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Critical Review

FATE AND EFFECTS OF POLY- AND PERFLUOROALKYL SUBSTANCES IN THE AQUATIC ENVIRONMENT: A REVIEW

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Abstract: Polyfluoroalkyl and perfluoroalkyl substances (PFASs) are distributed ubiquitously in the aquatic environment, which raises concern for the flora and fauna in hydrosystems. The present critical review focuses on the fate and adverse effects of PFASs in the aquatic environment. The PFASs are continuously emitted into the environment from point and nonpoint sources such as sewage treatment plants and atmospheric deposition, respectively. Although concentrations of single substances may be too low to cause adverse effects, their mixtures can be of significant environmental concern. The production of C_8-based PFASs (i.e., perfluorooctane sulfonate [PFOS] and perfluorooctanoate [PFOA]) is largely phased out; however, the emissions of other PFASs, in particular short-chain PFASs and PFAS precursors, are increasing. The PFAS precursors can finally degrade to persistent degradation products, which are, in particular, perfluoroalkane sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs). In the environment, PFSAs and PFCAs are subject to partitioning processes, whereby short-chain PFSAs and PFCAs are mainly distributed in the water phase, whereas long-chain PFSAs and PFCAs tend to bind to particles and have a substantial bioaccumulation potential. However, there are fundamental knowledge gaps about the interactive toxicity of PFAS precursors and their persistent degradation products but also interactions with other natural and anthropogenic stressors. Moreover, because of the continuous emission of PFASs, further information about their ecotoxicological potential among multiple generations, species interactions, and mixture toxicity seems fundamental to reliably assess the risks for PFASs to affect ecosystem structure and function in the aquatic environment. *Environ Toxicol Chem* 2014;33:1921–1929. © 2014 SETAC

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BACKGROUND

Polyfluoroalkyl and perfluoroalkyl substances (PFASs) have received global public attention because of their persistence, bioaccumulation potential, and possible adverse effects on living organisms [1,2]. In addition, they have the capability for long-range transport through the atmosphere and water [3,4]. As a consequence, perfluorooctane sulfonate (PFOS), one of the most frequently detected PFASs in the environment [5,6], and its precursors have been added to Annex B of the Stockholm Convention on Persistent Organic Pollutants list in 2009, which resulted in a global restriction on its production and use [7]. In addition, a number of PFASs have been regulated and voluntarily phased out in many countries across the world [8]. However, PFASs comprise a diverse group of chemicals with significant economic value; for example, the markets for stain repellents and for polishes, paints, and coatings are worth approximately $1000 million and $100 million, respectively [9]. Hence, the utilization of other PFASs has continued unbroken until the present. The economic importance of PFASs is further underpinned by their application in numerous residential, commercial, and industrial applications, such as surfactants in fluoropolymer production, metal plating, aqueous film-forming foams (AFFFs), paper, textile, and household products [7,10].

This broad spectrum of applications, as well as the associated ubiquity in products used daily, goes along with their continuous release via point and nonpoint sources into the aquatic environment. There, PFASs are subjected to various transport, partitioning, and degradation processes, depending on their physicochemical properties and environmental conditioning [6]. Moreover, these substances are pervasively detected as complex mixtures that may adversely affect autotrophic and heterotrophic food webs. For example, PFOS is very persistent, has a high bioaccumulation potential [1], and causes acute and chronic effects at the individual, population, and community levels [11,12]. In this context, the present review focuses on the fate of PFASs as well as multigenerational effects, multiple stressors, and impacts of PFASs on aquatic organisms. Moreover, by evaluating ecotoxicological knowledge in the light of field-relevant exposure scenarios, fundamental knowledge gaps in the risk evaluation of PFASs are identified that may stimulate future research.

