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## Comprehensive review of PFAS occurrence, regulatory frameworks, analytical, and remediation methodologies: emphasis on the Arabian Gulf and arid regions

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Per- and polyfluoroalkyl substances (PFAS) constitute a diverse class of highly stable synthetic organofluorines increasingly recognized for their environmental persistence, bioaccumulative behavior, and toxicological significance. It is especially concerning that they are frequently found in environmental matrices such as soil, groundwater, surface water, and biota globally. The impact is expected to be more severe in regions such as the Middle East and North Africa (MENA), where climatic conditions and water scarcity amplify the impact of even trace-level contamination. Groundwater, a critical resource in these regions, is especially vulnerable to PFAS infiltration from industrial effluents, landfill leachates, and aqueous film-forming foams (AFFFs). These unique pressures underscore the urgent need for a comprehensive assessment of PFAS in water systems across the Arabian Gulf and other arid regions. The review highlights several key insights. While PFAS have been detected in water systems across the region, available monitoring studies are limited compared to other parts of the world. In addition, regulatory frameworks for PFAS remain nonexistent, while international regulatory agencies such as the U.S. EPA and ECHA have established frameworks for legacy PFAS like PFOA and PFOS. On the analytical side, sample collection, preparation, and preservation are critical challenges due to the broad spectrum of PFAS chemistries and complex matrices. In addition, established analytical methods such as LC-MS/MS face barriers related to infrastructure cost and technical expertise. Concerning treatment technologies, conventional treatment methods have proven largely ineffective, with advanced methods like ion exchange resins and other sorption techniques leading the current research and large-scale treatment landscape. Overall, a regionally tailored, multidisciplinary approach is imperative to mitigate PFAS risks. Given the region's high *per capita* industrial footprint, extreme climatic conditions, and water insecurity, a significant pollution burden is anticipated, and extensive monitoring campaigns are recommended.

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### Water impact

This review emphasizes PFAS contamination risks in water, focusing on arid regions and the Arabian Gulf. It examines occurrence, regulatory gaps, analytical challenges, and potential remediation technologies. Findings underscore the critical need for targeted water management strategies to mitigate PFAS impacts on already scarce water supplies, thus, protecting public health and environmental sustainability in vulnerable regions.

## 1 Introduction

Per- and polyfluoroalkyl substances (PFASs) comprise a class of chemicals that has attracted much attention since the early 2000s.<sup>1</sup> Initially introduced in the 1940s, these

substances are now integrated into many products, numbering in hundreds. Their applications include creating stain- and water-resistant fabrics and carpets, and being present in cleaning products, paints, and fire-fighting foams.<sup>2–4</sup> Furthermore, specific types of these substances have received authorization from the FDA for restricted use in items such as cookware, food packaging, and equipment used for food processing.<sup>5</sup> PFAS have been classified by the U.S. Environmental Protection Agency (EPA) as emerging contaminants due to concerns about their potential effects

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on human health and the environment.<sup>6,7</sup> PFAS do not readily degrade in the environment or within the human body; instead, they remain intact and can build up over time.<sup>8</sup> The acronym “PFAS” stands for “per- and polyfluoroalkyl substances”. No individual chemical in the PFAS family can simultaneously be classified as perfluorinated and polyfluorinated; the term encompasses various substances with varying properties and uses. They are characterized by multiple fluorine atoms attached to an alkyl chain, which imparts unique properties such as resistance to degradation and repellent characteristics.<sup>9</sup> PFAS molecules, consisting of linked carbon and fluorine atoms, are chemicals that are extensively utilized and persist for extended periods, degrading at a very gradual rate.<sup>10</sup> Because of their extensive use and long-lasting nature in the environment, numerous PFAS are found in the blood of humans and animals and occur at low concentrations in various foods and consumer goods.<sup>11</sup> PFAS are accumulated in aquatic systems and soil.<sup>7,12</sup> Some studies proved the presence of PFAS in oysters and plasma in significant levels near superfund sites.<sup>13</sup> They were even found in bottled water at a high potential level.<sup>14</sup> Also, they were detected in commercial fish species,<sup>15</sup> high-protein food products, and human breast milk, showing vast exposure through various routes.

Synthetic short chain organofluorine compounds have been developed as potentially less toxic alternatives to legacy PFAS. Notable examples include GenX (hexafluoropropylene oxide dimer acid, HFPO-DA, and its ammonium salt), ADONA (4,8-dioxa-3H-perfluorononanoic acid, C7), which serves as a replacement for PFOA, and PFBS (perfluorobutane sulfonic acid, C4), introduced as a substitute for PFOS (Fig. 1). However, it still possesses properties such as bioaccumulation in living tissues, high water solubility, chemical stability and high mobility. It was also demonstrated that GenX can bind to blood albumin at both molecular and cellular levels.<sup>16</sup> As reported by the EPA, toxicity studies on oral animals (rat and mouse) showed toxicity on liver and kidney, adverse effects on immunity and development and revealed that the exposure will lead to cancer at a dose span from a low 0.5 mg kg<sup>-1</sup> per day to a high 1000 mg kg<sup>-1</sup> per day.<sup>17</sup>

Removing PFAS compounds from the wastewater stream is extremely challenging due to their unique properties such as oleophobicity, resistance to heat and water, high-energy carbon–fluorine bonds and hydrophobicity. Due to 5000 or more compounds of the same class at a trace level from pg L<sup>-1</sup> to mg L<sup>-1</sup>, developing a universal method is always

challenging. Removing short-chain compounds from the environment is even more challenging due to their high mobility and solubility. Biological methods are also applied and found effective, but they break PFAS into a more hazardous short chain.

Regulatory actions are already in place, led by the EPA and listed by the Stockholm Convention on Persistent Organic Pollutants (POPs).<sup>18</sup> Exposure to chlorinated polyfluoroalkyl ether sulfonic acid (F-53B), an alternative to perfluorooctane sulfonate (PFOS), was proven to have an effect on birth growth and lactation during pregnancy.<sup>19</sup>

PFAS prevalence in arid and semi-arid regions is a significant issue because of its potential consequences for human health, environmental behavior, and water resource management. Groundwater, a vital drinking water source in these regions, faces contamination risks from PFAS accumulation driven by high evaporation rates. Consumption of contaminated seafood further exacerbates health risks, particularly for children and marine wildlife.<sup>20</sup> Unique hydrological cycles in arid climates, including minimal precipitation and high evapotranspiration, contribute to PFAS persistence near the surface, while salinity alters PFAS solubility and adsorption dynamics, complicating management efforts.<sup>21</sup> Irrigation practices and surface water–groundwater exchanges facilitate PFAS migration, threatening drinking water supplies. Urban sources like wastewater treatment plant discharges and runoff significantly contribute to contamination, with short-term rainfall events mobilizing PFAS. Despite these challenges, research on PFAS in arid regions remains limited, with gaps in understanding their transport, fate, and behavior in saline environments.<sup>22,23</sup> Continuous monitoring and baseline data are essential for developing tailored management and remediation strategies, including soil amelioration techniques. The need for region-specific guidelines highlights the importance of further investigation to address the unique challenges of arid climates, hydrology, and hydrochemistry in effectively mitigating PFAS contamination.<sup>24</sup>

PFAS exposure in arid climates, such as those in the GCC region, poses unique health risks due to environmental factors like frequent dust storms. These storms can act as carriers of PFAS, depositing them into soils, sands, and road dust, which may then be inhaled or ingested by humans and animals.<sup>25</sup> Consuming water, food, or dust contaminated with PFAS can result in significant health problems, such as cardiovascular diseases, diabetes, thyroid dysfunction, and developmental issues in children, and increased risks of cancers such as kidney and testicular cancer.<sup>26</sup> In arid

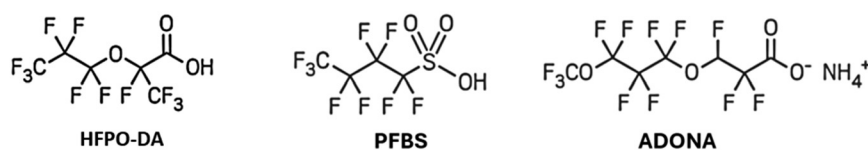


Fig. 1 Structural formula for some legacy PFAS replacements.



regions, where water scarcity often necessitates wastewater reuse, PFAS contamination in treated wastewater further amplifies risks, potentially affecting drinking water safety and agricultural practices.<sup>27</sup> Thus, to synthesize the available knowledge, Scopus-indexed articles and relevant grey literature, including country reports, were retrieved, emphasising studies published in the past five years. The literature was screened using targeted keywords across four thematic areas: occurrence, regulatory frameworks, analytical techniques, and treatment technologies. In total, 135 publications were incorporated into this review.

## 2 Sources, transport, and distribution dynamics of PFAS

PFAS in aquatic ecosystems originate from multiple release pathways, with wastewater being a major contributor. Industrial effluents have exhibited PFAS concentrations up to 27 100 ng L<sup>-1</sup>, while domestic effluents typically contain around 1000 ng L<sup>-1</sup>.<sup>28</sup> Conventional wastewater treatment processes are not very effective at removing PFAS. To complicate matters, the concentration of PFAS may be higher even while treatment is ongoing due to the transformation of precursor compounds. This phenomenon was demonstrated in an industrial wastewater treatment plant where 6:2 fluorotelomer carboxylic acid (FTCA) concentrations escalated from 188 000 ng L<sup>-1</sup> to 592 000 ng L<sup>-1</sup> post-activated sludge treatment.<sup>29</sup> The transformation is attributed to specific operational conditions in biological treatment systems, where mesophilic temperatures and aerobic/nitrate-reducing conditions promote microbial conversion of fluorotelomer alcohols (FTOHs) to perfluorocarboxylic acids (PFCAs).<sup>30</sup> Further studies on long-term PFAS trends in effluent from domestic WWTPs across the USA affirm this issue, showing an average increase of 6.0 ng L<sup>-1</sup> in PFOA from influent to effluent,<sup>31</sup> and a 100% detection frequency of PFAS like PFOA, PFNA, PFBS, and PFHxS.<sup>32</sup> In summary, the ineffectiveness of conventional treatments, coupled with the potential for increased PFAS concentrations in effluents, highlights the major role of wastewater discharge in the widespread contamination of aquatic ecosystems.

