



Review

Speciation and biogeochemical behavior of perfluoroalkyl acids in soils and their environmental implications: A review

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ARTICLE INFO

Keywords:

Perfluoroalkyl acids
Per- and polyfluoroalkyl substances
Extraction and analysis methods
Contamination remediation
Speciation

ABSTRACT

Perfluoroalkyl acids (PFAAs) are emerging organic pollutants that have attracted significant attention in the fields of environmental chemistry and toxicology. Although PFAAs are pervasive in soils and sediments, there is a paucity of research regarding their environmental forms and driving mechanisms. This review provides an overview of the classification and biotoxicity of per- and polyfluoroalkyl substances (PFAS), organic pollutant forms, PFAS extraction and analytical methods, the prediction of PFAS distribution in soils, and current PFAS remediation strategies. Four predominant PFAA forms have been proposed in soils: (i) aqueous-extracted PFAAs, (ii) organic-solvent extracted PFAAs, (iii) embedded or sequestered PFAAs, and (iv) covalently bound PFAAs. Furthermore, it suggests suitable extraction methods and predictive models for different PFAA forms, which are instrumental in the research on PFAA speciation and prediction in soils. Simultaneously, it was proposed that elemental cycling and microbial activity may affect the speciation of PFAS. Additionally, the categorization of PFAA forms facilitated the analysis of pollution remediation. Understanding the interplay between PFAA speciation, element cycling, and bacterial activity during soil remediation is essential for understanding remediation mechanisms and assessing the long-term stability of remediation methods. Future studies should expand the investigation of varying PFAA forms in different media, consider the potential binding forms of PFAAs to minerals, organic matter, and microbes, and evaluate the possible mechanisms of PFAA speciation variation.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of organic compounds in which hydrogen atoms bound to C atoms are partially or entirely replaced by fluorine atoms [1]. Products containing PFAS are widely used in textiles, lubricants, surfactants, food packaging, nonstick coatings, electronics, fire protection gears, fire-extinguishing foams, and various other fields [1,2]. During the production and use of substances containing PFAS, their release into the atmosphere and waterways leads to the global dispersion of pollutants. Furthermore, PFAS can migrate through various environmental media, including the atmosphere, water, soil, and sediment. They accumulate within organisms through the food chain, and pose a range of environmental and health risks [3–5]. Thus, solid media such as sediments and soil are highly enriched media for PFAS.

Over 3000 PFAS types are present in the environment and exhibit varying transport behaviors. PFAS are categorized as short and long chains based on the number of C atoms. For instance, long-chain PFAS include perfluorocarboxylic acids (PFCAs) with seven or more C atoms and perfluorosulfonic acids (PFSAs) with six or more C atoms [6,7] (Fig. 1). Long-chain PFAS, like perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), exhibit longer elimination half-lives and greater bioaccumulation potential when compared to short-chain PFAS [8,9]. Therefore, perfluoroalkyl acid (PFAA)-series substances, such as PFOA and PFOS, have attracted more attention from researchers than other PFAS.

These functional groups significantly influence the physicochemical properties of PFAS. Common PFAS can be classified into six categories (Fig. 1). Fluoroalkanes (C_nF_{2n+2}), exemplified by perfluoroheptane (C_8F_{18}) and perfluorohexadecane ($C_{16}F_{34}$), are PFAS that lack functional

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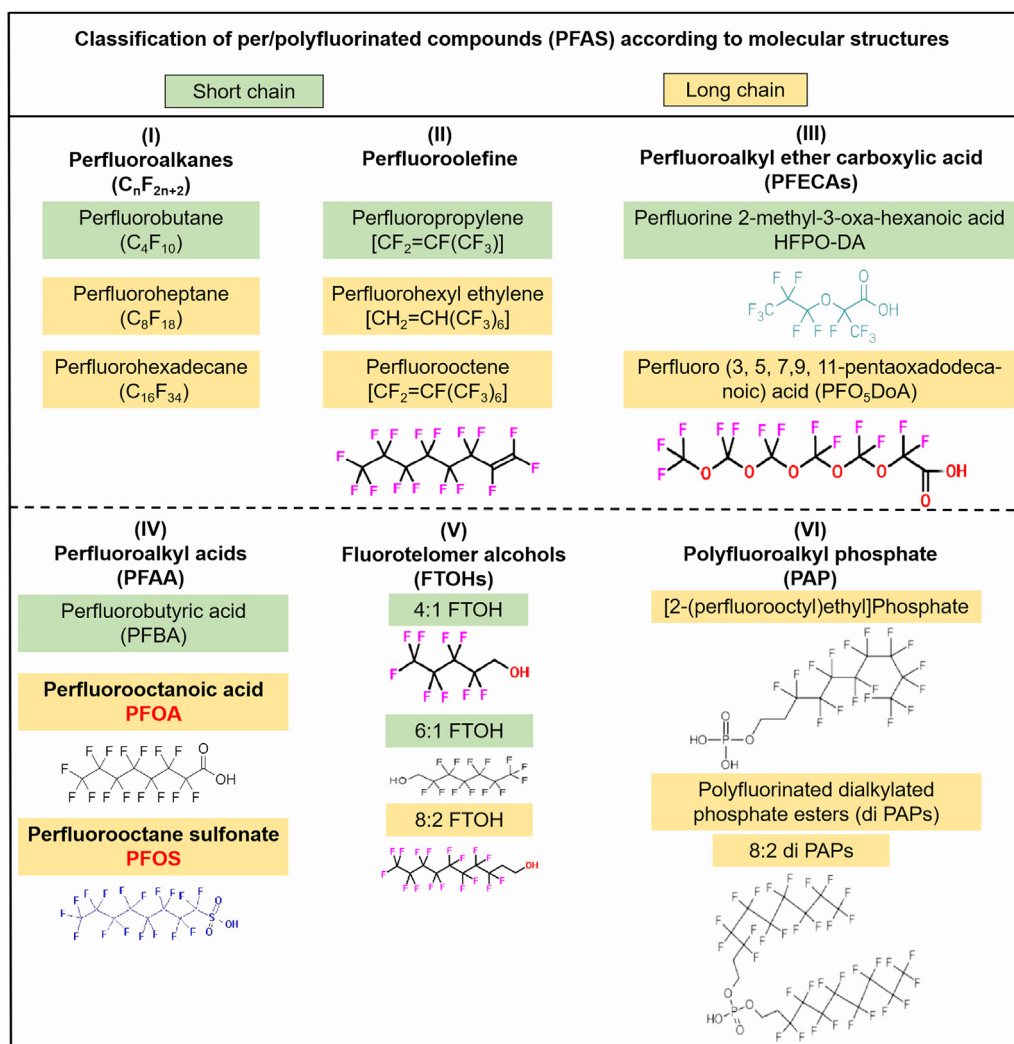


