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Review

In situ remediation of per- and polyfluoroalkyl substances by colloidal activated carbon in groundwater and vadose zone

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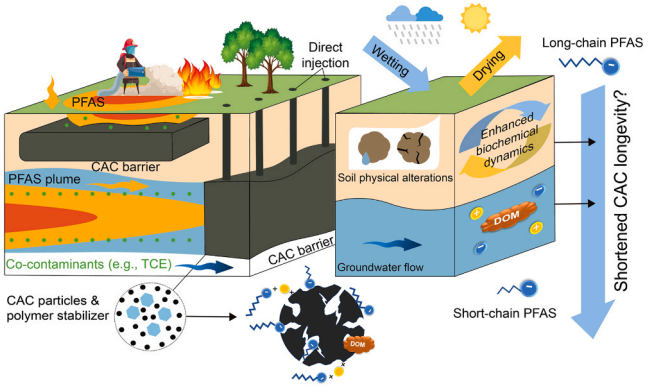
HIGHLIGHTS

- CAC-enabled *in situ* remediation of PFAS-impacted groundwater and vadose zone is reviewed.
- PFAS properties, groundwater hydrogeochemistry, and co-contaminants affect technology performance.
- Mathematical modeling can predict the longevity of CAC barrier in groundwater remediation.
- Unique vadose zone processes affect CAC performance for *in situ* PFAS remediation.

GRAPHICAL ABSTRACT



Abbreviations: AC, Activated carbon; AFFF, Aqueous film forming foam; AWI, Air–water interface; Bgs, Below ground surface; CAC, Colloidal activated carbon; C–C, Carbon–carbon; C–F, Carbon–fluorine; CMC, Carboxymethyl cellulose; CVOC, Chlorinated volatile organic compound; DGBE, Diethylene glycol butyl ether; DLVO, Derjaguin–Landau–Verwey–Overbeek; DOC, Dissolved organic carbon; DoD, Department of Defense; DOM, Dissolved organic matter; DRO, Diesel-range organics; EMM, Equilibrium mixing model; EPA, Environmental Protection Agency; EPS, Extracellular polymeric substance; F_{CAC}, Colloidal activated carbon injection dose; F_{OC}, Fraction of organic carbon; FOSA, Perfluorooctane sulfonamide; FTS, Fluorotelomer sulfonate; GAC, Granular activated carbon; GenX or HFPO, Hexafluoropropylene oxide; IX, Ion exchange; K_d, Solid–liquid partitioning coefficient; K_F, Equilibrium adsorption capacity parameter; MCL, Maximum contaminant level; MCLM, Modified competitive Langmuir model; MT3DMS, Modular three–dimensional multispecies transport model; MTBE, Methyl tert-butyl ether; NAPL, Non-aqueous phase liquid; NOM, Natural organic matter; OATZ, Oxic–anoxic transition zone; PAH, Polycyclic aromatic hydrocarbon; PFAS, Per- and polyfluoroalkyl substances; PFBA, Perfluorobutanoic acid; PFBS, Perfluorobutanesulfonic acid; PFCA, Perfluoroalkyl carboxylic acid; PFDA, Perfluorodecanoic acid; PFHpA, Perfluoroheptanoic acid; PFHpS, Perfluoroheptanesulfonic acid; PFHxA, Perfluorohexanoic acid; PFHxS, Perfluorohexanesulfonic acid; PFNA, Perfluorononanoic acid; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctanesulfonic acid; PFPeA, Perfluoropentanoic acid; PFPeS, Perfluoropentanesulfonic acid; PFSA, Perfluoroalkyl sulfonic acid; PFUnDA, Perfluoroundecanoic acid; PolyDM, Polydiallyldimethylammonium chloride; SMC, Surface-modified clay; SRNOM, Suwanee River natural organic matter; TCE, Trichloroethylene; TOC, Total organic carbon; TRL, Technology readiness level; USGS, U.S. Geological Survey; VOC, Volatile organic compound; WDC, Wetting–drying cycle.

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) have reached global occurrence in the environment, including groundwater and vadose zone. Therefore, developing technologies to remediate PFAS in groundwater and vadose zone is urgent, especially for *in situ* remediation. Colloidal activated carbon (CAC) has emerged as a cost-effective adsorbent that shows potential to *in situ* immobilize PFAS in groundwater and vadose zone. This review provides state-of-the-art assessment of CAC-enabled technologies to *in situ* remediate PFAS-impacted groundwater and vadose zone, focusing on the technology feasibility, effectiveness, efficiency, longevity, and environmental factors affecting technology performance. The adsorption mechanisms of CAC for various types of long-chain and short-chain PFAS are discussed to evaluate technology effectiveness and efficiency. Significant efforts are devoted to assessing and predicting the longevity of CAC-based barriers for treating PFAS plumes in groundwater by mathematical modeling and field observations. Key factors on how nonuniform distribution, plume migration, and potential loss of CAC affect the barrier continuity and PFAS breakthrough are elucidated. The unique processes in the vadose zone, such as dynamic wetting-drying cycles, air-water interfacial partitioning, and oxic-anoxic transition zones are highlighted, since they may significantly affect CAC adsorption and migration capacities, underscoring the urgent needs for systematic studies and long-term monitoring efforts. Future research frontiers and challenges on CAC-enabled technologies for *in situ* remediation of PFAS-impacted groundwater and vadose zone are identified, contributing to the global efforts in addressing PFAS pollution.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of emerging contaminants, consisting of more than 15,000 manmade chemicals [1]. Among these diverse chemical species, their common structural hallmarks are the hydrophobic perfluorinated carbon backbones (i.e., carbon chains) and hydrophilic headgroups (Fig. 1) [2]. Due to their stable thermal and chemical properties, PFAS show a wide spectrum of

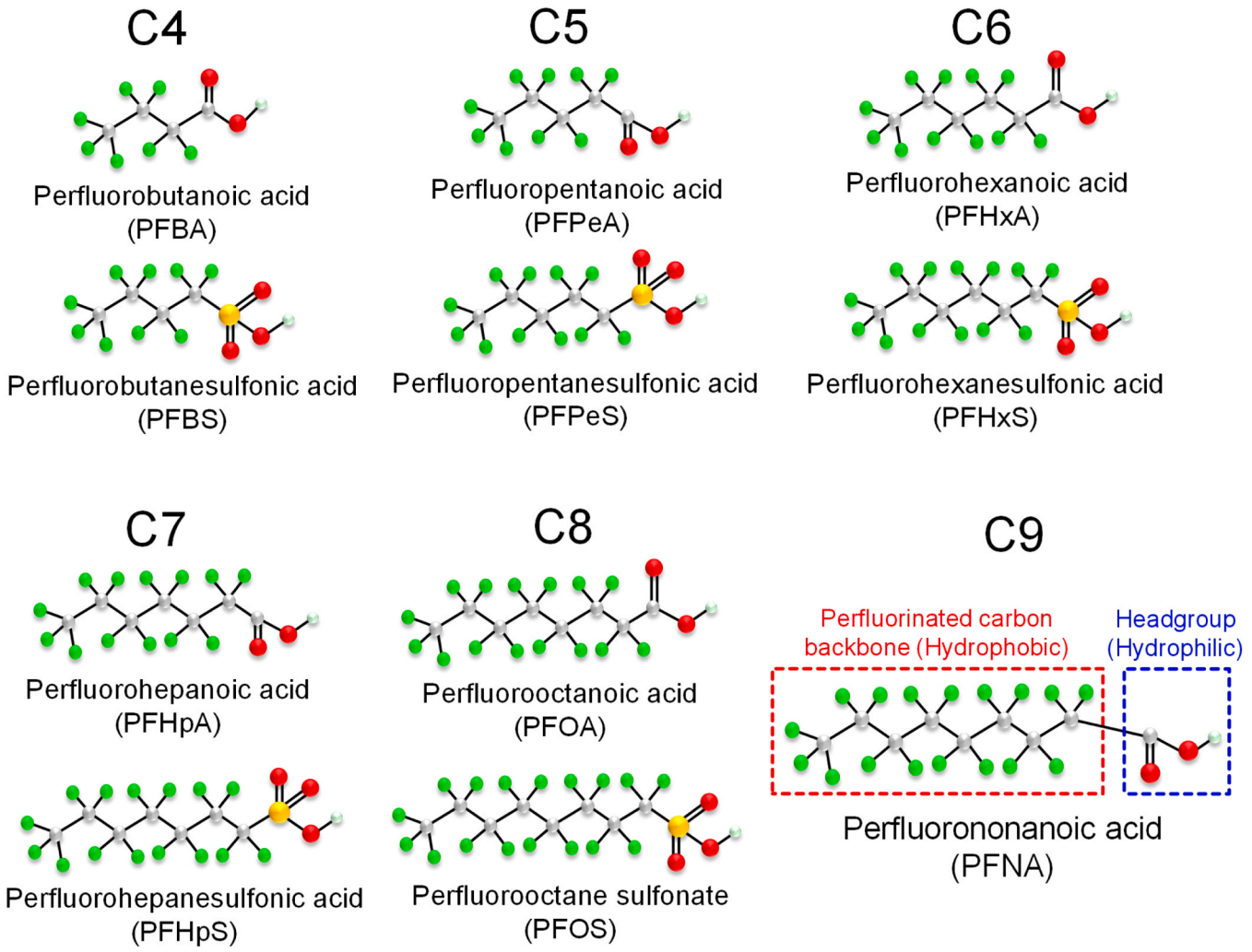

Fig. 1. Molecular structures of representative PFAS with total carbon numbers from four (C4) to nine (C9). The perfluorinated carbon backbone (in red box) is hydrophobic, while the headgroup (in blue box) is hydrophilic. The longer the carbon backbone, the greater the hydrophobicity. Color code: C (grey), F (green), O (red), S (yellow), and H (white).

industrial and commercial applications, such as nonstick cookware, aqueous film forming foams (AFFFs), food packaging, and semiconductor materials [3]. Yet, the widespread use and unregulated disposal of PFAS-containing products have caused global occurrence of PFAS in the environment [2,4–6]. For example, a recent study conducted by the U.S. Geological Survey (USGS) indicated that the Biscayne Principal Aquifer in Florida exhibited the highest total PFAS concentration (24 PFAS) at 29 ng/L in groundwater in the United States [6]. Considering the environmentally persistent, toxic, and bioaccumulative nature of PFAS [7], extensive studies have reported strong associations between PFAS exposure and adverse health outcomes (e.g., cancer and liver damage), even at very low concentrations (ng/L levels) [8]. Therefore, in April 2024, the U.S. Environmental Protection Agency (EPA) [9] recommended that the ideal goal of PFAS in drinking water is essentially zero (e.g., PFOA and PFOS; Fig. 1).

Beyond their pronounced environmental persistence, PFAS contamination is also characterized by highly variable mobility, particularly in the context of groundwater contamination [10]. This is because PFAS migrating through the vadose zone represents one of the primary sources of groundwater PFAS contamination [11]. Upon initial release, highly mobile PFAS species can rapidly transport to reach the groundwater via infiltration [2]. In contrast, PFAS with relatively lower mobility that remain in soils for longer periods may still migrate slowly or undergo transformation, generating transformation intermediates and final products with greater mobility and thereby driving prolonged secondary contamination plumes into the groundwater for years and even decades [12,13]. These unique, yet complex processes in the vadose zone raise significant human health concerns of PFAS discharge in groundwater, which is one of the main sources of drinking water in the United States [14].

Over the past decade, substantial efforts have been devoted to developing and testing technologies that can remediate PFAS in water and soil, such as groundwater and vadose zone. However, relatively few technologies have been demonstrated to successfully treat PFAS *in situ*. Among these technologies, colloidal activated carbon (CAC) has emerged as one of the few adsorbents that show promising potential to remediate PFAS-impacted groundwater and vadose zone *in situ*. Therefore, this review aims to provide the first, state-of-the-art assessment of CAC-enabled technologies for *in situ* remediation of PFAS-impacted groundwater and vadose zone. A literature review shows that most published studies on CAC-based technologies are performed to treat PFAS-impacted groundwater, with a small fraction of studies focusing on vadose zone. Consequently, this review focuses on the discussions using findings harnessed from CAC-enabled *in situ* remediation in groundwater. Nonetheless, some findings (if not all) gathered from groundwater literature are also applicable to guide CAC-enabled *in situ* remediation for vadose zone. Therefore, this review also details the current advancement of CAC-based technologies for *in situ* remediation of PFAS-impacted vadose zone, especially with respect to the issues and challenges encountered due to the unique processes and pathways occurring in vadose zone.

To provide a structurally smooth workflow of this review, we first provide a brief overview of various PFAS remediation technologies (Section 2), followed by a methodology review (Section 3) that identifies key references specifically documenting CAC-enabled *in situ* remediation. Afterwards, comprehensive discussions of CAC-based technologies for *in situ* remediation of groundwater (Section 4) and vadose zone (Section 5) were presented. Critical factors, such as PFAS properties, CAC characteristics, groundwater geochemistry, hydrological variability, competitive adsorption, and mathematical modeling are carefully discussed to evaluate and predict the performance (feasibility, effectiveness, efficiency, and longevity) of CAC-based technologies for *in situ* remediation of PFAS-impacted groundwater and vadose zone. We conclude this review by identifying future research frontiers and challenges of using CAC-based technologies for treating PFAS-impacted groundwater and vadose zone *in situ* (Section 6), contributing to the global efforts for addressing PFAS pollution.

To our knowledge, this is the first review dedicated to CAC-enabled *in situ* remediation of PFAS in both groundwater and vadose zone systems, rather than conventional *ex situ* PFAS adsorption technologies. Unlike previous PFAS reviews that broadly summarize remediation technologies, this review provides a high-level focused and critical synthesis of CAC-based remediation by integrating: (i) field-scale applications and technology readiness; (ii) mechanistic understanding of PFAS adsorption, transport, and competitive interactions under subsurface conditions; (iii) mathematical modeling approaches for predicting CAC barrier longevity; and (iv) the unique hydro-biogeochemical processes in vadose zones, including wetting–drying cycles (WDCs), air–water interface (AWI) partitioning, and oxic–anoxic transition zones (OATZs) that may greatly affect CAC performance.

2. A brief overview of PFAS remediation technologies

A wide array of technologies has been developed to treat PFAS-impacted matrices, including water and soil [13,15–17]. These treatment technologies [13] can be generally classified into (1) non-destruction technologies that separate PFAS from environmental media without breaking down their molecular structures (e.g., adsorption of PFAS by adsorbents), (2) destruction technologies that break carbon–fluorine (C–F) and carbon–carbon (C–C) bonds of PFAS into less harmful or harmless compounds (e.g., thermal, electrochemical, advanced oxidation and reduction processes, plasma, and supercritical water oxidation), and (3) treatment train technologies that integrate non-destruction and destruction treatments [18–22]. Among these technologies, the adsorption-based technology exhibits high technology readiness level (TRL) and technological reliability [23]. Therefore, adsorption is the most widely used technology for PFAS removal, with activated carbon (AC) [24,25] and ion exchange (IX) resin [26,27] being the top two adsorbents (Table 1, TRL = 9) [28]. While showing high TRLs, AC is not effective to adsorb short-chain PFAS (e.g., PFBA; Fig. 1) [32] and IX resin is relatively expensive that prohibits its large-scale application (e.g., *in situ* groundwater remediation). Recently, biochar (TRL = 4; Table 1) [28] produced by the pyrolysis of agricultural and forestry wastes under oxygen-limiting conditions has been proposed as a cost-effective and efficient adsorbent for PFAS [18–20,33,34], although the overall adsorption performance of biochar for PFAS removal is generally lower than that of AC and IX resin.

Another alternative adsorbent is surface-modified clay (SMC, Table 1, TRL = 7–8), which has been evaluated in laboratory- and pilot-scale column studies [35]. The reported removal performance of PFAS by SMCs is typically greater than granular activated carbon (GAC), but lower than IX resins [31,36]. While recent studies have incorporated unit media cost and levelized cost analyses, the economic competitiveness of SMCs depends largely on site- and water quality-specific conditions, so further evaluation is needed to assess their long-term feasibility and suitability for widespread application [31]. Other new adsorbents for PFAS adsorption include polymers (e.g., cyclodextrin), chitosan, and metal-organic frameworks (MOFs) [31,37–40]. Yet, these new adsorbents are not ready for large-scale (e.g., pilot and field) application for PFAS remediation (e.g., relatively low TRLs), due to issues associated with their large-scale production, costs associated with production, operation, and maintenance, along with other technical barriers during *in situ* remediation.

