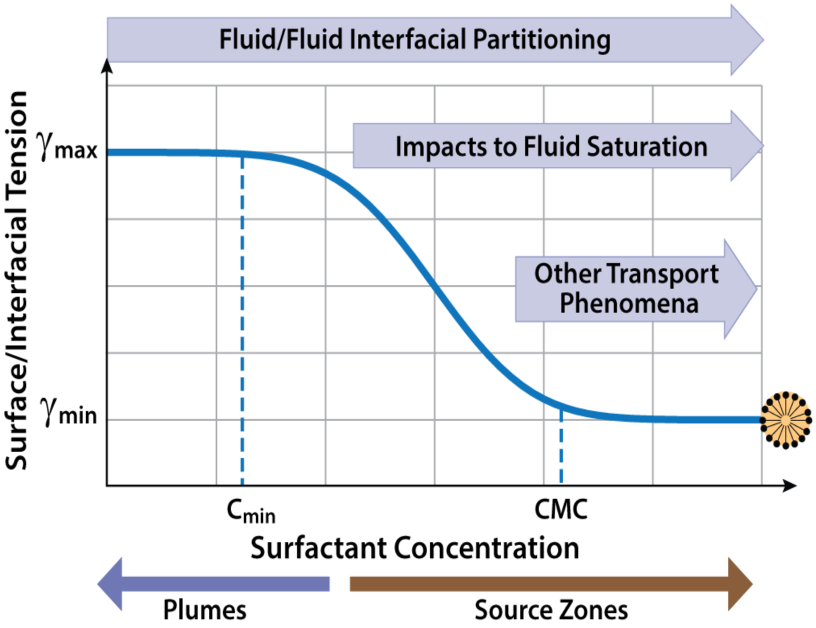

Figure 3.2. Conceptual illustration of surface/interfacial tension γ as a function of concentration C. The graph is divided into three main regions based on γ characteristics: (1) at low C, γ reflects measurements of surfactant-free water; (2) as C increases, γ significantly decreases, and (3) γ reaches a minimum value at large concentration. The arrows across the top of the figure indicate key processes, whereas the arrows at the bottom indicate areas where those processes are relevant.

concentrations (parts per billion levels or smaller), this partitioning may not impact surface properties such as surface tension for air-water systems, interfacial tension for liquid/liquid systems, or contact angles for three-phase systems. If surfactants are present in sufficient quantities, however, partitioning may alter the surface properties (***Figure 3.2***).

Why is surfactant fluid/fluid interfacial partitioning important?

Partitioning at fluid/fluid interfaces (e.g., air/water or NAPL/water), and the associated implication for subsurface transport, is one important distinction when PFAS contaminants are compared with more traditional organic contaminants. The first important implication for fluid/fluid interfacial partitioning is that it impacts contaminant mass distribution (***Figure 3.3***). Understanding how contaminant mass is distributed in the subsurface is vital to proper site characterization and remediation.

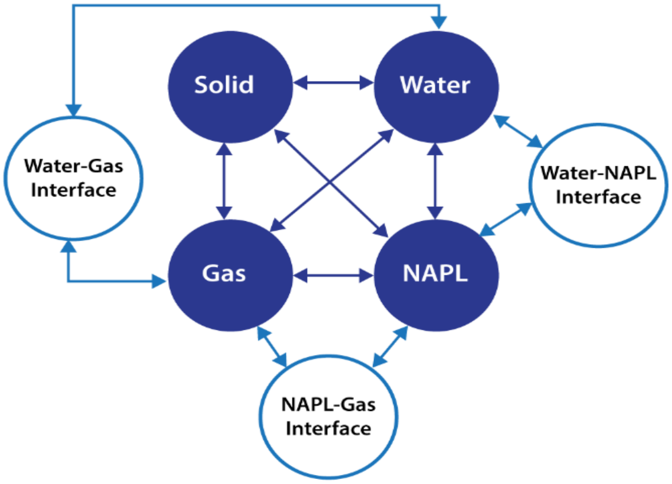

Figure 3.3. Subsurface phases and interface partitioning. The blue circles illustrate contaminant phase partitioning relationships for organic contaminants without surfactant properties (i.e., typical organic contaminants) between subsurface solids and fluids (i.e., water, NAPL, and gas). Note: in vadose zone applications, air is the gas. When considering a contaminant with surfactant properties, and when two or more immiscible fluids are present, fluid/fluid interfacial partitioning should also be considered. The open circles represent fluid/fluid interfacial partitioning.