TERMINOLOGY AND CLASSIFICATION

This section gives an overview of the terminology and classification of PFASs as described by Buck et al. [8]. Polyfluoroalkyl and perfluoroalkyl substances are commonly divided into 3 classes: perfluoroalkyl substances (PerFASs), polyfluoroalkyl substances (PolyFASs), and fluorinated polymers. In Table 1, PerFASs and PolyFASs are briefly displayed and exemplified. The PerFASs, such as perfluoroalkane sulfonates (PFSAs; $C_nF_{2n+1}SO_3^-$), perfluoroalkyl carboxylates (PFCAs; $C_nF_{2n+1}COO^-$), perfluoroalkyl phosphonates (PFPAs; $C_nF_{2n+1}[O]P[OH]O^-$), perfluoroalkyl sulfonamides (FASAs; $C_nF_{2n+1}SO_2NH_2$), perfluoroalkyl sulfonamidoethanols (FASEs; $C_nF_{2n+1}SO_2NHCH_2CH_2OH$), and perfluoroalkyl sulfonamidoacetic acids (FASAAs; $C_nF_{2n+1}SO_2NHCH_2COOH$), have a fully fluorinated alkyl chain. The PolyFASs have a partly fluorinated alkyl chain (but containing at least 1 fluorine atom)

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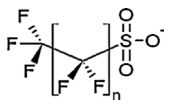
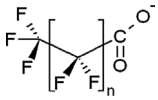
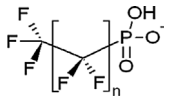
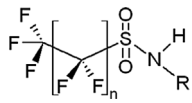
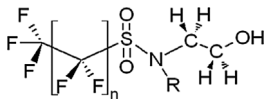
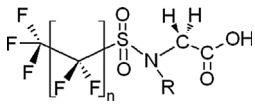
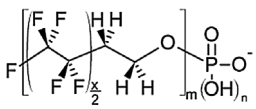
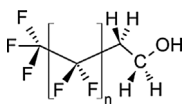
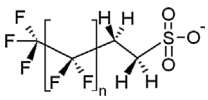
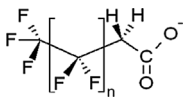
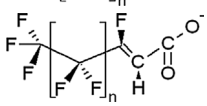
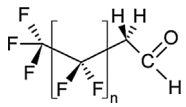
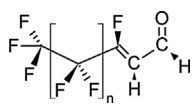
Table 1. Environmentally relevant groups of polyfluoroalkyl and perfluoroalkyl substances (PFASs) in the aquatic environment

Compound groups	Acronym	Formula	Chemical structure	Typical PFASs[a]
Perfluoroalkyl substances				
Perfluroalkyl sulfonates	PFSAs	$C_nF_{2n+1}SO_3^-$		n = 3–9
Perfluoroalkyl carboxylates	PFCAs	$C_nF_{2n+1}COO^-$		n = 1–17
Perfluoroalkyl phosphonates	PFPAs	$C_nF_{2n+1}(O)P(OH)O^-$		n = 4, 6, 8
Perfluoroalkyl sulfonamides	FASAs	$C_nF_{2n+1}SO_2NH_2$		n = 8, R = H n = 8, R = CH_3 n = 8, R = C_2H_5 n = 4, R = CH_3
Perfluoroalkyl sulfonamidoethanols	FASEs	$C_nF_{2n+1}SO_2NHCH_2CH_2OH$		n = 8, R = CH_3 n = 8, R = C_2H_5 n = 4, R = CH_3
Perfluoroalkyl sulfonamidoacetic acids	FASAAs	$C_nF_{2n+1}SO_2NHCH_2COOH$		n = 8, R = H n = 8, R = CH_3 n = 8, R = C_2H_5
Polyfluoroalkyl substances				
Polyfluoroalkyl phosphoric acid esters	PAPs	$(O)P(OH)_{3-x}$ $(OCH_2CH_2C_nF_{2n+1})_x$		m = 1, n = 2, x:2 monoPAP m = 2, n = 1, x:2 diPAP
n:2 Fluorotelomer alcohols	n:2 FTOHs	$C_nF_{2n+1}CH_2CH_2OH$		n = 4, 6, 8, 10
x:2 Fluorotelomer sulfonates	x:2 FTSAs	$C_nF_{2n+1}CH_2CH_2SO_3^-$		n = 4, 6, 8, 10
n:2 Fluorotelomer carboxylates	x:2 FTCA	$C_nF_{2n+1}CH_2COO^-$		n = 4, 6, 8, 10
n:2 Fluorotelomer unsaturated carboxylates	x:2 FTUCA	$C_{n-1}F_{2n-1}CF=CHCOO^-$		n = 3, 5, 7, 9
n:2 Fluorotelomer saturated aldehydes	n:2 FTALs	$C_nF_{2n+1}CH_2CHO$		n = 4, 6, 8, 10
n:2 Fluorotelomer unsaturated aldehydes	n:2 FTUALs	$C_{n-1}F_{2n-1}CF=CHCHO$		n = 3, 5, 7, 9

