


Analysis of colloidal activated carbon alternatives for in situ remediation of a large PFAS plume and source area

Grant R. Carey^{1,2} | Richard H. Anderson³ | Paul Van Geel² | Rick McGregor⁴  | Keir Soderberg⁵ | Anthony Danko⁶ | Seyfollah Gilak Hakimabadi⁷ | Anh Le-Tuan Pham⁷ | Mia Rebeiro-Tunstall¹

¹Porewater Solutions, Ottawa, Ontario, Canada

²Department of Civil and Environmental Engineering, Carleton University, Ottawa, Ontario, Canada

³Air Force Civil Engineer Center, Joint Base, San Antonio, Texas, USA

⁴InSitu Remediation Services Limited, St. George, Ontario, Canada

⁵S.S. Papadopoulos & Associates, Rockville, Maryland, USA

⁶Naval Facilities Engineering Command, Engineering and Expeditionary Warfare Center, Port Hueneme, California, USA

⁷Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, Ontario, Canada

Correspondence

Grant R. Carey, Porewater Solutions, 2958 Barlow Crescent, Ottawa, ON K0A 1T0, Canada.
Email: gcarey@porewater.com

Funding information

Strategic Environmental Research and Development Program, Grant/Award Number: project ER21-3959

Abstract

This study evaluated optimal locations for in situ remediation of per- and poly-fluoroalkyl substances (PFAS) in groundwater with colloidal activated carbon (CAC). New Freundlich isotherms for PFAS adsorption to CAC were estimated to illustrate the effect of competitive adsorption with dissolved organic carbon and other PFAS in a groundwater sample. A hypothetical model scenario was constructed based on source area characteristics similar to a site impacted by aqueous film forming foam in South Dakota. Modeling indicates that, even with high PFAS concentrations, CAC would still be capable of maintaining concentrations below proposed maximum contaminant levels in the adsorption zone for at least 30–40 years. Two-dimensional areal modeling indicates that the future breakthrough of PFAS is likely to occur in the localized core of the plume, and that the corresponding future reinjection of CAC will only need to be conducted over a smaller portion of the original injection footprint. The benefits of implementing a phased remedial approach at PFAS sites are discussed. Source area and mid-plume CAC treatments are shown to be ineffective at attenuating PFAS concentrations at the downgradient property boundary within a reasonable timeframe when PFAS travel time is relatively slow. Among the CAC alternatives evaluated here, a downgradient CAC permeable reactive barrier has the best performance with respect to protecting downgradient receptors.

1 | INTRODUCTION

Aqueous film-forming foam (AFFF) containing PFAS has been used historically for fire training activities since the mid-1960s (Leeson et al., 2021), resulting in high concentration PFAS source areas and groundwater plumes at some military and civilian airports in the United States (Adamson et al., 2020; Carey et al., 2022; Interstate

Technology and Regulatory Council ITRC, 2022; Leeson et al., 2021). One common approach for these sites consists of groundwater extraction and ex-situ treatment with adsorbents such as granular activated carbon (GAC) or ion exchange resin (IER). Over time, ex-situ adsorbents eventually become less effective (i.e., “spent”) at removing the chemicals, and spent adsorbent containing PFAS has to be either disposed of in landfills, incinerated, or re-activated using

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thermal or solvent technologies (Grieco et al., 2022; Kucharzyk et al., 2017; Meegoda et al., 2022; NGWA, 2018; Winchell et al., 2021). The problem with disposal or trying to reactivate these adsorbents is that PFAS may be subsequently released to the environment beyond the location of the original site (Berg et al., 2022). For example, the US Department of Defense was recently temporarily prohibited from incinerating PFAS-laden materials due to uncertainties regarding the products of incomplete combustion (Department of Defense [DoD], 2022).

At some sites, there is an urgent need for in situ remedial alternatives which may be used to reduce the PFAS mass flux from a source area or across a downgradient property boundary. Injection of colloidal activated carbon (CAC) to facilitate in situ PFAS sequestration has been demonstrated to be an effective technology (Carey et al., 2019; Carey et al., 2022; Hakimabadi et al., 2023; McGregor, 2018, 2020a, 2020b, 2023; McGregor & Benevenuto, 2021; McGregor & Zhao, 2021; Mole et al., 2023). For example, Carey et al. (2022) presented a summary of 17 field sites where CAC was successfully employed to reduce PFAS mass flux in groundwater. The fraction of CAC in soil (f_{cac}) at these 17 sites ranges from 0.0002 to 0.008 g/g (i.e., 0.02%–0.8%).

After CAC injection, PFAS will adsorb to the CAC that is attached to soil particles, resulting in the immobilization of PFAS in the CAC zone. If PFAS mass flux continues into the CAC zone at sufficiently high rates over a period of time, then eventually the CAC will become spent and PFAS will breakthrough the downgradient boundary of the CAC zone. Longevity is defined as the time for the first PFAS of concern (POC) to breakthrough the downgradient boundary of the CAC zone at a concentration that exceeds the target cleanup criterion.

PFAS mass flux into a CAC permeable reactive barrier (PRB) is expected to exhibit some degree of decline over time; for example, Carey et al. (2019) conducted a screening model analysis to estimate a source depletion half-life of 30 years when back-diffusion is the main contributing process to mass discharge from a source area. Naturally occurring source depletion or enhanced PFAS remediation upgradient of a CAC zone will effectively increase the CAC longevity. Desorption of PFAS from within a CAC PRB into a downgradient plume may occur when the concentration of PFAS within and at the downgradient CAC zone boundary are higher than the downgradient plume outside the CAC zone. Carey et al. (2023) demonstrated how this may occur at coastal sites where a CAC PRB is constructed close to the shore, where groundwater flow direction reversals are occurring intermittently due to tidal oscillations. Carey et al. (2023) demonstrate that a CAC PRB is still capable of achieving orders of magnitude mass flux reduction downgradient of a PRB at these coastal sites. Desorption of short-chain PFAS may also occur due to competitive adsorption as long-chain PFAS advance slowly through a CAC zone (Singh et al., 2023), although this may only influence the downgradient plume when the long-chain PFAS are close to breakthrough.

One advantage of a CAC remedy is that it may be used to passively reduce PFAS mass flux immediately. If the in situ CAC

becomes spent, there is the option to expand a PRB by injecting CAC directly downgradient of the original PRB location. If CAC becomes spent several decades after injection, it is possible that new destructive or other types of PFAS technologies may be available at that time to facilitate in situ destructive PFAS treatment. For example, thermal destruction (Wilton et al., 2022) and biodegradation (Ruiz-Uriguen et al., 2022) technologies are undergoing development. It may be possible in the future to use a destructive approach for treating PFAS that have been sequestered and concentrated in the CAC zone.

Feasibility studies typically involve calculating the net present value (NPV) to facilitate the comparison of costs for different remedial alternatives. The cost of CAC reinjection or the implementation of newly available technologies several decades into the future will have only a minor influence on the remedy cost, because NPV assumes that future expenditures will be discounted as a result of the interest rate on invested funds being greater than inflation (e.g., see Exhibit 4-1 in Environmental Protection Agency [EPA], 2000). A CAC remedy that is designed to have a longevity of at least 30–40 years allows for the deferral of future remedy costs well into the future with little influence on the NPV of the remedial alternative.

The purpose of this study was to evaluate the viability of a CAC remedy for a scenario involving AFFF impacts to groundwater. The study evaluates the benefits and limitations of placing a CAC remedy in three potential locations: (1) a source area (herein referred to as a “grid” application), (2) a mid-plume PRB, and (3) a downgradient plume PRB near the property boundary. This evaluation includes an assessment of PFAS concentration trends and the modeled longevity for each CAC remedial alternative.

A hypothetical site scenario was generated for this assessment, with source characteristics based on those reported previously for a former fire-training area in South Dakota (Anderson et al., 2022; McGuire, 2013; McGuire et al., 2014; WSP, 2022). This South Dakota site includes a former fire-training area that has relatively high PFAS concentrations in groundwater. Currently, the two PFAS that are the focus at this site from a regulatory perspective are perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) which have similar magnitudes of concentrations in the source area. PFOS adsorbs more strongly to CAC than PFOA (Carey et al., 2022; Hakimabadi et al., 2023), so modeling conducted for this study focuses only on PFOA because it will govern the longevity of a CAC remedy relative to PFOS in this scenario.

Model simulations required the development of temporal mass discharge functions which varied for CAC applications in a source area grid versus a plume PRB. New PFAS-CAC four-species solution isotherms were developed to improve our understanding of competitive adsorption factors which affect CAC longevity. Two-dimensional plan view modeling was conducted to evaluate CAC PRB performance across the width of a large plume (approximately 400 m wide) where the range in PFAS concentrations is more than four orders of magnitude. Findings from this study may be used to guide future site characterization, feasibility studies, remedial design, and remedy optimization at PFAS sites.

2 | CONCEPTUAL MODEL FOR CAC REMEDIATION AT AFFF-IMPACTED SITES

2.1 | PFAS distribution and fate

PFAS released due to AFFF impacts include polyfluoroalkyl precursors and recalcitrant perfluoroalkyl acids (PFAAs). PFAAs consist of two classes: (i) perfluoro sulfonic acids (PFSAs) which include PFOS, perfluorohexanesulfonic acid (PFHxS), and perfluorobutanesulfonic acid (PFBS); and (ii) perfluorocarboxylic acids (PFCAs) including PFOA. The fluorocarbon chain length of these PFAAs affects the relative toxicity and hydrophobicity of these compounds. PFSAs adsorb more strongly to CAC than PFCAs with the same chain length (Carey et al., 2022; Hakimabadi et al., 2023).

While there may be hundreds of PFAS present at AFFF-impacted sites, there are only several PFAAs which are currently of concern. The two most common POCs are PFOS and PFOA, and the next three most common POCs are PFHxS, PFBS, and perfluorononanoic acid (PFNA) (Carey et al., 2022). The US Environmental Protection Agency (EPA) recently proposed maximum contaminant levels (MCLs) for PFOS and PFOA of 0.004 µg/L each (EPA, 2023). EPA also proposed hazard index-based MCLs for four combined chemicals: PFHxS, PFBS, PFNA, and hexafluoropropylene oxide dimer acid (also referred to as GenX). The health-based water concentrations proposed by EPA for use in the denominator in calculation of the hazard index for these four compounds are 0.009, 2.0, 0.01, and 0.01 µg/L, respectively. (GenX is typically not present at historical AFFF-impacted sites and is not discussed further herein) Carey et al. (2022) and Mole et al. (2023) present a statistical analysis of PFAS concentrations at 96 AFFF-impacted sites including PFOA, PFOS, PFHxS, PFNA, and PFBS. These statistical analyses indicate that maximum groundwater concentrations at AFFF-impacted sites for these five PFAAs are typically three to five orders of magnitude higher than EPA's proposed MCLs.

Adamson et al. (2020) present an analysis of the mass distribution of precursors and PFAAs at an AFFF-impacted site. Some of the findings of Adamson et al. (2020) may apply to a wide range of AFFF-impacted sites, and are relevant to the implementation of CAC for in situ remediation. Specifically:

- Precursors, which may be degraded into the regulated PFAAs, such as PFOS and PFOA, are largely retained in the source area.
- Naturally occurring biotransformation of precursors to PFAAs is generally a slow process.
- In the source area at the site studied by Adamson et al. (2020), 93% of total PFAS mass and 99% of precursor mass was in low permeability soil such as silt and clay, indicating that back-diffusion of this mass into more permeable zones may be an important process contributing to aqueous PFAA concentrations in the source area.