Overall, the current PFAS remediation industry is evolving rapidly, with AC receiving the greatest attention due to its high TRL, high efficiency for PFAS adsorption, and relatively low costs (vs. IX resin). It should be noted that, from both cost and performance perspectives, SMC appears to be a competitive alternative; however, at present, CAC remains the only technology that can be directly injected for *in situ* remediation of groundwater and vadose zone.

Table 1
Summary of PFAS treatment technology and its technology readiness level (TRL).

Application	Technology	Media	Cost ($/kg)	Longevity	TRL
Adsorption	Granular activated carbon (GAC)	Water, soil*	~$2.8	Years	9
Adsorption	Colloidal activated carbon (CAC)	Water*, soil*	~$10	Years	8–9
Hydrophobicity	Foam fractionation (FF)	Water*	NA	NA	8–9
Adsorption	Surface-modified clay (SMC)	Water, soil*	~$6.3	Months – years	8–9
Ion exchange	Ion exchange (IX) resin	Water	~$17.6	Months – years	6
Adsorption	Biochar (colloidal)	Water, soil	~0.35	Months – years	4
Adsorption	New adsorbent (e.g., MOFs)	Water, soil	NA	NA	≤ 3
TRL = 1, 2, 3		TRL = 4, 5, 6		TRL = 7, 8, 9	

Technology Readiness Levels (TRLs): (1) basic principles observed and reported, (2) technology concept and/or application formulated, (3) analytical and experimental critical function and/or characteristic proof of concept, (4) component and/or breadboard validation in laboratory environment, (5) component and/or breadboard validation in the relevant environment, (6) system/subsystem model or prototype demonstration in an operational environment, (7) system prototype demonstration in an operational environment, (8) actual system completed and "flight qualified" through test and demonstration, and (9) actual system flight proven through successful mission operation [28,29]. Cost data were obtained from the literature [30,31]. * indicates *in situ* applicability of this media. NA: Not applicable.

3. Literature search and review methodology

Literature relevant to CAC applications for PFAS remediation was primarily identified through the Web of Science database on May 24, 2026, using the keyword combination "colloidal activated carbon" AND "PFAS" across all searchable fields, which initially yielded 30 records. To ensure comprehensive coverage of the rapidly evolving field, additional relevant publications were further identified through backward and forward citation tracking, as well as targeted searches of key authors, research groups, and references associated with CAC-enabled PFAS remediation. The collected literature was subsequently screened based on its direct relevance to CAC applications for *in situ* PFAS remediation in groundwater and vadose zone systems. Studies included in this review were categorized into several major themes, including: (i) laboratory-scale investigations of PFAS adsorption mechanisms and adsorption behavior in relation to CAC physicochemical properties; (ii) effects of groundwater chemistry, co-contaminants, and environmental conditions on CAC performance; (iii) field-scale applications and implementation strategies of CAC barriers; and (iv) modeling approaches for evaluating PFAS transport, breakthrough behavior, and CAC barrier longevity. Studies lacking direct relevance to CAC-enabled PFAS remediation or focusing only on unrelated adsorbents or *ex situ* treatment systems were excluded from detailed analysis. The selected studies (21 papers on groundwater and 7 papers on vadose zone soils) were then critically synthesized and discussed in the following sections to provide a comprehensive and state-of-the-art assessment of CAC-enabled *in situ* remediation technologies for PFAS.

4. CAC-enabled in situ remediation of PFAS in groundwater

Remediating PFAS in groundwater is rather challenging. Pump-and-treat is a common *ex situ* groundwater remediation technique, in which the contaminated water is extracted from the ground using extraction wells and then transported to aboveground treatment systems for treating various contaminants, including PFAS and others, such as chlorinated solvents, metals, fuel oils, pesticides, and volatile organic compounds (VOCs). However, pump-and-treat technique is often cost prohibitive especially with respect to PFAS remediation, due to the strong C–F covalent bond [10], and stringent regulatory requirement (e.g., ng/L level) [9,41]. In addition to high operational costs, this approach may simply translocate contamination from one location to another by producing PFAS-saturated residuals that require further disposal or treatment. As PFAS are classified as hazardous substances, the associated disposal costs and legal liabilities of such residuals are expected to increase over time. In contrast, *in situ* remediation at the source zones has been identified as a more sustainable and cost-effective alternative. Since all treatment processes occur underground, it eliminates waste generation and thus greatly reduces the need for surface infrastructure and environmental disturbance, offering long-term benefits in both performance and environmental responsibility [42].

As one of the leading technologies for *in situ* remediation, CAC at TRL = 8–9 has been commercially applied since 2015. It has been used to treat a wide range of groundwater contaminants, including chlorinated VOCs (CVOCs such as ethene and ethane), petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), methyl tert-butyl ether (MTBE), and pesticides [43,44]. CAC is the colloidal form of AC with particle diameter typically between 0.5 and 2 micrometers (μm). The smaller particle size of CAC compared to GAC (500–1000 μm) and powdered activated carbon (PAC, 10–100 μm) sets it apart from other AC products. The large specific surface area (>1000 m^2/g) of CAC make it especially suitable for PFAS adsorption [28]. CACs are generally produced at high temperatures, normally above 1000 °C, which results in a material with a high carbon content compared to other carbon-based materials produced at lower temperatures (e.g., biochar) [45]. Therefore, CAC is relatively stable when deployed into the subsurface environments. The CAC particles exhibit colloidal stability and transport properties in aqueous solutions (similar to colloids), which can be readily applied for *in situ* remediation in groundwater without structural breakdown or significant migration from the treatment source zone.

Generally, CAC particles are dispersed in a water-based medium to create a liquid, colloidal form of AC with CAC mass typically ranging from 1% to 5% [42]. Unlike other AC forms such as GAC, which is typically used in a fixed bed or packed column, CAC can be used in suspension allowing for more versatile and cost-effective applications, such as *in situ* groundwater remediation via direct injection (Fig. 2). After injection, CAC particles attach to the surrounding geologic matrix (e.g., clay, silt, sand, and gravel), becoming immobilized in the subsurface and forming a site-specific, *in situ* treatment zone that immobilizes contaminants as groundwater passes through [46]. This is because PFAS are adsorbed much more strongly to CAC than to the native matrices (e.g., soil particles and sediments), due to hydrophobic and oleophobic interactions, electrostatic interactions, hydrogen bonds, interfacial behaviors, along with other interactions [2]. Often, PFAS-impacted sites also include other types of organic contaminants that have already been treated by CAC, such as CVOCs, PAHs, pesticides, and MTBE [44,46]. These co-contaminants exhibit a wide range of physicochemical properties, encompassing both highly hydrophobic compounds that readily adsorb to soil and highly hydrophilic compounds with strong mobility. Similar to the PFAS family, those organic contaminants often co-occur in the source zones, persisting in both saturated and unsaturated zones with long-term environmental persistence. The broad-spectrum applicability and high sorption performance of CAC in treating those organic contaminants (e.g., 85–90%

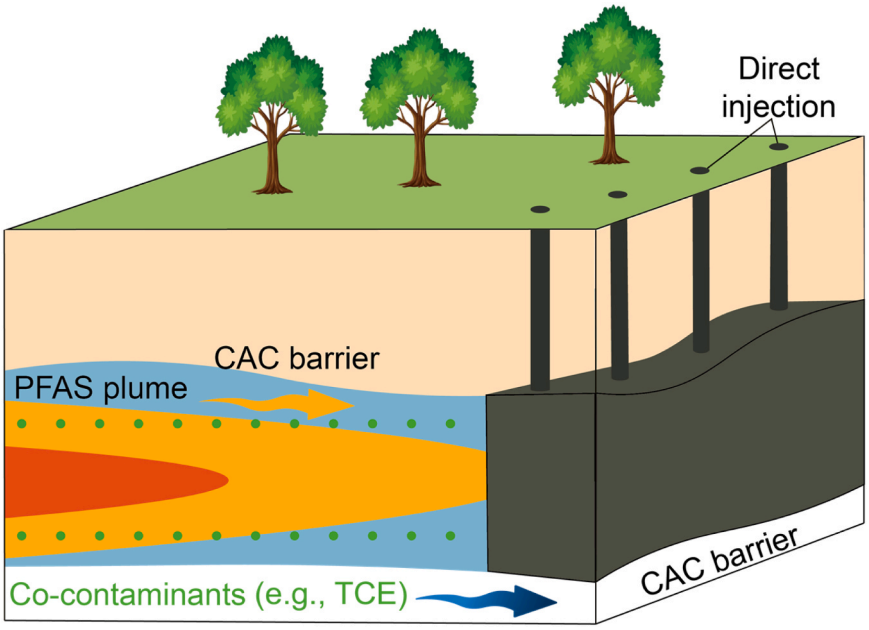

Fig. 2. Schematic showing CAC-enabled *in situ* remediation of PFAS in groundwater (CAC barriers are formed).

concentration reduction within 90 days) have demonstrated its potential as a low-cost and environmentally friendly material for *in situ* PFAS remediation [43,44,46].

4.1. Field applications of CAC-enabled in situ remediation of PFAS in groundwater

Many laboratory-scale studies have demonstrated high PFAS removal efficiency by CAC, with solid-liquid partitioning coefficients (K_d; L/kg) typically ranging from 10^2 to 10^5, generally increasing with PFAS chain length (Fig. 1) [47–49]. Consequently, CAC amendment substantially increases PFAS retardation within the treated zone, reducing downgradient PFAS concentrations and limiting plume migration, while groundwater seepage velocity remains unchanged. CAC has been commercialized by multiple vendors for groundwater plume and source-zone treatment applications in the United States such as REGENESIS (San Clemente, CA) and CASCADE (Bothell, WA) and internationally (Intraplex/Intropore, Germany). Up until now, the CAC commercial products have been applied to *in situ* immobilize PFAS plumes on more than 60 sites globally, including airport, industrial, landfill, manufacturing, and military/fire-training sites in the United Kingdom, Canada, Sweden, Belgium, Germany, and the United States. Representative examples include AFFF-impacted military sites in South Dakota and Michigan (USA), airport and industrial sites in Ontario (Canada) and the United Kingdom, pilot-scale CAC barriers near Arboga (central Sweden), and PFAS-impacted industrial/manufacturing facilities in Sweden and Belgium [42,44,46,50–53]. The CAC commercial products produced from different vendors normally have different physicochemical properties, such as particle size, size distribution, specific surface area, surface charge, surface functional groups, surface modification by stabilizing agents, among others [54–57]. These physicochemical properties of CACs are expected to affect their colloidal stability, transport, and sedimentation behaviors in aqueous solutions (e.g., groundwater), which ultimately affect their effectiveness, efficiency, and longevity for *in situ* PFAS remediation.

Recent field-scale investigations further strengthen the feasibility of CAC-enabled technologies for *in situ* PFAS remediation in groundwater. For example, Hatton et al. [58] conducted a field demonstration using polymer-stabilized activated carbon to treat PFAS-impacted groundwater through push–pull injection tests and aquifer-cell evaluations. They reported substantial PFAS concentration reductions ranging from ~90% to > 99.9%, with some locations exhibiting reductions of up to four orders of magnitude after 10 months of treatment. Their findings further demonstrated that polymer-stabilized activated carbon can be effectively distributed within aquifer materials, while maintaining strong PFAS retention under realistic groundwater flow conditions [58]. Importantly, the study also highlighted the significance of groundwater residence time, treatment-zone continuity, and carbon distribution uniformity in controlling PFAS breakthrough behavior and long-term barrier performance. Overall, these field observations support the potential of CAC-based permeable treatment zones as a cost-effective and sustainable alternative to conventional pump-and-treat systems for long-term management of PFAS plumes in groundwater.

Currently, there are some ongoing demonstration projects funded by the Department of Defense (DoD) of applying CACs for *in situ* remediation of PFAS plumes in groundwater at AFFF-impacted DoD sites [59]. To evaluate the feasibility and affordability (mainly costs) of different treatment techniques for PFAS, recent study estimated that the projected CAC costs are approximately one-third ($7.2 M vs. $19 M) of the pump-and-treat costs over the project periods of 15–100 years [42]. It is important to emphasize that CAC has a relatively short history of field application, with initial deployments occurring around 2015. As a result, the available information on long-term performance and maintenance cost is derived from modeling efforts and may not fully capture future field-scale performance.

4.2. Longevity of a CAC barrier for in situ remediation of PFAS in groundwater

Longevity is considered as one of the most critical performance factors to evaluate the CAC barriers for *in situ* PFAS remediation, as it determines how long the technology can maintain regulatory compliance before re-injection of CAC is required. Generally, the longevity of a CAC barrier is defined as the time duration between the initial injection of CAC and the time when the concentration of PFAS of interest exceeds applicable regulatory or guidance criteria (e.g., maximum contaminant concentrations (MCLs) of PFOA and PFOS at 4 ng/L by the U.S. EPA) [9] at the downgradient boundary of the CAC zone (Fig. 2) [60]. The CAC barrier is designed to function with a longevity at years to decades [42], thereby offering more time for the scientific and remediation

communities to develop and validate *in situ* PFAS destruction technologies. In practice, however, the long-term performance of a CAC barrier depends on (i) the remaining adsorption capacity of CAC for PFAS retention and (ii) the persistence and stability of the barrier within the subsurface. Physical processes such as particle mobilization, nonuniform distribution, preferential flow, erosion, dilution, sediment redistribution, and potential detachment or migration of CAC particles beyond the designed treatment zone may reduce the effective CAC mass and create untreated flow pathways, thereby compromising barrier performance even before PFAS concentrations exceed regulatory thresholds at monitoring wells. Therefore, long-term CAC barrier performance depends on both physicochemical adsorption processes and the stability and retention of CAC particles within the subsurface porous media.

As mentioned above, different CAC commercial products offered by different vendors are expected to have different longevities for *in situ* site remediation, but no study is available to systematically compare the physicochemical properties and longevity of different CAC commercial products. This lack of comparative data creates large uncertainties for site-specific design and longevity estimation. While CAC demonstrated a more than 90–99% reduction of PFAS concentrations at 14 of 16 field sites, the observed durations (1–7.5 years) reflect the relatively recent implementation of CAC, and its actual long-term (decades) effectiveness remains to be verified [60–62].

The longevity of a CAC barrier for PFAS remediation in groundwater relies on a wide range of site-specific factors. These factors mainly include: (i) the hydrogeology of the site (e.g., groundwater flow rate and direction) [63], (ii) the location [50] and amount (dosage) of CAC injected [50,60] and its distribution in the groundwater, (iii) the mass flux and type of PFAS (e.g., short- and long-chain PFAS; Fig. 1) entering the CAC barrier, and (iv) the groundwater chemistry (e.g., ionic strength and composition, dissolved organic matter (DOM), and co-occurring contaminants) [42,51,56].

Estimating longevity begins with a careful characterization of PFAS background at the contaminated site. In real-world scenarios, PFAS are typically released as complex mixtures of multiple compounds over extended periods of time [12,64]. PFAS contamination is often categorized as originating from point sources on a regional scale. However, at the site scale, PFAS release often resembles line or area sources due to diffusive entry into groundwater [50]. There are three primary PFAS loading pathways to the CAC barrier, including: (1) above the water table, where PFAS from the vadose zone leach downward into the barrier; (2) upgradient sources, where PFAS already in groundwater, or infiltrating from the vadose zone along the flow path, move toward the barrier; and (3) within the groundwater body itself, where PFAS are released from natural organic matter (NOM), non-aqueous phase liquids (NAPLs), NAPL-water interfaces, transformation of PFAS precursors, or back diffusion from high-sorption soil matrices (e.g., clays) [50,65]. Once PFAS loading pathways and directions are characterized, the remaining parameters control the rate and spatial pattern of PFAS transport into the barrier. For example, groundwater velocity governs the PFAS mass flux delivered to the CAC barrier, which directly controls the rate of sorbent loading and, consequently, barrier longevity. PFAS speciation (chain length, headgroup, and fluorination) determines adsorption affinity [56], while groundwater chemistry (e.g., ionic strength, pH, DOM, and co-contaminants) modifies interactions by competitive sorption [50,66]. Subsurface geology further affects spatial distribution and physical retention of CAC within the porous subsurface, which in turn alters PFAS access to sorption sites and the spatial continuity of *in situ* treatment zone [46]. These factors co-determine the rate of CAC site depletion and time-dependent decline in sorption capacity, ultimately influencing the operational lifespan of the barrier.