Fig. 1. Classification of PFAS according to chain length or functional group.

groups and have primary applications in chemosynthesis [10]. Perfluoroolefins, including perfluoropropylene [$CF_2=CF(CF_3)$] and perfluorohexylethylene [$CH_2=CH(CF_3)_6$], are PFAS that contain a double bond and are primarily used in pharmaceutical synthesis [11]. Fluoroalkyl ether carboxylic acids (PFECAs), such as perfluorine 2-methyl-3-oxa-hexanoic acid and perfluoro (3, 5, 7, 9, 11-pentaoxadodecanoic acid), are PFAS characterized by ether bonds [12]. PFECAs with discontinuous CF_2 structures have been developed as substitutes for traditional PFAS in industrial applications [13]. PFAAs are the most commonly used PFAS and are frequently detected in the environment, primarily comprising PFSAs and PFCAs. PFOS and PFOA are the representatives of PFSAs and PFCAs, respectively [14,15]. Fluorotelomer alcohols (FTOHs), such as 4:1 FTOH (C_5F_9HO) and 8:2 FTOH ($C_{10}F_{17}H_5O$), are volatile PFAS that can migrate through the atmosphere and decompose into PFAAs in the natural environment [16,17]. Polyfluoroalkyl phosphates, including [2-(perfluorooctyl)ethyl] phosphate and 8:2 polyfluorinated dialkylated phosphate esters (8:2 diPAPs), are PFAS with phosphate groups that are mainly used in food packaging, cosmetics, and personal care products [18,19]. PFAS with different functional groups may react differently to the environmental matrix, and it has been difficult to obtain consistent results in previous studies. Therefore, in this review, we focus on typical long-chain PFAA.

PFAS with various functional groups undergo gradual degradation in the environment and are predominantly transformed into PFSAs and PFCAs. Despite certain PFAAs being currently phased out, including

typical long-chain PFAAs such as PFOA and PFOS, they continue to be prevalent in the natural environment [15,20,21]. Recent research has identified abundant sulfonamide-PFASs derived from electrochemical fluorination as sources of PFAAs because of environmental transformations, particularly in soils [22,23]. In recent years, global pollution levels of PFOA or PFOS have ranged from 0.2 to 100 ng/g or ng/L [15]. Recently, in severely contaminated areas, PFOA concentrations have reached an alarming 400,000 ng/L [24]. Research has indicated that PFAA pollution is becoming increasingly serious. In addition, the PFOS and PFOA concentrations per unit mass/volume in sediments surpass those in water [15,25]. Therefore, special attention must be paid to solid phases (e.g., soil and sediment) in the investigation of typical long-chain PFAAs.

PFAS exist widely in the atmosphere, water, soil, sediment, plants, and various animal organs [26,27]. Typically, point-source PFAS are transported by surrounding rivers. Consequently, according to most existing studies, PFAS concentrations are highest in rivers and streams, followed by lakes, reservoirs, and coastal and marine systems [28,29]. Most of environmental PFAS contain hydrophilic functional groups and hydrophobic C and fluorine chains. Therefore, short-chain PFAS are more prevalent in water, whereas long-chain PFAS are more prevalent in suspended particles and sediments [30,31].

Geochemical processes can affect the occurrence of PFAS in the environment by increasing or decreasing their mobility [32,33]. Taking Fe and microbes as examples, Fe(II) can absorb anionic PFAS from the

environment and fix them in minerals during mineralization [34,35]. Microorganisms are important in the formation and dissolution of Fe minerals [36]. Additionally, the degradation of PFAS branches and functional groups by microorganisms affects the binding between PFAS and minerals [37]. PFAS embedded in environmental matrices such as mineral or organic matter (OM) cannot be directly extracted by conventional organic solvent extraction methods, which need to destroy the structure of the matrix before extraction [38,39].

The human body efficiently absorbs most perfluorinated compounds and distributes them through the bloodstream to various organs and tissues with high blood flow, including the liver, kidneys, lungs, heart, skin, testes, brain, spleen, and bones [40]. In contrast to hydrophobic organic pollutants, which accumulate in fat, PFAS are more concentrated in protein components, occupying active sites on proteins and consequently causing physiological toxic effects [41]. Human exposure studies have linked elevated blood levels of PFAAs to kidney and testicular cancers, increased cholesterol, liver disease, reduced fertility, thyroid issues, altered hormone function, compromised immune system, and adverse developmental effects [42,43]. Given the widespread use of PFAAs and the persistence of long-chain PFAS, most toxicity studies have concentrated on PFOA and PFOS [44].

Accordingly, PFAAs are more widely used and persistent than other PFAS. Typical long-chain PFAA, such as PFOA and PFOS, are highly prevalent in the solid phase and pose toxicity risks to humans [45]. Environmental transmission of PFAA from a point source to the bodies of animals and plants is an indispensable process. The variation in PFAA forms is a crucial factor in investigating PFAA transport. However, research has rarely focused on the forms of PFAA in soils. Building on these studies, we review and discuss the speciation of PFAA forms in soils and their environmental implications. The specific objectives were to (i) identify the typical long-chain PFAA forms in soils, (ii) classify PFAS extraction and detection technologies for different PFAA forms, (iii) elucidate the environmental factors influencing PFAA speciation and prediction models for PFAA migration, and (iv) highlight the significance of classifying PFAA forms for remediating PFAS.