2.2 | Conceptual models for mass discharge into CAC zones

When modeling the longevity of CAC at PFAS sites, it is important to consider the various processes which may be contributing to the mass discharge of POCs into a CAC zone. Figure 1a illustrates the conceptual model for POC contributing processes in a source area that extends up to the water table. There are three potential mass discharge terms which represent POC input terms to the CAC zone: (1) mass discharge from upgradient groundwater (Md_{UG}), (2) mass discharge from above the water table (Md_{AWT}) into the CAC zone, and (3) mass discharge from processes occurring inside the CAC zone below the water table (Md_{BWT}). There are up to five processes which may be contributing to Md_{BWT} , including:

- Desorption from natural organic matter (NOM) below the water table;
- Back-diffusion;
- Biotransformation of precursors into POCs;
- Desorption from NAPL-water interfaces; and/or,
- Dissolution from nonaqueous phase liquid (NAPL) in which POCs are entrained.

The last two processes relating to dissolution or desorption from NAPL are assumed to be negligible in the hypothetical scenario considered in this study. This assumption likely holds for former fire training areas that have already been at least partially remediated for chlorinated solvents and petroleum hydrocarbons. However, these processes could play a role at sites where NAPL and PFAS are co-located. CAC zones that represent PRBs have a different conceptual model for POC mass discharge contributions (Figure 1b). In PRBs, the only two processes that are expected to contribute POC mass are upgradient groundwater flow (Md_{UG}) and the desorption of PFAS from NOM within the CAC zone.

2.2.1 | Predicting POC postinjection concentration

A simple mass balance equation is used to estimate the initial aqueous PFAS concentrations immediately after CAC injection, using a Freundlich isotherm to represent PFAS partitioning to CAC (Carey et al., 2019):

$$C_{\text{post}} = \left[\frac{C_o(\theta + K_{oc} f_{oc} \rho_b)}{K_f f_{cac} \rho_b} \right]^{1/a}, \quad (1)$$

where C_o and C_{post} are the pre- and postinjection aqueous PFAS concentrations (mg/L), θ is effective porosity (m^3/m^3), ρ_b is the soil dry bulk density (g/mL), K_{oc} is the organic carbon partitioning coefficient (mL/g), f_{oc} is the fraction of organic carbon in soil (g/g), K_f is the Freundlich coefficient ($(\text{mg/kg})/(\text{mg/L})^{-a}$), f_{cac} is in g/g, and a is the Freundlich exponent (dimensionless). This mass balance assumes that PFAS mass will be predominantly adsorbed to CAC over NOM and, thus, it may not be valid to use Equation (1) to estimate postinjection concentrations for short-chain PFAS or where f_{oc} is high.

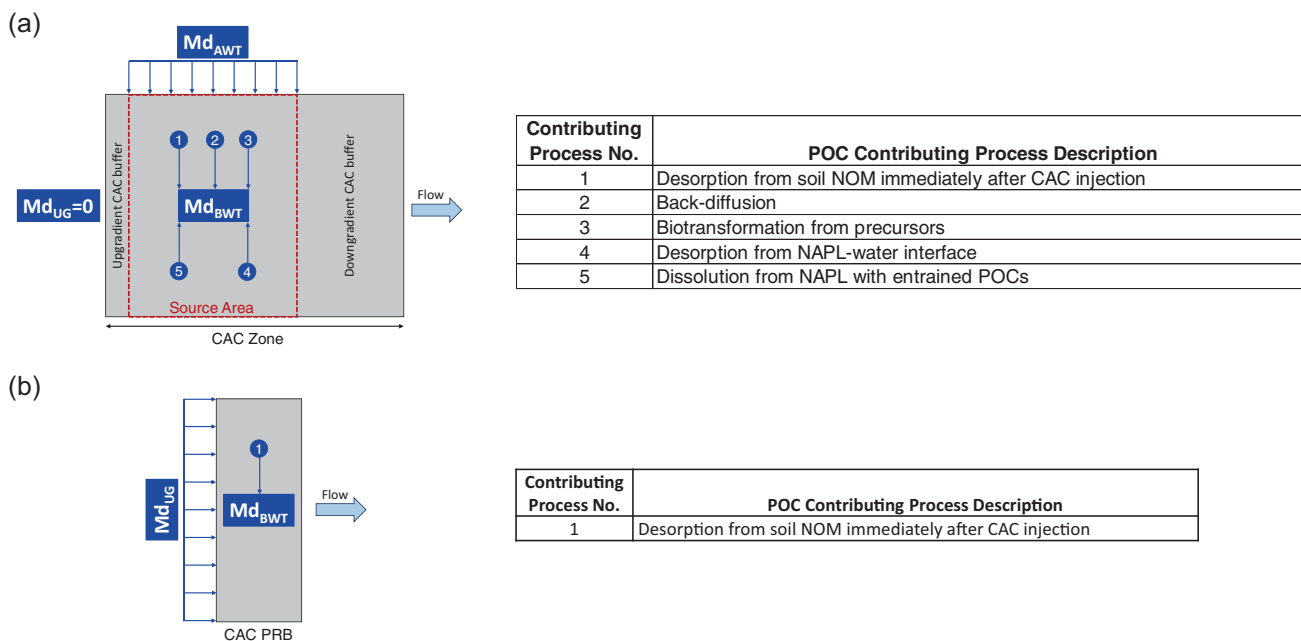


FIGURE 1 Conceptual models used to represent CAC zones in this study, showing the processes contributing to POC mass discharge into the aqueous phase below the water table within a CAC zone for: (a) source area grid; and (b) PRB intercepting a plume downgradient of the source area. Arrow lengths are not scaled proportionally with mass discharge. CAC, colloidal activated carbon; Md_{AWT} , POC mass discharge to the water table from the source in the vadose zone; Md_{BWT} , POC mass discharge into the aqueous phase from sources present below the water table; Md_{UG} , POC mass discharge from upgradient groundwater; NAPL, nonaqueous phase liquid; NOM, natural organic matter; POC, PFAS of concern; PRB, permeable reactive barrier. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/rem.21772)]

When designing a CAC remedy, it is important to analyze what the postinjection concentrations will be immediately after the injection event. If the postinjection concentration is higher than the target cleanup criterion in the CAC zone (e.g., EPA's proposed MCL), then the design f_{cac} may need to be increased to reduce C_{post} below this target criterion. This is one of the means by which the CAC dose and corresponding f_{cac} may be engineered to ensure that the remedy will meet the remedial action objective (RAO).

For example, the relationship between PFOA C_{post} and C_o based on Equation (1) is shown in Supporting Information S1: Figure 1 for f_{cac} values of 0.02%, 0.08%, 0.2%, and 0.8%, and for: (a) $f_{oc} = 0.1\%$ and (b) $f_{oc} = 0.25\%$. These graphs are based on $\rho_b = 1.6 \text{ mL/g}$, $\theta = 0.2$, $K_{oc} = 120 \text{ mL/g}$, $K_f = 580 \text{ (mg/kg)(mg/L)}^{-a}$, and $a = 0.25$. Assuming $C_o = 160 \text{ }\mu\text{g/L}$ and $f_{cac} = 0.4\%$, C_{post} is calculated to be $8 \times 10^{-5} \text{ }\mu\text{g/L}$ for $f_{oc} = 0.1\%$ (i.e., 50 times below the proposed PFOA MCL), and $7 \times 10^{-4} \text{ }\mu\text{g/L}$ for $f_{oc} = 0.25\%$ (i.e., five times below the proposed MCL). C_{post} increases when f_{oc} increases because a higher f_{oc} results in a larger mass of PFOA adsorbed to NOM before CAC injection, which results in a higher aqueous concentration after CAC injection and the subsequent re-equilibration between phases.

2.3 | Predicting CAC longevity

Carey et al. (2019) and Carey et al. (2022) present PFAS-CAC Freundlich isotherms based on batch tests conducted using a

groundwater sample from an AFFF-impacted site. Hakimabadi et al. (2023) and Singh et al. (2023) present single-species, two-species, and three-species PFAS isotherms with CAC that demonstrate the effect of competition between several PFAS. In this present study, new isotherms were developed for a four-species PFAS solution with similar constituents and concentrations that were present in the groundwater sample from an AFFF-impacted site (See Supporting Information S1: Section 1 for more details on the methodology and discussion of results). Comparison of PFOA isotherms for these different solutions facilitates quantification of the effects of adding different PFAS, calcium, magnesium, and DOC on adsorption to CAC.

The fitted Freundlich PFOA isotherms for the four-species solutions and the groundwater sample are shown in Figure 2a. Supporting Information S1: Table 1 presents a summary of the Freundlich isotherms for all constituents used in these seven series of batch tests. The calculated PFOA adsorbed concentrations to CAC for each of these solutions based on an aqueous concentration of $1 \text{ }\mu\text{g/L}$, which was within the range of all seven batch tests discussed above, are shown in Figure 2b. Figure 2b demonstrates that with the progressive addition of multiple PFAS, the adsorbed concentration of PFOA will decrease due to increased competition among PFAS.

For the four-species solution with the addition of calcium and magnesium shown in Figure 2b, there was a dramatic increase of close to one order of magnitude in the PFOA adsorbed concentration relative to the four-species solution without calcium and magnesium. This suggests that high concentrations of calcium and magnesium