The extent of interfacial partitioning depends on several factors. Partitioning will depend on the PFAS chemical structure itself, with carbon chain length, functional group, and counterion type being important factors (Brusseau & Van Glubt, 2019). In general, interfacial partitioning is dependent on concentration, but linear partitioning can be assumed at low concentrations (e.g., Silva et al., 2021) and has been demonstrated through direct measurements of surfactant per interfacial surface area or surface excess (e.g., Brusseau, 2021). However, nonlinear behavior has also been suggested (Schaefer et al., 2019). Partitioning is also sensitive to background electrolyte concentrations (Brusseau & Van Glubt, 2019; Costanza et al., 2019; Le et al., 2021; Wang & Niven, 2021) and may vary because of the presence of other surfactants (Schaefer et al., 2019; Silva et al., 2021). Other factors include temperature, pH, and co-solutes.

The second important implication of fluid/fluid interfacial partitioning is that it may create retardation. This retardation mechanism is the underlying principle for previous research related to interfacial tracers (e.g., Costanza-Robinson & Henry, 2017, and references therein). More recent studies have noted the potential importance that fluid/fluid interfacial partitioning may have on subsurface PFAS transport (e.g., Brusseau, 2018; Costanza et al., 2019; Schaefer et al., 2019; Silva et al., 2019), especially due to partioning at the air-water interface in the vadose zone. Laboratory experiments have demonstrated retardation of injected PFAS beyond that expected due to solid sorption alone (e.g., Brusseau et al., 2019; Li et al., 2021; Lyu et al., 2018), and numerical modeling work has supported the hypothesis that fluid/fluid interfacial partitioning is the explanation (Brusseau et al., 2019; Silva et al., 2020). Retardation due to fluid/fluid interfacial partitioning may be quite significant, exceeding that due to solid-phase sorption in some (Brusseau, 2018) but not all cases (Silva et al., 2020).

Empirical evidence of PFAS retardation in laboratory studies is used to infer immobility of the PFAS relative to bulk fluid motion when partitioned at the air/water interface. However, net movement of a solute partitioned on the interface has been reported in at least one reference, which suggests the potential for interfacial advection (Kim et al., 1999). In surface chemistry, the Marangoni effect refers to the movement of water due to viscous forces associated with surface tension gradients of a surfactant film spreading across the interface (Adamson & Gast, 1997). The spreading of a surfactant film suggests another potential transport mechanism that is not routinely considered. Finally, at least one reference has investigated the concept of interfacial velocity (i.e., the velocity with which the fluid/fluid interface itself moves through the porous media; Nordhaug et al., 2003). It is unclear whether these processes have practical application in subsurface PFAS transport and fate, but it may be prudent to acknowledge that more research is needed to better understand what role, if any, solute motion on the fluid/fluid interface, and movement of the interface itself, may have in subsurface PFAS transport and fate.

As surfactant concentration increases, surface tension (or interfacial tension) will eventually begin to decrease (see ***Figure 3.2***). Once significant decreases in surface tension have occurred, impacts are expected to occur in capillary pressure, fluid saturation, and relative permeability. This behavior has been documented in a series of papers based on modeling and experimental work (Henry et al., 2002; Henry & Smith, 2002, 2003, 2006; Smith et al., 2011) using a long-chain alcohol, which demonstrated that water drains from areas of high alcohol concentration to areas of low concentration. Reductions in water saturation likewise reduce relative permeability, which impact subsequent infiltration patterns (i.e., infiltrating water flows around areas where water previously drained due to surfactant enhanced flow). This may have important implications for the persistence of PFAS contamination, for example, in the vadose zone. Impacts also depress the capillary fringe. This behavior is not expected in areas of dilute plumes but may occur where high concentrations are expected (i.e., on the order of parts per million [ppm]). Releases of AFFF are a prime example of an incident that may result in such impacts. A modeling study by Guo et al. (2020) illustrated impacts to vadose-zone fluid distributions due to PFOS concentration levels.

