

Monitored natural attenuation to manage PFAS impacts to groundwater: Potential guidelines

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Abstract

Practical guidelines based on a three-tiered lines of evidence (LOEs) approach have been developed for evaluating monitored natural attenuation (MNA) at per- and polyfluoroalkyl substances (PFAS)-impacted groundwater sites using the scientific basis described in a companion paper (Newell et al., 2021). The three-tiered approach applies direct measurements and indirect measurements, calculations, and more complex field and modeling methods to assess PFAS retention in the subsurface. Data requirements to assess the LOEs for quantifying retention in both the vadose and saturated zones are identified, as are 10 key PFAS MNA questions and 10 tools that can be applied to address them. Finally, a list of potential methods to enhance PFAS MNA is provided for sites where MNA alone may not effectively manage the PFAS plumes. Overall, a practical framework for evaluating PFAS MNA that can result in more efficient, reliable management of some PFAS sites is provided.

1 | INTRODUCTION

This paper builds upon a companion paper that described the scientific basis for using monitored natural attenuation (MNA) to managing per- and polyfluoroalkyl substances (PFAS) impacts to groundwater (Newell et al., 2021). While MNA is often thought to depend on the presence of destructive processes like biodegradation, it explains how nondegrading chemicals of concern (COCs; e.g., some metals, metalloids, and radionuclides) are amenable to MNA if geochemical conditions are suitable for significant geochemical retention. For PFAS recognized nondestructive attenuation processes such as dispersion can contribute to MNA; however, the degree and nature of PFAS retention in the subsurface will likely be the most significant process that determines the efficacy of MNA as a remedy. This retention is divided into two main forms: (1) chemical retention, where PFAS are retained in the precursor form rather than the more closely regulated perfluoroalkyl acid (PFAA) form, and (2) geochemical retention via sorption (hydrophobic, electrostatic,

interphase partitioning, and, potentially, self-assembly phenomena) and matrix diffusion into low-permeability media. Many of the PFAS retention processes are nondestructive and reversible, so that the key attenuation benefit of these processes is "peak-shaving" where the original peak mass discharge of PFAS from the source is attenuated to lower, albeit longer-lasting mass discharge downgradient (Newell et al., 2020).

The following guidelines for PFAS MNA are based on three-tiered lines of evidence (LOEs) approach, which leads to specific recommendations regarding the collection and analysis of field data and the application of computer models.

2 | MNA EVIDENCE AND METRICS

Evaluation of PFAS MNA requires both data and metrics that reflect the unique characteristics of PFAS. MNA evaluations often rely on predictive modeling, and modeling of PFAS is currently challenging given

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the complexities of PFAS sites (Simon et al., 2019). However, additional research is ongoing to improve predictive models and provide guidance on input parameters for PFAS (e.g., Anderson et al., 2021). The fact that PFAS do not appear to completely degrade to non-PFAS end products in the environment means PFAS plume behavior may be different than hydrocarbon or chlorinated solvent plumes. Newell et al. (2021) proposed that Plume Assimilative Capacity Zones may be an important component of PFAS MNA in groundwater where some degree of plume expansion would be allowable where migrating PFAS could be retained.

Based upon these considerations, a highly data-driven monitoring approach to assess PFAS MNA is warranted, with an emphasis on direct measurements of transport and retention, supported by modeling to evaluate and guide characterization and monitoring efforts. In addition, as recommended by relevant guidelines for other compounds, it is important to demonstrate that the PFAS plume being evaluated poses no risk of near-term impacts to groundwater users before commencing an MNA remedy and/or that appropriate response measures have mitigated such risks. MNA evaluation plans should reflect the need to refine predictions over time and include appropriate contingency measures, as additional data become available.

2.1 | Proposed PFAS MNA LOE

As a starting point to evaluate PFAS MNA, a modified set of LOEs has been developed for site-specific applications (Table 1). This includes direct and indirect measurements of retention as the first and second LOEs, respectively, with more complex tools/computer models as a third LOE. As of 2021, not all of these LOE are completely understood

with existing proven methods to obtain the necessary data (e.g., rate of precursor transformation). However, this framework for a potential LOE can serve as a roadmap for identifying key data gaps and important research targets to improve our understanding and encourage the implementation for PFAS MNA at appropriate sites.

Given the complexities of PFAS sites (e.g., broad mixtures of PFAS; high mobility; large masses of precursors; the presence of other COCs, especially at aqueous film-forming foam sites; multiple interacting retention and release processes, etc.), model predictions may not sufficiently address uncertainties so as to provide a primary basis for decision-making at this time but may become key tools for evaluation of PFAS MNA in the near future. Ongoing work to develop planning-level models that reflect improved mechanistic understanding of the relevant PFAS retention processes may improve the ability to achieve reliable modeling predictions (Anderson et al., 2021). A data-driven approach is warranted, with an emphasis on direct measurements of transport and retention, supported by modeling to guide characterization and monitoring efforts. As more confidence is developed with applying groundwater fate and transport models to PFAS sites, these models may become important tools to evaluate PFAS MNA, similar to the commonly used MNA models such as BIOSCREEN and BIOCHLOR, which are used to evaluate other COCs (hydrocarbons and chlorinated solvents).