[a]The abbreviations n, m, and R represent different chemical groups in the chemical structure.

and include such substances as polyfluoroalkyl phosphoric acid esters (PAPs; $[O]P[OH]_{3-x}[OCH_2CH_2C_nF_{2n+1}]_x$), fluorotelomer alcohols (FTOHs; $C_nF_{2n+1}CH_2CH_2OH$), x:2 fluorotelomer sulfonates (FTSAs; $C_nF_{2n+1}CH_2CH_2SO_3^-$), x:2 fluorotelomer carboxylates (FTCA; $C_nF_{2n+1}CH_2COO^-$), x:2 fluorotelomer unsaturated carboxylates (FTUCA; $C_{n-1}F_{2n-1}CF=CHCOO^-$), n:2 fluorotelomer saturated aldehydes (FTALs; $C_nF_{2n+1}CH_2CHO$), and n:2 fluorotelomer unsaturated aldehydes (FTUALs; $C_{n-1}F_{2n-1}CF=CHCHO$) (Table 1). The class of fluorinated polymers includes a large variety of chemicals and also is divided into 3 subclasses: fluoropolymers, perfluoropolyethers, and side-chain fluorinated polymers [8]. Long-chain PFASs are referred to PFCAs and PFSAs with a perfluorocarbon chain length of $\geq C_7$ and $\geq C_6$, respectively (including their precursor compounds). Polyfluoroalkyl and perfluoroalkyl substances have unique physicochemical properties that vary depending on the chain length and functional group [12–14].

SOURCES

Polyfluoroalkyl and perfluoroalkyl substances are released into the aquatic environment throughout their whole life cycle (i.e., during their production, along the supply chains, product use, and disposal of industrial and consumer products). Direct emission sources of PFASs are defined as emissions throughout their product cycle, and indirect emission sources are defined as emissions from transformation of their precursors [8]. The total (direct + indirect) historic emissions of perfluorooctylsulfonyl fluoride (POSF)-based substances (i.e., PFOS and its precursors), the major precursor for several PFASs, are estimated to be 6800 tons to 45 300 tons (1972–2002), whereas total emissions of PFCAs range between 3200 tons and 7300 tons (1951–2004) [7,10]. The majority of these emissions (>95%) are directly released into the aquatic environment, whereas emissions through the atmosphere are considered to be rather small (<5%) [7,10]. However, a reliable quantitative assessment of their production, direct and indirect emission, and environmental inventory is lacking.

The emissions of POSF-based fluorochemicals (C_8 fluorocarbon) decreased after the voluntarily phase-out of POSF by the 3M Company in 2002 [7] and other regulations [15]. In addition, the emissions of PFOA are expected to decrease after institution of the US Environmental Protection Agency PFOA Stewardship program, under which the 8 major companies of the perfluoropolymer industry committed to eliminate emissions and product content of PFOA and related chemicals by 2015 [16]. Although POSF-based production has continued in China [17], production of these PFASs has generally shifted to other substances of this group. Currently, short-chain PFASs such as perfluorobutane sulfonate and perfluorobutanoate, and PFAS precursors that can finally degrade to persistent degradation products (e.g., PFCAs and PFSAs) are frequently applied [18,19]. However, the release of long-chain PFASs into the aquatic environment will continue in the future from degradation of PFAS precursors, or from historical products still in use or deposed, and they can be remobilized into the water phase, for example, from soil, sediment, and ice [6]. In addition, the emissions of other PFASs, in particular short-chain PFASs and PFAS precursors are increasing.