Atmospheric deposition represents another significant transport pathway. Analysis of 42 rainwater samples in southeastern Florida revealed PFAS in 95% of samples, with mean PFOS and PFOA concentrations (0.24 ng L<sup>-1</sup> and 0.32 ng L<sup>-1</sup>, respectively) exceeding EPA drinking water guidelines.<sup>33</sup> The airborne PFAS originated from diverse sources, including African dust storms, vehicular emissions, power plants, and incineration facilities.<sup>33,34</sup> This widespread atmospheric distribution is further evidenced by a Wisconsin study analyzing 89 precipitation samples, which detected PFAS concentrations ranging from 0.7 to 6.1 ng L<sup>-1</sup>, with PFCAs representing a major constituent class.<sup>35</sup> The significance of atmospheric transport was quantitatively demonstrated in a study examining long-range transport (>150 km) originating from a manufacturing plant that

produces fluoropolymers in North Carolina, USA. Of the facility's annual PFAS emissions of 109 000 kg, over 95% were transported beyond the 150 km radius, with only a minor fraction depositing within the immediate vicinity of the facility.<sup>36</sup> This finding underscores the potential for atmospheric transport to facilitate widespread PFAS contamination well beyond point sources.

The persistence of legacy PFAS, particularly long-chain perfluoroalkyl acids ( $\geq$ C7 PFCAs and  $\geq$ C6 PFSAs), remains a significant concern despite their phase-out since the early 2000s.<sup>37</sup> This persistence is evidenced by groundwater monitoring near a landfill, where PFAS concentrations (including legacy PFAS) decreased from 4400 ng L<sup>-1</sup> to 1900 ng L<sup>-1</sup> over a decade, while concentrations in downgradient wells increased, demonstrating both compound stability and transport dynamics.<sup>38</sup> Similarly, analysis of residential soils across China revealed substantial concentrations of legacy PFOA ( $\sim$ 370 pg g<sup>-1</sup>) and PFOS ( $\sim$ 200 pg g<sup>-1</sup>), alongside emerging short-chain analogues ( $\sim$ 400 pg g<sup>-1</sup>) and alternative compounds like F-53B.<sup>39</sup>

Contemporary aquatic systems show an increasing prevalence of short-chain PFAS ( $\leq$ C6 PFCAs and  $\leq$ C5 PFSAs) and ultrashort-chain compounds, reflecting the industrial transition away from legacy PFAAs.<sup>40,41</sup> For instance, perfluoropropanoic acid (PFPrA) and trifluoromethanesulfonic acid (TFMS) have been detected in bottled water at levels up to 18.9 ng L<sup>-1</sup> in the USA and 15 ng L<sup>-1</sup> in Sweden.<sup>14,41</sup> While this shift to shorter-chain alternatives was intended to reduce the persistence, bioaccumulation, and toxicity associated with longer-chain PFAS, emerging evidence suggests that this transition has not eliminated environmental and health concerns and may have introduced new ones. High concentrations of GenX (reaching 4000 ng L<sup>-1</sup>), a prominent short-chain replacement for PFOA, have been detected in freshwater sources, including potable water wells, in an industrial area in North Carolina.<sup>42</sup> An increasing number of studies report on the environmental prevalence of GenX and suggest toxicological outcomes comparable to PFOA.<sup>42,43</sup> In one *in vitro* study, GenX predisposed human liver cells to increased apoptosis and intracellular ROS generation, comparable to PFOA, especially at higher doses.<sup>44</sup> Similarly, studies on photocatalytic degradation and removal have reported that GenX demonstrated less effective removal (79%) and defluorination (33%) when compared to PFOA, which achieved complete removal (100%) and a higher defluorination rate (69%).<sup>45</sup> This was due to GenX's lower adsorption onto the photocatalytic material and increased production of ultra-short-chain transformation products.<sup>45</sup>

Surface water PFAS composition analysis reveals complex distribution patterns. In Hulun Lake, short-chain PFCAs (C4–C7) dominated at 33.6%, followed by long-chain PFCAs (C8–C12) at 26.2%, long-chain PFSAs at 15.3%, hexafluoropropylene oxide dimer acid (HFPODA) at 12.2%, and short-chain PFSAs at 5.9%.<sup>46</sup> Source apportionment indicated contributions from wastewater, cosmetics,



Table 1 PFAS concentrations in different water sources

Major PFAS detected	Location	Water source	Concentration	Sediment	Ref.
PFCA, PFSA, <i>n</i> :2 FTSS, <i>n</i> :2 diPAPs, 8Cl-PFOS, and HPFO-DA	Hulun Lake, China	Surface water	3.67 to 8.84 ng L <sup>-1</sup>	0.97 to 1.73 μg kg <sup>-1</sup>	46
PFCA, PFBS, and PFOS	Yellow River, China	Surface water	44.7 to 1520 ng L <sup>-1</sup>	8.19 to 17.4 ng g <sup>-1</sup>	48
PFCA, PFSA, PFECA, PFESA, and FTSA	East China Sea, China	Surface water	1.1 to 100 ng L <sup>-1</sup>	0.26 to 1.9 ng g <sup>-1</sup>	51
PFCA, PFSA, 6:2 FTS, and PFOA	Victoria, Australia	Surface water	1 ng L <sup>-1</sup> to 75 ng L <sup>-1</sup>	1 ng L <sup>-1</sup> to 29 ng L <sup>-1</sup>	47
PFCAs, PFASAs, and FTSS	Biscayne Bay, USA	Surface water	0.6 to 26.4 ng L <sup>-1</sup>	—	52
PFSA, PFCA, PFES, and PFECA	Central Kentucky, USA	Surface water	~10 to ~1000 ng L <sup>-1</sup>	0.06 to ~6 ng g <sup>-1</sup>	61
PFOS and PFOA	Cauvery Basin, India	Surface water	Up to 1800 ng L <sup>-1</sup>	—	62
PFOS and PFOA	Cauvery Basin, India	Groundwater	Up to 900 ng L <sup>-1</sup>	—	62
PFCA and PFSA	Utrechtse Heuvelrug, Netherlands	Groundwater	Up to 1900 ng L <sup>-1</sup>	—	38
PFCA and PFSA	Utrechtse Heuvelrug, Netherlands	Groundwater	Up to 4400 ng L <sup>-1</sup>	—	63
PFCA and PFSA	Utrechtse Heuvelrug, Netherlands	Drinking water	5.5 ng L <sup>-1</sup>	—	38
PFCA and PFSA	South Florida, USA	Rainwater	0.2 to 21.0 ng L <sup>-1</sup>	—	33
PFBS and PFOA	Chennai, India	Groundwater	0.1 to 136.3 ng L <sup>-1</sup>	—	64
PFBS and PFOA	Adyar river, India	Surface water	0.2 to 59.8 ng L <sup>-1</sup>	—	64
PFCA and PFSA	Lake Victoria, Uganda	Surface water	5.2 to 26.6 ng L <sup>-1</sup>	—	65
PFCA and PFSA	Kampala and Entebbe, Uganda	Tap water	5.2 to 7.3 ng L <sup>-1</sup>	—	65
PFOA, PFOS, PFHxS, and PFHpA	Hartbeespoort Dam and Roodeplaat Dam, South Africa	Surface water	1.4 to 346.3 ng L <sup>-1</sup>	—	66
PFOS	Rivers across 3 geopolitical zones, Nigeria	Surface water	3.9 to 10.1 ng L <sup>-1</sup>	5.1 to 10.4 ng g <sup>-1</sup>	67
PFBA, PFPeA, PFBS, PFOS, PFNS, PFOA, and PFDA	Nairobi River Basin, Kenya	Surface water	6.7 to 26.2 ng L <sup>-1</sup>	22.3 to 51.9 ng g <sup>-1</sup>	68
PFCAs	Lake Tana, Ethiopia	Surface water	0.073 to 5.6 ng L <sup>-1</sup>	0.22 to 0.55 ng g <sup>-1</sup>	69
TFMS	Flanders, Belgium	Bottled water	<0.03 and 15.0 ng L <sup>-1</sup>	—	41
PFBA, PFBS, and TFMS	Flanders, Belgium	Tap water	0.1 to 12.0 ng L <sup>-1</sup>	—	41
PFCAs	Wisconsin, USA	Rainwater	0.7 to 6.1 ng L <sup>-1</sup>	—	35
PFCAs, PFASAs, cyclic PFSA	Nabeul, Tunisia	Tap Water	≤5.0 ng L <sup>-1</sup>	—	70
PFCAs, PFASAs, cyclic PFSA, FASAs, FASAAs, ether-PFAS	Isfahan, Iran	Tap Water	≤5.0 ng L <sup>-1</sup>	—	70
PFCAs, PFASAs, cyclic PFSA, FASAs, FASAAs	Tehran, Iran	Tap Water	≤5.0 ng L <sup>-1</sup>	—	70
PFCAs, PFASAs, cyclic PFSA, FASAs, FASAAs, ether-PFAS	Meknes, pr, Morocco	Tap Water	≤5.0 ng L <sup>-1</sup>	—	70
PFCAs, PFASAs, cyclic PFSA, FASAs, FASAAs, ether-PFAS	Kenitra, Morocco	Tap Water	≤5.0 ng L <sup>-1</sup>	—	70
PFCAs, PFASAs, cyclic PFSA, FASAs, FASAAs	Tizi Ouzou, Algeria	Tap Water	≤5.0 ng L <sup>-1</sup>	—	70
L-PFOS, br-PFOS, ∑PFOS, PFOA, PFHxS	Egypt	Surface Water	0.06 to 0.53 ng L <sup>-1</sup>	—	71
L-PFOS, br-PFOS, ∑PFOS, PFOA, PFHxS	Tunisia	Surface Water	0.21 to 1.17 ng L <sup>-1</sup>	—	71
PFCA, PFAA, PFSA, and 6:2 FTS	Red Sea, Saudi Arabia	Coastal water	<LOQ to 956 ng L <sup>-1</sup>	—	72
PFOS	Tubli Bay, Bahrain	Coastline sediments	—	<0.05–1.4 ng g <sup>-1</sup>	73
PFOS, PFOA, PFBA, PFHpS, and PFHxA	Riyad, Saudi Arabia	Artificial pond	Mean of 55 ng L <sup>-1</sup> (108 ng L <sup>-1</sup> peak and 29.7 ng L <sup>-1</sup> median)	Mean of 25 ng g <sup>-1</sup> (116 ng g <sup>-1</sup> peak and 5.7 ng g <sup>-1</sup> median)	74



firefighting foams, and textile/paper products. The predominance of PFCAs, particularly short-chain variants, in surface waters and sediments is consistently reported,<sup>47,48</sup> attributable to their widespread use after replacing legacy PFAS and leachability from polytetrafluoroethylene (PTFE) at temperatures exceeding 200 °C.<sup>49</sup>

Secondary PFAS release through biosolid application presents additional environmental concerns. Analysis of industrial sludge from nine wastewater treatment plants revealed 41 distinct PFAS compounds, with concentrations varying significantly by industry: grain/oil processing (1106 ng g<sup>-1</sup>), polymer fiber production and printing/dyeing (>100 ng g<sup>-1</sup>), food processing (22.4 ng g<sup>-1</sup>), galvanizing (22.2 ng g<sup>-1</sup>), laundry detergent manufacturing (11.3 ng g<sup>-1</sup>), and landfill operations (4.7 ng g<sup>-1</sup>).<sup>50</sup> Land-use studies correlate PFAS prevalence with urbanization, showing PFOS detection frequencies of 42% in urban areas, compared to 22% in mixed-use areas, 16% in agricultural zones, and 5% in remote locations.<sup>47</sup>

Marine environments also exhibit significant PFAS contamination. The part of the East China Sea that is closer to the coast, known as its inner shelf, contained 32 of 41 analysed PFAS compounds in water (1.1–100 ng L<sup>-1</sup>) and 19 in sediments (0.26–1.9 ng g<sup>-1</sup>).<sup>51</sup> This contamination extends to marine biota, as evidenced by cumulative PFAS concentrations in Biscayne Bay fisheries, with wet weight concentrations ranging from 0.2–3.4 ng g<sup>-1</sup> in blackfin tuna and 0.4–5.2 ng g<sup>-1</sup> in lobster.<sup>52</sup> Table 1 provides a summary of PFAS concentrations in different water sources.