Table 1 incorporates several important considerations about PFAS fate and transport in groundwater. As noted above, our current understanding of PFAS fate and transport suggests that there may be relatively fewer shrinking or completely stable PFAS plumes compared to hydrocarbon or chlorinated solvent plumes. However, at sites with strong retention processes in the saturated zone and with depleting source mass discharge, some plumes may be quasi-stable where the

TABLE 1 Potential lines of evidence (LOEs) for PFAS MNA

	First LOE: Direct measurements of retention	Second LOE: Indirect measurements of retention	Third LOE: More complex field programs/computer models
Partitioning-based and matrix diffusion-based retention	<ul style="list-style-type: none"> Soil and/or groundwater sampling to show significant retention in key compartments (air-water partition, sorbed mass, matrix diffusion) High retained versus mobile mass percent 	<ul style="list-style-type: none"> Conditions amenable for matrix diffusion (e.g., significant geologic heterogeneity) Conditions amenable for adsorption (high foc, charged minerals, high salinity) 	<ul style="list-style-type: none"> Computer model of plume (computer model must include matrix diffusion)¹ Chromatography effect of low-sorption PFAS versus high-sorption PFAS
Chemical retention	<ul style="list-style-type: none"> Soil and/or groundwater sampling to indicate precursor mass versus PFAA mass 	<ul style="list-style-type: none"> Anaerobic conditions in zones with high precursor mass Field studies to measure rate of precursor transformation 	<ul style="list-style-type: none"> Calculations or data that show rate of precursor transformation
Impact retention is having on attenuating plume migration	<ul style="list-style-type: none"> Concentrations and/or mass flux decreasing along plume centerline Shrinking, stable, or slowly increasing plume concentrations and plume length Clean line for regulated PFAS downgradient of plume or downgradient of an Plume Assimilative Capacity Zone 	<ul style="list-style-type: none"> Comparison of unattenuated plume length (plume length without retention) to actual plume length with retention Simple transport models or empirical relationships that combine the effect of dispersion, sorption, and matrix diffusion to suggest if and how much the plume will expand in the future¹ 	<ul style="list-style-type: none"> Detailed groundwater modeling study focusing on dispersion, sorption, and matrix diffusion² Mass flux calculations showing no adverse impact to receptors

Abbreviations: MNA, monitored natural attenuation; PFAA, perfluoroalkyl acid; PFAS, per- and polyfluoroalkyl substances.

¹An uncertainty and sensitivity analysis would be part of this study to explore model behavior across the range of input parameters.

plume expansion is too slow to measure. At other sites, measurable PFAS plume expansion could be slow enough to be managed by MNA in a Plume Assimilative Capacity Zone (Newell et al., 2021). More research is needed to understand how many PFAS plumes are shrinking, stable, or quasi-stable, or expanding slow enough to apply MNA with a Plume Assimilative Capacity Zone. From a historical perspective, there have been several emerging contaminants that the groundwater remediation field once thought would migrate for long distances in groundwater, but were later shown to exhibit significant attenuation (Newell et al., 2020). At any given site, the actual behavior of the plume (stable, shrinking, etc.) will require a site-specific assessment.

Different PFAS sites will require varying levels of effort based on site-specific conditions (e.g., size of source and plume, presence of nearby receptors, relative concentrations in groundwater). A three-tiered data acquisition hierarchy is thereby proposed for candidate PFAS MNA sites based upon different levels of complexity.

- *Tier 1: For small, simple PFAS sites*, an MNA study comprised of several groundwater monitoring wells and several soil sampling locations could suffice in evaluating the effectiveness of MNA. These sampling results would be used to compile data under the first and second LOEs. In addition, an optional computer modeling study could prove useful for data interpretation and projections.
- *Tier 2: For sites with more complexity*, more detailed first LOE and second LOE would be conducted to better understand the key retention processes to characterize the site per the *Compartmental Retention Framework* shown in Table 3 of Newell et al. (2021). In addition, a simple second LOE modeling study would be performed based upon a simple groundwater flow regime but incorporating matrix diffusion effects (e.g., a model such as the ESTCP REMChlor-MD model (Falta & Wang, 2017; Farhat et al., 2018; Muskus & Falta, 2018).
- *Tier 3: For more complex, potentially high-cost sites*, high-resolution site characterization techniques similar to those employed by Adamson et al. (2021, 2020) would be added to the first and second LOEs to improve the understanding of the mass distribution between different compartments, the degree of chemical retention at the site, and the mass flux versus distance from the source. A more refined three-dimensional model could be applied for the third LOE to better account for complex groundwater flow patterns and geologic heterogeneity. In this regard, it is important to note that many finite-difference groundwater flow and transport models have significant limitations for modeling matrix diffusion (Farhat et al., 2020). Therefore, steps to mitigate or account for these limitations may be necessary to effectively evaluate PFAS MNA at many sites.

2.2 | PFAS MNA success metrics

Metrics to demonstrate the success of an MNA program for PFAS will include site-specific measures of retention, the performance of the MNA program as either a sole remedy or the final step in a treatment train, and compliance with applicable regulatory criteria. Site-specific conditions that may provide a useful measure of success include:

- PFAS concentrations or mass flux (mass discharge) are decreasing along the plume centerline from the source to the downgradient edge of the plume.
- Temporal trends in PFAS concentrations show a plume that is shrinking, stable, or quasi-stable or is increasing slow enough that the plume can be managed with a PFAS MNA Plume Assimilative Capacity Zone.
- Retention timescales that are long compared to PFAS migration (e.g., the ratio of PFAS mass to PFAS mass flux in the vadose zone is high), and there are no credible processes that would result in a rapid, complete loss of retention.
- If the PFAS plume discharges to a surface water body and, based on consideration of mixing zones and other site-specific factors, the rate of mass discharge of PFAS does not impair the use of that water body, subject to applicable water quality criteria.
- The PFAS plume does not pose a risk of impact to water well users or other receptors.
- The PFAS MNA approach is found to be more sustainable over the lifetime of project-based key sustainability metrics such as carbon footprint, water use, air emissions, worker safety (AFCEC, 2010; ESTCP, 2013), and/or other sustainability metrics compared to active remediation approaches such as pump-and-treat, excavation, or other active remediation technologies.