Recently, Zheng et al. [67] addresses the mechanistic question behind longevity prediction: whether PFAS adsorption by CAC can be treated as equilibrium sorption or whether mass-transfer limitations cause earlier breakthrough. Their column experiments and two-site kinetic transport model showed that mass-transfer limitations were needed to reproduce laboratory PFOA/PFOS breakthrough and elution profiles [67]. However, field-scale modeling indicated that under natural hydraulic gradients, mass-transfer limitations are generally not important because groundwater residence times in CAC barriers are long enough for near-equilibrium sorption; they become important mainly under active pumping or short residence-time conditions [47,60].

While current studies primarily focus on barrier performance, limited information is available regarding PFAS desorption, rebound effects, changes in adsorption reversibility, or potential remobilization of PFAS once CAC sorption capacity becomes depleted under long-term field conditions (i.e., exhausted CAC barriers). Follow-up injection of CAC is one of the most practical management approaches currently proposed for maintaining long-term barrier effectiveness. Since CAC is directly injected into subsurface treatment zones, additional CAC amendments may potentially be applied when monitoring data indicate increasing PFAS breakthrough concentrations or declining adsorption performance. Follow-up injections could help replenish adsorption capacity, reinforce nonuniform treatment zones, and extend barrier service life without extensive excavation or replacement of subsurface materials. Yet, the effectiveness of repeated CAC injections remains unclear under realistic field conditions. Important uncertainties include how previously emplaced CAC affects subsequent particle transport and distribution, whether pore clogging or permeability reduction may occur after multiple injections, how aging and biofouling affect newly injected CAC interactions, and whether residual PFAS sorbed on older CAC phases could alter competitive adsorption behavior. Repeated injections may also create increasingly heterogeneous subsurface distributions of CAC, potentially affecting preferential flow paths and localized PFAS breakthrough behavior.

4.3. *Modeling approaches for predicting the longevity of a CAC barrier in groundwater*

Currently, most existing CAC barriers have not been operated for a sufficiently long period of time (e.g., more than 5 years) to reliably evaluate their longevity (via personal communication with remedial project managers). Therefore, modeling studies have been used to predict the longevity of the CAC barrier for treating PFAS in groundwater [47,50,60]. The fundamental mechanisms governing PFAS retention by CAC are through adsorption, which is commonly described by the Freundlich isotherm due to its flexibility in representing nonlinear sorption behavior across environmentally relevant conditions [51]. The Freundlich model assumes heterogeneous distribution of sorption sites with varying affinities, where high-affinity sites are occupied first, followed by sorption onto lower-affinity sites at a slower rate. It also allows for experimental determination of the equilibrium adsorption capacity parameter (K_F) as well as the Freundlich exponent term (n), which reflects the degree of sorption nonlinearity and controls how adsorption capacity evolves with changing PFAS concentrations. To estimate the operational longevity of CAC barriers for PFAS-impacted groundwater, site-specific modeling approaches are often employed.

Different transport models have been used to simulate PFAS plume migration in saturated zones, such as the modular three-dimensional (3D) multispecies transport model (MT3DMS) and its *in situ* reactive extension (ISR)—ISR-MT3DMS [47,60,62,63]. These transport models are typically coupled with MODFLOW, which generates groundwater flow fields based on actual site hydrogeologic parameters. Together, the coupled modeling framework enables the prediction of PFAS mass fluxes reaching the CAC barrier and time-dependent sorption depletion, providing realistic estimates of barrier lifespan under field-relevant conditions [62]. In practice, MODFLOW uses field-measured parameters such as hydraulic conductivity, aquifer thickness, hydraulic gradient, and boundary conditions derived from well logs and site investigations. MT3DMS requires inputs, including the initial PFAS concentration distribution and dispersivity parameters. ISR-MT3DMS further incorporates reactive transport parameters such as the fraction

of CAC in soil (f_{CAC}), fraction of organic carbon (f_{OC}), dissolved organic carbon (DOC) content, and adsorption parameters (e.g., Freundlich K_F and n values). Together, these inputs allow for site-specific simulations of PFAS mass flux arriving at the CAC barrier and its time-dependent sorption capacity exhaustion, enabling more realistic projections of CAC longevity under *in situ* conditions.

One classic application of the ISR-MT3DMS model was conducted to compiled median PFAS concentrations from 96 AFFF-impacted airport sites (PFOS = 12 μg/L, PFHxS = 7 μg/L, and PFOA = 2 μg/L) [60]. Representative site parameters for the model simulation included f_{OC} = 0.1%, post-injection f_{CAC} = 0.08%, and DOC concentration = 23.8 mg/L, along with sorption parameters fitted from batch tests using actual PFAS-contaminated groundwater. Assuming a 12 m-long CAC barrier, the simulation results predicted that downgradient PFAS concentrations would remain below 1 ng/L (EPA's current MCLs is 4 ng/L for PFOA and PFOS, and 10 ng/L for PFHxS) for 936 years for PFOS, 265 years for PFOA, and 235 years for PFHxS, respectively. Even when f_{CAC} was reduced to 0.02%, the predicted longevity for PFOA remained over 60 years. Another study was conducted for a specific site to incorporate detailed field parameters using data from a high-concentration PFAS site at a military facility in South Dakota, USA (maximum PFOA concentration of 321 μg/L with average at 118 μg/L). At that site, a CAC permeable barrier with an injection dosage ranging from 0.02% to 0.8% by soil weight was predicted to stop a large, advancing PFAS groundwater plume for at least 30–40 years [50]. The model simulations showed that approximately two billion liters of groundwater could be treated to non-detectable PFAS levels, avoiding the pumping and waste generation typical of the pump-and-treat alternative. If further remediation is required after 30 years, re-injection of CAC would be an option [68] to reduce PFAS concentrations to the levels set by regulatory agencies, such as U.S. EPA.

In addition to the comprehensive 3D transport modeling approach, Carey et al. also developed a simplified equilibrium mixing model (EMM) to provide a rapid preliminary estimate of CAC performance within the PFAS source zone [47]. The EMM employs a mass-balance approach to simulate aqueous PFAS concentrations over time in a single mixing cell, assuming persistent source loading from vadose zone leaching and within the waterbody. While multi-dimensional models are vital for high-resolution simulations, a simplified 1D model offers a practical alternative in early-stage remediation. With minimal reliance on site-specific parameters, it can be implemented in spreadsheets (no need for high-performance computing or specialized software) to quickly estimate the longevity of a CAC barrier under varying PFAS source strengths [47]. EMM is especially useful for diffusion-controlled systems. For example, Carey et al. [47] applied the EMM to a legacy fire-training site in Central Canada with a permeable, homogeneous aquifer and minimal ongoing PFAS input, the results closely matched with those obtained from full ISR-MT3DMS simulations conducted at the same site [47,52]. In such slowly migrating systems, EMM can provide conservative longevity estimates, support sensitivity analyses, and help complete more complex models such as ISR-MT3DMS. Since Freundlich parameters (K_F and n) are often uncertain or variable, such simplified models enable preliminary assessment of how CAC dosage may affect the overall longevity of CAC barrier [51].

Based on previous frameworks (MODFLOW–ISR-MT3DMS and EMM), Newell et al. [62] recently developed a user-friendly tool to rapidly estimate the longevity of CAC barriers in PFAS-impacted groundwater. The tool combines regression equations and graphical outputs to estimate breakthrough times of PFOS, PFOA, and PFHxS using common site parameters (e.g., f_{CAC}, hydraulic gradient, and influent concentration). Instead of full reactive transport simulations, it draws on precomputed MODFLOW–MT3DMS outputs calibrated using batch isotherms from an AFFF-contaminated site in South Dakota [60]. In one scenario with moderate PFOA flux (3.8×10^{-3} kg/m^2/year) and f_{CAC} (0.24%), the tool predicted CAC's longevity of 47 years, closely matching the 50-year result from Carey's full simulations [62]. Input data were compiled from 17 published field sites and the AFFF site database maintained by Northeastern University [60,62]. While the tool does not consider competitive sorption or time-varying inputs, its simplicity and low data requirements make it suitable for early-stage design and rapid scenario screening.

While the above models provide important quantitative insights into PFAS retardation and CAC barrier performance, they rely on some simplifying assumptions and site-specific input parameters that may introduce uncertainties when extrapolating short-term observations to long-term field conditions. For example, Carey et al. [47] highlighted that the actual desorption and redistribution behaviors of PFAS under field conditions remain uncertain and may vary substantially depending on site hydrogeology, PFAS composition, and groundwater chemistry. The Freundlich parameters derived from laboratory-controlled experiments or a single groundwater sample may not adequately represent heterogeneous field environments with varying DOC, ion composition, competitive adsorption, and fluctuating PFAS source loading. The predictive performance of CAC longevity models is also highly sensitive to assumptions regarding PFAS mass flux, groundwater velocity, CAC loading fraction (f_{CAC}), and PFAS-specific adsorption affinity. The models also generally assume relatively uniform CAC emplacement and idealized adsorption conditions, whereas actual subsurface environments often exhibit preferential flow pathways, spatially heterogeneous permeability, nonuniform CAC distribution after injection, and localized breakthrough zones. Additionally, competitive adsorption between long-chain and short-chain PFAS, co-occurring hydrocarbons, and NOM may also progressively alter adsorption behavior and breakthrough patterns over time. Therefore, the current modeling outputs should be interpreted as planning-level or scenario-based estimates rather than definitive predictions of CAC service life. Future studies are highly needed to include long-term field monitoring datasets, post-injection characterization of CAC distribution, site-specific PFAS-CAC adsorption experiments under representative groundwater chemistry, and uncertainty/sensitivity analyses within future reactive transport models.

4.4. Practical factors affecting the longevity of a CAC barrier in groundwater

The longevity of a CAC barrier ranges widely from a few years to many decades (based on modeling), depending on CAC type (different vendors), injection dosage, and site geochemistry, especially with respect to PFAS characteristics (type and concentration). The above models collectively represent a shift from detailed mechanistic simulations to preliminary cost estimation tools. However, in the absence of long-term field monitoring data on CAC service life, the current modeling approaches that consider a range of hydrogeological parameters and use PFAS adsorption coefficients fitted from site-specific or analogous groundwater experiments, provide CAC longevity estimates that are subject to uncertainty and dependent on the selection of input parameters [50,60,62]. Although these models have incorporated certain chemical and physical site characteristics, the parameters used are often generalized or representative rather than directly measured at the target site.

While modeling studies provide valuable longevity estimates under controlled assumptions, actual field performance is often influenced by additional physical, chemical, and biological factors that can deviate from these modeling predictions. For example, chemical factors include the intrinsic adsorption properties of CAC and effect of background groundwater geochemistry on PFAS adsorption. Physical factors include uncertainties in transport, distribution, and effective barrier formation of CAC particles within the subsurface environment. It is also rather challenging to accurately simulate these processes, because they require high site-specific data and detailed physicochemical parameters, which are often unavailable. For instance, the specific PFAS adsorption coefficients at AFFF-impacted sites used in the modeling efforts (K_F = 4900 mg/kg for PFOS) were derived from one location in South Dakota

[60,62]. While these parameters better represent field conditions compared to laboratory-formulated solutions, they are still only representative of that specific site and may not be broadly applicable to other locations with distinct hydrogeological or biogeochemical conditions.

While *in situ* field monitoring efforts on the overall performance (e.g., longevity) of CAC barriers in groundwater are still ongoing, more laboratory-controlled experiments are increasingly designed and conducted to better understand the adsorption mechanisms of PFAS, mimicking real groundwater and vadose zone. For example, CAC is expected to exhibit different adsorption performances (kinetics and capacities) for different types of PFAS (e.g., long- and short-chain), which will likely to be further impacted by competitive adsorption among different types (PFAS mixture) and water chemistry in the groundwater and vadose zone. Below, we systematically review the effects of PFAS type, competitive adsorption of PFAS mixture, and water chemistry on the adsorption behaviors and mechanisms of different PFAS by CAC to enable better assessment and prediction of CAC barrier for *in situ* remediation of PFAS-impacted sites.

4.4.1. *Effects of PFAS type on the adsorption by CAC*

Generally, CAC can effectively adsorb long-chain PFAS, such as C8 PFOS and PFOA (Fig. 1) for decades, whereas short-chain PFAS (e.g., C4 PFBA) break through much faster (e.g., a few years or even less) due to lower adsorption affinity and capacity. Laboratory batch sorption experiments reported a clear chain-length dependent adsorption trend for seven PFAS by the CAC (REGENESIS), following the order: PFOS > 6:2 fluorotelomer sulfonate (FTS) > PFHxS > PFOA > PFBS > PFPeA > PFBA (i.e., the longer the carbon chain length, the greater the adsorption; Fig. 1) [51]. This pattern is consistent with adsorption dominated by hydrophobic interactions that increase with increasing -CF_2- units (more hydrophobic than -CH_2-CH_2- backbones; e.g., PFOS > 6:2 FTS), and are higher for sulfonate headgroups than for carboxylate groups (sulfonates are more hydrophobic than carboxylates; e.g., PFOS > PFOA) [51]. Similar patterns were observed in soil column experiments using 0.031% CAC in a sandy soil matrix, where log K_d values increased linearly with -CF_3 units (+0.26 for PFCAs, +0.32 for PFSAs, +0.20 for FTSs) and PFSAs averaged 0.05 log units higher than PFCAs of the same chain length [48].

To conceptually summarize these effects at the molecular level, a radar chart (Fig. 3**a**) was developed to illustrate how chain length, hydrophobicity, headgroup, molecular rigidity/branching, and competitive stability affect CAC adsorption for various PFAS (PFOS, PFOA, PFBS, and GenX) [56]. They further simulated breakthrough times under baseline water chemistry, normalized to PFOA (= 1.00), as PFBS (0.27), GenX (0.15), PFHxA (0.06), PFPeA (0.02), and PFBA (0.001; ~8.76 h) [56]. Notably, GenX (5 CF_2; Fig. 3**b**) showed a longer breakthrough time than PFPeA and PFHxA despite its shorter CF_2 unit and lower hydrophobicity. This finding suggests that branching and molecular rigidity enhance PFAS-CAC interactions beyond simple chain length or headgroup effects.

4.4.2. *Effects of competitive adsorption among different PFAS by CAC*

Competitive adsorption among different PFAS in a PFAS mixture solution is strongly affected by chain length and hydrophobicity, with long-chain species dominating active sorption sites and short-chain species being more susceptible to being replaced. For example, Niarchos et al. employed a systematic experimental design to examine PFAS competitive adsorption in multi-solute and bi-solute systems [64]. In multi-solute systems, the average adsorption efficiency of all PFAS decreased by ~10% compared to single-solute systems (77% average), with short-chain compounds (e.g., PFPeA and PFBS) showing the most significant reduction (25% and 24%, respectively). In a bi-solute system consisting of two C8 PFAS, the co-adsorption of perfluorooctane sulfonamide (FOSA) and charged PFOS reduced PFOS adsorption by 43%, while the neutral FOSA remained largely unaffected. This highlights the hydrophobicity-driven nature of PFAS adsorption to CAC in which neutral, long-chain compounds exhibit a distinct competitive advantage over their charged counterparts (e.g., PFSAs and PFCAs) in mixed systems. The substantial drop in PFOS adsorption under competitive conditions also indicates that electrostatic interactions, although secondarily important to hydrophobic interactions, still contribute to high initial adsorption. Niarchos et al. [64] further observed concentration-dependent sorption behavior: short-chain PFAS (e.g., PFBA and PFPeA) exhibited increasing K_d values with increasing concentration, possibly due to multilayer adsorption or the formation of hemimicelle-like structures. In contrast, long-chain PFAS showed a decrease in K_d values at higher concentrations, suggesting site saturation effects.

