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PNNL-35136

Development of Scalable Reactive Transport Framework for PFAS

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Summary

Ongoing research into per- and polyfluoroalkyl substances (PFAS) chemicals is extensive, including analytical quantification, determination of properties, toxicology, ex situ treatment, and in situ remediation. PFAS chemicals are very stable and thus persistent/recalcitrant in the environment. Although there are many unknowns about PFAS chemicals, degradation pathways, reaction rates, etc., many different sorption, oxidation, reduction, biological, and innovative treatment approaches are being developed. Sorption with activated carbon is currently the only fully available in situ treatment technology for PFAS-impacted groundwater. Given the wide array of PFAS chemicals and transformation products, remediation may need multi-step treatment trains to fully address the PFAS contamination.

The work here provides kinetic reaction modules that represent an initial offering at functionality representing PFAS migration and reaction in groundwater aquifer flow and transport models. One reaction kinetics module provides a method to model kinetically limited adsorption using a mass transfer model. The second reaction module represents biological transformation of 8:2 FTOH and daughter species, illustrating how a complex reaction pathway network can be represented. Both reaction modules allow for spatially variable parameter values so that a variety of remediation approaches (e.g., a permeable reactive barrier or volumetric treatment or variations in geochemical conditions) can be simulated. The intent with these PFAS reaction modules is to provide tools for practitioners to aid in the selection, design, and assessment of potential in situ PFAS remediation strategies. Application of these modules will require that practitioners determine whether these reaction modules are relevant to a particular site and remediation approach, and whether the assumptions and uncertainty are acceptable. That is, professional judgement and site-specific information will play a role in whether these reaction modules are suitable for remediation decision-making at a given site. It is anticipated that, as PFAS remediation technologies and scientific understanding advances, these modules would be refined or replaced to match new knowledge.

Acknowledgments

This work was funded by the U.S. Department of Energy Office of Environmental Management Headquarters, who are gratefully acknowledged.

Acronyms and Abbreviations

AFFF	aqueous film-forming foam
ATSDR	Agency for Toxic Substances and Disease Registry
CAC	colloidal activated carbon
CEC	cation exchange capacity
DLL	dynamic link library
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOM	dissolved organic matter
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FTOH	fluorotelomer alcohol
GAC	granular activated carbon
GAC	granular activated carbon
ITRC	Interstate Regulatory and Technology Council
NSF	National Science Foundation
OC	organic carbon
OM	organic matter
PAC	powdered activated carbon
PFAAs	perfluoroalkyl acids
PFASs	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutanesulfonic acid
PFCAs	perfluorinated carboxylates
PFHpA	perfluoroheptanoic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexanesulphonic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPeA	perfluoropentanoic acid
PFSAs	perfluorinated sulfonates
PNNL	Pacific Northwest National Laboratory
PRB	permeable reactive barrier
RT3D	Reactive Transport in 3-Dimensions code
SERDP	Strategic Environmental Research and Development Program
TOSD	tempered one-sided stable density
QA	quality assurance
ZVI	zero valent iron

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1.0 Introduction

Per- and polyfluoroalkyl substances (PFAS) pollution in the environment is an emerging concern, with much ongoing research into health effects, analytical chemistry methods, characterization, monitoring approaches, and environmental restoration technologies. The U.S. Environmental Protection Agency (EPA) is actively developing policy and technical approaches to address PFAS (https://www.epa.gov/pfas/key-epa-actions-address-pfas). The U.S. Department of Defense (DoD) actively funds basic research and field demonstrations of PFAS-related technology through their Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP). The U.S. Department of Energy (DOE) has conducted an initial assessment (DOE 2022), drawing upon survey responses collected from 53 DOE sites to summarize the current knowledge about the uses and releases of PFAS, with drinking water being an area of particular focus. DOE has also issued a PFAS Strategic Roadmap, PFAS Environmental Sampling Guidance, and other related guidance and policy documents (see https://www.energy.gov/pfas/pfas-and-polyfluoroalkyl-substances).

As DOE site-specific groundwater data is being collected and treatment technologies mature, data science and modeling tools will be needed to integrate multisource experimental and site-specific data with fundamental treatment technology principles to predict PFAS movement in the subsurface, aid in the design of effective field-scale remedies and evaluate potential impacts to existing site remedies. The work described in this report is a first step towards developing tools for modeling reactive contaminant transport in groundwater aquifers.

1.1 Background

Per- and polyfluoroalkyl substances (PFAS) are a group of several thousand anthropogenic chemicals which are fully (per-) or partly (poly-) fluorinated. The carbon fluorine bond is the strongest in organic chemistry, imparting valuable properties relative to biological, chemical, and thermal stability, but these properties result in extreme persistence (Houtz et al. 2013; Simon et al. 2019; Wang et al. 2017, 2018; Weber et al. 2017). PFAS have been developed and used in a broad range of commercial applications, such as the manufacturing of surfactants, stain repellents, fire suppressants, paper products, semiconductors, and textiles, since the 1950s (Paul et al. 2009; Prevedouros et al. 2006; Wang et al. 2017, 2018). In humans, exposure to certain types and levels of PFAS is indicated to lead to adverse health effects, including increases risk of some cancers, developmental delays in children, hormone interference, reduced immunity, and decreased fertility (ATSDR 2021; DeWitt 2015).

PFAS pollution is a widespread and long-term issue that is prompting regulatory actions. PFAS enter the environment through a variety of pathways and during all product lifecycle stages (i.e., manufacturing, use, and disposal). The widespread use of products containing PFAS, including certain firefighting foams used in the defense, mining, and aviation industries, has resulted in widespread contamination of soil and groundwater (IRTC 2021; Kjoholt et al. 2015; Lyu et al. 2022; Zhao et al. 2022). Furthermore, PFAS contaminated soils can act as a decadal source to groundwater, leading to almost indefinite contamination, despite regulation (Brusseau et al. 2020; Høisæter et al. 2019; Johnson et al. 2022; Maizel et al. 2021; McMahon et al. 2022; Zhao et al.

2022). Given the nature of PFAS pollution, EPA is taking actions to enforce stricter water quality standards on resource stewards (Simon et al. 2019; EPA 2022, 2023).

The unique chemical properties of PFAS present challenges in monitoring and remediation (Vecitis et al. 2009). PFAS chemicals are emerging contaminants of concern in that their ubiquity and associated environmental impacts were not considered until the early 2000s (Espana et al. 2015). Analytical methods applied to identifying environmentally relevant concentrations of PFAS did not become widely available until the early 2010s (IRTC 2021). PFAS have thus far been found to be resistant to typical environmental degradation processes, with the production of potentially more toxic and more mobile byproducts a concern (Bruton and Sedlak 2017; Guelfo and Higgins 2013). There are no proven analytical technologies which have been demonstrated to detect all potential fluoro-organic byproducts of PFAS degradation processes, and remediation efforts have the potential to miss precursors and/or byproducts that could continue to be a long-term source of contaminants (Horst et al. 2020; Nickerson et al. 2021).

There are multiple conceptualizations to organize the wide array of PFAS chemicals (e.g., Mahinroosta 2020; Wang et al. 2018). Figure 1 based on ITRC (2022) provides a simplified visual for the classification of selected PFAS compounds, namely the perfluoroalkyl acids (PFAAs), comprising perfluorinated carboxylates (PFCAs) and perfluorinated sulfonates (PFSAs).

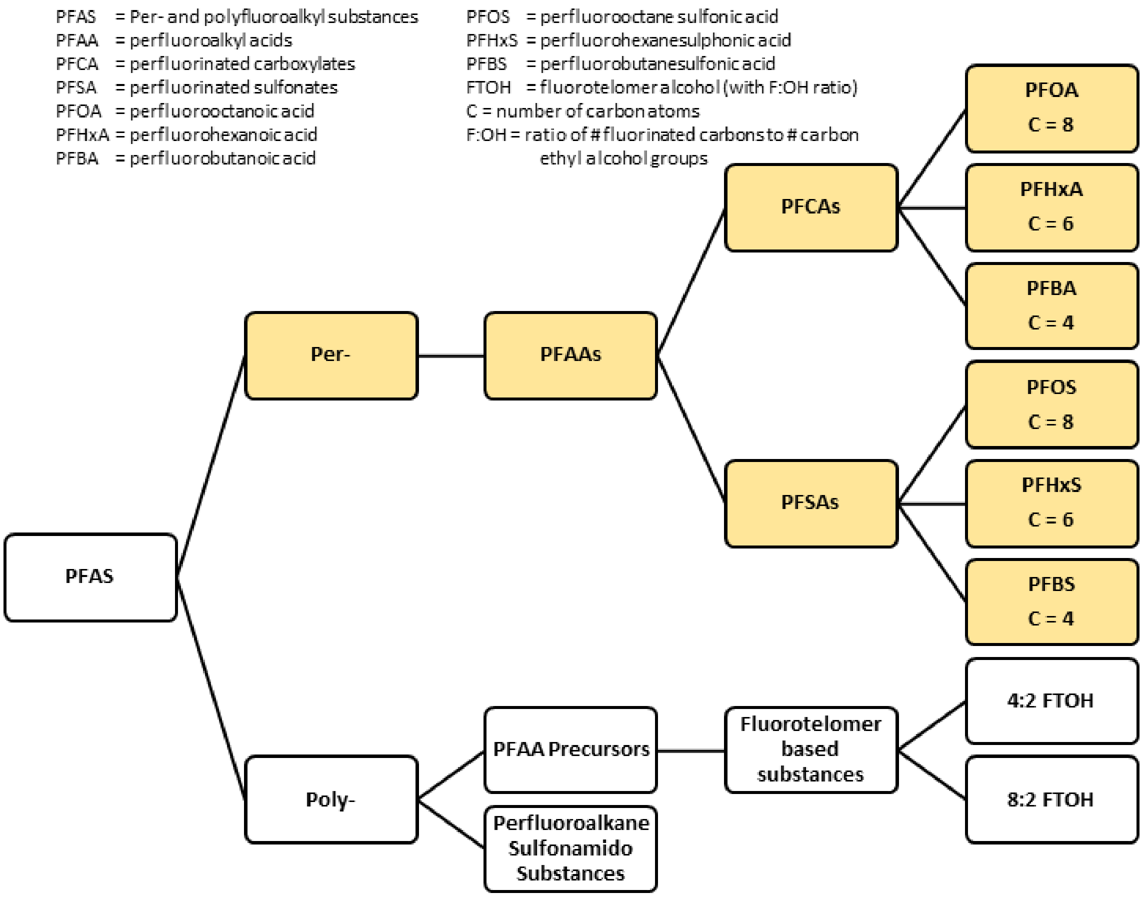

Figure 1. Simplified categorization of PFAS compounds (based on information in ITRC 2022).

