

Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Scientific Basis

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Abstract

Sites impacted by per- and polyfluoroalkyl substances (PFAS) pose significant challenges to investigation and remediation, including very low cleanup objectives, limited information on natural PFAS degradation processes in the subsurface, and the apparent mobility and persistence of PFAS. Consequently, monitored natural attenuation (MNA) may be considered less applicable to PFAS compared to biodegradable classes of chemicals such as petroleum hydrocarbons and chlorinated solvents that can completely biodegrade to innocuous end products. However, MNA has proven effective for certain non-degrading metals, metalloids, and radionuclides (e.g., chromium, arsenic, and uranium). To assess the applicability of MNA to PFAS, this paper reviews the fate and transport properties of PFAS in conjunction with the various physiochemical factors that control the subsurface movement of chemicals. This analysis demonstrates that two important retention processes: (1) chemical retention in the form of PFAS precursors, and (2) geochemical retention in the form of sorption and matrix diffusion to mitigate the movement and potential impacts of PFAS in groundwater that may form the scientific basis for applying MNA to PFAS contamination. This paper describes the scientific and regulatory basis for using MNA to manage PFAS-impacted groundwater.

Introduction

Sites impacted with per- and polyfluoroalkyl substances (PFAS) may prove difficult and costly to remediate in some cases, due to a combination of several challenges, including:

1. part-per-trillion (ppt) cleanup objectives;
2. the lack of proven destructive in-situ remediation technologies;
3. the number of PFAS in source zones and the limited ability to comprehensively evaluate the PFAS composition;
4. limited information on natural PFAS degradation processes in the subsurface;
5. the mobility and persistence of PFAS in the subsurface;
6. the large size of some PFAS plumes (Simon et al. 2019); and
7. the potentially large number of PFAS sites requiring remediation (see three estimates in Newell et al. 2020).

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Monitored natural attenuation (MNA) represents one opportunity to manage such sites more efficiently while still protecting potential receptors. MNA refers to “*the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods*” (USEPA 1999). Despite past skepticism of its effectiveness, MNA is now considered one of several remedial technologies that can be employed at contaminated sites, as long as the science behind natural attenuation (NA) processes is well understood and MNA helps manage the chemicals of concern (COCs) in groundwater (Adamson and Newell 2014). There is an extensive collection of MNA protocols and guidance for implementing MNA for a wide variety of COCs in groundwater (Wiedemeier et al. 1995; National Research Council 2000; Pope et al. 2004; Ford et al. 2007a; ITRC 2010). Depending on site conditions, MNA can be applied in several different ways: (1) to manage an entire plume with or without source remediation; (2) to manage a portion of the plume, based on horizontal/vertical location and contaminant type; (3) as a polishing step after plume remediation. MNA is generally utilized where NA processes manage a groundwater plume, whereas a related technology, Natural Source Zone Depletion (NSZD), is utilized where NA processes manage source zones (typically LNAPL source zones) (Garg et al. 2017).

While the authors are not aware of any PFAS sites where MNA has been applied to date, MNA likely will be

an important component of PFAS site management strategies in the future. Therefore, this evaluation aims to foster efficient and effective MNA assessments at PFAS sites and to promote an effective response to PFAS impacts on groundwater resources. The authors summarize the rationale for using MNA at appropriate PFAS sites and the key processes responsible for NA. A companion paper (Newell et al. 2021) describes the lines of evidence used for MNA determinations and the methods available to screen sites for MNA potential, including quantifying NA rates and capacities.

History of MNA as a Groundwater Remediation Tool

Development of MNA as a groundwater remediation tool began during the 1990s. MNA was used for two of the most common groundwater contaminant classes (petroleum hydrocarbons and chloroethene solvents) (Figure 1) historically. Developing the necessary scientific knowledge about MNA processes and then establishing the technologies and strategies to assess MNA required several years. More recently, MNA has been applied to other groundwater COCs as the understanding of attenuation processes expanded. Published MNA guidance documents and technical papers have been prepared for 9 metals/metalloids and other inorganics (e.g., chromium [Ford et al. 2007b]), 10 radionuclides (e.g., uranium [Ford et al. 2008]), methyl tert-butyl ether (MTBE) (Wilson et al. 2005), and 1,4-dioxane (Adamson et al. 2015). Overall, MNA has been applied to a broad assortment of COCs in groundwater with widely different

fate and transport processes, including some COCs that do not completely degrade in-situ (see Table 1).

Applicability of MNA as a Remediation Tool for PFAS in Groundwater

PFAS comprise a large group of man-made fluorinated compounds that have recently emerged as significant COCs for groundwater (Hu et al. 2016). PFAS pose several challenges regarding remediation, notably their wide range of chemical properties, their high mobility, and recalcitrance of some PFAS, which can cause regulatory concern (Simon et al. 2019). While these properties may make MNA more challenging, some physio-chemical properties of PFAS can result in significant retention of PFAS in both the vadose and saturated zones of the subsurface. Thus, these retention processes can provide a credible scientific basis for MNA at many PFAS sites.

Thousands of individual PFAS exist, with a wide range of properties affecting their fate and transport in the subsurface. However, the PFAS of greatest regulatory concern are the long-chain perfluoroalkyl acids (PFAAs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). PFAAs, and many other PFAS, are surfactant molecules, with hydrophobic alkyl tails and anionic acidic, hydrophilic head groups (e.g., anionic [or deprotonated] acidic, hydrophilic head groups). Under common environmental conditions, PFAAs exist in the dissociated anionic form and are relatively water-soluble with low vapor pressures (Prevedouros et al. 2006; Rayne and Forest 2009;