As a final note regarding fluid/fluid interfacial partitioning, any activity that introduces immiscible fluids into subsurface locations with suspected PFAS contamination should be evaluated for its potential to enhance PFAS transport. Examples include air sparging, which introduces air into the saturated zone and therefore creates air-water interfaces. Another example is the injection of an emulsified product to promote biodegradation. Emulsions consist of immiscible oil droplets in water, and PFAS contaminants may partition at the droplet interfaces.

3.2.4 Surfactant Self-Assembly

Because of an inherent repulsion between hydrophobic tails and water molecules, surfactants will assemble into molecular structures that minimize the contact between hydrophobic tails with the surrounding water molecules. One such structure is a micelle, and another is a vesicle (**Figure 3.4a**; micelle on the left, vesicle on the right). In solutions, micelles develop at only a sufficiently large concentration, referred to as the critical micelle concentration (CMC). However, increasing concentration will not always lead to micelle formation. For ionic surfactants, the Krafft point is defined as the intersection of two curves: solubility versus temperature and the CMC versus temperature (Kissa, 2001). For temperatures below the Krafft point, increasing concentration will not reach the CMC but will reach a solubility limit (see **Figure 3.5a**). The CMC can be reached only at temperatures above the Krafft point. This may have important ramifications when considering subsurface conceptual models for surfactant contaminants.

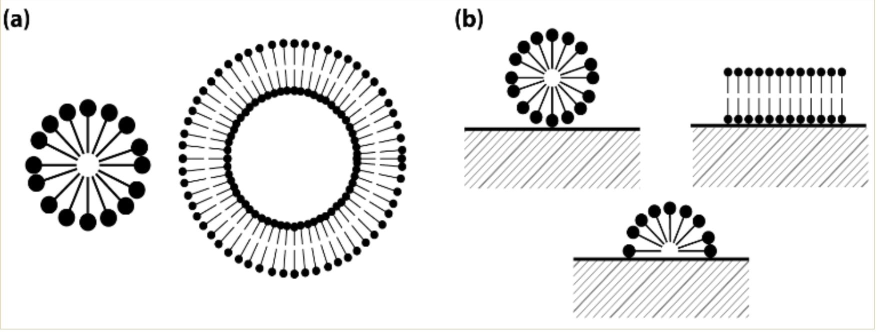

Figure 3.4. Conceptual illustration of surfactant self-assembly: (a) micelle and vesicle in solution, and (b) examples during solid sorption

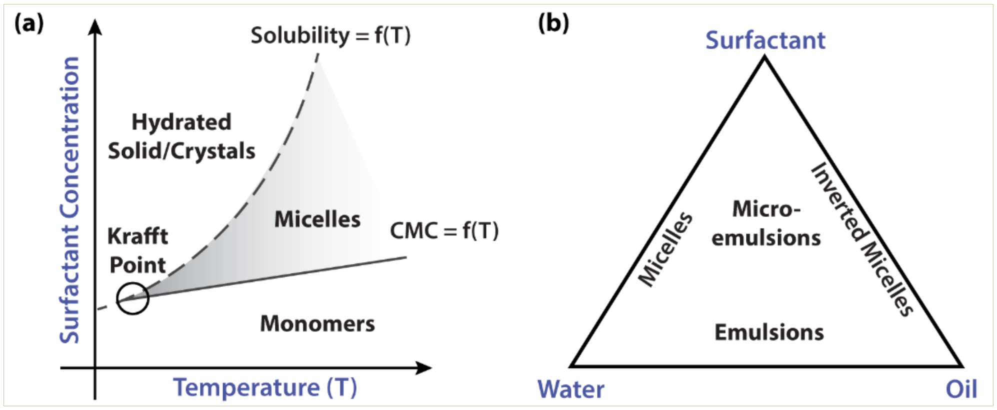

Figure 3.5. Conceptual diagrams of (a) the Krafft point for ionic surfactants, and (b) phase behavior for water-oil-surfactant systems. Note that the term "inverted micelle" is use here synonymously with "reverse micelle".

Why is surfactant self-assembly important?