1.2 Objectives

The objective of this work was to provide initial functionality for representing PFAS migration and reaction in groundwater aquifer flow and transport models through development of kinetic reaction modules. The intent with these PFAS reaction modules was to provide tools for practitioners to consider for the selection, design, and assessment of potential in situ PFAS remediation strategies. Application of these modules will require that practitioners determine whether these reaction modules are relevant to a particular site and remediation approach, and whether the assumptions and uncertainty are acceptable. That is, professional judgement and site-specific information will play a role in whether these reaction modules are suitable for remediation decision-making at a given site.

The RT3D (Reactive Transport in 3 Dimensions) code (Clement 1997; Clement et al. 1998) was selected as the framework for developing kinetic reaction modules, though the reaction kinetics could be adapted for use with other transport codes. RT3D is a multi-species, 3-D reactive transport simulation software for groundwater systems (https://www.pnnl.gov/projects/multi-species-reactive-transport-simulation-software-groundwater-systems) that provides flexibility to simulate a wide range of reaction kinetics. RT3D is part of the widely used MODFLOW/MT3D family of codes (Harbaugh 2005; Zheng and Wang 1999).

The specific objectives of this work were to:

- Conduct a literature survey to consolidate information about known PFAS reactions (pathways and rates), remedial technologies, and potential case study information for use in validation. The literature information and data inform the development of reaction modules.
- Develop a reactive transport module for PFAS kinetic sorption on geological media and/or sorbent materials with spatially variable sorption properties (i.e., to capture site-specific biogeochemical characteristics and remedy approaches).
- Develop a reactive transport module for spatially variable PFAS transformation reactions for biological/chemical transformation from parent PFAS compounds to daughter products.

2.0 Overview of Current PFAS Remediation Technologies

A lot of energy is going into research and development to determine effective PFAS remediation technologies for both ex situ water treatment and for in situ groundwater remediation. PFAS treatments are being investigated by researchers in academia, industry, and organizations such as the DoD, EPA, and the National Science Foundation (NSF). The range of potential technologies includes immobilization (adsorption/sequestration), transformation/destruction (e.g., bioremediation, chemical oxidation, chemical reduction, or thermal destruction), and removal (capture/extraction) technologies. The thermal stability of PFAS chemicals and their strong binding capacity to soil and/or organic matter mean that applying remediation technologies that have been used for typical organic and inorganic pollutants are challenging or even ineffective for treating PFAS (Bentel et al. 2019; Kucharzyk et al. 2017; Mahinroosta and Senevirathna 2020; Vecitis et al. 2009; Wang et al. 2017, 2018; Lim 2021; Berhanu et al. 2023).

Work continues to develop suitable ex situ and in situ remediation strategies, with some successes being seen with ion exchange/sorption, advanced oxidation, thermal, and biological/enzymatic technologies (Vo et al. 2020; Dixit et al. 2021; Kang et al. 2023; Yadav et al 2022; Duchesne et al. 2020; Sun et al. 2023; Yu et al. 2022; Zhang et al. 2022; Grgas et al. 2023). Ex situ water treatment technologies that can be applied for waste sites and wastewater treatment of aqueous phase PFAS have had a lot of focus (Alalm and Boffito 2022; Espana et al. 2015; Horst et al. 2020; Kucharzyk et al. 2017; Olsavsky et al. 2020). Another area of focus has been on technologies for adsorption or destruction of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), which are classified as long-chain (with 8 or more carbon atoms, $C \geq 8$) PFAS chemicals. In situ treatment technologies are also being investigated as less expensive and more permanent solutions to subsurface PFAS contamination, but challenges in scale and site-specific application persist (Mahinroosta and Senevirathna 2020).

A brief survey of current remediation approaches for PFAS is presented below. Ex situ technologies are discussed, though the in situ processes are more relevant to the work here.

2.1 Ex Situ Remediation Technologies

Ex situ treatment of water for the most common PFAS chemicals is relatively well established, with published research demonstrating effective removal of PFOA and PFOS (Grieco et al. 2022). Adsorption (e.g., granular activated carbon [GAC]) and ion exchange (e.g., resins), are the most well established, ‘field implemented’ ex situ treatments and are currently in use at military installations and by private water companies (IRTC 2021). Ex situ technology is often deployed within existing remediation systems targeted at other contaminants, however; the presence of co-contaminants can impact the choice and efficacy of the treatment technology. Furthermore, management of spent sorption media is an important consideration for practitioners. Most common options are off-site disposal via thermal destruction, reuse through regeneration, and landfilling (IRTC 2021). Enhanced methods of sorption for the removal of PFAS in ex situ applications continues to be an ongoing area of research (Mahinroosta and Senevirathna 2020).

Pilot-scale ex situ treatment technologies using a multi-method approach (i.e., treatment train) have recently been investigated, and in some instances, successfully demonstrated. For example, a field-based study in Australia using a treatment train approach of foam fractionation and nanofiltration was able to achieve 99% removal efficiency of PFAS from approximately 4 million gallons (15 million liters) of aqueous film forming foam (AFFF) impacted wastewater (McDonough 2019). The method used ozofractionation to remove PFAS compounds, including short chain variations, while also destroying organic co-contaminants. The ozonfractionation method was shown to convert C6 precursors to perfluorohexanoic acid (PFHxA) and perfluoropentanoic acid (PFPeA), which could then be removed with nanofiltration. The concentrated effluent was then thermally destroyed offsite.

More recently, novel treatment techniques have targeted the full degradation of PFOA, PFOS, and their intermediates through defluorination (Kucharzyk et al. 2017), effectively eliminating the need for off-site, high energy, thermal destruction. Degradation of PFCAs and PFSAs is achieved by removing a carboxyl or sulfur trioxide group to release carbon dioxide (decarboxylation) or sulfur trioxide. Fluorine is replaced with hydrogen atoms (defluorination), and the carbon-carbon bonds are cleaved. Innovative degradation methods include electrochemical, sonochemical, photocatalytic, mechanochemical, plasma, radiolytic, and other oxidative and reductive processes (Bentel et al. 2019). Table 1 briefly summarizes selected recent research efforts for innovative ex situ treatment methods for PFAS.

Table 1. Sample of recent innovative ex situ PFAS treatment studies.

Method (Reference)	Scale	Research Summary
Photolysis with UV-generated hydrated electrons (Bentel et al. 2019)	Lab-based	This work investigated the structural factors of PFAS that may control the rate and extent of defluorination. Decay of perfluorinated carboxylic acids (PFCAs; ($C_nF_{2n+1}COO^-$)) was found to be complete within 8-12 hours for compounds of n = 1 -10. Multiple reaction pathways were identified, leading to the formation of variable defluorination products. Perfluorinated sulfonates with short fluoroalkyl chains were slow to react and recalcitrant to oxidation. Therefore, practical applications should use caution due to the likelihood of PFAS contamination being present as a mixture of diverse structures.
Non-thermal plasma as an advanced oxidation method (Khan et al. 2022)	Lab-based environmental field samples	The work specifically targeted the destruction of PFOA, PFOS, and a mixture of PFOA and PFOS in distilled water to isolate effectiveness of non-thermal plasma treatment. PFOA degradation was found to be nonlinear. A higher degradation rate was measured for PFOS than PFOA (average 35% higher treatment efficiency for PFOS compared to PFOA). Treatment time was found to be the main influence on the effectiveness of PFAS degradation and overall cost of the treatment. Most PFAS were completely degraded and not transformed to short-chain PFAS compounds. Efficiency of degradation decreased to 70% after 60 minutes in groundwater samples from soil-contaminated sites, providing further challenges in scaling this method. No reaction pathway was provided.

Method (Reference)	Scale	Research Summary
Sonolytic degradation (Shende et al. 2019)	Lab-based	The sonolytic degradation of aqueous PFOA and PFOS was found to be a function of adsorption at the cavity-water interface. Findings contest the previously theorized degradation mechanics, and instead suggest the cleavage of an ionic head group is dependent on the structural orientation of the PFAS at the time of adsorption to the cavity-water interface. PFOS was found to be less degradable under high-frequency ultrasound experimental conditions, compared to PFOA. Degradation follows pseudo-first-order reaction kinetics, and a proposed pathway is provided.
Radiolytic decomposition of PFOS using an electron beam and activated persulfate treatment (Kim et al. 2019)	Lab-based	One of the first studies on the effects of adding oxidants to the radiolytic degradation of PFOS and to suggest the degradation mechanism. The addition of persulfate was found to be able to lower the required absorbed dose, thus reducing energy consumption. Overall, PFOS requires a higher absorbed dose than other recalcitrant organic contaminants, which poses challenges for upscaling efforts.
Gamma irradiation (Patch et al. 2022)	Lab-based	Solutions containing 15 PFAS and precursor compounds were gamma irradiated, followed by high-resolution mass spectrometry to identify more than 80 fluorinated transformation products formed during the degradation process. Gamma irradiation can produce hydroxide radicals, aqueous electrons, and hydrogen radicals as reactive species. The addition of methanol was shown to improve degradation of PFCAs through the enhanced release of aqueous electrons. Degradation efficiency in these experiments was found to be a function of chain length and pH. First-order and zero-order rates for all PFAS were calculated. A unified reaction schematic for PFAS irradiation in water was presented, with three pathways and 16 steps.

2.2 In Situ Remediation Technologies

In contrast to ex situ treatment, in situ remediation occurs in the subsurface in the vadose zone (unsaturated) or a groundwater aquifer (saturated). The subsurface presents additional challenges in characterization, implementation, and performance assessment. As part of the 2nd PFAS Experts Symposium held in June 2021 (Newell et al. 2022), the In Situ Remediation Technologies Committee prepared a review of “available” in situ technologies for PFAS, i.e., those technologies that are verified at the field scale and available for use now or in the near future (Abrams et al. 2022). According to the results of their review, sorption with activated carbon is the only fully available in situ treatment for PFAS-impacted groundwater. However, long-term performance of adsorptive activated carbon technologies is still an area of ongoing research (Carey et al. 2022; Liu et al. 2020; McGregor 2018, 2020; Son and An 2022). Other emerging methods that have been demonstrated at the lab or pilot scale include degradation technologies such as bioremediation and chemical oxidation/reduction (Abrams et al. 2022; Leung et al. 2022). A non-exhaustive overview of in situ sorption and degradation information and technologies is provided in the following sections.