Irrespective of these shortcomings in our scientific knowledge, PFASs are introduced through both point and nonpoint (diffuse) sources. Point sources of PFASs include, for example, landfills, manufacturing plants, and application of PFAS-containing products at a concentrated area (e.g., application of AFFFs) [20–23]. Industrial and municipal sewage treatment plants were identified as major contributors [20–22]. The total discharge of PFASs into the aquatic environment ranged between 10 g d^{-1} [21,22] and 10 000 g d^{-1} [18], depending on the water usage in the community connected to the sewage treatment plant. These documented releases of PFASs from conventional sewage treatment plants may be explained by the ineffectiveness of implemented technologies to remove micropollutants in general [24]. In addition, PFAS precursors can be degraded and even increase PFCA and PFSA loads released into the receiving aquatic ecosystem [20]. Advanced water treatment techniques such as activated carbon and nanofiltration may be suitable amendments to current techniques to help reduce PFAS concentrations [25,26]. As suggested by Ahrens [6], among other authors, the application of AFFFs can be a PFAS source of serious local concern causing massive concentrations in adjacent water bodies but also soils [27]. However, leaching of PFASs from soils to ground and surface water bodies is not fully understood and requires further investigation to allow for a reliable judgment of the contribution of such a source to the overall exposure [28,29].

An important nonpoint source for PFASs is wet and dry atmospheric deposition, while the original sources are manufacturing plants, sewage treatment plants, landfills, and households [30–32]. Volatile PFASs (e.g., FTOHs, FASAs, FASEs) have been detected in outdoor air samples, even in very remote regions [4,33,34].Volatile PFASs enter the atmosphere, where they can degrade, form intermediates during atmospheric oxidation, or transform into more persistent PFASs such as PFSAs and PFCAs, which may finally end up in the aquatic environment [35]. Moreover the metabolic transformation of PFAS precursors (e.g., PAPs, FTCAs, FTUCAs, FTSAs, FASAAs) can be an important source of PFSAs and PFCAs in the aquatic environment. Another important nonpoint source is runoff from contaminated land or streets as a result of biosolid application or wet and dry atmospheric deposition [36–38].

The described variety of point and nonpoint sources releasing PFASs into aquatic ecosystems reflects the broad spectrum of specific substances with their inherent environmental properties as well as their application range. This pattern indicates, in addition, a continuous exposure of the aquatic ecosystems to complex mixtures of PFASs.

ENVIRONMENTAL FATE

The environmental fate of PFASs describes their transport, partitioning, and transformation processes after their release into the environment (Figure 1). During or after the production and usage of PFAS-containing products, PFASs can, as detailed in the *Sources* section, be released into the aquatic environment

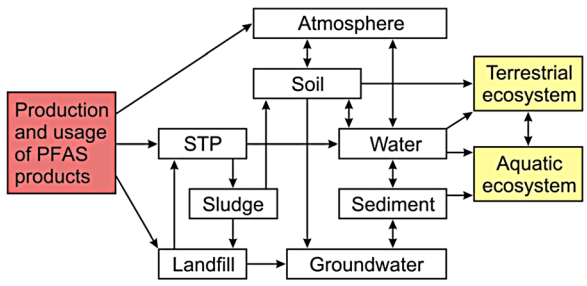


Figure 1. Pathways of polyfluoroalkyl and perfluoroalkyl substances (PFASs) into the environment and their fate. Adapted from Ahrens [6]. STP = sewage treatment plant.

from point and nonpoint sources. The PFAS precursors are typically transported via the atmosphere because of their volatile to semivolatile properties and subsequently can be degraded to, for example, PFSAs and PFCAs [35,39]. The PFAS precursors (e.g., FTOH, FASAs, FASEs, PAPs) are subject to a variety transformation pathways in the atmosphere or under aerobic and anaerobic conditions in other environmental compartments [19,39]. Moreover, intermediate degradation products (i.e., FTUALs, FTALs, FTUCAs, FTCAs) formed during both atmospheric transformation and biotransformation are very reactive [35,40] and have shown acute and chronic toxicity to aquatic invertebrates and green algae [41–43]. The transport processes of these final degradation products proceed mainly in the water phase but can also occur via seaspray or gas-phase and particle-bound transport in the atmosphere [3,44,45]. For remote regions such as the Arctic Ocean, it was estimated that the long-range transport of PFCAs is 1 to 2 orders of magnitude higher in the water phase compared with transport in the atmosphere [4,46,47]. However, it is still under debate whether the atmospheric transport or transport via the water phase is the dominant transport pathway for ionizable PFASs, whereas for neutral, volatile PFASs, gas-phase transport is likely to be the dominant pathway to remote regions [6].