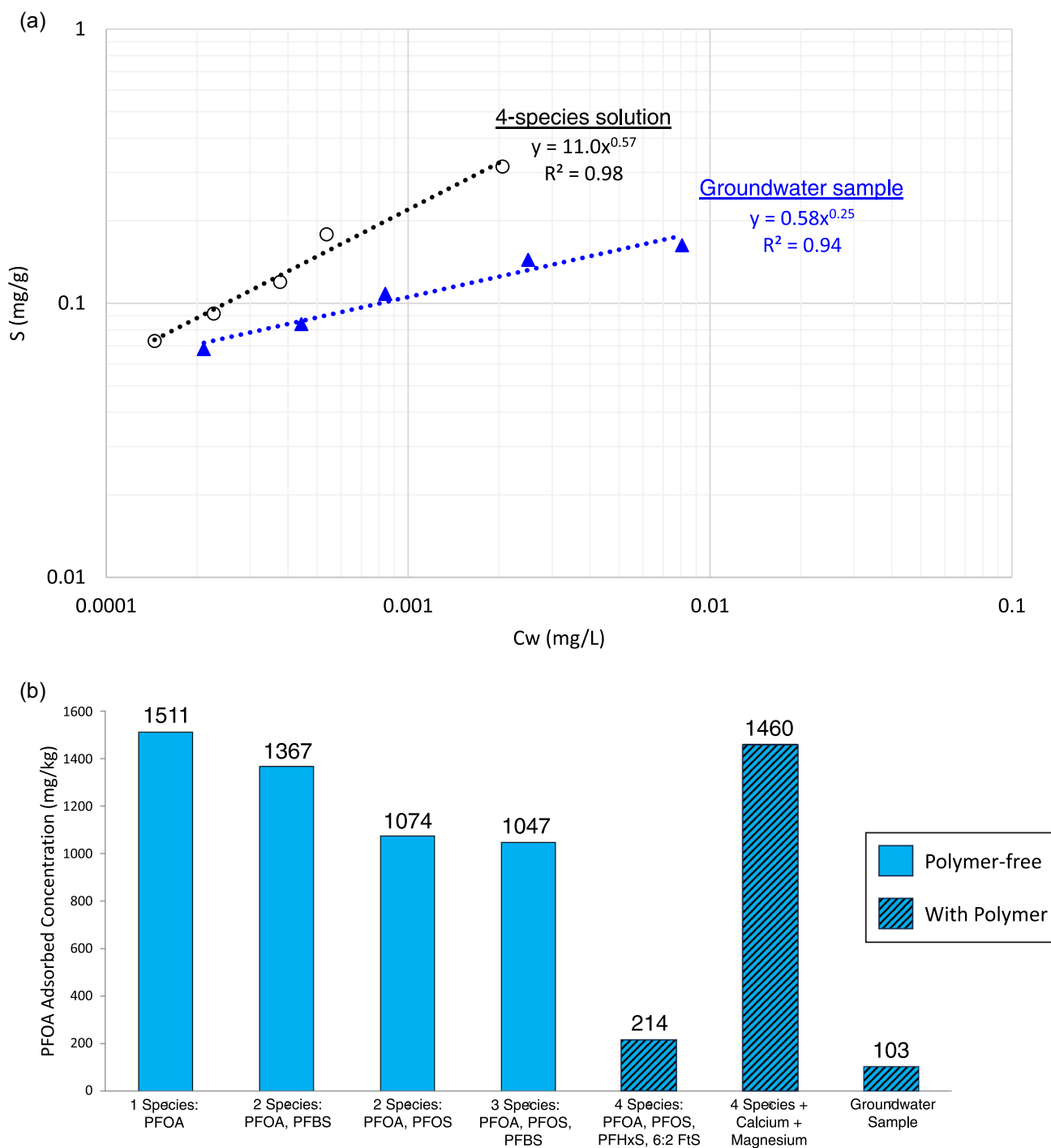


FIGURE 2 (a) PFOA-CAC Freundlich adsorption isotherms for the four PFAS species solution (this study) and a groundwater sample from an AFFF-impacted site (Carey et al., 2022). Symbols represent average concentrations from duplicate batch test results. Dotted lines represent the regression of the Freundlich isotherm based on the Power Law model in Microsoft Excel. The four species solutions were conducted using the same PFAS initial concentrations as were present in the groundwater sample. (b) Calculated concentration of PFOA adsorbed to CAC corresponding to $C = 1 \mu\text{g/L}$ for various PFAS solutions, based on the Freundlich isotherms shown in Figure 2a and Supporting Information S1: Table 1. Solid bars represent solutions dosed with polymer-free CAC, and hatched bars represent solutions that were dosed with CAC mixed with polymer. This polymer may be competing with PFOA for available CAC adsorption sites in the four-species and groundwater sample solutions. 6:2 FtS, 6:2 fluorotelomer sulfonate; CAC, colloidal activated carbon; PFBS, perfluorobutanesulfonic acid; PFHxS, perfluorohexanesulfonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonic acid. [Color figure can be viewed at wileyonlinelibrary.com]

may enhance PFAS adsorption as was shown by Hakimabadi et al. (2023) for a synthetic solution. Hakimabadi et al. (2023) potentially attribute this enhanced adsorption of PFAS to the calcium ions acting as a bridge between the PFAA molecule head and the surface of CAC, which was a hypothesis advanced by Wang et al. (2022).

Figure 2b shows that the PFOA adsorbed concentration for the groundwater sample (with similar concentrations of calcium and magnesium and DOC at 23.8 mg/L) is about half of the adsorbed concentration for the four-species solution sample (without calcium, magnesium, and DOC). This lower adsorbed concentration for the single-species groundwater sample compared to the four-species solution is likely due to competition between PFOA and DOC in the groundwater sample. It is possible that a large proportion of the calcium and magnesium cations in the groundwater sample are tied up via aqueous complexation reactions with other ions in the sample, which inhibits the cationic bridging effect. This demonstrates the importance of conducting isotherm batch tests using groundwater samples collected in the field. These field samples will have different composition and aqueous speciation characteristics relative to synthetic solutions that are produced in the laboratory.

2.3.1 | Reactive transport modeling

Carey et al. (2022) provides an example of how a single-species PFOA reactive transport model may be used to predict longevity. Carey et al. (2022) used the PFOA isotherm that was derived using the groundwater sample from an AFFF-impacted site. This isotherm represents the effects of competition between PFOA and other PFAAs and precursors that were also present in the groundwater sample, as well as DOC.

In a PRB, PFAS with a lower affinity for adsorption to CAC will have smaller retardation coefficients and more advanced fronts in the PRB, relative to PFAS with a higher affinity for adsorption. Lower affinity PFAS will, therefore, breakthrough the CAC zone sooner than higher affinity PFAS. This process is referred to as chromatographic separation (Haggerty & Gorelick, 1994; Valocchi et al., 1981). In the absence of higher affinity PFAS, the lower affinity PFAS will exhibit greater adsorption strength because there is less competition for available CAC adsorption sites. For example, the PFOA front in a PRB will be more advanced (i.e., farther downgradient in the PRB) than the PFOS front due to this chromatographic separation front. In the absence of PFOS in this downgradient region of the PRB, PFOA will have a higher adsorption affinity for CAC as shown in Figure 2a,b.

The PFOA adsorption isotherm used for this study is based on the groundwater sample where PFOA is present with high initial concentrations of other PFAS that have a higher affinity for adsorption to CAC, including PFOS, 6:2 FtS, and PFHxS; as well as DOC at 23.8 mg/L (Carey et al., 2019). Using this isotherm may be conservative with respect to modeling PFOA adsorption to CAC in a PRB in regions where the PFOA front has moved ahead of higher affinity PFAS due to chromatographic separation effects. For example, Carey (2023) demonstrated that accounting for the effect

of enhanced PFOA adsorption downgradient of PFHxS and PFOS fronts in a PRB may result in a significant increase in the estimated CAC longevity.

There may also be aging effects with activated carbon that can reduce longevity to some degree. The potential effect of aging on CAC in situ has not yet been quantified. In addition, chromatographic separation is not expected to be as significant in source areas where there is essentially a line source function along the groundwater flow path that includes competing PFAAs and precursors. Using the groundwater sample isotherm is reasonable for PFOA because even when chromatographic separation does occur in a PRB, PFOA adsorption will still be affected to some degree by competition with a number of short-chain PFASs and PFCAs that are typically present at AFFF-impacted sites. In contrast, to estimate the longevity of CAC for short-chain PFAS, such as PFBS, the use of a competitive adsorption model and representation of the chromatographic separation that occurs may be more important because it is expected that the longevity of short-chain PFAS is more significantly influenced by chromatographic effects.

3 | SOURCE AREA CHARACTERISTICS AT SOUTH DAKOTA SITE

The model scenario developed for this study is based on the general source area characteristics reported for a former fire training area at a site in South Dakota (Anderson et al., 2022; McGuire, 2013; McGuire et al., 2014; WSP, 2022). AFFF was used in fire training activities in an unlined pit from the early 1970s to 1990. This source area is referred to as FT001P and is approximately 2 acres in size. Historical soil grading activities, overspray, and AFFF runoff (McGuire, 2013; McGuire et al., 2014) may have contributed to the current source area extent which is larger than the former burn pit area (see Figure 3). Radial diagrams on Figure 3 illustrate that groundwater concentrations of PFOA, PFOS, PFHxS, and PFBS generally increase along the flow path. The maximum source area concentrations are shown as a separate data series on these radial diagrams to facilitate a visual inspection of spatial changes in concentration between wells.

PFNA is not shown on this figure because PFNA is at least an order of magnitude below PFOA concentrations in the source area (Supporting Information S1: Table 2). PFHxS groundwater concentrations are typically about four times higher than PFOS and PFOA in the source area. (The relative longevity of a CAC barrier for PFHxS vs. PFOA is evaluated below for the source area alternative.) The radial diagrams in Figure 3 indicate that the ratios of these four constituents are similar throughout the source area, although the overall concentrations increase along the flow path as mentioned above. This trend is consistent with a source line function, where mass discharge from the vadose zone and below the water table is occurring continuously along the flow path through the source area.

The two POCs at this site are PFOS and PFOA. PFOS and PFOA have similar magnitudes of groundwater concentrations in the source area (Supporting Information S1: Table 2). Given that PFOS has a

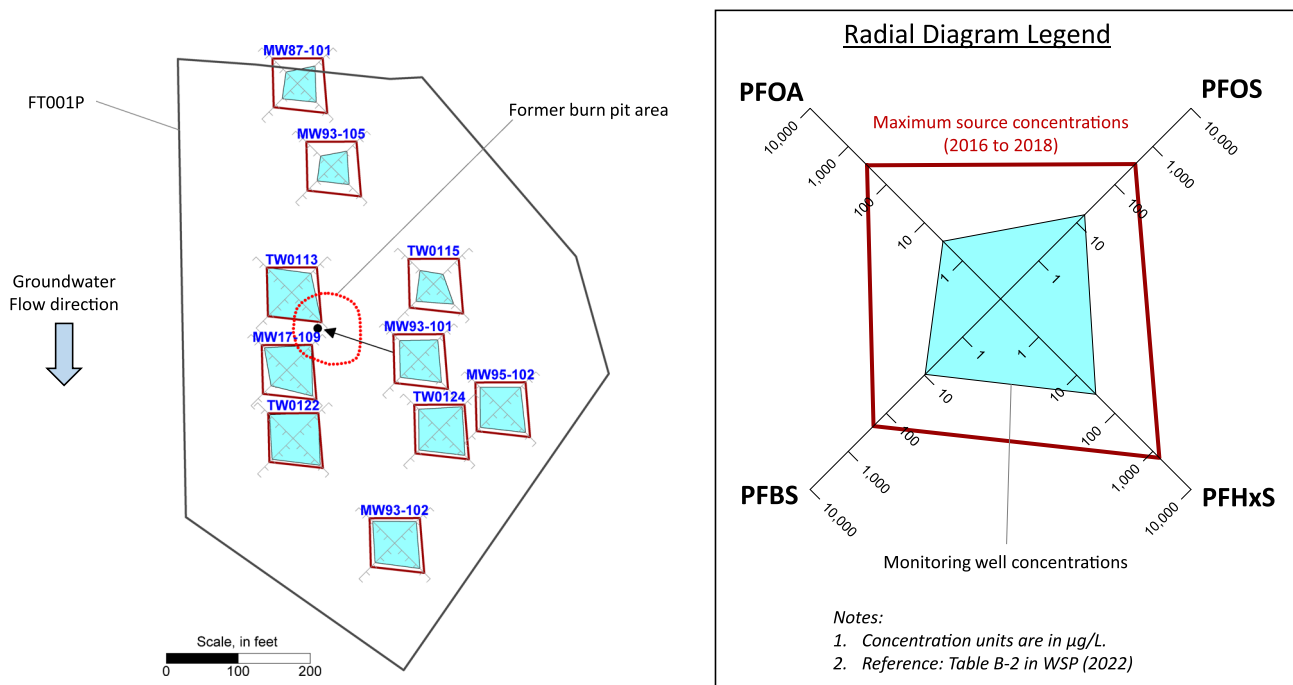


FIGURE 3 PFAS 2016–2018 groundwater concentrations in the vicinity of the former fire training area (FT001P) at the South Dakota site. 6:2 FtS, 6:2 fluorotelomer sulfonate; PFBS, perfluorobutanesulfonic acid; PFHxS, perfluorohexanesulfonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctanesulfonic acid. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/rem.21772)]

significantly stronger affinity for CAC than PFOA (Carey et al., 2022; Hakimabadi et al., 2023), PFOA is expected to be the POC in this setting that will govern the longevity of a CAC remedy because it will breakthrough a CAC zone before PFOS.