Based on the PFAS situation report the mixed picture regarding water contamination in Egypt, Lebanon, and Jordan can be explained. In Lebanon, significant groundwater contamination from PFOS is acknowledged at numerous sites due to major historical use of these substances, particularly from the 1970s to 2002. An estimated 56 to 167 kg of PFOS were released from firefighting foams between 2004 and 2014, indicating substantial potential for widespread water pollution from fire incidents and practice areas, though specific contamination levels in actual environmental water samples were not included in the initial inventory or identified in peer-reviewed studies. For Egypt, there is a notable lack of information concerning PFAS production, use, or direct contamination levels in environmental water samples. Studies identified for Egypt focused on PFAS presence in dust and food packaging materials, rather than water. In Jordan, while initial PFAS levels in wastewater were not explicitly provided, laboratory studies on biochar filters for PFAS removal from wastewater show varying efficiencies (e.g., 20% for PFBA, 60% for PFHxS), implying the presence of these contaminants in local wastewater streams. This widespread human exposure strongly suggests substantial environmental, including water, contamination. Firefighting foams are identified as a “likely major source” of PFAS in Jordan, contributing to this pollution. The country also lacks comprehensive data on imported PFAS volumes,

complicating the assessment of overall water contamination.<sup>53–55</sup>

With reference to Table 1, globally, PFAS monitoring has been conducted extensively across diverse regions including Asia, Africa, Europe, Australia, and North America, covering a wide range of water sources such as surface water, groundwater, drinking water, tap water, bottled water, rainwater, and coastal systems. In contrast, available data from the MENA region remain very limited, with only a handful of studies reported from Egypt, Tunisia, Saudi Arabia, and Bahrain, mainly restricted to surface water, coastal water, sediments, and artificial ponds. This uneven distribution of research highlights a significant knowledge gap, as critical sources such as groundwater, drinking water, rainwater, and tap water remain largely unexplored in the MENA region despite their direct relevance to human exposure and public health.

Another form of PFAS compounds, in gaseous form namely volatile PFAS or volatile fluorinated compounds (VFCs), typically comprise C1–C8 species with boiling points below approximately 100 °C and are widely detected in the atmosphere.<sup>56</sup> This group includes neutral volatile compounds such as fluorotelomer alcohols (FTOHs), fluorooctane sulfonamides (FOSAs), and fluorooctane sulfonamide ethanols (FOSEs), along with potent greenhouse gases like volatile anesthetics (e.g., sevoflurane and desflurane).<sup>57,58</sup> Major sources of volatile PFAS emissions include manufacturing facilities, incinerators, thermal treatment processes (which generate products of incomplete combustion/destruction, PICs/PIDs), landfills, households, and wastewater treatment plants where vigorous aeration promotes aerosolization and atmospheric release. Among these compounds, tetrafluoromethane (CF<sub>4</sub>) is often reported as the most abundant VFC in the atmosphere, while short-chain PFAS, particularly 6:2 FTOH, are frequently observed at elevated concentrations in ambient air. Trifluoroacetic acid (TFA), the most volatile perfluorocarboxylic acid (VPFCA), dominates the atmospheric PFCA burden across urban, rural, and remote environments.<sup>59</sup> Spatial distribution patterns reveal higher concentrations of volatile PFAS, such as 6:2 FTOH and TFA, in urban areas, correlating with population density and industrial activity.<sup>60</sup> Critically, volatile PFAS like FTOHs act as atmospheric precursors that undergo oxidative transformation to form persistent PFCAs, representing a major pathway for long-range transport and global contamination, even in remote ecosystems. Monitoring arid climates is crucial to understand their occurrence, transport, and transformation under extreme temperature and low humidity conditions, which can influence their atmospheric persistence and deposition patterns (Fig. 2).

### 3 PFAS prevalence in aquatic systems of arid regions

Comprehensive data on PFAS occurrence in water and their distribution into the environment is scarce in regions like





Fig. 2 Distribution of detected compounds in the MENA region from data in Table 1.

the Arabian Gulf region and sub-Saharan Africa. This scarcity is primarily due to limited infrastructure and resources for monitoring these micropollutants.<sup>27,75</sup> This hinders effective risk assessment and policy making, specifically identifying toxicological concerns and bioaccumulative potential. A recent review paper broadly focusing on PFAS in the GCC reported that Saudi Arabia accounts for the highest number of available monitoring studies (five), with one additional study reported in Bahrain.<sup>27</sup> The limited data available, however, highlights the need for increased attention to this

issue. For example, a study in Saudi Arabia examining PFAS concentrations in serum among a population in Jeddah reported a significant association between PFAS detection and osteoporosis.<sup>76</sup>

Furthermore, PFAS such as PFBA, PFOA, PFOS, and PFBS have been detected in various food items in Saudi Arabia, including cereals, fish, and milk.<sup>77</sup> Though limited in scope, these findings underscore the potential for human exposure and the urgent need for comprehensive PFAS monitoring and regulation in these regions to protect public health and the

Table 2 Peculiarities influencing PFAS pollution in the Arabian Gulf region

Factor	Regional peculiarity	Implication for PFAS occurrence
Climate & atmosphere	Frequent dust storms, high wind speeds	Facilitates atmospheric transport and deposition of PFAS-bound particles over wide areas
	Extreme heat and high solar irradiation	Enhances degradation/leaching of PFAS-containing materials (plastics, coatings, landfill waste) and alters mobility
Hydrology & Water Resources	Scarcity of natural freshwater; reliance on desalination and fossil groundwater	PFAS entering aquifers are highly persistent with little natural dilution or flushing. Possible accumulation in desalination brine and sludge
	Industrial activities	Increases potential for PFAS use in processing, firefighting foams, and waste streams
Transport & Infrastructure	High density of oil & gas, petrochemical industries, and refineries	Potential hotspots for PFAS accumulation and recycling back into the environment
	Large desalination and wastewater treatment infrastructure	Airports are known PFAS hotspots due to historical and ongoing firefighting foam usage
Military presence	Major international airports (e.g., Hamad, Dubai, Abu Dhabi)	Vehicle-related PFAS sources (fluoropolymer coatings, lubricants, brake dust, tire wear) may contribute significantly
	Dense road networks and high vehicle ownership	Use of firefighting foams and PFAS-containing materials at bases increases localized contamination risks
Consumer & trade Patterns	Concentration of military bases and training facilities	Continuous introduction of PFAS through food packaging, textiles, and other fluorinated materials
	Heavy reliance on imports of packaged goods and consumer products	Potential acceleration of PFAS leaching from disposed materials into soils and leachates
Waste management	Landfills often exposed to intense heat and solar radiation	Potential underestimation of occurrence and exposure risks compared to regions with stricter controls
	Regulation & Monitoring	Limited PFAS-specific regulations and monitoring programs



environment. In addition to the climatic conditions, economic, industrial, and waste management practices unique to these regions may influence PFAS transport and fate differently than temperate zones, underscoring the urgent need for localised research and baseline environmental studies. Some potential peculiarities of the Gulf and MENA region that could influence PFAS prevalence are highlighted in Table 2.

Due to the insufficient data from our region, we emphasize the trends in multiple arid regions worldwide. For example, in the Dahei River basin of China, surface water concentrations ( $\sum 30\text{PFASs}$ ) observed varied, ranging from a minimum of  $3.13\text{ ng L}^{-1}$  to a maximum of  $289.1\text{ ng L}^{-1}$ , with an average of  $25.40\text{ ng L}^{-1}$ . Among the substances measured, perfluorooctanoic acid (PFOA) exhibited the highest average concentration at  $2.44\text{ ng L}^{-1}$ . It was found in every sample tested, followed by perfluorohexanoic acid (PFHxA) (mean:  $1.34\text{ ng L}^{-1}$ ), and perfluorohexane sulfonate (PFHxS) (mean:  $12.94\text{ ng L}^{-1}$ ). Emerging PFAS like HFPO-DA and 4:2 FTS were detected with 100% frequency, indicating their ubiquitous presence in this Yellow River basin region. In the Hetao Irrigation District, another typical arid area in China, total PFAS ( $\sum\text{PFASs}$ ) in surface water ranged from 29 to  $232\text{ ng L}^{-1}$ , while groundwater concentrations were lower, ranging from 2 to  $77\text{ ng L}^{-1}$ . Perfluorobutanoic acid (PFBA) was the predominant component in both surface water (39% of  $\sum\text{PFASs}$ ) and groundwater (45%). PFAS were also detected in soil ( $0.09$  to  $0.58\text{ ng g}^{-1}$ ) and aquifer solid samples, with higher clay content than sandy samples.<sup>21,78</sup>