The environmental cycling of PFASs depends on environmental conditions (e.g., organic carbon content, temperature, salinity, concentration of atmospheric oxidants) and the physicochemical properties inherent in the substance. The latter is mainly determined by the PFASs' chain length and their functional groups [1,48]. For example, short-chain PFASs are dominantly hydrophilic and are generally more mobile in hydrosystems, whereas long-chain PFASs have a higher hydrophobicity and hence tend to bind to particles and have a substantial bioaccumulation potential [1,49]. Among the environmental media, the largest global reservoirs of PFASs are proposed to be oceans and sediment [47].

EXPOSURE, BIOACCUMULATION, AND EFFECTS IN THE AQUATIC ECOSYSTEM

PFASs have a high binding affinity to serum albumin and fatty acid binding proteins, which results in a tissue-dependent distribution in biota [1,50–52]. For example, the tissue distribution for PFASs in various freshwater fish species from Beijing, China decreased from blood over liver and brain to muscle [52]. Moreover, the bioaccumulation potential of PFASs varies among individual organisms and species and also depends on the physicochemical properties of PFASs, such as branched or linear chain, chain length, and functional group [1,48,53,54]. It also has been shown that the elimination rate depends on the PFAS structure. For example, branched isomers are eliminated faster than linear isomers [55]. In addition, the accumulation and elimination of PFASs depends on the species, gender, and reproductive status [56,57].

PFASs are ubiquitously present in the environment, even in pristine regions, and can possibly biomagnify along the food chain [2,5,58–64]. In biota, PFOS (C_8 fluorocarbon) is typically the dominant PFAS, and the PFOS concentration increases along the food chain, showing its high bioaccumulation potential. In contrast, perfluorooctanoate (PFOA; C_7 fluorocarbon) has a low bioaccumulation potential and is relatively similar among species from different trophic levels. For example, the maximum concentrations of PFOS and PFOA in invertebrates [59–61,65,66] are in a similar range, whereas in fish [60,61,65–68], reptiles [69–71], birds [59–61,68,72,73], and mammals [60,63,67,68,71,72,74,75], the maximum PFOS concentration is up to 3 orders of magnitude higher compared with PFOA (Figure 2). The lower bioaccumulation potential of PFOA may be driven by the shorter perfluorocarbon chain length and different functional group compared with PFOS [1]. In recent years, PFSA concentrations showed decreasing trends in biota because of the phase-out of PFOS in 2002 [7,58,76]. However, the concentrations of other PFASs, such as long-chain PFCAs, show no clear trend and are even increasing depending on the compound, trophic level, and geographical location [62].

Hence, PFASs can be considered as persistent in the environment as a whole, whereas PFAS precursors are degradable to PFCAs and PFSAs [19]. The PFASs are permanently introduced into aquatic ecosystems, which can result in a continuous exposure of those compounds for organisms located downstream of the discharges. These insights indicate a long-term (chronic) exposure of species in aquatic ecosystems suffering from wastewater discharge and other point and nonpoint sources of PFASs. In contrast to the large number of studies investigating acute and chronic effects of PFASs, which were reviewed by Giesy et al. [11] and more recently by Ding and Peijnenburg [12], only a very few studies address implications over multiple generations. Drottar and Krueger [77,78] assessed the survival of juveniles (over 48 h and 96 h) released from PFOS-exposed *Daphnia magna*

