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Environmental Significance

Per- and polyfluoroalkyl substances (PFAS) represent one of the most challenging classes of recently emerged contaminants due to their extreme persistence, global distribution, mobility, and potential adverse effects on human and ecosystem health. This review provides a comprehensive synthesis of PFAS sources, environmental occurrence, fate and transport, analytical challenges, toxicological risks, regulatory responses, and remediation technologies. It highlights critical knowledge gaps associated with emerging PFAS, precursor compounds, complex mixtures, and cumulative risk assessment, while examining limitations in current monitoring and regulatory frameworks. By integrating advances in analytical science, environmental risk assessment, and remediation, this review identifies key priorities for research, policy harmonization, and sustainable management strategies needed to address PFAS contamination at local, regional, and global scales.



ARTICLE

Per- and Polyfluoroalkyl Substances (PFAS): A Global Review of Sources, Contamination, Risks, Analytical Challenges, and Remediation Strategies

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Per- and polyfluoroalkyl substances (PFAS) are a large class of synthetic fluorinated compounds extensively used in industrial applications and consumer products due to their exceptional chemical stability and resistance to degradation. These same properties, however, contribute to their environmental persistence, leading to global contamination and growing concern over their ecological and human health impacts. This review provides a comprehensive synthesis of current knowledge on PFAS sources, environmental distribution, and transport across water, air, soil, sediments, and biota. It highlights regional disparities in regulatory frameworks and underscores limitations in existing monitoring efforts, including analytical detection challenges and the underrepresentation of emerging PFAS. The toxicological profile of PFAS is examined, with emphasis on bioaccumulation, endocrine disruption, immunotoxicity, and developmental effects. Remediation strategies are critically assessed, including activated carbon adsorption, reverse osmosis, advanced oxidation processes, electrochemical degradation, and in situ stabilization. While progress is being made in reducing exposure and remediation, substantial knowledge gaps remain, particularly regarding methods to characterize and assess the cumulative risk posed by complex mixtures of PFASs. This includes methods to assess the risk posed by PFAS “precursor” compounds, including polyfluoroalkyl substances, that can degrade to “terminal” perfluoroalkyl substances recalcitrant to further degradation. PFAS represent a large and diverse group of fluorinated compounds whose persistence, bioaccumulation, and global distribution have created unique regulatory and remediation challenge. Their chemical diversity and ubiquity call for cross-sector collaboration supported by advanced analytical approaches and adaptive policy frameworks. Therefore, improving PFAS detection and assessment capabilities is essential for developing effective and sustainable remediation strategies. In addition, stronger international collaboration is proposed to address the global nature of PFAS contamination, as addressing the long-term risks posed by PFAS will require an integrated approach grounded in innovation, lifecycle-based regulation, and global coordination.

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Introduction

Per- and polyfluoroalkyl substances (PFAS) constitute a diverse class of synthetic organofluorine compounds known for their exceptional chemical and thermal stability (1). This resilience, attributed to the strength of the carbon–fluorine bond, has made PFAS widely attractive for use in industrial and consumer applications since the 1950s, including aqueous film-forming foams (AFFF), non-stick cookware, water- and stain-resistant textiles and paper products, and metal plating (2, 3). However, the very characteristics that make PFAS useful also render them environmentally persistent and biologically active, leading to their classification as contaminants of emerging concern (CECs) by agencies such as the United States Environmental Protection Agency (4). Due to their widespread use and extreme chemical stability, PFAS have emerged as some of the most persistent and ubiquitous environmental contaminants of the 21st century (5).

A persistent challenge in PFAS research is the lack of universal agreement regarding what constitutes a PFAS. For the purposes of this review, PFAS are defined according to the OECD framework as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (OECD, 2021). This broad definition encompasses thousands of compounds, including perfluoroalkyl acids, fluorotelomer-based compounds, side-chain fluorinated polymers and precursor compounds.

Alternative definitions have also been proposed. For example, Schymanski et al. (2023) advocated for a structurally broader classification to improve transparency in chemical inventories and hazard assessment. Depending on the definition adopted, estimates of the total number of PFAS range from approximately 4,000 to over 15,000 compounds globally. This definitional variability has important implications for regulation, monitoring, toxicology and remediation because it determines which compounds are included in analytical target lists and regulatory frameworks. This definitional complexity underpins many of the challenges discussed throughout this review, particularly those associated with analytical detection, regulatory classification, risk assessment and remediation of PFAS-contaminated environments.

PFAS are distinguished by their amphiphilic nature and strong carbon–fluorine bonds, which confer exceptional resistance to thermal, chemical, and biological degradation (6, 7). PFAS encompass anionic, cationic, zwitterionic, and neutral forms (8, 9). Their behaviour in the environment is further complicated by diverse chain lengths, functional groups, and physicochemical properties. This vast chemical diversity complicates regulatory classification, analytical detection, and toxicity

prediction, with only a small fraction of the PFAS compounds being adequately studied or regulated to date.

PFAS have now been detected in virtually every environmental compartment, including soil, groundwater, rain, surface water, air, and biological tissues and even in remote locations - highlighting their global pervasiveness and environmental mobility (1, 10). Their distribution is driven by both point sources (e.g., industrial discharges, military bases) and diffuse sources (e.g., atmospheric transport, consumer products), with significant implications for environmental management and public health.

More than 15,000 PFAS-related compounds are either known or commercially active (11). Although legacy compounds such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have been restricted or phased out in several jurisdictions, they are increasingly being replaced by short-chain and polymeric alternatives whose fate and toxicological behavior remain poorly understood (12, 13). This transition—often referred to as "regrettable substitution"—has led to the continued environmental loading of novel PFAS compounds, which present new analytical and regulatory challenges due to their variable structures, lack of toxicological data and poorly characterized environmental pathways.

The environmental fate and transport of PFAS are dictated by their chain length, hydrophobicity, and functional groups. Long-chain PFAS tend to bioaccumulate most readily and sorb strongly to soils and sediments, persisting in terrestrial systems, while short-chain PFAS and precursors are more water-soluble and mobile, facilitating long-range transport through groundwater and surface water (6, 14). This mobility has resulted in contamination of critical resources such as agricultural systems, drinking water aquifers and aquatic biota.

In parallel, toxicological research continues to identify a broad spectrum of potential health impacts linked to PFAS exposure, including immunotoxicity, endocrine disruption, reproductive and developmental disorders, hepatic effects, and certain cancers (15, 16). These effects are often mediated by molecular pathways involving nuclear receptors such as PPAR α , as well as oxidative stress and hormonal disruption (17). Alarming, PFAS have been detected in maternal and cord blood as well as in breastmilk, indicating potential transgenerational risks (18).

Growing awareness of PFAS health risks has prompted more stringent regulatory scrutiny.



Epidemiologists in the USEPA, for example, recently proposed toxicity factors for PFOA and PFOS and four other compounds that would equate to drinking water advisory levels well below one part per trillion and below levels detectable by commercial laboratories (19-22). Regulatory limits were ultimately set at much higher levels (i.e. PFOS and PFOA MCLs of 4 ppt) deemed to be measurable and achievable (21, 22). Debates have also arisen over the scientific defensibility of toxicity factors based on epidemiological studies versus more controlled animal studies (23-26). As a result, regulatory approaches remain fragmented. While the European Union has moved toward class-based restrictions under REACH, other countries like the United States, Canada, Japan, and Australia continue to regulate PFAS on a compound-by-compound basis, leading to inconsistencies in exposure limits and management strategies (27).

Monitoring PFAS in the environment presents additional challenges. Despite the availability of advanced analytical techniques such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) and high-resolution mass spectrometry (HRMS), many programs still focus on a limited suite of legacy compounds (28). Novel methods like total organic fluorine (TOF) and total oxidizable precursor (TOP) assays offer broader screening potential but lack standardization and clarity between agencies regarding toxicological relevance.

Beyond science and regulation, PFAS also present profound social and economic challenges. Affected communities—often located near contamination sources—face disproportionate exposure risks, environmental injustice, and barriers to remediation or compensation. Meanwhile, industries, municipalities, and governments bear the growing financial burden of cleanup and legal liabilities. In the United States alone, PFAS remediation costs are projected to reach tens of billions of dollars over the next decade (19).

In this context, a comprehensive review is urgently needed to synthesize the expanding body of knowledge on PFAS sources, pollution patterns, analytical methods, risks, and remediation approaches. As shown conceptually in Figure 1, this paper critically examines:

1. Environmental sources and pathways of PFAS contamination;
2. Global pollution trends and regulatory responses;
3. Analytical methods for PFAS detection and monitoring;

4. Toxicological risks to humans and ecosystems;
5. Environmental fate and transport mechanisms;
6. Emerging remediation technologies;
7. Key research and regulatory gaps.

Expanded information on these topics is provided in (29). Through this integrative review, we aim to provide a foundation for improved environmental governance, regulatory harmonization, and the development of safer chemical alternatives.

Given these challenges, crcCARE organised a PFAS experts' symposium with a view to determining key research gaps with particular emphasis on Australian conditions. The team of experts included regulatory representatives from Australia, the United States, Canada, and Finland and practitioners currently engaged with PFAS assessment and remediation.