To further quantify these competitive adsorption effects, Singh et al. [69] analyzed batch adsorption data with a modified competitive Langmuir model (MCLM). The MCLM demonstrated strong predictive performance, especially for short-chain PFAS that are more susceptible to suppression in multi-component environments. Under a CAC dosage of 0.3372 g/L, the K_d of PFBS decreased from ~140 L/g in single-solute conditions to ~21.9, ~29.0, and ~26.2 L/g, respectively, in the co-presence of PFHxS, PFOA, and PFOS (80–90% reduction). In contrast, the K_d values of PFHxS, PFOA, and PFOS showed much smaller changes under co-contaminant conditions, indicating a more stable sorption behavior. In various binary and ternary systems, the MCLM consistently outperformed conventional models such as the ideal adsorbed solution theory and classical competitive Langmuir model in predicting the behavior of low-affinity PFAS. These studies confirm the "long-chain dominance notion" as a robust and reproducible trend in PFAS competitive adsorption on CAC.

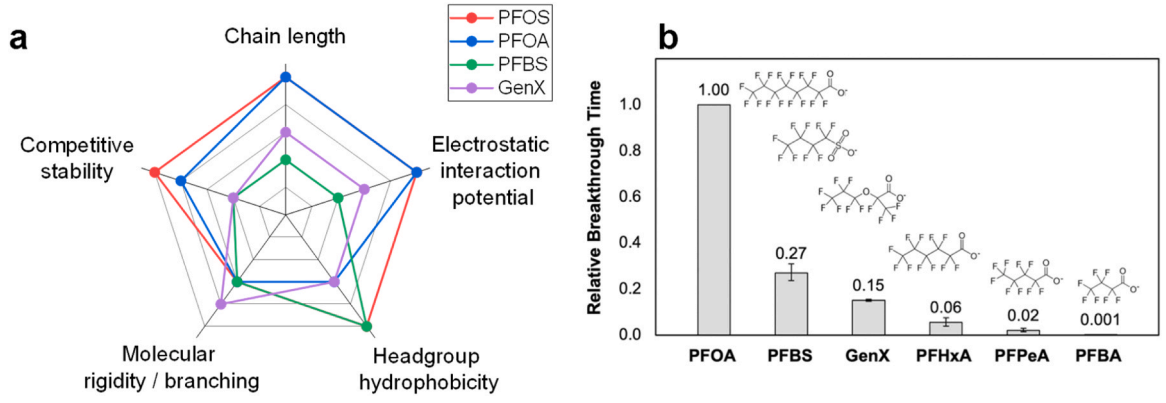

Fig. 3. (**a**) Conceptual radar plot summarizing key physicochemical factors influencing PFAS adsorption by CAC. Scores are qualitative and were assigned based on reported adsorption trends, chain-length-dependent K_d relationships, headgroup effects, and modeled breakthrough behavior from Hakimabadi, Taylor and Pham [51], Niarchos et al# [48], and Mole et al# [56]. (**b**) Relative base case breakthrough times for all PFAS normalized to PFOA (1.00). Source: [56].

4.4.3. Effects of water chemistry on PFAS adsorption by CAC

Competitive adsorption due to the mixed nature of PFAS contamination has been recognized as a critical factor influencing the performance and longevity of CAC barriers. However, this competition becomes more complex under real environmental conditions, where water chemistry, including DOM, inorganic ions, and co-occurring organic contaminants, can significantly alter the adsorption behaviors (Fig. 4).

4.4.3.1. Effects of organic components (DOM and Stabilizers) on PFAS adsorption by CAC. Several studies have revealed the effects of DOM on PFAS adsorption by CAC [49,51,56,61]. Generally, higher DOM concentrations reduce the adsorption capacity for all PFAS types, with the magnitude of reduction depending on DOM molecular size and concentration. In batch experiments, Mole et al. [56] found that 10 mg/L DOM reduced PFOA adsorption by 50%, lowered PFPeA by an order of magnitude, and completely suppressed PFBA adsorption. Similarly, Hakimabadi et al. [51] observed ~3.8-fold and ~3.6-fold reduction for PFOS and PFOA adsorption in the presence of 20 mg/L DOM. The primary mechanism was physical clogging of CAC pores, where small-molecular-weight DOM (e.g., Suwannee River humic acid; SRHA) first blocked macropores and then restricted micropore access. Comparisons with a high-molecular-weight synthetic polymer (CMC of 90, 000 g/mol at 0.01 mg/mL) showed negligible effects on PFAS adsorption, consistent with the assumption that large DOM molecules have limited pore access and, at low concentrations, minimal surface coverage [56]. In contrast, a proprietary commercial stabilizer caused slight reductions, likely due to its smaller molecular size and higher concentration [51]. While the effects of DOM on PFAS adsorption likely depend on molecular size and concentration, DOM is heterogeneous in nature. Its composition and behavior vary greatly depending on the biological, chemical, and climatic context of a given site. Therefore, its effects on PFAS adsorption and CAC barrier longevity can be far more complex in real-world applications.

4.4.3.2. Effects of inorganic ions on PFAS adsorption by CAC. Electrostatic interactions, while less important compared to hydrophobic forces in overall CAC performance, are important for the adsorption of short-chain PFAS and can be strongly influenced by ionic strength and composition (e.g., Na^+, Ca^{2+}, Cl^-, and SO_4^{2-}). This is particularly relevant at AFFF-impacted military sites, many of which are located in groundwater-seawater interaction zones (47% of Navy sites on the National Priorities List) [70], where saline conditions are common. Hakimabadi et al. [51] showed that Na^+ and Ca^{2+} markedly enhanced PFOA adsorption on unmodified CAC. As NaCl concentration increased from 0 to 100 mM, K_d values of PFOA increased from 824 ± 172 L/g to 6010 ± 716 L/g, indicating a strong "salting-out" effect. PFOS, already removed at ~99.9% under salt-free conditions, showed little further improvement in adsorption. Isolating the effect of Ca^{2+}, they maintained a total ionic strength at 7 mM and increased Ca^{2+} concentration from 0.1 to 2 mM, which boosted PFOS K_d from 9579 to 66,047 ± 14,715 L/g and PFOA K_d from 824 to 8457 ± 2220 L/g. This enhancement is attributed to cation bridging [71], where divalent Ca^{2+} links anionic PFAS head groups (carboxylate or sulfonate) to negatively charged CAC sites, creating additional sorption opportunities beyond the original high-affinity sites. While these findings focused on long-chain PFAS, Mole et al. [56] also explored the effects of ionic strength on the adsorption of short-chain PFCAs (PFHxA, PFPeA, and PFBA) using a positively charged commercial CAC (Intraplex, Intrapore, Germany) (via personal communication). Increasing background anion concentrations reduced their adsorption, consistent with competition theory for limited positively charged sites. Under high ionic strength conditions, hydrophilic short-chain PFCAs are thus more vulnerable to being replaced by inorganic anions.

More importantly, the effects of DOM and ionic strength can be synergistic or antagonistic (Fig. 5**a**). In Mole et al.'s test with 10 mg/L DOM and 100 mM NaCl, PFOA adsorption (slightly suppressed by DOM) was partially recovered via NaCl's salting-out effect, as shown by a modest K_d increase [56]. In contrast, PFPeA and PFBS reached their lowest adsorption under dual interferences (Fig. 5**b**). Note that the adsorption experiments conducted by Mole et al. [56] were performed over a 72-hour contact period under the assumption that adsorption equilibrium had been reached. The observed reductions in PFAS adsorption (Fig. 5**b**) in the presence of DOM may reflect a combination of competitive adsorption, diffusion limitations, delayed mass transfer, and potential pore blockage effects. This is especially the case that DOM may dynamically alter pore accessibility, surface wettability, and adsorption site availability over time, particularly under environmentally relevant groundwater conditions. Therefore, at sites where salt and DOM co-occur, controlling the transport of short-chain PFAS may be the greatest challenge to ensure the high performance of CAC-enabled *in situ* remediation in PFAS-impacted sites (groundwater and vadose zone).

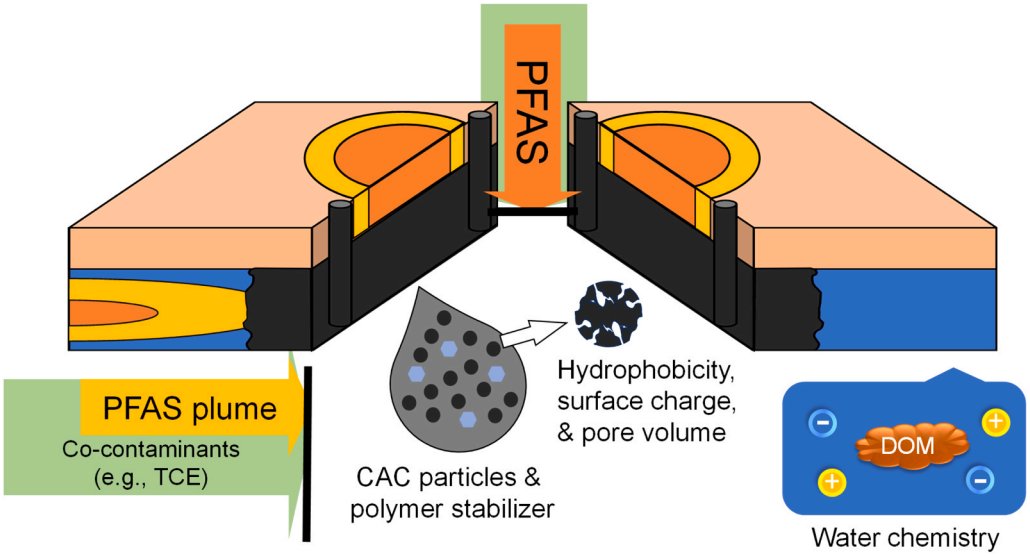

Fig. 4. Schematic showing water chemistry influencing PFAS adsorption by CAC. PFAS and co-contaminants (e.g., trichloroethylene; TCE) infiltrate into (or plume interaction) the polymer-stabilized CAC barrier, where hydrophobicity, surface charge, and pore volume of CAC control adsorption efficiency. Water chemistry, such as DOM and inorganic ions may compete for adsorption sites via electrostatic and steric effects.

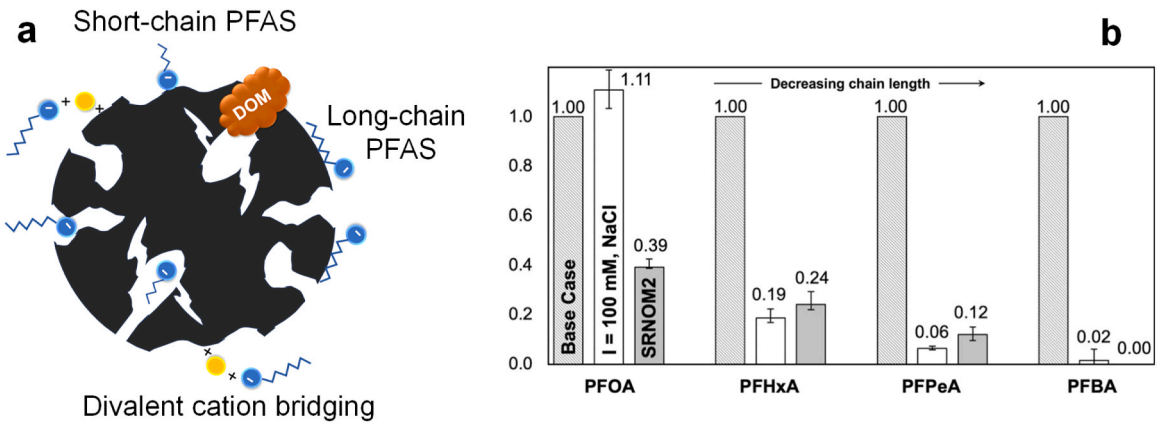

Fig. 5. (**a**) Schematic illustrating the adsorption mechanisms of PFAS, DOM, and divalent cations on CAC surface. The long-chain PFAS primarily adsorb via hydrophobic tail interactions, short-chain PFAS adsorb via electrostatic interactions, divalent cation bridging facilitates long-chain PFAS adsorption, and DOM blocks macropores. (**b**) Relative breakthrough times of individual PFAS under changes in water chemistry normalized to the base case condition. Base case: 1 mM $NaHCO_3$ at pH 7.5; I (ionic strength = 100 mM NaCl), and SRNOM2 (Suwanee River natural organic matter 2 = 10 mg/L). Source: [56].

4.4.3.3. Effects of co-contaminants on PFAS adsorption by CAC. Organic co-contaminants commonly present at AFFF-impacted sites and may also affect PFAS adsorption, ultimately affecting the longevity of CAC barriers. These co-contaminants include diethylene glycol butyl ether (DGBE; 10–100 mg/L), NAPLs such as benzene (0.5–4.8 mg/L) and TCE (0.5–8 mg/L), and diesel-range organics (DRO; 1.4 mg/L). Some of those compounds are components of AFFF formulations (e.g., DGBE), while others originate from historical industrial activities or fuel spills.

Hakimabadi et al. found that DGBE significantly decreased PFOS and PFOA adsorption onto CAC, with a stronger inhibitory effect than DOM (e.g., 1–10 mg/L) [51]. Being a small, highly hydrophilic molecule, DGBE can readily penetrate CAC micropores and occupy key sorption sites, thereby reducing PFAS adsorption. Given its widespread use in AFFF formulations, DGBE may play a critical role in modulating PFAS mobility, which should be carefully considered during *in situ* remediation design. Under similar conditions, benzene and TCE showed compound-specific effects. At 0.5–4.8 mg/L, both benzene and TCE changed little for PFOS adsorption (e.g., K_d from 6932 ± 982 L/g to 6634 ± 1963 L/g). However, at 8 mg/L TCE, PFOA adsorption is increased by ~2.5-fold. This is due to the possible formation of trace NAPL phases within CAC pores, allowing PFOA to partition into hydrophobic domains or facilitating its transfer to high-affinity sorption sites. These results indicate that non-fluorinated organic contaminants can exhibit opposite effects depending on PFAS structure. Specifically, hydrophobic PFAS are more likely to experience competition and reduced adsorption, whereas more hydrophilic PFAS may benefit from multiphase partitioning induced by the presence of co-contaminants.

Similarly, Mole et al. noted that even at concentrations below their aqueous solubility limits (often >1000 mg/L), benzene and TCE may still form stable organic phases within CAC pores [56]. However, the promoting effect of NAPLs is not universal. In Mole et al.'s following study [61], PFOA adsorption decreased in the presence of DRO (1.4 mg/L), likely due to its lower concentration and complex composition compared to single-solute benzene used by Hakimabadi et al. [51]. Overall, the copresence of DGBE, benzene, TCE, and DRO in groundwater systems at AFFF-impacted sites is important for assessing CAC barrier performance, warranting further mechanistic investigations and field observations.

4.4.4. Physical effect of hydrogeologic conditions on the longevity of a CAC barrier

The long-term performance of CAC-based barriers is also affected by physical and hydrodynamic factors that control the distribution, retention, and potential remobilization of CAC particles in the subsurface. In field applications, physical factors such as injection method, site selection, and water flow direction and velocity also control CAC distribution and the formation of effective adsorption barriers. These physical controls, in turn, can determine PFAS breakthrough behavior and ultimately impact the long-term performance of CAC-enabled *in situ* remediation.

Most modeling studies assume uniform CAC distribution within the treatment zone. Yet, achieving this uniformity in the subsurface is rather challenging. At a PFAS- and BTEX-impacted site in central Canada, PlumeStop CAC was injected at approximately 0.08% (by soil weight) into a silty sand matrix containing a thin, high-permeability sand lens [46]. TOC analyses after injection showed clear vertical variation, with higher TOC in the sandy lens (13.0 g/kg) compared to surrounding silty material (7.4 g/kg). This indicates that CAC preferentially accumulated in more permeable zones (sand is more permeable than silt), rather than a uniform distribution. In addition to soil texture and grain size heterogeneity, topographic variation also affects CAC distribution. Field application typically uses low-pressure, multi-well grid injections to avoid hydraulic fracturing and improve subsurface coverage [46,53]. In McGregor and Benevenuto's study, injection points were spaced on a 2.5-m grid (totaling 20 points) [46]. Yet, the 12-month post-injection monitoring still recorded PFAS rebound and the emergence of new PFAS species in some wells. Breakthrough was particularly evident in shallow fractured bedrock zones, where the scarcity of fine-grained material may have limited CAC retention. Moreover, site-measured horizontal groundwater velocities (~12 m/year in silt and up to 220 m/year in sand) suggest that PFAS could bypass CAC-enriched zones via high-velocity preferential flow paths, contributing to localized barrier failure. A similar rebound occurred at a Swedish site, where high-conductivity pathways in low-permeability soils likely allowed plume bypass, potentially influenced by seasonal groundwater flow shifts [72].