2. Speculation of typical long-chain PFAA forms in soils

Compared with PFAAs, research on the forms of traditional organic pollutants in soils is more comprehensive. Based on bioavailability, the forms of traditional organic pollutants (e.g., polycyclic aromatic hydrocarbons and organochlorine pesticides) in soils can be categorized into three groups [46,47]: bioavailable, non-bioavailable but chemically extractable, and non-extractable residues (NERs) (Fig. 2). Among them, NERs are substances that remain in the soil after common (not destroy soil structure) chemical extraction [48]. NER PFAAs are present in soil

[49]; therefore, we speculated that PFAAs exist in different forms in the environment.

2.1. Forms of traditional organic pollutants in soils

Based on these generation mechanisms, the European Chemicals Agency further subdivided the NERs of organic pollutants into three categories. Type I NERs involve noncovalent binding to the soil matrix, utilizing adsorption, entrapment, and sequestration as binding modes [50,51]. The binding forces include ionic forces, ligand exchange, charge transfer, hydrogen bonds, van der Waals forces, and hydrophobic effects [50]. Additionally, the size of the apertures and the expansion and contraction of the matrix affect the embedding efficiency of the type I NERs [52]. Type II NERs form stronger bonds with the soil matrix than type I NERs, which are fixed by covalent bonds [53,54]. Esters, ethers, or C–C bonds produced by enzymes, free radical reactions, or photochemical catalysis reactions play key roles in the generation of type II NERs [50]. Moreover, variations in environmental factors, such as wet-dry or freeze-thaw alternations, affect the formation, release, and speciation of type I and II NERs [55]. In isotope-labeling studies, degraded organic pollutant atoms can be found in the protein structure of bacteria; these degraded organic pollutants are referred to as type III NERs [50]. Type III NERs are a form of bioassimilation that cannot be reversed into type I and II NERs. According to the classification of traditional organic pollutants, PFAAs in solid media may exist in bioavailable form, chemical extraction form, and type I and II NERs. Because PFAAs are extremely difficult to biodegrade in soil, the presence of type III NERs is negligible.

2.2. Prediction of typical long-chain PFAA forms in soils

Many studies on the transport of PFAS have overlooked their various forms in soils. A study concentrating on PFOS NER in soils discovered significant conversion of PFOS to NER during prolonged interactions between PFOS and soil [49]. The study revealed that PFOS NER reached its peak at 60 days. However, 50% of the NER was subsequently released between days 60 and 180, and the newly formed NER exhibited poor stability [49]. This result is consistent with the characteristics described for traditional organic pollutants, specifically type I and II NERs [49,50]. In addition, an ecological effects study simulating PFOA found that after 120 days of in situ environmental simulation incubation, only 40% of the total PFOA was extracted using organic solvents at its minimum point [56]. The aforementioned studies on typical long-chain PFAAs have demonstrated a high percentage of NER PFAAs in the solid phase. However, there is a lack of detailed classifications of PFAA forms in soil. According to research on traditional organic pollutant forms and PFAA NERs and considering the bioavailability of PFAAs in soils or sediments [49,50], typical long-chain PFAAs can be categorized into four forms in the solid phase (Fig. 3), namely (i) aqueous-extracted [57], (ii) organic solvent-extracted [49], (iii) embedded or sequestered [50], and (iv) covalently bound PFAAs [16]. The biological availability of PFAAs gradually decreases from (i) to (iv), and the four PFAA forms can be interconverted by changes in environmental factors [49]. Based on the above classification, it is helpful to conduct more research on the environmental behavior of PFAS, including microscopic mechanism research on the interaction between different PFAS forms and environmental substrates, as well as quantitative research, such as the prediction of kinetic models.

3. PFAS extraction and detecting technologies for different forms of PFAAs

Because PFAS extraction methods vary in their processing procedures, the sample types can be categorized into four groups: water, soil or sediment, air, and biological. At present, a more comprehensive and highly recognized PFAS extraction method is the US EPA 1633 method, which analyzes PFAS in aqueous, solid, biosolid, and tissue samples using

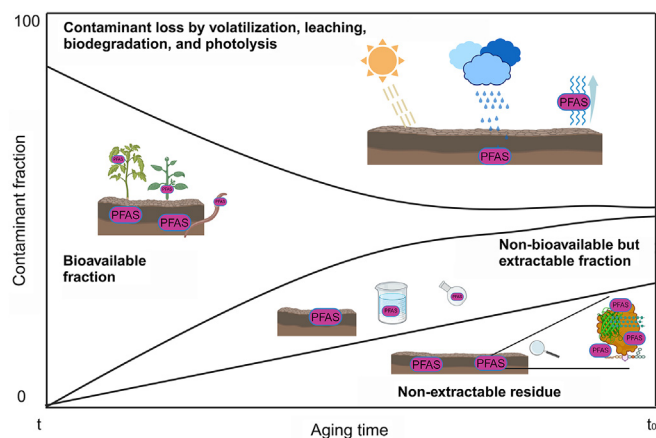


Fig. 2. Forms of traditional organic pollutants in the environment. The figure information was obtained from Kästner's research [50].

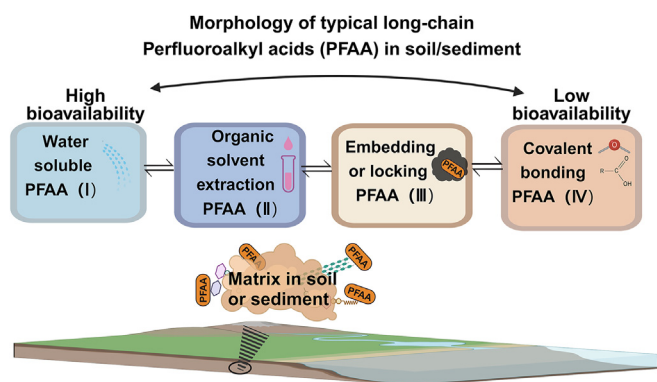


Fig. 3. Four types of possible PFAA forms in soils or sedimentary environments.

LC–MS/MS (<https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P101687F.txt>). The following section introduces some of the PFAS extraction methods that have been used (Table 1). Notably, most existing extraction and analysis techniques do not consider the different PFAS forms in the environment.

3.1. Extraction methods of PFAS

Water samples typically require filtration before extraction. Preferably, polypropylene should be used as the filter material rather than glass. Following filtration, seawater samples require the addition of sodium thiosulfate to eliminate residual chlorine [58]. In most environmental water samples, the PFAS concentration is often below the detection limit of the instrument and requires further concentration after filtration [58,59]. Solid-phase extraction (SPE) is the primary enrichment method, and SPE columns are commonly categorized as hydrophobic, mixed hydrophobic/polar, and polar wax-fixed equal types [59].

