Per- and Polyfluoroalkyl Substances (PFAS) in Aquatic Environments: Occurrence, Bioaccumulation, and Risk

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Abstract

PFAS have become a prominent class of contaminants to study in aquatic environments due to the combination of persistence, mobility, bioaccumulation potential and analytical complexity. This is a narrative review that summarises the peer-reviewed evidence of PFAS presence, sources, bioaccumulation and risk in freshwater systems, estuarine systems and marine systems. The literature demonstrates that a combination of direct industrial discharges, wastewater treatment plant discharges, landfill leachate, aqueous foams which form films, diffuse urban runoff, biosolid-amended catchments and atmospheric deposition drive aquatic pollution. Long-chain perfluoroalkyl acids, especially PFOS and longer-chain perfluorocarboxylic acids, continue to be the focus of bioaccumulation and trophic-transfer issues, whereas short-chain and replacement PFAS have other issues due to their higher mobility and difficulty to eliminate in water. The behaviour of PFAS in aquatic food webs has been shown to be inexplicable in terms of the traditional hydrophobic-partitioning assumptions; protein binding, chain length, functional group, precursor conversion and routes of exposure peculiar to the matrix are all essential. Uncertainty exists in risk assessment due to the predominance of a small number of target analytes in environmental monitoring, disproportionate toxicity data among species and life stages, and inability to resolve mixture effects. The review suggests that the future assessment of aquatic PFAS needs to change its compound-by-compound monitoring to class-conscious, source-conscious, and effects-linked management.

Keywords: PFAS, aquatic environments, bioaccumulation, trophic transfer, wastewater, ecological risk

1. Introduction

PFAS are a broad family of fluorinated organic substances, the use of which in industries and consumer products dates back to the 1970s due to their ability to confer resistance against heat, water, oil, and chemical attack. What makes them useful is the same chemical stability that contributes to their environmental significance. The stability of carbon-fluorine bonding, along with surfactant-like behaviour of many PFAS, permits many compounds and transformation products to remain, travel in hydrological systems, and be incorporated into food webs. PFAS are not just another category of trace contaminants to aquatic scientists. They dismantle conventional beliefs regarding the partitioning of pollutants between water, sediment, and biota, the types of exposure measurements that should be used to assess them, and the comparisons that should be made of risks across compounds (Buck et al., 2011; Ahrens, 2011; Evich et al., 2022).

PFAS includes the legacy perfluoroalkyl acids perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), shorter-chain homologues, fluorotelomer-based materials, perfluoroether acids, sulfonamides and numerous precursor materials. Such chemical diversity causes a discrepancy between the reality of the environment and the limited focus of most monitoring programmes. In the past, PFAS studies have focused on PFOS and PFOA since the two chemicals were produced in large quantities, were often detected and linked to persistence, bioaccumulation and toxicity. Nevertheless, subsequent authors have indicated that thousands of PFAS have been utilized or put on the market, and most replacement compounds and precursors are not detected with a regular target analysis (Wang et al., 2017; Xiao, 2017; Gluge et al., 2020).

Aquatic systems are of particular significance since they combine various release pathways. Wastewater effluents, industrial discharges, stormwater, contaminated groundwater and leachates of landfills and waste sites are collected in rivers. Riverine input is also received in estuaries and coastal waters, which also serve as mixing zones wherein partitioning is affected by salinity, suspended solids and organic matter. PFAS can be long-term stored in lakes and reservoirs in water, sediment and biota, and in the marine system moved over long distances by mobile compounds. This implies that the data of aquatic occurrence are both indicators of local sources and indicators of more widespread environmental circulation (Loos et al., 2009; Ahrens, 2011; Kurwadkar et al., 2022).

The risk story of PFAS in the water is not a straightforward high-concentration story around known sources. In most water bodies, dissolved phase levels can be low relative to legacy hydrophobic contaminants, but biologically significant exposure may still ensue due to some PFAS binding to proteins, accumulating in blood and liver, and amplifying through some food webs. On the other hand, short-chain PFAS can demonstrate less classical

bioaccumulation factors but endure in water, travel longer distances and make drinking-water treatment more difficult. Therefore, occurrence, bioaccumulation and risk must not be viewed as two distinct issues but as a unit (Conder et al., 2008; Ng and Hungerbuhler, 2014; Brendel et al., 2018).