Laboratory studies have observed comparable heterogeneity-driven CAC redistribution. In a 15-cm dynamic soil column test, Niarchos et al. initially mixed CAC at 0.031% (w/w) to evaluate PFAS removal. About 22% of CAC was transported downstream during the experiment, leading to carbon depletion near the column inlet and accumulation at the column outlet [48]. This redistribution coincided with PFAS breakthrough, particularly for short-chain PFAS. Long-chain PFAS, such as perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA), exhibited delayed breakthrough, but were not fully retained. These results highlight that both emplacement operations and site matrix properties can greatly affect barrier effectiveness: uneven CAC distribution or locally high groundwater velocities may create "escape pathways" that compromise long-term containment. Note that the pore water velocity used in the column test (~0.7 m d^{-1}) exceeds typical

groundwater velocities by 10–100 times, suggesting that field-scale CAC redistribution may be less severe than that observed under laboratory conditions. Also, the pre-incorporation of CAC into sediment by Niarchos et al. [48] likely produces a more homogeneous distribution and stronger physical retention of CAC particles compared to dynamic injection conditions, where deposition, filtration, aggregation, and preferential attachment processes may vary spatially throughout the porous medium. Consequently, the remobilization behavior, particle retention efficiency, and hydraulic impacts observed in these laboratory columns may differ from those occurring under actual field injection scenarios. Future studies are needed to investigate CAC transport and remobilization behaviors under more realistic injection-based conditions that better simulate heterogeneous aquifer environments and transient groundwater flow regimes.

As discussed above, common groundwater constituents (e.g., Ca^{2+} and DOM) affect PFAS adsorption through electrostatic shielding, cation bridging, and competitive adsorption [51,56,71]. However, their effects also impact the deposition, retention, and remobilization of CAC particles in porous media, thereby altering the spatial continuity and long-term effectiveness of CAC-based barriers. Guan et al. used saturated column experiments to show that, at a fixed total ionic strength of 100 mM, increasing Ca^{2+} concentration from 0 to 10 mM markedly increased carboxymethyl cellulose (CMC)- stabilized CAC deposition in quartz sand and reduced subsequent remobilization from 77% to nearly 0% [73,74]. In contrast, DOM suppressed the deposition and promoted the release of CAC upon deionized (DI) water flushing.

To improve CAC immobilization during injection and counter hydrodynamic forces that may induce particle detachment, biodegradable stabilizers are often added to enhance the colloidal stability of CAC [46]. A persistent challenge is to balance mobility and retention: excessive mobility risks gradual loss via groundwater flow, whereas premature immobilization can limit dispersion from injection points. The effectiveness of polymer coatings is highly dependent on site-specific geochemical conditions. For example, Guan et al. compared uncoated CAC, CMC-CAC, and polydiallyldimethylammonium chloride (PolyDM)-CAC in quartz sand under varying ionic strengths. At low ionic strength (0.1 mM), both polymer-coated CACs transported well, while bare CAC was nearly immobilized due to aggregation [55]. At high ionic strength (100 mM), only CMC-CAC had ~30% mobility loss, while others were fully retained (~100% mobility loss) [55]. Upon ionic strength reduction, CMC-CAC remobilized significantly, whereas PolyDM-CAC remained attached due to stronger adhesion. These results suggest CMC is suited for applications requiring wide dispersion, while PolyDM favors stable barriers under high ionic strength or saline environments. Similarly, Georgi et al. found that CMC enhances CAC stability at high concentration (11 g/L) and high ionic strength (5 mM divalent cations) via electrosteric stabilization [54]. Ndubueze et al. further showed that pH, Ca^{2+}, and DOM jointly affect aggregation and sedimentation of polymer-stabilized CAC, primarily through surface charge modulation and Ca^{2+}–DOM bridging, consistent with Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and the role of porous media surface heterogeneity [57].

Stabilizers such as CMC or PolyDM are primarily introduced to facilitate the initial injection and emplacement of CAC, but their persistence and effectiveness over the full operational lifespan of a barrier remain uncertain. For example, stabilizer concentrations may decrease over time due to dilution, desorption, biodegradation, chemical aging, or interaction with groundwater constituents, meaning that short-term laboratory observations may not fully represent long-term CAC stability, retention, or remobilization behavior under field conditions. Also, while previous work [55] provided useful mechanistic insight into how ionic strength, Ca^{2+}, DOM, and polymer coatings influence CAC deposition and remobilization, the column-scale experiments, including the short transport length, primarily simulate near-injection or early-stage mobility rather than field-scale transport across meters to tens of meters. The observed mobility or remobilization of polymer-coated CAC should not be directly extrapolated to field applications without considering aquifer heterogeneity, longer residence times, repeated groundwater flushing, stabilizer aging, preferential flow, and potential changes in CAC surface chemistry. Future studies should evaluate polymer-coated CAC under longer columns, larger-scale flow cells, realistic groundwater chemistry, and extended aging periods to determine whether stabilizer-assisted mobility persists over the actual service life of CAC barriers.

5. CAC-enabled in situ remediation of PFAS in vadose zone

The application of CAC for *in situ* remediation of PFAS-impacted vadose zone requires careful consideration of its mobility, resistance to leaching, and long-term adsorption stability. One major PFAS source relevant to *in situ* groundwater remediation (discussed above) is the vadose zone, from which PFAS in unsaturated soils can leach downward and reach the CAC barrier. After accumulating PFAS for many decades, vadose zones at many AFFF-impacted sites serve as reservoirs of PFAS. Site investigations estimate that the vadose zone stores approximately 23–97% of the total PFAS mass, including up to 99% of PFAS precursors that can slowly transform into more stable perfluoroalkyl acids (PFAAs such as PFOS and PFOS) under natural conditions [75]. The extensive presence of AWI in the vadose zone leads to strong interfacial adsorption of PFAS (especially for long-chain PFAS) which can result in slow, long-term release into the underlying groundwater even decades after site closure (with estimated vertical mass discharge rates typically ranging from <0.01% to ~0.2% per year, depending on PFAS type) [76,77]. Furthermore, negatively charged soil particles can electrostatically sorb substantial amounts of cationic or zwitterionic PFAA precursors, further increasing retention and subsequent release of PFAAs. PFAS in the vadose zone can also volatilize into the atmosphere, be mobilized by surface runoff to areas of human activity, or be taken up by plants and released to the atmosphere via phytovolatilization [11]. Consequently, the vadose zone is the first point of contact and a major reservoir for PFAS where precursor transformation drives secondary contamination. The resulting risks to surrounding communities, groundwater, and downstream receptors from PFAS in the vadose zone make it an urgent target for *in situ* remediation.

5.1. Laboratory evaluation of CAC-enabled in situ remediation of PFAS in vadose zone

A key consideration for CAC performance in the vadose zone is the leaching resistance. In laboratory studies, CAC fixation performance was tested under extreme conditions at two time points (1 week and 4 years), including acidic (pH 4) and alkaline (pH 10.5) environments, repeated leaching (five extractions), and high liquid-to-solid ratios (L: S = 20: 1) [78]. CAC initially reduced total PFAS leaching by 86–93%, improved to 94–97% after 4 years, and maintained no more than 3% leaching under alkaline conditions [78]. Note that the leaching experiments were conducted using PFAS-contaminated soils amended with CAC [78], where the observed leaching behavior reflected PFAS release and transport from the contaminated soil system in the presence of CAC, rather than PFAS leaching directly from CAC itself. Another study involving 10 types of soils found highest sorption for medium-chain PFAS (C4-C9; PFOA = 81%; PFHxS = 86%; and 6:2 FTSA = 85%) and poorer sorption for short chains (PFBA ≈ 0; but PFBS ≈ 73%) [49]. As in groundwater, high organic carbon reduced CAC effectiveness, but high clay content enhanced it [49,56]. Because excavation-and-mixing can overcome hydraulic conductivity constraints on CAC distribution, clay-rich, low-conductivity zones could be prioritized for protective *in situ* remediation tests.

Recent studies indicate that the overall performance of CAC-based *in situ* PFAS remediation in soil and vadose zone environments is controlled not only by PFAS adsorption capacity, but also by the surrounding soil chemistry, redox dynamics, and long-term particle

stability [65,73,74,79]. For example, Niarchos et al. [79] highlights that DOC as a major limitation for CAC-amended soils. Using dynamic column experiments with 14 PFAS, they showed that DOC significantly reduced PFAS sorption in CAC-treated soils and increased aqueous PFAS concentrations, meaning that CAC performance in vadose zone/source zone soils may be overestimated if DOC/DOM competition is ignored [79]. Gunarathne et al. [80] further expands CAC evaluation into more realistic soil biogeochemical conditions by testing CAC against a novel adsorptive organoclay under dynamic redox regimes. This is important because vadose zone and capillary fringe soils often experience fluctuating oxic–anoxic conditions, which can alter PFAS immobilization, amendment behavior, and microbial communities. The study [65] therefore supports evaluating CAC under time-varying redox conditions rather than static batch or column systems alone. In contrast, [73,74] addresses a different but critical issue: whether CAC remains immobilized after placement. They showed that subsurface aging can trigger CAC mobilization from saturated porous media by changing interaction energy barriers, potentially compromising barrier continuity and increasing the risk of CAC-facilitated PFAS transport [73,74]. This finding is highly relevant to long-term vadose-zone and groundwater-interface performance, where CAC may undergo physical, chemical, or biogeochemical aging after injection. Therefore, successful CAC application in vadose zone soils requires site-specific assessment of DOC/DOM levels, redox variability, soil microbial response, wetting–-drying or saturation changes, and CAC aging/mobility.

5.2. *Field applications of CAC-enabled in situ remediation of PFAS in Vadose Zone*

Unsaturated vadose zone conditions may limit the mobility of liquid CAC. Fig. 6 shows *in situ* remediation of vadose zone soils by injecting a commercial CAC suspension (SourceStop, REGENESIS) in Grayling, Michigan. The vadose zone soils were first excavated, followed by the injection of CAC suspension. After injection, the excavated soils were thoroughly mixed with the CAC suspension to maximize contact between CAC and PFAS-contaminated soils. Site-specific parameters included (1) treatment area: 225 square feet, (2) soil volume treated: 0–10 feet below ground surface (bgs), (3) maximum total PFAS in leachate: 84 cubic yards, and (4) surficial geology: sand, top-soil cover. As discussed above, most CAC commercial products (e.g., REGENESIS) have various capping or stabilizing agents, such as polymer coatings [54,55] to improve their affinity to soil particles (including sands) and aquifer sediments, ultimately enhancing their performance for PFAS adsorption. The concentrations of PFOS and other PFAS in the soil leachates were monitored before CAC treatment (baseline data), right after the CAC treatment, 6-months after CAC treatment, and 12-months after CAC treatment, respectively. The baseline soil leachates showed PFOS and other PFAS concentrations at ~1050 ng/L and ~200 ng/L, respectively. Right after the CAC treatment, 99% of total PFAS was removed from the soil leachates. No PFAS was detected after 6-months treatment, and still 99% of total PFAS was removed from soil leachates after 12-months treatment [68]. These results show the effectiveness and efficiency of CAC in immobilizing PFAS (e.g., long-chain PFOS) in source zone soils, mainly vadose zone areas. However, long-term field monitoring efforts (over 2–5 years) of both soil and soil leachates are still needed to further test the effectiveness and efficiency of using CAC for *in situ* PFAS remediation. The desorption of PFAS, including kinetics and extent, from CAC in the treated soils needs to be carefully investigated. Some environmental factors, such as temperature, dissolved oxygen content (redox potential), water content (e.g., rainfall events), pH, and microorganisms are likely to be involved into the desorption of PFAS from CAC during *in situ* remediation [2,81]. All the above factors need to be carefully considered to evaluate the performance (effectiveness, efficiency, and longevity) of CAC for PFAS remediation in vadose zone.

5.3. *Factors affecting CAC-enabled in situ remediation of PFAS in vadose zone*

While CAC applications in soil have been proposed, systematic studies under vadose zone conditions remain rather limited. Existing data are mostly derived from laboratory leaching tests where CAC was

Fig. 6. CAC-enabled *in situ* remediation of PFAS-impacted vadose zone soil. Source: REGENESIS.

pre-mixed with soil. However, such results are far from sufficient to guide field-scale implementation. As detailed above, multiple factors can affect the performance and longevity of CAC during vadose zone remediation, including soil composition, organic carbon content, ionic strength and divalent cation bridging, competitive (or synergistic) adsorption among PFAS mixtures and co-contaminants, material aging, surface chemistry changes, subsurface heterogeneity, hydraulic variability, and commercial stabilizers (Fig. 7). However, unlike saturated conditions, the vadose zone exhibits strongly heterogeneous moisture distributions (e.g., AWIs) and ubiquitous wetting-drying cycles (WDCs) driven by rainfall, groundwater table fluctuation, and surface water-groundwater interaction (hyporheic zone). This spatiotemporal variability makes transport and reaction processes rather complex, which is likely to amplify or reshape the roles of those controlling factors for CAC performance. Yet systematic studies on this aspect remain scarce.

In vadose zone, WDCs continuously create dynamic OATZs that are not restricted to static interfaces at the groundwater table (Fig. 7). Specifically, pore spaces become water-filled and anaerobic during infiltration events, then re-aerated upon drainage or evaporation, bringing dissolved oxygen back into the pores and temporarily transforming the region into an OATZ. Such redox oscillating zones occur frequently in rainfall-dominated or tidally influenced regions, also on a periodic basis at most sites, as water cycling is the principal driver of reactivity. Unlike groundwater, these unique spatiotemporal characteristics introduce substantial uncertainty into contaminant management. The extent of such uncertainty is tightly linked to site-specific soil composition, mineral content, organic carbon, and microbial communities, while also modulated by climatic conditions, especially precipitation regimes, humidity, and temperature (Fig. 7) [78,86]. The coupling of these factors further amplifies vadose-zone heterogeneity and makes cross-site generalization difficult [86].

From a mechanistic perspective, the dynamic OATZ imposes both biochemical and physical perturbations. Biochemically speaking, key processes include (1) rapid redox fluctuations, (2) transient dissolved oxygen diffusion, (3) competitive microbial dynamics, (4) active mineral cycling such as Fe(II)/Fe(III) transformations producing highly reactive secondary phases, and (5) *in situ* production of short-life reactive oxygen species, such as hydrogen peroxide (H_2O_2) and hydroxyl (•OH) radicals [82–86]. These biochemical activities may affect the effectiveness and longevity of CAC barriers by competing with PFAS for adsorption sites (or increasing sites through cation bridging) and by aging CAC materials to reduce its adsorption capacity. Physically speaking, WDCs reshape soil structures and change AWIs through (1) swelling-shrinkage of fine particles (e.g., clays), (2) altering pore connectivity, and (3) promoting aggregate breakdown and reformation, often accompanied by compaction, cracking, redeposition, and clogging (Fig. 7). These changes can cause localized, dynamic variations in porosity and hydraulic conductivity, shifting water flow pathways, inducing threshold flow events, and increasing uncertainty in CAC migration and fixation. These processes become especially significant during early stages when stabilizer-coated particles are not yet well integrated with soils.

The extensive AWIs in vadose zone deserve particular attention. PFAS strongly partition to AWIs, a process already emphasized in vadose-zone modeling studies where AWI adsorption is treated as a key driver [87,88]. When combined with CAC adsorption from porewater, this dual pathway suggests that *in situ* remediation in the vadose zone could be particularly promising. However, it raises some important questions: during infiltration, will PFAS adsorbed at AWIs be efficiently captured by CAC, or will repeated WDCs and aging cause redistribution and desorption? Could the surface activity of CAC stimulate biogeochemical processes in the OATZ, potentially accelerating precursor transformation and secondary pollution? These uncertainties remain largely unexplored.