Groundwater in the Loess Plateau, northwest China, characterized by a continuous arid climate, showed  $\sum\text{PFAS}$  ranging from  $2.78$  to  $115\text{ ng L}^{-1}$ . Emerging PFAS like HFPO-DA and 4:2 FTS were also detected. In the Las Vegas Wash watershed, Southern Nevada, USA, an arid, urban, wastewater-dominated area, the mean total measured PFAS concentration in the mainstem Las Vegas Wash was  $72\text{ ng L}^{-1}$ . Short-chain PFPeA (48% molar) and PFHxA (32% molar) comprised the majority of PFAS, followed by PFOA (9%). Mean PFOA was  $8.8\text{ ng L}^{-1}$  and mean PFOS was  $1.4\text{ ng L}^{-1}$  in the Wash. High levels were found in shallow groundwater near the major airport (*e.g.*,  $1658\text{ ng L}^{-1}$  PFOS).<sup>21,79</sup>

A statewide assessment conducted from 2020 to 2024, in new Mexico, investigated perfluoroalkyl and polyfluoroalkyl substances (PFAS) in New Mexico's major rivers. The study found PFAS present in all major rivers, exhibiting high temporal and spatial variability, with concentrations ranging from below detection to  $156\text{ ng L}^{-1}$ . PFAS concentrations generally increased downstream of urban areas, notably showing an order of magnitude increase in the Rio Grande as it flows through Albuquerque. Urban runoff from stormflow events and treated wastewater discharge were identified as significant sources. PFBS was the most frequently detected and highest concentration PFAS. Importantly, several sites exceeded the EPA's drinking water standards for PFOA and PFOS. The research offers crucial insights to guide future PFAS sampling efforts.<sup>80</sup> In

Saskatoon, Canada, characterized as a semi-arid, cold region, the average total concentration of PFAS in stormwater was  $9.0\text{ ng L}^{-1}$ , and eleven different PFAS compounds were identified in snowmelt samples. Landfills have also been identified as major pollutant sources. In a case study assessing PFAS contamination from historic landfill groundwater plumes discharging to surface waters, endobenthic zones experienced the highest concentrations ( $>4000\text{ ng L}^{-1}$  pond site;  $>20\,000\text{ ng L}^{-1}$  urban stream site) year-round. Epibenthic exposure in non-flowing systems showed spatiotemporal variability, reaching  $\sim 4000\text{ ng L}^{-1}$ . Pelagic zones had elevated levels ( $>120\text{ ng L}^{-1}$  pond site;  $>60\text{ ng L}^{-1}$  urban stream site) despite dilution, indicating year-round exposure. Downstream mass loadings for short-chain + long-chain PFAA were  $15\text{ g}$  per year (pond site) and  $36\text{ g}$  per year (stream). The study also detected ultra-short-chain PFAS (TFMS, PFPrA, PFPrS), affirming historic landfills as significant, year-round PFAS sources to aquatic ecosystems.<sup>81</sup>

Considering that the Arabian Gulf is a partially enclosed marine system influenced by surrounding arid and semi-arid regions, the total PFAS concentrations in seafood varied from  $2.3$  to  $6.1\text{ ng g}^{-1}$ , with PFOS being the most common compound. PFAS have likewise been identified in sediments and fish from other saltwater coastal areas adjacent to arid regions, such as the Eastern Red Sea and Xiamen Bay.<sup>20,22</sup> PFAS contamination has been detected in various water systems and environmental matrices across several Middle Eastern countries. In Saudi Arabia, a study found total PFAS concentrations up to  $956\text{ ng L}^{-1}$  in marine water from the Red Sea coast near Jeddah, with the highest levels in lagoons receiving treated sewage effluents.<sup>72</sup> The predominant compounds were PFHxA, PFHxS, and 6:2 FTS. Municipal and industrial wastewater discharges and aqueous film-forming foams (AFFFs) used in firefighting are the suggested sources. Jordanian research on the Zarqa River, which receives significant wastewater effluent, showed total PFAS concentration levels ranging between  $16$  and  $27\text{ ng L}^{-1}$  in the river water, with PFPeA, PFOA, and PFDA as dominant compounds.<sup>82</sup> The Assamra wastewater treatment plant effluent had comparable concentrations ( $14$ – $24\text{ ng L}^{-1}$ ), indicating poor PFAS removal. While soil samples showed low levels, no PFAS were detected in alfalfa and mint crops. In Iran, PFOS and PFOA were detected in the Karun River, and PFAS compounds were identified in seafood from the Persian Gulf, suggesting bioaccumulation.<sup>20</sup> PFAS compounds have been identified in both tap and bottled water in Turkey, raising questions about the safety of drinking water. Research carried out in Lebanon detected PFAS in blood serum and breast milk samples from pregnant women, indicating a potential link to exposure *via* contaminated drinking water.<sup>83</sup>

Conversely, information on PFAS assessment in water systems is limited in the United Arab Emirates, highlighting the need for targeted research. Similarly, no study or research data on PFAS occurrence in any water sources in Qatar has been available for the last 5 years. The sources emphasize the



necessity for regular monitoring in regions lacking data to understand the prevalence of PFAS and compare values against international standard guidelines. This can also help set guidelines for controlling substances that lead to water source contamination. Overall, the findings across the regions studied underscore the impact of wastewater discharges and other potential sources like AFFFs on water contamination and the potential for individuals to be exposed through the consumption of drinking water and seafood highlights the importance of implementing monitoring and regulatory measures.

## 4 Global PFAS regulations

Establishing uniform regulations across different countries is particularly challenging due to the evolving nature of standard methods for environmental monitoring of PFAS and the associated costs. These costs include the need for specialized technical expertise, expensive analytical equipment, and chemicals. Consequently, routine monitoring of PFAS in water and their exposure effects remains a formidable challenge, especially for low-income countries. In this section of the review, we shall go over some of the recent regulations that pertain to drinking water and surface water contamination.

General global or national regulations and guidelines include the Stockholm Convention listing PFOS and PFHxS,<sup>78</sup> China's ban on PFOS and PFOA production/use with exemptions, IARC classification of PFOA and PFOS as carcinogens, US EPA health advisories, MCLs, and reference values for various PFAS in drinking water, EU maximum levels for PFAS in certain foodstuffs, and Canadian guidelines for wildlife diet.<sup>20</sup> However, none of the sources describe specific environmental guidelines or regulations for PFAS concentrations or management practices designed explicitly for arid or semi-arid environments, noting the lack of such considerations for dry and cold climates. Current regulatory strategies for surface waters do not account for occurrences in arid climates, which points to a possible gap in knowledge or policy.<sup>24</sup>

The European Union (EU), through its recast Drinking Water Directive (EU) 2020/2184, has established a stringent limit of 500 ppt for all PFAS compounds in drinking water, requiring compliance from all member states by 2026.<sup>84</sup> Similarly, USEPA enacted a National Primary Drinking Water Regulation (NPDWR) for six PFAS compounds in April 2024, drawing upon data assessed from over 120 000 sources and comprehensive stakeholder engagement.<sup>85</sup> This new regulation, enforceable under the Safe Drinking Water Act, mandates all public water systems to undertake initial monitoring of selected PFAS classes to establish baseline data by 2027, followed by compliance monitoring. The water operators must publicly disclose PFAS concentrations in drinking water starting in 2027. Should PFAS levels exceed the established maximum contaminant levels (MCLs), operators have until 2029 to implement corrective measures

to reduce PFAS concentrations to within acceptable limits.<sup>85</sup> This regulatory shift follows a series of non-enforceable health advisory limits issued in 2016 and 2022,<sup>86</sup> highlighting a move towards stricter, enforceable standards as more data become available. Notably, the advisory limits set in 2022 for PFOA and PFOS were significantly lower than those in 2016, reflecting increased concerns over their health impacts—PFOA was limited to 0.004 ppt and PFOS to 0.02 ppt, compared to 70 ppt in 2016.<sup>87</sup> Additionally, 2022 marked the introduction of advisory limits for hexafluoropropylene oxide dimer acid (HFPO-DA) and its ammonium salts at 10 ppt. The revision of these limits reflects growing data supporting stricter regulation, particularly following the classification of PFOA as a class 1 human carcinogen by the WHO.<sup>88</sup>

In Australia, the National Health and Medical Research Council (NHMRC) has proposed new guideline limits for four PFAS compounds in drinking water as of October 2024.<sup>89,90</sup> Reflecting an evolving understanding of health impacts, the recommended limit for PFOA has been significantly reduced from 560 ng L<sup>-1</sup> in 2018 to 200 ng L<sup>-1</sup> in the latest draft, responding to updated evidence of its carcinogenic potential.<sup>90</sup> Similarly, the guideline for PFOS has been drastically lowered from 70 ng L<sup>-1</sup> to 4 ng L<sup>-1</sup>, driven by concerns about its effects on bone marrow.<sup>89,90</sup> The limit for PFHxS has also been adjusted from 70 ng L<sup>-1</sup> to 30 ng L<sup>-1</sup>, influenced by new findings on its thyroid impacts.<sup>89,90</sup> Notably, the 2024 draft introduces a limit for PFBS for the first time, set based on its thyroid effects, indicating a proactive approach to emerging health data.<sup>90</sup> Notably, the regulatory limits in the United States are significantly stricter than those in Australia, reflecting differences in legislative approaches toward carcinogenic substances. In the U.S., any substance with potential carcinogenic effects is mandated to be reduced to as close to zero as possible, aligning with a more precautionary legislative stance. In contrast, Australian limits are based on a risk threshold approach, where acceptable levels are determined by the substance's estimated risk to public health.<sup>90</sup>

PFAS regulations have progressively evolved in Canada as more research findings become available. Initially, in 2018, regulatory limits were established at 600 ppt for PFOS and 200 ppt for PFOA.<sup>91,92</sup> By 2019, these regulations had expanded to include nine PFAS compounds, with limits ranging from as low as 20 ppt for PFNA to as high as 30 000 ppt for PFBA. Table 3 shows the most recent guidelines for permissible limits of PFAS in drinking water and surface water across the globe. These evolving regulations underscore a global shift towards tighter control of PFAS in drinking water, driven by increasing scientific understanding and public health concerns. With future enforcement targets already established, there is a clear trajectory towards more rigorous PFAS management, signalling a critical period for innovation in water treatment technologies to meet these upcoming challenges.