3 | PFAS FIELD METHODS

Field methods that can be used to evaluate the LOEs for PFAS MNA described above are summarized in Tables 2 (vadose zone) and 3 (saturated zone). There is a focus on collecting field data rather than obtaining data from laboratory experiments (e.g., bench-scale leaching tests) because of the potential for soil cores to be disturbed and alter key properties.

3.1 | Laboratory testing of target analytes

Based on the analytical method, laboratory capabilities, and regulatory requirements, target analyte lists specifying which PFAS should and/or can be analyzed may vary from site to site and should be evaluated in detail. Some regulatory jurisdictions mandate a minimum analyte list. Target analytes may include both PFAAs and key precursors or other PFAS of concern. Additionally, the limit of detection and the limit of reporting can vary with both method and laboratory. Several published methods are currently available to analyze PFAS in environmental media (UCMR3, USEPA 537.1, USEPA 533, ISO 25101:2009, ASTM D7979-20, ASTM D7968-17a). ITRC (2020, Table 11-4) lists the compounds included in each of these methods. Specialty or academic laboratories have also developed their own analytical methodologies using high-resolution approaches that attempt to quantify a larger number of nontarget PFAS analytes (Barzen-Hanson et al., 2017; Jacob et al., 2021; Liu et al., 2019; Nakayama et al., 2019; Newton et al., 2017; Pan et al., 2020; Wang et al., 2020; Xiao, 2017).

TABLE 2 Vadose zone: Summary of relevant data needs and applicable data acquisition methods for characterization of PFAS mass retention

Relevant data	Data acquisition method	Significance
Subsurface geology to quantify matrix diffusion effects	Soil cores and boring logs; other stratigraphic tools	Site-specific heterogeneity and specific low-permeability layers to evaluate the impact of matrix diffusion
PFAS mass in transmissive versus low-permeability zones	Soil sampling in both transmissive and low-permeability geologic media	Quantifies mass retained by matrix diffusion and increases the reliability of matrix diffusion modeling
Sorption parameters in soil: Total organic carbon/fraction organic carbon; bulk density; cation/anion exchange capacity	Standard lab analysis of soil samples collected using direct push technology (DPT), hollow-stem auger, or other methods	Evaluate impact of hydrophobic sorption and electrostatic interactions
High-resolution sampling of soil/groundwater focused at the water table (Tier 3)	Depth-discrete, colocated soil and groundwater sampling using DPT	Provides mass distribution data to evaluate retention at air-water interfaces
Recharge rate through vadose zone	Soil type, precipitation data, lysimeter data	Needed for estimating source strength
Mass discharge from vadose zone	Recharge estimate and leachate sampling	Provides quantitative measurement of mass per time entering the saturated zone to better estimate source strength

Note: Some of these data do not have well-defined, accepted methods for acquiring the data, but are now the target of significant research. Abbreviation: PFAS, per- and polyfluoroalkyl substances.

TABLE 3 Saturated zone: Summary of relevant data needs and applicable data acquisition methods for characterization of PFAS mass retention

Relevant data	Data acquisition method	Significance
Hydrogeological parameters: Hydraulic conductivity (K), hydraulic gradient, Darcy velocity	Monitoring wells or DPT	Site-specific heterogeneity and specific low-K layers to evaluate the impact of matrix diffusion
Mass flux and mass discharge estimates	Various methods (ITRC, 2010)	Mass discharge estimates from the source zone and downgradient transects
Sorption parameters in soil: Total organic carbon/fraction organic carbon; bulk density; cation/anion exchange capacity	Standard lab analysis of soil samples collected using DPT or hollow-stem auger	Evaluate magnitude of hydrophobic sorption and electrostatic interactions and effect on PFAS retention
Matrix diffusion modeling parameters (T/low-k ratio; interfacial area; representative thickness) (Falta & Wang, 2017)	DPT, soil cores/boring logs	Can be used to model PFAS retention from matrix diffusion processes
Mass discharge from vadose zone	Time series lysimeter measurements within the source area	Provides quantitative measurement of current source strength and for understanding/modeling retention
Concentration versus time data	Temporal groundwater monitoring data	Indirect indicator of the degree of retention

Abbreviations: DPT, direct push technology; PFAS, per- and polyfluoroalkyl substances.

In addition to the target analytes described above, some analytical methods can provide bulk measurements of fluorine and/or data that can be used as a surrogate for bulk PFAS concentrations (including precursors and other nontarget PFAS; ITRC, 2020) and may be useful at some sites. Key methods that could prove useful for PFAS MNA evaluation include the following:

- Total oxidizable precursor assay (Houtz & Sedlak, 2012; McDonough et al., 2019);
- Total organic fluorine assays that may be useful for mass balance assessments (methods reviewed in Trojanowicz et al., 2011);
- Total elemental fluorine using particle-induced gamma-ray emissions spectroscopy (McDonough et al., 2019; Ritter et al., 2017); and
- Adsorbable organic fluorine paired with combustion ion chromatography that measures the organofluorine content as fluoride (von Abercron et al., 2019; ASTM International Inc., 2019; Cousins et al., 2020; Han et al., 2021; McDonough et al., 2019; Wagner et al., 2013; Willach et al., 2016).