2.2.1 Sorption

Several factors influence the fate and transport of PFAS in the subsurface, including compound-specific chemical properties and site-specific characteristics. Most of the commonly studied PFAS chemicals contain a carbon-fluorine tail (hydrophobic and lipophobic) and a nonfluorinated, polar functional head group (hydrophilic). The competing head and tail structures and the length of the carbon chain result in multiple partitioning mechanisms affecting PFAS, including hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors. In general, adsorption of long-chain PFAS chemicals are dominated by hydrophobic interactions, while short-chain PFAS chemical adsorption is dominated by electrostatic interactions (Qi et al. 2022). In the saturated zone, PFAAs (e.g., PFOA and PFOS) are relatively mobile, but sorption and retardation increase with increasing carbon chain length, and PFSAs generally sorb more strongly than PFCAs. Soil properties also impact sorption behavior, with the most important properties being organic matter (OM) content, pH, pore volume, and cation exchange capacity (CEC) (Li et al. 2018; Lyu et al. 2022; Mahinroosta and Senevirathna 2020; Milinovic et al. 2015). The magnitude of these impacts also depends on PFAS chain length and the nature of the functional head group. Table 2 summarizes key points of properties[1] influencing the sorption of PFAS.

Table 2. Influence of soil and PFAS compound characteristics on sorption.

Property	Effect	References
Dissolved Organic Matter (DOM)	▪ Competes with PFAS for sorption sites ▪ Strongly influences removal rate ▪ DOM bound PFAS have increased solubility ▪ DOM can also promote desorption ▪ Stronger influence over anionic PFAS	(Li et al. 2018; Milinovic et al. 2015; Qi et al. 2022)
pH	▪ Soil sorption coefficients increases when pH decreases ▪ Stronger influence on long chain (C>6) behavior compared to short chain	(Nguyen et al. 2020)
Soil micropore volume	▪ Correlates more strongly to sorption capacity of anionic PFAS with C > 6	(Nguyen et al. 2020; Park et al. 2020)
PFAS Chain Length	▪ Less strongly impacts sorption compared to compound ionic state ▪ Longer chain PFAS have increased soil sorption coefficients, implying hydrophobicity is the driving force for sorption ▪ Longer chain PFAS are dominated by hydrophobic interactions ▪ Shorter chain PFAS are dominated by electrostatic interactions	(Higgins and Luthy 2006; Milinovic et al. 2015; Nguyen et al. 2020, 2022; Qi et al. 2022)
Compound Molecular Weight	▪ No relationship between sorption and smaller PFAS (shorter-chain PFAS, molecular weight < 350 g/mol) ▪ Positive, linear relationship between sorption and larger molecules (longer chain, molecular weight > 350 g/mol) ▪ For the C6 and C8 perfluorinated compounds, PFSAs will exhibit stronger sorption compared to PFCAs due to the increased molecular weight of PFSAs	(Maimaiti et al. 2018; Nguyen et al. 2020)

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[1] CEC was not included in Table 2 due to its co-dependence on other physiochemical properties and the lack of specific measurements of CEC of soils used in sorption experiments (Li et al. 2018).

2.2.1.1 Sorption Technologies

Several sorption-based treatments are commercially available, and small-scale studies, most often at fire training areas or military installations, have shown success with these treatments. Stewart and McFarland (2017) used a novel aluminum hydroxide-based adsorption product to demonstrate remediation of soil leachate to levels below 0.3 µg/L (based on Minnesota Department of Health guidance for drinking water standards) for a suite of 20 PFAS compounds, including PFOA and PFOS. The material was determined to be a rapid and cost-effective remediation strategy for AFFF impacted soils. McGregor (2020) conducted one of the first groundwater pilot-scale in situ studies at a site co-contaminated by hydrocarbons and PFAS. Four adsorbent reagents were investigated as part of the study, including a colloidal activated carbon (CAC) product. Groundwater monitoring was conducted for 18 months following reagent injection. Of the treatments tested, the CAC was the only reagent not to experience breakthrough after 18 months, demonstrating effective attenuation of 23 PFAS compounds.

Improving current sorption treatments, particularly for newly identified PFAS compound sequestration and effectiveness and moving beyond the laboratory scale, continues to be an ongoing research area. Between 2009 and 2017, 455 new PFAS compounds were identified, highlighting knowledge gaps in understanding the fate and transport of PFAS in contaminated environments, including about transformation of precursor products (Xiao 2017; Barzen-Hanson 2017). Xiao et al. (2017) compared the removal of 30 PFAS compounds, including 13 newly identified substances, using granular activated carbon of different particle sizes in laboratory batch experiments. Their research indicated the smallest particle size tested on AFFF-impacted water had the highest removal rate after 5 days at equilibrium. Subsequently, more research into developing a stable aqueous suspension of powdered activated carbon and assessing the longevity of injected colloidal activated carbon has recently been undertaken (Carey et al. 2022; Liu et al. 2020; Son and An 2022). However, pilot-scale studies remain critically important to validate the effectiveness of sorption technologies in the saturated zone in real environmental settings due to the known, complex interactions between physical soil properties, chemical compound structure, and solution chemistry (Liu et al. 2019).

2.2.1.2 Sorption Modelling

Modelling PFAS adsorption is important for assessing effective remediation strategies, with multiple methods proposed for modelling sorption under varied environmental settings. Sima and Jaffé (2021) provide a comprehensive overview of modeling PFAS in the soil-water environment, including sorption and desorption to soils and artificial sorbents (i.e., activated carbon and other treatment technologies). Table 3 summarizes common approaches for mathematically representing PFAS sorption. For the purposes of this work, PFAS sorption at the air-water and NAPL-water interfaces are not discussed further, but more information is available (Sima and Jaffé 2021; Schaefer et al. 2022; Brusseau and Guo 2022).

Table 3. Common approaches to modelling sorption of PFAS at equilibrium.[1]

Isotherm / Model	Mathematical Model Equation	Comment
Linear Isotherm	$C_s = K_dC_w$ (1) C_s - PFAS concentration at equilibrium in the solid phase (µg/g) C_w - PFAS concentration at equilibrium in the aqueous phase (µg/mL) K_d - partition coefficient (mL/g)	▪ K_d increases with solution ionic strength and fraction organic carbon ▪ Measured K_d values increase with carbon chain length ▪ Field based K_d values are larger than those measured in at the laboratory scale ▪ Applicable to low environmental PFAS concentrations
Freundlich Isotherm	$C_s = K_FC_w^N$ (2) K_F - partition coefficient (mL/g) N - Freundlich constant (—)	▪ Represents nonlinear sorption ▪ Sorption becomes nonlinear as K_d decreases with increasing PFAS concentration ▪ K_f varies with PFAS compound and sorbent characteristics ▪ Research suggests a linear K_d value can be used at low PFAS concentrations depending on soil-PFAS-solvent interactions ▪ Applicable to higher environmental concentrations of PFAS
Virial Isotherm	$C_s = K_{vi}C_we^{-bC_s}$ (3) K_{vi} - sorption distribution constant (mL/g) b – adjustable parameter (g/µg) related to interfacial capacitance	▪ Less common ▪ Based on linear isotherm with correction for heterogeneity or soil surface electrostatic energy ▪ Comparable to the Freundlich isotherm
Langmuir Isotherm	$C_s = S_m\frac{b_LC_w}{1 + b_LC_w}$ (4) S_m – maximum sorption capacity (µg/g) b_L – constant (mL/µg)	▪ Accounts for sorption capacity (may be more appropriate in environments with coexisting PFAS) ▪ Comparable to Freundlich when describing non-linear PFAS sorption onto a range of sorbents ▪ Applicable to higher environmental concentrations of PFAS

PFAS sorption kinetics can be described by a range of models, including first order, pseudo first order, pseudo second order, intraparticle diffusion, and mass transfer. Additional advanced representations have also been investigated in response to the need to reliably quantify adsorption kinetics for various PFAS compounds in different soils. Zhou et al. (2021) proposed a universal physical law for PFAS adsorption by interpreting the adsorption kinetics as a nonequilibrium process with multiple rates, following the tempered one-sided stable density (TOSD) distribution. Several PFAS adsorption kinetic studies were reviewed and described, and then the TOSD-based models were successfully validated against these published data. In addition, a recent study by

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[1] Equations and corresponding comments in Table 3 are based on Sima and Jaffé (2021).

(Fabregat-Palau et al. 2021) represented sorption behavior of PFAs compounds in soil by modelling relative sorption at organic carbon and mineral sites. The distribution coefficient (K_d) of was predicted for PFCAs and PFSAs ($3 \geq C \geq 11$) using only the organic carbon (OC) and silt/clay content information for the soil.

PFAS concentrations in the subsurface tend to be very low, resulting in linear sorption isotherms being appropriate for the majority of practical modelling requirements (Brusseau and Van Glubt 2019). Sorption kinetics are generally most important during the initial exposure of sediment to PFAS (for which the time scales are relatively under natural conditions) and when the system hydraulics are changing (Zhang et al. 2019; Haggerty and Gorelick 1994). Although desorption kinetics can affect the efficiency of a remediation process, few studies have measured desorption kinetics (Sima and Jaffé 2021). Haggerty and Gorelick 1994 describe an immobile/mobile system for contaminant transport with kinetic adsorption/desorption based on a mass transfer approach. Their "one-site" first-order mass transfer approach generically represents processes for (1) sorption of contaminants onto and off of mineral and organic matter surfaces (chemical nonequilibrium), (2) diffusion into and out of minerals and organic matter (intra-sorbent diffusion non-equilibrium) and (3) diffusion into and out of lithologies of low permeability and smaller stagnant zone (transport-related, or physical nonequilibrium).

2.2.2 Transformation and Degradation

PFAS chemistry generally results in strong persistence and recalcitrance under natural environmental conditions, posing challenges for remediation, compared to other better-understood contaminants (e.g., petroleum hydrocarbons, chlorinated solvents, metals, etc.). Transformation through biological (e.g., microbial) or chemical (e.g., oxidation/reduction) processes has been demonstrated for ex situ processes, and in situ approaches are being investigated. A brief review of select potentially applicable in situ transformation/degradation technologies is provided below, although most technologies are yet to be experimentally verified beyond bench-scale.