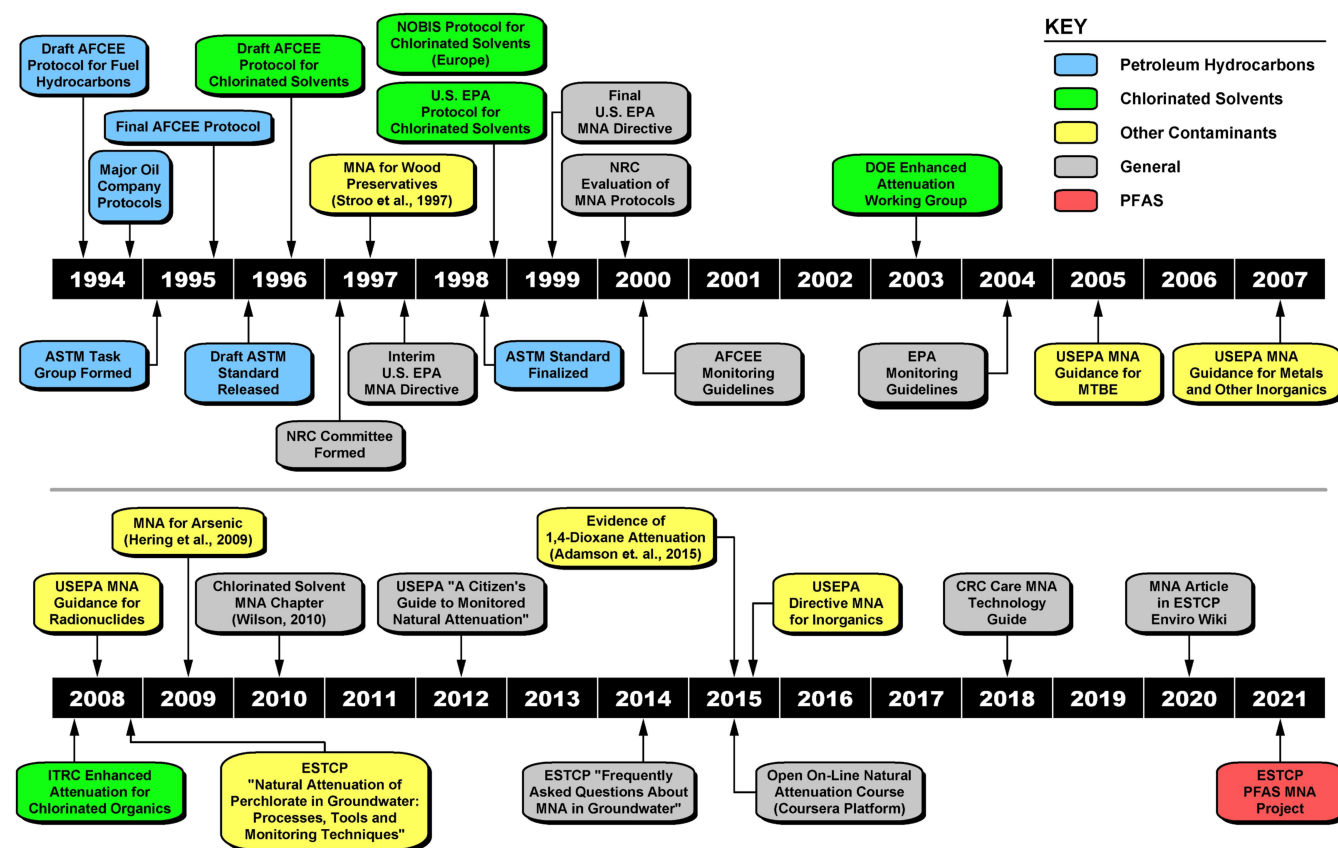


Figure 1. Development of MNA (updated from ITRC 2008). The authors will be working on an upcoming ESTCP PFAS MNA project in 2021 (USEPA 2015).

Table 1

Comparisons of PFAS to Conventional COCs in Groundwater Plumes

Property or Process	Organics (e.g., chlorinated solvents, hydrocarbons)	Inorganics (e.g., metals, radio-nuclides)	PFAS
Chemical bond	C—Cl, C—H (high electronegativity)	Varies (low electronegativity)	C—F (most electronegative)
Physical structure	Generally hydrophobic	Generally hydrophilic	Hydrophobic tail and hydrophilic head
Degradability in groundwater	Many are completely biodegradable to innocuous end products. Rates vary considerably between COCs	Generally non-degradable though radionuclides undergo natural radioactive decay	PFAS are not thought to degrade to innocuous products but may transform from parent to intermediate PFAS and finally to perfluoroalkyl acids (PFAAs) as terminal end products
Partitioning	Primarily partitioning to organic matter	Variety of partitioning and precipitation processes controlled by groundwater/ soil geochemistry	Partitioning onto organic matter and to a lesser degree for some PFAS classes, charged minerals
Ionic state	Generally non-polar	Generally anions	Anions, cations, zwitterions, and neutrally charged species
Volatility	High volatility	Non-volatile	Most extremely low volatility
Solubility	Variable	Variable	Variable (increases as chain length decreases)
MNA used as remediation tool?	Extensively used based on USEPA and other guidance documents	Extensively used based on USEPA guidance documents	Focus of this paper
Key MNA processes	Biodegradation	Retention	Retention

Rahman et al. 2014). PFAAs are also resistant to chemical or biological degradation because of their strong C—F bonds (Nzeribe et al. 2019; ITRC 2020) and can be generated by the biological transformation of PFAA precursors.

In groundwater, the major PFAS transport processes are advection, dispersion, diffusion, and sorption (ITRC 2020). Sorption can be very important for PFAAs and many other PFAS in the vadose and saturated zones. Sorption in the saturated zone occurs via two significant mechanisms: (1) electrostatic interaction of the charged functional group heads (such as the anionic heads' interaction with positively charged surfaces of a porous media), and (2) hydrophobic interaction of their perfluoroalkyl tail with non-polar sites of the porous media (Higgins and Luthy 2006; Guelfo and Higgins 2013; Du et al. 2014) or hydrophobic sorption of non-fluorinated hydrocarbon alkyl structures and associated functional groups. In unsaturated systems, such as soils, many PFAS partition strongly to the air-water interfaces (Lyu et al. 2018; Brusseau et al. 2019). For example, air-water partitioning was shown to comprise up to 50 to 78% of the total PFOS retention in laboratory experiments (Brusseau 2018; Costanza et al. 2019). Using empirically derived values for adsorption coefficients, Brusseau (2018) estimated that PFOS would exhibit a retardation factor of 140 based on air-water interfacial adsorption, which is seven times higher than the estimated retardation factor of 20 for solid-phase adsorption alone for a soil with a fraction organic carbon content (f_{oc}) of 0.002 and 0.4 water saturation (pore space 40% filled with water). By comparison, retardation factors in groundwater, where completely saturated aquifer soils rule out contributions from air-water interfacial adsorption, are expected to be lower. For example, Newell

et al. (2020) estimated PFOS would have a hydrophobic-only retardation factor of 6.0, vs. 2.0 for TCE and 1.3 for benzene (for soils with f_{oc} of 0.01), and the REMChlor-MD model user's manual states that typical retardation factors in groundwater range from 1 to 3 for BTEX compounds (benzene, toluene, ethylbenzene, xylenes) and 2 to 5 for many chlorinated solvents (Farhat et al. 2018).