Once the CMC is reached, micelle formation may introduce a mechanism for enhanced transport of co-contaminants. The interior of the micelle is a hydrophobic region where other hydrophobic organic contaminants may partition. For this purpose, surfactants have been used for remediation of NAPL contamination in groundwater (e.g., Pennell et al., 2014, and references therein). If PFAS contaminants are released at concentrations that meet or exceed their CMC, then they also could form micelles and enhance transport of other contaminants (***Figure 3.6***). The CMC is typically on the order of ppm (see Bhhatarai & Gramatica, 2011, or Le et al., 2021, for summary information), which suggest enhanced transport of other contaminants due to PFAS micelles may be limited to source areas with large concentrations.

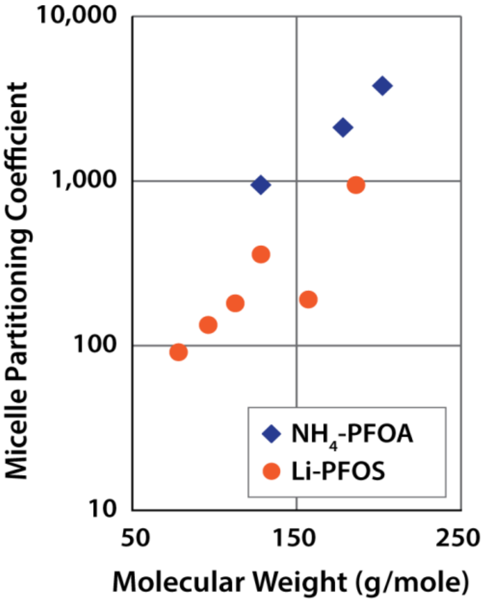

Figure 3.6. Micelle partitioning coefficients (i.e., the ratio of chemical concentration in the micelle to that in the aqueous phase) plotted as a function of co-contaminant molecular weight (MW). This figure illustrates the potential for enhanced transport of co-contaminants by PFAS micelles. Data reflect aromatic hydrocarbons as co-contaminants, ranging from benzene (lowest MW) to pyrene (highest MW). The blue diamonds represent results based on micelles of ammonium PFOA (An et al., 2002), and the orange circles represent results based on micelles of lithium PFOS (Simmons and McGuffin, 2007). Results are plotted as a function of MW for summary purposes only and do not suggest MW as a sole factor in the partitioning relationships. For example, Simmons and McGuffin (2007) suggest a relatively large partitioning coefficient for hexafluorobenzene into lithium PFOS micelles may be due to similarity in the chemical structures of those compounds.

For traditional organic contaminants, adsorption on solid surfaces is the primary mechanism for contaminant retardation in the subsurface. Solid phase adsorption relevant to PFAS contamination is summarized elsewhere (e.g., Rovero et al., 2021) and will not be discussed in detail here. However, the ability of surfactants to self-assemble even in the context of solid adsorption is a complexity worth noting given the focus of this technical brief. ***Figure 3.4b*** illustrates a few simple structures that may occur, but even more complex structures are possible depending on solid surface heterogeneity (e.g., Striolo, 2019, and references therein). Moreover, these structures may occur at bulk phase concentrations less than the CMC (Schwarzenbach et al., 2003). More research is needed to better understand what role surfactant self-assembly may have in PFAS solid phase sorption in the subsurface.

3.2.5 Emulsions and Foams

Emulsions and foams consist of binary fluid mixtures stabilized by surfactants. In an emulsion, surfactants act to stabilize droplets of one (discontinuous) liquid in the other (continuous) liquid (***Figure 3.5b***). Two common types of emulsions are an oil-in-water emulsion and a water-in-oil emulsion (Adamson & Gast, 1997). Microemulsions are a special class of emulsions, distinguished by their transparent appearance, consisting of a dispersed liquid with droplet diameters ranging from approximately 10 to 100 nm (Rosen, 1989). Likewise, foams consist of a discontinuous gas dispersed as bubbles throughout a continuous liquid. Surfactants in the foam promote liquid film (i.e., lamellae) elasticity, which prevent the lamella between gas bubbles from rupturing (Rosen, 1989).

Although likely not a significant factor in subsurface transport, aerosols are another mixture consisting of small solid particles or discontinuous liquid droplets dispersed throughout a continuous gas phase. Aerosols may, however, be significant in atmospheric PFAS transport (e.g., Faust, 2022). Surfactants are used in enhanced oil recovery operations for emulsions and foams and to alter wetting characteristics. Murphy and Hewat (2008) provide a mini-review specific to the use of fluorocarbon surfactants for enhanced oil recovery. In addition, foams have been investigated for subsurface contaminant remediation (e.g., Maire et al., 2015).