2.2.2.1 Chemical Oxidation

Chemical oxidation is a common in situ treatment method for certain environmental contaminants. Typically, such technologies use direct transfer of electrons to electron acceptors to transform or degrade the target contaminant (Leung et al. 2022). The highly electronegative fluorine atoms within PFAAs, however, reduce the electron density of functional groups thus preventing oxidative attacks under general oxidizing conditions. To overcome this challenge, more reactive free radicals have been investigated (Kucharzyk et al. 2017; Vecitis et al. 2009). Mitchell et al. (2013) investigated degradation of PFOA by a catalyzed hydrogen peroxide process that generates additional reactive oxygen species, such as perhydroxyl radicals, superoxide radical anions, and hydroperoxide anions. In reactions where hydroperoxide was generated as the sole reactant in solutions at an elevated pH, PFOA was reduced by 80% with no detectable degradation products. A more cost-effective and field-applicable strategy, however, may be thermally activated persulfate, which produces sulfate radicals that can degrade PFAS. Park et al. (2016) achieved complete decomposition of PFOA using thermally activated (60 °C) persulfate, even in the presence of polycyclic aromatic hydrocarbon co-contaminants. Notably, however, PFOS did not degrade under the range of thermal experimental conditions applied, suggesting that a multi-faceted treatment system would likely be needed to address both PFOA and PFOS.

Crimi et al. (2017) conducted a comprehensive investigation using a ‘treatment train’ approach involving low cost in situ horizontal reactive media wells. Granular activated carbon was used to sorb and concentrate PFAS from AFFF impacted media, followed by contaminant destruction and GAC regeneration using activated persulfate oxidation. Although degradation of PFOA was enhanced (95% degradation within 24 hours) using multiple oxidant doses of lower concentrations, results confirmed previous findings that PFOS is resistant to degradation by heat-activated persulfate (S. Park et al., 2016).

2.2.2.2 Chemical Reduction

Based on experience with other contaminants, such as halogenated hydrocarbons (Burris et al. 1996; Dror and Schlautman 2004; Gantzer and Wackett 1991), reductive dehalogenation through chemical methods should be an applicable mechanism for PFAS remediation through fluoride elimination. Several studies have investigated reductive defluorination approaches, with PFAA degradation testing using reductants such as zero valent iron (ZVI), modified Fenton’s reagent, and dithionite (Leung et al. 2022; Mitchell et al. 2013; Vellanki et al. 2013; Xia and Liu 2020). In one study (Ochoa-Herrera et al. 2008), catalyzed reductive dehalogenation of PFOS was achieved by electron transfer mediators under anoxic conditions and at increased temperatures (70 °C). The process occurred more rapidly for branched versus straight-chain PFAS chemicals. Lee et al. (2017) investigated the use of titanium(III) citrate in the presence of catalysts (vitamin B_{12} and nano zero valent copper) to reductively defluorinate PFOA. The degradation pathway involved the removal of electrons from PFOA by vitamin B_{12} and the formation of cobalt-carbon intermediates. The precursor complex was adsorbed on the surface of the nano copper where a reaction then formed less-fluorinated products. The overall reaction efficiency was shown to increase under basic pH conditions. The study (Lee et al. 2017) reported 65% PFOA removal with no release of short chain intermediates when using an initial pH of 9.0 and a temperature of 70 °C.

2.2.2.3 Microbial Degradation

There is growing evidence that PFAS compounds are reactive and will transform in the environment through biological processes mediated by bacteria, fungi, and enzymes (Yu et al. 2022; Zhang et al. 2022; Berhanu et al. 2023; Grgas et al. 2023). For example, PFAA precursors, including PFOA and PFOS, can biodegrade through various polyfluorinated intermediates to produce more mobile PFAAs as terminal products (Newell et al. 2021). Biodegradation of PFAS is generally understood to involve enzymes that directly remove fluorine atoms by either adding oxygen or electrons across the F-C bond, allowing other normal assimilation enzymes to break down the rest of the compound (Shahsavari et al. 2021). Studies have elucidated potential degradation and/or transformation pathways under certain natural and laboratory settings, but detailed kinetic information is lacking, and transformation products are often not able to be verified experimentally (Mejia-Avendaño et al. 2016; Nickerson et al. 2021; Weber et al. 2022; Zhang et al. 2022). Conversion is generally slow, with low product yields. Reaction pathways often have multiple intermediates, are generally branched, and mass balance accounting is a major challenge (Zhang et al. 2022).

Emerging trends in PFAS biodegradation and/or biotransformation are summarized below.

- Combined biotic/abiotic degradation or transformation shows a direct correlation to soil nutrient status and PFAS sorption.
- High molecular weight PFAS compounds break down to a diverse catalog of less well-known, low molecular weight chemicals that cannot yet be measured reliably.
- Molecular weight is a good indicator of compound stability (stability generally increases with decreasing molecular weight).
- Many reactions target and transform the functional group of PFASs, yielding varied polyfluorinated compounds.
- Proposed pathways for different compounds substantiate defluorination reactions, however, the specifics are not well understood.

Specific biodegradation for PFOA and PFOS was described by Huang and Jaffé (2019) for a pure culture of an autotroph strain *Acidimicrobium* sp. A6, which is known to promote the Feammox process. The Feammox process is a relatively novel pathway in the nitrogen cycle by which the anaerobic oxidation of ammonium (NH_4^+) occurs under iron-reducing conditions. The study reported the strain is common at iron rich sites where soil pH is < 7. After 100 days of incubation, 50% of detected POFA was transformed to intermediate products of perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA) in enriched microbial cultures. The proposed mechanism of degradation is defluorination while reducing iron and using ammonium or hydrogen as the electron donor.

Currently, the best described biotic pathways are the aerobic degradation of 8:2 and 6:2 FTOH (Liu et al. 2010; Wang et al. 2009; Harding-Marjanovic et al. 2015; Yan et al. 2022). Proposed pathways have largely been derived from laboratory-scale investigations. The recent study by Yan et al. (2022) investigated the biotransformation of 8:2 FTOH under nitrate-, iron-, and sulfate-reducing conditions in microcosms of AFFF impacted soils, which is a closer representation of fate in the natural environment. Different transformation products were detected, depending on the reducing agent, and two new compounds were identified during the biotransformation of 8:2 FTOH. Furthermore, biotransformation was found to be fastest under oxic conditions. The biotransformation pathways proposed by Yan et al. (2022) for 8:2 FTOH under various redox conditions are shown in Figure 2.

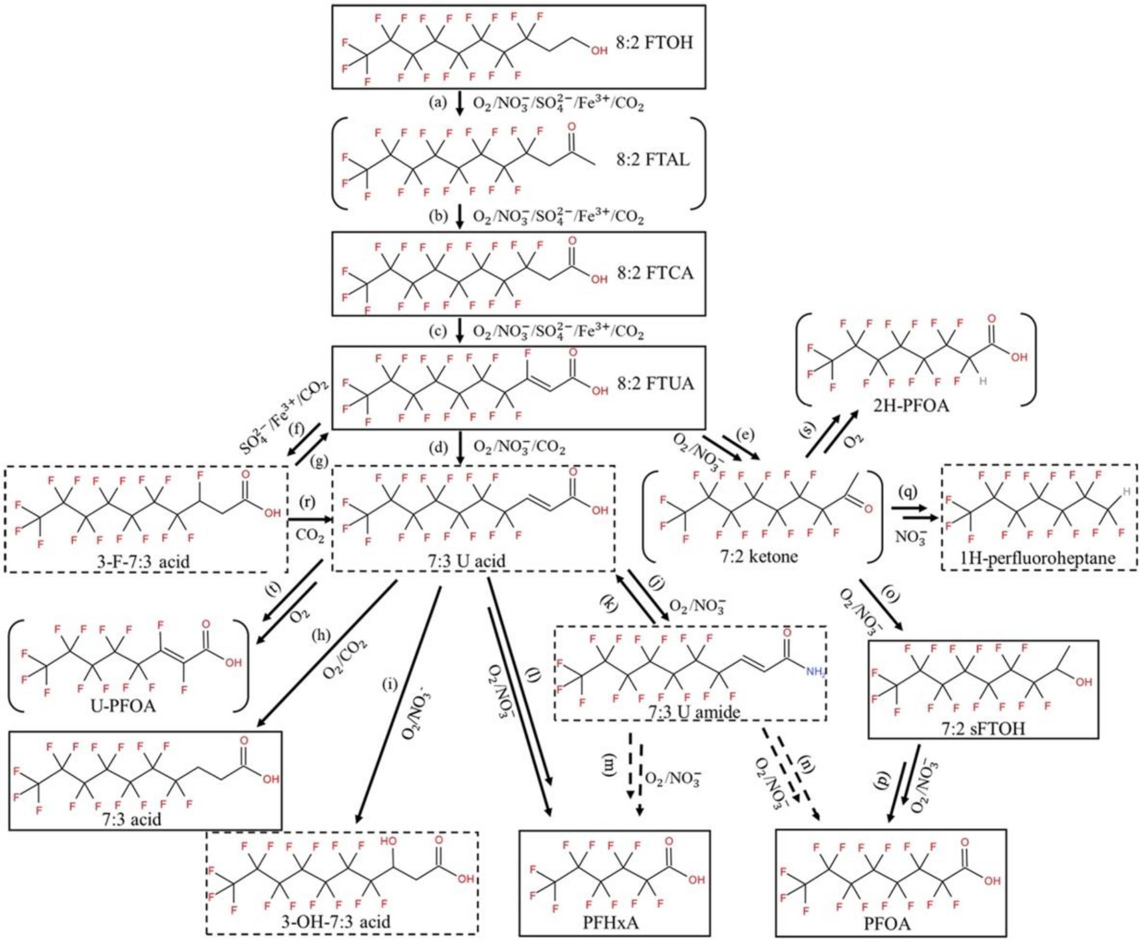

Figure 2. 8:2 FTOH biodegradation pathways proposed by Yan et al. (2022). Chemicals in rectangular boxes (solid and dashed) were detected in the study, while chemicals in brackets were not (though the paths are proposed in other studies). Solid arrows are expected paths, dashed arrows are uncertain paths, with double arrows indicating a multi-step process. Figure from Yan et al. (2022).