5.4. *Aging and biogeochemical effects during oxic-anoxic transition zone (OATZ)*

The long-term integrity of CAC can be compromised by dynamic physical, chemical, and biological processes that operate over years to decades at some sites. These processes, including material aging, hydrogeological fluctuation, and microbial colonization, may

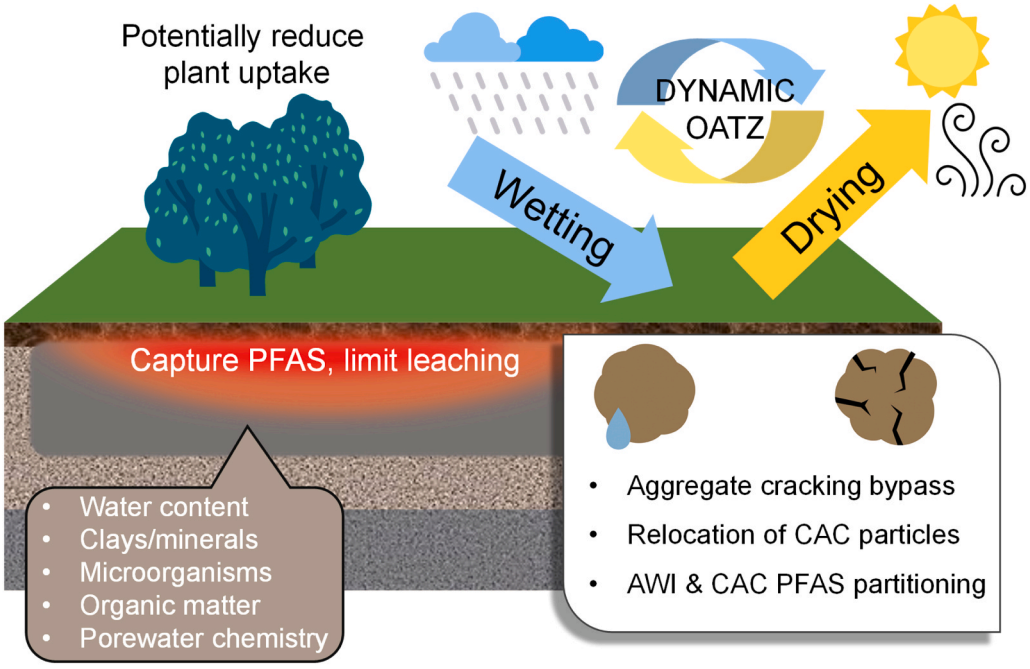

Fig. 7. Conceptual illustration of CAC in the vadose zone. CAC captures PFAS in soil and limits their leaching potential into groundwater. Soil factors (water content, clays/minerals, microorganisms, organic matter, and porewater chemistry) influence CAC performance. Repeated wetting-drying cycles (WDCs) create dynamic oxic-anoxic transition zones (OATZs), promoting biogeochemical reactions, while also inducing physical changes that affect CAC performance, such as aggregate cracking, particle redistribution, and PFAS partitioning between the air-water interface (AWI) and CAC.

progressively alter CAC's physicochemical properties and reduce its adsorption capacity for PFAS, especially during OATZs that are characterized with enhanced biogeochemical cycling and fast turnover of various species in this enhanced reactivity zone (Fig. 7). Although laboratory experiments may involve more aggressive conditions than those encountered in the field, their short duration does not ensure that CAC performance over the decades proposed for field applications will be better than that observed under accelerated aging conditions.

Very recently, Jiang et al. simulated four accelerated aging processes (WDCs, H_2O_2, Fenton reaction, and mineral acid treatments) in water matrix to systematically evaluate their effects on CAC adsorption of PFAS (PFOS, PFOA, PFHxA, PFPeA, PFBA, and PFBS) [66]. Except for PFOS, K_F values decreased by 17.7–55.8% (WDCs), 24.0–56.4% (H_2O_2), and 50.4–76.2% (Fenton reaction) [66], indicating substantially decreased adsorption for both short-chain and long-chain PFAS (Fig. 8). All treatments reduced the average breakthrough time to below 50%, with PFBS and PFPeA falling below 20%, whereas PFOS retained > 99% removal under all conditions. Aging caused pronounced changes in CAC surface properties. These include: (1) reduced specific surface area (e.g., −10.5% after Fenton treatment and −35.2% after acid aging), (2) increased surface oxygen-containing functional groups (e.g., carboxyl and carbonyl) leading to lower hydrophobicity (C/O ratio decreasing from 11.7 to 5.0 and 4.6), (3) decreased pH of point of zero charge (pH_{PZC} from 8.8 to 3.9 and 3.1) shifting the surface charge from positive to negative under typical subsurface environmental pH conditions, and (4) substantial loss of anion exchange capacity (from 11.5 cmol/kg to 6.0 and 0.8 cmol/kg) [66].

Many of these processes (e.g., WDCs, Fenton reactions, and hydrogen peroxide treatment) can naturally occur within the dynamic OATZs [89–92], which are geochemically complex regions at the interface of oxic and anoxic zones [93]. Such zones (present at ~78% of surveyed U. S. Navy installations) [70] exhibit sharp redox gradients, high biological and chemical reactivity, and frequent shifts in dissolved oxygen content [94,95]. The two typical OATZ settings are (1) the interface where oxygenated surface water meets sub-oxic to anoxic groundwater, and (2) the capillary fringe immediately above the saturated zone. These dynamics can stimulate active mineral cycling, microbial reactivity, and contaminant transformation [96,97]. Within an OATZ field trial, McGregor et al. injected CAC at the gas-water interface of a shallow aquifer (5.0–6.2 m bgs; capillary fringe) [98]. Over 18 months, sulfate

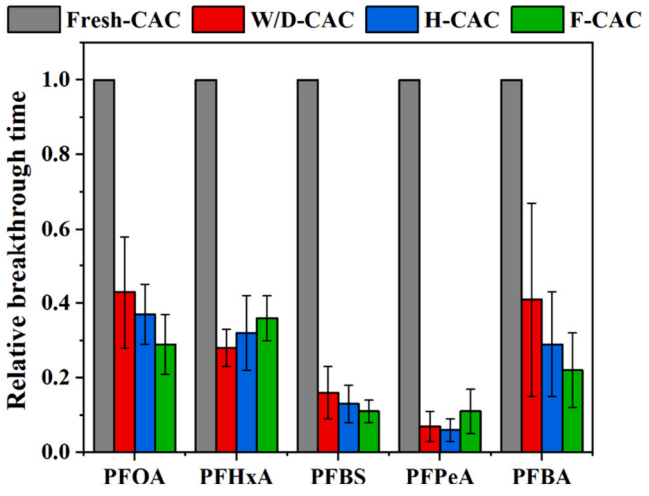

Fig. 8. Relative longevity of CAC for PFAS adsorption when considering the different aging impacts. The estimate of longevity was based on the breakthrough time for tested PFAS compounds normalized to fresh CAC. W/D: wetting-drying cycles, H-: hydrogen peroxide treatment, F-: Fenton reaction results of PFOS are not available due to the complete adsorption (>99%) of PFOS in both fresh and aged CAC groups in the batch isotherm experiments. Source: [66].

concentration decreased (36–11.5 mg/L), dissolved iron content increased (0–0.82 mg/L), pH slightly decreased, and alkalinity increased, suggesting carbon release from CAC stimulated microbially driven reducing processes [98]. By the end of the 18th month, long-chain PFAS were undetected, but PFPeA reappeared (50–40 ng/L). This clearly indicates reduced retention capacity of short-chain PFAS by CAC under dynamic conditions [98].

In coastal OATZs, seawater-groundwater mixing and subsequent interaction add more complexities. Carey et al. modeled a U.S. coastal site and found that high nearshore ionic strength (84 mM) enhanced PFOA/PFOS adsorption to CAC by ~50% via salting-out effect [63]. The model predicted > 99.9% PFOA mass flux reduction and a 20–40 years barrier longevity, while PFOS removal was slower but still effective [63]. However, tidal flow reversals caused downgradient PFOA accumulation and sustained concentrations above cleanup criteria (4–10 ng/L) for decades [63]. These predictions assumed constant CAC performance, uniform distribution, and no particle migration. Indeed, OATZ cycling may accelerate CAC aging. While high salinity can improve CAC attachment to soils and enhance long-chain PFAS adsorption (bridging and salting-out), aging-induced changes in surface charge (positive to negative) and hydrophobicity could reduce PFAS adsorption, potentially shortening the actual service life of CAC barriers.

Note that biological effects are not considered in the prediction of the longevity of the CAC barrier. Microorganisms can colonize onto CAC and secrete extracellular polymeric substances (EPS), which alter hydraulic conductivity and oxygen distribution [99]. While no studies have directly examined the effects of EPS on CAC performance, EPS concentration has been shown to exert non-linear effects on bacterial transport in saturated sand media. At low to moderate concentrations, EPS can increase microbial mobility, while at high concentration, EPS may promote aggregation and clogging (increased retention) [100,101]. These findings raise questions for *in situ* PFAS remediation: EPS could block adsorption sites, encapsulate particles, or promote migration in high-conductivity zones, while potentially enhancing retention in low-conductivity zones. Although not tested, these mechanisms require further investigations into biologically active transition zones (e.g., OATZs). Additionally, while still under significant debate [102–104], microorganisms could involve into some of the transformation and degradation processes, pathways, and reactions for some PFAA precursors, which will likely affect the longevity of CAC for certain PFAS during *in situ* remediation.

Many of the above discussions regarding vadose zone applications are partially extrapolated from groundwater studies and emerging conceptual understanding, rather than from extensive direct field validation. The unique vadose zone processes, including WDCs, AWI partitioning, preferential flow, fluctuating moisture conditions, and oxic–anoxic transition dynamics, may substantially alter CAC transport, retention, and PFAS adsorption behaviors compared to saturated groundwater systems. For example, the importance of AWI partitioning, transient moisture content, preferential flow pathways, and dynamic WDCs on PFAS retention and transport in vadose zones is well recognized in the broader PFAS subsurface literature. However, their direct effect on CAC mobility, distribution uniformity, colloidal stability, and long-term adsorption performance remains insufficiently quantified. Therefore, the proposed impacts of WDCs on CAC redistribution, aggregation, pore accessibility, and adsorption/desorption dynamics are currently mechanistic hypotheses inferred from colloid transport theory, PFAS interfacial behavior, and unsaturated flow processes, rather than conclusively demonstrated CAC field observations. Similarly, the OATZs are likely to cause changes in redox-sensitive geochemistry, dissolved organic matter composition, microbial activity, ionic strength, and mineral surface properties that may alter CAC surface interactions and PFAS partitioning behavior, but these coupled hydro-biogeochemical effects have not yet been systematically evaluated for CAC-amended vadose zone systems.

Therefore, many proposed vadose zone mechanisms and long-term

performance predictions should be viewed as important conceptual frameworks and future research priorities requiring controlled laboratory experiments, advanced multiphase reactive transport modeling, pilot-scale demonstrations, and long-term field monitoring efforts before generalized conclusions can be established. While CAC shows promising potential for vadose zone remediation, its long-term effectiveness, distribution behavior, and longevity under unsaturated subsurface conditions remain insufficiently understood and require systematic laboratory studies, pilot-scale testing, and long-term field monitoring before broad conclusions can be drawn.

On the other hand, the biological processes and aging effects discussed for the vadose zone may also play important roles in groundwater systems and potentially influence the long-term lifespan of CAC barriers. This is because groundwater environments are not biologically or chemically static, and long-term exposure to subsurface geochemical and microbiological conditions may progressively alter CAC physicochemical properties, adsorption behavior, and remobilization potential. For example, biofilm growth and EPS can alter CAC surface wettability, reduce pore accessibility, block adsorption sites, and modify PFAS mass-transfer kinetics. Groundwater constituents such as DOM, co-occurring hydrocarbons, ionic strength, and redox-sensitive species may interact synergistically with aging and biofilm development processes to further influence CAC adsorption performance and PFAS breakthrough behavior over long operational timeframes. Nonetheless, these coupled biological and aging processes remain insufficiently understood for both saturated groundwater and unsaturated vadose-zone systems, particularly under field conditions spanning years to decades. Future research should systematically evaluate long-term biological aging, biofilm-mediated pore blockage, changes in CAC surface chemistry, and their combined effects on PFAS adsorption, desorption, and barrier longevity under realistic groundwater conditions.

5.5. Opportunities for CAC-enabled in situ remediation in vadose zone

Given that vadose zone is a major reservoir of PFAS, the difficulties noted above should be viewed not only as obstacles, but rather as opportunities to advance field-oriented remediation science. Importantly, commercial CAC formulations have already been deployed under unsaturated conditions (Fig. 6), providing a valuable starting point for the broader *in situ* applications. This enables site-scale observations focusing on practical outcomes, such as the degree of downward PFAS leaching and its potential correlation with climatic drivers. Using SourceStop CAC (Fig. 6) as an example, a 2–5 years field monitoring program of both bulk soil and soil leachates is recommended to further evaluate the effectiveness and efficiency of CAC-based *in situ* PFAS immobilization. It is particularly important to characterize the kinetics and magnitude of PFAS desorption from CAC in treated soils. Environmental factors including temperature, oxygen availability (redox potential), water content (rainfall event), pH, and microbial activity may affect desorption during *in situ* operations [2,81]. Furthermore, soil-mixing approaches (excavation and blending) require higher upfront investment than direct injection, but they can also provide greater control over the distribution of CAC and site conditions. Comparable carbon-based amendments, such as biochar, have been reported to reduce plant uptake of PFAS, with a 70–84% decrease in PFAS accumulation in tomato following biochar amendment [105]. Meanwhile, composted manure and biosolids often contain high PFAS concentrations (e.g., 209–455 μg/kg) [106]. This highlights the risk of PFAS transfer into the food chain and motivates evaluation of CAC-based soil amendments in agricultural settings. Collectively, despite uncertainties arising from complex physicochemical processes, the vadose zone remains a promising frontier for CAC-based research, demonstration, and application *in situ*.

6. Conclusions and future research frontiers

As the only *in situ* groundwater remediation technology that has been implemented for PFAS to date, CAC builds upon the mature and highly stable production processes of conventional AC, while incorporating distinct engineering advantages associated with colloidal materials. The small particle size nature of CAC provides a large specific surface area and abundant pore structure, while simultaneously enabling injectability and high adaptability to heterogeneous subsurface conditions, collectively promoting PFAS adsorption and supporting its application across a range of remediation scenarios in groundwater and vadose zone.

Although no standardized, side-by-side comparison of commercial CAC products has been published, available studies and technical reports provide useful product-specific information [51]. PlumeStop is the most extensively reported CAC product in the peer-reviewed literature. It is generally described as a polymer-stabilized CAC suspension with particle sizes commonly around 1–2 μm, enabling low-pressure subsurface injection and attachment to aquifer solids. Laboratory studies using PlumeStop showed PFAS adsorption following the general affinity order: PFOS > 6:2 FTS > PFHxS > PFOA > PFBS > PFPeA > PFBA, with adsorption dominated by hydrophobic interactions. However, polymer stabilizers, DOM, AFFF co-solvents, and some co-contaminants can reduce adsorption capacity [51]. Dynamic column experiments further showed that CAC-treated soils strongly retarded PFAS transport, with K_d values of approximately 10^{3}–10^{5} L/kg for individual PFAS and 99.7% greater PFAS retention than untreated reference soil, although about 23% of added CAC eluted during the experiment [48]. Field summaries for PlumeStop report generally successful short-term performance at 17 sites, with monitoring periods of 0.3–6 years and > 90–99% PFAS reductions at 14 of 16 sites with available data [60]. Modeling studies predict much longer potential longevity under favorable assumptions, including 915–936 years for PFOS, 262–268 years for PFOA, and 233–235 years for PFHxS in a base-case AFFF-impacted airport scenario. However, these estimates are strongly dependent on CAC dose, PFAS influent concentration, groundwater velocity, and Freundlich adsorption parameters.

Other commercial CAC products are less represented in peer-reviewed PFAS literature. Intraplex has been reported by the vendor as an injectable CAC technology for PFAS adsorption barriers with claimed pollutant reductions up to 98% and projected barrier lifetimes of several decades (https://intrapore.com/en/products/intraplex/). Cascade's ColloidalChem is described as a 2–3 μm high-surface-area colloidal carbon suspension, and ColloidalChem + Anchor incorporates an anchoring technology intended to control CAC mobility in permeable reactive barrier applications (https://www.cascade-env.com/resources/blogs/managing-pfas-risk-plume-treatment-with-colloidalchem/). FluxSorb RP RA is reported by the supplier to contain 6–15 wt% activated carbon, particle size < 3 μm, viscosity around 2000 cP, and density of 1.0 g/mL (https://hepure.com/products/colloidal-carbon/), but independent PFAS adsorption and longevity data remain limited. These findings indicate that commercial CAC products share common design goals—micron-scale particle size, injectability, high surface area, and subsurface persistence—but differ in stabilizer chemistry, anchoring strategy, carbon loading, mobility control, and reported adsorption capacity. Therefore, the key knowledge gap is not the absence of product-specific information, but the absence of standardized comparative studies evaluating multiple commercial CACs under identical PFAS mixtures, groundwater chemistries, porous media, injection conditions, and long-term field monitoring frameworks.