Another motivation to assess PFAS in aquatic environments is the evolving regulation and analysis environment. Some of the older PFAS are currently limited or have guideline limits, yet aquatic surveillance is still showing some compounds that were not included in older regulations. This poses a moving target to scientists and environmental organizations. An aquifer or river that is deemed to be acceptable based on one set of analytical panels could have a different interpretation when precursors, short-chain homologues or ether-based substitutes are taken into account. The work of aquatic review must go beyond the summary of concentrations and thus consider the influence of the evidence base itself on the availability of methods, regulatory focus, and historical production trends (Wang et al., 2017; Xiao, 2017; Gobelius et al., 2018).

The objective of this narrative review is to provide a synthesis of the existing evidence regarding the occurrence of PFAS in aquatic environments and answer three related questions: where and why PFAS are present in aquatic environments; how various PFAS interact in the water, sediment and organisms; and what gaps remain to interpret ecological and human-health risks. The review will prioritize peer-reviewed articles in the past 10 years, but will keep older foundational papers that defined PFAS terminology, global wildlife detection and aquatic food-web behaviour. The main point is that in order to detect aquatic PFAS, the synthesis across sources, matrices, compounds, and biological endpoints requires greater strength. In the absence of such integration, monitoring can underestimate exposure, bioaccumulation studies can not consider the relevant precursors, and risk assessment can be limited to a small portion of the PFAS that is present.

2. Review Approach and Literature Selection

The paper is written in the style of a narrative review as opposed to a systematical review or meta-analysis. The aim was to construct a critical synthesis around occurrence, bioaccumulation and risk as opposed to calculating pooled effect sizes. Major scientific databases and publisher platforms were searched with a combination of terms such as PFAS, perfluoroalkyl substances, aquatic environment, surface water, groundwater, sediment, biota, wastewater, landfill leachate, aqueous film-forming foam, bioaccumulation, trogic transfer, ecotoxicity, risk assessment and non-target screening. Studies reporting aquatic matrices, source-pathways, organism data, analytical challenges or ecological impacts were favored.

The review retained about three types of literature. First, there were foundational papers; where they are still crucial in terminology or other early global occurrence or bioaccumulation concepts (Giesy and Kannan, 2001; Martin et al., 2004; Houde et al., 2006; Buck et al., 2011). Second, the growing PFAS universe, wastewater and landfill routes, aquatic presence and bioaccumulation dynamics were framed with the help of recent review and synthesis papers (Wang et al., 2017; Lenka et al., 2021; Evich et al., 2022; Khan et al., 2023). Third, the field and experimental studies were incorporated in case they demonstrate noteworthy patterns of evidence, including river-basin contamination, AFFF-impacted waters, marine toxicity endpoints, food-web transfer or methodological limitations (Campo et al., 2015; Gobelius et al., 2018; Hayman et al., 2021; Ali et al., 2021).

The review does not purport to be a comprehensive review of PFAS publications since the area of focus is quite extensive and is growing at a considerable pace. It instead focuses on highly cited, methodologically influential, recent, or directly related to aquatic occurrence, bioaccumulation and risk studies. References were verified in terms of author names, year, journal and DOI where possible. The synthesis also does not assume that all the PFAS are toxicologically identical. Simultaneously, it acknowledges that a compound-by-compound methodology has grown increasingly inadequate due to the possibility of precursor transformation, replacement chemistry and unknown organofluorine fractions having significant impacts on exposure interpretation (Houtz and Sedlak, 2012; Barzen-Hanson et al., 2017; Xiao, 2017).

3. Sources and Pathways of PFAS in Aquatic Environments

Table 1. Major PFAS groups and aquatic relevance.

PFAS group / examples	Aquatic relevance	Main concern	Key references
Long-chain perfluoroalkyl sulfonates (e.g., PFOS)	Often detected in fish, birds and higher trophic organisms; sorbs more strongly than short-chain acids.	Bioaccumulation, trophic transfer and ecological criteria.	Giesy and Kannan (2001); Kelly et al. (2009); Ankley et al. (2021)
Perfluorocarboxylic acids (e.g., PFOA, PFNA, PFDA)	Mobile in water; longer chains may bioaccumulate more than shorter chains.	Drinking-water exposure and food-web accumulation depending on chain length.	Conder et al. (2008); Ng and Hungerbuhler (2014)

Short-chain PFAS (e.g., PFBA, PFHxA, PFBS)	Highly mobile and frequently detected in aqueous systems and landfill leachate.	Persistence, transport and treatment difficulty.	Brendel et al. (2018); Hamid et al. (2018)
Fluorotelomer and sulfonamide precursors	Can transform to terminal perfluoroalkyl acids during environmental or treatment processes.	Hidden precursor burden and changing profiles.	Houtz and Sedlak (2012); Lenka et al. (2021)
Perfluoroether and replacement PFAS	Associated with industrial substitution and emerging contamination cases.	Analytical coverage and uncertain toxicity.	Sun et al. (2016); Xiao (2017)

