

Tool 2.1: Guide to PFAS Fate and Transport in Subsurface Environments

The following document describes the mechanisms by which PFAS may be transported in subsurface environments and the factors determining its eventual fate.

Per - and Polyfluoroalkyl Substances (PFAS) in Subsurface Environments
<p>Environmental characteristics including potential hydrogen (pH), organic matter content and type, salinity, ionic exchange capacity, moisture, flushing, presence of colloidal materials*</p> <p>* Colloids are homogeneous non-crystalline substances consisting of large molecules or ultramicroscopic particles of one substance dispersed through a second substance. Colloids include gels, sols, and emulsions. Colloids do not settle and cannot be separated out of a solution by filtration or centrifugation.</p>
<p>Relevance: Determines the presence or absence of ionic forms of PFAS affecting their mobility, the surface charges of soil minerals which affect electrostatic interactions with ionic PFAS, and subsurface conditions favoring PFAS tendency to accumulate at surfaces.</p>
<p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p> <p>pH - In the case of perfluoroalkyl acids (PFAAs), both the carboxylic and sulfonic perfluoroalkyl classes are in the ionic forms (i.e., as anions) in most environments, except at low pH values, when they are present as acids. In their ionic forms, they are negatively charged, being repelled by soil particles (mostly negatively charged) and resulting in higher mobility through soil.</p> <p>Organic matter - PFAS are expected to be more retarded in soils with high organic carbon content, however, this will be influenced also by PFAS charge and ionic exchange capacity of the soil. The type of organic matter in soil may also influence PFAS sorption and migration in subsurface, with PFAS sorption potential of pyrogenic carbonaceous material (for example, biochar) reported to be 14–780 times higher than that of humic-based material with a comparable fraction of organic carbon (Zhi and Liu 2018).</p> <p>Salinity - PFAS are more retarded in high salinity soils (Lyu and Brusseau 2020).</p>

<p>Per - and Polyfluoroalkyl Substances (PFAS) in Subsurface Environments</p> <p><u>Anionic/Cationic exchange capacity of soils</u> - The exchange capacity may help evaluate the strength of electrostatic interactions of ionic PFAS in soil. Cation exchange capacity positively impacted the sorption of the cationic 6:2 fluorotelomer sulfonamide amine (FtSaAm) and zwitterionic fluorotelomer sulfonamide betaines (FtSaBs) precursor-type of compounds (Barzen-Hanson, et al. 2017).</p> <p><u>Moisture</u> – The presence of moisture in soil provides soil/water and air/water interfaces where PFAS tend to accumulate. Therefore, a moist soil may have higher retention capacity for PFAS as compared to a dry soil (Interstate Technology and Regulatory Council 2020).</p> <p><u>Flushing+17:91 - PFAS soil-to-groundwater concentration ratios across multiple sites were shown to be strongly influenced by the degree of flushing that occurred (Anderson, Adamson and Stroe 2019). This contributes to increased soil retention at poorly flushed sites, as in those with low precipitation and deep groundwater.</u></p> <p><u>Presence of colloids</u> – PFAS may partition to mobile colloids in soils resulting in facilitated colloidal transport and increased mobility (Interstate Technology and Regulatory Council 2020).</p>
<p>Subsurface Geochemistry</p>
<p>Relevance: Refers to PFAS chemical structure affecting their properties and mobility.</p>
<p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p> <p><u>Pore spaces</u> - The greater the number of spaces within a porous media, the higher the potential for air/water and soil/water surface areas and the higher the retardation potential of PFAS migration due to the general PFAS tendency to accumulate at interfaces. Therefore, PFAS are expected to migrate slower through sandy soils than through clayey soils (Anderson, Adamson and Stroe 2019).</p> <p><u>Soil composition and chemistry</u> – Dictates the ionic charges of soil particles and subsequent interaction with PFAS polar groups; similar charges of soil particles and PFAS compounds would increase PFAS migration through soil, while opposing charges would slow PFAS migration in subsurface soils.</p> <p><u>Specific subsurface conditions</u> - PFAS retention in subsurface soils is enhanced in the vadose zone and the capillary fringe (Hatton, Holton and DiGuseppi 2018).</p> <p><u>Bedrock aquifers</u> – PFAS plumes were reported to migrate quickly in bedrock aquifers (Interstate Technology and Regulatory Council 2022).</p>
<p>Type of Released PFAS</p>
<p>Relevance: Refers to PFAS chemical structure affecting their properties and mobility.</p>