Field monitoring efforts are normally operated on a quarterly basis for a period of 2–5 years to test and monitor the effectiveness and efficiency of the CAC barrier for *in situ* PFAS remediation in groundwater and vadose zone. The field monitoring efforts provide critical information on when re-injection (post-injection) of CAC is needed to meet the regulatory requirements for PFAS of interest. Although commercial CAC

products have been applied at multiple sites worldwide, field monitoring records rarely exceed a decade, far shorter than the multi-decade service life predicted by modeling studies. Consequently, field-based evidence for evaluating the long-term performance and durability of CAC barriers under realistic conditions remains limited.

While CAC commercial products have already been used for *in situ* site remediation in different countries, a number of potentially important processes remain insufficiently quantified beyond the factors identified by existing laboratory studies and modeling efforts. These include mechanisms controlling their colloidal stability, transport, and aggregation behaviors, as well as differences in adsorption mechanisms among PFAS species. PFAS desorption from CAC has also been reported, and the kinetics and extent of desorption may be strongly affected by competing ions, DOM, and co-occurring organic contaminants; therefore, potential PFAS desorption during practical applications warrants careful consideration. These knowledge gaps limit our ability to reliably evaluate the long-term performance of CAC under realistic field conditions. Additionally, CAC has been proposed for *in situ* remediation in vadose zone, where uncertainties may be even more pronounced. Physicochemical heterogeneity, WDCs, AWIs, and OATZs can collectively reshape CAC adsorption, migration, stability, and long-term effectiveness, further complicating performance assessment of CAC-enabled technology. Importantly, differences in CAC formulations among different vendors, including particle size distribution, stabilizing agents, surface functional groups, colloidal stability, injection methods, and proprietary modifications, can complicate direct comparisons among published studies and may influence CAC transport, retention, adsorption affinity, and longevity. Therefore, vendor-specific variations for CAC commercial products need to be considered in future studies.

In addition to CAC, SMC has also been proposed to *in situ* remediate PFAS since both CAC and SMC have a high TRL at 8–9. Yet, this technology is currently limited to soil treatment. For groundwater applications, cost-effective biochar, especially the modified biochar with large specific surface area and rich functional groups is reported to exhibit high adsorption performance for both long- and short-chain PFAS. The colloidal biochar may have a similar potential (like CAC but with a lower sorption capacity for PFAS) to be injected into groundwater or soil for *in situ* PFAS remediation, but future pilot and field studies are still needed. Moreover, no systematic comparative data is currently available on the physicochemical properties, adsorption performance, and long-term field longevity of different commercial CAC products. Addressing these gaps through standardized laboratory protocols, extended field monitoring, and explicit inclusion of vadose zone processes will be critical to improving predictive models and optimizing barrier design for sustained PFAS containment.

Finally, there are also other knowledge gaps, including the lack of standardized experimental protocols, limited independent field validation studies, insufficient reporting of CAC physicochemical properties, limited data on short-chain PFAS behavior, minimal information on long-term CAC aging and redistribution in subsurface environments, and the scarcity of studies evaluating multiphase vadose-zone processes. Especially, many reported CAC performance metrics, including PFAS removal efficiency, longevity estimates, and barrier effectiveness, are derived from relatively short-term monitoring periods, site-specific case studies, and modeling assumptions rather than standardized long-term comparative evaluations across multiple hydrogeological settings. Important factors such as DOM, ionic strength, competing ions, co-contaminants, pH, redox conditions, PFAS mixtures, and subsurface heterogeneity may interact in highly complex and site-specific ways that are not yet fully understood. Future studies should address these knowledge gaps to further the CAC-enabled *in situ* remediation technologies.

Environmental implications

CAC, a colloidal form of activated carbon, has recently emerged as a cost-effective and efficient adsorbent with strong potential for *in situ* immobilization of PFAS in groundwater and vadose zone environments. This review provides the first comprehensive and state-of-the-art assessment of CAC-enabled technologies to *in situ* remediate PFAS-impacted groundwater and vadose zone. Key challenges and critical knowledge gaps associated with CAC-enabled PFAS remediation are systematically evaluated, focusing on technology feasibility, effectiveness, efficiency, longevity, and environmental factors affecting technology performance, contributing to the global efforts in addressing PFAS pollution.

CRediT authorship contribution statement

Bo Guo: Writing – review & editing, Conceptualization. **Rafael Muñoz-Carpena:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization. **Chongyang Wang:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Dengjun Wang:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

[1] USEPA 2026. CompTox Chemicals Dashboard. U.S. Environmental Protection Agency (EPA), ⟨https://comptox.epa.gov/dashboard/⟩.
[2] Lyu, X., Xiao, F., Shen, C., Chen, J., Park, C.M., Sun, Y., Flury, M., Wang, D., 2022. Per- and polyfluoroalkyl substances (PFAS) in subsurface environments: occurrence, fate, transport, and research prospect. Rev Geophys 60 (3) e2021RG000765.
[3] Gluge, J., Scheringer, M., Counsins, I.T., DeWitte, J.C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C.A., Trier, X., Wang, Z., 2020. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). Environ Sci Proc Impacts 22 (12), 2345–2373.
[4] Evich, M.G., Davis, M.J.B., McCord, J.P., Acrey, B., Awkerman, J.A., Knappe, D.R. U., Lindstorm, A.B., Speth, T.F., Tebes-Stevens, C., Strynar, M.J., Wang, Z., Weber, E.J., Henderson, W.M., Washington, J.W., 2022. Per- and polyfluoroalkyl substances in the environment. Science 375 (6580), eabg9065.
[5] Grunfeld, D.A., Gilbert, D., Hou, J., Jones, A.M., Lee, M.J., Kibbey, T.C.G., O'Carroll, D.M., 2024. Underestimated burden of per-and polyfluoroalkyl substances in global surface waters and groundwaters. Nat Geosci 17, 340–346.
[6] Tokranov, A.K., Ransom, K.M., Bexfield, L.M., Lindsey, B.D., Watson, E., Dupuy, D.I., Stackelberg, P.E., Fram, M.S., Voss, S.A., Kingsbury, J.A., Jurgens, B. C., Smalling, K.L., Bradley, P.M., 2024. Predictions of groundwater PFAS

occurrence at drinking water supply depths in the United States. Science 386 (6723), 748–755.
[7] Fenton, S.E., Ducatman, A., Boobis, A., DeWitte, J.C., Lau, C., Ng, C., Smith, J.S., Roberts, S.M., 2021. Per- and polyfluoroalkyl substance toxicity and human health review: current state of knowledge and strategies for informing future research. Environ Toxicol Chem 40 (3), 606–630.
[8] Wee, S.Y., Aris, A.Z., 2023. Revisiting the "forever chemicals", PFOA and PFOS exposure in drinking water. npj Clean Water 6 (1), 57.
[9] USEPA 2024. Per- and Polyfluoroalkyl Substances (PFAS) - Final PFAS National Primary Drinking Water Regulation. U.S. Environmental Protection Agency (EPA), ⟨https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas⟩.
[10] O'Hagan, D., 2008. Understanding organofluorine chemistry. An introduction to the C–F bond. Chem Soc Rev 37 (2), 308–319.
[11] Sharifan, H., Bagheri, M., Wang, D., Burken, J.G., Higgins, C.P., Liang, Y.N., Liu, J.X., Schaefer, C.E., Blotevogel, J., 2021. Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone. Sci Total Environ 771.
[12] Zhang, H., Xu, H.C., Qin, B., Fu, Y.F., Yao, Y., Zhao, Y.S., Qin, C.Y., 2025. Review on the sources, distribution and treatment of per- and polyfluoroalkyl substances in global groundwater. Environ Res 275.
[13] SERDP-ESTCP, 2022. Summary Report: Strategic Workshop on Management of PFAS in the Environment. DoD SERDP-ESTCP Program.
[14] USGS 2018. Groundwater Use in the United States. U.S. Geological Survey (USGS), ⟨https://www.usgs.gov/water-science-school/science/groundwater-use-united-states⟩.
[15] Kucharzyk, K.H., Darlington, R., Benotti, M., Deeb, R., Hawley, E., 2017. Novel treatment technologies for PFAS compounds: a critical review. J Environ Manag 204, 757–764.
[16] Lu, D., Sha, S., Luo, J., Huang, Z., Zhang, X., 2020. Treatment train approaches for the remediation of per- and polyfluoroalkyl substances (PFAS): a critical review. J Hazard Mater 386, 121963.
[17] Ross, I., McDonough, J., Miles, J., Storch, P., Kochunarayanan, P.T., Kalve, E., Hurst, J., Dasgupta, S.S., Burdick, J., 2018. A review of emerging technologies for remediation of PFASs. Remediat J 28 (2), 101–126.
[18] He, J., Boersma, M., Song, Z., Krebsbach, S., Fan, D., Duin, E.C., Wang, D., 2024. Biochar and surfactant synergistically enhanced PFAS destruction in UV/sulfite system at neutral pH. Chemosphere 353, 141562.
[19] Jafarinejad, S., He, J., Wang, D., 2025. Regeneration of biochars (pristine and modified/engineered) and economic analysis of their use in the removal of per- and polyfluoroalkyl substances (PFAS) from water/wastewater. Front Environ Sci Eng 19, 20.
[20] Song, Z., He, J., Kouzehkanan, S.M.T., Oh, T.S., Olshansky, Y., Duin, E.C., Carroll, K.C., Wang, D., 2024. Enhanced sorption and destruction of PFAS by biochar-enabled advanced reduction process. Chemosphere 363, 142760.
[21] Wang, D., Zhang, W., Hao, X., Zhou, D., 2013. Transport of biochar particles in saturated granular media: Effects of pyrolysis temperature and particle size. Environ Sci Technol 47 (2), 821–828.
[22] Wang, D., Zhang, W., Zhou, D., 2013. Antagonistic effects of humic acid and iron oxyhydroxide grain-coating on biochar nanoparticle transport in saturated sand. Environ Sci Technol 47 (10), 5154–5161.
[23] Worch, E., 2012. Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling. De Gruyter, Boston.
[24] Liu, C.J., Werner, D., Bellona, C., 2019. Removal of per- and polyfluoroalkyl substances (PFASs) from contaminated groundwater using granular activated carbon: a pilot-scale study with breakthrough modeling. Environ Sci Water Res Tech 5 (11), 1844–1853.
[25] Park, M., Wu, S., Lopez, I.J., Chang, J.Y., Karanfil, T., Snyder, S.A., 2020. Adsorption of perfluoroalkyl substances (PFAS) in groundwater by granular activated carbons: roles of hydrophobicity of PFAS and carbon characteristics. Water Res 170, 115364.
[26] Dixit, F., Dutta, R., Barbube, P., Mohseni, M., 2021. PFAS removal by ion exchange resins: a review. Chemosphere 272, 129777.
[27] Boyer, T.H., Fang, Y., Ellis, A., Dietz, R., Choi, Y.J., Schaefer, C.E., Higgins, C.P., Strathmann, T.J., 2021. Anion exchange resin removal of per- and polyfluoroalkyl substances (PFAS) from impacted water: a critical review. Water Res 200, 117244.
[28] DiGuiseppi, W.H., Newell, C.J., Carey, G.R., Kulkarni, P.R., Xia, Z., Stults, J., Maher, T.L., Houtz, E.F., More, R., Wice, R., Tomiczek, P.W., Richardson, S.D., Xiong, J., Hale, J., Hnatko, J.P., McGregor, R., McDonough, J.T., Oka, A., Thomas, R., Fenstermacher, J., Hatton, J., 2024. Available and emerging liquid treatment technologies for PFASs. Remediat J 34, e21782.
[29] NASA 2017. Technology Readiness Level Definitions. National Space and Aeronautics Administration, ⟨https://www.nasa.gov/wp-content/uploads/2017/12/458490main_trl_definitions.pdf?emrc=da53fb⟩.
[30] Campion, L., Bekchanova, M., Malina, R., Kuppens, T., 2023. The costs and benefits of biochar production and use: a systematic review. J Clean Prod 408, 137138.
[31] Murray, C.C., Safulko, A., Vatankhah, H., Liu, C.J., Tajdini, B., Marshall, R.E., Bellona, C., 2023. PFAS adsorbent selection: the role of adsorbent use rate, water quality, and cost. J Hazard Mater 454, 131481.
[32] Gagliano, E., Sgroi, M., Falciglia, P.P., Vagliasindi, F.G.A., Roccaro, P., 2020. Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. Water Res 171, 115381.
[33] Krebsbach, S., He, J., Adhikari, S., Olshansky, Y., Feyzbar, F., Davis, L.C., Oh, T. S., Wang, D., 2023. Mechanistic understanding of perfluorooctane sulfonate (PFOS) sorption by biochars. Chemosphere 330, 138661.
[34] Krebsbach, S., He, J., Oh, T.S., Wang, D., 2023. Effects of environmental factors on the sorption of per- and polyfluoroalkyl substances by biochars. ACS ES&T Water 3 (10), 3437–3446.
[35] McDonough, J.T., Anderson, R.H., Lang, J.R., Liles, D., Matteson, K., Olechiw, T., 2022. Field-Scale Demonstration of PFAS Leachability Following In Situ Soil Stabilization. ACS Omega 7 (1), 419–429.
[36] Tajdini, B., Vatankhah, H., Pezoulas, E.R., Zhang, C., Higgins, C.P., Bellona, C., 2025. Adsorbability of a wide range of per- and polyfluoroalkyl substances on granular activated carbon, ion exchange resin, and surface modified clay. Water Res 268, 122774.
[37] Wu, C., Klemes, M.J., Trang, B., Dichtel, W.R., Helbling, D.E., 2020. Exploring the factors that influence the adsorption of anionic PFAS on conventional and emerging adsorbents in aquatic matrices. Water Res 182, 115950.
[38] Ateia, M., Alsbaiee, A., Karanfil, T., Dichtel, W., 2019. Efficient PFAS removal by amine-functionalized sorbents: Critical review of the current literature. Environ Sci Technol 6 (12), 688–695.
[39] Li, R., Adarsh, N.N., Lu, H., Wriedt, M., 2022. Metal-organic frameworks as platforms for the removal of per- and polyfluoroalkyl substances from contaminated waters. Matter 5 (10), 3161–3193.
[40] Liu, L., Liu, Y., Gao, B., Ji, R., Li, C., Wang, S., 2020. Removal of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from water by carbonaceous nanomaterials: a review. Crit Rev Environ Sci Technol 50 (22), 2379–2414.
[41] USEPA 2025. CompTox Chemicals Dashboard. U.S. Environmental Protection Agency (EPA), ⟨https://comptox.epa.gov/dashboard/⟩.
[42] Birnstingl, J., Wilson, J., 2024. A cost comparison of pump-and-treat and in situ colloidal activated carbon for PFAS plume management. Remediat J 35 (1), e70005.
[43] Basaleh, A., Hassan, A., Tawabini, B., Mahmoud, M., Alghamdi, F., Althubiti, A., Alrayaan, M., Al-Nasser, R., 2025. Removal of MTBE and BTEX pollutants from contaminated water using colloidal activated carbon (CAC). ACS Omega 10 (1), 509–519.
[44] McGregor, R., Zhao, Y., 2021. The in situ treatment of TCE and PFAS in groundwater within a silty sand aquifer. Remediat J 31, 7–17.
[45] Karume, I., Bbumba, S., Tewolde, S., Mukasa, Ih.Z.T., Ntale, M., 2023. Impact of carbonization conditions and adsorbate nature on the performance of activated carbon in water treatment. BMC Chem 17 (1), 162.
[46] McGregor, R., Benevenuto, L., 2021. The effect of heterogeneity on the distribution and treatment of PFAS in a complex geologic environment. Front Environ Chem 2, 729779.
[47] Carey, G.R., McGregor, R., Pham, A.L.-T., Sleep, B., Hakimabadi, S.G., 2019. Evaluating the longevity of a PFAS in situ colloidal activated carbon remedy. Remediat J 29 (2), 17–31.
[48] Niarchos, G., Ahrens, L., Kleja, D.B., Fagerlund, F., 2022. Per- and polyfluoroalkyl substance (PFAS) retention by colloidal activated carbon (CAC) using dynamic column experiments. Environ Pollut 308, 119667.
[49] Sorengard, M., Kleja, D.B., Ahrens, L., 2019. Stabilization of per- and polyfluoroalkyl substances (PFASs) with colloidal activated carbon (PlumeStop®) as a function of soil clay and organic matter content. J Environ Manag 249.
[50] Carey, G.R., Anderson, R.H., Van Geel, P., McGregor, R., Soderberg, K., Danko, A., Hakimabadi, S.G., Pham, A.L., Rebeiro-Tunstall, M., 2024. Analysis of colloidal activated carbon alternatives for in situ remediation of a large PFAS plume and source area. Remediat J 34 (1).
[51] Hakimabadi, S.G., Taylor, A., Pham, A.L.T., 2023. Factors affecting the adsorption of per- and polyfluoroalkyl substances (PFAS) by colloidal activated carbon. Water Res 242, 120212.
[52] McGregor, R., 2018. situ treatment of PFAS-impacted groundwater using colloidal activated carbon. Remediat J 28, 33–41.
[53] McGregor, R., 2020. Six pilot-scale studies evaluating the in situ treatment of PFAS in groundwater. Remediat J 30, 39–50.
[54] Georgi, A., Schierz, A., Mackenzie, K., Kopinke, F.D., 2015. Colloidal activated carbon for in-situ groundwater remediation — Transport characteristics and adsorption of organic compounds in water-saturated sediment columns. J Contam Hydrol 179, 76–88.
[55] Guan, X., Kong, L., Liu, C., Fan, D., Anger, B., Johnson, W.P., Lowry, G.V., Li, G., Danko, A., Liu, X., 2024. Polymer coatings affect transport and remobilization of colloidal activated carbon in saturated sand columns: Implications for in situ groundwater remediation. Environ Sci Technol 58 (19), 8531–8541.
[56] Mole, R.A., Velosa, A.C., Carey, G.R., Liu, X., Li, G., Fan, D., Danko, A., Lowry, G. V., 2024. Groundwater solutes influence the adsorption of short-chain perfluoroalkyl acids (PFAA) to colloidal activated carbon and impact performance for in situ groundwater remediation. J Hazard Mater 474, 134746.
[57] Ndubueze, E.U., Boparai, H.K., Xu, L., Sleep, B.E., 2024. Colloidal properties and stability of colloidal activated carbon: effects of aqueous chemistry on sedimentation kinetics. Environmental Science Nano 11 (10), 4391–4408.
[58] Hatton, J., Yan, P.F., Liu, C., Jo, S., Popovic, J., Rhiner, B.L., Wong, J., Mitchek, M., Li, J., Arnold, W.A., Simick, M.F., Pennell, K.D., 2025. Field demonstration of polymer stabilized activated carbon for in situ treatment of per- and polyfluoroalkyl substances (PFAS)-impacted groundwater. J Hazard Mater 499, 140292.
[59] SERDP-ESTCP, 2025. Situ Treatment of PFAS-Impacted Groundwater. DoD SERDP-ESTCP Program. ⟨https://serdp-estcp.mil/focusareas/db535794-ba25-4f8c-9f18-950e2aa8e2bf/in-situ-treatment-of-pfas-impacted-groundwater⟩.
[60] Carey, G.R., Hakimabadi, S.G., Singh, M., McGregor, R., Woodfield, C., Van Geel, P.J., Pham, A.L., 2022. Longevity of colloidal activated carbon for in situ PFAS remediation at AFFF-contaminated airport sites. Remediat J 33 (1), 3–23.