4 | TEN PFAS MNA QUESTIONS AND TOOLS

Key questions for a PFAS MNA demonstration program and tools that may be helpful to address these questions are described below. These include both proven approaches and emerging concepts, the latter of

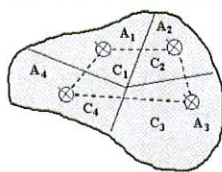
which, in some cases, may be theoretical in nature and not presently implementable using available methodologies. Questions 1–6 address vadose zone retention, which at some sites may not be a primary focus of a PFAS MNA demonstration for managing PFAS plumes in groundwater. Questions 7–10 focus directly on the saturated zone and the retention processes attenuating the migration of the PFAS plume itself.

PFAS MNA question

Key tools

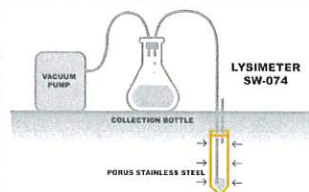
1. How much of the PFAS mass is in the vadose zone versus saturated zone?

Due to PFAS air/water partitioning, knowledge of the mass in the vadose zone versus saturated zone can help understand the timescale of the retention of the vadose zone PFAS mass. Mass calculations can be performed by averaging soil sampling data in the PFAS source zone and multiplying by the volume of the source zone. A geographic information system or the SourceDK tool (Farhat et al., 2004) can also be used to interpolate the data, integrate by volume, and calculate the total mass.



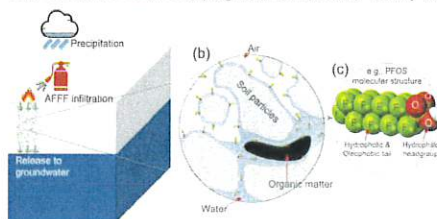
2. What is the concentration of the PFAS in leachate that is transported from the vadose zone to the saturated zone?

Soil lysimeters can be used to collect residual pore water in the vadose zone for the measurement of PFAS concentrations. Several lysimeter designs are available; the design of one type is shown below (SMS, 2020). The U.S. Air Force is deploying lysimeters at PFAS sites to better define the strength of vadose zone PFAS sources (Anderson, 2019). With this information, a defensible basis for the need/effectiveness of soil remediation can be determined. The DoD is also funding studies where lysimeters are being used to more accurately estimate soil-to-groundwater ratios during leaching (e.g., ESTCP, 2021; Project ER20-5088).



3. How can the mass discharge (mass per time) from the vadose zone to the saturated zone be estimated?

Vadose zone models (e.g., Guo et al., 2020; Silva et al., 2020) can be used to estimate the mass discharge from the vadose zone due to leaching and accounting for various retention processes, including air–water partitioning. While these models are primarily research tools, some are being adapted for use by practitioners. Figure below reprinted with permission from Guo et al. (2020). Copyright (2020) John Wiley and Sons.



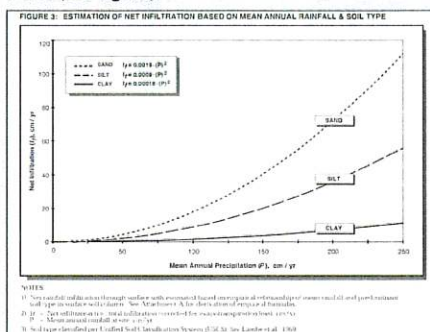
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PFAS MNA question

Key tools

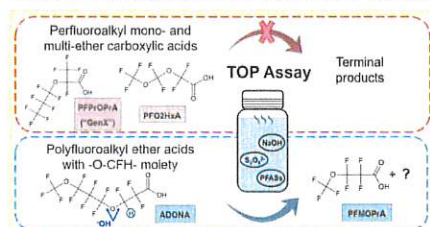
4. How can the infiltration rate through the vadose zone be estimated?

Computer models such as the HELP model (USEPA, 2020) can be used to model the water balance at landfills and for natural soils. A simpler method based on infiltration estimates from 100 sites (Stevens, 1996) was developed by Connor et al. (1997) and described in Wiedemeier et al. (1999), where annual precipitation and soil type can provide general estimates of infiltration at a site (see figure).



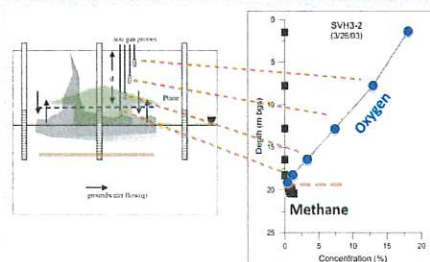
5. How can the degree of chemical retention be estimated at a PFAS site?

Soil sampling where PFAAs and a total oxidizable precursors (TOP) assay (e.g., Zhang et al., 2019) can be used to determine if more of the PFAS mass is chemically retained as less mobile precursors versus more mobile PFAAs. Figure below reprinted with permission from Zhang et al. (2019). Copyright (2019) American Chemical Society.



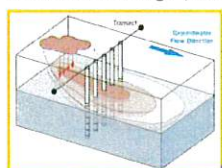
6. How can the rate of oxygen diffusion from the surface into a subsurface reservoir of biodegradable precursors be estimated?

Publications on natural source zone depletion (NSZD) provide several methods to estimate NSZD rates at petroleum hydrocarbon sites (e.g., Kulkarni et al., 2020). One approach, the Gradient Method, is based on measuring the oxygen gradient vertically from the ground surface to the water table to determine the vertical oxygen gradient (Lundegard & Johnson, 2006, see figure). When this gradient is multiplied by a representative effective diffusivity coefficient for unsaturated soils, the oxygen flux from the surface can be calculated. This method could be adapted for the consumption of oxygen by PFAS precursors, although the presence of other aerobically biodegradable co-COCs would need to be considered.