In addition to drinking and surface water guidelines, various countries have also implemented restrictions to



**Table 3** Global trends of PFAS permissible limits in drinking and surface water

Country	Regulatory and year	Water source	PFAS type	Permissible limit	Ref.
USA	USEPA-2024	Drinking water	PFOA	4 ppt	85
			PFOS	4 ppt	
			PFHxS	10 ppt	
			PFNA	10 ppt	
			HFPO-DA	10 ppt	
Mixture of two or more	1 (no unit) using hazard index				
USA	USEPA-2022	Freshwater	PFOA	49 ppm (acute water column)	93
		Marine water	PFOA	7 ppm (acute water column)	
		Freshwater	PFOS	3 ppm (acute water column)	
USA	USEPA-2022	Marine water	PFOS	0.55 ppm (acute water column)	94
		Freshwater	PFOS	0.55 ppm (acute water column)	
Australia	Australian NHMRC-2024	Drinking water	PFOS	4 ppt	89
			PFOA	200 ppt	
			PFHxS	30 ppt	
			PFBS	1000 ppt	
Australia	Environmental Protection Authority Victoria-2023	Recreational water	PFOS + PFHxS	2000 ppt	95
		Drinking water	PFOA	10 000 ppt	
New Zealand	New Zealand Water Services Drinking Water Standards-2022	Drinking water	PFOS + PFHxS	70 ppt	96
			PFOA	560 ppt	
			PFOS + PFHxS	70 ppt	
New Zealand	Taumata Arowai Recreational Water Quality Guidelines-2022	Recreational water	PFOS + PFHxS	2000 ppt	97
			PFOA	10 000 ppt	
Canada	Health Canada-2023	Drinking water	Sum of 25 individual PFAS	30 ppt	91 and 92
EU	EU Water Framework Directive-2013	Surface water	PFOS	0.65 ppt	98
	EU recast Drinking Water Directive-2020	Drinking water	Sum of 20 individual PFAS	100 ppt	84
England	England Drinking Water Inspectorate-2024	Drinking water	Sum of all PFAS	500 ppt	99
		Drinking water	Sum of 48 PFAS	100 ppt	
Scotland	Scotland Drinking Water Quality Regulator-2022	Drinking water	Sum of 20 PFAS	100 ppt	100
Japan	Environment Ministry-2020	Drinking water	PFOS+PFOA	50 ppt	101
China	Chinese Drinking Water Standard	Drinking water	PFOS	40 ppt	102
Global	WHO-2022	Drinking water	PFOA	80 ppt	89 and 103
			PFOS	100 ppt	
			PFOA	100 ppt	
			Total PFAS	500 ppt	

curtail the production of goods containing PFAS-active ingredients. The EU was among the pioneers, phasing out PFOS under the Persistent Organic Pollutants (POP) Regulation as early as 2009, with subsequent bans on PFOA and PFHxS in July 2020 and August 2023, respectively.<sup>104</sup> The UK has similarly prohibited PFOA and PFOS.<sup>16</sup> In the United States, the Food & Drug Administration (USFDA) banned PFAS-containing materials used in food packaging for grease-proofing purposes as recently as February 2024.<sup>105</sup> However, regulatory measures are not uniformly implemented worldwide. PFAS remain under-regulated in Asia, Africa, and Latin America. Japan stands out in Asia with bans on the production of PFOS and PFOA and stringent drinking water limits set at 50 ng L<sup>-1</sup> for both substances.<sup>102,106</sup> In Latin America, Brazil has taken steps towards regulation with the proposed Brazilian National PFAS Control Policy bill to establish a comprehensive framework for monitoring and

mitigating PFAS impacts.<sup>106</sup> Contrastingly, despite detecting significant PFAS concentrations in drinking and surface waters in Africa, regulatory frameworks remain notably inadequate, with little to no guidance on water quality or restrictions on PFAS-laden products.<sup>107,108</sup> This disparity in regulatory approaches highlights a critical need for a more unified global strategy to manage PFAS contamination effectively. Bridging these gaps will be essential for protecting public health and the environment from the pervasive impacts of these enduring chemical compounds.

## 5 Sample preparation for PFAS analysis

Sample preparation constitutes a pivotal stage in determining PFAS, primarily due to their occurrence at trace levels, wide-ranging physicochemical properties, and the complexity of



environmental matrices. The principal objective of preparation strategies is to improve analytical sensitivity and selectivity by pre-concentrating the target analytes and minimizing matrix interferences. However, several challenges persist, including matrix-induced signal suppression or enhancement, background contamination from laboratory consumables and glassware, analyte losses arising from volatility during thermal or drying steps, and the limited availability of isotopically labelled internal standards. Consequently, rigorous optimization is required to establish reliable, cost-effective, and field-applicable analytical protocols.

Commonly employed pretreatment and preparation techniques include solid phase extraction (SPE), which is extensively applied across diverse matrices to enrich PFAS; liquid-liquid extraction (LLE) and its microextraction variants, although often associated with high solvent consumption; and stir bar sorptive extraction (SBSE), a more sustainable, low-solvent microextraction approach

particularly suitable for volatile PFAS. Passive sampling strategies are also utilized for preliminary monitoring in aqueous and atmospheric environments.<sup>109,110</sup> Solid-phase microextraction (SPME) is another solvent-free, integrated sample preparation method combining sampling, cleanup, and preconcentration, ideal for ultra-trace detection of PFAS. It uses a sorbent-coated fiber or film to extract analytes from liquid, solid, or gaseous matrices through equilibrium partitioning. The extracted compounds are thermally or solvent-desorbed for GC-MS or LC-MS analysis. It provides a greener, more efficient alternative to conventional extraction methods such as SPE, reducing analyte loss and solvent use. SPME effectively extracts both volatile PFAS precursors (*e.g.*, FTOHs, FOSAs, FOSEs) using HS-SPME/GC-MS and ionic PFAS (*e.g.*, PFOA, PFOS, GenX) using LC-MS/MS.<sup>111</sup> Optimized conditions—such as heated or cycloid agitation—enhance diffusion-limited analyte recovery. Innovations like SPME-arrow designs increase sorbent volume, sensitivity, and linear range, while advanced coatings (*e.g.*, HLB-WAX/PAN)

**Table 4** Summary of sample preparation techniques and their respective challenges

Sl#	Technique	Disadvantages/challenges
1	Solid phase extraction (SPE)	<ul style="list-style-type: none"> <li>• Costly, time-consuming, labor-intensive</li> <li>• Requires large sample volumes, risk of clogging from suspended solids</li> <li>• Incomplete matrix removal and poor recovery at ultra-trace levels</li> <li>• Contamination risk from PTFE and adsorption to glassware</li> <li>• Automated systems need close monitoring</li> </ul>
2	Solid-phase microextraction (SPME)	<ul style="list-style-type: none"> <li>• Limitation in extraction capacity</li> <li>• Matrix effects</li> <li>• Fiber fragility and limited lifetime</li> <li>• Limited analyte range</li> <li>• Carryover and memory effects</li> </ul>
3	Liquid-liquid extraction (LLE) & microextraction variants	<ul style="list-style-type: none"> <li>• High solvent consumption, less environmentally sustainable</li> <li>• Limited automation</li> <li>• Incomplete extraction of short-chain PFAS; prone to emulsion formation</li> <li>• Possible overestimation from fluorinated materials</li> <li>• Multi-step, complex procedures</li> </ul>
4	Sportive/passive sampling (SBSE, passive sampling)	<ul style="list-style-type: none"> <li>• Wall effect: adsorption of analytes to glass surfaces</li> <li>• Strong matrix effects in complex samples (<i>e.g.</i>, wastewater influent)</li> <li>• May require derivatization for GC-MS (<i>e.g.</i>, perfluorocarboxylic acids)</li> <li>• Limited compound coverage and sensitivity</li> <li>• Total fluorine methods cannot differentiate individual PFAS</li> </ul>
5	TOP assay	<ul style="list-style-type: none"> <li>• Long preparation time (<math>\geq 6</math> h)</li> <li>• May miss precursors oxidizing to unmonitored PFAS</li> <li>• Can form intermediate fluorinated compounds not measured</li> <li>• Captures mainly precursors oxidized to PFAAs, not full PFAS spectrum</li> </ul>
6	TOF/TF ( <i>e.g.</i> , PIGE, CIC)	<ul style="list-style-type: none"> <li>• Results highly dependent on preparation method</li> <li>• PIGE costly, rarely used, requires gamma radiation (measures only surface fluorine, risk of overestimation)</li> <li>• CIC cannot resolve individual PFAS; response differs for organic <i>vs.</i> inorganic fluorine</li> </ul>
7	Derivatization & supporting steps (centrifugation, drying, homogenization, dilution)	<ul style="list-style-type: none"> <li>• Significant matrix interference</li> <li>• Multiple, complex steps (pH adjustment, washing, phase separation)</li> <li>• Incomplete derivatization or transfer <math>\rightarrow</math> underestimation</li> <li>• Suspended solids reduce recovery</li> <li>• Drying (<i>esp.</i> at high <math>T^\circ</math>) causes volatile PFAS loss</li> <li>• Risk of cross-contamination, poor homogenization leads to non-representative results</li> </ul>
8	Internal standards (isotopically labeled)	<ul style="list-style-type: none"> <li>• Over-dilution may cause false negatives, requiring re-analysis</li> <li>• Limited availability of labeled PFAS standards</li> <li>• Different isotopic labels may require MS parameter changes</li> <li>• Recovery must meet strict acceptance limits</li> <li>• Failure may require re-analysis or data qualification</li> </ul>



improve selectivity through hydrophobic and ion-exchange interactions. Mechanically robust recessed SPME rods allow *in situ* monitoring with minimal matrix effects (−13.7% to 11.1%) and quantification at part-per-trillion levels.<sup>112</sup> The method is easily automated, portable, and offers good analyte stability, aligning with green analytical chemistry principles. However, limitations include long extraction times (>22 h) due to strong matrix interactions, competitive adsorption reducing low-affinity analyte recovery, limited sorbent volumes (0.028–0.612  $\mu\text{L}$ ), and coating stability issues. Additionally, excessive agitation may increase variability (RSD up to 17%), and non-selective sorbents can intensify matrix effects.<sup>113</sup> For non-target or precursor analysis, total oxidizable precursor (TOP) assays and total organic fluorine (TOF) determinations provide comprehensive insight into PFAS burden.<sup>114</sup> Additionally, derivatization may be necessary when employing gas chromatography-based analytical workflows. The commonly employed techniques, their methodology and a comparative outline of their respective advantages and limitations are presented in Table 4.<sup>115,116</sup>

## 6 Analytical methods for the identification and quantification of PFAS

Measuring the levels of PFAS pollution in the environment is crucial to establishing water quality standards. A few procedures, including sample collection, preservation, preparation, and detection methodology for qualitative and quantitative analysis, are involved in measuring PFAS in a water matrix.

Several analytical techniques for identifying and tracking PFAS are available. The golden standard methodology used for PFAS determination is liquid chromatography. Due to its excellent sensitivity and selective compound identification technique, LC-MS/MS leads to trace-level analysis. Protocols for the analysis were developed and demonstrated. USEPA has established specific methods for testing water: method 537.1 and method 533 are designated for analyzing drinking water, while method 8327 is used for groundwater, surface water, and wastewater.