Why are emulsions and foams important?
Microemulsions may impact contaminant mass distributions and facilitate NAPL transport. Kostarelos et al. (2021) investigated mixtures of AFFF and Jet Fuel A and found that a Winsor type II solution was consistently produced for the conditions investigated. This type of solution is characterized by two separate phases: aqueous and a water-in-oil microemulsion. Microemulsions were generally found to be much more viscous than the AFFF solution or Jet Fuel A, suggesting a greater chance for trapping in the subsurface. Results from column studies indicated that almost 80% of measured PFAS were retained in the microemulsions, suggesting the possibility of a long-term PFAS source.

By design, AFFF is a product that creates a foam. Foams are less permeable than groundwater or air and may therefore alter flow patterns in the subsurface. Kostarelos et al. (2021) state it is likely that AFFF, released as a foam at ground surface, will dissipate before entering the subsurface as a foam, and the separated liquid will then infiltrate into the ground. However, Høisæter et al. (2019) noted observations of foam penetration into the top of soil columns during laboratory experiments where AFFF was applied as a foam. If foam does penetrate into the soil, it seems reasonable to suspect the foam will not persist, given its instability. However, activities that inject air into PFAS-impacted areas, such as air sparging, may create foam in the porous media. Surfactant-enhanced air sparging has in fact been proposed as an alternative to air sparging, and the ability to create foam as a result has been reported (Kim et al., 2022). However, this is likely a concern only in PFAS source zones with potentially high (ppm-level) total surfactant concentrations. This does not preclude, of course, foam formation in areas with smaller PFAS concentrations during activities such as treatment with foam fractionation, provided other mechanical actions or chemical additives are used to create the foam.

3.3 Summary

Currently, the PFAS of most environmental concern are fluorocarbon surfactants. As surfactants, they have characteristics that may impact subsurface transport and fate, resulting in differences when compared with the characteristics of more traditional organic contaminants. ***Table 3.1*** summarizes subsurface transport and fate processes that may be impacted by surfactant properties. In the case when only a single fluid is present, such as groundwater in the saturated zone, surfactant self-assembly may be a factor in solid phase sorption, even at concentrations less than the CMC. Surfactant self-assembly may also be a factor in source zones with high concentrations, in which case, surfactants may self-assemble into structures called micelles.

Other organic co-contaminants, if present, may partition into micelles, resulting in an enhanced transport mechanism. These two processes may also be factors when multiple fluids are present in the subsurface, but the presence of multiple fluids also raises what may be the most important difference. Surfactants partition at fluid/fluid interfaces, such as the interface between air and groundwater in the vadose zone, or the interface between a NAPL and groundwater. Empirical evidence suggests this partitioning mechanism may create significant retardation (i.e., transport rates much less than advection) under some, but not necessarily all, conditions.

The extent of partitioning at fluid/fluid interfaces will depend on site geochemistry, porous media characteristics, and other surfactants, including other PFAS. Moreover, remedial activities, such as air sparging or injecting emulsions, may introduce immiscible fluids into the subsurface. This may impact PFAS transport not only because of possible phase partitioning, but also because of partitioning at the interfaces between the immiscible fluids. In source zones with high PFAS concentrations (ppm-level), partitioning at fluid/fluid interfaces may alter surface or interfacial tension. Partitioning at fluid/solid interfaces may also alter contact angles. Alteration of either of these two surface chemistry properties may, in turn, alter the distribution and flow of immiscible fluids in the subsurface.

Table 3.1. Summary of subsurface transport and fate processes potentially influenced by contaminant surfactant properties

Transport process	**Fluids in porous media**	
	Single fluid (e.g., groundwater)	**Multiple fluids (e.g., groundwater and air; groundwater and NAPL; or groundwater, air, and NAPL)**
Advection	N/A	Surfactant enhanced flow, with the potential for changes in flow patterns
Sorption	Self-assembly during sorption	Self-assembly during sorption
Interfacial partitioning	N/A	Partitioning at the interface between fluids
Other enhanced transport processes	Enhanced transport of other contaminants through micelles	Enhanced transport of other contaminants through micelles, and emulsions when NAPL is present

Note: Transport processes not included in the table (i.e., diffusion, dispersion, transformation, and phase partitioning) may likewise be important, but are not influenced by surfactant properties.