Figure 1: Key features of this review article.

We conclude by identifying critical research needs and policy priorities to support more effective and coordinated responses to this persistent and complex environmental challenge.

Impacted Environmental Media: Sources and Pathways of PFAS Contamination

PFAS are pervasive across nearly all environmental compartments, driven by their chemical stability, high mobility, and widespread use (5, 30, 31). Understanding their distribution in water, air, soil, sediments, and biota is critical for assessing environmental fate, informing regulatory actions, and guiding effective remediation efforts. This section synthesizes current knowledge on



PFAS occurrence across environmental media and examines the primary pathways and mechanisms contributing to their contamination.

A significant global knowledge gap remains regarding PFAS occurrence across the Global South. Most occurrence data originate from North America, Europe, China, Japan and Australia, reflecting stronger analytical infrastructure and regulatory investment in these regions. In contrast, data from Africa, South America, Southeast Asia and many small island nations remain sparse.

Where monitoring has been undertaken in developing regions, elevated PFAS concentrations are frequently associated with manufacturing zones, fluorochemical production facilities, airports, military installations, landfill leachate disposal and wastewater reuse systems. This suggests that contamination patterns are strongly linked to both industrial activity and waste management practices, although under-reporting remains substantial due to limited monitoring capacity.

Water (Surface Water and Groundwater)

Aquatic systems are among the most affected by PFAS contamination due to the high solubility, persistence, and resistance to degradation of these compounds (5, 32). Surface water and groundwater serve both as reservoirs and transport pathways, with contamination originating from sources such as firefighting foams, industrial discharges, and landfill leachate (30). These compounds can be transported far from their sources via stormwater, river systems, and infiltration pathways (33). In Australia, PFAS levels in surface water have reached median concentrations of 63.5 ng/L across 33 compounds, with some sites reporting up to 526 ng/L (34). Groundwater samples have revealed mean concentrations as high as 8,740 ng/L for 27 compounds. The presence of PFAS in the atmosphere also contributes to PFAS presence in precipitation, with PFOS and PFOA median levels ranging from 3 to 10 ng/L (35).

Air and Atmospheric Transport

The atmosphere, though often underrepresented in PFAS monitoring, plays a critical role in their global dispersion. Volatile precursors such as fluorotelomer alcohols (FTOHs) are emitted from manufacturing, firefighting activities, and consumer products (36). These substances undergo long-range atmospheric transport and reaction to perfluorinated carboxylic acids (PFAAs) (37) and are redeposited via precipitation and dust, enabling PFAS detection in remote areas (38). Indoor air and dust are notable pathways for human exposure. PFAS levels in household and fire station dust often exceed 100 ng/g, with concentrations of N-EtFOSAA - primarily used for

water and stain resistance in textiles, carpets, paper and insecticides, reaching up to 1,800 ng/g (39). This suggests that indoor environments can act as persistent secondary exposure sources.

Soil and Sediment

Soils and sediments act as both sinks and secondary sources of PFAS contamination. Inputs include industrial emissions, atmospheric deposition, biosolid application, and AFFF use at military and airport sites (40). PFAS can leach into groundwater, being carried into surface water bodies by runoff or be taken up by vegetation, enabling transfer through terrestrial and aquatic food webs (41). In Australian sediments, average concentrations of four or more legacy PFAS species such as PFOA and PFOS reach 0.35 ng/g dry weight (34), while lake sediments globally have reported concentrations ranging from 1.038 to 6.979 ng/g (42). Sediments in contaminated zones may release PFAS through desorption and remobilization, especially under dynamic redox conditions (43).

Wastewater Treatment Plant Effluent and Sludges

The presence of PFAS in municipal and industrial wastewater effluent and sludges (biosolids) is well documented (44-48). PFAS are present in wastewater both from point sources, and also pervasively from the use of PFAS in a wide range of consumer products. Methods such as Total Oxidizable Precursor assays and analysis for Total Organic Fluorine indicate a complex mix of identifiable as well as unidentifiable terminal endpoint compounds, precursor compounds and partially oxidized intermediates. Effluents from municipal wastewater treatment plants that lack significant industrial input tend to be dominated by ultrashort (and shorter-chain compounds). This can include PFASs such as perfluoroethanoic acid (trifluoroacetate) formed from pharmaceuticals containing a CF₃-group and perfluoropropanoate as well as other organofluorine compounds and can dominate wastewater effluent – (49, 50). The high organic content of sludges serves as a sponge for broad range of compounds, including longer-chain PFASs.

The specific types of PFAS compounds present and potential risks to human health and the environment posed by these compounds requires additional research. Adverse uptake of these compounds into food crops cultivated in fields amended with sludges and biosolids or irrigated with PFAS-contaminated wastewater is a rapidly evolving field of research (51-58). Crops are especially vulnerable to uptake of more mobile, short-chain and ultrashort compounds. Dissolve-phase, longer-chain compounds can also be taken up if present in irrigation



water or water in newly applied sludges. Longer-chain PFAS pose the highest potential for uptake and accumulation into livestock, such as cattle, and there is growing evidence of elevated consumer exposures to non-regulated long-chain PFAS (such as PFDA) where livestock are raised on land treated with biosolids (59).

Biota (Plants and Animals)

Biota serve as both receptors and indicators of PFAS exposure. These compounds bioaccumulate through ingestion, inhalation, or dermal contact, impacting organisms at multiple trophic levels (60). Plant uptake from contaminated soil or water is species-dependent (61, 62). PFAS is also readily taken up into terrestrial invertebrates such as earthworms (63, 64), resulting in significant food-chain accumulation through terrestrial ecosystems, or in foraging livestock such as chickens, which readily pass PFAS into eggs, resulting in potential human exposure (65). Aquatic species are particularly vulnerable. PFAS concentrations in Australian freshwater turtles have reached ~3.70 mg/kg (66), and Burrunan dolphins show hepatic levels up to 19.5 mg/kg across 25 compounds (67). In livestock, PFAS accumulation in organs such as the liver and in muscle (meat) and milk raises concerns about dietary exposure from meat and dairy (68, 69), particularly for longer-chain PFAS. These findings highlight the systemic and potentially intergenerational risks associated with PFAS contamination.

Critical Knowledge Gaps

Despite growing research and regulatory attention, several key knowledge gaps continue to limit our understanding of PFAS behaviour, exposure pathways, and long-term risks:

- Limited monitoring of emerging PFAS: Most environmental surveillance focuses on a small group of well-known legacy compounds (e.g., PFOA, PFOS), overlooking emerging, ultrashort, short-chain, or proprietary PFAS with unknown environmental persistence and toxicological profiles.
- Underdeveloped understanding of atmospheric transport: Although atmospheric pathways are recognized as important for long-range PFAS dispersion, quantitative models describing precursor transformation, transport, and deposition dynamics remain insufficiently developed.
- Scarcity of long-term studies of PFAS uptake in biota and ecosystems toxicity data: Data on chronic exposure, biomagnification, trophic

transfer and health effects particularly within terrestrial ecosystems are limited. This is especially the case for PFAS other than the well-known legacy compounds. This impedes our ability to assess ecosystem-level impacts or uptake into human foodstuffs.

- Uncertainty in soil interactions: The behaviour of PFAS in soil, including sorption, leaching, and potential degradation, especially for short-chain and novel compounds is poorly characterized, limiting the accuracy of predictive transport models.
- Inadequate linkage between environmental levels and human exposure: The relationship between environmental PFAS concentrations and human internal dose is complex and poorly quantified for the majority of PFAS compounds, highlighting the need for integrated multimedia exposure assessments and expanded biomonitoring.

Filling these knowledge gaps is critical for improving risk assessments, establishing science-based regulatory thresholds, and informing the development of targeted remediation strategies and effective policy responses.

Global PFAS Pollution Trends and Regulatory Frameworks for Environmental Media

PFAS are now recognized as pervasive global contaminants, present in nearly all environmental compartments—including soil, groundwater, surface water, sediments, and biota. Their extreme persistence, mobility, and potential for bioaccumulation have resulted in PFAS being detected across diverse ecosystems, from Arctic snowpacks to agricultural and urban groundwater (2, 70). Increasing concentrations in drinking water, agricultural zones, and urban catchments have been traced to point sources such as industrial facilities, airports, wastewater treatment plants, and legacy use of aqueous film-forming foams (71, 72).

Recent international alignment efforts have emerged, with Australia, Canada, and the EU progressively harmonizing PFAS health-based guidelines with (4) revisions for PFOA and PFOS. However, variability in toxicity values, which includes discrepancies in toxicity assessment methodologies, could lead to inconsistencies across jurisdictions, complicating health risk assessments (73). Also, the enormity of the PFAS inventory further exacerbates prioritization challenges, which points to the



importance of adaptive, tiered regulatory testing frameworks (74).

Regulatory Responses and Fragmentation

Global regulatory responses to PFAS contamination remain highly fragmented, varying across countries and environmental media. Drinking water has received the most regulatory attention. For example, the USEPA recently finalized enforceable Maximum Contaminant Levels (MCLs) for six PFAS, including a cumulative hazard index for mixtures (20). Drinking water standards for four of the compounds - GenX, PFHxS, PFNA, and PFBS, have since been challenged in court and are anticipated to be rescinded (19). The European Union, under the Drinking Water Directive, has adopted a group-based regulatory approach and is advancing broad restrictions under the REACH framework for over 10,000 PFAS (27).