2.3 Remediation Technologies Summary

Research on PFAS chemicals is extensive and covers all aspects, including analytical quantification, determination of properties, toxicology, ex situ treatment, and in situ remediation. The stability of PFAS chemicals results in strong persistence and recalcitrance (particularly under natural environmental conditions in the subsurface), posing challenges for remediation. There are many unknowns, including what PFAS chemicals there are (with new ones continuing to be identified), degradation pathways, reaction rates, etc. Many different treatment approaches have been developed using traditional principles (e.g., adsorption, ion exchange, advanced oxidation, thermal, and biological) and innovative methods (e.g., photolysis, non-thermal plasma, sonolytic, radiolytic). To date, sorption with activated carbon is the only fully available in situ treatment for PFAS-impacted groundwater, though long-term performance is still being investigated. Work is progressing on other technologies for in situ PFAS transformation/degradation, with many proposed approaches, mechanisms, reaction pathways, and modeling approaches. Reactive approaches have challenges in detecting/verifying transformation products (which have the potential to be more problematic that the parent chemicals) and thus with closing the mass balance. Given the wide array of PFAS chemicals and transformation products, remediation may need multi-step treatment trains to fully address the PFAS contamination. There is a lot of promise in the current research on PFAS treatment/remediation, but there is also a lot left to learn.

3.0 Reaction Kinetics Modules

The objective of this work was to provide initial functionality for representing PFAS migration and reaction in groundwater aquifer flow and transport models through development of kinetic reaction modules. The intent with these PFAS reaction modules was to provide tools for practitioners to aid in the selection, design, and assessment of potential in situ PFAS remediation strategies. Toward this objective, two reaction modules were selected for development: kinetically limited adsorption and reactive transformation/degradation. As noted previously, the reaction modules were developed for application with the RT3D multi-species, three-dimensional reactive contaminant transport code for groundwater modeling (Clement 1997; Clement et al. 1998). Implementation of reaction modules for RT3D is convenient because the reaction mechanisms are encapsulated in a code module that is compiled into a dynamic link library (DLL). Thus, no changes are needed to the RT3D code. Rather, the RT3D code is simply run with the correct "rxns.dll" file for the reaction kinetics of interest. Note that RT3D (as with sister codes such as MT3DMS) uses the MODFLOW (Harbaugh 2005) flow solution to simulate reactive contaminant transport.

Note that application of either of these reaction modules will require that practitioners determine their relevance to a particular site and remediation approach, and whether the assumptions and uncertainty are acceptable. That is, professional judgement and site-specific information will play a role in whether these reaction modules are suitable for remediation decision-making at a given site.

The following sections describe the reaction modules for kinetically limited sorption and transformation of parent PFAS compounds in a reaction network. These reaction modules were based on selected approaches discussed in the PFAS remediation technologies overview in Section 2.0. It is anticipated that, as PFAS remediation technologies and scientific understanding advances, these modules would be refined or replaced to match new knowledge.

3.1 Kinetically Limited Adsorption Reaction Module

Out of the wide range of research and approaches related to PFAS adsorption are discussed in Section 2.2.1, the mass transfer approach of Haggerty and Gorelick (1994) was selected to describe kinetically limited adsorption/desorption for a system with both mobile (dissolved phase) and immobile (sorbed phase) constituents.

3.1.1 Description of the Kinetics and Code

The mass transfer approach equations generically account for chemical nonequilibrium, intra-sorbent diffusion non-equilibrium, and transport-related physical nonequilibrium. In this scheme, the concentration difference between dissolved and sorbed phases is the driving force and the rate of adsorption (positive difference) or desorption (negative difference) is controlled by the mass transfer coefficient. Figure 3 shows the differential equations that describe the kinetically limited adsorption for the two tracked species. Note that the "Kd" variable is used to translate the sorbed-phase concentration (e.g., µg/g) into an aqueous concentration (µg/L) based on linear equilibrium. If a different equilibrium distribution approach were more appropriate, the code could be modified to use the Langmuir, Freundlich, or other isotherm (see Section 2.2.1.2). The porosity and bulk density used in the groundwater model are intended to reflect subsurface formation properties, which may be spatially variable. The first order mass transfer coefficient, eta, can also be specified as spatially variable to reflect variations in geochemistry/mineralogy or distribution of remediation amendments (e.g., activated carbon). The appropriate values for the mass transfer coefficient and distribution coefficient will depend on the specific PFAS chemical involved, formation properties, and the geochemical conditions.

```
!     rxns_PFAS_sorption
!     ------------------
!       Two-species, spatially variable model for modeling kinetic mass
!       transfer of contaminants between aqueous and sorbed-phases.
!       The approach here is based on the mass-transfer model described by
!       Haggerty and Gorelick (1994, Water Resources Research, 30(2):435-446).
!       The model is given by the differential equations:
!
!              d(Caq)                  /        Cs  \
!              -----  =        - eta × | Caq - ---- |
!                dt                    \        Kd  /
!
!              d(Cs)                   /        Cs  \
!       rhob × -----  =  poros × eta × | Caq - ---- |
!                dt                    \        Kd  /
!
!        where eta   = first-order mass transfer coefficient [1/T]
!              Kd    = distribution (partition) coefficient [L³/M]
!              Cs    = solid-phase concentration [M/M]
!              Caq   = aqueous concentration [M/L³]
!              rhob  = bulk density [M/L³]
!              poros = effective porosity [--]
!              t     = time [T]
```

Figure 3. Differential equations used in the kinetically limited adsorption reaction module.

3.1.2 Example Reaction Module Application

The kinetically limited adsorption reaction module is flexible enough to allow users to investigate a range of remediation scenarios. The reaction module allows specification of the mass transfer rate (and the distribution coefficient) as spatially variable values. Thus, the user could define (based on laboratory or field studies) how the adsorption varies as a result of differing formation geochemistry or mineralogy. Another scenario that can be simulated is spatial variations in adsorption due to application of a permeable reactive barrier (i.e., PRB or in situ treatment wall/zone) or other volumetric distribution of sorbent in situ. This reaction module does not track transport of sorbent as a species (and RT3D does not have functionality for tracking colloid transport). However, changes in adsorption due to changes in sorbent distribution over time can be tracked by breaking up the groundwater simulation into multiple stress periods where each stress period has a different spatial distribution of sorbent, as reflected by the mass transfer coefficient values.

As an example to illustrate application of this kinetically limited adsorption reaction module, a groundwater model was configured with flow from left to right, a PRB treatment zone, and a contaminant source entering from the left. Figure 4 shows simulation results for this example with a constant contaminant source and compares the results for plain linear equilibrium adsorption to the kinetically limited adsorption. As with any adsorptive technology, as the sorbent approaches or reaches its loading capacity, contaminant mass will migrate through that zone of loaded sorbent. Sorbents that can concurrently sequester (such as strontium-90 incorporation into apatite minerals) or facilitate degradation provide an extra element of treatment. Regardless, a constant source will be challenging for an adsorption approach.

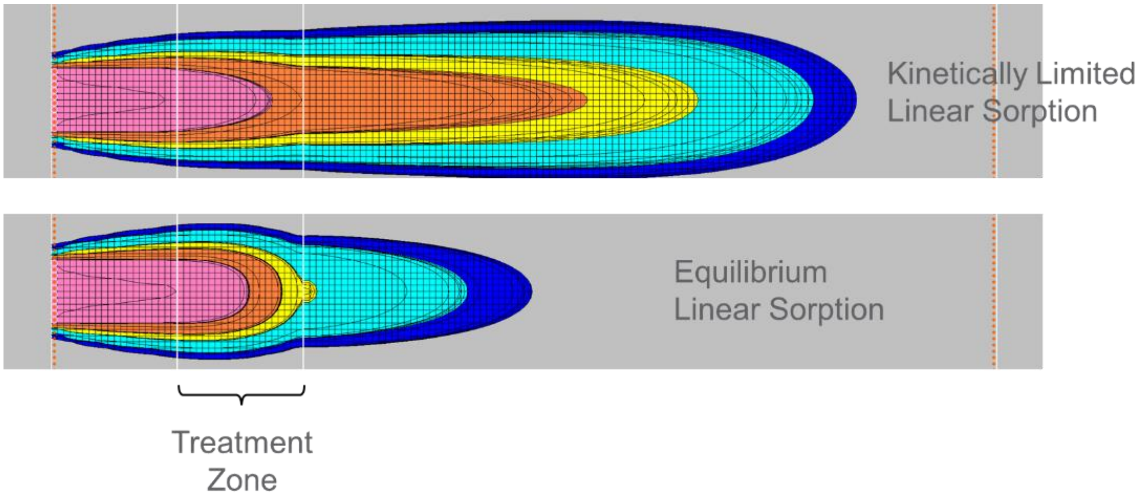

Figure 4. Comparison of equilibrium linear sorption and kinetically limited sorption for the same simulation duration and a constant contaminant source as the contamination passes through an adsorptive treatment zone.

When a site either had a single, finite release or if the source has been removed/controlled, then the dissolved phase plume is only dealing with a finite plume, instead of a continued supply of contamination from a source. A finite or "detached" dissolved phase plume can be a more tractable remediation problem. Figure 5 shows the same simulation configuration as in Figure 4, but the source is a pulse that has a finite initial duration before it is removed/controlled. The images in Figure 5 represent dissolved phase plume migration over time as it encounters a treatment zone and part of the mass is sorbed while part of the mass continues downgradient. Figure 6 shows the same simulation, but in a 3D view with both the dissolved phase and the sorbed phase.