3.4 Contacts

Michael C. Brooks (Brooks.Michael@epa.gov)[1]
Jingjing Chen,[2] Aderonke Adegbule,[3] Junqi Huang,[4] Carolyn Acheson[5]

[1] Retired, U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Subsurface Remediation Branch

[2] Formerly, Oak Ridge Institute for Science and Education (ORISE) Postdoctoral Associate, U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Subsurface Remediation Branch

[3] U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Office of Pollution Prevention and Toxics, Existing Chemicals Risk Assessment Division, Risk Assessment Branch

[4] U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Groundwater Characterization and Remediation Division, Subsurface Remediation Branch

[5] Retired, U.S. Environmental Protection Agency, Center for Environmental Solutions and Emergency Response, Land Remediation and Technology Division, Contamination Analysis and Innovative Solutions Branch

3.5 References

Adamson, A. W. & Gast, A. P. (1997). *Physical chemistry of surfaces* (6th ed.). Wiley.

An, Y., Carraway, E. R., & Schlautman, M. A. (2002). Solubilization of polycyclic aromatic hydrocarbons by perfluorinated surfactant micelles. *Water Research*, *36*, 300–308. https://doi.org/10.1016/s0043-1354(01)00205-6

Bhhatarai, B. & Gramatica, P. (2011). Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals. *Environmental Science & Technology*, *45*, 8120–8128. https://doi.org/10.1021/es101181g

Brusseau, M. L. (2018). Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface. *Science of the Total Environment*, *613–614*, 176–185. https://doi.org/10.1016/j.scitotenv.2017.09.065

Brusseau, M. L. (2021). Examining the robustness and concentration dependency of PFAS air-water and NAPL-water interfacial adsorption coefficients. *Water Research*, *190*, 116778. https://doi.org/10.1016/j.watres.2020.116778

Brusseau, M. L., & Van Glubt, S. (2019). The influence of surfactant and solution composition on PFAS adsorption at fluid-fluid interfaces. *Water Research*, *161*, 17–26. https://doi.org/10.1016/j.watres.2019.05.095

Brusseau, M. L., Yan, N., Van Glubt, S., Wang, Y., Chen, W., Lyu, Y., Dungan, B., Carroll, K. C., & Holguin, F. O. (2019). Comprehensive retention model for PFAS transport in subsurface systems. *Water Research*, *148*, 41–50. https://doi.org/10.1016/j.watres.2018.10.035

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwenkket, S. P. J. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, *7*(4), 513–541. https://doi.org/10.1002/ieam.258

Costanza, J., Arshadi, M., Abriola, L. M., & Pennell, K. D. (2019). Accumulation of PFOA and PFOS at the air-water interface. *Environmental Science and Technology Letters*, *6*, 487–491. https://doi.org/10.1021/acs.estlett.9b00355

Costanza-Robinson, M. S., & Henry, E. J. (2017). Surfactant-induced flow compromises determination of air-water interfacial areas by surfactant miscible-displacement. *Chemosphere*, *171*, 275–283. https://doi.org/10.1016/j.chemosphere.2016.12.072

Faust, J. A. (2022). PFAS on atmospheric aerosol particles: A review. *Environmental Science: Processes &*

Impacts, *2*. https://doi.org/10.1039/d2em00002d

Glüge, J., Scheringer, M., Cousins, I. T., DeWitt, J. C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C. A., Trier, X., & Wang, Z. (2020). An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science Processes & Impacts*, *22*(12), 2345–2373. https://doi.org/10.1039/d0em00291g

Guo, B., Zeng, J. & Brusseau, M. L. (2020). A mathematical model for the release, transport, and retention of per- and polyfluoroalkyl substances (PFAS) in the vadose zone. *Water Resources Research*, *57*. https://doi.org/10.1029/2019WR026667

Henry, E. J. & Smith, J. E. (2002). The effect of surface-active solutes on water flow and contaminant transport in variably saturated porous media with capillary fringe effects. *Journal of Contaminant Hydrology*, *56*(3–4), 247–270. https://doi.org/10.1016/S0169-7722(01)00206-6

