Bioaccumulation of emerging contaminants in aquatic food chains and its implications for public health

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Abstract

Emerging contaminants (ECs), including per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), micro- and nanoplastics, novel flame retardants, pesticide metabolites, and other substances that have entered the environment, pose ecological and human health problems. They remain in water and exhibit complex behaviors that facilitate the accumulation of organisms and the magnification of other organisms at higher trophic levels. Accumulation of ECs in primary producers and invertebrates, and in higher-trophic-level freshwater, estuarine, and marine ecosystem animals such as fish and marine mammals, has been documented across all three ecosystem types. Human exposure occurs through the consumption of contaminated seafood, with some mixtures exceeding risk thresholds for endocrine disruption, immunotoxicity, and developmental impacts. Subsistence fishers and coastal communities with high seafood consumption are the most exposed and thus most vulnerable. This review aims to consolidate what is known about the mechanisms of distribution and the health implications of ECs' bioaccumulation, assess exposure assessment and analytical consistency data gaps, and identify regulatory and research gaps to better protect public health through monitoring, regulation, and research.

Keywords: Bioaccumulation, Biomagnification, PFAS, Pharmaceuticals, Microplastics, Trophic transfer, Risk assessment

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Introduction

Emerging contaminants (ECs) have been increasingly detected in the environment over the last couple of decades, affecting both the environment and public health. These include per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), micro- and nanoplastics, novel flame retardants, and pesticides' metabolites. They are not fully regulated and should be bioactive, persistent, and capable of long-range transport. The constant discharge from industrial, agricultural, and domestic activities poses a low chronic exposure risk, leading to ecological imbalance in freshwater, estuarine, and marine ecosystems and potentially disrupting the safety of the human food supply (Anagnostopoulos and Varga, 2021; Assegid and Ketema, 2023). Bioaccumulation is the net gain of a substance from all the exposure pathways, which are water, sediment, and food, while bioconcentration is specifically concerning uptake from the water, and biomagnification is the increase of a substance in successive trophic levels (Hu *et al.*, 2024). Traditional hydrophobic organic contaminants are associated with lipid partitioning, but many ECs, especially PFAS and ionizable pharmaceuticals, are not traditional and exhibit atypical behaviors associated with protein and phospholipid binding. This challenges classic modeling based on the octanol–water partition coefficient (K_ow) and illustrates the need for new, refined bioaccumulation approaches (Xie *et al.*, 2017).

The bioaccumulation of ECs in aquatic food chains presents potential human exposure risks as contaminated fish and seafood are consumed (Parolini *et al.*, 2023). Highly dependent on seafood populations, including coastal communities and subsistence fishers, are at heightened risk of chronic exposure. Furthermore, vulnerable populations, for instance, pregnant women and children, are at increased endocrine, immunological, and developmental health effects risks due to certain ECs. This review examines the mechanisms and extent of EC bioaccumulation in food webs and corridors across freshwater, estuarine, and marine environments, and assesses the human health and regulatory policy implications (Hou *et al.*, 2021). This paper aims to consolidate widely dispersed studies, differentiated by chemical class and trophic structure, to identify methodological and critical research gaps and propose actionable steps to improve risk assessments and risk management for emerging contaminants in the aquatic environment.

Materials and Methods

Bioaccumulation of emerging contaminants (ECs) within the food web of aquatic organisms occurs through complex interactions among physicochemical, biological, and ecological processes that shape the food web (Pereira *et al.*, 2015). Explanatory mechanisms behind gradient accumulation and high predictive exposure risk models require an understanding of these processes. Within aquatic organisms, the pathways of contaminant acquisition include gill absorption, gastrointestinal uptake, and

dermal absorption. For waterborne contaminants, gill uptake is the principal route of absorption, driven by diffusion through the membranes and by gill vascularization, which influences composition, surface area, and ventilation rate (Suedel *et al.*, 1994). For higher-trophic-level organisms, dietary absorption via the gut is more important. For instance, microplastics and hydrophobic organic compounds associated with particulates are contaminants that gastrointestinal absorption aids in the acquisition of. While basal dermal absorption is of minor importance, permeable skin and, in some cases, larval stages of some species make dermal absorption reasonable (Carbery, O'Connor and Palanisami, 2018). The partitioning of ECs between the dissolved and particulate phases determines their bioavailability, as strong partitioning into organic matter and microplastics decreases uptake. Capture and transformation of contaminants in the gut and subsequent modification of assimilation efficiency due to microbiome activity are suggestive of an intermediary role (Nilsen *et al.*, 2019).