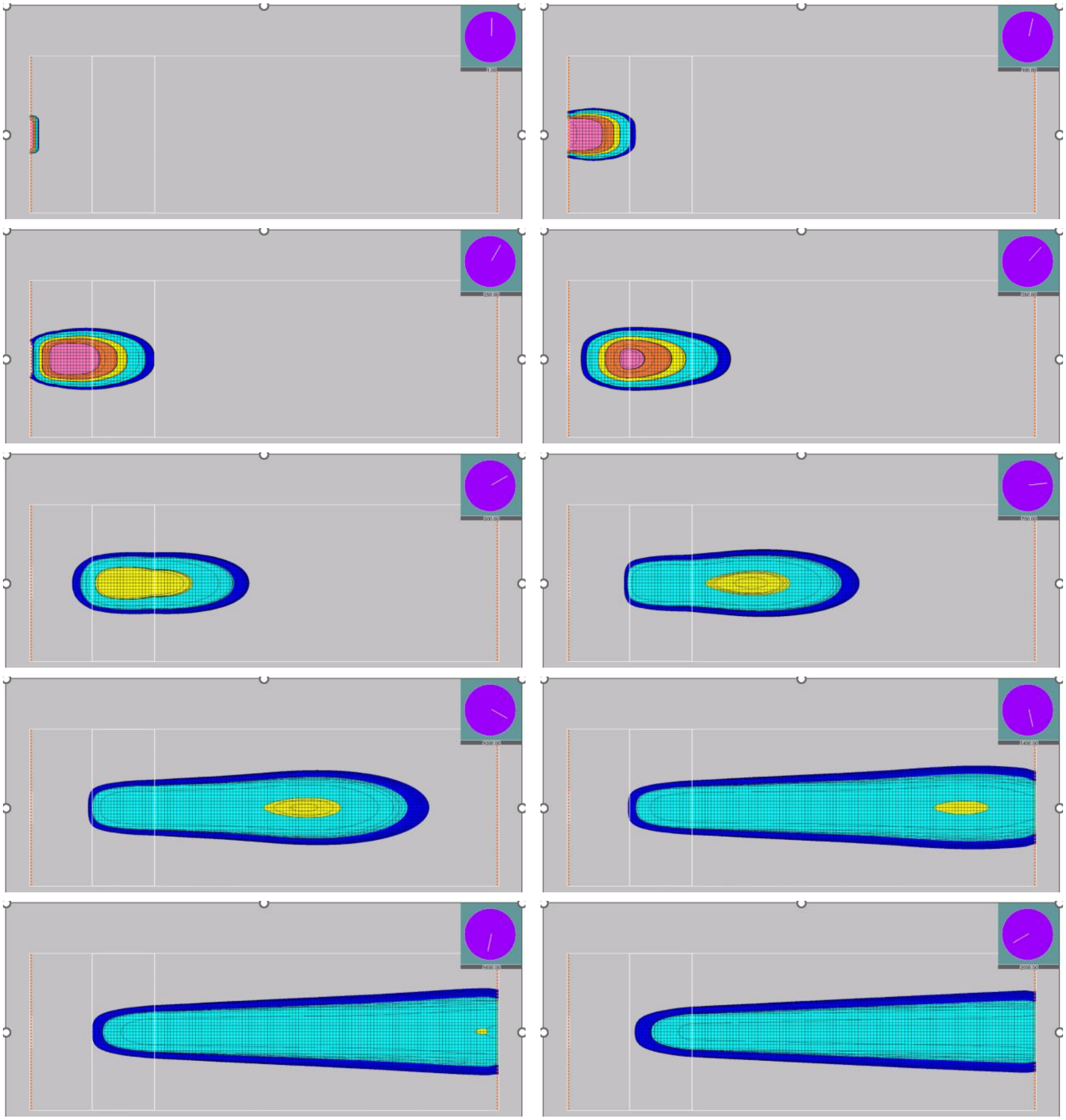

Figure 5. Time series plan view of dissolved contaminant transport and kinetic adsorption through a reactive zone for a pulse (transient release) of contaminant from a source.

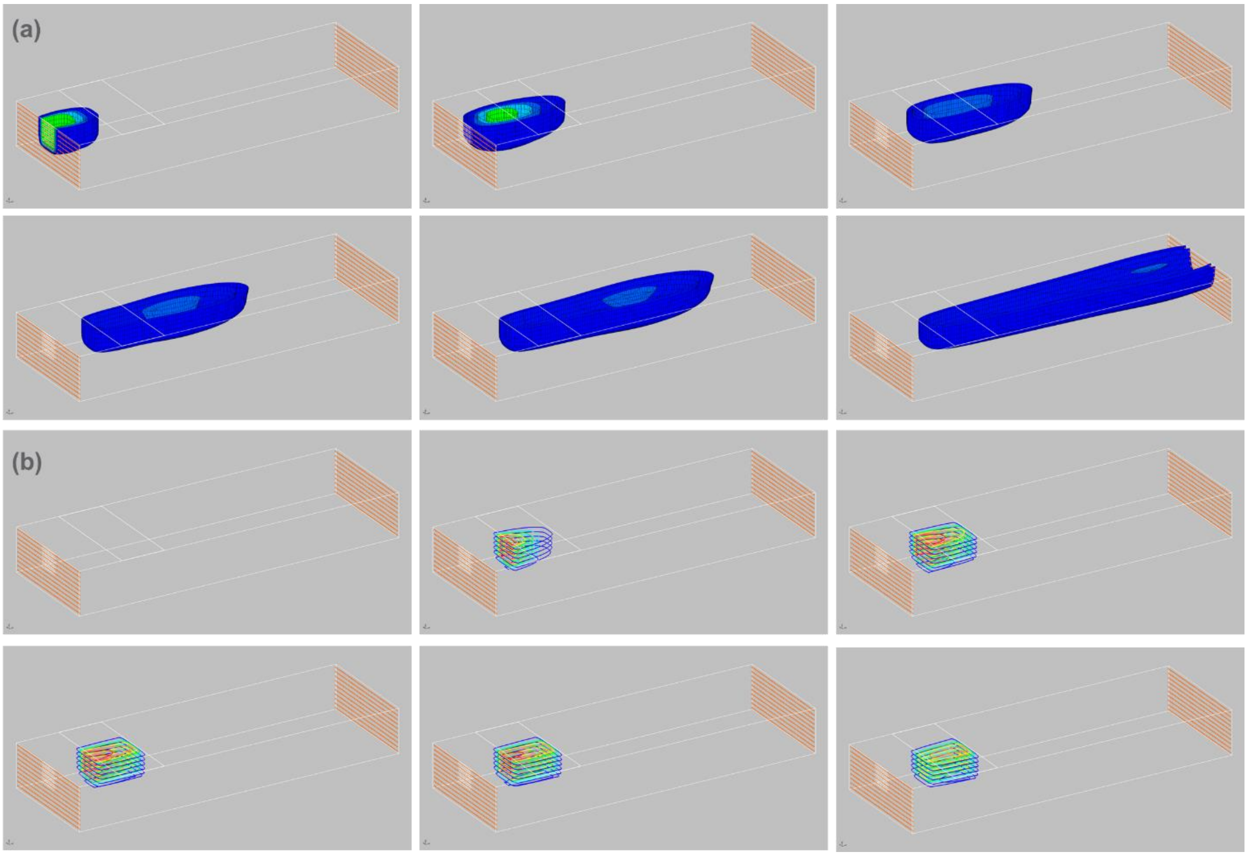

Figure 6. Three-dimensional view of time series dissolved (a) and sorbed (b) concentrations as a pulse of a contaminant transports through a treatment zone where kinetically limited sorption occurs (same simulation conditions as for Figure 5).

3.2 FTOH Degradation Reaction Module

The objective for the second RT3D reaction kinetics module was to develop a reactive transport module for spatially variable PFAS transformation reactions from parent compounds to daughter products. As discussed in Section 2.2.2.3, one of the best described biotic degradation pathways is that for transformation of 8:2 FTOH, which has been observed in the laboratory to occur under a range of aerobic and reducing conditions. The reaction scheme described in Yan et al (2022) was selected for implementation because it was deemed a closer representation of AFFF contaminant fate in the natural environment. Figure 7 shows the reaction network of interest, starting with 8:2 FTOH and continuing with transformation to multiple daughter products. The chemical species that were not observed by Yan et al. (2022) were not included in this scheme.

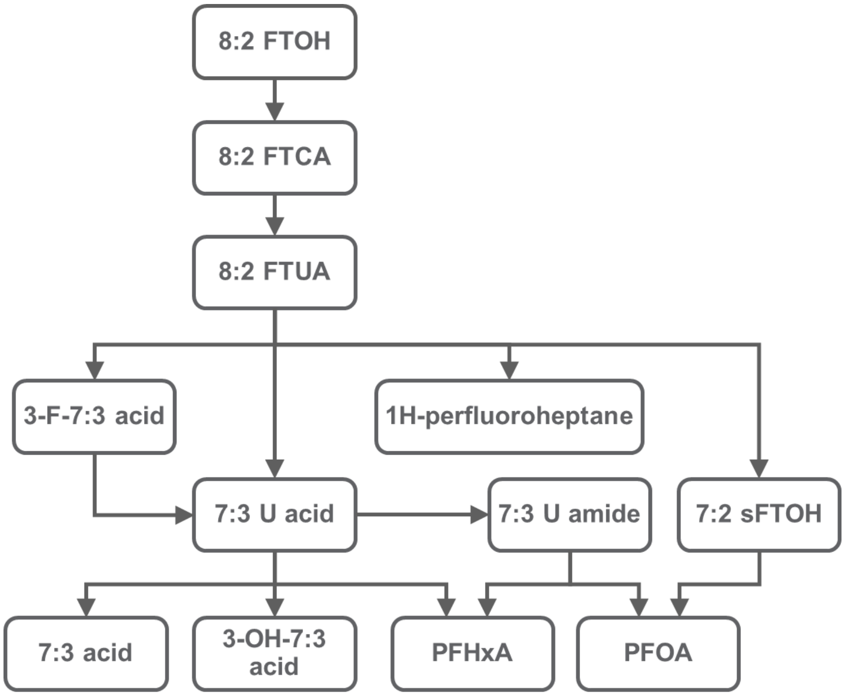

Figure 7. FTOH biological degradation reaction pathways after Yan et al. (2022), excluding chemical species not observed (see Figure 2). The reaction module allows user control over the active pathways and rates, including spatially variable activity.

3.2.1 Description of the Kinetics and Code

The reaction network of Figure 7 was translated into a set of differential equations to describe the first-order transformation from a parent to one or more daughter products. Figure 8 describes the terminology used for the variables and the chemical species names. There are three key variables related to the transformation reactions. The f_<daughter>_<parent> parameters represent the “mass yield” of daughter species that is produced from a parent species. The mass yield is simply the ratio of the molecular weights. Setting the mass yields to 1.0 is equivalent to running a simulation in mol/L (instead of mass units such as µg/L). The y_<daughter>_<parent> parameters represent the stoichiometric yield of a given daughter species from transformation of a parent species. For example, stoichiometric yields of 0.3 and 0.7 for two daughter products that come from the same parent species means that 30% of the transformation of one mole of parent results in one daughter species while the other daughter species is 70% of the mole of parent transformed. If a reaction pathway is inactive for a given set of conditions, then the stoichiometric yield would be zero. The final key parameters are the k_<parent> values, which represent the first-order degradation rate of a chemical species. Another way to turn off a reaction pathway is to set the degradation rate to a value of zero. The full set of parameters used in this reaction module are listed in Table 4, in the required order and with an indication of whether the parameter is constant or if it can be constant or spatially variable. For parameters 15-40, they must either all be spatially constant or all spatially variable.

```
!  dydt(i)                  = change in ith species concentration over time [mol/L/d or mg/L/d]
!  reta(i)                  = retardation factor for the ith species  [—]
!  f_<daughter>_<parent>  = mass yield of daughter from parent [(g/mol) / (g/mol)]
!  y_<daughter>_<parent>  = stoichiometric yield of daughter from parent [mol / mol]
!  k_<parent>               = first-order decay rate of parent species [1/d]
!
!   ftoh82    = 8:2 FTOH
!   ftca82    = 8:2 FTCA
!   ftua82    = 8:2 FTUA
!   acid3f73  = 3-F-7:3 acid
!   pfh1h     = 1H-perfluoroheptane
!   acid73u   = 7:3 U acid
!   amide73u  = 7:3 U amide
!   sftoh72   = 7:2 sFTOH
!   acid73    = 7:3 acid
!   acid3oh73 = 3-OH-7:3 acid
!   pfhxa     = PFHxA
!   pfoa      = PFOA
```

Figure 8. Terminology for the variables used in the FTOH biological degradation reaction module code.