The maximum groundwater concentration of PFOA in the source area is 321 µg/L, and the average PFOA concentration in the downgradient region of the source area is 118 µg/L (Supporting Information S1: Table 3). To put this site in context, Supporting Information S1: Figure 2 compares the statistical distribution of maximum groundwater concentrations at 96 AFFF-impacted sites (modified from Carey et al., 2022) to the maximum PFOA concentration of 321 µg/L at this site. The median site of the 96 AFFF-impacted sites had a maximum PFOA concentration of only 7 µg/L, and the 75th percentile site had a maximum concentration of 41 µg/L. This illustrates that the South Dakota site has high PFOA concentrations relative to most other AFFF-impacted sites. As such, the groundwater concentrations at this site represent a good test case for the viability of an in situ CAC groundwater remedy.

Anderson et al. (2022) present the results of a lysimeter study which was conducted at the South Dakota site to characterize PFAS mass discharge from the vadose zone down to the underlying aquifer. Quarterly sampling of shallow and deep paired lysimeters in the vadose zone indicate that PFAS concentrations were consistent at 10 of 12 locations over the 1-year monitoring period. Based on a regional infiltration rate of 3.5% of precipitation (Driscoll et al., 2002) and a total equivalent rainfall of 52.6 cm/y at the site where the climate is semiarid, the mass discharge of PFOA to the underlying

aquifer was estimated by Anderson et al. to be approximately 17 g per year (g/y). This represents 0.06% of the total PFOA mass (28 kg) estimated to occur in the vadose zone (Anderson et al., 2022). Importantly, this estimate reflects current conditions which likely have lower mass discharge than when AFFF operations were occurring at the site. At this site currently, the predominant process contributing to groundwater concentrations is believed to be back-diffusion from low-permeability soils and/or the shallow bedrock matrix below the water table, based on the relatively low infiltration rate from the vadose zone and the high PFAS concentrations in groundwater within the source area.

4 | REMEDIAL ALTERNATIVES ANALYSIS

4.1 | Approach

Two-dimensional plan view modeling of various remedial alternatives was conducted to: (1) determine the design f_{cac} that results in at least 30–40 years of CAC longevity; (2) assess PRB performance across a large plume where PFOA concentrations from the plume centerline to the outer extent varied by more than four orders of magnitude; (3) evaluate how the transient width and intensity of the expanding plume affect CAC performance in the downgradient PRB; (4) assess the integrated performance of multiple PRBs installed at the same time; and (5) improve our understanding of differences in PFAS transport behavior in CAC zones for PRB versus source area grid implementations.

MODFLOW (Harbaugh & McDonald, 1996) was used to simulate steady-state groundwater flow for the two-dimensional model domain representing an unconfined aquifer. The proprietary In-Situ Remediation Model, or ISR-MT3DMS (Porewater Solutions, 2022) was used to simulate PFOA transport both before and after CAC injection. The features in ISR-MT3DMS used to simulate CAC longevity are discussed in more detail in Carey et al. (2019) and Carey et al. (2022).

Characteristics at the South Dakota site were used as the basis for defining the source area in this scenario. The hypothetical hydrogeologic setting used in this study is simpler than the South Dakota site; therefore, the modeled remedial alternatives are not applicable to the South Dakota site. To create the baseline plume for the remedial alternatives analysis, PFOA transport was simulated to occur over a 50-year period (i.e., from 1973 to 2023) before CAC injection. Using this "current" plume as the initial condition, the following three CAC remedial alternatives were modeled for a 100-year postinjection simulation period:

- Alternative No. 1: PRB with a width of 6 m constructed down-gradient of the expanding PFAS plume;
- Alternative No. 2: Mid-plume PRB with a width of 6 m constructed where the PFOA plume was stable, combined with the same downgradient PRB modeled in Alternative 1 to allow for an assessment of the integrated performance of these two PRBs; and,
- Alternative No. 3: Source area grid treatment.

4.1.1 | Model construction

The two-dimensional model was used to simulate the following hydrogeologic setting:

- Unconfined aquifer;
- Aquifer bottom that generally sloped downward along the groundwater flow path, resulting in increasing saturated thickness with distance from the source area;
- Semiarid conditions with an infiltration rate of 2 cm/y which is consistent with the rate assumed for the South Dakota site (Anderson et al., 2022);
- Hydraulic conductivity of 7.6 m/day; and,
- Effective porosity of 0.20.

The modeled PFOA mass discharge from the source area of 270 g/y is based on the average downgradient PFOA concentration at the South Dakota site (118 mg/L), and the following parameters from the hypothetical hydrogeologic setting: groundwater velocity of 24 m/y; source area width of 80 m; and a saturated thickness of 6 m. The PFOA mass discharge from the vadose zone to the water table ($M_{d_{AWT}}$) was specified to be 17 g/y based on the South Dakota site (Anderson et al., 2022). This means that approximately 94% of the mass discharge from the source area in this scenario is contributed from processes occurring below the water table (i.e., $M_{d_{BWT}}$ is 253 g/y).

Model construction details are shown in Supporting Information S1: Table 3 and Figure 4. Further details on the model construction are provided in Supporting Information S1: Section 2. The simulated groundwater velocity declined by about 30% between the source area and downgradient PRB location due to the increasing saturated thickness (Supporting Information S1: Figure 3). When modeling CAC injection into the source area grid (i.e., Alternative No. 3), it was required to consider which mass discharge processes contributing to PFOA aqueous concentrations in the source area would continue after CAC injection, and which would cease after CAC injection. Figure 5 shows the assumed allocation of PFOA mass discharge for various contributing processes before and after CAC injection in the source area.

For the source area alternative (i.e., Alternative No. 3), it was assumed that 70% of the total PFOA mass discharge from the source area was due to back-diffusion from low-permeability soil and precursor biotransformation. This was specified as part of this hypothetical scenario, and a sensitivity analysis on this parameter is discussed below for Alternative No. 3. As discussed above, 6% of the total mass discharge was due to infiltration from the vadose zone. The remaining 24% of the mass discharge before CAC injection was due to desorption from NOM (Figure 5). The ISR-MT3DMS model assumes that re-equilibration of mass between three compartments (aqueous, sorbed to CAC, and sorbed to NOM) occurs as an instantaneous step immediately after CAC injection; therefore, this portion of the mass discharge term (24%) does not continue in the model after CAC injection and the mass re-equilibration step. The resulting source area mass discharge function declined by 24% immediately after CAC injection.

Since modeling CAC longevity involves simulations over multiple decades, it is also important to consider the rate of mass discharge decline that is expected to occur after CAC injection. Carey et al. (2019) estimated an approximate source depletion half-life of 30 years for back-diffusion from secondary sources in low permeability soil based on a simple screening model application. This source depletion half-life was also applied to the mass discharge function for all three alternatives. The mass discharge temporal function used to model the PRB and source area grid remedial alternatives is shown in Supporting Information S1: Figure 4. Based on these mass discharge functions, the source area mass discharge declined by about one order of magnitude over the 100-year postinjection simulation period. The application of CAC in a source area may increase the back-diffusion mass discharge and its rate of decline; however, this potential influence was not considered in this study, and is being evaluated as part of a modeling study for a different site.

For this hypothetical scenario, an f_{oc} of 0.25% was assumed, resulting in a PFOA retardation coefficient of 3.4 and a PFOA travel time which is 70% longer relative to the unattenuated groundwater velocity. Based on the average simulated groundwater velocity of 20 m/y downgradient from the source area, the PFOA attenuated velocity is 6 m/y, resulting in a travel time of about 100 years between the source area and the downgradient PRB.

Two values of longitudinal dispersivity were utilized in the model domain: 10 m to represent site-wide average dispersion in the plume,

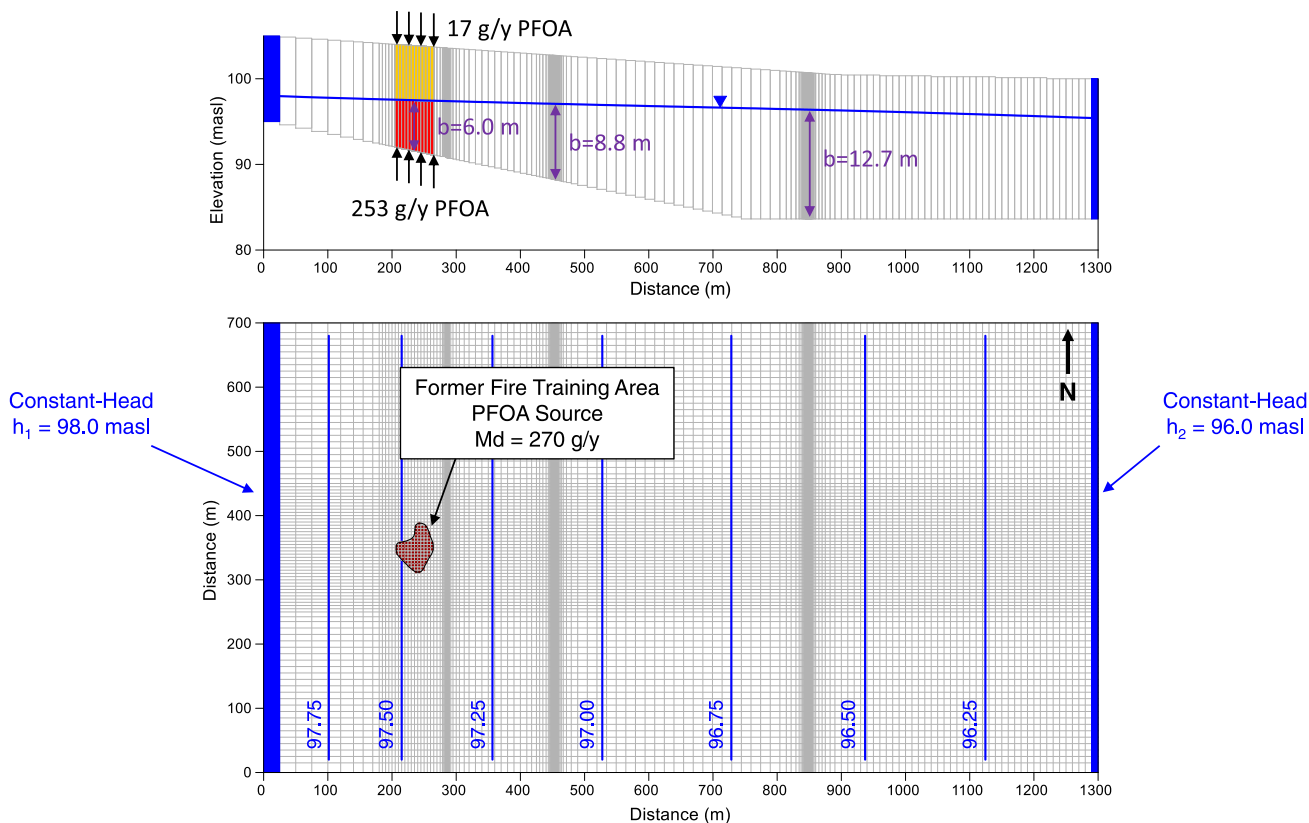


FIGURE 4 Model domain extent, grid discretization, boundary conditions, and simulated groundwater elevation contours. masl, meters above mean sea level. [Color figure can be viewed at wileyonlinelibrary.com]