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<p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p> <p>The longer the fluorinated carbon chain, the stronger the hydrophobicity and the affinity to soil organic matter, resulting in a higher soil retention of longer chain PFAS.</p> <p>The functional groups may also affect subsurface migration of PFAS. Specifically, the type and ionic charge of PFAS functional groups may result in slower or faster migration through subsurface media.</p> <p>Negatively charged PFAS (anionic forms such as for carboxylic and sulfonic perfluorinated carboxylates and sulfonates) are expected to migrate faster than positively charged PFAS (cationic forms such as amines), while zwitterionic forms (that contain both positive and negative charges – such as betaines) migrate slower than anionic forms, but higher than cationic forms. Perfluorosulfonic acids (PFSAs) tend to adsorb more strongly than perfluoroalkyl carboxylic acids (PFCAs) of equal chain length (Interstate Technology and Regulatory Council 2020). For some of the studied fluorotelomers, sorption is strongest for FtSaAm, and less for FtSaBs and least for fluorotelomer sulfonates (FtSs) (Barzen-Hanson, et al. 2017).</p> <p>Linear vs. branched structures PFAS isomers are also known to affect subsurface mobility of released PFAS with faster migration expected for branched PFAS isomers (Interstate Technology and Regulatory Council 2020).</p> <p>Specific observations - For perfluorooctanesulfonic acid (PFOS), desorption was reported to occur more slowly than adsorption in soil; therefore, its potential retardation in soil may be significant (Interstate Technology and Regulatory Council 2020).</p>
Presence of Co-Contaminants
<p>Relevance: Determines the potential for additional either delay or increase in PFAS migration.</p>
<p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p> <p>Nonaqueous phase liquid (NAPL) – PFAS from Aqueous Film-Forming Foams (AFFF) are typically released along with other organic contaminants that may have caused fires, such as petroleum NAPL; PFAS may accumulate at water/NAPL interfaces (Brusseau 2018), further delaying PFAS environmental migration in subsurface; PFAS may also tend to partition into the organic NAPL phases (Guelfo and Higgins 2013), (McKenzie, Siegrist, et al., The Influence of a Non-aqueous Phase Liquid (NAPL) and Chemical Oxidant Application on Perfluoroalkyl Acid (PFAA) Fate and Transport 2016), (Brusseau 2018).</p> <p>Trichloroethylene (TCE) NAPL – Was reported to increase sorption of PFAS compounds with 3-5 carbon atoms in the chain, while decreasing sorption of larger PFAS molecules (Hatton, Holton and DiGuseppi 2018).</p>

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<u>Anionic sodium dodecyl sulfate</u> – May compete with PFAS for adsorption to organic carbon therefore, increasing subsurface mobility of PFAS (Guelfo and Higgins 2013).
Presence of Remedial Products
Relevance: Determines the potential for additional either delay or increase in PFAS migration.
<i>Specific factors to be evaluated and their effect on PFAS fate and transport:</i>
<u>Permanganate</u> – Is reported to increase PFAAs mobility and transport in subsurface media due to liberating soil organic matter (McKenzie, Siegrist, et al. 2015) (McKenzie, Siegrist, et al., The Influence of a Non-aqueous Phase Liquid (NAPL) and Chemical Oxidant Application on Perfluoroalkyl Acid (PFAA) Fate and Transport 2016).
<u>Peroxide</u> – Is reported to increase PFAS mobility and transport in subsurface media (McKenzie, Siegrist, et al. 2015) (McKenzie, Siegrist, et al., The Influence of a Non-aqueous Phase Liquid (NAPL) and Chemical Oxidant Application on Perfluoroalkyl Acid (PFAA) Fate and Transport 2016).
<u>Persulfate</u> – Is reported to decrease PFAS mobility and transport in subsurface media (McKenzie, Siegrist, et al. 2015) (McKenzie, Siegrist, et al. 2016).
<u>Polyvalent cations</u> – Are reported to reduce mobility of PFAS (Hatton, Holton and DiGuseppi 2018).
Release Type and Amount
Relevance: Dictates the concentration of released PFAS that, in turn, may affect their environmental mobility and migration distance.
<i>Specific factors to be evaluated and their effect on PFAS fate and transport:</i>
<u>Released PFAS concentration</u> - PFAS will adsorb more strongly at low PFAS concentrations than at high concentrations. Therefore, PFAS released in high concentrations (e.g., sudden and accidental releases) are expected to migrate faster through subsurface soils than PFAS released at low concentrations (for example, gradual leaks and spills).