Aquatic PFAS pollution has its roots in a combination of point sources, diffuse releases and delayed secondary sources. Direct industrial discharges are the most obvious sources, since they may produce specific chemical fingerprints and local high levels. The release of both legacy and replacement PFAS to wastewater, surface water and ground water can occur during fluorochemical manufacturing, metal plating, textile treatment, paper and packaging applications, semiconductor production and other industrial applications. In these environments, manufacturing history and regulatory substitution tend to be more evident in the profile of PFAS: the trend of legacy compounds may decrease, and short-chain or ether-based compounds take the center stage (Wang et al., 2017; Gluge et al., 2020; Evich et al., 2022).

The second significant route is the wastewater treatment plant. Traditional treatment was tailored to eliminate biodegradable organic content, nutrients, and pathogens, rather than highly recalcitrant fluorinated surfactants. PFAS can be added to wastewater through domestic sources, industrial effluents, commercial items, landfill leachate returns and stormwater flows. PFAS profiles are movable by treatment as certain precursor compounds are changed to terminal perfluoroalkyl acids in the process of biological and chemical treatment. Consequently, the effluent occasionally has increased amounts of the chosen terminal PFAS compared to the influent, not due to the generation of fluorine, but due to the formation of measurable end products of less easily measurable precursors (Arvaniti and Stasinakis, 2015; Lenka et al., 2021).

Landfills are long-term secondary storage. PFAS can be discharged to leachate by consumer products containing PFAS over prolonged time, contaminated textiles, carpets, paper, packaging, industrial wastes and treatment residues. The examination of landfill systems reveals that in many cases, perfluoroalkyl acids are detected in leachate, and short-chain compounds are frequent due to their higher mobility and stability in water. The management of leachates can thus pass the PFAS to wastewater treatment facilities, surface waters or groundwater in case of incomplete containment and treatment (Hamid et al., 2018; Masoner et al., 2020).

In the area of military bases, airports, firefighting-training locations and accidental fire spots, aqueous film-forming foams (AFFF) are particularly significant. Formulations of AFFF include complicated combinations of fluorinated surfactants and precursors, many of which are not covered by initial target lists of analytes. The mass spectrometry studies at high resolution have shown that there are a plethora of classes of PFAS in the AFFF-impacted groundwater and surface waters, explaining why the historical monitoring might have underestimated contamination. The case of AFFF also demonstrates that the risk of PFAS may be latent over decades due to the spatial localisation of sources but transportation via groundwater plumes, stormwater drains and related streams (Place and Field, 2012; Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2017).

Diffuse pathways pose more control challenges. Urban runoff has the potential to mobilise PFAS on traffic surfaces, building materials, consumer residues, atmospheric deposition and contaminated soils. The agricultural systems can also be helped by the use of biosolids, reclaimed water, and drainage of the contaminated catchments in irrigation. Another route of transport and deposition to remote water bodies is through atmospheric transport and deposition, particularly with volatile precursors, which are later decomposed to form long-lasting acids. Such processes are the reason that PFAS are found not only downstream of known sources but also in distant lakes, coastal and wildlife waters (Giesy and Kannan, 2001; Ahrens, 2011; Sunderland et al., 2019).

4. Occurrence and Distribution of PFAS in Aquatic Systems

Table 2. Principal aquatic PFAS sources and transport pathways.

Source category	Typical pathway to water	Expected signature	Management implication
Industrial manufacture and use	Direct discharge, sewer inputs, contaminated soil and groundwater	Site-specific mixture including legacy and replacement PFAS	Source control and industrial pretreatment are critical
Wastewater treatment plants	Effluent discharge and sludge handling	Terminal PFAAs plus transformed precursors	Conventional treatment is often insufficient
Landfills	Leachate to WWTPs, surface water or groundwater	Short-chain acids, PFOA and precursor residues	Leachate monitoring and treatment need PFAS-specific design
AFFF sites	Groundwater plumes, runoff and drainage	Complex mixtures with many unmeasured surfactants	Historical site inventories and HRMS screening are needed
Urban and agricultural diffuse sources	Stormwater, biosolids, reclaimed water and runoff	Low-level mixtures across broad catchments	Catchment-scale monitoring is required

Patterns of occurrence within the aquatic environments are regional, source, matrix and scope of analysis based. PFAS are frequently dominant in the surface waters as most of them are ionic, mobile, and not easily degraded. PFAS has been widely detected in river water; its concentrations tend to be the highest in proximity to industrialised catchments, wastewater discharges and identified contaminated locations (Loos et al., 2009; Ahrens, 2011; Gobelius et al., 2018). PFOS, PFOA and shorter-chain perfluorocarboxylic acids are the most frequently reported compounds, but the profile varies greatly depending on the analytes that are incorporated into the method.