Polyfluorinated compounds, including those that have been identified as PFAA precursors, can be cationic and zwitterionic. In vadose and saturated zones, these polyfluorinated compounds can be retained as a result of additional electrostatic interactions with soils which typically are negatively charged. Overall these precursor properties can result in long-term retention of some PFAS in vadose zones, which is a promising process for MNA even where residual sources are present (Shin et al. 2011; Xiao et al. 2015; Brusseau et al. 2020). As such, PFAA precursors can be considered chemically retained PFAAs as long as the precursors do not transform to PFAAs. This concept is described in more detail in a later section of this paper.

On initial review, PFAS would be considered an unlikely class of chemicals for MNA in groundwater. The U.S. Environmental Protection Agency's 1999 MNA Directive (USEPA 1999) states that "*when relying on natural attenuation processes for site remediation, EPA prefers those processes that degrade or destroy contaminants.*" However, as shown in Figure 1, the USEPA developed an extensive three-volume set of MNA guidance documents explaining how to implement MNA for metals, metalloids, radionuclides, and groundwater contaminants that do not degrade in-situ (Ford et al. 2007a, 2007b, 2008; Truex et al. 2011). MNA projects for non-degrading groundwater contaminants have

been evaluated at several field sites (e.g., arsenic by Reisinger et al. 2005; heavy metals by Krishna et al. 2010; chromium by Rouse et al. 2006 and Truex et al. 2017). Thus, there is precedent and a scientific basis for not immediately ruling out MNA as a potential groundwater management tool at PFAS sites.

PFAS characteristics and processes that support the case for MNA as a remediation alternative for PFAS include:

- MNA via retention is a recognized remediation alternative for some groundwater COCs, as described in Table 1 (Ford et al. 2007a; Truex et al. 2011).
- PFAAs and precursors are subject to several processes that can retain mass and limit mobility, leading to significant attenuation with distance.
- PFAS retention can significantly reduce transport in both vadose zones (Anderson et al. 2019) and groundwater plumes (Adamson et al. 2020).
- PFAS plumes are subject to matrix diffusion effects (Adamson et al. 2020).
- Compared to other COCs, the ratio of typical source concentrations to regulatory criteria may actually be lower for PFAS plumes compared to COCs that have conventionally impacted groundwater (Newell et al. 2020).

Finally, there is a growing recognition that at some sites, matrix diffusion and other long-term retention processes occur, indicating that active remediation will have a limited impact on reducing the remediation timeframe (e.g., Sale et al. 2008; Hadley and Newell 2014; Sale et al. 2013).

Potential Benefits of MNA for PFAS Management

Currently, remediation strategies for PFAS-impacted groundwater are limited to pump and treat technologies, as there are no available, reliable, cost-effective, in-situ treatment options that destroy or remove PFAS (Simon et al. 2019). Ex-situ treatment of extracted groundwater relies on sorption using granular activated carbon, although novel, destructive treatment technologies such as sonolysis, electrochemical oxidation, and enhanced contact plasma are now being actively studied (Leeson et al. 2021). Groundwater pump and treat (P&T) systems can be effective for controlling the migration of conventional COCs. However, such systems commonly cannot restore aquifers to their original conditions and are often operated indefinitely (National Research Council 1994). For P&T systems in the United States, 2003 surveys indicate an average capital cost of \$2.4 million per site and an average annual cost of \$424,000 for operation and monitoring (NAVFAC 2003).

Many PFAS groundwater plumes may eventually require some type of environmental management (Newell et al. 2020). Remediation costs for COCs with properties similar to that of PFAS have proven very significant. Existing ex-situ (and in-situ) groundwater treatment technologies for PFAS plumes could be more costly than conventional COCs because of the C—F bond and associated energy requirements to break that bond (Coyle et al. 2021). Clearly, there are significant practical and economic incentives to use MNA as a remediation tool, where appropriate.

The PFAS Experts Symposium (Simon et al. 2019) proposed a triage approach to PFAS site management:

- *Minor PFAS sites* may be addressed by source removal (if the sources are very small) combined with MNA or, if needed, pump and treat.
- *Intermediate PFAS sites* may be addressed by partial source remediation or complete removal or source control such as capping, together with MNA at sites where there are long-term risks that need to be controlled.
- *Major PFAS sites* (e.g., semi-regional sites) may be addressed by “partial removal or control of some of the known sources., but because of the large extent of the PFAS plume, alternative water supply or point-of-use treatment is employed for both domestic and municipal users of PFAS-impacted groundwater.”

Simon et al. (2019) noted that NA for PFAS “will not likely involve destructive reactions, but be driven by processes such as matrix diffusion, sorption, dispersion, and dilution.” MNA for PFAS plumes will be different than MNA for other COCs. MNA for PFAS will require understanding the processes responsible for attenuation and transformation of a wide variety of PFAS, as well as the methods available to evaluate NA rates and the site-specific capacity for in-situ retention that relies on physicochemical processes. While MNA is not likely to be applicable to all PFAS sites, we believe it is likely that some fraction of PFAS sites are amenable to management with MNA.

PFAS Attenuation Processes

The key processes affecting PFAS attenuation in vadose and saturated zones include partitioning/adsorption, matrix diffusion, biodegradation of PFAA precursors, and dispersion. An additional process known as “salting out” can be important where PFAS in fresh groundwaters mix with saline groundwater.

Partitioning/Retention

Several naturally occurring partitioning/sorption processes can influence PFAS transport in the subsurface (Naidu et al. 2020; Anderson et al. 2021). Here, partitioning is defined as any process that leads to the distribution of a compound between two phases (e.g., aqueous phase and NAPL phase) and is an equilibrium condition. Adsorption refers to the accumulation of a constituent at the solid:water, air:water, or NAPL:water interface. Sorption is a more general term for processes that can include both adsorption and absorption.

Figure 2 summarizes the potential interfacial interactions and the relevant physical and chemical properties that affect PFAS retention.