Before extraction, the soil must be ground to remove large particles. Various extraction methods have been employed for soil, sediment, or particulate matter samples, including Soxhlet extraction, pressurized solvent extraction (PLE), steam extraction, and ultrasonic extraction after grinding into small particles [60,61]. Selecting an appropriate extraction temperature is critical for PFAS extraction. For instance, the temperature of PLE ranges from 50 to 200 °C. Generally, increasing the temperature enhances the solubility of the target substance in the solvent, thereby improving the extraction efficiency [62]. Nevertheless, higher temperatures may destroy the target compound, form unextractable complexes, and increase interfering components in the matrix [63,64]. Generally, a mixed solvent of acetone and methanol (1:3) at 100 °C was suitable for extracting long-chain PFAAs from sediments [65]. The recovery rate of pure organic solvent extraction is relatively insufficient, and an acidified methanol solution used to extract PFAA from sediment achieves an overall recovery rate > 73% [60]. A better recovery rate can be obtained through ultrasonic extraction, which extracted PFAS from sediment samples and achieved recoveries of 95.3%–97.6% [66]. PLE was the most efficient extraction method between Soxhlet extraction, PLE, steam, and ultrasonic extraction of PFAS from sludge [67]. PFAS in aqueous film-forming foam (AFFF)-contaminated soil is a popular topic of research. An innovative method involves the use of acidic (HCl) and basic

(NH₄OH) MeOH solvent extraction, which can extract 97% of the total PFAS mass from AFFF-polluted soil [68].

Collecting PFAS samples from the atmosphere requires separating gases and particles from air. One separation method employs a polyurethane foam and a quartz fiber filter membrane to collect gas and particle samples, respectively [69]. In addition, polystyrene resins such as XAD-2 and XAD-4 can adsorb PFAS in air [61]. Polyurethane foam, quartz fiber filter membranes, or polystyrene resins can be further extracted via Soxhlet extraction [61,69]. Because PFAS accumulates in organisms, methods for extracting PFAS from biological tissues have garnered significant attention. Mixed organic solvent extraction is an early method that employs acidified ether and n-hexane (8:2) to extract PFCAs from blood, urine, and liver homogenates using GC-ECD after methylation [70]. Silica column chromatography is also useful for separating perfluorinated compounds from biological samples using the phase partition method, which utilizes a silica column for purification and elution with ethyl ether and trifluoroacetic acid (100:1) [71].

Pickling or alkaline digestion is indispensable for extracting PFAS from biological tissue samples [72,73]. A comparative study of the extraction methods of PFAS from plant samples showed that the use of formic acid to extract plant samples was not ideal [73]. In addition, digestion of biological tissue samples using potassium hydroxide is recommended by the EPA's 3rd Draft Method 1633 Analysis of Per- and Polyfluoroalkyl Substances in Aqueous, Solid, Biosolids, and Tissue Samples using LC–MS/MS (<https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P101687F.txt>). Therefore, alkali digestion is a commonly used and effective method for the extraction of PFAS in tissue samples.

3.2. Analysis methods of PFAS

Numerous methods have been developed to determine PFAS over time, using different detection principles (Table 2). Relatively reliable detection methods include gas and liquid chromatography–tandem mass spectrometry (GC/LC–MS). PFAS analysis methods can be divided into PFAS-specific methods, such as gas and liquid chromatography [62,74,75], and nonspecific PFAS methods, such as chemical absorption [76], electrode detection method [77], combustion ion chromatography [78], and ultraviolet absorbance and fluorescence [79].

The earliest method used to determine organic fluoride was oxidation. Briefly, the sample was vaporized in a hydrogen-oxygen flame chamber and rapidly decomposed into CO₂ and HF. The produced gas was further absorbed by a NaOH solution, and the remaining NaOH was neutralized with HNO₃ [76]. This nonspecific method can determine the presence of fluorine; however, it is challenging to identify specific organic fluorides. Additionally, combustion may lead to incomplete decomposition, resulting in measured values lower than the actual amounts of perfluorinated compounds [80]. The electrode detection method quantifies PFAS by measuring the fluoride ion concentration. The combination of oxidation and ion-selective electrodes was an early-stage method [77]. This process converts organic fluorine into HF through combustion, and its concentration is determined using an ion-selective electrode. Another method involves the release of fluorine ions from the C–F bond through a chemical reaction and detection using fluorine ion-sensitive electrodes [81]. However, it is challenging to confirm whether the detected fluorine ions originate from PFAS.

Table 1

The summary of different PFAS sample collection, pretreatment, and extraction methods.

Sample types	Collect or pretreatment	Extraction methods	References
Water sample	Pre-filtering	Solid-phase extraction	[58,59]
Soil or sediment Sample	Grinding and crushing	Soxhlet extraction, US EPA1633 Pressurized liquid extraction, steam extraction method, ultrasonic extraction, acidic and basic MeOH solvent extraction, US EPA1633	[60–68]
Atmospheric sample	Separately collected the gas and particle phases	Soxhlet extraction	[61,69]
Biological sample	Cell disruption; pickling or alkali digestion	Organic solvents extraction and solid phase extraction, US EPA1633	[70–73]

Table 2

The summary of PFAS sample analysis methods and characteristics.

Analytic strategies	Analysis methods and characteristics	References
Non-specific PFAS method	<ul style="list-style-type: none"> Gas chromatography–tandem mass spectrometry, suitable for detecting volatile PFAS; Liquid chromatography–tandem mass spectrometry, suitable for detecting most soluble PFAS. 	[62,74,75]
Specific PFAS method	<ul style="list-style-type: none"> Chemical absorption, acid-base neutralization reaction detects fluorine ions; Electrode detection method, electrodes detect fluoride ions; Combustion ion chromatography, ion chromatography detects fluorine ions; Ultraviolet absorbance and fluorescence, low cost, and fast detection. 	[76–79]

In contrast to chemical absorption and electrode methods, GC/LC–MS allows clear qualitative and quantitative analyses [71,82,83]. GC–MS can be employed to identify volatile PFAS, including amides, fluorotelomers, alkenes, and derivatized PFAS [69,71]. The most common PFAS can be detected using LC–MS equipped with suitable separation columns [62]. GC–MS is an effective method for determining PFAS in air. However, before GC analysis, derivatization of PFAAs is required, which poses challenges for reproducibility [69]. Similarly, LC–MS is suitable for detecting PFAS in wastewater, achieving detection limits for PFOA, PFNA, PFDA, PFOS, and PFOSA ranging from 0.20 ng/L to 0.47 ng/L [84]. LC–MS is more commonly utilized in PFAS detection studies than GC–MS.