Table 4. Reaction parameters for the FTOH biological degradation reaction module.

#	Type*	**Mass Yield** (g/mol) / (g/mol)
1	C	y_ftca82_ftoh82
2	C	y_ftua82_ftca82
3	C	y_acid3f73_ftua82
4	C	y_pfh1h_ftua82
5	C	y_acid73u_ftua82
6	C	y_sftoh72_ftua82
7	C	y_acid73u_acid3f73
8	C	y_amide73u_acid73u
9	C	y_acid73_acid73u
10	C	y_acid3oh73_acid73u
11	C	y_pfhxa_acid73u
12	C	y_pfhxa_amide73u
13	C	y_pfoa_amide73u
14	C	y_pfoa_sftoh72

#	Type*	**Stoichiometric Yield** (mol / mol)
15	C / V	f_ftca82_ftoh82
16	C / V	f_ftua82_ftca82
17	C / V	f_acid3f73_ftua82
18	C / V	f_pfh1h_ftua82
19	C / V	f_acid73u_ftua82
20	C / V	f_sftoh72_ftua82
21	C / V	f_acid73u_acid3f73
22	C / V	f_amide73u_acid73u
23	C / V	f_acid73_acid73u
24	C / V	f_acid3oh73_acid73u
25	C / V	f_pfhxa_acid73u
26	C / V	f_pfhxa_amide73u
27	C / V	f_pfoa_amide73u
28	C / V	f_pfoa_sftoh72

#	Type*	**First-order Decay Rate** (1/d)
29	C / V	k_ftoh82
30	C / V	k_ftca82
31	C / V	k_ftua82
32	C / V	k_acid3f73
33	C / V	k_pfh1h
34	C / V	k_acid73u
35	C / V	k_amide73u
36	C / V	k_sftoh72
37	C / V	k_acid73
38	C / V	k_acid3oh73
39	C / V	k_pfhxa
40	C / V	k_pfoa

* C = spatially constant reaction parameter, C / V = can be either spatially constant or spatially variable

Figure 9 describes the differential equations for each chemical species in the FTOH reaction network. The transformations for a given chemical species may involve production from a parent, degradation to form daughter species, or both.

```
! Differential Reaction Equations
!- ftoh82
      dydt( 1) = (- k_ftoh82 * ftoh82 )
     &              / reta(1)
!- ftca82
      dydt( 2) = (  y_ftca82_ftoh82 * f_ftca82_ftoh82 * k_ftoh82 * ftoh82
     &            - k_ftca82 * ftca82 )
     &              / reta(2)
!- ftua82
      dydt( 3) = (  y_ftua82_ftca82 * f_ftua82_ftca82 * k_ftca82 * ftca82
     &            - k_ftua82 * ftua82 )
     &              / reta(3)
!- acid3f73
      dydt( 4) = (  y_acid3f73_ftua82 * f_acid3f73_ftua82 * k_ftua82 * ftua82
     &            - k_acid3f73 * acid3f73 )
     &              / reta(4)
!- pfh1h
      dydt( 5) = (  y_pfh1h_ftua82 * f_pfh1h_ftua82 * k_ftua82 * ftua82
     &            - k_pfh1h * pfh1h )
     &              / reta(5)
!- acid73u
      dydt( 6) = (  y_acid73u_ftua82 * f_acid73u_ftua82 * k_ftua82 * ftua82
     &            + y_acid73u_acid3f73 * f_acid73u_acid3f73 * k_acid3f73 * acid3f73
     &            - k_acid73u * acid73u )
     &              / reta(6)
!- amide73u
      dydt( 7) = (  y_amide73u_acid73u * f_amide73u_acid73u * k_acid73u * acid73u
     &            - k_amide73u * amide73u )
     &              / reta(7)
!- sftoh72
      dydt( 8) = (  y_sftoh72_ftua82 * f_sftoh72_ftua82 * k_ftua82 * ftua82
     &            - k_sftoh72 * sftoh72 )
     &              / reta(8)
!- acid73
      dydt( 9) = (  y_acid73_acid73u * f_acid73_acid73u * k_acid73u * acid73u
     &            - k_acid73 * acid73 )
     &              / reta(9)
!- acid3oh73
      dydt(10) = (  y_acid3oh73_acid73u * f_acid3oh73_acid73u * k_acid73u * acid73u
     &            - k_acid3oh73 * acid3oh73 )
     &              / reta(10)
!- pfhxa
      dydt(11) = (  y_pfhxa_acid73u * f_pfhxa_acid73u * k_acid73u * acid73u
     &            + y_pfhxa_amide73u * f_pfhxa_amide73u * k_amide73u * amide73u
     &            - k_pfhxa * pfhxa )
     &              / reta(11)
!- pfoa
      dydt(12) = (  y_pfoa_amide73u * f_pfoa_amide73u * k_amide73u * amide73u
     &            + y_pfoa_sftoh72 * f_pfoa_sftoh72 * k_sftoh72 * sftoh72
     &            - k_pfoa * pfoa )
     &              / reta(12)
```

Figure 9. Code listing for the differential equations used in the FTOH biological degradation reaction module (see Figure 8 for terminology).

3.2.2 Example Reaction Module Application

Four different cases (A-D) with different (and arbitrary) initial conditions (Table 5) and reaction parameter values (Table 6) were simulated as examples of applying the FTOH reaction module.

Table 5. Initial species concentrations [a] for the FTOH reaction module example simulations.

	Initial Concentration (mol/L)			
Species Name	**Case A**	**Case B**	**Case C**	**Case D**
8:2 FTOH	100	100	100	100
8:2 FTCA	0	0	60	90
8:2 FTUA	0	0	20	80
3-F-7:3 acid	0	0	0	70
1H-perfluoroheptane	0	0	0	60
7:3 U acid	0	0	0	50
7:3 U amide	0	0	0	40
7:2 sFTOH	0	0	0	30
7:3 acid	0	0	0	20
3-OH-7:3 acid	0	0	0	10
PFHxA	0	0	0	0
PFOA	0	0	0	0

Table 6. Reaction parameter values [a] for the example FTOH reaction module simulations.

Reaction Parameter Name	Case A	Case B	Case C	Case D
f_ftca82_ftoh82	1	1	1	1
f_ftua82_ftca82	1	1	1	1
f_acid3f73_ftua82	0.25	0.5	0.5	0.25
f_pfh1h_ftua82	0.25	0	0	0.25
f_acid73u_ftua82	0.25	0.2	0.1	0.25
f_sftoh72_ftua82	0.25	0.3	0.4	0.25
f_acid73u_acid3f73	1	1	1	1
f_amide73u_acid73u	0.25	0.2	0.1	0.25
f_acid73_acid73u	0.25	0.3	0.3	0.25
f_acid3oh73_acid73u	0.25	0.4	0.1	0.25
f_pfhxa_acid73u	0.25	0.1	0.5	0.25
f_pfhxa_amide73u	0.5	0.4	0.2	0.5
f_pfoa_amide73u	0.5	0.6	0.8	0.5
f_pfoa_sftoh72	1	1	1	1
k_ftoh82	0.3	0.3	0.3	0.3
k_ftca82	0.2	0.2	0.2	0.2
k_ftua82	0.1	0.1	0.1	0.1
k_acid3f73	0.06	0.06	0.06	0.06
k_pfh1h	0	0	0	0
k_acid73u	0.03	0.03	0.03	0.03
k_amide73u	0.2	0.2	0.2	0.2
k_sftoh72	0.04	0.04	0.04	0.04
k_acid73	0	0	0.003	0
k_acid3oh73	0	0	0.002	0
k_pfhxa	0	0	0.001	0
k_pfoa	0	0	0	0

[a] Shaded cells differ from Case A.

Figures 10 - 13 show the time series concentration data for Cases A-D, respectively. As the initial concentrations, reaction pathway stoichiometry, and transformation rates are adjusted, a different blend of transformation products is produced, with differing concentration magnitudes and rates of accumulation and loss. The reaction parameter values selected were entirely arbitrary (and the mass yields were all set to 1.0 to use mol/L concentrations), so these results are **not** intended for interpretation of actual rates. Site-specific microcosms and/or field studies would be used in a real-world application to determine appropriate parameter values.

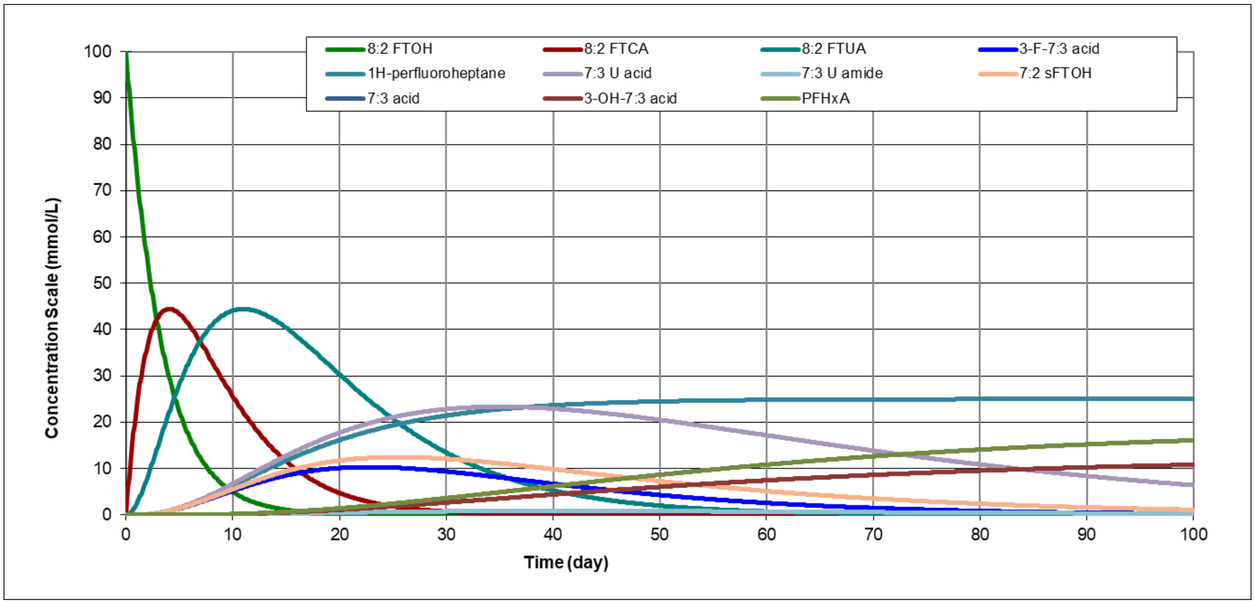

Figure 10. Time series data for the transformation reactions in FTOH reaction module Case A.