The current knowledge of PFAS partitioning processes differs among various environmental media (Brusseau 2018; Sima and Jaffé 2021). Adsorption by the solid phase has been the topic of several investigations, which have successfully demonstrated the multiple mechanisms that influence this partitioning phenomenon. These mechanisms include hydrophobic and electrostatic interactions, which are a function of pH, ionic strength, organic carbon content, the charge of soil particles, chain lengths, and charge of the functional group of the PFAS (Nguyen et al. 2020). The

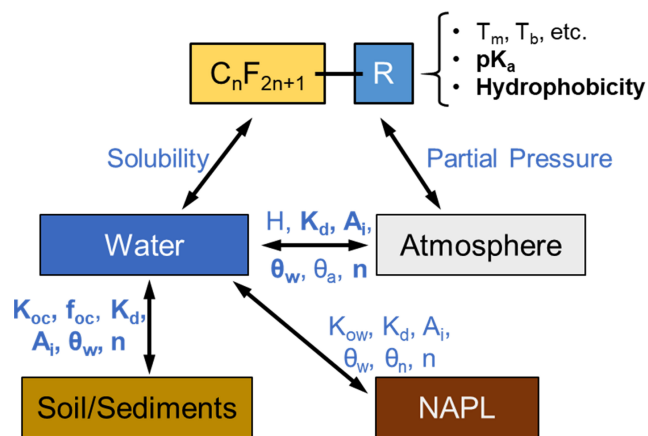


Figure 2. Potential interactions of PFAS compounds among the phases in the subsurface. Some of the physical and chemical properties of PFAS that will affect the interfacial interactions are listed. R, retardation Factor; T_m , melting point; T_b , boiling point; pK_a , acid dissociation constant; K_d , adsorption coefficient at a certain interface; and A_i , specific surface area of the interface; θ_w , volumetric water content, n , porosity; NAPL, non-aqueous phase liquids (from ITRC 2020).

relative importance of these processes has been documented at PFAS field sites (Weber et al. 2017; Adamson et al. 2020; Nickerson et al. 2021). For example, a field-scale evaluation of a former fire training area where aqueous film-forming foam (AFFF) had been released showed that zwitterionic and cationic precursors were strongly retained within the source area relative to PFAAs due to preferential sorption characteristics (Adamson et al. 2020; Nickerson et al. 2021). Differences in PFAS distribution among solid and liquid phases as a function of carbon chain length were also noted. These findings are consistent with several studies showing that, among PFAAs, the shorter-chain compounds are generally more mobile and less strongly retained, and that, for PFAS of equal chain length, perfluorinated sulfonates sorb more strongly than perfluorinated carboxylates because of their sulfonic headgroup (Guelfo and Higgins 2013; Nguyen et al. 2020).

The influence of processes, other than solid-phase adsorption, on PFAS fate and transport has been identified in other PFAS characterization studies (Xiao et al. 2015; Weber et al. 2017; Brusseau et al. 2020). In unsaturated systems, many PFAS will strongly adsorb to the air-water interfaces in vadose zone soils (Brusseau 2018; Lyu et al. 2018; Silva et al. 2019) and to NAPL-water interfaces for conventional NAPLs in the vadose and saturated zones (Nelson and Brusseau 1996; Saripalli et al. 1998; Cain et al. 2000; Brusseau et al. 2003; Silva et al. 2019). Accumulation at air-water interfaces can be particularly important for PFAS MNA as it can result in long-term retention of a large fraction of the PFAS mass, especially in fine-grained soils (Brusseau et al. 2019; Costanza et al. 2019). This adsorption of PFAS in the vadose zone can be nonlinear and subject to hysteresis, therefore increasing the retention of PFAS compared to systems with linear sorption/desorption (Costanza et al. 2019; Sima and Jaffé 2021). Retention by NAPLs can also be significant (McKenzie et al. 2016; ITRC 2020; Van Glubt and Brusseau 2021) at sites where PFAS was entrained in LNAPL or

DNAPL released from fire-fighting activities. The degree of retention by these mechanisms is a function of the partition coefficient of a particular PFAS compound and the interfacial area between the two phases of interest. Reasonable estimates of air: water and NAPL:water partitioning can be made for many PFAS (Brusseau 2018; Schaefer et al. 2019; Silva et al. 2019) and the NAPL literature provides several methods to measure and predict air:water as well as NAPL:water interfacial areas in the subsurface (Karkare and Fort 1996; Saripalli et al. 1998; Cho and Annable 2005; Brusseau et al. 2006; Chen and Kibbey 2006; Dobson et al. 2006).

With respect to PFAS volatilization, several studies have reported the measured Henry's constants of one or more PFAS. These results indicate that the partitioning of PFOA and PFOS to air would be insignificant under static conditions (no advection-driven transport). However, volatilization of other PFAS (such as fluorotelomer alcohols [FTOH]) can be significant and may contribute to their wider distribution in the environment (Ellis et al. 2003; Goss 2008; Ahrens 2011; Ding and Peijnenburg 2013). Nonetheless, a modeling study performed by Brusseau (2018) found the degree of partitioning of PFOA, PFOS, and FTOH to the soil atmosphere was relatively insignificant compared to other transport processes.

The sum of these processes impacts the fate and transport of PFAS in the subsurface. For locations where PFAS are associated with AFFF released from a fire-fighting area, several general observations have emerged from lab-based studies and site characterization projects:

- A considerable mass of PFAS can be retained in the vadose zone due to partitioning on the air-water interfaces in soils.
- Cationic/zwitterionic PFAS are typically less mobile than anionic compounds and may be retained in soil in the source zones to a greater extent than PFAAs (Adamson et al. 2020).
- PFAS precursors in aerobic subsurface environments can be transformed in-situ to PFAAs (see Biodegradation discussion below).
- PFAAs will not further break down and will migrate farther than most other non-PFAAs.
- Shorter-chain PFAAs in the plume generally migrate longer distances than their longer-chain counterparts (ITRC 2020).

Matrix Diffusion

Groundwater plumes can persist for long periods because of the chemical mass that slowly diffuses into, and then back out of, lower-permeability geologic media (National Research Council 2003; Chapman and Parker 2005; Payne et al. 2008; Hadley and Newell 2014). This process, called matrix diffusion, can make the sequestered mass challenging to treat because liquid or solid remediation amendments cannot be delivered easily into lower-permeability soils. In general, plumes subjected to significant matrix diffusion effects are generally better candidates for less-intensive management strategies that focus on reducing mass discharge rates, stabilizing the plume, and protecting potential downgradient receptors (Sale et al. 2013).