		Contributing Process	Pre-Injection	Post-Injection
Above water table	}	Vadose zone infiltration to WT	6%	6%
		Desorption from NAPL-water interface below WT	24%	0%
Below water table	}	Desorption from NOM below WT		
		Dissolution from NAPL below WT		
		Precursor biotransformation	70%	70%
		Back-diffusion below WT		
		<i>Total:</i>	100%	76%

Processes continue after CAC injection

FIGURE 5 Potential contributing processes to PFOA mass discharge from the source area before and after CAC injection. The process of desorption from NOM below the water table is simulated to occur as an instantaneous step immediately after CAC injection, and thus is not represented as a continuing mass discharge contribution process after this step has been simulated. CAC, colloidal activated carbon; NAPL, nonaqueous phase liquid; NOM, natural organic matter; PFOA, perfluorooctanoic acid; WT, water table. [Color figure can be viewed at wileyonlinelibrary.com]

and 0.18 m in the 6-m wide CAC PRBs and in the downgradient region of the source area grid. This low dispersivity is about 3% of the transport length in the vicinity of the PRBs and represents local-scale transport where concentrations varied by up to six or seven orders of magnitude over short distances at the downgradient extent of the CAC zone. The utilization of the local-scale dispersivity in the CAC zone helps to reduce the potential for artificial dispersion between the CAC zone and the adjacent groundwater plume. The potential for artificial dispersion “in the opposite direction of groundwater flow,” which is referred to as upstream dispersion, was studied by Irvine et al. (2021).

4.2 | CAC remedial alternative simulations

Figure 6 shows the current (i.e., preremediation) PFOA plume after 50 years of migration. The extent of the plume is defined based on EPA’s proposed MCL for PFOA of 0.004 µg/L. The current PFOA plume in this scenario was modeled to extend approximately 535 m downgradient from the source area. This model does not consider forward diffusion of PFOA into low permeability layers which would have resulted in a shorter plume (Adamson et al., 2022).

Figure 6 also shows the location of the three CAC zones that were modeled for different alternatives. The downgradient PRB

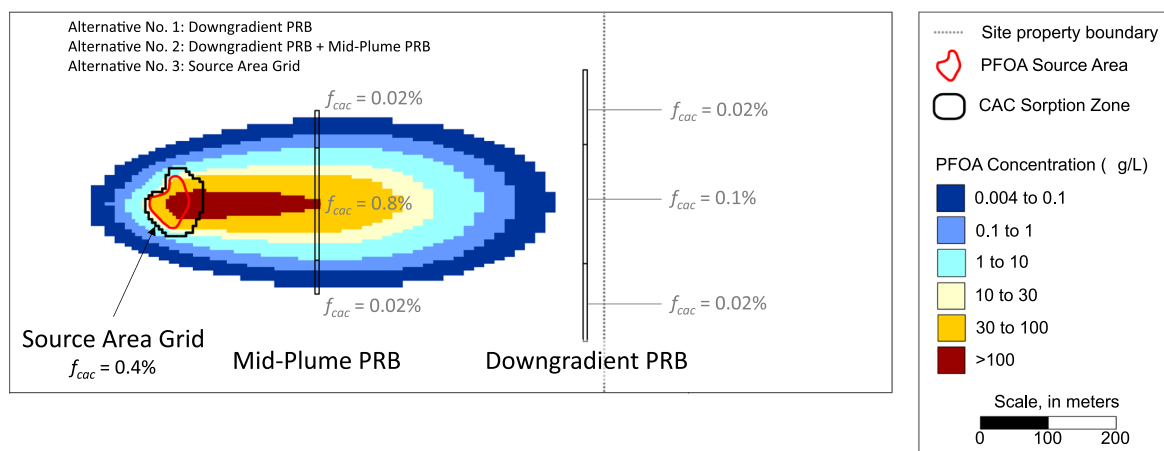


FIGURE 6 Simulated preinjection PFOA plume based on a constant source mass discharge function for a 50-year period. The potential locations of the three different CAC zones considered (i.e., source area grid, mid-plume PRB, and/or downgradient PRB) are illustrated with the fraction of CAC (f_{cac}) values used in the various remedial alternative simulations. The plume concentration intervals are plotted directly for each model grid cell based on the simulated concentration at a specific time; concentrations are not interpolated across the model domain. Simulated plume represents current conditions just prior to CAC injection. CAC, colloidal activated carbon; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier. [Color figure can be viewed at wileyonlinelibrary.com]

(Alternative No. 1) was simulated to be 400 m long, 6 m wide, and 12.7 m thick vertically (total soil volume of approximately 30,000 m³). The mid-plume PRB (Alternative No. 2) was simulated to be 290 m long, 6 m wide, and 8.8 m thick vertically (total soil volume of approximately 15,000 m³). The downgradient PRB is longer than the mid-plume PRB because the modeled PFOA plume in this scenario is expanding in both length and in width. This demonstrates the importance of predicting future plume dimensions and intensity when installing a PRB downgradient of an expanding plume. By comparison, the source area grid area soil volume, based on a saturated thickness of 6.0 m, was approximately 36,000 m³. This source area grid is a large volume that also requires a larger CAC dose than the downgradient PRB given the high PFOA concentrations in the source area.

The f_{cac} values determined to provide a longevity of at least 30 to 40 years in each placement area are also shown in Figure 6. These f_{cac} values were determined through a trial-and-error process to ensure that the target longevity was attained (data not shown). The source area grid treatment f_{cac} was specified to be 0.4%. The source area CAC zone shown in Figure 6 (Alternative No. 3) includes a short buffer zone upgradient of the source area, and a longer buffer zone downgradient of the source area. This buffer is included in the CAC zone because there will be some uncertainty regarding the actual upgradient and downgradient extent of source material above and below the water table. The longer downgradient buffer also provides additional attenuation capacity which may be required if the remedial action objective is to sustain concentrations downgradient from the CAC zone below the proposed MCL of 0.004 µg/L.

For the two plume PRBs (mid-plume and downgradient), different amounts of CAC were specified for the plume core and the plume fringes. For the mid-plume PRB, the f_{cac} was specified to be 0.8% for the plume core, and only 0.02% for the plume fringes where PFOA concentrations

are orders of magnitude lower. These f_{cac} values are consistent with the minimum and maximum site f_{cac} values cited in the 17 field-scale studies summarized by Carey et al. (2022). In wide plumes, it may be beneficial to consider different CAC doses for the plume core and fringes to improve the cost-effectiveness of the remedy. For the downgradient plume, the f_{cac} was specified to be 0.2% in the plume core and 0.02% in the plume fringes. The plume core f_{cac} in the downgradient PRB is lower than the value specified for the core at the mid-plume PRB because PFOA concentrations and mass flux were substantially lower for several decades after installation of the downgradient PRB. While these f_{cac} values were predicted with the model to be sufficient, it may be advisable to consider using higher CAC doses to account for uncertainty in model predictions of long-term field-scale performance, as well as site-specific factors such as geologic heterogeneity, competitive adsorption effects, and seasonal velocity variations.

Groundwater flow modeling in this study is considered to be representative of the average groundwater flow direction for this hypothetical scenario. Most sites experience seasonal changes in groundwater flow direction and PFAS mass flux at specific points where a PRB is to be installed; the average annual mass flux is the determining factor when evaluating CAC longevity, not short-term transient fluctuations due to seasonal shifts in the groundwater flow direction. It is important, however, to characterize the average and ranges in groundwater flow direction and velocity, and temporal and spatial variability in PFAS mass flux across the cross-sectional area of a future PRB.

4.2.1 | Alternative No. 1: Downgradient plume PRB

The downgradient PRB was placed downgradient of the expanding plume to mitigate future PFAS transport beyond the site boundary.

Supporting Information S1: Figure 5 shows the PFOA concentration profile for a transect through the plume perpendicular to the groundwater flow direction, at a distance of about 1 m upgradient of this PRB. PFOA concentrations directly upgradient of the PRB do not exceed EPA's proposed MCL of 0.004 $\mu\text{g/L}$ until 5 years after CAC injection. The width and intensity of the plume continue to expand over time, as shown in Supporting Information S1: Figure 5. This shows the importance of predicting the future plume width and intensity when installing a PRB in front of an expanding plume.

Video animation of the downgradient PRB performance from 0 to 70 years after CAC injection is shown in Supporting Information S2: Exhibit 1. CAC longevity for this this passive PRB scenario was modeled to be 66 years. By comparison, a groundwater pump-and-treat system providing hydraulic containment at the downgradient property boundary would require active treatment of approximately 2 billion liters of water over this same time period.

The initial breakthrough in the CAC PRB occurred across a 75 m length of the PRB directly downgradient from the plume core, which is less than 20% of the total PRB length (Figure 7). For this remedial alternative, performance monitoring would be conducted to provide an indication of when breakthrough will actually occur. If breakthrough is observed with wells downgradient of the PRB, or if monitoring in the PRB indicates that breakthrough is likely to happen at some point in the near future, then one option would be to reinject CAC in an expanded PRB directly downgradient of the first PRB in the localized area(s) where breakthrough is expected to occur soon. As shown in Figure 7, breakthrough will occur in a small portion of the plume core where PFOA concentrations and mass flux are the highest; so this reinjection could be done in a smaller volume (and at lower cost) compared to the original PRB injection event. Another option with installing a PRB downgradient of an expanding plume is to phase the injections over time, which reduces the

uncertainty of the full extent of PRB needed; and this may be more cost-effective than constructing the full PRB at one time.

The plume extent and degree of PFOA penetration into the downgradient PRB at simulation times of 50 and 60 years after CAC injection are compared in Figure 8. After 50 years, the PFOA plume has penetrated a maximum of 42% into the plume core zone in the PRB, and 17% in the plume fringe zone. Only 10 years later, the PFOA maximum plume front penetration into the PRB has approximately doubled: 75% penetration in the plume core zone, and 38% in the plume fringe zone. This faster rate of plume front penetration into the PRB between 50 and 60 years is due to the increasing PFOA plume concentrations directly upgradient of the PRB (see Supporting Information S1: Figure 5). Figure 8 also indicates that there is very little PFOA penetration in much of the plume fringe zones of the PRB, due to the low PFOA mass flux in these regions. One may also need to consider how far to extend the PRB to account for potential future changes in groundwater flow direction. This may depend on whether the RAO is mass flux reduction, which is accomplished mainly in the plume core zone; or whether the goal is to prevent any plume migration beyond a compliance point (i.e., where the plume is specified to be where POCs exceed applicable groundwater cleanup criteria).

PFOA concentrations versus distance within the PRB are shown in Supporting Information S1: Figure 6. The PFOA plume front in the PRB is indicated by the steep slope in PFOA concentrations corresponding to each time data series. This figure also shows that the rate of penetration through the PRB is increasing over time, based on the greater distance between the plume front as time increases in 10-year intervals.

The average PFOA plume front retardation coefficient versus time for this downgradient PRB simulation is shown in Figure 9. The retardation coefficient decreases over time as a result of the increasing plume concentration in the expanding PFOA plume.