The kinetics of Elimination Control systems can be viewed as the balance between the removal function k_2 and the uptake function k_1. In addition to the steady-state body burden, temporary 'grew dilution' (tissue dilution) also occurs, in which the body burden concentration is reduced without any loss of chemical. For highly polar and ionizable ECs, classic octanol-water partitioning is of no utility. Take PFAS, for example. PFAS bioaccumulate atypically and within the liver and blood water compartments, which are highly proteinaceous, because they preferentially bind to serum proteins, not lipids. Charged pharmaceuticals also present issues similar to PFAS, including variable charge states, bimodal uptake, and effects on the gill surface and membrane transporters. Linking the mechanistic models of protein-ligand binding and active transport will undoubtedly improve predictions of bioaccumulation (Bhatt and Chauhan, 2023). Trophic transfer of contaminants is driven by biomagnification - the increase of contaminant concentration at successive levels and through trophic systems. Predators further amplify biomagnification by assimilating prey that has body burdens above the equilibrium concentration, a state of ontogenetic dilution. Excessive lipid content drives and controls the biomagnification of hydrophobic ECs. For many pharmaceuticals that retain a significant substrate for metabolic biotransformation, the biomagnification potential is expectedly reduced. In contrast, non-degradable metabolites, such as long-chain PFAS or specific brominated flame retardants, are subject to strong trophic magnification factors (TMFs). Temperature, salinity, and food-web structure also impact these by altering energy flow and metabolism, as seen in Figure 1.

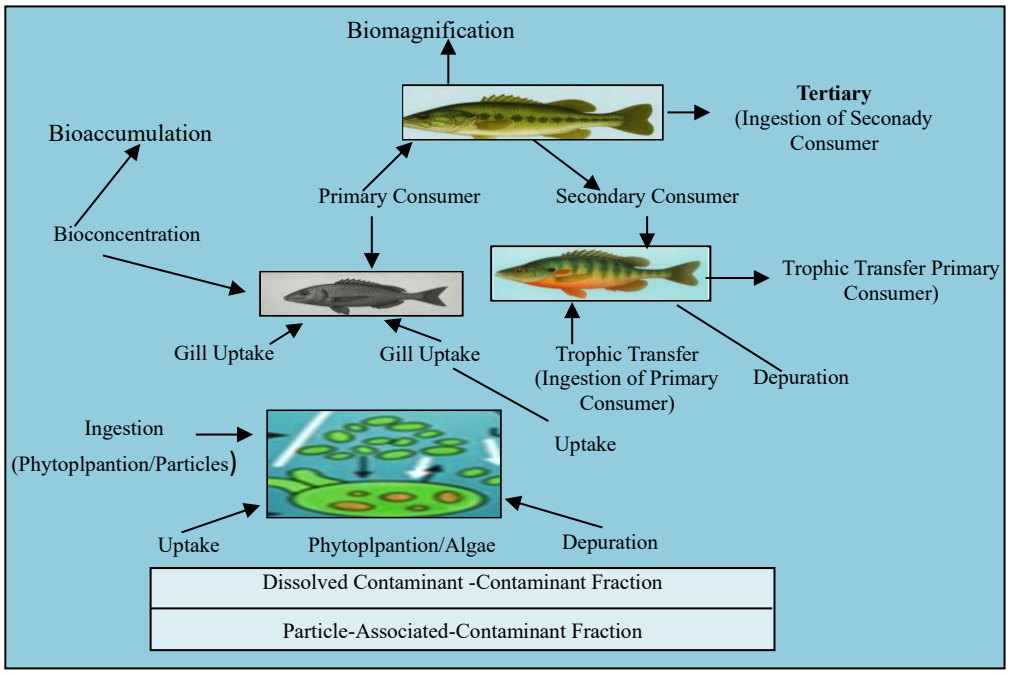

Figure 1: Flow diagram of contaminant transfer and bioaccumulation in aquatic food chains.