In contrast, standards for PFAS in soil, sediment, and groundwater are either absent or inconsistent across jurisdictions. Australia's PFAS National Environmental Management Plan (NEMP 3.0) provides detailed guidance values for various media, yet most countries lack binding cleanup criteria or harmonized risk assessment methods (75). Additionally, where guidance values are available, they often do not consider the exposure pathways driving potential risks (for example, uptake into foodstuffs). Indeed, assessment of such pathways will in many instances require case-specific analysis due to variability in soil and crop type. Regulatory agencies often lack in-house expertise and diverge in how PFAS mixtures, precursors, and total organofluorine (TOF) are assessed, complicating remediation planning and liability assessments.

Policy Gaps and Conservative Approaches

Despite growing evidence of PFAS-related hazards, policy responses have been largely reactive and narrow in scope. Most frameworks continue to target a limited set of legacy compounds (e.g., PFOA, PFOS), overlooking the vast number of emerging ultrashort and short-chain PFAS now in circulation or the longer-chain PFAS associated with biosolids applications, and which are known to have high bioaccumulation potential. The limited availability of guidance for characterization and assessment of complex mixtures of PFASs as well as enforceable thresholds in soil, sediment, drinking water and food limits effective risk management, particularly in contexts such as land redevelopment or wastewater and biosolid reuse (28).

Attempts to consider the full scope of PFAS potentially present in environmental media have

been inconsistent. Regulatory inertia is often driven by the presence or absence of in-house expertise, analytical challenges, economic implications of phase-outs, and industry opposition. Many governments also lack the institutional capacity or political will to implement comprehensive investigation guidance, group-based restrictions or adopt lifecycle-based chemical management strategies (76).

Challenges of PFAS Group-Based Regulation

One of the most significant regulatory challenges in PFAS management is determining how PFAS should be grouped for assessment and regulation. Given the large number and structural diversity of PFAS compounds, and the practical difficulty of regulating each individually, many jurisdictions are increasingly moving toward group-based regulatory approaches (77, 78). However, defining meaningful PFAS groups remains scientifically complex. Grouping based on **chain length** (e.g., short-chain versus long-chain PFAS) is widely used because it often correlates with environmental mobility, bioaccumulation potential and toxicokinetics; however, this approach may oversimplify important differences in toxicity and environmental behaviour within individual compound classes (79). **Functional group-based classification**, including perfluoroalkyl carboxylic acids, perfluoroalkane sulfonic acids, fluorotelomer compounds and fluoropolymers, provides improved chemical specificity but remains challenging due to transformation pathways and the presence of precursor compounds (80). Further complexity arises when distinguishing **precursor compounds from terminal degradation products**, as many precursor compounds transform over time into persistent perfluoroalkyl acids, complicating both risk assessment and regulatory monitoring (76). More recently, **mobility-based grouping** has gained increasing attention due to the potential for highly mobile PFAS to contaminate groundwater and drinking water supplies, while **persistence-based grouping** has also been proposed because extreme environmental persistence is a defining characteristic shared across many PFAS regardless of toxicological profile (8, 78). While each grouping strategy offers practical regulatory advantages, none is universally applicable across all policy or environmental contexts. Ultimately, PFAS group-based regulation requires balancing **practicality, enforceability and analytical feasibility** with **scientific defensibility**, toxicological uncertainty and the evolving understanding of PFAS behaviour across environmental and biological systems.

The Challenge Ahead



Addressing the global PFAS crisis will require a shift from chemical-specific regulation toward more holistic, precautionary, and adaptive policy frameworks. This includes expanding monitoring to capture emerging PFAS and transformation products, improving methods to assess the cumulative risk posed by complex mixtures of PFASs, developing total PFAS metrics (e.g., Total Organofluorine [TOF] and total fluorine [TF]), and adopting remediation standards that are both technically and economically feasible and socially equitable. International harmonization of standards and guidance for assessment of PFAS risk, coupled with site-specific flexibility, is essential for addressing the transboundary nature and systemic risks of PFAS contamination.

Analytical Methods for Detection and Quantification of PFAS: Advances, Limitations, Data Use and Research Needs

Recent advances in analytical chemistry have led to the identification of PFAS in soil, water, and plant matrices. Because of the high chemical diversity within this class and the lack of reliable standards, LC-MS/MS, which remains the analytical benchmark, frequently quantifies less than 100 distinct PFAS (81). Nontarget high-resolution mass spectrometry (NTS-HRMS) can currently detect multiple PFAS from many chemical classes in biological and environmental samples. This method significantly enhances our understanding of contamination complexity (82, 83).

Accurate detection and quantification of PFAS across environmental media are essential for site assessment, regulatory compliance, and remediation. The chemical diversity, ultra-low concentrations (often ppt levels), and presence of numerous precursors and transformation products complicate analysis. Despite advances, challenges remain in sensitivity, compound coverage, and standardization. Utility of the more comprehensive data likewise remains limited due to the lack of toxicity factors for precursor compounds and partially degraded or transformed PFAS that characterize wastewater, sludges and other environmental media.

Sample Preparation Approaches and Associated Limitations

Sample preparation remains a critical step in PFAS analysis, as the accuracy, sensitivity and reproducibility of instrumental detection are strongly influenced by extraction efficiency, matrix interferences and analyte recovery (84, 85). Selection of an appropriate sample preparation method depends on sample type, target

analytes, expected concentration range and the analytical platform employed.

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Among the most widely applied techniques, solid-phase extraction (SPE) remains the dominant method for aqueous matrices including groundwater, surface water, wastewater and landfill leachate. SPE offers efficient analyte pre-concentration, improved method sensitivity and cleaner extracts for downstream LC-MS/MS analysis (84, 86). However, SPE recoveries can vary substantially depending on cartridge sorbent chemistry, sample pH, dissolved organic carbon concentration, ionic strength and the physicochemical properties of individual PFAS compounds. Matrix suppression resulting from co-eluting dissolved constituents remains a significant challenge, particularly in complex matrices such as landfill leachate, biosolids extracts and industrial wastewaters (87, 88).

For solid matrices including soils, sediments, biosolids and biological tissues, solvent extraction methods are widely used, typically employing methanol, acetonitrile or alkaline solvent mixtures to desorb PFAS from solid phases prior to analysis (89). Ultrasonic extraction is also frequently applied to improve extraction efficiency by enhancing desorption from mineral and organic surfaces. While these approaches are practical and broadly applicable, extraction efficiency is often matrix-dependent and influenced by organic matter content, mineral composition, moisture content and PFAS chain length. In addition, co-extraction of natural organic matter, lipids and dissolved organics may interfere with subsequent instrumental analysis and contribute to ionisation suppression or enhancement during electrospray ionisation LC-MS/MS (90).

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) approaches have also been increasingly explored for PFAS extraction, particularly in food matrices, biological tissues and other complex environmental samples. These methods offer advantages in simplicity, speed and throughput; however, application to PFAS remains less standardised compared with SPE-based workflows, and extraction efficiencies may vary significantly between compound classes and matrices (91, 92).

In contrast, direct injection approaches are increasingly applied for relatively clean aqueous matrices or targeted screening applications where PFAS concentrations are elevated. These methods minimise sample handling, reduce contamination risks and enable faster analysis. However, they are generally more susceptible to matrix interference and typically provide higher detection limits compared with extraction-based methods, particularly when ultra-trace quantification is required (86).

Beyond conventional grab sampling, passive sampling approaches such as Polar Organic Chemical Integrative Samplers (POCIS) and sorbent-based passive samplers are increasingly being used for PFAS monitoring in surface waters, porewaters and wastewater systems. These approaches provide time-integrated concentration



estimates and are particularly useful where PFAS concentrations vary over time or where long-term monitoring is required (93). However, uncertainties in uptake kinetics, compound-specific sampling rates, environmental conditions and calibration remain limitations to broader application and standardisation.

Despite significant analytical progress, PFAS sample preparation continues to face several challenges. These include matrix suppression during electrospray ionisation, poor or variable recoveries—particularly for short-chain PFAS and precursor compounds—co-extraction of dissolved organic matter and background fluorinated contaminants, and the lack of harmonised protocols across laboratories and environmental matrices (88, 89). Continued efforts toward method harmonisation, improved quality assurance procedures and inter-laboratory standardisation will be essential to improve comparability and confidence in PFAS monitoring worldwide.

Targeted Analytical Techniques

Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)

LC-MS/MS is currently the most widely used technique for PFAS analysis due to its high sensitivity, selectivity, and ability to quantify compounds at ng/L or ppt levels in complex matrices. Targeted LC-MS/MS methods rely on pre-defined compound lists, typically covering 20–50 well-characterized PFAS, including legacy substances such as PFOA, PFOS, and PFHxS (94, 95).

Sample preparation often includes solid-phase extraction (SPE), filtration, and concentration steps tailored to specific media (e.g., water, soil, sediment, biota). Method validation is guided by protocols from agencies such as the USEPA (e.g., Method 1633, 2024) and International Standards Organization (ISO), though analytical performance can vary depending on laboratory proficiency and matrix complexity (4).