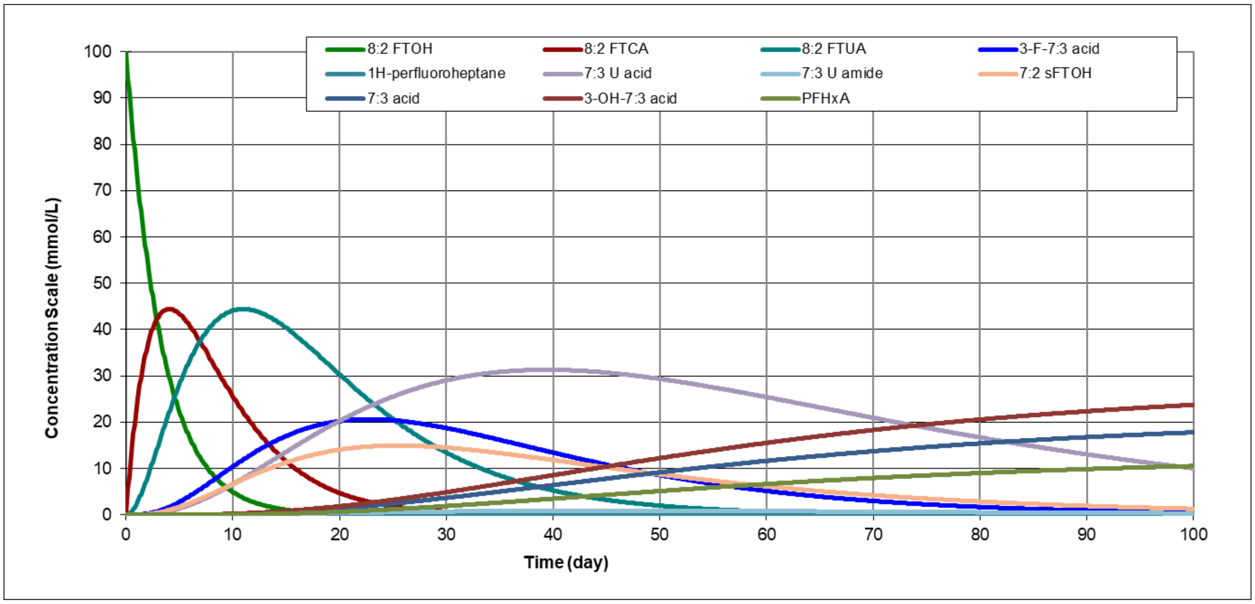

Figure 11. Time series data for the transformation reactions in FTOH reaction module Case B.

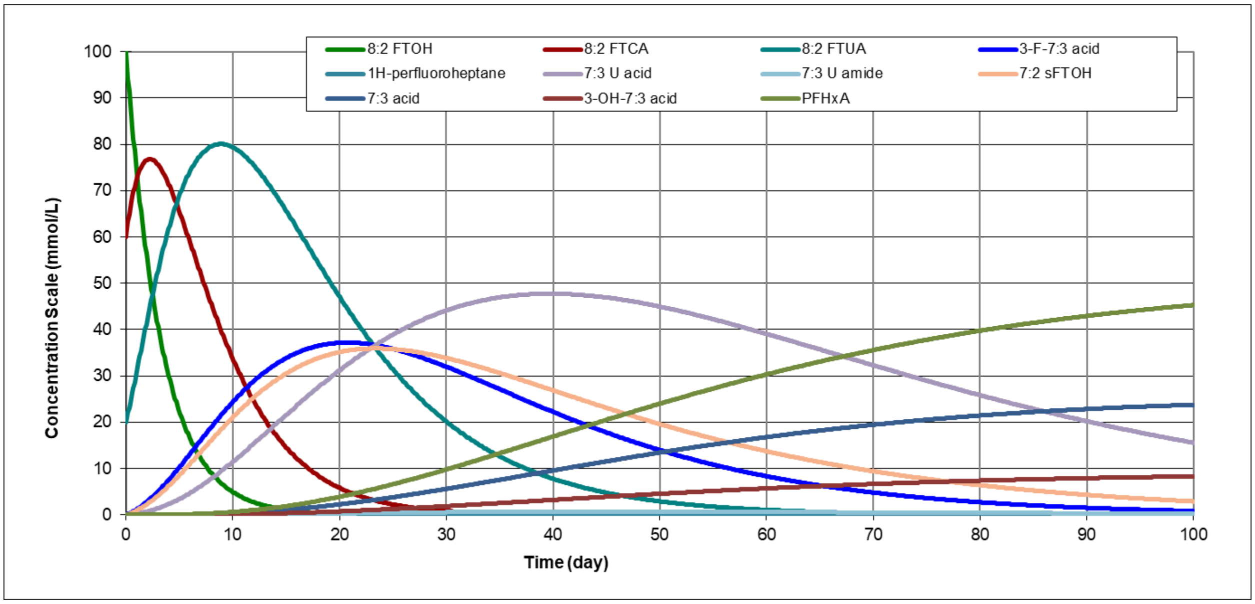

Figure 12. Time series data for the transformation reactions in FTOH reaction module Case C.

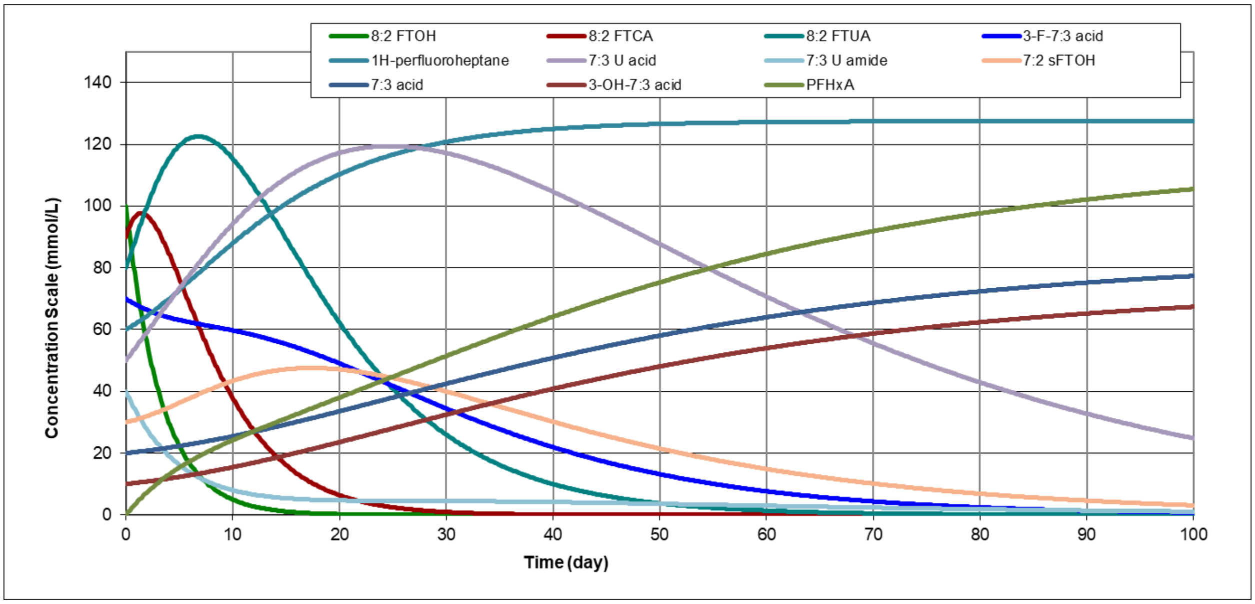

Figure 13. Time series data for the transformation reactions in FTOH reaction module Case D.

4.0 Summary

As discussed in Section 2.3, ongoing research on PFAS chemicals is extensive and covers all aspects, including analytical quantification, determination of properties, toxicology, ex situ treatment, and in situ remediation. PFAS chemicals are very stable and thus persistent/recalcitrant in the environment. Although there are many unknowns about PFAS chemicals, degradation pathways, reaction rates, etc., many different sorption, oxidation, reduction, biological, and innovative treatment approaches are being developed. Sorption with activated carbon is currently the only fully available in situ treatment technology for PFAS-impacted groundwater. Given the wide array of PFAS chemicals and transformation products, remediation may need multi-step treatment trains to fully address the PFAS contamination.

The work here provides kinetic reaction modules that represent an initial cut at functionality representing PFAS migration and reaction in groundwater aquifer flow and transport models. One reaction kinetics module provides a method to model kinetically limited adsorption using a mass transfer model. The second reaction module represents biological transformation of 8:2 FTOH and daughter species, illustrating how a complex reaction pathway network can be represented. Both reaction modules allow for spatially variable parameter values so that a variety of remediation approaches (e.g., a PRB or volumetric treatment or variations in geochemical conditions) can be simulated. The intent with these PFAS reaction modules is to provide tools for practitioners to aid in the selection, design, and assessment of potential in situ PFAS remediation strategies. Application of these modules will require that practitioners determine whether these reaction modules are relevant to a particular site and remediation approach, and whether the assumptions and uncertainty are acceptable. That is, professional judgement and site-specific information will play a role in whether these reaction modules are suitable for remediation decision-making at a given site. It is anticipated that, as PFAS remediation technologies and scientific understanding advances, these modules would be refined or replaced to match new knowledge.

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