The evaluation of ecological risk posed by emerging contaminants (ECs) and bioaccumulation potential in aquatic food webs relies on advanced analytical methodologies capable of pinpointing minute concentrations in various environmental matrices (Parolini *et al.*, 2023). The selected matrices, extraction methods, and analytical frameworks can each impact the quality and the comparability of the bioaccumulation data. Interpretation of the data on bioaccumulation and risk assessments will, therefore, require study harmonization at the risk of equating disparate results (Khan, Burgess and Cantwell, 2023). Typical sampling strategies involve the selection of water, sediment, and biological tissues, each representing a different quadrant of the aquatic environment. Since large volumes of water need to be processed to isolate contaminants, water samples are subject to preliminary concentration by solid-phase extraction (SPE) or liquid-liquid extraction (LLE). Extracts of sediment and particulate matter are often processed with accelerated solvent extraction (ASE) or Soxhlet extraction, which is followed by the removal of co-extracted organic matter using silica gel and Florisil column clean-up. For biological materials, sample preparation is dictated by the tissue compositional class, which is mostly muscle, liver, and whole-body homogenates. Following residual lipid removal by gel permeation chromatography (GPC) after lipid extraction, signal enhancement is achieved. As part of the standard protocol, the incorporation of blanks, matrix spikes, and surrogate standards is used to assess recovery efficiency and analytical bias.

There has been a marked improvement in ECs detection owing to the implementation of high-sensitivity mass spectrometry. Liquid chromatography in tandem with mass spectrometry (LC–MS/MS) remains the gold standard in the quantification of polar and semi-polar contaminants, including PFAS, pharmaceuticals, and personal care

products. The use of isotopically labelled internal standards increases precision and mitigates the impact of matrix effects. For gas chromatography–mass spectrometry (GC–MS) and pyrolysis–GC/MS, the focus is on hydrophobic or polymeric contaminants where flame retardants and polymer fragments of microplastics are identified. Additional micro-spectroscopic techniques are used in polymer characterization of micro- and nanoplastics and in the determination of some of their morphological features, including type and shape, via micro-Fourier transform infrared (FTIR) and Raman microscopy. The validity of the dataset is ensured through the implementation of quality assurance and control (QA/QC) measures, including calibration, detection limits, and precision of the instrumentation. Detection limits for most ECs in biota are now routinely in the low nanogram per gram ($ng \cdot g^{-1}$) range, although inter-study inconsistency remains prevalent due to matrix complexity.

One of the ongoing difficulties in EC bioaccumulation studies is the absence of consistent documentation units. In the documentation reviewed in Table 1, the concentrations in studies on aquatic organisms are reported on wet-weight, dry-weight, and lipid-basis or combinations, complicating inter-study evaluations (Ray and Shaju, 2023). For proteinophilic contaminants like PFAS, the use of protein-normalized (e.g., per gram of total protein) is more relevant than lipid-based, as it captures the more closely bound metrics of proteins and the biological relevance of the protein metrics. Inconsistent estimations of the trophic magnification factor (TMF) arise from unharmonized documentation, coupled with differences in analytical recovery correction and detection limits from which TMF estimations are drawn. Incorporating harmonized TMF calculations alongside comprehensive metadata (e.g., sample type, extraction recovery, and analytical uncertainty) would greatly improve cross-system comparability as well as meta-analytical synthesis.

Results

Table 1: Detection methods and reporting criteria for environmental contaminants.

Contaminant class	Typical matrix	Extraction / clean-up	Detection method	Detection limit ($ng \cdot g^{-1}$)	Reporting basis
PFAS	Water, sediment, biota (liver, muscle)	SPE, protein precipitation, GPC	LC–MS/MS	0.1–1.0	Wet weight / protein-normalized
Pharmaceuticals (PPCPs)	Water, sediment, biota	SPE, ASE, SPE–GPC	LC–MS/MS	0.5–5.0	Wet weight
Microplastics	Water, sediment, gut contents	Density separation, peroxide oxidation	Micro-FTIR, Raman microscopy	Size ≥10 µm	Particle count / mass
Flame retardants (BFRs, OPFRs)	Sediment, biota (lipid-rich tissues)	Soxhlet / ASE, silica clean-up	GC–MS or GC–MS/MS	0.1–2.0	Lipid-normalized
Pesticides and metabolites	Water, sediment, biota	LLE or QuEChERS	GC–MS/MS or LC–MS/MS	0.1–1.0	Wet or lipid-normalized