7. How can the mass discharge (mass flux) of a PFAS groundwater plume be estimated?

The ITRC (2010) guide provides a detailed description of five methods to determine mass flux and/or mass discharge of groundwater plumes: (i) transect method (graphic adapted from Einarson and Mackay (2001, see figure)), (ii) well capture method, (iii) passive flux meters, (iv) isocontour method, and (v) computer modeling. Passive flux meters for PFAS are currently being tested (e.g., Pohlmann et al., 2019). The ESTCP Mass Flux Toolkit is a useful tool for calculating mass flux/mass discharge (Farhat et al., 2013).

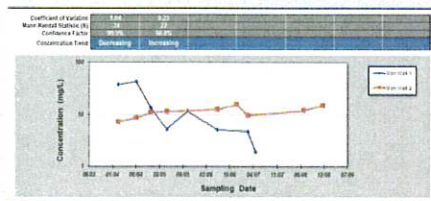


PFAS MNA question

Key tools

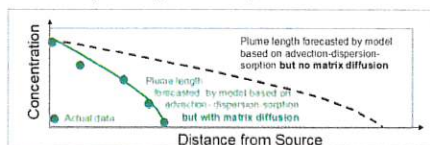
8. How can I determine if the PFAS plume is relatively stable, or expanding slowly enough to be suitable for MNA?

There are a number of statistical packages that can be used to analyze trends in groundwater monitoring data. The MAROS tool (Aziz et al., 2003) is based on the Microsoft Access platform. The GSI Mann-Kendall Toolkit (Connor et al., 2012) is a spreadsheet-based tool. Both MAROS and the M-K Toolkit can be downloaded at www.gsi-net.com.



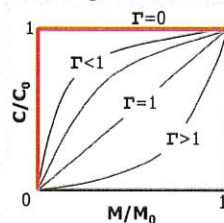
9. How can the future migration of a PFAS plume be estimated?

Retention-based MNA without degradation means that some degree of long-term plume expansion may occur at many PFAS sites, and tools are needed to determine the level of expansion acceptable to site stakeholders (Newell et al., 2021). While fate and transport modeling of PFAS groundwater plumes is in the early stages of development, it will likely be an important tool for forecasting the degree of PFAS plume expansion. In an early attempt at modeling PFAS retention processes, Adamson et al., (2021, 2020) found that matrix diffusion was a key retention process for PFOS at one AFFF site. The REMChlor-MD groundwater model was applied to better understand the PFOS plume from an AFFF site and how matrix diffusion could attenuate a nondegrading plume, and found that it was much easier to match observed field data when matrix diffusion was incorporated into the model (Adamson et al., 2021, see conceptual figure above).



10. How can the PFAS source be linked to a groundwater transport model?

The "power model" or "gamma model" is a relatively simple method used to define the relationship between the remaining chemical mass in the source and the long-term concentration (or mass discharge) being discharged from NAPL source zones (e.g., Falta et al., 2007; Rao et al., 2001). A gamma of zero is a step function (red line), while a gamma of one is an exponential decay). This model is used in combination with three commonly used models for conventional COCs: REMFuel, REMChlor, and REMChlor-MD (Falta et al., 2007; Falta & Wang, 2017). This relationship could provide a simple way to link the rate of mass flux from the PFAS source zone to PFAS groundwater transport models.



5 | ENHANCED ATTENUATION FOR PFAS PLUMES

Enhanced attenuation (EA) is a plume remediation strategy that provides a bridge between source zone treatment and MNA, or between MNA and more aggressive plume remediation methods (ITRC, 2008, 2017; NRC, 2013; Truex et al., 2011, 2006). In general, EA is the use of low-energy, sustainable technologies when MNA is insufficient to manage a groundwater plume. Several potential EA technologies for PFAS plumes can be implemented in both the vadose and saturated zones (see accompanying text boxes).

Potential EA technologies for PFAS plumes implemented in the vadose zone:

- Capping sites to reduce PFAS leaching to groundwater.
- Managing the soil moisture to maximize retention via air-water partitioning.
- Reducing the oxygen influx to reduce the aerobic transformation of precursors.
- Adding sorbents to increase retention.
- Emplacing sorbents in horizontal barriers at the water table.
- Stabilizing water table fluctuations to prevent flushing of PFAS to groundwater.
- Using phytoremediation to reduce infiltration and/or to remove PFAS.

Potential EA technologies for PFAS plumes implemented in the saturated zone:

- Continually sparging gas into the formation to increase air–water partitioning.
- Constructing a cut-off trench and sparging gas within the trench to retain/separate PFAS.
- Adding sorbents to increase retention.
- Reducing the mass flux from the source using physical barriers to reduce groundwater flow through the source.
- Using phytoremediation for hydraulic control and/ to remove PFAS.

6 | CONCLUSIONS

Building on the scientific basis for a retention-based PFAS MNA approach described in Newell et al. (2021), potential practical guidelines for evaluating MNA PFAS sites were developed using a three LOE approach. The first LOE consists of direct measurements of chemical retention, retention via partitioning and matrix diffusion, and the impact of retention on plume migration. The second LOE comprises indirect indicators of retention, including more detailed field data collection and use of simple modeling tools to evaluate plume migration. The third LOE consists of more detailed tools such as high-resolution field characterization and the application of more complex computer models. Three different tiers of PFAS demonstrations are described for simpler sites (Tier 1) ranging to more complex sites (Tier 3).