Groundwater is quite important as it can relate historical sources with rivers, lakes, and drinking-water sources. Groundwater contamination could be longer-term than surface water contamination due to slowed dilution and more challenging removal. AFFF-contaminated aquifers demonstrate the influence of precursors in source zones to form complex plumes in the long term. In others, there are replacement PFAS or transformation products present with the legacy PFAS, making it difficult to interpret the age of sources and the compliance with regulations (Place and Field, 2012; Barzen-Hanson et al., 2017; Sun et al., 2016).

PFAS do not necessarily occur in the dominant reservoir, which is often the sediments, yet it should not be overlooked. In the presence of organic carbon, proteins, mineral surfaces, or black carbon, the long-chain compounds and sulfonates are more likely to sorb than short-chain carboxylates. Sediments are thus able to maintain source histories and form benthic exposure pathways. Nevertheless, the partitioning of PFAS compared to hydrophobic contaminants like PCBs is different since, unlike the latter, PFAS do not accumulate under the lipid affinity. This renders it challenging to contrast risks of sediment at different sites without uniform approaches and matrix normalisation (Ahrens and Bundschuh, 2014; Campo et al., 2015).

Water alone may not exhibit such obvious risk indicators as aquatic biota. PFAS has been detected in river basins and food webs in fish, invertebrates, birds and marine mammals. PFOS is frequently found as a dominant chemical in higher trophic organisms, although longer-chain perfluorocarboxylic acids can also be accumulated. PFAS were found in the Llobregat River ecosystem, e.g. in water, sediment, and biota with greater concentrations in the sediments and the organisms compared to the water column. This is an example of a common problem: even lower or moderate levels of water may not imply an insufficient biological exposure (Campo et al., 2015; Khan et al., 2023).

Temporal trends are also significant. In a situation where there is repeated monitoring, certain legacy compounds demonstrate decreases following production modifications or limitations, however, not all matrices demonstrate consistent trends. Water can also react more quickly to the reduction of the source than sediment or long-lived biota and groundwater plumes could persist in releasing the PFAS even after the initial emission has ceased. Reported values can also be affected by seasonal hydrology due to dilution, storm mobilisation or vary in wastewater contribution. This is why single-time sampling is effective in screening and not in trend analysis. Long-term tracking is required to be able to differentiate between real decrease in the source and a transient hydrological fluctuation (Ahrens, 2011; Gobelius et al., 2018; Kurwadkar et al., 2022).

Regulatory change is also reflected in regional patterns. A decrease in both the PFOS and the PFOA in certain monitored systems may be a result of phase out and restriction, but this decrease does not imply that the PFAS issue is resolved. Substitute compounds, short-chain PFAS and unknown organofluorine fractions can be enhanced or not well characterised. This shift between a legacy-PFAS issue to a larger PFAS-mixture issue is one of the primary strains in the literature. This has enhanced monitoring, even though the list of compounds measured on a regular basis is still minimal compared to the chemical universe that has been identified (Wang et al., 2017; Xiao, 2017; Evich et al., 2022).

5. Bioaccumulation and Trophic Transfer

The bioaccumulation of PFAS is not comparable to the behaviour of most other persistent organic pollutants due to the fact that lipid partitioning does not govern the behaviour of most compounds. PFAS tend to stick to proteins, phospholipids and tissues rich in blood. Thus, different PFAS profiles may be observed in tissues like liver, blood, kidney and muscle and whole-body or fillet-based measurements might not reflect the same biological burden. This becomes especially significant in the case of fish since assessments of human exposure typically target edible muscle, whereas ecological impacts might be associated with metabolic, reproductive and immune metabolism-related organs (Houde et al., 2006; Ng and Hungerbuhler, 2014; Khan et al., 2023).