A recent research study determined that matrix diffusion contributed significantly to PFAS retention within source areas at an AFFF site and in the overall attenuation of the plume (Adamson et al. 2020). The results “highlight the importance of retention processes on the potential migration of PFAS, with the benefits of low mass discharge rates, limited plume expansion, and the subsequent reductions in the potential risk to downgradient receptors.” Approximately 82% of the total PFAS mass was associated with soils classified as lower-permeability material compared to the clean sands that had the highest transmissivity for groundwater flow.

Biodegradation

At this time, most PFAS are generally considered non-biodegradable under natural conditions; however, PFAAs precursors can biodegrade (often through other polyfluorinated intermediates) to produce the more mobile PFAAs as terminal products (Dinglasan et al. 2004; Harding-Marjanovic et al. 2015). These precursor transformations typically occur via aerobic biodegradation (Liu and Avendaño 2013; O’Carroll et al. 2020) and can be stimulated by aeration such as biosparging used to treat commingled hydrocarbon plumes (McGuire et al. 2014) or by chemical oxidation (Houtz and Sedlak 2012). Because precursor mass can equal or exceed the mass of PFAAs (Adamson et al. 2020), it is important to include their transformations in modeling and MNA assessments. More importantly, because PFAAs are often the key PFAS of concern in groundwater, PFAA precursors can be considered “chemically retained” PFAS mass. This unique feature of PFAS results in biodegradation processes having an opposite effect at chlorinated solvent/hydrocarbon sites compared to PFAS sites: biodegradation is a sink for solvents/hydrocarbons, but a source of PFAAs at PFAS sites.

Dispersion

Mechanical dispersion refers to the spread of a groundwater plume as solutes move through porous media, a process that has long been recognized as a component of MNA for groundwater plumes (USEPA 1999; Wiedemeier et al. 1999). In groundwater systems, two different processes are associated with dispersion: (1) molecular diffusion, and (2) mechanical dispersion. Traditionally, mechanical dispersion has been explained as the result of pore-scale bifurcation of groundwater streamlines that result in mixing

of impacted groundwater and clean groundwater (Payne et al. 2008). Dispersion occurs in the direction of groundwater flow (longitudinal dispersion in the X-direction) and transverse to groundwater flow in two directions (transverse in the Y-direction and vertical in the Z-direction) (Payne et al. 2008). However, there has been a slow change in thinking about dispersion when modeling groundwater plumes (Payne et al. 2008; Zech et al. 2015). Overall, while dispersion is still an important fate and transport process, its perceived importance as an attenuation process has diminished over time (Hadley and Newell 2014).

PFAS Salting Out

The aqueous solubility of some organic compounds displays an inverse dependency on the ionic strength of the groundwater, a phenomenon known as “salting out” (Xie et al. 1997; Turner and Carl Rawling 2001; Turner 2003). That is, increased salinity enhances the retention of certain organic compounds on the solid matrix. Similarly, the ionic strength of groundwater has been observed to impact PFAS sorption (Brusseau et al. 2019; Silva et al. 2019; Li et al. 2020; Lyu and Brusseau 2020). Several researchers have reported the salting out of PFAS in estuarine systems as freshwater PFAS plumes mix with salt water, resulting in increased plume salinity and increased sorption of PFAS to solids, with a commensurate decrease in the aqueous phase concentrations. However, the authors are not aware of any studies of PFAS salting out in groundwater systems to date.

You et al. (2010) evaluated PFAS sorption/desorption at the sediment–water interface and concluded that “...PFOS can be largely removed from the water with increasing salinity, and get trapped onto sediments irreversibly. These phenomena could be explained by salting-out...” In the You et al. (2010) study, the amount of PFOS sorbed to suspended sediment was up to six times greater in seawater systems than in freshwater. More research is underway; however, PFAS salting out may be an important attenuation process for PFAS where freshwater plumes mix with more saline groundwater, a common occurrence in marine environments.

Conceptual PFAS MNA Model

The conceptual model of PFAS attenuation (Figure 3) is based on the following key PFAS retention processes:

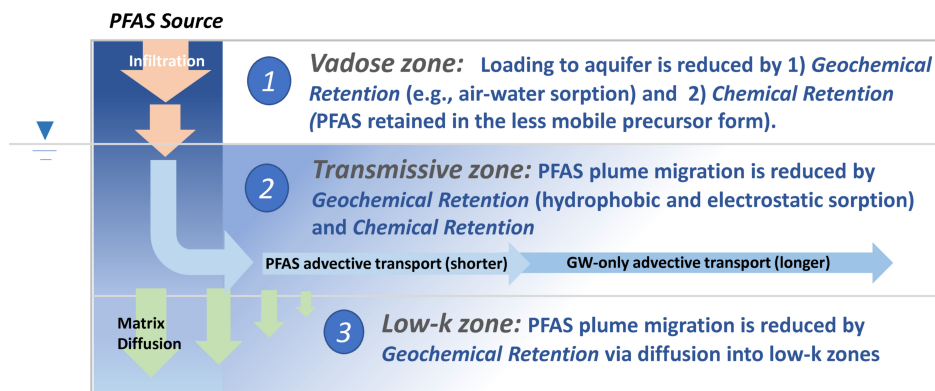


Figure 3. Key PFAS retention processes by subsurface zone. Note that not all retention processes are shown.

1. Partitioning of PFAS at air-water interfaces in the vadose zone and capillary fringe, which reduces the mass discharge of PFAS to the saturated zone that occurs via leaching relative to the discharge rates of conservative solutes,
2. Sorption of PFAS to soils in the vadose and saturated zones via hydrophobic and electrostatic processes, and
3. Matrix diffusion of PFAS in low-permeability zones within the vadose zone and groundwater-bearing unit.

Another retention process, accumulation at NAPL:water interfaces, can be significant in some cases where significant NAPL is present but overall may be a second-order process compared to the three processes described above.

Figure 3 references “chemical retention,” where PFAS in the form of precursors have greater retention and less mobility than their more mobile degradation products (e.g., PFAAs). This concept is discussed in more detail below.