The relevant data needs and applicable data acquisition methods for the characterization of PFAS mass retention are provided for both the vadose zone and saturated zone. Ten key data acquisition and data analysis tools are presented and described. Finally, several potential methods to enhance PFAS MNA are suggested.

Overall, PFAS MNA has a sound scientific basis built around the retention of PFAS in the subsurface that attenuates the migration of PFAS plumes in groundwater. There are a number of existing practices, technologies, and tools that can be applied to evaluate PFAS MNA and determine if it is applicable at a particular site. Increasing the use and development of these PFAS MNA tools will lead to greater confidence and reliance on MNA as a remedial option at PFAS sites. As our knowledge about PFAS fate and transport increases, the potential PFAS MNA guidelines described in this paper will likely evolve based on practical experience, new technologies, and new scientific knowledge.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

REFERENCES

- von Abercron, E., Falk, S., Stahl, T., Georgii, S., Hamscher, G., Brunn, H., & Schmitz, F. (2019). Determination of adsorbable organically bound fluorine (AOF) and adsorbable organically bound halogens as sum parameters in aqueous environmental samples using combustion ion chromatography (CIC). *Science of the Total Environment*, 673, 384–391. <https://doi.org/10.1016/j.scitotenv.2019.04.068>
- Adamson, D. T., Kulkarni, P. R., Newell, C. J., Mohanty, S. K., Borthakur, A., & Mahendra, S. (2021). *Final report: Natural retardation of per- and polyfluoroalkyl substances (PFAS)*. Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC).
- Adamson, D. T., Nickerson, A., Kulkarni, P. R., Higgins, C. P., Popovic, J., Field, J., Rodowa, A., Newell, C., DeBlanc, P., & Kornuc, J. J. (2020). Mass-based, field-scale demonstration of PFAS retention within AFFF-associated source areas. *Environmental Science & Technology*, 54(24), 15768–15777. <https://doi.org/10.1021/acs.est.0c04472>
- Air Force Civil Engineer Center (AFCEC). (2010). *Sustainable remediation tool (SRT), version 2.1*. GSI Environmental Inc.
- Anderson, H. (2019). *PFAS source aones: How to define source strength?* SETAC North America Focused Topic Meeting Environmental Assessment of PFAS. SETAC.
- Anderson, R. H., Thompson, T., Stroo, H. F., & Leeson, A. (2021). US Department of Defense–funded Fate and transport research on per- and polyfluoroalkyl substances at aqueous film–forming foam–impacted sites. *Environmental Toxicology and Chemistry*, 40(1), 37–43. <https://doi.org/10.1002/etc.4694>
- ASTM International, Inc. (2019). *ASTM WK68866: New test method for determination of adsorbable organic fluorine in waters and waste waters by adsorption on activated carbon followed by combustion ion chromatography*.
- Aziz, J. J., Ling, M., Rifai, H. S., Newell, C. J., & Gonzales, J. R. (2003). MAROS: A decision support system for optimizing monitoring plans. *Ground Water*, 41(3), 355–367. <https://doi.org/10.1111/j.1745-6584.2003.tb02605.x>
- Barzen-Hanson, K. A., Roberts, S. C., Choyke, S., Oetjen, K., McAlees, A., Riddell, N., McCrindle, R., Ferguson, P. L., Higgins, C. P., & Field, J. A. (2017). Discovery of 40 classes of per-and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. *Environmental Science & Technology*, 51(4), 2047–2057. <https://doi.org/10.1021/acs.est.6b05843>
- Connor, J., Farhat, S. K., Vanderford, M. V., & Newell, C. J. (2012). *GSI Mann-Kendall toolkit*. GSI Environmental Inc.
- Connor, J. A., Bowers, R. L., Paquette, S. M., & Newell, C. (1997). Soil attenuation model for derivation of risk-based soil remediation standards, *Petroleum hydrocarbons and organic chemicals in groundwater conference*. National Ground Water Association.
- Cousins, I. T., DeWitt, J. C., Glüge, J., Goldenman, G., Herzke, D., Lohmann, R., Miller, M., Ng, C. A., Scheringer, M., Vierke, L., & Wang, Z. (2020). Strategies for grouping per-and polyfluoroalkyl substances (PFAS) to protect human and environmental health. *Environmental Science: Processes & Impacts*, 22(7), 1444–1460. <https://doi.org/10.1039/D0EM00147C>