PFOS and various longer-chain perfluoroalkyl acids most clearly have evidence of trophic transfer. Initial food-webs of Lake Ontario, the Arctic showed that PFAS was present in plankton, invertebrates, fish, birds and marine mammals, and some compounds were more concentrated in higher trophic levels (Martin et al., 2004; Kelly et al., 2009). According to a recent meta-analysis of a large number of food webs, it was discovered that trophic magnification is common and heterogeneous, supporting the notion that PFAS should not be regarded as a homogeneous group (Ricolfi et al., 2025). The magnitude of biomagnification is observed to be affected by chain length, functional group, species physiology, habitat utilization and food-web arrangement.

PFAS with short chains make interpretation of bioaccumulation difficult. They usually exhibit reduced bioaccumulation parameters in the traditional terms, but they are very mobile and recalcitrant to treatment, which causes them to be the drivers of persistent exposure in water. This creates a perceived paradox: certain short-chain PFAS can be less bioaccumulative in individual organisms, but harder to contain on a catchment scale due to their extensive distribution and inability to be removed by standard treatment methods. However, long-chain PFAS, conversely, can be less mobile than short-chain ones but more prone to accumulation in organisms and sediments. The key to this argument is the idea of a regrettable substitution (Conder et al., 2008; Brendel et al., 2018; Cousins et al., 2020).

Exposure of aquatic organisms occurs via a variety of pathways such as direct water absorption, prey ingestion, sedimentary and maternal contact. The relative importance of these pathways differs among algae, plankton, benthic invertebrates, fish and marine mammals. Water and diet can prevail in the case of pelagic species, whereas in benthic organisms, sediment-bound PFAS and porewater can play a larger role. Salinity, dissolved organic matter and suspended particles can change partitioning and enter into food-webs in estuaries and coastal systems. These complexities contribute to the reason why field-derived bioaccumulation factors can be quite different across sites of the same compound (Ahrens and Bundschuh, 2014; Ali et al., 2021; Khan et al., 2023).

The species-specific physiology is important too. PFAS uptake, elimination, and tissue distribution studies in the laboratory in fish and invertebrates indicate that growth rate, life stage, metabolic capacity, and exposure duration affect these processes. Other trophic level indicators like nitrogen stable isotopes are commonly applied in field studies to estimate food-web position, although they do not completely track movement between habitats or seasonal changes in diet. Thus, trophic magnification factors are not to be perceived as universal chemical constants but as food-web-specific ones (Martin et al., 2004; Kelly et al., 2009; Ricolfi et al., 2025).

Table 3. Evidence themes from aquatic occurrence and bioaccumulation studies.

Evidence theme	Representative finding	Interpretive caution	References
River occurrence	PFAS are detected widely in rivers, with higher values near industrial and wastewater inputs.	Sampling frequency and target-analyte lists strongly influence reported occurrence.	Loos et al. (2009); Campo et al. (2015); Kurwadkar et al. (2022)
AFFF-impacted waters	Groundwater and surface waters can contain many PFAS classes outside routine monitoring lists.	Discovery does not always equal full quantification without standards.	Place and Field (2012); Barzen-Hanson et al. (2017); D'Agostino and Mabury (2017)
Food-web transfer	PFOS and several longer-chain compounds can biomagnify in aquatic food webs.	TMFs depend on food-web structure, tissue type and trophic-level estimation.	Martin et al. (2004); Kelly et al. (2009); Ricolfi et al. (2025)
Marine biota	PFAS occur in diverse marine organisms, with compound-specific accumulation patterns.	Edible tissue may not represent whole-organism ecological burden.	Ali et al. (2021); Khan et al. (2023)
Wastewater influence	Effluent and leachate inputs can maintain PFAS loading even after restrictions.	Precursors may transform during treatment, altering effluent profiles.	Arvaniti and Stasinakis (2015); Lenka et al. (2021); Masoner et al. (2020)

6. Ecotoxicological Effects and Risk Assessment

The assessment of aquatic PFAS risk is not yet certain due to imbalanced hazard data among the compounds, species and endpoints. PFOS and PFOA have been the subject of much more toxicological scrutiny than the majority of replacement or precursor compounds. The effects of concentrations on survival, growth, development, reproduction, oxidative stress, endocrine signalling, immune function, metabolism and behaviour have been reported in experimental studies, but the range of concentrations that have an effect varies widely across taxa and test designs (Li, 2009; Ankley et al., 2021; Hayman et al., 2021). This disparity is not healthy since exposure to the environment will seldom be as PFOS or PFOA.

PFOS is also typically a matter of special ecological interest due to a combination of environmental persistence, bioaccumulation and relatively high aquatic toxicity relative to most other PFAS. Marine toxicity assessments have demonstrated that species sensitivity may vary significantly across standard test organisms and that PFOS and PFOA cannot be considered to be similarly toxic. These types of studies can be used to derive protective thresholds, although they indicate that aquatic criteria are susceptible to endpoint selection, test species and statistics (Hayman et al., 2021; Ankley et al., 2021).