Other approaches, such as total oxidizable precursor (TOP)<sup>117</sup> and high-resolution accurate mass spectrometry, help to identify the molecular structure of the PFAS and the species. This mainly targets unknown PFAS compounds, which are oxidized and, in this method, the oxidized PFAS compounds were converted into detectable or measurable known PFAS compounds.<sup>118</sup> Non-target analysis combined with HRMS allows the identification of unknown compounds. An overall estimate of the PFAS can be calculated from the total organic fluorine content (TOF) using combustion ion chromatography (CIC) and particle-induced gamma ray emission (PIGE) spectroscopy. However, these methods do not provide information on specific PFAS compounds; they do give an estimate of overall PFAS concentration.

Modified LC-MS/MS methods are also in place, which use a reverse phase column for separating short and long chain PFAS, followed by a hybrid/ion exchange column for separating ultra-short and short chain PFASs. A trap column packed with weak ion exchange (WAX) sorbent enriches the ultrashort-chain PFAS, which was not retained by the RP column.<sup>119</sup> Table 5 summarizes methodologies employed for PFAS detection and their potential challenges.

### 6.1 Indirect detection methods

The  $\mu$ -MIP sensor was used for detecting GenX and PFOA, using a “turn-off” electrochemical mechanism. The sensor is fabricated by electropolymerizing *o*-phenylenediamine on a gold microelectrode, forming GenX-specific cavities. It demonstrates high sensitivity (LOD: 250 fM) and selectivity against environmental interferents, with a linear detection range of 1 pM to 5 nM. Electrochemical techniques like DPV assess current changes using redox mediators (*e.g.*, dissolved oxygen). Validated with Haw River water samples, the sensor minimizes distortions in high-resistance samples, enabling *in situ* application. This platform supports continuous GenX monitoring, empowering citizen scientists in water quality management.<sup>124</sup>

In another method, researchers used differential pulse stripping voltammetry (DPSV) at a  $\mu$ ITIES array for detecting perfluorooctanesulfonate (PFOS) in environmental water samples. A 5 minute preconcentration time was used to achieve a detection limit of 0.03 nM (0.015  $\mu\text{g L}^{-1}$ ) in an aqueous electrolyte solution. The researchers then tested their method on drinking water, laboratory tap water, and seawater. They observed a matrix effect, where the water samples altered the electrochemical signal, likely due to interactions between PFOS and matrix components, like the adsorption of PFOS to particulate matter. This suggests that matrix effect minimization strategies, such as standard addition calibration, will be needed to improve the accuracy of this method in real-world applications.<sup>125</sup>

Due to the presence of inorganic fluorine in the experimental solutions, which can lead to underestimation of total fluorine during targeted LC-MS/MS analysis, the AOF and EOF methods captured a more comprehensive picture of organic fluorine, revealing that the above was correct. This study has two optimized methods for measuring total organic fluorine (TOF) in various matrices: the AOF method, which uses activated carbon adsorption, and the EOF method, which employs solid-phase extraction. Both methods involve combusting the extracted organic fluorine to convert it into inorganic fluoride, which is then measured by ion chromatography. The researchers aimed to improve the recovery of organic fluorine while minimizing the co-extraction of inorganic fluorine, which can lead to artificially high TOF measurements. Both methods successfully quantified TOF in industrial wastewater, river water, and air samples. The EOF method demonstrated slightly higher recoveries and lower detection limits than the AOF method.



Table 5 Methodologies employed for PFAS detection and their potential challenges

Method	Compounds	Water sample matrix type	Sample preparation technique	Challenges	Interferences	Detection limits	Ref.
LC-MS/MS	Class 1 <sup>a</sup>	<ul style="list-style-type: none"> <li>➤ Wastewater</li> <li>➤ Surface Water</li> <li>➤ Ground water</li> <li>➤ Leachate</li> </ul>	Solid-phase extraction (SPE)	<ul style="list-style-type: none"> <li>Isotope dilution</li> <li>Cleanup procedure</li> </ul>	<ul style="list-style-type: none"> <li>➤ Contamination by laboratory materials</li> <li>➤ Cross-contamination</li> <li>➤ Co-extracted interferences</li> <li>➤ Fluoropolymers</li> <li>➤ Bile salts</li> </ul>	LOQ from 1 to 4 ng L <sup>-1</sup>	120
TD-GC-MS	PFHpA PFOA PFNA PFDA PFUnA PFDoA PFTeDA PFHxDA PFODA	<ul style="list-style-type: none"> <li>➤ Tap Water</li> <li>➤ River water</li> <li>➤ Influent and effluent samples from WWTPs</li> </ul>	Derivatization and extraction	For achieving low detection limits a pre-concentration step may be needed	Matrix effects for wastewater samples	<b>21.17 to 73.96 ng L<sup>-1</sup></b>	121
CIC	PFBA PFOA PFUnDA PFBS PFOS PFDoDs 6:2 FTSA MeFOSA 8:2 FTOH 8:2diPAP PFOPa 6:2 Cl-PFESA HFPO-DA	Spiked deionized Water and blood	Solid-phase extraction (SPE) and ion-pair extraction	Combustion efficiencies for different matrices	Presence of caution and matrix (for biological samples such as blood)	LOD – 50 ng mL <sup>-1</sup>	115
PIGE	HFPO-DA PFBS PFPeA PFHxA PFHxS PFHpA PFOA PFOS PFNA PFDA	Bottled water	Filtration and solid phase extraction	This can only be used for screening	Not to be used at very low pH	LOD – 50 µg L <sup>-1</sup>	122
HR-CS-GFMAS	PFCAs PFSAs FTOHs FECAs/ FESAs FOSAs diPAPs	Spiked sample	Solid phase extraction (SPE)	<ul style="list-style-type: none"> <li>PFAS volatility</li> <li>Species specific</li> <li>Response</li> <li>Matrix effect</li> <li>Modifier optimization</li> <li>Time temperature program tuning</li> </ul>	<ul style="list-style-type: none"> <li>➤ Chlorine</li> <li>➤ Aluminum</li> <li>➤ Magnesium</li> <li>➤ Persulphate</li> </ul>	(LOD) – <b>β(F) 1.71 µg L<sup>-1</sup></b> (LOQ) – <b>β(F) 5.13 µg L<sup>-1</sup></b>	123

<sup>a</sup> Class 1: PFCAs, PFSAs, FTOHs, FECAs, FESAs, FOSAs, and diPAPs (full breakdown can be found in Table S1). LC-MS/MS – liquid chromatography coupled with tandem mass spectrometry; TOF – total organic fluorine content; CIC – combustion ion chromatography; PIGE – particle-induced gamma ray emission (PIGE) spectroscopy; TD-GC-MS – thermal desorption unit coupled with gas chromatography-mass spectrometry; HR-CS-GFMAS – high resolution-continuum source-graphite furnace molecular absorption spectrometry.

However, the choice between the two methods depends on factors like sample volume, analysis time, and cost.<sup>114</sup>

A straightforward, quick, and reliable analytical technique called SBE-TD-GC-MS was utilized to extract and quantify fluorotelomer alcohols (FTOHs) present in water. This

method uses stir bar sorptive extraction (SBSE) combined with thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). It was refined using three frequently found FTOHs—specifically 6:2, 8:2, and 10:2 FTOH—as representative compounds. The process involves



two primary stages: first, FTOHs are extracted from water samples using a stir bar coated with polydimethylsiloxane (PDMS). In the thermal desorption step, the stir bar is placed in a thermal desorption unit where the FTOHs are released and moved to a GC-MS system. Within the GC-MS system, the FTOHs are separated and then analyzed using the selected ion monitoring (SIM) mode. The method proved good linearity, consistent repeatability, and effective recovery rates, with detection limits (LODs) varying from 2.16 ng L<sup>-1</sup> to 16.7 ng L<sup>-1</sup>. The refined method successfully identified 6:2 FTOH and 8:2 FTOH in wastewater samples at very low concentrations, specifically at the parts per trillion (ppt) level. This approach is considered environmentally friendly and sustainable because it needs just a small sample volume (20 mL) and a minimal amount of organic solvent (1 mL of methanol) for monitoring FTOHs in water.<sup>126</sup>

The combustion chromatography method identifies PFAS as the sum of total, adsorbable and extractable organic fluorine.<sup>127</sup> This is the best approach for the analysis of the complex matrix.<sup>128</sup> Analysis and combustion efficiencies of 13 different PFAS were studied, ranging from 66 to 110%.<sup>115</sup> The authors concluded that different functional groups could lead to different thermal degradation profiles, affecting combustion efficiency. For example, the combustion efficiencies of perfluoroalkyl carboxylic acids (PFCAs) decreased as chain length increased. The sources explain that it is important to consider these variations in combustion efficiency when analyzing environmental samples, as assuming a constant combustion efficiency of 100% could lead to an underestimation of PFAS content.

Additionally, the study evaluated the potential for matrix interferences from surface water and whole blood samples and found that they did not impact the CIC analysis. However, the sources emphasize that this study's absence of matrix effects cannot be generalized to other matrices or extraction methods. The authors suggest utilizing a matrix-matched sample to ensure that co-extracted matrix components do not affect the analysis of EOF content when using CIC.