Quantitative Comparison of PFAS Retention

To illustrate the relative impact of different retention processes, the authors developed a simplified, hypothetical PFAS source and plume to compare different retention processes (Table 2). This hypothetical site is not representative of all sites, having an assumed distribution where 75% of the PFAS mass is in the form of precursors and an assumed hydrogeologic setting with a large fraction of fine-grained soils. The source was assumed to reside in an unsaturated sandy soil 30m wide, 30m long, and 5 m thick with an aqueous phase PFOS concentration of 10,000 ng/L (e.g., this is the PFOS concentration of the water held within the unsaturated soils assuming 0.78 water saturation). This source was assumed to have created a uniform concentration of PFOS groundwater plume in the saturated zone of 10,000 ng/L that was 200 m long, 100 m wide, and 10 m thick. Using (1) retention factors from Brusseau (2018), (2) a simple assumption that electrostatic sorption was about 10% of conventional hydrophobic sorption (Brusseau et al. 2019), and (3) matrix

Table 2

PFOS Mass Distribution in Hypothetical Sandy Vadose Zone Source and Groundwater Plume in Heterogeneous Geology Assuming Constant Aqueous Phase Concentration of 10 µg/L

		Basis
Mass comparison starting assumptions		
Source zone dimensions	30m×30m×5m	Generally based on source in Adamson et al. (2020)
Plume dimensions	200m×100m×10m	Generally based on source in Adamson et al. (2020)
Assumed uniform PFOS concentration in plume	10µg/L	Low end evaluated by Brusseau (2018)
Assumed soil type in source	Sandy	Evaluated by Brusseau et al. (2019)
Mass in hypothetical PFOS source zone and plume, PFOS mass (kg)		
Unsaturated zone source		
Aqueous phase	0.015	Assumed aqueous phase concentration 10 µg/L
Air/water interface	3.5	Retard. Factor from Brusseau (2018; table 4)
Hydrophobic sorption	0.2	Brusseau (2018; table 4) for $f_{oc} = 0.002$
Electrostatic sorption	0.011	Brusseau et al. (2019) 10% estimate
Total	3.8	
Saturated zone		
Transmissive geologic media	0.6	28% Distribution based on Adamson et al. (2020)
Low permeability geologic media	2.3	82% Distribution based on Adamson et al. (2020)
Total	2.9	
Grand total	6.7	
Mass distribution of precursor vs. PFAAs in this hypothetical source/plume system		
Unsaturated + saturated zone (%)		
Precursors	75	Assumed for this hypothetical source/plume system
PFAAs (primarily PFOS/PFOA)	25	Assumed for this hypothetical source/plume system
Mass distribution by percent in this hypothetical source/plume system		
Compartment (rounded %)		
% mass in unsaturated zone	57	Calculated from mass distribution above
% mass in saturated transmissive media	9	Calculated from mass distribution above
% mass in saturated low permeability media	35	Calculated from mass distribution above
Total	100	

Note: Different PFAS and different site conditions can result in very different distribution characteristics.

diffusion retention values from the site characterized by Adamson et al. (2020), the PFOS mass and mass distribution were calculated (Table 2) (see spreadsheet in Supporting Information). Although specific conditions can vary significantly by site and by different PFAS, these calculations illustrate two important points: (1) retention in the vadose zone can be significant at PFAS sites for certain PFAS, and (2) matrix diffusion can be important once the PFAS enter the saturated zone.

Favorable and Unfavorable Site Characteristics for PFAS MNA

Not all sites will be amenable for managing PFAS plumes using MNA. As with other contaminants, the MNA calculus for a PFAS plume is based on a wide variety of factors, including:

- The chemical composition of the PFAS source and the relative risk (ratio of current concentration to key environmental criteria) associated with a particular mix of PFAS;
- PFAS source concentrations (see ITRC 2020 for information on PFAS concentrations for different types of sites, such as fire-fighting sites vs. landfill; see Newell et al. 2020 for median PFOS source zone concentrations two PFAS databases);
- Relative contribution from vadose zone vs. saturated zone source materials;
- The rate of PFAS release from different source compartments, such as dissolved phase PFAS vs. sorbed phase vs. PFAS held in the matrix diffusion compartment vs. PFAS in the air/water partitioning compartment (see Guo et al. (2020) for research on the contributions from unsaturated PFAS source zones);
- The configuration of the PFAS plume, such as a narrower, longer plume vs. a wider, shorter plume;
- Hydrogeologic factors, such as the groundwater seepage velocity;
- The location of the plume relative to potential receptors and, in some cases, relative to property boundaries;
- The distribution of between precursors which are retained more in the subsurface compared to more mobile PFAAs (“Chemical Retention”). While one interpretation is that having considerable precursors is a negative condition at a particular site, this can be considered a type of retention where mobile mass is retained with a time delayed release;
- The amount of “Geologic Retention” via sorption to aquifer solids and matrix diffusion removing mass from the plume (based on prevalence of low-permeability layers).

In general, characteristics that will be more favorable for PFAS MNA will be smaller, lower concentration sources that slowly release PFAS to low velocity groundwater with long travel time to key receptors, and significant chemical and geologic retention of the PFAS mass. Note that though the PFAS regulatory criteria for PFAS plumes are more stringent than conventional contaminants, the median source concentrations are lower. Overall PFAS sites may require less concentration reduction compared to chlorinated solvent sites (Newell et al. 2020).

On the other hand, characteristics that will be less favorable for PFAS MNA will be larger, higher concentrations sources that rapidly release PFAS to groundwater, fast-moving groundwater and nearby key receptors, and low chemical and geologic retention.

Why Chemical and Geologic Retention Are Important for PFAS MNA

Applying MNA for plumes comprised of familiar groundwater contaminants like chlorinated solvents and petroleum hydrocarbons often focuses on demonstrating ongoing degradation processes. Because PFAS do not completely degrade to innocuous end products, PFAS MNA will likely rely on retention processes, in particular chemical retention and geologic retention. This retention dichotomy is used as the basis for a PFAS MNA classification system described below.

Researchers have developed classification systems to better understand the potential of MNA for several groundwater COCs. For example, Wiedemeier et al. (1995) developed a three-class system for chlorinated solvent sites comprised of Type 1 sites (biodegradation driven by anthropogenic electron donors), Type 2 sites (biodegradation driven by natural electron donors), and Type 3 sites (relatively little electron donors). In addition, Truex et al. (2006, 2011) developed a scenario system for estimating the potential for MNA at chlorinated solvent sites and inorganic/radionuclide sites.