Historically, risk assessment has been based on water-column concentrations and compound-specific thresholds. This is a method that is needed but not fully applicable to PFAS. In the case of bioaccumulative compounds, tissue-based criteria can be more directly related to the exposure in predators and humans that feed on aquatic organisms. In the case of mobile short-chain compounds, water-column surveillance can still be necessary since the biological accumulation is not so high yet drinking-water exposures and long-range transport can play a significant role. An integrated water-sediment-biota framework is thus needed over a single-matrix assessment (Ng and Hungerbuhler, 2014; Ankley et al., 2021; Khan et al., 2023).

One of the poorest areas of existing evidence is mixture toxicity. Aquatic life are exposed to combinations of PFAS with metals, pesticides, nutrients, pharmaceuticals and microplastics. Combined exposure can have additive or interactive effects even in cases when individual PFAS are below effects thresholds. Nevertheless, the toxicological information is too limited to make effective mixture risk models of most PFAS groups. This presents a risk-management dilemma: the need to wait until the full compound-by-compound toxicity data is available can potentially delay actions, whereas the need to regulate only the best-studied PFAS can overlook important exposure fractions (Cousins et al., 2020; Ankley et al., 2021; Evich et al., 2022).

The risk thresholds are also disputed as there are divergent benchmarks due to varying protection objectives. A level that seems to be safe in direct aquatic toxicity might not prove to be protective to fish-eating wildlife or humans in case the compound biomagnifies. On the other hand, a tissue-based value might prove hard to implement when only water data are present. This disparity between the metric of exposure and the target of protection is one of the reasons why the PFAS criteria have been slow to develop and vary in some jurisdictions. A clear risk evaluation must then indicate whether it is safeguarding aquatic life, benthic communities, piscivorous wildlife, seafood consumers or drinking-water users, since each endpoint might need different data (Ng and Hungerbuhler, 2014; Ankley et al., 2021).

Aquatic systems are also associated with human-health risk, particularly, via drinking water and seafood. In this review, the focus is on aquatic environmental risk, but the line between ecological and human exposure is not clear. Sources of aquatic contamination are linked to dietary and community-level exposures in fish, shellfish and drinking-water sources. Exposure pathway reviews indicate that contaminated water and food may also play an important role in the populations affected, particularly around industrial or AFFF sources (Sunderland et al., 2019; Sun et al., 2016). In the case of aquatic research, this implies that ecological monitoring is of public-health interest and cannot be separated off of catchment management.

7. Analytical and Methodological Challenges

PFAS research is not only analytically challenged by detecting low concentrations. It is determining what proportion of the universe of PFAS is under measure. Known compounds with available standards are well-captured by targeted LC-MS/MS methods, but only a list of compounds is captured. Numerous precursors, branched isomers, replacement products and new fluorinated surfactants might not be on regular lists. This poses the structural underestimation issue: a sample may seem to be low-risk when it is evaluated based solely on a small target panel despite having a significant amount of unidentified organofluorine (Wang et al., 2017; Xiao, 2017; Evich et al., 2022).

The total oxidisable precursor assay was devised as a means of exposing concealed pools of precursors by transforming oxidisable precursors into quantifiable perfluoroalkyl acids. It has found specific application to urban runoff, AFFF-contaminated locations, and wastewater situations where precursor compounds would otherwise be overlooked. The assay is however not a total measure of all PFAS; it is dependent on the reaction conditions, sample matrix and the oxidisability of compounds present. It must hence be viewed as a measure of precursor burden as opposed to a universal total-PFAS measure (Houtz and Sedlak, 2012).

High resolution mass spectrometry has broadened the area as it has made possible screening of suspect and non-targets. AFFF studies are a significant example as they demonstrated that numerous fluorinated compounds were not in the traditional lists of targets. Non-target screening, however, also creates confidence-level issues: provisional

results can not be based on authentic standards, quantification can be semi-quantitative and cross-laboratory consistency is hard to achieve. Consequently, discovery methods that are non-target need to be considered essential but should be effectively coupled with targeted confirmation and source studies (Place and Field, 2012; Barzen-Hanson et al., 2017; Xiao, 2017).