PFAS exhibit unique protein-affinity phenomena. Concentrations in the liver, blood, and kidneys are higher than in the muscle due to serum protein and phospholipid binding. The chain length and functional group structure affect bioaccumulation (Du *et al.*, 2019). Long-chain perfluoroalkyl acids (PFOS, PFNA, PFDA) and some precursor substances are associated with higher body burdens and frequently exhibit a TMF > 1, especially in protein-rich diet predators. Short-chain PFAS and ether-PFAS are more water-soluble, more mobile, and tend to have lower trophic magnification. Patterns are modulated by organismal traits (metabolic capacity, growth rate) and food-web structure, as well as salinity. From a human exposure perspective, predatory fish and seafood offal (liver products) significantly contribute to dietary PFAS, and vulnerable populations (children, pregnant people, subsistence fishers) are disproportionately affected (Table 2).

Table 2: PFAS in aquatic food webs: tissue patterns and trophic metrics.

Ecosystem	Dominant species/tissue	Key PFAS	Normalization	BAF/BMF	TMF	Key observation
Freshwater	Planktivorous fish (muscle)	PFOS, PFNA	ww	—	—	δ^{15}N-based TMF near unity
Estuarine	Benthic invertebrates (whole)	PFOS, PFHxS	ww	—	—	Gradient with salinity
Marine	Predatory fish (liver)	PFUnDA, PFOS	protein	—	>1	Strong biomagnification
Riverine	Omnivorous fish (muscle)	PFOA, PFHxA	ww	—	~1	Low chain length = low TMF
Coastal	Seabirds (blood)	PFNA, PFOS	protein	—	>1	High protein binding

Ionizable PPCPs behave differently depending on environmental conditions. Uptake behavior is still determined by gill surface chemistry, transporters, and membrane partitioning. Continuous inputs of PPCPs, with low and moderate BAF/BMF values and common BMF values under 1, demonstrate pseudo-persistence as a consequence of metabolic biotransformation and weak membrane partitioning. The remaining BMF >1 conditions are noted for antidepressants or antihistamines with strong membrane transporter interaction, incomplete metabolism, and high protein binding due to a marked concentration of residues in the brain and liver. Growth dilution, rapid depuration, or a combination of both can suppress trophic magnification of synthesized compounds, even in the prey.

From zooplankton to fish, ingestion occurs, and egestion takes place within hours to days, with retention increasing for smaller particles and fibrous morphologies. There is evidence for trophic transfer (prey → predator gut); however, consistent biomagnification of particle counts at any trophic level remains unsubstantiated. Several studies demonstrate transfer without clear magnification, attributable to egestion and gut clearance. The effects of vectors (sorption/desorption of additives and co-contaminants) are situation dependent: additives that strongly bind to plastics (like certain flame-retardant additives), or conditions with low-DOC (dissolved

organic carbon) waters, increase the potential for plastics to provide an unintentional chemical load, whereas in organic-rich waters, the contribution of plastics to chemical load is negligible compared to the natural particulate and dietary particulates (Table 3).

Table 3: Micro/nanoplastics, BFRs/OPFRs, and pesticides.

Ecosystem	Analyte/class	Metric	BMF/TMF	Notable feature
Freshwater	PE fragments	items·g^{-1}	—	Rapid egestion
Estuarine	PET fibers	items·ind^{-1}	~1	Transfer without magnification
Marine	Novel BFRs	ng·g^{-1}	>1?	Lipid-based accumulation
Riverine	OPFRs (TDCIPP)	ng·g^{-1}	≤1	Labile; metabolic loss
Agricultural drainage	Pyrethroids	ng·g^{-1}	—	Event-driven spikes