PFAS concentrations can be analyzed using methods other than GC/LC–MS. Reflectance chemistry methods have been used to investigate the distribution and degradation of PFOA in various organisms. After adding isotopically labeled PFOA, samples of different components were analyzed using a radioactive scintillator to reveal the biological metabolic processes of PFOA [75]. Researchers used nuclear magnetic resonance (NMR) to quantify PFAS concentration based on the NMR peak area of ^{19}F to quantify CF_3 at the end of a single compound; however, the results were less stable [62]. The attenuated total reflectance Fourier transform infrared spectroscopy rapidly detects PFAS in water, with a detection limit of 0.03 $\mu\text{mol/L}$ to 0.7 $\mu\text{mol/L}$ [74]. Aung et al. employed ultraviolet absorbance and fluorescence to predict the removal ratio of 11 short-chain PFAS via activated C adsorption [79]. In addition, combustion ion chromatography can non-specifically measure total organic fluorine (TOF) in industrial wastewater, river water, and air. Compared with LC–MS/MS, this method measures a higher TOF in industrial wastewater, river water, and air samples [78]. Although some PFAS analysis methods have advantages over GC/LC–MS, they are mostly inferior in terms of stability and application. The most popular method currently remains GC/LC–MS, particularly LC–MS.

3.3. Extraction and detection technologies for different PFAA forms

Currently, there are no specific studies on the classification of different PFAS forms in soils; therefore, extraction methods for different PFAS levels have not been accurately described. In terms of analysis, GC/LC–MS is a relatively better method. However, in terms of extraction, for PFAAs that have high binding affinities to the matrix, chemical reagents should be used to destroy the structure or break the chemical bond before extraction. One study divided PFOS in 240-day soil experiments into conventional extraction and NER states, employing different extraction methods [49]. The method for extracting NER PFOS was similar to that of extracting covalently bound traditional OM. It uses alkaline hydrolysis and chemical reagents to break covalent bonds, thereby releasing NER PFOS from the soil matrix [49,50].

The conventional extraction state can be subdivided into bioavailable (water-soluble) and hard-to-bioavailable but extractable (organic solvent extraction) states [48]. The NER state can be further subdivided into noncovalently bonded (embedded or locked) type I NERs and covalently bonded type II NERs [49,50] (Fig. 3). According to previous studies, the extraction methods for the four PFAA forms (Fig. 3) may be as follows: (i) using deionized water to extract the bioavailable form of PFAAs [57], (ii) using organic solvent to extract the hard-to-bioavailable but extractable form of PFAAs [25], (iii) disrupting soil structure to release the

embedded or locked form of NER PFAAs [38], and (iv) breaking the covalent bond between soil and PFAAs to release the covalently bonded form of PFAAs [39]. GC/LC–MS is a suitable instrument for accurate quantitative detection of the four PFAA forms [71,82,83]. The above extraction methods focused on PFAA speciation research, while the US EPA 1633 standard for extracting PFAS from solid samples (<https://nep.is.epa.gov/Exe/ZyPURL.cgi?Dockey=P101687F.txt>) is a more convenient method in most studies focusing on PFAS concentration.

4. Environmental factors influencing PFAA speciation and prediction model for PFAA migration

Previous studies on PFAA processes in soil focused solely on fixation and neglected various forms of PFAAs [85,86]. Although there are differences between PFAA fixation and speciation processes, van der Waals, interionic, and hydrophobic forces exist in both [87,88]. Therefore, factors influencing PFAA speciation can be derived from PFAA fixation. Numerous factors, including OM, minerals, ions, and pH, impact the behavior of PFAA allocation (K_d) [85,89]. Most studies have posited that hydrophobic and electrostatic forces are pivotal in the PFAA allocation process (Fig. 4). In addition, various biotic and abiotic geochemical processes, such as Fe cycling and microbial community variation, can affect the migration of PFASs.

4.1. Factors affecting PFAA retention in soils

The adsorption of PFAAs on the matrix, caused by hydrophobic and electrostatic interactions, can convert aqueous-extracted PFAAs (type I) into organic solvent-extracted PFAAs (type II). Research on PFAA fixation in sediments indicates that OM and minerals influence the adsorption behavior of PFAAs [85]. The hydrophobic perfluoroalkyl group of PFAAs interacts with OM through hydrophobic interactions, whereas the acidic functional group engages in electrostatic interactions with minerals in the soil [86]. The hydrophobic perfluoroalkyl group of PFAAs interacts

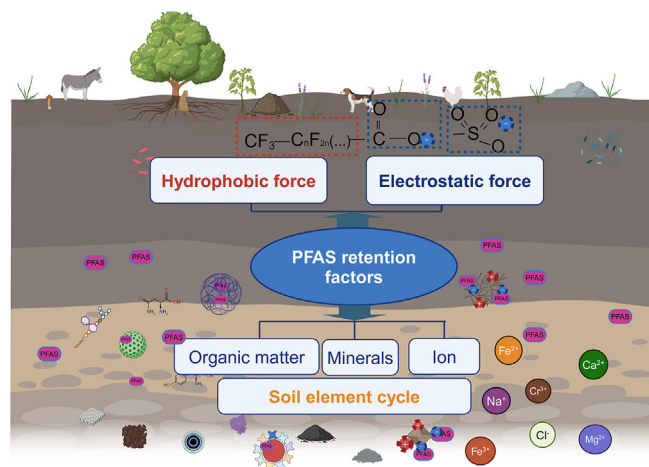


Fig. 4. The possible forces and factors of PFAA form speciation in soils or sediment.

with OM through hydrophobic interactions, whereas the acidic functional group engages in electrostatic interactions with minerals in the soil [86]. Some researchers believe that the adsorption of PFAAs in sediments is primarily affected by OM. The organic C content of sediments is a decisive factor influencing the adsorption behavior of PFOA. When the OM content in sediments increased from 0.56% to 9.66%, the K_d value of PFOA increased from undetectable to 11.93 [86]. Moreover, the K_d value showed a significant positive correlation with organic C in the soil. Furthermore, an increase in dissolved OM (DOM) significantly decreases the adsorption of PFOA in sediment [88]. These results indicate that hydrophobic interaction between DOM and PFOA is a key factor in the adsorption process.