Henry, E. J. & Smith, J. E. (2003). Surfactant-induced flow phenomena in the vadose zone: A review of data and numerical modeling. *Vadose Zone Journal*, *2*, 154–167. https://doi.org/10.2136/vzj2003.1540

Henry, E. J. & Smith, J. E. (2006). Numerical demonstration of surfactant concentration-dependent capillarity and viscosity effects on infiltration from a constant flux line source. *Journal of Hydrology*, *329*(1–2), 63–74. https://doi.org/10.1016/j.jhydrol.2006.02.008

Henry, E. J., Smith, J. E., & Warrick, A. W. (2002). Two-dimensional modeling of flow and transport in the vadose zone with surfactant-induced flow. *Water Resources Research*, *38*(11), 1251. https://doi.org/10.1029/2001WR000674

Høisæter, Å., Pfaff, A., & Breedveld, G. D. (2019). Leaching and transport of PFAS from aqueous film-forming foam (AFFF) in the unsaturated soil at a firefighting training facility under cold climatic conditions. *Journal of Contaminant Hydrology*, *222*, 112–122. https://doi.org/10.1016/j.jconhyd.2019.02.010

Interstate Technology Regulatory Council. (2023). *Technical resources for addressing environmental releases of per- and polyfluoroalkyl substances (PFAS)*. https://pfas-1.itrcweb.org/

Kim, H., Cho, M., & Annable, M. D. (2022). Analysis of facilitated air intrusion during surfactant-enhanced air sparging using surface tension-reducing chemicals: Surfactants and alcohols. *Soil and Sediment Contamination: An International Journal*, *31*(2), 133–151. https://doi.org/10.1080/15320383.2021.1913574

Kim, H., Rao, P. S. C., & Annable, M. D. (1999). Gaseous tracer technique for estimating air-water interfacial areas and interface mobility. *Soil Science Society of America Journal*, *63*(6), 1554–1560. https://doi.org/10.2136/sssaj1999.6361554x

Kissa, E. (2001). *Fluorinated surfactants and repellents* (2nd ed.). Marcel Dekker, Inc.

Kostarelos, K., Sharma, P., Christie, E., Wanzek, T., & Field, J. (2021). Viscous microemulsions of aqueous film-forming foam (AFFF) and Jet Fuel A inhibit infiltration and subsurface transport. *Environmental Science & Technology Letters*, *8*, 142–147. https://doi.org/10.1021/acs.estlett.0c00868

Le, S., Gao, Y., Kibbey, T. C. G., Glamore, W. C., & O'Carroll, D. M. (2021). A new framework for modeling the effect of salt on interfacial adsorption of PFAS in environmental systems. *Science of the Total Environment*, *796*, 148893. https://doi.org/10.1016/j.scitotenv.2021.148893

Le, S., Kibbey, T. C. G., Weber, K. P., Glamore, W. C., & O'Carroll, D. M. (2021). A group-contribution model for predicting the physicochemical behavior of PFAS components for understanding environmental fate. *Science of the Total Environment*, *764*, 142882. https://doi.org/10.1016/j.scitotenv.2020.142882

Li, Z., Lyu, X., Gao, B., Xu, H., Wu, J., & Sun, Y. (2021). Effects of ionic strength and cation type on the transport of perfluorooctanoic acid (PFOA) in unsaturated sand porous media. *Journal of Hazardous Materials*, *403*, 123688. https://doi.org/10.1016/j.jhazmat.2020.123688

Lyu, Y., Brusseau, M. L., Chen, W., Yan, N., Fu, X., & Lin, X. (2018). Adsorption of PFOA at the air–water interface during transport in unsaturated porous media. *Environmental Science & Technology*, *52*(14), 7745–7753. https://doi.org/10.1021/acs.est.8b02348

Maire, J., Coyer, A., & Fatin-Rouge, N. (2015). Surfactant foam technology for in situ removal of heavy chlorinated compounds-DNAPLs. *Journal of Hazardous Materials*, *299*, 630–638. https://doi.org/10.1016/j.jhazmat.2015.07.071

Murphy, P. M., & Hewat, T. (2008). Fluorosurfactants in enhanced oil recovery. *The Open Petroleum Engineering Journal*, *1*, 58–61. https://doi.org/10.2174/1874834100801010058

Nordhaug, H. F., Celia, M., & Dahle, H. K. (2003). A pore network model for calculation of interfacial velocities. *Advances in Water Resources*, *26*(10), 1061–1074. https://doi.org/10.1016/S0309-1708(03)00100-3

Pennell, K. D., Cápiro, N. L., & Walker, D. I. (2014). Surfactant and cosolvent flushing. In B. H. Kueper, H. F. Stroo, C. M. Vogel, & C. H. Ward (Eds.), *Chlorinated solvent source zone remediation* (pp. 353–394). Springer. https://doi.org/10.1007/978-1-4614-6922-3_11

Rosen, M. J. (1989). *Surfactants and interfacial phenomena* (2nd ed.). Wiley.