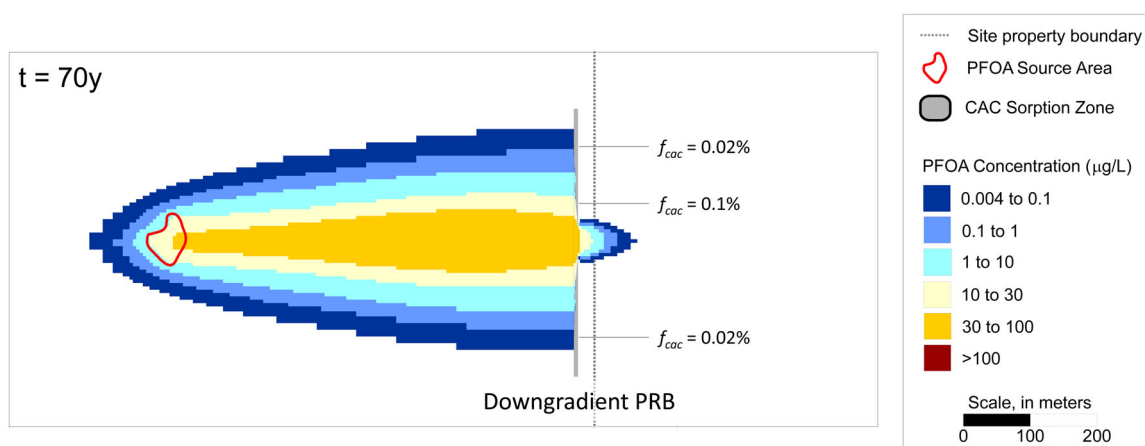


FIGURE 7 Simulated PFOA plume for Alternative No. 1 at a time of 70 years after CAC injection. Localized breakthrough is shown to have occurred in the center of the core portion of the downgradient PRB where PFOA concentrations are highest. CAC, colloidal activated carbon; f_{cac} , fraction of CAC; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier. [Color figure can be viewed at wileyonlinelibrary.com]

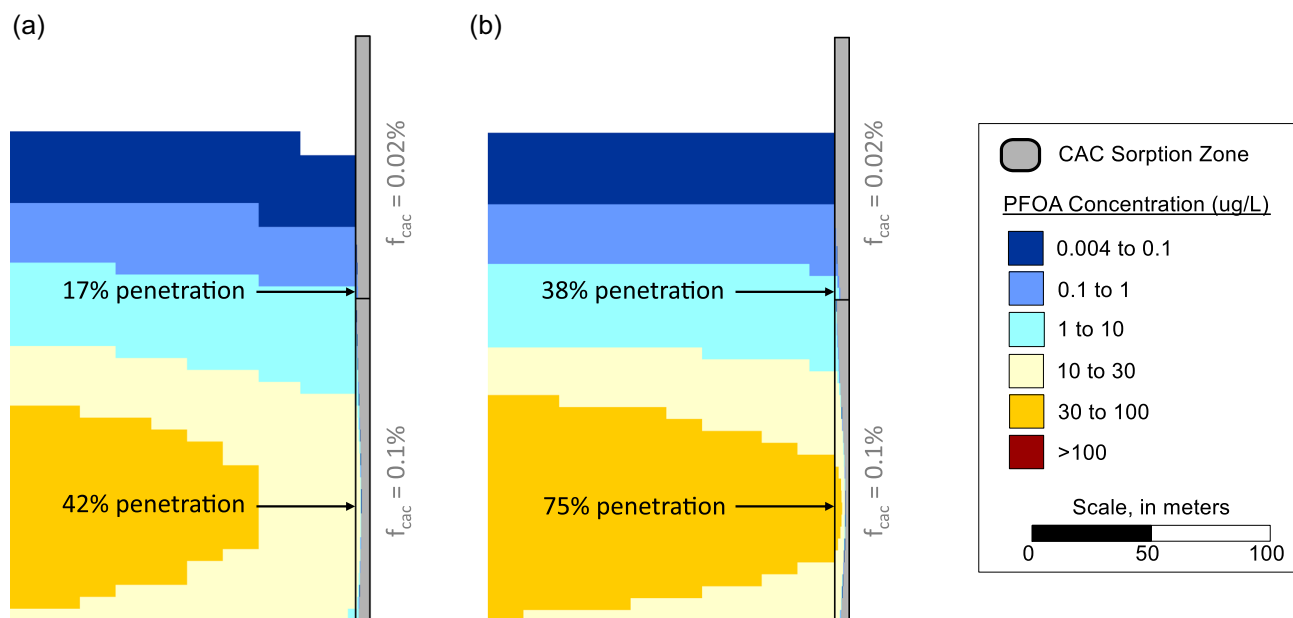


FIGURE 8 Comparison of simulated PFOA plumes for Alternative No. 1 at times after CAC injection of (a) 50 years; and (b) 60 years. The unpenetrated portions of the core and north fringe segments of the downgradient PRB are illustrated with gray shading. The percent penetration is based on the ratio of the maximum plume front penetration into the downgradient PRB in each CAC zone segment, relative to the total PRB width of 6 m parallel to groundwater flow. For example, 75% penetration implies that the PFOA plume front has broken through 75% of the width of the PRB to a distance of 4.5 m. CAC, colloidal activated carbon; f_{cac} , fraction of CAC; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/rem.21772)]

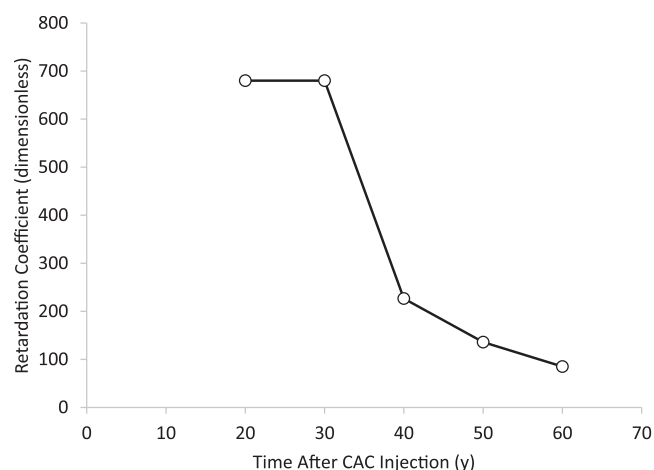


FIGURE 9 Retardation versus distance in downgradient PRB. Average retardation coefficient versus time at the centerline of the plume core in the downgradient PRB (Alternative No. 1). The average retardation coefficient at each point in time is calculated based on the ratio of the attenuated velocity of the PFOA front within the PRB, versus the average linear groundwater velocity. This profile shows that the average retardation coefficient of the PFOA front declines over time for the expanding plume due to the increasing plume mass flux entering the PRB. CAC, colloidal activated carbon; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier.

This shows that the retardation coefficient for an expanding plume will decrease in time, whereas the retardation coefficient is generally constant for a PRB installed in a stable plume (data not shown).

4.2.2 | Alternative 2: Integrated mid- and downgradient plume PRBs

Figure 10 shows the simulated performance of the combined construction of two PRBs (mid-plume PRB and downgradient PRB) at simulation times of 1, 5, 10, 20, 30, and 50 years after CAC injection. Video animation of the integrated PRB performance from 0 to 70 years after CAC injection is shown in Supporting Information S3: Exhibit 2. The purpose of this simulation was to assess how a mid-plume PRB would impact the longevity of the downgradient PRB for this scenario. Before CAC injection, the total PFOA mass in the aquifer between the two PRBs was 491 g, with 144 g in the aqueous phase and 347 g adsorbed to NOM. The relatively high adsorbed PFOA mass in this scenario results in a longer time to desorb PFOA between the two PRBs after CAC injection. This illustrates the importance of characterizing the ratio of soil to groundwater concentrations (i.e., the effective K_d) downgradient of a planned barrier or pump-and-treat system.

The longevity of the mid-plume PRB was simulated to be about 50 years, even with a relatively high f_{cac} of 0.8%. The longevity of the downgradient PRB was simulated to be 68 years, which is only 2 years longer than the simulated longevity without the mid-plume PRB. This demonstrates that there is little benefit of upgradient source control or a mid-plume PRB with respect to improving the performance (i.e., longevity) of the downgradient PRB. However, upgradient CAC zones are expected to have a larger benefit at sites with a faster travel time (e.g., Carey, 2023).

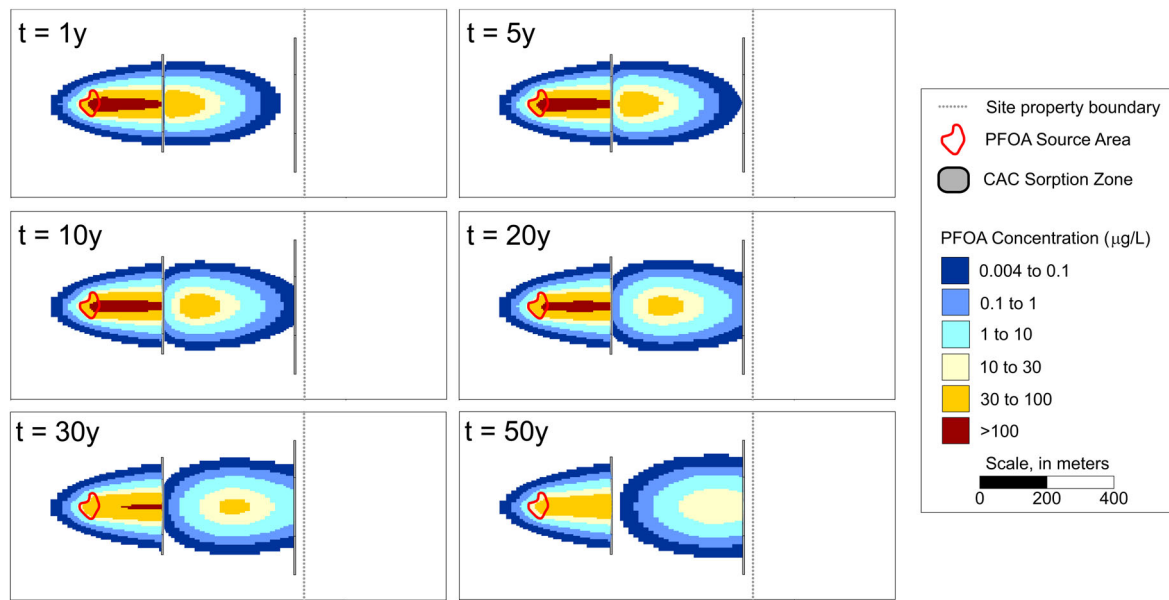


FIGURE 10 Simulated PFOA plume for Alternative No. 2 (i.e., combined mid-plume and downgradient PRBs) at simulation times of 1, 5, 10, 20, 30, and 50 years after CAC injection. CAC, colloidal activated carbon; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier. [Color figure can be viewed at wileyonlinelibrary.com]

The simulated incoming PFOA concentration at the downgradient PRB is shown in Figure 11 for Alternative No. 1 and 2. This figure shows that the mid-plume PRB only causes a decrease in the incoming PFOA concentration at the downgradient PRB starting at a time of about 50 years after CAC injection, when there has already been significant penetration of the PFOA front into the downgradient PRB. Although the incoming PFOA mass flux did start to decline after 50 years, it was not a sufficiently large decline to cause a significant increase in the CAC longevity for this downgradient PRB.