High-Resolution Mass Spectrometry (HRMS)

High-resolution instruments such as quadrupole time-of-flight (QTOF) or Orbitrap mass spectrometers enable suspect and non-target screening of PFAS beyond standard analyte lists. HRMS is particularly useful for identifying unknown compounds, precursors, and transformation products (96). However, this technique requires extensive data processing and high-level expertise, and compound identification is often limited by the availability of reference standards and spectral libraries.

Gas Chromatography Mass Spectrometry (GCMS) View Article Online DOI: 10.1039/D6VA00165C

While LC-MS/MS remains the dominant analytical platform for ionic PFAS, GC-MS plays an important role in measuring volatile and semi-volatile PFAS precursors, particularly fluorotelomer alcohols and neutral precursor compounds in air, dust and indoor environments.

Emerging and Complementary Approaches

Total Oxidizable Precursor (TOP) Assay

Individual laboratory identification and assessment of risk posed by the multitude of PFAS precursor compounds potentially present in contaminated, environmental media is currently not practicable. The TOP assay is designed to oxidize PFAS precursors—such as fluorotelomer-based compounds—into terminal perfluoroalkyl acids (PFAAs), which can then be measured using LC-MS/MS (97). The types and concentrations of additional, “secondary” terminal PFASs generated by TOP processing of samples is used by some agencies to quantify the collective health risk posed by precursors in samples (98).

Examples include the use of TOP processing of soil impacted by releases of “modern” AFFF and 6:2 FtTAoS, a primary PFAS used in many types of AFFF since 2005 (99). Potential exposure risk is quantified based on the types and concentrations of short-chain terminal endpoint compounds generated, for example PFHxA and PFHpA. Reliance on only data for primary terminal endpoint PFASs originally present in the sample such as PFOS and PFHxS could significantly underestimate risk for post-2005 releases of modern AFFF, since these compounds are no longer used in AFFF.

Field studies that incorporated TOP assay have documented a dominance of PFAS precursor compounds in sludges generated by wastewater treatment plants (46–48). TOP processing methods can also provide an estimate of the total precursor burden in a sample and be particularly useful for assessing treatment design and efficacy. Improvements in TOP methods to ensure more complete oxidation of precursor compounds are underway by research institutes and commercial laboratories in conjunction with an increasing understanding of the toxicity and risk posed by precursor compounds.

Total Organic Fluorine (TOF)

TOF analysis provides a measure of the total fluorine associated with organic fluorinated substances within a sample. Because fluorine content varies between compounds, TOF does not directly quantify the mass concentration of individual PFAS or total organic



compound concentration. Techniques such as combustion ion chromatography (CIC) and particle-induced gamma-ray emission (PIGE) are frequently used to estimate total fluorine or extractable organofluorine. However, unless combined with appropriate sample preparation or subtraction approaches, these techniques generally do not distinguish organic fluorine from inorganic fluoride species. This limitation should be considered when interpreting TOF data in environmental matrices. Methods for testing of TOF in air or vapor samples are currently in development. Current field and laboratory methods are limited to quantification of Total Fluorine in industrial stack emissions (100).

TOF lacks specificity and cannot differentiate between PFAS and other fluorinated organics attributable to non-PFAS-related sources. Knowledge of the source and comparison of the concentration of organic fluorine predicted by individual identified PFASs to the concentration of TOF measured in a sample can, however, be used to identify the presence of additional PFAS-related compounds in environmental media. Nontargeted analysis can help identify the specific type or types of compounds associated with the excess organic fluorine but not the concentrations of the compounds. The concentration of excess organic fluorine identified in a sample in conjunction with nontargeted analysis is used by some agencies to assign a composite toxicity factor to this group of compounds and use the data to help quantify the total (cumulative) risk posed by the mixture of PFAS in the sample as a whole (98) (refer to Section 6). TOF analysis can also be valuable for estimation of the total PFAS burden and design of remedial actions when specific compounds are unknown or undetectable using targeted methods (101).

Media-Specific Analytical Challenges

Analysing PFAS across various environmental media presents unique technical difficulties. Water samples typically allow for high analytical sensitivity; however, they are often affected by matrix interferences such as natural organic matter, dissolved ions, and surfactants, which can complicate detection and quantification. In contrast, soils, sediments and sludges pose challenges due to the strong sorption of PFAS to mineral and organic components, necessitating rigorous extraction and cleanup protocols to ensure accurate results. Biota and food matrices add further complexity, requiring controlled digestion methods that preserve the chemical integrity of PFAS while ensuring efficient recovery. Meanwhile, air and dust samples are particularly difficult to analyse due to the volatility and trace-level concentrations of PFAS precursors, such as fluorotelomer

alcohols, which often demand highly sensitive techniques and specialized sampling methods (102).

Table 1 summaries key analytical methods used for PFAS detection, including their principles, target compounds, strengths, limitations, and applicability across environmental media (water, soil, sediment, air, and biota). Selection of a specific method is dependent on the media of interest as well as the objectives of the investigation.

Table 1 Summary of PFAS Analytical Methods and Their Applications Across Environmental Media (See appendix)

Key Limitations and Analytical Gaps

Despite advancements in PFAS detection, several analytical limitations continue to hinder comprehensive assessment. One major challenge is the limited compound coverage—most targeted analytical methods detect only a small fraction of the estimated 15,000+ PFAS compounds currently in use (70). Expansion of detection capabilities can help better understand PFAS sources and toxicity. Additionally, there is a lack of standardized and validated protocols for emerging and complex matrices such as landfill leachate, biosolids, and construction materials, which further complicates consistent monitoring efforts. The scarcity of commercially available reference standards and toxicity factors for many novel PFAS also restricts accurate quantification and inter-laboratory comparability. This issue is compounded by significant variability in recovery rates, detection limits, and quantitation accuracy across laboratories, as noted by (28). Detection and quantification of PFAS precursors presents an additional layer of complexity, as these compounds often transform in unpredictable ways. Grouping of PFAS in a manner that focuses on terminal endpoint compounds originally present in a sample and terminal endpoint compounds generated by TOP processing of a sample combined with consideration of TOF data can help avoid the need to identify each individual compound present in the targeted media (refer to Section 6; (98)). Refinement of the test methods and approaches to assess risk will be necessary, however, as our understanding of these complex mixtures of compounds expands.

Emerging Opportunities: Machine Learning and Artificial Intelligence in PFAS Analysis

Emerging machine learning (ML) and artificial intelligence (AI) tools may offer an important pathway to address several current analytical limitations in PFAS science. Predictive modelling approaches can assist in prioritising PFAS compounds lacking analytical standards, estimating physicochemical properties, supporting suspect screening workflows, and predicting environmental



behaviour, transport or toxicity where empirical data remain unavailable. Machine learning algorithms have also shown increasing potential for interpreting high-resolution mass spectrometry datasets, identifying unknown PFAS signatures, and improving compound annotation in non-target screening applications. As PFAS monitoring continues to move beyond targeted analysis toward broader chemical intelligence, AI-assisted analytical workflows may play an increasingly important role in accelerating compound identification, improving data interpretation and supporting risk-based decision-making in complex environmental systems.

Future Directions

To address current analytical challenges in PFAS detection, several key priorities must be advanced. Expanding the use of non-targeted and suspect screening approaches is essential, particularly when supported by comprehensive spectral libraries and shared databases that facilitate the identification of unknown or emerging PFAS. Standardizing extraction and analytical protocols across a range of complex environmental matrices—such as biosolids, leachates, and building materials—is equally critical to ensure consistency and comparability of results. Additionally, increasing the availability of analytical standards, especially isotopically labelled surrogates for novel compounds, will significantly enhance the accuracy and scope of PFAS quantification. A more integrated approach that combines complementary methods, including LC-MS/MS, TOP assays, and TOF analysis, can provide a more complete profile of PFAS contamination and cumulative toxicity. To improve data reliability, strengthening quality assurance and quality control (QA/QC) procedures and promoting inter-laboratory harmonization are vital. Finally, the development of portable, field-deployable sensors could enable more rapid and cost-effective PFAS screening at contaminated sites, supporting real-time decision-making and broader environmental monitoring efforts. Aligning analytical capabilities with evolving regulatory frameworks particularly group-based or total PFAS metrics will be critical for accurate exposure assessment and remediation monitoring, especially in non-aqueous matrices such as concrete, biosolids, and landfill leachate.

Environmental Fate, Transport Behaviour, and Exposure Pathways of PFAS: Current Knowledge, Gaps, and Future Needs

A critical aspect of understanding and managing PFAS contamination lies in elucidating their fate and transport mechanisms, particularly within the

unsaturated (vadose) and saturated zones of the subsurface. This understanding underpins the development of accurate risk assessments, regulatory frameworks, and site-specific remediation strategies.

In both unsaturated and saturated zones, advection, dispersion, and sorption dominate PFAS transport (74). Amphiphilic PFAS can form multi-layered assemblies on surfaces such as concrete and firefighting infrastructure, making desorption more difficult and extending their persistence in built environments. These physicochemical interactions require mechanistic models that incorporate surface partitioning and precursor transformation to predict site-specific behaviour (14).