Rovero, M., Cutt, D., Griffiths, R., Filipowicz, U., Mishkin, K., White, B., Goodrow, S., & Wilkin, R. T. (2021). Limitations of current approaches for predicting groundwater vulnerability from PFAS contamination in the vadose zone. *Groundwater Monitoring & Remediation*, *41*(4), 62–75. https://doi.org/10.1111/gwmr.12485

Schaefer, C. E., Culina, V., Nguyen, D., & Field, J. (2019). Uptake of poly- and perfluoroalkyl substances at the air−water interface. *Environmental Science & Technology*, *53*(21), 12442−12448. https://doi.org/10.1021/acs.est.9b04008

Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (2003). *Environmental organic chemistry* (2nd ed.). Wiley.

Sharifan, H., Bagheri, M., Wang, A., Burben, J. G., Higgins, C. P., Liang, Y., Liu, J., Schaefer, C. E., & Blotevogel, J. (2021). Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone. *Science of the Total Environment*, *771*, 145427. https://doi.org/10.1016/j.scitotenv.2021.145427

Silva, J. A. K., Martin, W. A., Johnson, J. L., & McCray, J. E. (2019). Evaluating air-water and NAPL-water interfacial adsorption and retention of perfluorocarboxylic acids within the vadose zone. *Journal of Contaminant Hydrology*, *223*, 103472. https://doi.org/10.1016/j.jconhyd.2019.03.004

Silva, J. A. K., Martin, W. A., & McCray, J. E. (2021). Air-water interfacial adsorption coefficients for PFAS when present as a multi-component mixture. *Journal of Contaminant Hydrology*, *236*, 103731. https://doi.org/10.1016/j.jconhyd.2020.103731

Silva, J. A. K., Šimůnek, J., & McCray, J. E. (2020). A modified HYDRUS model for simulating PFAS transport in the vadose zone. *Water*, *12*, 2758. https://doi.org/10.3390/w12102758

Simmons, R. N. & McGuffin, V. L. (2007). Modeling transport effects of perfluorinated and hydrocarbon surfactants in groundwater by using micellar liquid chromatography. *Analytica Chimica Acta*, *603*, 93–100. https://doi.org/10.1016/j.aca.2007.09.025

Smith, J. E., Henry, E. J., & Bashir, R. (2011). Solute-dependent capillarity-induced focused flow during infiltration into alcohol-contaminated soil. *Vadose Zone Journal*, *10*(1), 403–411. https://doi.org/10.2136/vzj2009.0081

Striolo, A. (2019). Studying surfactants adsorption on heterogeneous substrates. *Current Opinion in Chemical Engineering*, *23*, 115–122. https://doi.org/10.1016/j.coche.2019.03.009

Wallis, I., Hutson, J., Davis, G., Kookana, R., Rayner, J., & Prommer, H. (2022). Model-based identification of vadose zone controls on PFAS mobility under semi-arid climate conditions. *Water Research*, 225, 119096. https://doi.org/10.1016/j.watres.2022.119096

Wang, Z., DeWitt, J. C., Higgins, C. P., & Cousins, I. T. (2017). A never-ending story of per-and polyfluoroalkyl substances (PFASs)? *Environmental Science & Technology*, *51*(5), 2508–2518. https://doi.org/10.1021/acs.est.6b04806

Wang, J. & Niven, R. K. (2021). Unification of surface tension isotherms of PFOA or GenX salts in electrolyte solutions by mean ionic activity. *Chemosphere*, *280*, 130715. https://doi.org/10.1016/j.chemosphere.2021.130715

United States
Environmental Protection
Agency

EPA 600/R-25/153 I July 2025 I

Office of Research and Development (8101R)
Washington, DC 20460