The level of quality assurance is out of the ordinary in PFAS studies since contamination may be caused by sampling equipment, waterproof clothing, laboratory supplies and even background blanks. The apparent distribution of compounds across water, sediment and tissues can vary due to differences in extraction method, isotope-labelled standards, matrix correction and reporting limits. These concerns do not nullify the literature, but justify why cross-study comparisons should be done carefully. High transparency of methods is particularly required in narrative synthesis due to its ability to separate real environmental variation and analytical artefact in readers (Houde et al., 2006; Evich et al., 2022).

The sampling design influences conclusions to the same extent as instrumental choice. Grab samples can be missing episodic discharges, storm-event pulses or seasonal variation. Grain size, selection of organic matter and depth are some factors which bias sediment sampling. The sampling of biota may depend on species, age, sex, tissue type and migration behaviour. By these differences in methodology, occurrence and bioaccumulation data are hard to compare across regions. Synthesis-level interpretation requires stronger reporting of detection limits, recovery, and matrix effects, branched-linear isomer treatment, dry-weight or wet-weight basis, tissue type and quality assurance (Ahrens and Bundschuh, 2014; Ankley et al., 2021; Khan et al., 2023).

8. Discussion and Synthesis

Three general conclusions are supported in the literature. To begin with, PFAS prevalence in the water systems is concentrated but not uniform with the highest concentrations near the sources of point contamination and lower but consistent concentrations in diffuse and remote systems. Second, bioaccumulation of PFAS is compound-specific and cannot be explained by the hydrophobic partitioning only. Third, risk assessment is challenged by small lists of monitored, imbalanced toxicity information and lack of mixture knowledge. These conclusions are not independent. The organisms exposed to something are defined by occurrence studies; the compounds that move through the food webs are determined by bioaccumulation studies; and which exposures are biologically important is determined by toxicity studies.

One of the major tensions of the literature is that of substitution. The scientific basis of restrictions to legacy PFOS and PFOA is valid, but substitution by short-chain or ether-based PFAS does not necessarily decrease the concern of the environment. PFASs in short chains might exhibit reduced classical bioaccumulation, yet are also persistent, mobile and hard to eliminate in water. There are also some replacement compounds that have been observed in critical water supplies and might not be sufficiently removed using the older methods. This implies that substitution may alter the risk profile of bioaccumulation-dominated concern to mobility, persistence and treatment-resistance concern (Sun et al., 2016; Brendel et al., 2018; Cousins et al., 2020).

The other conflict is that of matrix choice. Water data are necessary to determine the relevance of transport and drinking-water, whereas biota data frequently have more ecological significance. Sediments might not be significant in short-chain compounds, but could harbor longer-chain PFAS and expose benthic life. The treatment of water, sediment and biota as separate compartments in a review overlooks the key aquatic issue: PFAS support inter-compartmental migration that is governed by functional group, chain length, ionic state, proteins, organic matter and food-web structure. Combined sampling in matrices is thus more educative than a standalone water surveillance (Ahrens, 2011; Campo et al., 2015; Khan et al., 2023).

It also proved that the risk of PFAS is not a concentration problem. It is a time issue. The persistent compounds emitted today can persist in water, sediment and biota well after emissions decrease. Uncertainty in the case of high-persistence chemicals should not be taken as safety, as the probability of prevention diminishes as contamination proliferates. This rationale is the basis of recent suggestions to treat PFAS as a chemical category, particularly when used non-essential (Cousins et al., 2020; Evich et al., 2022). Aquatic-management-wise, it is more realistic to control sources than to treat downstream once the compounds have dispersed across catchments.

It has also been recommended in the literature that the management of aquatic sources of PFAS should be structured around sources, rather than around compliance points at the downstream. When PFAS is washed away by rivers, estuaries or groundwater networks, it is costly to clean and is ecologically incomplete. Treatment at drinking-water plants could offer protection to customers but is not a guarantee to decreasing exposure of aquatic organisms or eliminate the issue of spent adsorbents and concentrated residuals. It is more sustainable interventions like source prevention, product substitution assessment, and industrial pretreatment and leachate control that are more durable than end-of-pipe monitoring (Hamid et al., 2018; Lenka et al., 2021; Evich et al., 2022).

Lastly, PFAS studies have become so advanced that superior data are insufficient. The domain requires an enhanced interrelationship between the types of data. There should be a connection between occurrence datasets and source inventories and hydrological pathways. Tissue-specific and food-web information should be involved in bioaccumulation studies. The environmentally relevant mixtures and species should be used in toxicity studies. Where feasible analytical studies are to report target, precursor and unknown organofluorine fractions. This kind of

integration would enable future reviews to rely less on independent blocks of evidence and more on helping to make decisions at the level of the catchment.