Particle-induced gamma-ray emission (PIGE) spectroscopy was used to identify PFAS in the water matrix. This method measures the total fluorine, representing the fluoride molecules associated with the PFAS compounds. The samples were filtered through activated carbon felt, which was then analyzed using PIGE. The felt was exposed to proton bombardment, causing the fluorine nuclei to emit gamma rays, which were utilized for identification and quantification. The method measured fluorine from PFAS below 50 µg L<sup>-1</sup> for a 2 L water sample and measured 64% of PFAS compounds from water samples. Working at a low pH below two prevented inorganic fluoride from binding to the filter. This can only be utilized as an initial screening method to pinpoint samples containing high fluoride

levels; a more sensitive technique is required for the conclusive measurement and assessment.<sup>122</sup>

## 6.2 Total oxidizable precursor (TOP) assay analysis

TOP assay is an indirect analytical method used to estimate the total concentration of oxidizable PFAS precursors in a sample. Its primary purpose is to provide a more comprehensive understanding of PFAS contamination, including those precursors not typically measured by standard targeted analysis. The core principle involves subjecting a sample aliquot to strong oxidative conditions. This is typically achieved by activating potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) with heat, often at 85 °C, under alkaline pH (>12). This process generates sulfate radicals (SO<sub>4</sub><sup>•-</sup>), which are quickly converted to hydroxyl radicals (-OH), the primary oxidants. These radicals convert oxidizable PFAA precursors into stable PFAAs, mainly perfluoro carboxylic acids (PFCAs). Under these conditions, terminal PFAAs (PFCAs and PFSAs) generally remain intact.<sup>129</sup> By comparing the concentrations of PFAAs in the sample before and after the oxidative treatment, the increase (ΔPFAA) estimates the amount of oxidizable precursors that were converted. The resulting PFAAs are then measured using standard targeted PFAS analytical techniques like UHPLC-HRMS or UHPLC-MS/MS. The TOP assay has been applied to diverse matrices, including environmental water, soil, sediment, and biological samples like human plasma.<sup>130</sup>

Despite its utility as a complementary approach to targeted analysis, the TOP assay has limitations. A significant challenge is that not all precursors may achieve complete oxidation. High organic matter content, insufficient oxidant, or other co-contaminants can reduce oxidation efficiency, potentially leading to underestimation of total precursors. Matrix effects, particularly from the high salt content after oxidation, can also pose issues for instrumental analysis. The oxidation process is not specific, producing a range of products, making it difficult to link increases to specific precursors.<sup>117</sup> While PFAAs are assumed stable, some studies report increases in PFAAs post-TOP, potentially from sulfonamide precursors or release of bound compounds.<sup>131</sup> The assay may not capture volatile precursors or efficiently convert PFAS with ether linkages. Various modifications and techniques have been explored to address these issues, including using different activation methods or oxidants. Table 6 summarizes the associated techniques.

## 6.3 Volatile per- and polyfluoroalkyl substances

The necessity for capturing and quantifying volatile per- and polyfluoroalkyl substances (V-PFAS), or volatile fluorinated compounds (VFCs), stems from their persistence and widespread emission from stationary sources like manufacturing facilities and waste thermal treatment. Inadequate destruction during thermal processes results in VFCs as products of incomplete combustion or destruction



**Table 6** Summary of the techniques/activators from TOP analysis

Technique/activator	Description/reported behavior	Performance
Thermal persulfate	The standard method uses heat ( <i>e.g.</i> , 80–85 °C) with alkaline persulfate to generate radicals	Varies with matrix complexity and precursor concentration, potentially leading to incomplete conversion
UV-activated persulfate	Uses UV light to activate persulfate	This can lead to quicker sample oxidation and potentially better preservation/yield for some compounds compared to thermal activation <sup>39</sup> . Still susceptible to matrix effects
Ozone	Used as an alternative oxidant, typically under neutral or near-neutral pH conditions	Degradation of products and efficiencies can vary significantly depending on the compound, oxidant type, pH, and matrix
Acidic persulfate digestion	Uses persulfate under acidic pH to primarily generate sulfate radicals. Can oxidize compounds without C–H bonds and can cause decarboxylation of PFCAs	Can significantly expand the range of oxidizable precursors compared to methods primarily relying on hydroxyl radicals. Results in different product distributions
Direct TOP (dTOP)	Oxidation of the whole sample (aqueous or solid) before extraction of PFAS	Aims to minimize losses during sample processing and extraction. Significantly higher total PFAS estimates compared to targeted analysis alone
Post-extraction oxidation	Extraction of PFAS from the sample first, followed by oxidation of the extract	Suggested to minimize matrix effects from the sample matrix. Might not capture all precursor types as effectively during the initial extraction step

(PICs/PIDs).<sup>56</sup> Quantification is crucial for highly volatile species like tetrafluoromethane (CF<sub>4</sub>), the most abundant VFC in the atmosphere emitted by these sources. Accurate measurement is required to determine the release of VFCs to air. Furthermore, V-PFAS act as atmospheric precursors that oxidize into persistent perfluorinated carboxylic acids (PFCAs), contributing to global contamination. To address this, the U.S. EPA developed Other Test Method (OTM)-50 for measuring VFC emissions.<sup>57,132</sup> Specialized tools, such as nylon-based passive air samplers for ultra-trace detection of gaseous PFCAs (C<sub>2</sub>–C<sub>6</sub>) and infrared spectral databases, are also essential for improving identification, quantification, and assessing the efficacy of treatment processes (Table 7).<sup>132</sup>

## 7 PFAS treatment technologies

Due to the chemical stability of the carbon–fluorine (C–F) bond, standard treatment methods like coagulation, sedimentation, and biological degradation have shown limited effectiveness in removing PFAS from water.<sup>136–139</sup> Consequently, the focus has shifted to alternative

remediation strategies, primarily categorized as physical separation and degradation techniques. As summarized in Fig. 3, common approaches include adsorption, membrane filtration, photocatalytic degradation, chemical oxidation, and biological treatments. While promising, many of these advanced technologies remain energy-intensive, costly, or face operational constraints that limit their feasibility for full-scale application.<sup>140,141</sup>

The performance of these technologies varies significantly. Advanced methods show greater potential than conventional wastewater treatment processes, which have low removal efficiencies (1–46%) and may even generate new PFAS from precursors.<sup>142</sup> For instance, advanced oxidation processes (AOPs) like electrochemical oxidation (EO) can achieve over 98% removal and 95% mineralization of certain PFAS, though it is associated with high operational costs. Higher removal rates (~100%) have been reported in systems that combine EO and membranes/adsorbents.<sup>143</sup> Other AOPs, such as UV-activated persulfate (PS/UV), can degrade 57% of PFBA, 80% of PFOA, and 60% of PFOS in controlled solutions, but their effectiveness is reduced in complex water matrices.<sup>143</sup>

**Table 7** Comparative sampling and detection methods for volatile PFAS

Sampling technique	Proposed analytical method	Target analytes	Application/source type	Ref.
U.S. EPA Other Test Method 50 (OTM-50)	Thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS)	Volatile fluorinated compounds (VFCs) C1–C8 compounds with C–F bonds	Stationary source emissions from fluorochemical manufacturing, incinerators, thermal treatment, pyrolysis, SCWO facilities	133
Nylon substrate passive air samplers (PAS)	IC-CD, IC-MS, GC-MS	Tetrafluoromethane Gaseous perfluoroalkyl carboxylic acids (PFCAs) such as TFA, PFPrA, PFBA, PFPeA, PFHxA	Ambient air	132
Passive sampling (combined)	GC-MS for neutrals/volatiles, and LC-MS/MS for ionic species	Volatile/neutral PFAS ( <i>e.g.</i> , 6:2 FTOH, 8:2 FTOH) Ionic PFAS ( <i>e.g.</i> , PFBA, PFOS)	Ambient air	60
Particulate matter (PM-10) sampling	LC-HRMS	Ionic PFAS (PFBA, PFHpA, PFOA, PFOS, <i>etc.</i> ) associated with aerosols	Activated sludge aeration (ASA) at wastewater treatment plants (WWTPs)	134
Active sampling (PM <sub>2.5</sub> )	SPE-LC-HRMS	Ionic PFAS (PFBA, PFHxA, PFOA, PFOS, <i>etc.</i> )	Residential indoor air	135



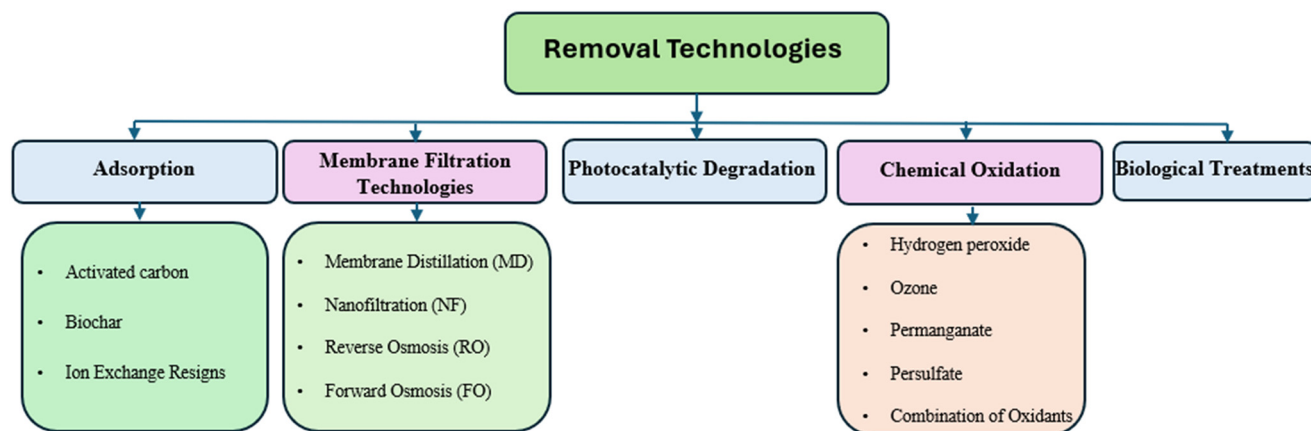


Fig. 3 Removal technologies for different PFAS compounds.

Biological treatments are eco-friendly but are typically slow and result in persistent byproducts. However, aerobic conditions are more suitable for polyfluorinated compounds, while anaerobic conditions are preferable for perfluorinated compounds.<sup>144</sup> To overcome the limitations of single technologies, integrated systems combining multiple methods are increasingly advocated for, with the potential to achieve removal efficiencies of 90–99%.<sup>145</sup> In the interim, more practical and cost-effective approaches employed on a large scale are activated carbon adsorption for WWTPs and biochar or ion exchange resins for households/remote communities.<sup>146</sup>

Currently, only a limited number of PFAS remediation technologies have reached full-scale application. Granular activated carbon (GAC), ion exchange resins, and high-pressure membranes (nanofiltration and reverse osmosis) are the most widely deployed in municipal drinking water treatment and industrial wastewater systems due to their proven effectiveness in capturing a broad range of PFASs.<sup>147</sup> These technologies are primarily applied in *ex situ* pump-and-treat configurations. They can achieve regulatory compliance levels, although they generate secondary waste streams such as spent adsorbents and brine that require further management. Thermal treatment (*e.g.*, incineration) has also been implemented at hazardous waste facilities for PFAS-concentrated wastes, but its sustainability and byproduct concerns remain debated.<sup>148</sup> In contrast, emerging methods such as foam fractionation, plasma reactors, and electrochemical oxidation are still at pilot or demonstration scales.<sup>149,150</sup> Therefore, large-scale remediation today remains dominated by adsorption- and membrane-based processes,

while destructive and *in situ* technologies continue to progress toward broader field deployment.