Table 2. Summary of Key PFAS Transport Mechanisms Across Environmental Media

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PFAS in the Unsaturated Zone

The unsaturated zone is often the first environmental compartment encountered by PFAS following release from sources such as firefighting foam application, biosolids, or landfill leachate. Transport in this zone is largely governed by advection, dispersion, and sorption, with the latter strongly influenced by site-specific factors such as soil moisture content, organic carbon content, and PFAS chain length (103, 104).

Long-chain PFAS typically show higher affinity for soil organic matter, while short-chain PFAS and precursors are more mobile and water-soluble (105). However, emerging evidence indicates that traditional sorption models—relying on organic carbon–water partition coefficients (K_{oc}) are insufficient to fully predict PFAS behaviour in unsaturated soils (14). Processes such as air–water interfacial sorption and surface tension effects also play a significant role in PFAS retention, particularly under low moisture conditions (106). These complexities challenge conventional contaminant transport models and necessitate new conceptual frameworks tailored specifically to PFAS. The use of soil column leaching methods to directly assess the potential for adverse leaching of PFASs from impacted soil offers one potential solution. Cost-effective use of such methods requires modification to accommodate larger and more representative field samples and a reduction in the number of leachate samples requiring analysis in order to answer specific investigation questions.

PFAS in the Saturated Zone

Once PFAS reach the saturated zone, they can persist for decades due to their low retardation factors and limited degradation under typical environmental conditions. Precursor compounds can be degraded in water substrates to terminal endpoint compounds by naturally occurring microorganisms. Unlike many organic pollutants, however, terminal endpoint PFAS are generally not readily biodegraded, leading to the development of persistent plumes that threaten drinking water supplies and aquatic ecosystems (14, 33).

PFAS transport in groundwater is influenced by a combination of hydrogeological heterogeneity, electrostatic interactions, and solution chemistry. For instance, divalent cations like calcium and magnesium can facilitate sorption of PFAS to mineral surfaces by modifying charge characteristics. In contrast, elevated pH and ionic strength can enhance PFAS mobility (107). Co-contaminants and fluctuating redox conditions further

complicate transport behaviour, yet these interactions are seldom incorporated into existing predictive models.

Knowledge Gaps and Research Challenges

Despite a growing body of literature, several key knowledge gaps continue to limit our ability to predict PFAS behaviour in complex environmental systems:

- **Partitioning and Interfacial Behaviour:** Most fate and transport models do not account for interfacial partitioning between air, water, and solids. This omission leads to underestimation of PFAS retention in the vadose zone and overprediction of vertical mobility (106).
- **Chemical Diversity and Transformation:** The PFAS class includes thousands of compounds, yet the majority of research focuses on a few legacy long-chain, terminal endpoint substances like PFOA and PFOS. Ultrashort, short-chain, polyfluorinated alkyl substances and polymeric alternatives may exhibit very different transport and transformation dynamics, which remain under-characterized (76, 108).
- **Degradation Mechanisms:** Although PFAS are generally resistant to biodegradation, some transformation can occur under specific conditions, such as anaerobic environments or in the presence of co-metabolites. The lack of clarity around precursor transformation pathways impedes the development of accurate models and risk assessments (17).
- **Coupled and Multiphase Processes:** PFAS often co-occur with other contaminants like hydrocarbons or chlorinated solvents. Their interactions and the influence of seasonal hydrological shifts are poorly understood and rarely incorporated into existing fate and transport models (28).

The Way Forward

Addressing these challenges will require interdisciplinary collaboration, expanded field-scale studies, and standardization of analytical protocols. Inadequately designed laboratory column studies, though valuable, often fail to replicate the heterogeneity and dynamics of real subsurface environments. More reliable and defensible sample collection methods, including the use of Decision Unit and Multi Increment Sample investigation methods, are also needed to expedite



characterization of environmental media, assess risk and design efficient remedial actions (109).

As regulatory thresholds tighten globally often reaching parts-per-trillion levels the need for precise, predictive modelling tools becomes increasingly urgent. Enhanced fate and transport models are essential for defining contaminant migration pathways, informing health-based exposure models, and guiding long-term monitoring and remedial design. Improved modelling frameworks should incorporate air–water interfacial sorption, precursor degradation, and coupled contaminant interactions.

In conclusion, advancing our understanding of PFAS fate and transport across both unsaturated and saturated zones is pivotal to mitigating long-term environmental and health risks. A more holistic, systems-based approach is required to support sustainable site management and effective policy development.

Health and Ecological Risks of PFAS: Current Knowledge, Emerging Evidence, and Data Gaps

PFAS have become a major global public health and ecological concern due to their persistence, widespread distribution, bioaccumulative nature, and growing evidence of toxicity (5). Over the past two decades, a substantial body of literature has documented associations between PFAS exposure and adverse outcomes in both human and ecological receptors. However, significant knowledge gaps remain, particularly regarding the toxicity of emerging PFAS compounds, mixture effects, low-dose exposures, and long-term ecological impacts.

Human Health Risks: Established and Emerging Evidence

Numerous epidemiological and toxicological studies have linked PFAS exposure—particularly from long-chain compounds such as PFOA, PFOS, PFHxS, and PFNA—to a wide range of adverse health effects. Short-chain and ultrashort compounds are considered to be less toxic, but toxicity factors published or estimated for these compounds are similar to toxicity factors published for contaminants such as arsenic, tetrachloroethylene and polychlorinated biphenyls (98). Key health risks include immunotoxicity, with evidence showing reduced vaccine efficacy and immune suppression in both children and adults (110). PFAS are also known endocrine disruptors, interfering with hormonal systems and affecting thyroid function, reproductive hormones, and metabolic pathways (111). Developmental toxicity is another major concern, as prenatal exposure has been associated with reduced birth weight, early puberty, and developmental delays (18). In addition, PFAS exhibit liver and kidney toxicity, demonstrated by elevated liver enzymes and cholesterol in exposed populations, as well as hepatotoxic and nephrotoxic effects in animal studies (17). PFOA has also been classified by the International Agency for Research on Cancer (IARC) as "possibly carcinogenic to humans" (Group 2B), with

epidemiological links to kidney and testicular cancers (16). The underlying toxicological mechanisms involve activation of nuclear receptors—particularly peroxisome proliferator-activated receptor alpha (PPAR α)—oxidative stress induction, disrupted lipid metabolism, and interference with endocrine and immune system signalling (17). However, extrapolating findings from animal studies to humans remains challenging due to interspecies differences in sensitivity and pharmacokinetics.

Ecological Risks: Bioaccumulation and Trophic Transfer

PFAS can pose significant risks to wildlife and ecosystems, particularly in aquatic and semi-aquatic environments, where they can bioaccumulate in organisms and biomagnify through food chains. This can lead to elevated concentrations in top predators such as fish, birds, turtles, and marine mammals (66, 67). Key ecological concerns include reproductive and developmental toxicity in amphibians, fish, and aquatic invertebrates—even at low concentrations (112). PFAS are also known to cause endocrine disruption in birds and mammals, affecting thyroid and sex hormone systems, while impairing immune responses and altering behaviour such as feeding. Both have potential consequences for population dynamics and overall ecological balance. Field studies have identified PFAS in wildlife, even in remote regions, underscoring their capacity for long-range atmospheric and aquatic transport (68). However, ecotoxicity data are heavily skewed toward a limited range of species and biological endpoints, leaving the ecological impacts of both legacy and newer PFAS compounds and their transformation products largely uncharacterized.

Exposure Pathways and Vulnerable Populations

Humans are exposed to PFAS through multiple pathways, with contaminated drinking water being a primary source of exposure for many communities (4). Dietary intake also contributes significantly to PFAS body burden, particularly through the consumption of fish, meat, and dairy products. The uptake of PFAS into food crops grown (113) or livestock raised in fields amended with sludges or irrigated with wastewater also poses a potentially important exposure pathway in some areas of the world. USEPA drinking water standards for PFAS apportion 20% of the tolerable daily intake (Reference Dose) to drinking water (22), implying that up to 80% of total exposure could come from food).

Global biomonitoring studies have consistently demonstrated widespread human exposure to PFAS, with measurable concentrations reported in blood serum across both occupationally exposed and general populations worldwide. PFAS—including PFOS, PFOA, PFHxS and PFNA—have been routinely detected in serum, plasma, breast milk and umbilical cord blood, indicating both widespread background exposure and potential intergenerational transfer (114, 115). In the general population, serum PFAS concentrations are typically associated with chronic low-level exposure through drinking water, diet, consumer products and indoor dust, with regional



differences reflecting historical use patterns, regulatory phase-outs and local contamination sources. Biomonitoring data further indicate that serum concentrations are often considerably higher among **occupationally exposed populations**, particularly firefighters, fluorochemical manufacturing workers and personnel involved in aqueous film-forming foam (AFFF) use, waste treatment or industrial PFAS handling, due to prolonged and repeated direct exposure (36, 116). Despite growing evidence from North America, Europe, Australia and parts of East Asia, substantial data gaps remain across **Africa, Latin America, Southeast Asia and many Pacific regions**, where PFAS biomonitoring remains limited. These geographical disparities restrict global understanding of human exposure patterns and highlight the need for broader international biomonitoring programs to better inform risk assessment, regulation and public health protection.