9. Research Gaps and Future Directions

The initial critical gap is the restricted coverage of PFAS outside of known target analytes. Numerous surveillance programmes continue to focus on PFOS, PFOA and a small number of homologues. Non-target screening and replacement chemistry evidence, however, indicates that aquatic systems may harbor a broader assortment of precursors and new PFAS. Future research ought to integrate focused analysis, precursor evaluations and high-resolution screening, especially around industrial, AFFF, landfill and wastewater locations (Houtz and Sedlak, 2012; Barzen-Hanson et al., 2017; Xiao, 2017).

The second gap is related to low and middle incomes and tropical areas. A great part of the best-developed evidence is that of North America, Europe, and China and few industrialised catchments. Most African, South Asian, Middle Eastern, Latin American and tropical island systems are still thinner in data, even with the rapid urbanisation, increasing wastewater demands, and increasing chemical consumption. This uneven distribution of geography restricts the interpretation of risk globally and could overstate the exposure to areas with low monitoring capabilities.

The third gap is the science of mixtures and transformation. The majority of toxicity testing is done on a single or limited number of compounds, whereas actual aquatic exposure is of mixtures and co-contaminants of PFAS. Additive effects, mixture interactions, precursor transformation during treatment and degradation to persistent terminal products need more work. Chemistry needs to be related to biological endpoints, not just concentration data, in such work (Lenka et al., 2021; Ankley et al., 2021).

The fourth gap is the food-web and tissue comparability. Available literature varies in terms of the species used, tissue used, wet-weight or dry-weight reporting, estimation of the trophic levels and quality assurance. The next generation of food-web research ought to apply stable isotope data, standardised tissue reporting and compound-specific measurements that can differentiate uptake of waterborne sources and dietary transfer of compounds. Special consideration must be given to edible fish and shellfish as top predators, benthic organisms and species utilized in regulatory criteria (Kelly et al., 2009; Ng and Hungerbuhler, 2014; Ricolfi et al., 2025).

The fifth gap is that the relationship between monitoring and management is weak. Numerous reports of occurrence do not assess source control, treatment feasibility or ecological thresholds. Future studies need to be structured on decision questions: what sources are predominant in exposure, what compounds cause risk, what matrices are used to give early signals, what organisms are to be monitored and what interventions will reduce long-term loading. This would transform aquatic PFAS studies on descriptive contamination mapping to prevention-oriented environmental management.

Table 4. Research gaps and future directions for aquatic PFAS studies.

Gap	Why it matters	Recommended direction
Narrow target lists	Many PFAS and precursors are missed by routine monitoring.	Combine target LC-MS/MS, TOP assay, EOF/TOF approaches and HRMS screening.
Limited mixture toxicity data	Aquatic organisms encounter PFAS mixtures plus co-contaminants.	Use mixture designs, realistic exposure ratios and sublethal endpoints.
Weak geographic coverage	Many regions with growing wastewater and industrial pressure are underrepresented.	Expand monitoring in tropical, arid and low-resource catchments.
Inconsistent biota reporting	Tissue, age, sex and trophic level affect bioaccumulation interpretation.	Standardise tissue basis, species metadata and stable isotope reporting.
Poor source-to-effect linkage	Occurrence studies often stop at concentration mapping.	Connect chemical profiles to sources, exposure pathways, toxicity and management options.

10. Conclusion

PFAS in aquatic environments represent a persistent and evolving challenge because occurrence, bioaccumulation and risk are connected but not always aligned. Water monitoring reveals mobility and source pathways, sediment and biota data reveal exposure reservoirs and food-web transfer, and toxicity studies define the biological meaning of those exposures. The strongest evidence indicates that legacy long-chain compounds such as PFOS remain central to bioaccumulation and ecological-risk concerns, while short-chain and replacement PFAS create a parallel problem of mobility, persistence and treatment difficulty. A narrow focus on a few regulated compounds is therefore insufficient.

This review concludes that aquatic PFAS assessment should become more class-aware, matrix-integrated and source-oriented. Monitoring programmes should include water, sediment and biota where possible; analytical strategies should combine targeted and discovery-oriented methods; and risk assessment should account for food-web transfer, tissue residues and mixtures. Because PFAS persistence makes delayed action costly, prevention and source control should be treated as core aquatic-management strategies rather than optional end points after contamination is detected. A more integrated research agenda will help aquatic scientists, regulators and environmental managers interpret PFAS contamination with greater confidence and design interventions that reduce long-term exposure.

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