Some studies have suggested the competitive adsorption of natural OM (NOM) and PFOA in water. NOM can adsorb onto the surface of organic components through hydrophobic actions and onto the surfaces of minerals through electrostatic actions [87]. The NOM typically comprises anionic compounds. When NOM adsorbs onto the sediment surface, its electronegative nature generates strong electrostatic repulsion between the sediment and PFOA, creating an unfavorable environment for PFOA adsorption [85]. These studies indicated that OM is an important factor in PFOA adsorption. Other researchers believe that the influence of inorganic components (e.g., metal oxides) is important for the adsorption of PFOA [90]. Similar to hydrophobic action, electrostatic action is a key mechanism for adsorption [90]. For example, Li et al. found that apart from the OM content, the amount of PFOS adsorbed was positively correlated with Fe oxides in sediments [91]. Zhao et al. discovered that clay mineral content (e.g., kaolin, goethite, and montmorillonite) was an important factor affecting the adsorption capacity of PFOA [92]. Wang et al. observed that PFOS is transported faster in sediments than in soils, which was attributed to the varying contribution rates of OM, metal oxides, silt, and clay components to PFOS adsorption [93]. The type of mineral surface charge influences the adsorption of PFAAs. Limestone, with a less negative charge, exhibits a stronger adsorption capacity for PFOA than that of quartz sand [89]. Overall, electrostatic action is also a key mechanism for the adsorption and fixation of PFAA in sediment.

In addition to minerals and NOM, ion concentrations and types also affect PFAA adsorption by altering electrostatic interactions. The amount of PFOA adsorbed in sediments increases with increasing anion concentrations [56]. With an increase in the anion concentration, the double electric layer on the sediment surface was continuously compressed, leading to a gradual weakening of its surface electronegativity and a significant decrease in the electrostatic repulsion between the sediment and PFOA. An increase in PFOA adsorption on the sediment surface was observed [88]. Some studies have found that ionic concentration does not affect the adsorption amount of PFOA in sediments. Unlike anions, the adsorption of cations onto PFAAs depends on their valence state. Under the same range of ionic concentration changes, Ca^{2+} significantly increased the adsorption of anionic PFAAs (such as PFOA and PFOS) in sediments but had almost no influence on Na^+ concentration. This may be due to the bridging effect of bivalent cationic metals, which can link anionic sites between the soil and PFAAs. In addition to the above factors, protein content, anion-exchange capacity, PFAA homologues, and surfactants also affect the adsorption of PFAAs on the sediment surface [94–96].

Generally, current research on the forces and factors affecting PFAS adsorption is relatively comprehensive. However, most studies did not consider the degree of binding between PFAAs and the matrix. Therefore, it is difficult to explicitly determine the long-term speciation of PFAA in soils solely through adsorption or fixation studies. Further studies should focus on the factors affecting PFAA speciation. Additionally, the dynamic cycling of major elements (such as Fe, C, N, and S) and the metabolic processes of bacteria are crucial factors influencing the long-term speciation of PFAA in soils. Researchers should also consider variable factors, such as microbial metabolism and elemental cycling when studying PFAA speciation.

4.2. Biogeochemical processes of elements impacting PFAS speciation in soils

In the environment, PFAA speciation may be influenced by a single factor and be linked to soil element cycling and microbial metabolic activities. However, identifying studies that combine PFAS speciation with mineral formation and microbial metabolism is challenging. Insights can be drawn from research on the interactions of organic C with minerals and bacteria in the soil. Fe minerals, including Fe oxides, (hydro)oxides, and (oxy)hydroxides, are widespread in soils and highly reactive to soil organic C [32,33]. It is reasonable to assume that this “highly reactive” nature also influences PFAAs, similar to various forms of organic C in soil.

The biogeochemical processes of Fe(II)/(III) are intricately linked to the fixation and mineralization of soil organic C (SOC). SOC protected by soil aggregates may also be released and decomposed by Fe cycling, particularly for Fe–SOC, which is considered a type of mineral-associated organic carbon (MAOC) sensitive to environmental conditions [97]. Similarly, PFAAs are embedded, locked, or covalently bound to soil. This may turn aqueous-extracted PFAAs (type I) or organic solvent-extracted PFAAs (type II) into embedded or sequestered PFAAs (type III) or covalently bound PFAAs (type IV). It can be speculated that the fixation and mineralization of matrix-bound PFAA are also closely related to the biogeochemical processes of Fe(II)/(III). Microbes play a crucial role in Fe cycling. Fe(II) oxidation can be driven by phototrophic microorganisms such as *Rhodospseudomonas palustris* TIE-1, *Rhodobacter* sp. SW2, *Chlorobium ferrooxidans*, and *Thiodictyon* sp. F4 [36]. This implies that activities related to the microbial community can also influence the speciation of PFAA. This is consistent with the theory proposed by Kästner that the formation of NERs combined with soil and organic pollutants is affected by bacteria [50]. In summary, elemental biogeochemical processes are key factors in PFAA speciation and should be considered in the prediction model of PFAA transmission fate and the remediation process of PFAA contamination.

The microbe- and Fe(II)-derived precursor transformation process of PFAS may also affect the speciation of PFAS [23,98]. Microbially driven dealkylation, oxidation, and hydrolytic reactions are important processes in AFFF-derived PFAAs [99]. Fe(II)-driven electrochemical defluorination also accelerates the transformation of PFAA precursors into PFAAs [23]. Research has shown that forming PFAAs via the transformation of precursors will likely impact the available PFAS forms in the environment, their retention, and mobility [100,101]. With the transformation of the PFAA precursor, the changed molecular structure and functional groups of PFAS affect their migration depth in the soil layer [37]. A soil column experiment showed that PFAAs were released more rapidly than PFAS precursors [102]. This implies that the speciation of PFAS in soil may be affected by differences in the molecular structure and functional groups of PFAS.