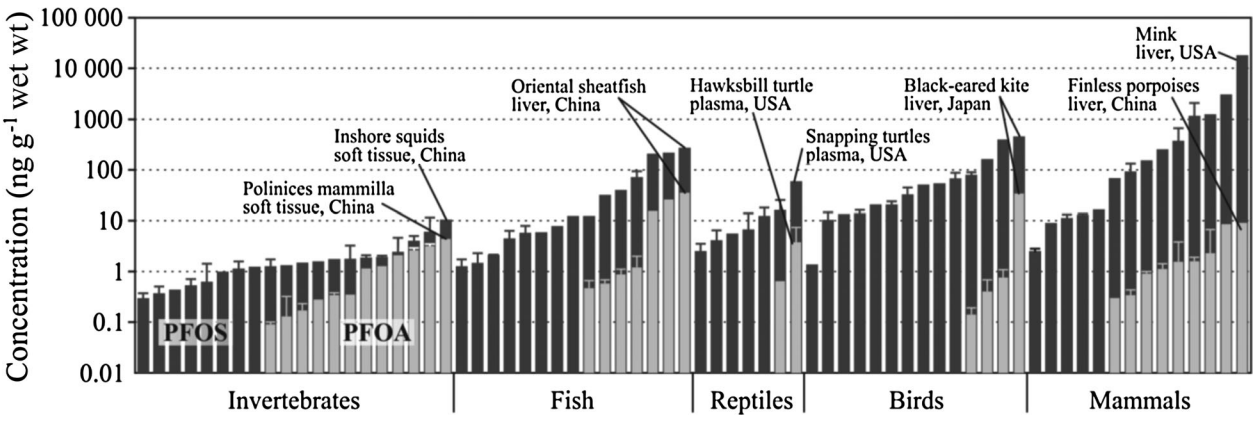


Figure 2. Average perfluorooctane sulfonate (PFOS; black bars) and perfluorooctane sulfonate (PFOA; gray bars) concentrations in wildlife from the aquatic environment including invertebrates (whole body) [59–61,65,66], fish (liver) [60,61,65–68], reptiles (plasma) [69–71], birds (liver) [59–61,68,72,73], and mammals (liver) [60,67,68,71,72,63,74,75].

(freshwater Cladocera) and *Mysidopsis bahia* (marine Mysida) in medium amended with the same PFOS concentration ($\mu g\ L^{-1}$ to $mg\ L^{-1}$ range) as the adults had been exposed to. Following this short-term exposure to PFOS, the F1 generation of both *Daphnia* and *Mysidopsis* exhibited no indication of a shift in sensitivity. In contrast to these studies with invertebrates, Japanese medaka (*Oryzias latipes*) exposed to either PFOA or PFOS (in the $\mu g\ L^{-1}$ range) released offspring that, even if cultured after hatching in control (PFAS-free) medium, showed higher mortality but also histopathological alterations compared with the offspring released from control animals. The effect size was even more pronounced if the exposure to PFOA or PFOS, respectively, is continued in the F1 generation [79]. These data suggest that effects on the next generation can already be observed if a species is exposed to PFASs for only 1 generation. However, and as detailed above, Polyfluoroalkyl and perfluoroalkyl substances are continuously introduced into aquatic environments and hence more than 1 generation may suffer from PFAS exposure, which requires an assessment of potential implications over multiple generations—especially for genera with a rather short generation time, such as *Daphnia* or *Chironomus*. The latter may be of particular interest because, for example, *C. tentans* survival, emergence, and growth was inhibited by 50% at a concentration slightly below $100\ \mu g\ L^{-1}$ of PFOS [80], which is 3 orders of magnitude below concentrations causing effects in daphnids, macrophytes, and algae (reviewed in Ding and Peijnenburg [12]). Multigeneration experiments should also consider whether effects persist even under control (PFAS-free) conditions, simulating the migration of species to nearby uncontaminated aquatic ecosystems. Overall, adverse effects of PFASs need to be evaluated considering a continuous exposure at environmentally relevant concentrations in the aquatic environment.