For PFAS sites, the authors propose the following classification system to explain the relative degree and type of retention of PFAS within the subsurface and therefore indicate the general likelihood that MNA could be applied (Table 3). The columns categorize the compartments where the PFAS mass is principally concentrated (as Types A, B, C), while the rows pertain to the chemical composition of the PFAS mass (Types 1, 2, 3). In this proposed system, sites are classified as Type A if the majority of PFAS mass is in the vadose zone. Type B sites are those where most of the mass is in the lower-permeability regions of the saturated

Table 3
Compartmental Retention Framework for Nine Types of PFAS Sites

	A. More Mass in Vadose Zone	B. More Mass in Low-Permeability Media in Saturated Zone	C. More Mass in Transmissive Media in Saturated Zone
1. Mostly Precursors	Type 1A: More Spatially and Chemically retained	Type 1B: More Chemically and Geologically retained	Type 1C: More Chemically retained
2. Mix Precursors, PFAAs	Type 2A: Spatially retained	Type 2B: Geologically Retained	Type 2C: Some Chemical retention
3. Mostly PFAAs	Type 3A: More Spatially retained	Type 3B: More Geologically Retained	Type 3C: More Spatially, Geologically, and Chemically mobile

Note: PFAS MNA is more likely for sites to the left and top of the table (green shading) and less likely for sites classified to the bottom right of the table (red shading).

zone, while most of the PFAS mass is present in the transmissive regions at Type C sites. Similarly, knowing the mass of PFAS in precursor form vs. PFAAs form (e.g., using Total Oxidizable Precursor [TOP] assay data) could be used to distinguish between Type 1, Type 2, and Type 3 sites.

Generally, the highest degree of retention is observed at sites where the bulk of the mass is located in the vadose zone, and the PFAS consist of longer-chain precursors. A Type 1A site has a much higher potential for PFAS MNA because both geologic and chemical retention processes are active compared to a Type 3C site where most of the PFAS are in the form of mobile PFAAs that are in highly transmissive geologic media. This is a very general framework because other factors besides mass distribution can control the applicability of PFAS MNA. For example, a receptor that is located near a Type 1A site might still need some type of active remediation to stop further plume migration. On the other hand, if receptors are distant from the leading edge of a Type 3C site, and if some limited plume migration is allowable, then MNA could still be a reliable approach to manage this plume. The classification system provides a general framework, but when site-specific factors are considered (source strength, plume size, hydrogeologic conditions, distance to potential receptors), there may be some Type 1A sites that are not amenable to MNA and some Type 3C sites that can be managed by MNA.

For example, the hypothetical source/plume system described in Table 2 would be classified as a *PFAS MNA Site Type 1A “More Spatially and Chemically Retained,”* as most of the PFOS mass is in the vadose zone, and most of the total mass is in the form of precursors. The classification system is intended to be flexible and accommodate available data. Table 2 used PFOS data to determine the mass distribution between different geologic compartments (the three columns), and a more general estimate of precursors/PFAAs was used to determine the rows. This type of site could be a good candidate for PFAS MNA.

A second example is the PFAS site delineated by Adamson et al. (2020) and Nickerson et al., (2021). At this site, PFAS concentrations in surface soils were measured, and the mass in the vadose zone was included in the total PFAS mass estimate for the site. However, the mass in the vadose zone was not calculated separately because the water table was close to the surface, and previous source excavation/remediation activities had likely redistributed the unsaturated source zone mass. Using three key site characteristics where: (1) most of the PFAS mass at this site was in the saturated zone; (2) about half of the total mass in the saturated zone was precursors and half PFAAs; and (3) PFAS concentrations decreasing away from the source (Figure 4), this site would be classified as a *PFAS MNA Site Type 2B “Geologically Retained.”* This type of site has a moderate potential for PFAS MNA.

The reliance on retention for PFAS plumes for MNA does have implications for potential plume expansion. Even though sorption retains PFAS mass at the air:water interface, sorption to aquifer materials, and matrix diffusion serve as sinks for groundwater solutes. These effects are not permanent, and PFAS can eventually come out of retention and potentially migrate in flowing groundwater. However, even in this case, sequestration by strong retention can pro-

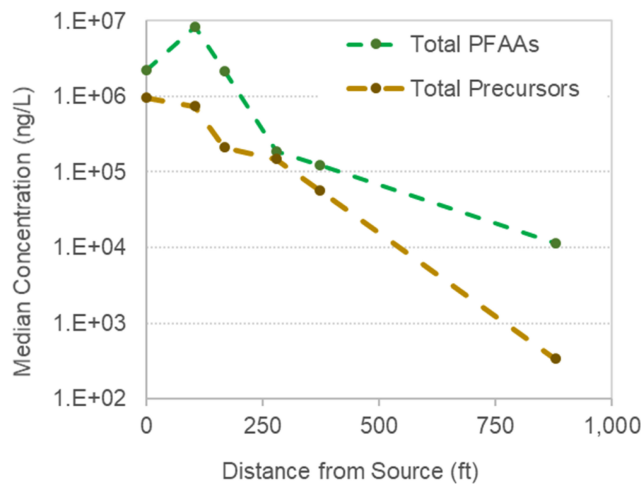


Figure 4. Median Concentrations of PFAAs and Precursors in the Saturated Zone with Distance from Source. Note each data point represents the median concentration of 4 to 12 depth-discrete samples.

vide significant protection to receptors by “peak-shaving,” that is, reducing the peak mass discharge of PFAS toward receptors to a lower, albeit longer-lasting discharge (Newell et al. 2020). Given sufficient natural sorption capacity, this strategy is similar to accepted enhanced attenuation technologies (e.g., injecting activated carbon).

There is precedent for relying on retention to protect groundwater receptors, both with MNA and engineered remedies. As noted earlier, other non-degrading inorganic COCs have been managed using MNA under appropriate geochemical conditions. In addition, retention capacity can be enhanced by injecting particulate sorbents (e.g., McGregor 2018), a technology that has been widely accepted for treating hydrocarbons, chlorinated solvents, and more recently, PFAS in groundwater. Remediation by natural retention operates on the same principles, but no added retention capacity is needed if adequate NA capacity can be demonstrated (Adamson and Newell 2014).