- Elnarson, M., & Mackay, D. (2001). Predicting impacts of groundwater contamination. *Environmental Science & Technology*, 35(3), 66A–73A. <https://doi.org/10.1021/es0122647>
- Environmental Security Technology Certification Program (ESTCP). (2013). *Quantifying life-cycle environmental footprints of soil and groundwater remedies*, ESTCP Project ER-201127.
- Environmental Security Technology Certification Program (ESTCP). (2021). PFAS leaching at AFFF-impacted sites: Insight into soil-to-groundwater ratios. <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Risk-Assessment/ER20-5088>
- Falta, R. W., Stacy, M. B., Ahsanuzzaman, A. N. M., Wang, M., & Earle, R. C. (2007). *REMChlor: Remediation evaluation model for chlorinated solvents, user's manual version 1.0*. R.S. Kerr Environmental Research Center, U.S. Environmental Protection Agency.
- Falta, R. W., & Wang, W. (2017). A semi-analytical method for simulating matrix diffusion in numerical transport models. *Journal of Contaminant Hydrology*, 197, 39–49. <https://doi.org/10.1016/j.jconhyd.2016.12.007>
- Farhat, S., Newell, C. J., & Nichols, E. M. (2013). Mass flux toolkit. Environmental Security Technology Certification Program. <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-200430>
- Farhat, S. K., Adamson, D. T., Gavaskar, A. R., Lee, S. A., Falta, R. W., & Newell, C. J. (2020). Vertical discretization impact in numerical modeling of matrix diffusion in contaminated groundwater. *Groundwater Monitoring & Remediation*, 40(2), 52–64. <https://doi.org/10.1111/gwmmr.12373>
- Farhat, S. K., de Blanc, M. B., Newell, C. J., Gonzales, J. R., & Perez, J. (2004). *SourceDK remediation timeframe decision support system, user's manual*. GSI Environmental Inc.
- Farhat, S. K., Newell, C. J., Falta, R. W., & Lynch, K. (2018). *REMChlor-MD users manual*, ESTCP Project ER-201426. Environmental Security Technology Certification Program.
- Guo, B., Zeng, J., & Brusseau, M. L. (2020). A mathematical model for the release, transport, and retention of per- and polyfluoroalkyl substances (PFAS) in the vadose zone. *Water Resources Research*, 56(2), e2019WR026667. <https://doi.org/10.1029/2019WR026667>
- Han, Y., Pullikkal, V. F., & Sun, M. (2021). Comprehensive validation of the adsorbable organic fluorine analysis and performance comparison of current methods for total per-and polyfluoroalkyl substances in water samples. *ACS ES&T Water*, 1(6), 1474–1482. <https://doi.org/10.1021/acsestwater.1c00047>
- Houtz, E. F., & Sedlak, D. L. (2012). Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science & Technology*, 46(17), 9342–9349. <https://doi.org/10.1021/es302274g>
- Interstate Technology & Regulatory Council (ITRC). (2008). *Enhanced attenuation: Chlorinated organics*. ITRC.
- Interstate Technology & Regulatory Council (ITRC). (2010). *Use and measurement of mass flux and mass discharge—technology overview*. ITRC.
- Interstate Technology & Regulatory Council (ITRC). (2017). *Remediation management of complex sites*. ITRC.
- Interstate Technology & Regulatory Council (ITRC). (2020). *Per- and polyfluoroalkyl substances (PFAS)*. ITRC.
- Jacob, P., Barzen-Hanson, K. A., & Helbling, D. E. (2021). Target and nontarget analysis of per-and polyfluoroalkyl substances in wastewater from electronics fabrication facilities. *Environmental Science & Technology*, 55(4), 2346–2356. <https://doi.org/10.1021/acs.est.0c06690>
- Kulkarni, P. R., Newell, C. J., King, D. C., Molofsky, L. J., & Garg, S. (2020). Application of four measurement techniques to understand natural source zone depletion processes at an LNAPL site. *Groundwater Monitoring & Remediation*, 40(3), 75–88. <https://doi.org/10.1111/gwmmr.12398>
- Liu, Y., D'Agostino, L. A., Qu, G., Jiang, G., & Martin, J. W. (2019). High-resolution mass spectrometry (HRMS) methods for nontarget discovery and characterization of poly-and per-fluoroalkyl substances (PFASs) in environmental and human samples. *TrAC, Trends in Analytical Chemistry*, 121, 115420. <https://doi.org/10.1016/j.trac.2019.02.021>
- Lundegard, P. D., & Johnson, P. C. (2006). Source zone natural attenuation at petroleum hydrocarbon spill sites—II: Application to a former oil field. *Ground Water Monitoring & Remediation*, 26(4), 93–106. <https://doi.org/10.1111/j.1745-6592.2006.00115.x>
- McDonough, C. A., Guelfo, J. L., & Higgins, C. P. (2019). Measuring total PFASs in water: The tradeoff between selectivity and inclusivity. *Current Opinion In Environmental Science & Health*, 7, 13–18. <https://doi.org/10.1016/j.coesh.2018.08.005>
- Muskus, N., & Falta, R. W. (2018). Semi-analytical method for matrix diffusion in heterogeneous and fractured systems with parent-daughter reactions. *Journal of Contaminant Hydrology*, 218, 94–109. <https://doi.org/10.1016/j.jconhyd.2018.10.002>
- Nakayama, S. F., Yoshikane, M., Onoda, Y., Nishihama, Y., Iwai-Shimada, M., Takagi, M., Kobayashi, Y., & Isobe, T. (2019). Worldwide trends in tracing poly-and perfluoroalkyl substances (PFAS) in the environment. *TrAC, Trends in Analytical Chemistry*, 121, 115410. <https://doi.org/10.1016/j.trac.2019.02.011>
- National Research Council (NRC). (2013). *Alternatives for managing the nation's complex contaminated groundwater sites*. The National Academies Press. <https://doi.org/10.17226/14668>
- Newell, C. J., Adamson, D. T., Kulkarni, P. R., Nzeribe, B. N., Connor, J. A., Popovic, J., & Stroo, H. F. (2021). Monitored natural attenuation to manage PFAS impacts to groundwater. Part 1: Scientific basis. *Ground Water Monitoring & Remediation*. Under review.
- Newell, C. J., Adamson, D. T., Kulkarni, P. R., Nzeribe, B. N., & Stroo, H. (2020). Comparing PFAS to other groundwater contaminants: Implications for remediation. *Remediation*, 30(3), 7–26. <https://doi.org/10.1002/rem.21645>
- Newton, S., McMahan, R., Stoeckel, J. A., Chislock, M., Lindstrom, A., & Strynar, M. (2017). Novel polyfluorinated compounds identified using high resolution mass spectrometry downstream of manufacturing facilities near Decatur, Alabama. *Environmental Science & Technology*, 51(3), 1544–1552. <https://doi.org/10.1021/acs.est.6b05330>
- Pan, Y., Wang, J., Yeung, L. W., Wei, S., & Dai, J. (2020). Analysis of emerging per-and polyfluoroalkyl substances: Progress and current issues. *TrAC, Trends in Analytical Chemistry*, 124, 115481. <https://doi.org/10.1016/j.trac.2019.04.013>
- Pohlmann, D. R., Morrish, A., Slowey, M., Marrs, M., & Rekowski, P. (2019). *Evaluation of PFAS flux measurement using passive flux meters*. https://www.uee.uliege.be/upload/docs/application/pdf/2019-10/219_gq19_annable_final.pdf
- Rao, P. S. C., Jawitz, J., Enfield, C., Falta, R., Annable, M., & Wood, A. L. (2001). Technology integration for contaminated site remediation: Cleanup goals and performance criteria. *Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution*, 275, 571–578.
- Ritter, E. E., Dickinson, M. E., Harron, J. P., Lunderberg, D. M., DeYoung, P. A., Robel, A. E., Field, J. A., & Peaslee, G. F. (2017). PIGE as a screening tool for per- and polyfluorinated substances in papers and textiles. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 407, 47–54. <https://doi.org/10.1016/j.nimb.2017.05.052>
- Silva, J. A., Kai, A., Šimunek, J., & McCray, J. E. (2020). A modified hydrous model for simulating PFAS transport in the vadose zone. *Water*, 12(10), 2757. <https://doi.org/10.3390/w12102758>
- Simon, J. A., Abrams, S., Bradburne, T., Bryant, D., Burns, M., Cassidy, D., Cherry, J., Ciang, S. Y., Cox, D., Crimi, M., Denly, E., Diguseppi, B., Fenstermacher, J., Florenza, S., Guarnaccia, J., Hagellin, N., Hall, L.,