IMPACT OF MULTIPLE STRESSORS

In addition to the ubiquitous presence and persistence of PFASs, environmental chemistry research has documented complex PFAS mixtures in surface water bodies [6]. In this context, however, more detailed ecotoxicological knowledge needs to be developed. Wang et al. [13] have suggested that mixtures of PFASs act additively on *Photobacterium phosphoreum*. However, mixtures of PFOA and PFOS exhibited complex toxic interactions on *Danio rerio* embryos, which were not predictable with either concentration addition (similar mode of action [81]) or independent action (dissimilar modes of action [82]) models [83]. Nonetheless, the studies of Liu et al. [84–86] indicated an increase in ecotoxicity with increasing molar ratio of PFOS in the investigated binary mixture. Moreover, the gene expression pattern of *Gobiocypris rarus* showed that a particular set of genes is expressed only if exposure to PFAS mixtures has taken place, whereas none of the single PFAS exposure scenarios resulted in a comparable pattern [87]. These studies suggest that mixtures of PFASs can cause unpredictable, species-specific effects. However, a systematic assessment of the potential implications of PFAS mixtures is required to understand whether and how these compounds might jointly affect the integrity of aquatic ecosystems.

Moreover, PFASs are usually detected in combination with other organic and inorganic chemical stressors with which they may interact. Studies report antagonistic, synergistic, or no interactions between PFOS (only one study also assessed PFOA) and metals [88,89], chlorinated compounds [90,91], and other organic compounds [90,92,93]. Liu et al. [92] linked the observed synergistic interaction between PFOS and pentachlorophenol, atrazine, and diuron in binary mixtures with their hydrophobicity, allowing for an uptake in algal cells. However, deeper insights supporting a prediction of potential interactions among PFASs and other natural or anthropogenic stressors are lacking, while the co-occurrence of these stressors in the field is certainly given [94]. This general lack of knowledge of interactions of other PFASs—besides PFOS and PFOA—with other natural and chemical stressors is particularly alarming because a variety of replacement compounds (e.g., short-chain PFSAs and PFCAs, and PAPS) are released into the aquatic environment [18,95].

COMPLEXITY IN SPECIES INTERACTION AND ECOSYSTEM FUNCTION

This section focuses on trophic interactions in the aquatic ecosystem, with special emphasis on autotrophic and heterotrophic food webs. In aquatic ecosystems, algae—and their photosynthetically generated biomass—are considered as the basis of autotrophic food webs. However, PFASs seem to have the potential to affect the functioning of these organisms' cell membranes, which is more pronounced with increasing PFAS chain length and lower proportion of indigestible structural components, such as cellulose, in the algal cell wall [96]. These processes may have implications in the food quality for algae-consuming animals, such as filtering and grazing invertebrates (Figure 3). Hence, it might be assumed that implications for reproduction of the standard test species *D. magna* [97] (among others) or the development of zooplankton communities [98,99] may be driven by not only direct exposure but also indirect exposure—via an altered nutritious quality of the ingested algae (Figure 3; [100]). This question can be addressed by applying simplified Dynamic Energy Budget models (DEBTox) [101]. This tool allows for an estimation of energy assimilation and expenditure processes (i.e., maintenance, growth, reproduction) that may be affected by a given stressor and hence would allow us to link the observed effects with relevant effect pathways [101].

In contrast to the autotrophic webs, heterotrophic food webs rely on the utilization of dead organic matter such as leaf litter. In this context, leaf litter decomposition is a fundamental ecosystem function, which fuels local and downstream aquatic communities [102]. As a first step in this process, microorganisms, especially bacteria and fungi, alter the physical and chemical structure of the leaf materials (conditioning), which increases their nutritious quality for leaf-shredding invertebrates [103]. The conditioning process, however, may be altered in the presence of PFASs by affecting (among other factors) leaf-associated bacteria, and any implications for fungi cannot be excluded, given the lack of data. Such effects may be hypothesized given the potential of PFASs for impacting the integrity of cell membranes (median effective concentrations have ranged from 0.28 mM to 12.8 mM for PFCAs) [96] and causing substantial cellular oxidative stress [104] (Figure 3). Such implications may alter the interaction between bacteria and fungi on leaves, as both groups are reported to depend on the activity of the other (synergistic interaction [105]) but can also be hampered (antagonistic interaction [106]) during conditioning. This in turn affects the nutritious value of the leaf material for leaf-shredding organisms, as displayed for various chemical stressors [107,108], leading to physiological implications in the shredders and shifts in the breakdown of leaves into finer