Plume Expansion

For many groundwater COCs, MNA is generally applied to demonstrate that attenuation processes have stabilized the rate of plume migration or have reversed plume growth to create a shrinking plume. Whereas for chemical classes such as hydrocarbons that are readily biodegradable, most plumes end up being relatively short and shrinking (Newell and Connor 1998; Wiedemeier et al. 1999; Connor et al. 2014).

However, even non-degrading plumes will eventually stabilize due to the effects of dispersion. Looney et al. (2006) observed that “*transverse dispersion can result in plume stability for a given C/C_0 even if there are no degradation mechanisms operating for a site*” (C/C_0 is the ratio of the concentration in a plume to the maximum concentration in the source). Plume stabilization occurs as a result of the mixing of impacted groundwater and freshwater along the edges of the plume, thereby reducing plume concentrations. Therefore, dispersion will eventually stabilize groundwater plumes, although long distances may be required.

Similarly, matrix diffusion can also contribute to plume stability. Lipson et al. (2005) described how matrix diffusion at a fractured rock aquifer “...acted as a solute sink, continuously removing solute from the groundwater flowing through fractures as the plume advances.” Modeling work based on the work of Sudicky and Frind (1982) determined the degree of plume attenuation attributable to matrix diffusion as a function of time and distance. Lipson et al. (2005) concluded that matrix diffusion manifests itself as increased apparent dispersion, increasing with travel distance so that a non-degrading plume will eventually stabilize and reach an asymptotic length.

Even with the combined effects of dispersion and matrix diffusion, some PFAS plumes may still expand for a number of years before reaching stability. Therefore, a different strategic approach for PFAS MNA may be needed, relying on groundwater use restrictions as an institutional control and some degree of limited, temporary PFAS plume expansion. There are regulatory precedents for acceptable plume expansion, such as the “Plume Management Zone” remedial response objective under the Texas Risk Reduction Program (TRRP) rule (TCEQ 2019), which allows for plume growth within a prescribed area. Similarly, under certain conditions, Illinois EPA guidelines allow excluding the groundwater ingestion exposure pathway for managing groundwater at a site if an ordinance adopted by a local government unit prohibits the installation of potable water supply wells.

Therefore, in theory, the applicability of PFAS MNA could be expanded by establishing a Plume Assimilative Capacity Zone, which defines longitudinal and transverse dimensions wherein retention factors will eventually cause the plume to stabilize. Overall, the degree and rate of plume expansion, the proximity of groundwater users, and the relevant regulatory criteria will influence the feasibility of PFAS MNA at a particular site.

Barriers to Implementing PFAS MNA

While there is a strong technical basis for using PFAS at MNA at suitable sites, there are several data gaps and other barriers to widespread adoption of the technology. Importantly, there are currently no generally accepted technical protocols for PFAS MNA, although the Environmental Security and Technology Demonstration Program (ESTCP) is currently funding a PFAS MNA project (ESTCP 2021a). Also, some allowance for minor plume expansion may be required at MNA PFAS sites, something that is not typically permitted under certain regulatory programs. Finally, there is not a rich body of fate and transport knowledge derived from multiple site databases like that of petroleum hydrocarbon, chlorinated solvent, 1,4-dioxane, and MTBE sites. Another barrier is the number and complexity of the PFAS mixtures present at many sites, which greatly complicate the implementation of any remediation technology, including MNA. Key data gaps include the limited longer-term data on PFAS source and plume behavior, the lack of robust predictive models of PFAS fate and transport, limited information on the properties of many PFASs, the impacts of common co-contaminants on attenuation, and the limited data on precursor transformation rates.

MNA for conventional contaminants faced similar challenges during the early years of its development. However,

progress was relatively rapid once the underlying scientific basis was understood, and monitoring protocols were developed. Similar rapid progress is expected for PFAS MNA. For example, ESTCP is also funding research on relevant PFAS models (ESTCP 2021b) and precursor transformations in-situ (ESTCP 2021c). Further, work on a PFAS MNA protocol has already begun with the companion paper “Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Potential Guidelines” (Newell et al. 2021).

Conclusions

Available information indicates that PFAS are resistant to complete degradation under natural conditions. Nevertheless, MNA can prove effective for managing PFAS at some sites due to natural processes that retain PFAS mass in the soil matrix, thereby limiting mass discharge to groundwater and consequent groundwater plume migration. As for other non-degrading COCs (e.g., metals, radionuclides), retention of PFAS can provide a reasonable scientific basis for PFAS MNA. Given the high cost and complexity of actively treating PFAS plumes, MNA has the potential to improve the effectiveness and sustainability of PFAS remediation at sites with appropriate conditions.

The scientific basis for MNA is primarily built around three main retention processes: (1) chemical retention where more mobile PFAAs are retained in less mobile precursor form, (2) retention via sorption, including hydrophobic, electrostatic, and two-phase partitioning such as air-water partitioning, and (3) retention via matrix diffusion. In general, sites with more retention will likely be more amenable to using MNA to manage PFAS in the subsurface. Two examples of this general PFAS MNA retention framework are presented herein; first, a hypothetical PFAS site with a PFAS mass distribution based in part on partitioning data from Brusseau (2018), and second, an actual site described by Adamson et al. (2020) and Nickerson et al. (2021). The scientific basis for PFAS MNA detailed in this paper was used to develop potential guidelines for implementing PFAS MNA, which are presented in a companion paper (Newell et al. 2021). In addition, the following key areas for future research for MNA implementation at PFAS-impacted sites were identified:

- Developing appropriate lines of evidence for PFAS MNA.
- Understanding how site conditions contribute to attenuation, including chemical retention of PFAS.
- Developing multiple site studies where information such as the PFAS plume length, source/plume concentrations, and plume mass discharge, matrix diffusion effects, plume attenuation characteristics, and the relative distribution precursor to PFAA concentrations.
- Evaluating if current methods for assessing plume stability are applicable to PFAS plumes.
- Identifying possible ways that existing or potentially new environmental regulations can be used to allow minor plume expansion for PFAS plumes.
- Developing and testing vadose zone PFAS transport models;
- Determining if existing matrix diffusion models such as REMChlor-MD can represent the general natural of PFAS transport in the saturated zone.

- Developing and testing methods to enhance PFAS MNA (Newell et al. 2021).

Supporting Information

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally not peer reviewed.

Appendix S1. PFOS retention comparison for generalized, hypothetical site.

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