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<p>High Vs. Low-mass sources – While PFAS released from high mass sources may travel great distances (for example, several miles), PFAS resulted from a low mass source may significantly attenuate at short distances from the source.</p>
Type of PFAS Source or Application
<p>Relevance: Help predict the potential and the process by which PFAS original composition may change from the source zone due to transformation of precursors (precursors are partially fluorinated PFAS, known as polyfluorinated alkyl substances. These compounds are less stable in the environment and tend to transform into fully fluorinated PFAS known as perfluoroalkyl substances. Fluorotelomers are examples of polyfluorinated PFAS) into distinct PFAS.</p>
<p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p> <p>Composition of the original released product containing PFAS – includes a specific mixture of both per- and polyfluorinated PFAS. While the perfluorinated PFAS are quite stable and will not typically transform in the environment, the polyfluorinated PFAS generally do transform into the more stable perfluorinated compounds, by losing the non-fluorinated carbons from the backbone or tail. The exact type of perfluorinated PFAS to be formed depends on the types of polyfluorinated PFAS present in the original spilled PFAS product. For example, fluorotelomers typically transform into perfluorocarboxylic acids (with lower carbon atoms in the tail), while polyfluorinated compounds present in PFAS mixtures manufactured by electrochemical fluorination (ECF) method may ultimately transform into perfluoro sulfonic acids. Therefore, PFAS migrating away from the source zone soils and reaching groundwater may have an altered fingerprint as compared to the original spilled product. The new PFAS mixture may have distinct fate and transport as compared with the mixture in the original spilled product.</p> <p>Total Oxidizable Precursor (TOP) This test determines individual PFAS in a sample before and after it is oxidized in the laboratory with the goal of evaluating the transformation of polyfluorinated precursors that cannot be analytically detected in detectable perfluorinated compounds. This may ultimately confirm the type of changes in PFAS composition that may be observed away from the release zone.</p>
Micelle Formation Potential
<p>Relevance: Determines the potential of significant decrease or increase in subsurface mobility for PFAS released at high concentrations.</p>
<p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p>

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<p><u>Released PFAS concentration</u> – If the released PFAS concentration is high enough (at critical micelle concentration (CMC)), micelles may be formed. The micelle formation will appear as a separate phase liquid floating on a water surface and may significantly impact mobility and vertical migration of PFAS compounds. Each individual PFAS compound will have distinct concentrations at which micelles may be formed. Those concentrations are much higher than typical environmentally reported PFAS concentrations. For example, in the case of PFOS, the CMC was reported between 500 - 5,000 milligrams per liter (mg/L) or parts per million (ppm) as compared with ppt or parts per billion (ppb) levels typically reported in environment. At lower concentrations, hemimicelles (partial micelles) and bilayers may also be formed impacting PFAS mobility in subsurface. Hemimicelles may be formed at 1,000 times lower concentrations than micelles. These concentrations are feasible to be found and have been reported for some PFAS at airport environments.</p> <p><u>Electrical charge of released PFAS and adsorbent environmental particles</u> – Depending on these charges, PFAS adsorption on soil minerals could be either enhanced or reduced, with potentially substantial effects on PFAS vertical migration at concentrations high enough for micelles, hemimicelles or bilayer formation. For example, adsorption of the anionic PFAS heads onto positively charged adsorbent surfaces can contribute to the formation and accumulation of hemimicelles near surfaces, increasing the near-surface aqueous concentration of PFAS relative to that measured in bulk solution (Yu, et al. 2009).</p>
Potential for Precursor Transformation into Commonly Monitored PFAS Compounds
<p>Relevance: Determines the potential for PFAS released to soils to change in the amounts and composition due to precursor.</p> <p>Specific factors to be evaluated and their effect on PFAS fate and transport:</p> <p><u>Total Oxidizable Precursor (TOP)</u> – Evaluation of the TOP may be done on representative soil samples (e.g., in source area and downward at various depths) in order to establish the potential of PFAS released to soils to generate higher total PFAS concentrations and change the original signature due to transformation of precursor PFAS compounds (polyfluorinated PFAS) into the measured and reported common PFAS compounds.</p> <p><u>Total Organic Fluorine (TOF)</u> - Evaluation of the TOF may be done on representative soil samples (e.g., in source area and downward at various depths) in order to confirm the trends observed via TOP analysis and evaluate the real extent of the presence of PFAS that may not be established due to analytical limitations, since only a very small fraction of PFAS potentially present may be measured via common laboratory analytical techniques (between 40-80 individual PFAS out of thousands of PFAS potentially present).</p>

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