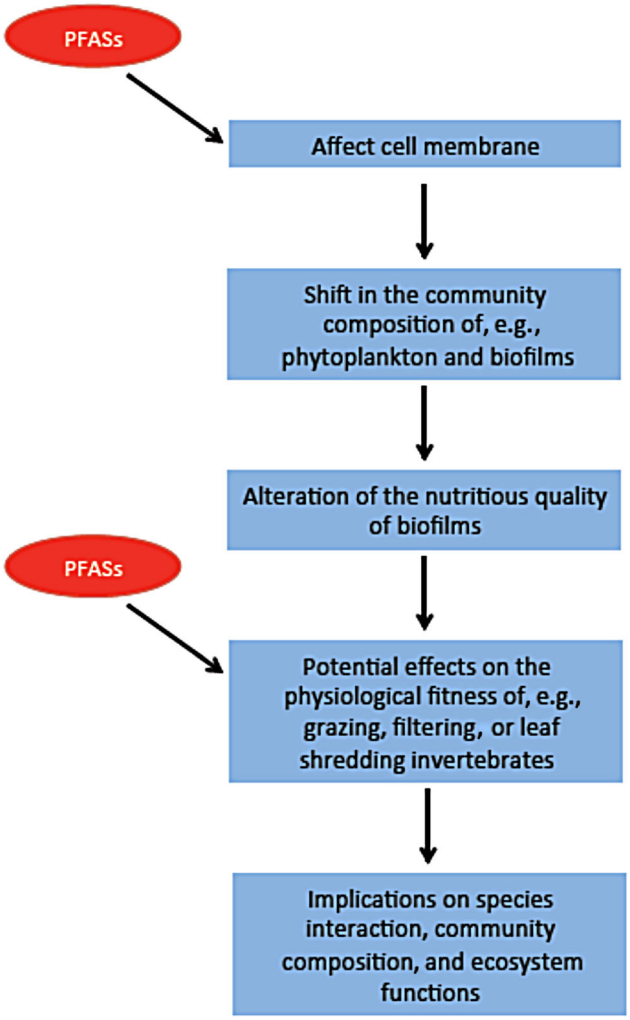


Figure 3. Potential (in)direct effect pathways of polyfluoroalkyl and perfluoroalkyl substances (PFASs) on grazing, filtering, and leaf shredding invertebrates as well as higher levels of ecological complexity as a result of alterations on the basis of autotrophic or heterotrophic food webs.

particles [109]. To the best of the authors' knowledge, no information regarding indirect (food quality–related) effect pathways of PFASs is available for autotrophic and heterotrophic food webs, despite the substances' continuous presence in the aquatic ecosystem (Figure 3). In addition, potential implications in terms of the consumption of contaminated food (e.g., algae or detritus) have not yet been properly considered in ecotoxicological investigations in spite of the potential importance of this issue, particularly for highly sorptive compounds [110]. Moreover, predator–prey interactions have not yet been addressed, although they can help predict potential effects among trophic levels in complex food webs [111,112].

CONCLUSIONS

Polyfluoroalkyl and perfluoroalkyl substances are subject to geochemical cycling processes in the aquatic environment, including indirect and direct emissions, transport, partitioning, and transformation processes. A better understanding of the influence of environmental conditions and the physicochemical properties of PFASs on these complex processes is needed. Although there is a large quantity of data in terms of potential acute and chronic effects of PFSAs and PFCAs, which allow us to conclude that the ecotoxicity of those compounds increases with the perfluorocarbon chain length, some fundamental challenges remain largely unsolved. Polyfluoroalkyl and perfluoroalkyl substances are continuously introduced into aquatic ecosystems and are ubiquitously present in complex mixtures. However, little is known about the interactive toxicity of PFAS mixtures at environmentally relevant concentrations or about interactions with other natural and anthropogenic stressors. In addition, because exposure to PFASs is continuous, further information about their ecotoxicological potential in multiple generations, species interactions, and energy transfer within and across ecosystem boundaries may help in judging the risks for PFASs to affect ecosystem structure (e.g., biodiversity) and function in the aquatic environment.

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