Occupational exposure is a major concern for certain groups, including firefighters and workers in chemical manufacturing industries, where PFAS use is prevalent (36). Additionally, indoor environments contribute to background exposure, as PFAS can be found in dust and air, especially in homes and workplaces containing PFAS-treated materials (102). Certain populations are especially vulnerable to PFAS exposure and its effects, including fetuses, infants, pregnant individuals, and people living near contaminated sites, due to both heightened exposure levels and greater physiological susceptibility (18).

Knowledge Gaps and Research Needs

Despite significant advancements in PFAS research, several critical gaps continue to hinder effective risk characterization and management. Most existing health studies focus on a limited set of legacy PFAS and fail to consider additive and synergistic health risks posed by complex mixtures of compounds (28). Except for GenX and PFBS; the toxicity and bioaccumulation potential of short-chain and emerging substitutes remain poorly understood (108). Additionally, PFAS are typically encountered as complex mixtures in the environment.

Methods to quantitatively assess cumulative risk posed by complex mixtures of PFAS have been developed and implemented by a limited number of regulatory agencies. Guidance published by (98), for example, separates complex mixtures of PFASs into three groups for assessment of cumulative risk: 1) "Primary Terminal PFAS" originally present in a sample, 2) "Secondary Terminal PFAS" generated by TOP degradation of precursor compounds and 3) "Excess Fluorine PFASs" identified by the presence of Total Organofluorine in a sample beyond that predicted by reported concentrations of Primary and Secondary Terminal PFAS. Data for Primary and Secondary Terminal Endpoint PFAS are compared to risk-based, soil or drinking water screening levels compiled for 20 terminal endpoint compounds and a Hazard Index calculated for each group. The latter assumes that the toxicity posed by precursors is driven primarily by the perfluoroalkyl chain of the terminal endpoint compounds that form the core structure of the

compounds. This approach negates the need to identify the specific precursor compounds present and simplifies the risk assessment process. The majority of excess organic fluorine is assumed to be associated with ultrashort PFAS compounds, based in part on nontargeted analysis of samples. Under the (98) approach, the calculated concentration of excess organic fluorine in a sample is converted to an equivalent concentration of perfluoropropanoate, one of only two ultrashort compounds with published toxicity factors and compared to risk-based screening levels for that compound. Cumulative "Total PFAS Risk" is calculated as the sum the Hazard Indices for Primary and Secondary Terminal Endpoint PFASs and the Hazard Quotient for Excess Fluorine PFASs. Although imperfect, the method allows for consideration of all PFAS-related compounds present in a sample in initial assessment of risk and decision making for additional actions.

Relative Potency Factors based on the molecular structure of compounds and other parameters have been for some PFAS that lack adequate toxicological studies (117). A promising approach by (118) derived relative potency factors for seven PFAS based detailed comparison of immune system effects. This allows for both a check of previously published toxicity for six of the seven the compounds as well as an alternative method to assess the combined toxicity of the compounds in a PFAS mixture. The number of compounds studied could potentially be expanded and used to help develop relative potency factors and corresponding toxicity factors for additional compounds, including phosphate-based PFAS in biosolids. Although not specifically discussed, it seems feasible that the approach could be expanded to assess the relative toxicity of case-specific, complex mixtures of mixtures of unknown PFAS in media such as wastewater effluent and sludges."

The impacts of low-dose and chronic exposure also remain difficult to evaluate, as long latency periods and confounding variables complicate the ability to detect subtle or delayed health effects. Furthermore, most human biomonitoring data come from North America and Europe, resulting in a lack of information on PFAS exposure trends in developing regions, particularly in the Global South. On the ecological side, data are limited for non-model species, making it difficult to assess species-specific risks or confidently extrapolate effects across different taxa and ecosystems.

Moving Forward: Toward Better Risk Assessment and Management

Addressing these critical knowledge gaps will require a multifaceted and forward-thinking approach. Expanded toxicological testing is essential, particularly the use of high-throughput and omics-based methods to efficiently screen a wide array of PFAS compounds and their impacts. Improved laboratory methods and toxicity factors are in particular needed for terminal endpoint compounds not currently considered in traditional risk assessments.

Regulatory strategies should also shift from evaluating individual chemicals to grouping PFAS into classes based on



shared properties and mechanisms of action, as this would enhance efficiency and consistency in risk assessment and management (3, 98, 119). Adequate assessment and management of PFAS as a group can only be achieved where efficient, user-friendly, tools for grouping and assessing PFAS (based on their relative toxicity, fate and transport properties and/or potential to breakdown into other PFAS) are available. In the current limited availability of such tools, the risks associated with the broader PFAS family, including precursors, are commonly unassessed, even when analysed for. While it is recognised that there is very limited information regarding the fate and transport properties and toxicity of many PFAS compounds, developing grouping approaches for PFAS using the currently available data (despite its limitations) is far superior to simply ignoring the problem until there is a comprehensive understanding of the risks posed by complex mixtures of these compounds, which might never be achieved, given the large and increasing number of PFAS-related compounds. Integrating human and ecological risk assessments will be crucial for setting more comprehensive health advisory levels and guiding remediation efforts. Additionally, epidemiological research must place greater emphasis on including vulnerable and susceptible populations, especially in underrepresented regions, to better understand global exposure disparities and health outcomes. Ultimately, a holistic, systems-based approach that incorporates multiple lines of evidence and considers cumulative risk will be essential for managing PFAS in a way that is both sustainable and equitable.

Remediation Strategies for PFAS-Contaminated Soil and Water: Technologies, Challenges, and Emerging Solutions

The persistent, mobile, and chemically resistant nature of PFAS presents significant challenges for remediation of contaminated environments. Traditional methods for treating organic pollutants such as natural attenuation or bioremediation are largely ineffective for PFAS due to their strong carbon-fluorine bonds and resistance to degradation beyond the initial breakdown of precursor compounds. As a result, PFAS contamination in soil and water can persist in perpetuity unless active remediation is undertaken. This section reviews current and emerging remediation strategies, highlights critical knowledge and technology gaps, assesses the economic and climate implications of large-scale PFAS cleanup, and outlines the integrated approach pioneered by *crcCARE*.

The Challenge of PFAS Remediation

Work by Ruyle et al (120) suggests that the soil reservoir of precursor compounds could continue to release PFAS for centuries at AFFF-impacted sites. Similar issues apply to agricultural fields amended with biosolids (56). While often lower in concentration, the sheer volume of PFAS containing wastewater generated by some facilities poses especially significant technical and economic challenges. Despite recent

advancements, most current technologies are unable to achieve complete PFAS mineralization. Adsorption improvements using polymer or biomass-derived materials have shown increased selectivity (121). The challenge of cost and scalability limits electrochemical oxidation and advanced oxidation processes (AOPs), which have shown promise for PFAS destruction (122, 123). Enzymatic defluorinases and genetically engineered microorganisms are gradually being recognized as feasible biotechnological possibilities (124, 125); nevertheless, further research is required for broader application.

PFAS remediation presents unique challenges due to several inherent factors. The extreme chemical stability of the compounds makes them resistant to natural attenuation processes such as hydrolysis, photolysis, and microbial degradation. The complexity of contaminated media, including the presence of co-contaminants, varying geochemical conditions, and diverse PFAS chain lengths, further inhibits treatment efforts. Additionally, effective technologies often require high energy inputs and specialized infrastructure, making remediation both costly and resource intensive. Regulatory uncertainty, with differing thresholds and standards across jurisdictions, also hinders the consistent implementation of treatment solutions. A major concern is the lack of technologies capable of fully mineralizing PFAS and breaking them down into harmless end products like fluoride and carbon dioxide. Most current or emerging methods either concentrate PFAS (such as through adsorption) or partially degrade them, which can result in the formation of intermediate compounds with unknown toxicity.

Soil Remediation Technologies

Soil Washing

Soil washing involves using aqueous solutions, often augmented with surfactants or solvents, to desorb PFAS from contaminated soil particles. This technique can effectively reduce PFAS concentrations, particularly for longer-chain compounds. However, it does not degrade PFAS; rather, it transfers them from soil to wash water, necessitating additional treatment of the liquid waste (126). The use of synthetic surfactants also raises concerns about secondary contamination.

Thermal Desorption and Incineration

High-temperature incineration remains one of the few methods capable of destroying PFAS in soil, especially when temperatures exceed 1,100°C. However, this method is energy-intensive, costly, and carries the risk of forming volatile fluorinated by-products if combustion is incomplete (127). Regulatory concerns about air emissions have restricted its widespread adoption.

Emerging catalytic thermal destruction technologies

Recent studies have shown that alkali and alkaline earth metal catalysts may significantly enhance PFAS mineralisation while reducing the temperatures required for thermal treatment (128, 129). Catalysts including calcium-, sodium- and potassium-based mineral systems have demonstrated potential to accelerate PFAS defluorination and improve fluoride release, thereby lowering the energy demand associated with conventional high-temperature PFAS destruction processes (130, 131). While still emerging and largely at laboratory or pilot scale, these catalytic approaches represent a promising



direction for improving the economic and environmental sustainability of PFAS destruction technologies.