In addition to Fe, other environmental factors, such as sulfate, nitrate, and pH, may also influence the forms of PFAAs. Microbes also affect the cycling of these elements. Building a model under the influence of microorganisms and multiple elements is an effective way to clarify the PFAA form variation process.

4.3. Prediction of PFAA migration in the natural environment

Currently, several prediction equations for PFAA migration have been developed based on the factors influencing PFAS allocation. Commonly used prediction equations include the Linear Isothermal, Freundlich, Langmuir, and Virial equations [95,103,104]. The Freundlich and Virial equations are used to predict the effects of different physical and chemical properties on the adsorption of PFAAs in soils [95]. However, similar to the studies on PFAA adsorption factors, most prediction studies can only simulate short-term PFAS migration, and the primary prediction methods are adsorption kinetic equations. Existing simulation equations make it challenging to simulate variations in the forms of PFAAs in the

environment. Thus, a more comprehensive kinetic model can be established for the separation of the different forms of PFAAs. Multiple environmental factors, including organic C, minerals, and element cycling, can be integrated into a comprehensive model that accurately simulates PFAA speciation in the environment. For example, by using kinetic transformation models, it is possible to quantify the contribution of Fe-related processes to the speciation of PFAS from multiple elements in the environment.

5. The significance of classifying PFAA forms for remediating PFAS

The Methods for remediating PFAA-contaminated soils can be categorized into three types: physical, chemical, and biological (Table 3). However, the most suitable methods for field applications involve physical adsorption or fixation. Therefore, classifying PFAA forms at different levels in soils during restoration and fixation is helpful to further clarify the effectiveness of remediation methods. Additionally, classifying PFAA forms can further elucidate remediation mechanisms and relate the effects of environmental factors by remediation methods to the speciation of PFAA forms.

5.1. Remediation methods for PFAS-contaminated soil

Physical remediation is the most prominent and highly applicable method and primarily involves adsorption, ion exchange, and physical degradation (Table 3). Many studies have used adsorption to treat PFAS contamination, which is broadly categorized into two types: C materials and the adsorption of other materials. C materials are frequently employed in the treatment of PFAS pollution because of their low cost and excellent adsorption performance [105]. Wood biochar and coconut shell biochar were used to remediate PFAS-contaminated soil, reducing contamination seeping from the soil by 90%. In a dynamic soil column experiment, the immobilization effect of PFAS was decreased by colloidal activated C in contaminated soil [106]. The retardation rate of long-chain PFAS in the treated soil was eight times higher than that in the blank group [106]. A comparison of the adsorption of six types of PFAAs between sewage sludge biochar and wood biochar showed that sewage sludge biochar has a similar adsorption ability to wood biochar [107]. In addition to C materials, researchers have explored the use of resin materials, metal materials, and metal-organic frameworks to dispose PFAS pollution. A comparison between the PFOA adsorption abilities of Zn-Al and Mg-Al-layered double hydroxides showed that the adsorbed materials were almost unaffected by NOM but could be disturbed by sulfates [108]. In addition, PFAAs can be adsorbed by Zr-based metal-organic frameworks, and the removal rate can reach 98% within 10 min [109]. The adsorption properties of resins, minerals, biomaterials, and polymers have been suggested for future PFAA restorations [110]. Physical adsorption mainly converts PFAAs (type I) to PFAAs (type II), and although it cannot eliminate PFAAs, it is highly applicable in pollution remediation.

The physical adsorption remediation of PFAA contamination is mainly accomplished by adding materials or applying physical

treatments, thereby altering the K_d value of PFAAs. Various physical methods are available for PFAA degradation, including photodegradation, sonic degradation, thermal degradation, and electron-beam decomposition. After 4 h of ultraviolet irradiation, 90% of the actively absorbed PFOA material was degraded [111]. In addition, sonic degradation is effective for mineralizing PFOA and PFOS [112]. Under the comprehensive consideration of application and economy, the thermal degradation process should be the focus of future studies [113]. Moreover, the use of high-energy electron beams has the potential for PFAS degradation, and the removal efficiency of seven types of PFAS ranged from 49% to 99.9% [114]. Hydrothermal alkaline treatment can effectively degrade PFAAs present in soil, which are mostly degraded to non-detectable levels after treatment [115]. Similarly, piezoelectric material-assisted ball milling is an effective method for PFAA degradation; approximately 80% of 21 targeted PFAAs were destroyed after 6 h of treatment [116]. Furthermore, soil washing/smoldering technologies and persulfate oxidation are in situ methods for degrading PFAAs in soil. According to current research, soil washing/smoldering technologies are more applicable than persulfate oxidation [117–119]. Most physical degradation methods directly destroy PFAA molecules and do not involve PFAA speciation.

In addition to physical methods for PFAS degradation, chemical reduction has proven to be effective. Chemical reduction and oxidation can efficiently degrade PFAS; however, most current methods are unsuitable for large-scale environmental applications. A chemical reaction model demonstrated the defluorination of PFOA by zero-valent Fe and Zn; however, a suitable catalyst was needed to optimize the reaction [120]. Several electrochemical degradation and oxidation methods have proven effective for PFAS remediation, but their viability must be demonstrated at the field scale [121]. In addition, a wetland investigation found that microbial community variation caused by an electron shuttle is important for PFAS removal [122]. Furthermore, vitamin B₁₂ is a new catalyst for branched PFAA defluorination, and the structural optimization and product degradation of vitamin B₁₂ are hot topics [123–125]. In addition to chemical methods, studies also use biological or regulatory ecosystem methods to control PFAS pollution.

Bioremediation methods for PFAS contamination can be divided into microbial degradation, phytoremediation, and mineral-enhanced ecological restoration. Currently, researchers are unable to defluorinate saturated C–F chains using microbes. However, there are effective ways to defluorinate non-saturated C–F chains, such as chlorinated PFCAs, GenX, and 3,3,3-trifluoropropionic acid [126–128]. For phytoremediation, the use of genetic engineering technology to enhance the ability of plants to repair PFAAs is a promising approach [129]. The application of minerals to regulate polluted ecosystems is also a popular method, such as using Fe minerals to enhance a wetland's ability to remove PFAAs and increase the number of bacteria with potential PFAS removal capability [130]. Bioremediation is more environmentally friendly than chemical remediation. However, currently, only phytoremediation has clear mechanisms and practical applications.