4.2.3 | Alternative 3: Source area grid treatment

Supporting Information S1: Figure 7 shows the simulated preremediation PFOA concentration contours in the vicinity of the source area. The extent of the CAC zone for grid treatment of the source area is also shown in Supporting Information S1: Figure 7. For this remedial alternative, a relatively long buffer of about 20 m beyond the known or suspected source area was included. It is expected that concentrations within the source area portion of the CAC zone will eventually increase above EPA's proposed MCL due to ongoing mass discharge contributions from various sources (see Figure 5). By adding the buffer zone downgradient of the source area, the longevity of the CAC for this alternative is extended significantly if the RAO is to ensure that cleanup criteria (e.g., proposed MCLs) are attained at the downgradient boundary of the CAC zone.

Note that the total volume of the modeled buffer zone (i.e., the portion of the CAC zone that is outside of the actual source area) is approximately the same as the volume within the source area. Which

means that the construction of this buffer zone effectively doubles the volume of the CAC zone, and would substantially increase cost. A smaller buffer zone could have been used to reduce upfront costs of the remedy, and then monitoring could be conducted and more CAC injected in the future to extend the length of the buffer zone as needed. Another option is to use a lower f_{cac} for the downgradient buffer zone if there is relatively low uncertainty about the downgradient extent of the source area.

Figure 12 shows the simulated PFOA plume at times of 1, 10, 20, 50, 80, and 100 years after CAC injection. Video animation of the source area CAC zone performance from 0 to 70 years after CAC injection is shown in Supporting Information S4: Exhibit 3. The simulated PFOA concentration within the source area eventually increases above EPA's proposed MCL approximately 10 years after CAC injection, and then above $0.1 \mu\text{g/L}$ in the source area within approximately 50 years after CAC injection. The PFOA plume front in the source zone has not penetrated significantly into the buffer area, however, and thus the downgradient plume is not affected by this localized increase in PFOA concentrations within the original source area. The plume continues to migrate downgradient of the source and disconnects from the source area as shown in Figure 12. Due to the relatively slow PFOA travel time simulated in this scenario, the PFOA plume concentration at the downgradient property boundary is simulated to be above $30 \mu\text{g/L}$ even 100 years after the initial CAC injection in the source area. This indicates that effective source control does not achieve the goal of mitigating PFOA transport beyond the site boundary; this goal is only achieved through the implementation of the downgradient PRB.

The modeled CAC longevity in the source area grid alternative has higher uncertainty than the PRB longevity estimates, because of

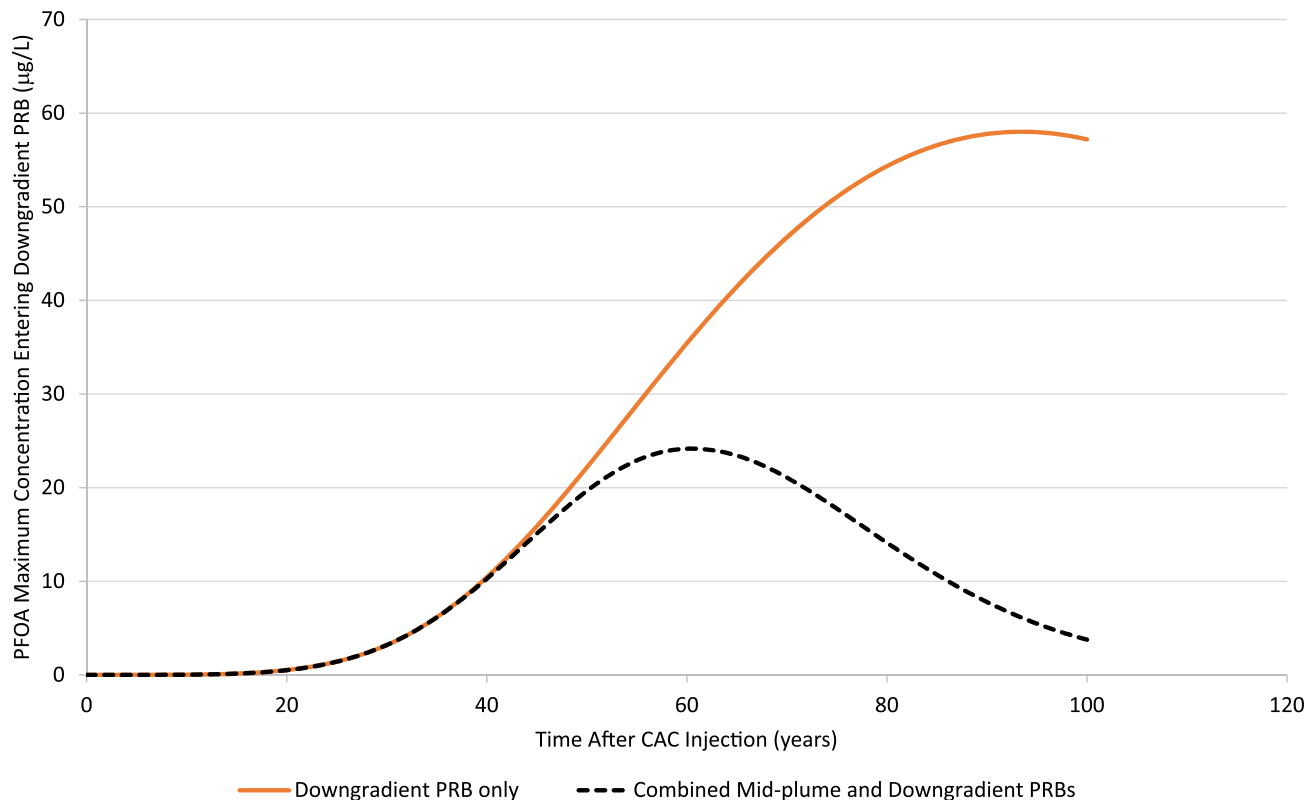


FIGURE 11 Simulated maximum PFOA concentration entering downgradient PRB versus time for Alternative No. 1 (downgradient PRB only) and Alternative No. 2 (combined mid-plume and downgradient PRBs). CAC, colloidal activated carbon; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier. [Color figure can be viewed at wileyonlinelibrary.com]

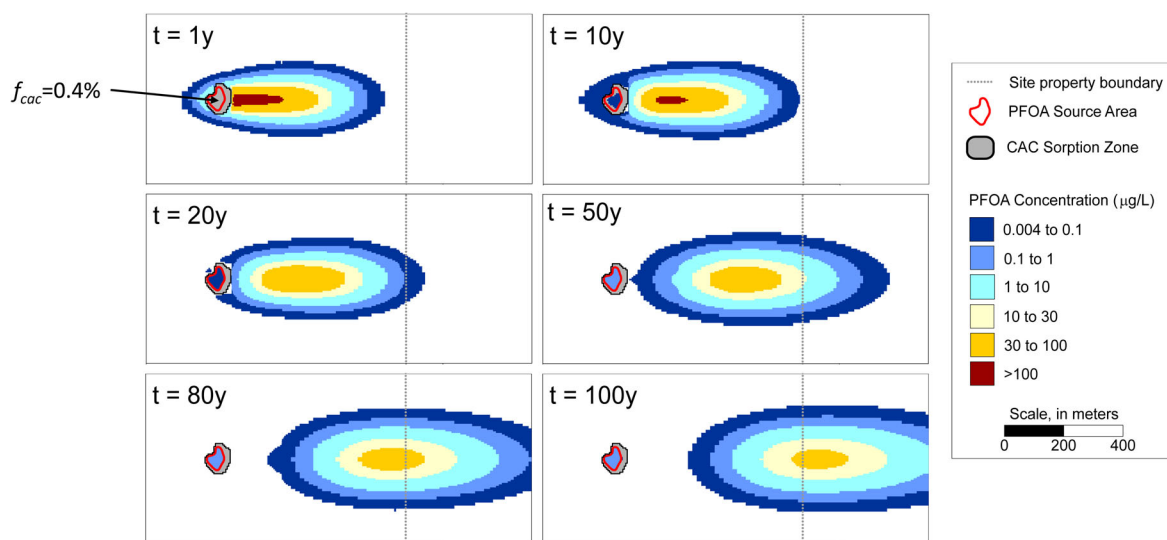


FIGURE 12 Simulated PFOA plume for Alternative No. 3 (i.e., source area grid) at times of 1, 10, 20, 50, 80, and 100 years after CAC injection. The plume shown at $t = 10$ years indicates that the PFOA concentration in the source area increased above the proposed MCL before 10 years after CAC injection; however, these plume maps also demonstrate that PFOA did not breakthrough the downgradient buffer zone even after 100 years postinjection. CAC, colloidal activated carbon; f_{cac} , fraction of CAC; PFOA, perfluorooctanoic acid; t , simulated time after CAC injection. [Color figure can be viewed at wileyonlinelibrary.com]

the large mass of precursors and long-chain PFAAs in the source area which may compete with PFOA for adsorption to CAC. The Freundlich isotherm used to represent PFOA adsorption to CAC was estimated based on a groundwater sample that was likely collected from a plume and not a source area. This isotherm may not represent the full extent of competitive adsorption occurring in the source area.

Simulated PFOA concentrations versus distance along a flow path through the center of the source area grid CAC zone are shown in Figure 13 for simulation times of 0, 1, 20, 40, 60, 80, and 100 years after CAC injection. The shape of the concentration versus distance curve for the source area grid (Figure 13) is different than the shape for the downgradient PRB (Supporting Information S1: Figure 6). The advancing PFOA front in the PRB over time is evident based on the steep changes in concentration with distance in the PRB. Figure 13 illustrates that there is not an analogous PFOA front in the source area; the PFOA concentration does not change significantly with distance in the source area because the model simulates the equivalent of a line source with incoming mass discharge throughout the source area. For this reason, chromatographic separation of PFOA from long-chain PFAAs and precursors is not expected to occur in the source area CAC zone. This is in contrast to what is expected to occur in a PRB where there will be more separation between fronts based on the relative affinity of PFAS for adsorption to CAC.

A sensitivity analysis was conducted to compare the CAC longevity for three scenarios: (1) the base case with PFOA and an initial source area mass discharge after CAC injection equal to 76% of the preinjection mass discharge (see Figure 5); (2) PFOA with an initial

postinjection mass discharge equal to 100% of the preinjection mass discharge; and (3) PFHxS with an initial postinjection mass discharge equal to 76% of the preinjection mass discharge. The PFHxS model scenario was simulated using a mass discharge rate equal to 3.7 times the PFOA mass discharge rate, which corresponds to the ratio of the PFHxS to PFOA concentrations in the source area (see Supporting Information S1: Table 2). The PFHxS Freundlich adsorption isotherm was specified as $K_f = 1240 \text{ (mg/kg)(mg/L)}^{-a}$, and $a = 0.24$ (Carey et al., 2022). The modeled PFOA and PFHxS concentrations versus distance through the center of the source area are shown in Supporting Information S1: Figure 8 at a simulated time of 100 years after CAC injection. This figure illustrates that the PFOA scenario with the higher initial mass discharge after injection results in a modeled concentration in the source area that is about double the base case concentration, but both scenarios have similar concentrations in the downgradient region of the CAC buffer area. The PFHxS scenario has a higher concentration in the source area and buffer area relative to the PFOA base case, as expected. PFHxS is simulated to be slightly above the proposed health-based water concentration of 0.009 $\mu\text{g/L}$ for PFHxS at the downgradient CAC zone boundary, which may be due to artificial upgradient dispersion as discussed earlier. This sensitivity analysis shows that PFOA and PFHxS have penetrated similar distances into the CAC buffer area downgradient of the source area 100 years after CAC injection.