Electrokinetic Remediation

This method uses electrical currents to mobilize PFAS in soil for subsequent extraction or degradation. Coupled with sorptive or oxidative electrodes, electrokinetics shows potential, particularly in low-permeability soils. However, scalability and field demonstrations remain limited.

Groundwater and Wastewater Treatment Technologies

Adsorption Technologies

Adsorption is the most widely applied approach for PFAS removal from aqueous media. Traditional materials like granular activated carbon (GAC) and ion exchange resins are commonly used in water treatment facilities. While effective for long-chain PFAS, these materials can struggle with short-chain and ultrashort variants.

Recent innovations include biochar, metal-organic frameworks (MOFs), and polymeric materials, which offer improved selectivity and capacity (121). However, adsorption only removes PFAS from water—it does not destroy them, and safe disposal or regeneration of the spent media is still a concern.

Electrochemical Methods

Electrochemical oxidation and electrocatalysis are emerging as powerful technologies for PFAS degradation. These methods employ reactive anodes (e.g., boron-doped diamond) that generate oxidative species capable of cleaving C–F bonds (123, 132). Electrocatalysis, in particular, shows promise for in situ treatment of groundwater plumes and ex situ applications in treatment plants.

Advanced Oxidation Processes (AOPs)

AOPs involve generating reactive radicals (e.g., hydroxyl, sulfate, or peroxymonosulfate radicals) to degrade contaminants. While traditional AOPs like ozonation are not highly effective against PFAS, combined processes—such as UV/sulfite or UV/persulfate—have demonstrated increased PFAS degradation rates (122).

Despite their promise, AOPs can form intermediates that are challenging to identify and may require downstream polishing steps to ensure complete detoxification.

Bioremediation

Bioremediation has long been considered ineffective for PFAS due to their resistance to microbial degradation. However, recent breakthroughs suggest that genetically engineered microorganisms may be capable of initiating PFAS defluorination (124). Additionally, enzymes such as defluorinases are under investigation for their ability to catalyze targeted breakdown.

While still at the proof-of-concept stage, bioremediation may eventually offer a low-cost, low-energy option for PFAS degradation—particularly in situ. Challenges include ensuring microbial viability in complex subsurface environments and

avoiding the creation of unintended transformation products, including short-chain and ultrashort PFAS compounds.

Integrated and Emerging Approaches

As no single technology offers a universal solution, there is growing interest in integrated remediation strategies that combine multiple methods. For example:

- Soil washing + electrochemical destruction of wash water.
- GAC adsorption + UV/sulfite AOP polishing.
- In situ barriers + groundwater plume treatment using electrochemical cells.

Emerging materials like photocatalysts, magnetic nanocomposites, and covalent organic frameworks (COFs) are also being investigated for PFAS remediation. However, real-world application requires validation at the pilot and field scales, with attention to cost, robustness, and regulatory acceptance.

crcCARE's Integrated in-Situ Approach

Recognizing the limitations of conventional methods, crcCARE has developed and tested in situ remediation technologies aimed at immobilizing and degrading PFAS directly within soil and groundwater systems (refer to Fig. 2):

PFAS Remediation Technologies



Fig 2: crcCARE's Integrated in-Situ PFAS remediation technologies

This approach reduces excavation, energy use, and long-term liabilities associated with containment-only strategies. It is especially relevant in complex, large-scale sites (e.g., military bases) where traditional remediation is cost-prohibitive or logistically unfeasible.

Barriers to Implementation

Despite promising lab-scale results, the translation of PFAS remediation technologies to full-scale operations is constrained by:

- High operational costs and energy requirements.



- Complexity of site conditions (e.g., varying PFAS types, co-contaminants).
- Regulatory uncertainties around destruction efficacy and by-product safety.
- Limited performance data from long-term field applications.

Further, most technologies are tailored toward legacy PFAS (e.g., PFOA, PFOS), while newer alternatives and precursors receive less attention but are increasingly prevalent in the environment. Treatment of more soluble and mobile short-chain and ultrashort compounds in soil, drinking water, wastewater and other environmental media beyond that necessary to address legacy compounds could be required in some cases to reduce residual risk to an acceptable level. Additional research on this important topic is urgently needed.

Table 3. Comparative Summary of PFAS Remediation Technologies

Table 4. PFAS Remediation Technologies: Cost-Effectiveness and Environmental Impact Matrix

This dual-table presentation offers a concise overview of current and emerging PFAS remediation options, helping stakeholders assess trade-offs between cost, sustainability, and technical viability.

Critical Knowledge Gaps and Future Research Priorities

Despite substantial advances in PFAS science over the past two decades, major knowledge gaps remain across analytical chemistry, toxicology, environmental behaviour, exposure assessment, remediation and regulation. Addressing these gaps will be essential to improve risk assessment, strengthen regulatory decision-making, and accelerate the development of sustainable remediation and management strategies. Several priority areas for future research are outlined below.

Analytical Gaps

Although analytical capabilities for PFAS have improved significantly, current monitoring approaches remain limited by incomplete compound coverage, insufficient analytical standards and challenges associated with complex environmental matrices. Most targeted methods capture only a small proportion of PFAS currently in commerce or present in contaminated environmental media. Continued advancement in high-resolution mass spectrometry, extractable organofluorine approaches and standardised sample preparation protocols is required to better characterise both known and unknown PFAS across environmental systems.

Toxicity Uncertainties

Toxicological understanding remains incomplete for the majority of PFAS compounds, particularly emerging PFAS

replacements, fluorinated polymers, precursor compounds and transformation products. Most health-based guideline values continue to rely on a relatively small number of well-studied compounds such as PFOS and PFOA, while toxicological data remain unavailable or limited for thousands of structurally related PFAS. Improved toxicokinetic, epidemiological and mechanistic toxicology studies are needed to support more robust human and ecological risk assessment.

Mixture Toxicity and Cumulative Exposure

Environmental PFAS rarely occur as single compounds; rather, they are present as complex mixtures often accompanied by co-contaminants such as hydrocarbons, metals, pharmaceuticals and microplastics. Current regulatory and toxicological frameworks are still largely compound-specific and do not adequately address mixture interactions, additive effects or cumulative exposure. Future research should prioritise mixture toxicity, cumulative risk modelling and improved understanding of PFAS interactions within complex environmental and biological systems.

Precursors and Transformation Products

A major uncertainty remains regarding the environmental behaviour and long-term significance of PFAS precursors and transformation products. Many precursor compounds may degrade over time to terminal perfluoroalkyl acids, extending contamination persistence and complicating site management. Current monitoring often underestimates this hidden PFAS burden. Improved identification, quantification and fate modelling of precursor compounds will be essential for accurate source tracking, exposure assessment and remediation planning.

Short-Chain PFAS

As regulatory restrictions on long-chain PFAS have increased, the use of short-chain alternatives has expanded globally. While often promoted as safer replacements due to lower bioaccumulation potential, short-chain PFAS are generally more mobile, more difficult to remove from water, and may persist extensively in environmental systems. Their long-term toxicity, transport behaviour and remediation challenges remain insufficiently understood and require greater research attention.

Soil-Plant Transfer and Food Chain Uptake

Important uncertainties remain regarding PFAS uptake by crops, soil-root interactions and transfer through terrestrial food chains. Soil physicochemical properties, organic matter content, PFAS chain length and co-contaminants all influence bioavailability and plant uptake, yet predictive understanding remains limited. Improved knowledge of soil-plant transfer mechanisms is particularly important for agricultural land impacted by biosolids application, wastewater irrigation and diffuse contamination sources, where food chain exposure may become a significant pathway for human exposure.

Global Inequity in Monitoring and Exposure Data



PFAS occurrence, exposure and biomonitoring data remain heavily concentrated in North America, Europe, Australia and parts of East Asia. Significant knowledge gaps persist across Africa, Latin America, Southeast Asia, the Pacific and other underrepresented regions where monitoring infrastructure and analytical capacity remain limited. These disparities constrain global understanding of PFAS contamination, human exposure and environmental risk. Expanding monitoring and analytical capability in the Global South will be critical for more equitable global risk assessment and management.

Policy Fragmentation and Regulatory Harmonisation

PFAS regulation remains fragmented internationally, with substantial differences between jurisdictions in definitions, analytical target lists, guideline values, grouping approaches and regulatory thresholds. This inconsistency complicates risk communication, trade, site assessment and remediation. Future progress will require greater harmonisation across regulatory frameworks, improved group-based classification strategies and stronger integration of lifecycle chemical management principles into PFAS policy.

Scalable and Sustainable Remediation Technologies

While many PFAS treatment technologies continue to advance, significant challenges remain in cost, scalability, long-term performance and destruction efficiency. Technologies capable of treating large volumes of contaminated soil, groundwater, wastewater, sludges and residuals in an economically viable and environmentally sustainable manner remain limited. Future research should prioritise field-scale validation, energy efficiency, long-term performance monitoring, and development of technologies capable of treating both terminal PFAS and precursor compounds across diverse environmental matrices.