Table 8 provides a comparative analysis of these key technologies' scalability, advantages, and limitations.

### 7.1 Considerations for adsorption

Adsorption is a scalable and cost-effective remediation strategy that relies on hydrophobic and electrostatic interactions between PFAS molecules and an adsorbent's surface. Activated carbon (AC), in granular (GAC) or powdered (PAC) form, can remove over 90% of long-chain PFAS but is less effective for short-chain variants (<60%).<sup>146,151,152</sup> Its performance is inhibited by competitive adsorption, where long-chain PFAS displace short-chain compounds, and by charge neutralization from background ions, a mechanism illustrated in Fig. 4. Biochar, a sustainable alternative, also shows higher efficiency for long-chain (70–85%) *versus* short-chain PFAS,<sup>153,154</sup> with its various interaction mechanisms shown in Fig. 5. Its performance is similarly hindered by dissolved organic matter and competing ions.<sup>155</sup> In contrast, ion exchange resins can achieve over 95% removal for both short- and long-chain PFAS, often outperforming AC and biochar, but are limited by higher costs and secondary waste generation.<sup>156</sup> Advanced developments like dual-functional resins aim to enhance removal efficiency while minimizing waste production.<sup>157</sup>

### 7.2 Considerations for membrane technologies

Membrane filtration technologies physically separate PFAS from water using mechanisms of size exclusion and

Table 8 Scalability of technologies considered for PFAS removal from water

Technology	Efficiency	Application scale	Advantages	Limitations
Activated carbon	70–95% (varies by PFAS)	Small to large	Cost-effective; proven	Short-chain PFAS removal low
Ion exchange resins	>95%	Small to medium	High removal rates	Expensive; frequent disposal
Nanofiltration	50–90%	Small to medium	Effective for long-chain	Fouling; energy-intensive
Reverse osmosis	>99%	Small to large	Comprehensive removal	High energy costs
Biological methods	<50%	Pilot/small	Eco-friendly potential	Slow degradation rates





Fig. 4 Inhibition of short-chain PFAS sorption on GAC. a) Hydrophobic long-chain PFAS induces desorption from the outmost sites, and b) reduction in electrostatic interaction with the GAC functional group is due to charge neutralisation by cations. Adapted with permission from ref. 158 with permission from Elsevier, copyright 2023.



Fig. 5 Mechanisms of adsorption of PFAS onto biochar and competition with dissolved organic matter (DOM). Adapted and reproduced from ref. 159 and 160 with permission from Springer Nature copyright 2024 and Elsevier copyright 2022, respectively.

electrostatic repulsion.<sup>151</sup> Reverse osmosis (RO) is the most effective technology, achieving over 99% removal for both long- and short-chain PFAS.<sup>161,137</sup> Nanofiltration (NF) is also highly effective for long-chain compounds (>90%), but its efficiency drops for short-chain PFAS (50–80%).<sup>139</sup> However, certain NF membranes (*e.g.*, NF90) have demonstrated rejection rates of over 97% for all PFAS, including ultrashort ones, in specific studies.<sup>162</sup> Both RO and NF are constrained by high energy consumption and membrane fouling.<sup>163</sup> Emerging alternatives include Forward Osmosis (FO), which offers lower energy costs but suffers from low permeate flux,<sup>164</sup> and mixed matrix membranes (MMMs), which incorporate nanomaterials to enhance performance and

have achieved 99.4% PFAS removal in certain configurations.<sup>165</sup>

### 7.3 Considerations for photocatalytic degradation

Photocatalysis utilizes a semiconductor photocatalyst that, upon light absorption, generates electron-hole pairs. These lead to the formation of reactive oxygen species (ROS) that break down PFAS molecules.<sup>166</sup> This degradation pathway is outlined in Fig. 6, showing the stepwise process where long-chain PFAS are broken into shorter-chain intermediates before mineralization.<sup>166</sup> Various catalysts have been explored, including TiO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, and metal-organic frameworks (MOFs).<sup>167,168</sup> High performance has been





Fig. 6 Mechanism of photocatalytic AOPs for degrading PFAS. Adapted from ref. 166, published by MDPI, copyright 2023 by the authors, under the terms of the CC BY 4.0 license.

reported with advanced materials; for example, a duo-functional tri-metallic-oxide (f-TMO) hybrid photocatalyst achieved 99.8% adsorption of PFOS and 95.5% degradation within 300 minutes. A high regeneration efficiency of the photocatalyst (>96.5%) was achieved after eight regeneration cycles.<sup>168</sup> Key challenges include reduced efficiency due to interference from natural organic matter, the higher resistance of short-chain PFAS to degradation, and the need to improve catalyst recyclability and cost-effectiveness for large-scale use.

#### 7.4 Considerations for chemical oxidation

Chemical oxidation employs strong oxidants to generate highly reactive radicals that can degrade PFAS. The effectiveness varies significantly by oxidant and conditions. Ozone is largely ineffective at neutral pH, but PFOA and PFOS can degrade by 85–100% under alkaline conditions, promoting superoxide radical formation.<sup>169</sup> Permanganate has been shown to degrade 46.8% of PFOS at elevated temperatures (65 °C) and acidic pH (4.2).<sup>170</sup> When activated by heat or UV light, persulfate generates potent sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) that are effective against both PFOA and PFOS.<sup>171</sup> A primary challenge is the variable effectiveness across different PFAS compounds and water matrices, making a universal solution unlikely. Additionally, some oxidation processes risk converting PFAS precursors into more stable and persistent perfluoroalkyl acids (PFAAs).

#### 7.5 Considerations for biological treatment

Bioremediation uses microorganisms or enzymes to degrade PFAS, but the strength of the C–F bond severely limits its application. Biodegradation utilizing bacteria such as *Pseudomonas* sp. has been investigated, but reported degradation rates are impractically low at less than 20%.<sup>172</sup> Enzymatic degradation shows slightly more promise, with studies achieving up to 50% degradation of long-chain PFAS under optimized laboratory conditions.<sup>173</sup> However, low degradation rates and challenges in scaling these

technologies for complex environmental conditions remain significant hurdles.

## 8 Recommendations and future directions

Scaling up biological methods, further improving adsorbents, and developing hybrid systems, including multiple remediation techniques, are considered the focus of future efforts in dealing with the pervasive challenge of PFAS contamination. Such examples may include integrating adsorption with membrane filtration or biological methods to exploit the strengths of each technology for better overall efficiency at reduced cost, as stated.<sup>174</sup> The development of functionalized adsorbents with higher selectivity and better regeneration potential is also an immediate need to overcome shortcomings of new adsorption technologies.

Additionally, advancements in membrane technology, such as developing anti-fouling surfaces and energy-efficient designs, could make these methods more accessible for large-scale applications. Much better discharge limits and financial incentives need to be instituted or, where promulgated, their enforcement becomes more binding to incentivize technology innovations in PFAS remediation methodologies to higher implementation rates. It urges governments, institutions, and industries to support a high degree of collaboration towards advancing cheaper, full-scale technologies of PFAS remediation. Public awareness campaigns can also go a long way in promoting these solutions by bringing to the fore the health and environmental risks that PFAS contamination poses. Future research should focus on hybrid systems incorporating physical and chemical remediation methods, such as membrane filtration and advanced adsorption techniques. These systems can achieve higher removal efficiencies while minimizing operational costs.

Further development in the fields of enzyme engineering and the design of microbial communities is expected to be crucial for improving efficiency and scaling biological treatments. Long-term monitoring and assessment of remediation performances are necessary to ensure effective and sustained operation. This should include the implementation of sound monitoring frameworks that allow the proper impact evaluation of PFAS remediation strategies and their fine-tuning concerning challenges emerging during a given period.

Due to their persistence and bioaccumulative nature, PFAS are a global concern, which leads to adverse public health and environmental impacts.<sup>167</sup> PFAS are challenging to remove with conventional water treatment technologies because they are present in low concentrations ( $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$ ), and their strong carbon–fluorine (C–F) bonds make them resistant to degradation.

Several noteworthy technologies have been developed to remove PFAS from water. Using materials like activated carbon and ion exchange resins, adsorption is common for



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concentrating PFAS before destruction. However, adsorption is not a destructive technique and generates secondary waste. Heterogeneous photocatalysis, a destructive method that uses semiconductor photocatalytic materials to degrade PFAS, shows promise for PFAS removal.<sup>175</sup> However, this method can be energy-intensive. Other technologies, such as membrane filtration (*e.g.*, nanofiltration and reverse osmosis), ozonation, electrochemical oxidation, and sonolysis, are also gaining traction. The choice of remediation technique depends on factors such as the type and concentration of PFAS, cost, and energy consumption.

## Conclusion

The growing awareness of PFAS as persistent, toxic, and globally distributed contaminants has driven urgent efforts to understand and mitigate their risks. While their use in industrial and consumer products has offered valuable benefits, PFAS are now widely recognized for their resistance to degradation and bioaccumulative potential, earning them the designation of “forever chemicals”. Exposure to PFAS has been linked to serious health effects, including endocrine disruption, immune system suppression, developmental toxicity, and cancer. Regulatory authorities such as the U.S. EPA and WHO have responded by establishing advisory levels and proposing maximum contaminant limits. Yet, detection, monitoring, and treatment challenges remain, particularly in data-scarce regions.

In arid regions such as the MENA, the risks are exacerbated by heavy reliance on vulnerable groundwater resources and limited water infrastructure. The region suffers from a critical lack of empirical data on PFAS occurrence in water, soil, and biota, hindering risk assessment, regulatory enforcement, and public awareness. This gap is primarily due to inadequate research funding, limited technical expertise, and the absence of region-specific monitoring protocols.

Advances in PFAS remediation technologies show considerable promise, though their scalability and cost-efficiency remain ongoing challenges. Conventional methods like GAC and RO are more established but often fail to treat short-chain PFAS and require energy-intensive operations.

Emerging artificial intelligence (AI) and machine learning (ML) tools offer new solutions by enhancing the detection, prediction, and treatment optimization of PFAS. These tools can improve source identification, predict toxicity, and support real-time monitoring through sensor integration. However, their success depends on access to high-quality datasets and region-specific environmental information.

## Author contributions

Arun K. K.: conceptualization, writing and editing; Haya Saleh Al Yasi: writing. Ojima Z. Wada: writing – editing. Fares AlMomani: supervision – review. Khaled A. Mahmoud: supervision – review.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Supplementary information is available (SI). See DOI: <https://doi.org/10.1039/d5ew00570a>.

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