Any type of PFAS remediation using a hydraulic, adsorptive, or physical barrier will leave POC mass in the subsurface downgradient of where the barrier is constructed. This includes PFAS mass adsorbed to NOM, or in diffusive secondary source zones in low

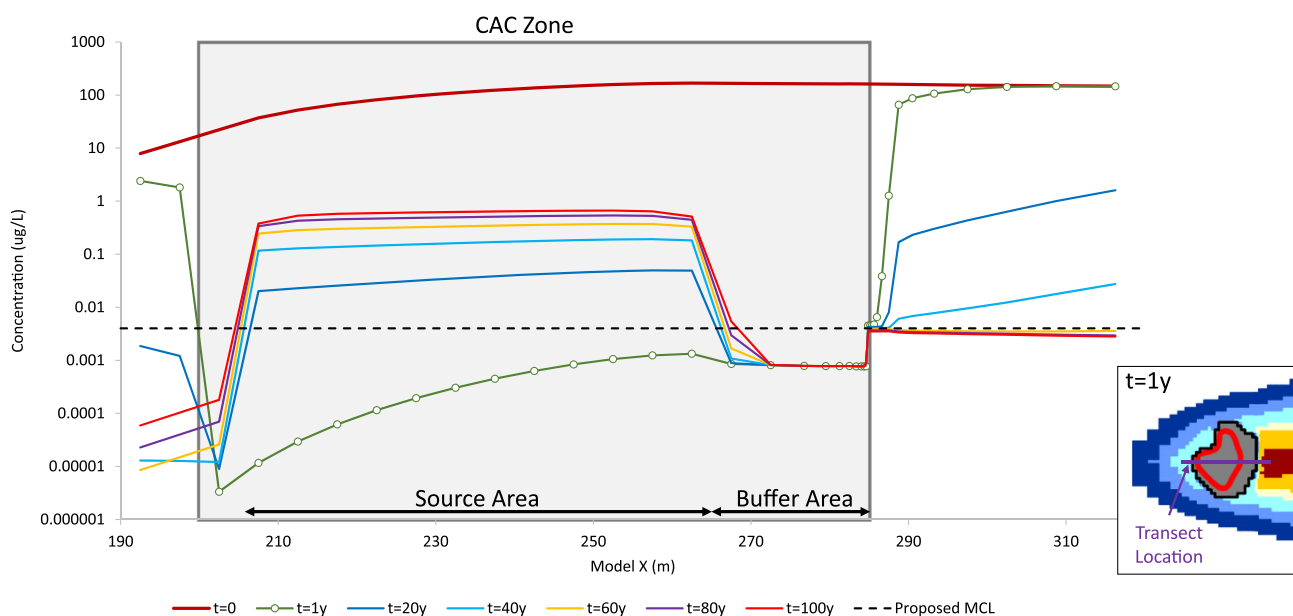


FIGURE 13 Simulated PFOA concentration versus Model X along the centerline through the source area CAC zone. The gray shaded area illustrates the extent of the CAC zone. The source area extent shown at the bottom of the chart is consistent with the red outlined source area in the inset map. Unlike the PRB where the PFOA front advances forward over time, the source area grid application of CAC results in generally similar PFOA concentrations throughout the source area which is consistent with a line source function. This illustrates that chromatographic separation is unlikely to occur within a source area after CAC injection. CAC, colloidal activated carbon; PFOA, perfluorooctanoic acid; PRB, permeable reactive barrier; t, simulated time after CAC injection. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

permeability soil downgradient of the barrier location. After implementing the remedial alternative, this downgradient mass may slowly desorb from NOM or back-diffuse from low permeability soil in the downgradient region, thereby sustaining POC plumes above the cleanup criteria for potentially a long period of time. This is independent of what technology is used for remediation, and should be considered when deciding where to place a barrier or groundwater extraction wells.

5 | CONCLUSIONS AND RECOMMENDATIONS

New PFAS-CAC isotherms based on four-species synthetic solutions were developed to quantify the effect of competitive adsorption on PFOA sorbed concentrations. DOC in a groundwater sample at a concentration of 23.8 mg/L apparently reduced the PFOA adsorption affinity by about a factor of two. The PFOA adsorption isotherm for the four-species solution with calcium and magnesium added indicates that these divalent cations substantially enhanced PFOA adsorption to CAC in the synthetic solution; however, this was not the case for the groundwater sample batch tests with similar calcium and magnesium concentrations. This suggests that calcium and magnesium are involved in aqueous complexation reactions with other ions in the groundwater sample, which inhibits cationic bridging between PFAS and CAC. Further research is recommended to assess the effects of geochemical speciation in groundwater samples on PFAS adsorption to CAC. Additional research is also recommended to be able to predict the field-scale performance of CAC for short-chain POCs.

A hypothetical model scenario was constructed with similar characteristics to a source area at a former fire training area at a South Dakota site. PFOA is the POC at this site which would govern the longevity of a CAC remedy. PFOA concentrations at the South Dakota site are shown to be substantially higher than most AFFF-impacted sites. Groundwater flow and reactive transport modeling indicates that CAC would still be capable of providing the desired longevity of at least 30–40 years using f_{cac} within the range of what has been measured or calculated for other sites (i.e., 0.02%–0.8%).

Two-dimensional modeling was conducted to facilitate visualization of PRB performance across a wide plume where PFOA concentrations vary by more than four orders of magnitude. This two-dimensional modeling also showed that when breakthrough occurs in a CAC PRB, it will only occur over a localized area where POC mass flux is the highest. Therefore, it will not likely be necessary to construct an entirely new PRB in the future; localized injections may be needed to expand a PRB length where monitoring indicates this is necessary. Two-dimensional modeling also proved useful for predicting future increases in plume width and intensity when a PRB is to be installed in front of an expanding plume.

PFAS transport characteristics in a CAC PRB are different than in a source area grid system. In a PRB, clear fronts will develop for each constituent, and chromatographic separation is expected to occur between PFAS with high and low affinity for adsorption to CAC. In a

source area grid system, mass discharge of precursors and PFAAs into the aqueous phase occurs throughout the source area; this suggests that chromatographic separation is not likely to be significant in a source area grid system. The modeling conducted for this study may be conservative with respect to predicting the longevity of a PRB because chromatographic separation effects were not considered; however, this will not be the case for the source area grid system that was modeled. There is higher uncertainty in longevity predictions for a source area CAC zone where precursors and other competing solutes have higher concentrations. A large proportion of precursors are retained in the source area and, thus, downgradient PRBs are less likely to have the same competitive adsorption effects as in the source area.

For the hypothetical scenario used in this study, source or mid-plume treatment did not provide a significant benefit; the downgradient PRB had the greatest benefit with respect to preventing PFAS migration beyond the site boundary. This indicates that for sites with a long distance between the source area and a downgradient property boundary, or slow POC travel times, source control may not be beneficial when a downgradient PRB is implemented; the best performance with respect to protection of downgradient receptors appears to be a downgradient PRB which has the most immediate benefit with respect to reducing mass flux off-site.

ACKNOWLEDGMENTS

This project was supported by Strategic Environmental Research and Development Program (project ER21-3959). The publication of this manuscript does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

ORCID

Rick McGregor  <http://orcid.org/0000-0002-3418-2901>

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AUTHOR BIOGRAPHIES

Grant R. Carey, PhD, P Eng, is President of Porewater Solutions in Ottawa, Ontario. Dr. Carey specializes in PFAS environmental forensics, litigation, groundwater modeling, NAPL remediation, and back-diffusion. Dr. Carey also develops modeling and visualization software, and is currently collaborating with various universities on PFAS remediation research. He received a BASc from the University of Waterloo, an M Eng from Carleton University, and a PhD from the

University of Guelph. He is an adjunct research professor in Environmental Engineering at Carleton University.

Richard H. Anderson, PhD, is an environmental scientist at the US Air Force Civil Engineer Center (AFCEC) in San Antonio, Texas. He provides technical expertise to AFCEC's Environmental Restoration Program in the areas of emerging contaminants, environmental engineering, environmental toxicology, and quantitative data analyses. Dr. Anderson also represents the AFCEC to the US Defense Department's Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) in the area of environmental restoration.

Paul Van Geel, PhD, is a professor of Environmental Engineering at Carleton University, and specializes in hydrogeology and solid waste management, flow and transport in the saturated and unsaturated zones, impacts of real world soil/NAPL wettability on migration, distribution and remediation of NAPL-contaminated sites. Dr. Van Geel received his BAsC and PhD from the University of Waterloo.

Rick McGregor, MSc, MBA, is a hydrogeologist with InSitu Remediation Services, Ltd based in Canada. Mr. McGregor has a BSc in geology and MSc in hydrogeology and geochemistry from the University of Waterloo along with an MBA from Wilfrid Laurier University. He has over 27 years of experience in research, consulting, and contracting. His current focus is on the remediation of impacted groundwater.

Keir Soderberg, PhD, is a geochemist with S. S. Papadopoulos & Associates, Inc. in Rockville, Maryland. Dr. Soderberg's research has focused on isotope geochemistry and ecohydrology, with a BSE from Princeton University, an MSc from the University of Cape Town, and a PhD from the University of Virginia. As a consultant, Dr. Soderberg has focused on environmental forensics, litigation, the allocation of remedial costs, site characterization, and the evaluation of remedial alternatives for impacted groundwater and sediments.

Anthony Danko, PhD, PE, is an environmental engineer with NAVFAC EXWC. He has a PhD in Environmental Engineering and is a licensed professional engineer. He is involved in various

NAVFAC projects and initiatives, including providing technical support to various remedial project managers, as well as the testing and demonstration of innovative technologies.

Seyfollah Gilak Hakimabadi, MS, is a PhD candidate in the Department of Civil and Environmental Engineering at the University of Waterloo. He received a BS in Chemical Engineering from the Amirkabir University of Technology, and an MS in Chemical Engineering from the Ferdowsi University of Mashhad, Iran.

Anh Le-Tuan Pham, PhD, is an Assistant Professor of Civil and Environmental Engineering at the University of Waterloo. His research group investigates contaminant fate and transformation. The current research focuses on developing novel technologies for the remediation of contaminated soil and groundwater, treatment of oil sands process water, and removal of emerging contaminants. He received his BS in Chemical Engineering from the Hanoi University of Technology, and MS and PhD in Civil and Environmental Engineering from the University of California, Berkeley.

Mia Rebeiro-Tunstall is a research assistant at Porewater Solutions, and is an undergraduate student in the Bachelor's of Science program with specialization in environmental science and toxicology at Queen's University in Kingston, Ontario.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Carey, G. R., Anderson, R. H., Van Geel, P., McGregor, R., Soderberg, K., Danko, A., Hakimabadi, S. G., Pham, A. L.-T., & Rebeiro-Tunstall, M. (2024). Analysis of colloidal activated carbon alternatives for in situ remediation of a large PFAS plume and source area. *Remediation*, 34, e21772. <https://doi.org/10.1002/rem.21772>