Role of Artificial Intelligence and Predictive Modelling

Emerging artificial intelligence, machine learning and predictive modelling tools offer substantial opportunity to accelerate progress across PFAS science. These tools may assist in prioritising compounds lacking analytical standards, predicting physicochemical properties and toxicity, interpreting non-target mass spectrometry data, identifying unknown PFAS signatures, modelling environmental fate and transport, and supporting decision-making for risk assessment and remediation. As PFAS datasets continue to expand in complexity and scale, AI-enabled approaches are likely to become increasingly important in both research and regulatory practice.

Author contributions

We strongly encourage authors to include author contributions and recommend using [ORCID](#) for standardised contribution descriptions. Please refer to our general [author guidelines](#) for more information about authorship.

Conflicts of interest

There are no conflicts to declare.

Data availability

NA

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Table 1. Summary of PFAS Analytical Methods and Their Applications Across Environmental Media

Method	Principle	Target Compounds	Strengths	Limitations	Applicable Media
LC-MS/MS (Targeted Analysis)	Liquid chromatography with tandem mass spectrometry	Legacy PFAS (e.g., PFOA, PFOS, PFHxS, PFNA)	High sensitivity (ppt levels), widely accepted, quantitative	Limited to target list; requires standards	Water, soil, sediment, biota
HRMS (Non-target/Suspect Screening)	High-resolution mass spectrometry (e.g., QTOF, Orbitrap)	Known & unknown PFAS, precursors, degradation products	Identification of novel PFAS; structural elucidation	Requires high expertise; interpretation complexity	Water, soil, sediment, biota
TOF (Total Organic Fluorine)	Combustion Ion Chromatography or PIGE spectroscopy	All organofluorines (non-specific)	Indicates total fluorine burden; useful for unknowns	Cannot distinguish PFAS from other fluorinated organic compounds	Water, wastewater, leachate, soil, sediment, sludges, AFFF-impacted media
TOP Assay (Precursors)	Chemical oxidation to convert precursors to terminal PFAAs	PFAS precursors (e.g., fluorotelomer compounds)	Reveals hidden PFAS burden; complements LC-MS/MS	Partial oxidation; not compound-specific	Water, wastewater, leachate, soil, sediment, sludges, AFFF-impacted media
GC-MS (Limited PFAS)	Gas chromatography with mass spectrometry	Volatile PFAS (e.g., FTOHs)	Suitable for PFAS precursors and volatile forms	Requires derivatization; limited compound range	Air, dust, indoor samples
SPE + LC Techniques	Solid-phase extraction followed by LC-based detection	Broad PFAS suite depending on SPE cartridge	Enhances recovery; customizable by media type	Matrix effects; multi-step process	Water, wastewater, landfill leachate
Immunoassay (ELISA)	Antibody-based detection (semi-quantitative)	Mainly PFOA and PFOS	Low cost, rapid, field-screening capable	Low specificity, cross-reactivity, not suitable for confirmation	Water, field test kits
Passive Sampling (e.g., POCIS, SIP)	Time-weighted sampling using diffusion/partitioning mechanisms	Mobile and bioavailable PFAS fractions	Suitable for long-term monitoring; low detection limits	Non-selective, may underrepresent less mobile PFAS	Surface water, porewater, wastewater

Legend:

LC-MS/MS = Liquid Chromatography-Tandem Mass Spectrometry

HRMS = High-Resolution Mass Spectrometry

TOF = Total Organic Fluorine

TOP = Total Oxidizable Precursor

GC-MS = Gas Chromatography–Mass Spectrometry

SPE = Solid Phase Extraction

ELISA = Enzyme-Linked Immunosorbent Assay

POCIS = Polar Organic Chemical Integrative Sampler

SIP = Sorbent-Impregnated Polymer



Table 2. Summary of Key PFAS Transport Mechanisms Across Environmental Media

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Environmental Zone	Primary Transport Mechanisms	Influencing Factors	Key Knowledge Gaps
Unsaturated Zone	- Advection & dispersion- Sorption- Air–water interfacial partitioning	- Soil moisture- Organic carbon content- PFAS chain length- Soil mineralogy	- Quantification of interfacial sorption- Modelling under variable moisture regimes
Saturated Zone	- Advection with groundwater- Sorption to aquifer materials- Ionic interactions	- Groundwater chemistry (pH, ionic strength)- Co-contaminants- Aquifer heterogeneity	- Limited in situ degradation data- Behaviour of short-chain and novel PFAS variants
Surface Water	- Dilution and dispersion- Sediment interaction- Flow dynamics	- Hydrological conditions- Particle binding- Photolytic and biotransformation potential	- Partitioning with suspended solids- Role of seasonal hydrology in redistribution
Atmosphere	- Volatilization (precursors)- Long-range transport- Wet/dry deposition	- Volatility of precursors (e.g., FTOHs)- Temperature & humidity- Wind patterns	- Limited data on atmospheric degradation- Transformation pathways during transport
Sediment/Soil	- Sorption/desorption- Diffusion- Leaching to groundwater	- Organic matter- Redox conditions- Particle size- Presence of metals or co-contaminants	- Long-term desorption behaviour- Bioavailability and transformation in anoxic or variable conditions
Biota	- Bioaccumulation- Trophic transfer- Bioconcentration	- Exposure route (water, diet)- PFAS structure- Organism protein content and metabolic rate	- Dynamics of short-chain PFAS in food webs- Role of precursors in tissue accumulation

Notes:

- **FTOHs = Fluorotelomer alcohols**



Table 3. Comparative Summary of PFAS Remediation Technologies

Technology	Target Media	Mechanism	PFAS Types Treated	Effectiveness	Advantages	Limitations	Technology Readiness
Excavation & Off-site Disposal	Soil	Physical removal	All PFAS (relocated, not treated)	High (if isolated)	Immediate risk reduction, well-understood	High cost; relocation of problem; limited long-term sustainability	Commercial
Granular Activated Carbon (GAC)	Groundwater, surface water	Adsorption	Long-chain PFAS	Moderate to high	Widely used; proven technology	Poor for short-chain PFAS; high replacement frequency	Commercial
Ion Exchange Resins	Groundwater, wastewater	Adsorption	Short- and long-chain PFAS	High	High selectivity; better for short-chain PFAS	Resin regeneration/disposal issues; higher cost than GAC	Commercial
Reverse Osmosis (RO)	Drinking water, leachate	Physical separation via membrane	All PFAS	Very high	Near-complete removal	Expensive; generates high-strength waste brine	Commercial
Soil Washing	Soil	Extraction with water/solvent	Mostly long-chain PFAS	Moderate	Can reduce source mass	Only partially effective; produces contaminated wash water	Commercial/pilot
Thermal Desorption/Incineration	Soil, biosolids	High-temperature volatilization/oxidation	All (including precursors)	High	Permanent destruction (if complete)	Very high energy use; possible toxic emissions	Commercial
Electrochemical Oxidation	Water (ex situ)	Destruction via anodic oxidation	Precursors and terminal PFAS	High (lab/pilot scale)	Breaks down PFAS to fluoride	Expensive; high energy demand; limited full-scale data	Pilot/early commercial
Plasma Treatment	Water (ex situ)	High-energy ionization	Long- and short-chain PFAS	High (lab scale)	Promising for complete destruction	Technical complexity; limited scalability	Pilot
crcCARE In Situ Stabilization	Soil, groundwater	Immobilization + oxidative treatment	Long- and some short-chain PFAS	Moderate to high	Minimal disturbance; lower cost and emissions	Long-term field performance still under evaluation	Demonstrated/pilot



Table 4. PFAS Remediation Technologies: Cost-Effectiveness and Environmental Impact Matrix

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Technology	Relative Cost	Effectiveness	Energy Use / Emissions	Scalability	Overall Cost-Effectiveness
Excavation & Disposal	\$\$\$\$\$	★★★★☆	★★☆☆☆	★★★★☆	★★☆☆☆
Granular Activated Carbon (GAC)	\$\$\$	★★★☆☆	★★★★☆	★★★★☆	★★★★☆
Ion Exchange Resins	\$\$\$\$	★★★★☆	★★★☆☆	★★★★☆	★★★★☆
Reverse Osmosis	\$\$\$\$\$	★★★★★	★☆☆☆☆	★★★★☆	★★★☆☆
Soil Washing	\$\$\$	★★★☆☆	★★★★☆	★★★★☆	★★★★☆
Incineration	\$\$\$\$\$	★★★★★	★☆☆☆☆	★★★★☆	★★★☆☆
Electrochemical Oxidation	\$\$\$\$	★★★★☆	★★★☆☆	★★★★☆	★★★★☆
Plasma Treatment	\$\$\$\$\$	★★★★☆	★★★☆☆	★★★★☆	★★★☆☆
crcCARE In Situ Remediation	\$\$-\$\$\$	★★★★☆	★★★★☆	★★★★★	★★★★☆



Data Availability Statement

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This paper is a review and does not involve the generation of new primary data. All information presented is derived from previously published sources, which have been appropriately cited within the manuscript. Any additional data or materials, if required, are available from the authors upon reasonable request. Interested readers are encouraged to contact the corresponding author to discuss access to relevant information.