[61] Molé, R.A., Correia de Velosa, A., Liu, X., Li, G., Fan, D., Danko, A., Lowry, G.V., 2025. Impacts of groundwater constituents and colloidal activated carbon (CAC) surface chemistry on the adsorption of perfluoroalkyl acids (PFAA) in aqueous film-forming foam (AFFF)-impacted groundwater. ACS ES&T. Water 5, 4541–4551.
[62] Newell, C.J., Smith, W.B., Kearney, K., Clay, S., Javed, H., Carey, G.R., Richardson, S.D., Werth, C.J., 2025. Tool and database for estimating potential longevity of colloidal activated carbon barriers for PFAS in croundwater. Remediat J 35 (3).
[63] Carey, G.R., Danko, A., Pham, A.L.T., Soderberg, K., Hoagland, B., Sleep, B., 2024. Modeling the influence of coastal site characteristics on PFAS in situ remediation. Groundwater.
[64] Niarchos, G., Georgii, L., Ahrens, L., Kleja, D.B., Fagerlund, F., 2023. A systematic study of the competitive sorption of per- and polyfluoroalkyl substances (PFAS) on colloidal activated carbon. Ecotoxicol Environ Saf 264, 115408.
[65] Gunarathne, V., Schauerte, M., Boie, F., Yang, X., Melo, T.M., Rinklebe, J., 2025. Poly-/perfluoroalkyl substance (PFAS) immobilization using a novel adsorptive organoclay compared with colloidal-activated carbon in soil under dynamic redox conditions and the response of microbial communities. ACS Omega 10 (45), 54441–54454.
[66] Jiang, L., Chen, X.J., Carey, G.R., Liu, X.T., Lowry, G.V., Fan, D.M., Danko, A., Li, G.B., 2025. Effects of physical and chemical aging of colloidal activated carbon on the adsorption of per- and polyfluoroalkyl substances. Environ Sci Technol 59 (7), 3691–3702.
[67] Zheng, Z., Cline, D.M., Shih, C.Y., Richardson, S.D., Newell, C.J., Mohtar, C.S.E., Hesse, M.A., Werth, C.J., 2026. Effects of mass transfer limitations on PFAS breakthrough in colloidal activated carbon groundwater barriers. ACS ES&T Eng 6 (5), 1629–1638.
[68] REGENESIS 2024. In Situ PFAS Remediation: A Low-Cost Approach to Avoiding Long-Term Risk and Liability. REGENESIS, ⟨https://regenesis.com/wp-content/uploads/2019/12/240827-US-eBook-PFAS-In-Situ-Remediation.pdf⟩.
[69] Singh, M., Hakimabadi, S.G., Van Geel, P.J., Carey, G.R., Pham, A.L.T., 2024. Modified competitive Langmuir model for prediction of multispecies PFAS competitive adsorption equilibria on colloidal activated carbon. Sep Purif Technol 345, 127368.
[70] NAVFAC 2020 Groundwater to surface water interface: Overview and management (part 1), Washington, D.C.
[71] Wang, J., Lin, Z., He, X., Song, M., Westerhoff, P., Doudrick, K., Hanigan, D., 2022. Critical review of thermal decomposition of per- and polyfluoroalkyl substances: mechanisms and implications for thermal treatment processes. Environ Sci Technol 56 (9), 5355–5370.
[72] Niarchos, G., Ahrens, L., Kleja, D.B., Leonard, G., Forde, J., Bergman, J., Ribeli, E., Schütz, M., Fagerlund, F., 2023. In-situ application of colloidal activated carbon for PFAS-contaminated soil and groundwater: a Swedish case study. Remed. J. 33 (2), 101–110.
[73] Guan, X., Fan, D.M., Yu, Y.C., Lowry, G.V., Li, G.B., Danko, A., Liu, X.T., 2025. Effects of calcium and natural organic matter on the transport and remobilization of colloidal activated carbon in saturated porous media: insights from Force Spectroscopy. ACS Es&T Eng.
[74] Guan, X., Jiang, L., Li, G., Fan, D., Lowry, G.V., Liu, X., 2025. Aging controls colloidal activated carbon mobilization from saturated sand columns through modulation of energy barriers. Environ Sci Technol Lett 13 (1), 158–163.
[75] 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. Environ Sci Technol 54 (24), 15768–15777.
[76] Anderson, R.H., Feild, J.B., Dieffenbach-Carle, H., Elsharnouby, O., Krebs, R.K., 2022. Assessment of PFAS in collocated soil and porewater samples at an AFFF-impacted source zone: Field-scale validation of suction lysimeters. Chemosphere 308, 136247.
[77] Weber, A.K., Barber, L.B., LeBlanc, D.R., Sunderland, E.M., Vecitis, C.D., 2017. Geochemical and hydrologic factors controlling subsurface transport of poly- and perfluoroalkyl substances, Cape Cod, Massachusetts. Environ Sci Technol 51 (8), 4269–4279.
[78] Navarro, D.A., Kabiri, S., Ho, J.A.T., Bowles, K.C., Davis, G., McLaughlin, M.J., Kookana, R.S., 2023. Stabilisation of PFAS in soils: Long-term effectiveness of carbon-based soil amendments. Environ Pollut 323.
[79] Niarchos, G., Ahrens, L., Kleja, D.B., Axmann, A.M.L., Fagerlund, F., 2025. Impact of dissolved organic carbon on per- and polyfluoroalkyl mobility in activated carbon-amended soils. Environ Pollut 384, 126928.
[80] Gunarathne, V., Melo, T.M., Schauerte, M., Groth, F., Slany, M., Rinklebe, J., 2025. Immobilization of per- and polyfluorinated alkyl substances (PFAS) from field contaminated groundwater by a novel organo-clay vs. colloidal activated carbon under flow conditions. J Hazard Mater 488, 137273.
[81] Kookana, R.S., Navarro, D.A., Kabiri, S., McLaughlin, M.J., 2022. Key properties governing sorption–desorption behaviour of poly- and perfluoroalkyl substances in saturated and unsaturated soils: a review. Soil Res 61 (2), 107–125.
[82] Salo, H., Virtanen, S., Laine-Kaulio, H., Koivusalo, H., Jacques, D., Kokkonen, T., 2023. Evolution of pH, redox potential and solute concentrations in soil and drainage water at a cultivated acid sulfate soil profile. Geoderma 436, 116559.
[83] Stewart, R.D., Flury, M., Ajami, H., Anderson, R.G., Green, T.R., Jin, Y., Patrignani, A., Shillito, R., Zhang, W., Najm, M.R.A., Babaeian, E., Berli, M., Brookshire, E.N.J., Daigh, A.L.M., Franklin, S., Giovando, J., Heinse, R., Heitman, J., Huang, J., Kelleners, T., Naseri, M., Ochsner, T.E., Radolinski, J., Sadeghi, M., Sasidharan, S., Shukla, M.K., Tuller, M., Wendroth, O., Wu, J., Wyatt, B.M., Yang, Y., Yu, Y., Zhang, Z.F., 2025. Emerging issues and research opportunities in vadose zone processes. Vadose Zone J 24 (4), e70030.
[84] Arora, B., Dwivedi, D., Faybishenko, B., Jana, R.B., Wainwright, H.M., 2019. Understanding and predicting vadose zone processes. Rev Mineral Geochem 85 (1), 303–328.
[85] Oh, S., Cho, K., Park, S., Kwon, M.J., Chung, J., Lee, S., 2023. Denitrification dynamics in unsaturated soils with different porous structures and water saturation degrees: a focus on the shift in microbial community structures. J Hazard Mater 445, 130413.
[86] Voggenreiter, E., Schmitt-Kopplin, P., ThomasArrigo, L., Bryce, C., Kappler, A., Joshi, P., 2024. Emerging investigator series: preferential adsorption and coprecipitation of permafrost organic matter with poorly crystalline iron minerals. Environ Sci Proc Impacts 26 (8), 1322–1335.
[87] 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 Resour Res 56 (2) e2019WR026667.
[88] Wallis, I., Hutson, J., Davis, G., Kookana, R., Rayner, J., Prommer, H., 2022. Model-based identification of vadose zone controls on PFAS mobility under semi-arid climate conditions. Water Res 225, 119096.
[89] Zhang, N., Bu, X., Li, Y., Zhang, Y., Yuan, S., Wen, Z., Tong, M., Lin, L., 2020. Water table fluctuations regulate hydrogen peroxide production and distribution in unconfined aquifers. Environ Sci Technol 54 (8), 4942–4951.
[90] Zhao, G., Wu, B., Zheng, X., Chen, B., Kappler, A., Chu, C., 2022. Tide-triggered production of reactive oxygen species in coastal soils. Environ Sci Technol 56 (16), 11888–11896.
[91] Peiffer, S., Kappler, A., Haderlein, S., Schmidt, C., Byrne, J., Kleindienst, S., Vogt, C., Richnow, H., Obst, M., Angenent, L., Bryce, C., McCammon, C., Planer-Friedrich, B., 2021. A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems. Nat Geosci 14.
[92] Piepenbrock, A., Dippon, U., Porsch, K., Appel, E., Kappler, A., 2011. Dependence of microbial magnetite formation on humic substance and ferrihydrite concentrations. Geochim Et Cosmochim Acta 75 (22), 6844–6858.
[93] Li, H.-Q., Li, H., Zhou, X.-Y., Shen, Y.-J., Su, J.-Q., 2021. Distinct patterns of abundant and rare subcommunities in paddy soil during wetting–drying cycles. Sci Total Environ 785, 147298.
[94] Kurt, Z., Mack, E.E., Spain, J.C., 2014. Biodegradation of cis-Dichloroethene and Vinyl Chloride in the capillary fringe. Environ Sci Technol 48 (22), 13350–13357.
[95] Boulton, A.J., Findlay, S., Marmonier, P., Stanley, E.H., Valett, H.M., 1998. The functional significance of the hypoheic zone in streams and rivers. Annu Rev Ecol Syst 29 (1), 59–81.
[96] Brune, A., Frenzel, P., Cypionka, H., 2000. Life at the oxic–anoxic interface: microbial activities and adaptations. FEMS Microbiol Rev 24 (5), 691–710.
[97] Dellwig, O., Leipe, T., März, C., Glockzin, M., Pollehne, F., Schnetger, B., Yakushev, E.V., Böttcher, M.E., Brumsack, H.-J., 2010. A new particulate Mn–Fe–P-shuttle at the redoxcline of anoxic basins. Geochim Et Cosmochim Acta 74 (24), 7100–7115.
[98] McGregor, R., 2023. The in situ treatment of PFAS within porewater at the air–water interface of a PFAS source zone. Remediat J 33 (4), 265–278.
[99] Rubol, S., Freixa, A., Carles-Brangarí, A., Fernàndez-Garcia, D., Romaní, A.M., Sanchez-Vila, X., 2014. Connecting bacterial colonization to physical and biochemical changes in a sand box infiltration experiment. J Hydrol 517, 317–327.
[100] Dutta, T., Carles-Brangarí, A., Fernàndez-Garcia, D., SimonettaRubol, Tirado-Conde, J. and Sanchez-Vila, X. 2016 Pore-scale oxygen (O2) dynamics of vadose zone under dry-wet cycles of 1 artificial recharge: A soil lysimeter experiment.
[101] Liu, Y., Du, M., Shu, S., Wei, J., Zhu, K., Wang, G., 2024. Bacterial surface properties and transport behavior actively respond to an extracellular polymeric substance gradient in saturated porous media. Sci Total Environ 944, 173889.
[102] Liu, J., Avendano, S.M., 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: a review. Environ Int 61, 98–114.
[103] Smorada, C.M., Sima, M.W., Jaffe, P.R., 2024. Bacterial degradation of perfluoroalkyl acids. Curr Opin Biotechnol 88, 103170.
[104] Wackett, L.P., 2022. Nothing lasts forever: understanding microbial biodegradation of polyfluorinated compounds and perfluorinated alkyl substances. Microb Biotechnol 15 (3), 773–792.
[105] Battisti, I., Trentin, A.R., Sabia, A., Masi, A. and Renella, G. 2024 Soil Amendment with Biochar Reduces the Uptake and Translocation of Perfluoroalkyl Substances by Horticultural Plants Grown in a Polluted Area.
[106] Goossen, C.P., Schattman, R.E., MacRae, J.D., 2023. Evidence of compost contamination with per- and polyfluoroalkyl substances (PFAS) from "compostable" food serviceware. Biointerphases 18 (3).