Overall, the most applicable remediation methods for PFAS pollution are fixation and adsorption (including physical and plant adsorption). Most fixation and remediation studies have focused on PFAA

Table 3
The summary of PFAS contamination remediation types and specific methods.

Remediation types	Remediation methods	References
Physical remediation	<ul style="list-style-type: none"> Carbon material adsorption: Active carbon, colloidal carbon, and commercial carbon; Other material: Zeolite, chitosan, bentonite, and ion exchange resin; Photodegradation, sonic degradation, thermal degradation, electron beam decomposition, hydrothermal and ball-milling, soil washing/smoldering, in situ oxidation. 	[105–119]
Chemical remediation	<ul style="list-style-type: none"> Chemical reduction or oxidation; Electrochemical reaction; Coenzymes (vitamin B₁₂) catalyze degradation. 	[120–125]
Biological remediation	<ul style="list-style-type: none"> Microbial degradation of functional groups or unsaturated fluorocarbon chains; Plants absorb PFAS from contaminated soil (phytoremediation); Minerals enhance ecological restoration. 	[126–130]

contamination, particularly that of PFOA and PFOS. Therefore, it is important to elucidate the speciation of long-chain PFAAs after fixation. Clarifying the ratios of different types of PFAAs in soils will help evaluate the long-term effectiveness of remediation methods for PFAA contamination. Additionally, the classification of PFAA forms could enhance the mechanism of PFAS remediation, such as using Fe minerals to increase the PFAS removal ability in wetlands. Further associations between PFAA forms, mineral forms, and bacterial communities could be revealed using a kinetic model.

6. Future research perspectives

Considering the widespread presence of PFAAs in soils and sediments, future research is needed in various fields, including environmental chemistry and modeling. This may involve more interdisciplinary collaborations. Based on the current knowledge, the topics proposed below are of general interest and warrant further investigation.

(i) The optimization of the extraction and analysis methods for the four PFAA forms is crucial. Research is required to discover new extraction methods for various PFAA forms, particularly to reduce the complexity and lack of determinacy of the extraction process. This may involve employing simpler extraction steps, milder reaction conditions, and reagents to minimize derivatization reactions and prevent damage to molecular structures. Additionally, further development of analytical instruments with high sensitivity and accuracy is necessary for better analysis of PFAA speciation, particularly at low sample sizes.

(ii) It is essential to establish a kinetic model for PFAA speciation in the environment. Further research requires a comprehensive kinetic model that integrates the four forms of PFAAs, elemental cycles, and microbial activity. One example is the model used for different metal forms [131]. A kinetic model generated by a multistep reaction equation can predict the potential speciation process of PFAAs under different environmental parameters during long-term pollution.

(iii) A biological exposure risk assessment method based on PFAA form classification is significant. Existing transport calculations rely on the PFAA concentrations extracted with organic solvents [12]. Following the classification of PFAA forms, it is essential to consider the bioavailability difference between PFAAs extracted using aqueous methods and those extracted using organic solvents and the re-release risk of soil-embedded or covalently bound PFAA, which could enable a more accurate assessment of the biosafety risks arising from PFAA contamination.

(iv) Classifying different PFAA forms in different media is vital. Suspended matrices exist in water and the atmosphere, providing opportunities for the adsorption, embedding, or covalent binding of PFAAs and influencing various assessments related to PFAA concentrations. There are typically fluctuations in the recovery of PFAAs in water samples [21], and changes in PFAA speciation caused by the interaction between the matrix and PFAAs may be one of the contributing factors. Considering the potential binding forms of PFAAs in minerals, OM, and microbes and evaluating the possible mechanism of PFAA speciation variation is a possible research direction for speciation classification on PFAAs.

(v) In the field of PFAS pollution remediation mechanism research and remediation effect evaluation, various methods are available for reducing the bioavailability of perfluorinated compounds in soils. Soil chemistry and microbial metabolic processes are crucial in the restoration processes [130,132]. PFAA classification can refine and clarify the fixation process involved in soil element cycling and microbial activities, providing a clearer explanation of the fixation mechanism. In addition, the effectiveness of PFAA remediation methods can be assessed using kinetic models based on the classification of PFAA forms.

(vi) Element cycling in the soil is one of the main driving forces for the speciation of PFAA forms. Exploring the relationship between PFAA speciation and elemental cycling (e.g., C, N, P, S, Fe, Al, and Ca) and other metals in soils is an important research direction. Clarifying the interaction between elemental cycling and the speciation of PFAA forms can

promote the development of PFAA pollution remediation technology under different environmental conditions. Most geochemical processes that influence the speciation of PFAAs also affect C and heavy metals in the soil [32,33,35]. Therefore, it is possible to consider greenhouse gas emission reduction and heavy metal passivation in PFAS pollution remediation.

CRedit authorship contribution statement

Chao Guo: Data curation, Software, Visualization, Writing – original draft. **Shiwen Hu:** Writing – review & editing. **Pengfei Cheng:** Conceptualization. **Kuan Cheng:** Investigation. **Yang Yang:** Methodology. **Guojun Chen:** Software. **Qi Wang:** Software. **Ying Wang:** Funding acquisition. **Tongxu Liu:** Conceptualization, Funding acquisition, Investigation, Supervision.

Declaration of competing interests

The authors have declared no conflicts of interest.

Acknowledgments

This study was supported by the Guangdong Major Project of Basic and Applied Basic Research (No. 2023B0303000006), National Natural Science Foundation of China (Nos. 42125704, 42261160644, 42277479, and 42077307), the Guangzhou Basic and Applied Basic Research Foundation (No. 2023A04J0931), and the GDAS' Project of Science and Technology Development (Nos. 2023GDASZH-2023010103, 2022GDASZH-2022010201-04, 2022GDASZH-2022010105 and 2019GDASYL-0102002-2), Guangdong Foundation for Program of Science and Technology Research (No. 2023B1212060044).

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