- Hesemann, J., Houtz, E., ... Wice, R. (2019). PFAS experts symposium: Statements on regulatory policy, chemistry and analytics, toxicology, transport/fate, and remediation for per- and polyfluoroalkyl substances (PFAS) contamination issues. *Remediation*, 29(4), 31–48. <https://doi.org/10.1002/rem.21624>
- Soil Measurement Systems (SMS). (2020). Stainless Steel Suction Lysimeter. <http://soilmeasurement.com/products/lysimeters>
- Stevens, D. B. (1996). *Estimation of infiltration and recharge at environmental sites*. American Petroleum Institute.
- Trojanowicz, M., Musijowski, J., Koc, M., & Donten, M. A. (2011). Determination of total organic fluorine (TOF) in environmental samples using flow-injection and chromatographic methods. *Analytical Methods*, 3(5), 1039–1045. <https://doi.org/10.1039/C0AY00719F>
- Truex, M., Brady, P., Newell, C. J., Rysz, M., Denham, M., & Vangelas, K. (2011). *The scenarios approach to attenuation-based remedies for inorganic and radionuclide contaminants*, SRNL-STI-2011-00459. Savannah River National Laboratory, U.S. Department of Energy. <https://gsi-net.com/en/publications/gsi-papers/papers.html>
- Truex, M., Newell, C. J., Looney, B. B., & Vangelas, K. (2006). *Scenarios evaluation tool for chlorinated solvent MNA*. Washington Savannah River Company, Savannah River National Laboratory, United States Department of Energy.
- U.S. Environmental Protection Agency (USEPA). (2020). Hydrologic evaluation of landfill performance (HELP) model.
- Wagner, A., Raue, B., Brauch, H. J., Worch, E., & Lange, F. T. (2013). Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography. *Journal of Chromatography A*, 1295, 82–89. <https://doi.org/10.1016/j.chroma.2013.04.051>
- Wang, X., Yu, N., Qian, Y., Shi, W., Zhang, X., Geng, J., Yu, H., & Wei, S. (2020). Non-target and suspect screening of per- and polyfluoroalkyl substances in Chinese municipal wastewater treatment plants. *Water Research*, 183, 115989. <https://doi.org/10.1016/j.watres.2020.115989>
- Wiedemeier, T. H., Rifal, H. S., Newell, C. J., & Wilson, J. W. (1999). *Natural attenuation of fuels and chlorinated solvents*. John Wiley & Sons.
- Willach, S., Brauch, H. J., & Lange, F. T. (2016). Contribution of selected perfluoroalkyl and polyfluoroalkyl substances to the adsorbable organically bound fluorine in German rivers and in a highly contaminated groundwater. *Chemosphere*, 145, 342–350. <https://doi.org/10.1016/j.chemosphere.2015.11.113>
- Xiao, F. (2017). Emerging poly- and perfluoroalkyl substances in the aquatic environment: A review of current literature. *Water Research*, 124, 482–495. <https://doi.org/10.1016/j.watres.2017.07.024>
- Zhang, C., Hopkins, Z. R., McCord, J., Strynar, M. J., & Knappe, D. R. U. (2019). Fate of per- and polyfluoroalkyl ether acids in the total oxidizable precursor assay and implications for the analysis of impacted water. *Environmental Science & Technology Letters*, 6(11), 662–668. <https://doi.org/10.1021/acs.estlett.9b00525>

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