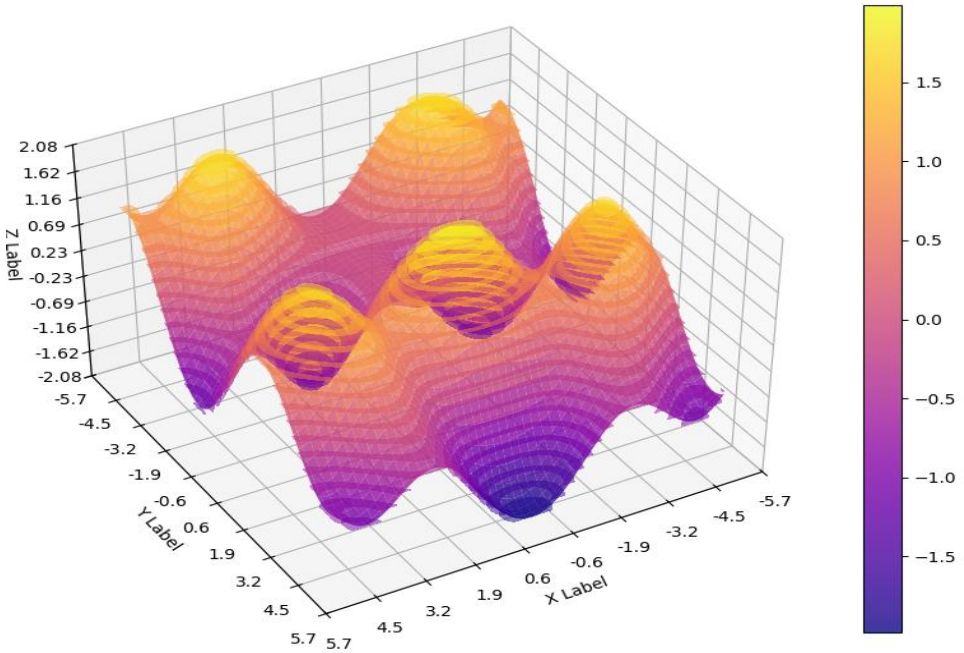

Figure 2: 3D Surface representation of sine and cosine wave interference with color intensity.

Figure 2 depicts the conversation surrounding the accumulation and biomagnification of contaminants in the aquatic ecosystem, more specifically, the paragraph pertaining to current-use pesticides, brominated flame retardants (BFRs), and organophosphate flame retardants (OPFRs). The figure demonstrates how contaminants move through food webs, beginning with phytoplankton (algae). Phytoplankton, along with other aquatic plants, uptake contaminants from dissolved and particle-associated fractions of water. When primary consumers, such as small fish, prey on phytoplankton and larger fish prey on the small fish, the contaminants accumulate and biomagnify within successive trophic levels. This is partially due to the bioaccumulation and biomagnification processes, the latter occurring in the upper trophic levels. It also depicts trophic transfer, the process by which contaminants are transferred from one host to another through the predation process. This is particularly evident in the case of lipophilic pesticides, BFRs, and

OPFRs, which concentrate in the adipose reserves and predaceous organisms at the upper trophic levels of the food web have substantially greater concentrations. In the case of current-use pesticides, metabolism prevents the biomagnification of certain pesticides, resulting in a biomagnification factor (BMF) of ≤ 1. Certain species may have slower metabolism or chronic exposure to certain pesticides in the environment, making biomagnification and accumulation possible. Also, biomagnification represents the potential accumulation of pesticides at greater trophic levels in a food web, regardless of the pesticides being eliminated from the organism by depuration. Persistent and highly hygroscopic brominated flame retardants (BFRs) have been reported in the literature to tropically magnify in food webs and exceed TMFs of 1, especially in lengthy food webs. Certain UV filters, industrial sugar, and caffeine are found in low concentrations in influent wastewater, and biomagnification of sugar and caffeine is not a significant concern. The diagram visually demonstrates the accumulation of various contaminants and biomagnification of various contaminants in the aquatic food web, beginning with primary producers and continuing to higher trophic levels.

Discussion

Among various contaminant classes, long-chain PFAS, persistent, and protein-binding compounds are the most tropically magnified and biomagnified from lower to apex trophic levels, especially in marine and estuarine systems. Most pharmaceuticals, UV filters, and newer flame retardants, in contrast, are minimally biomagnified, due in large part to metabolism and ionization, although limited localized accumulation can pose ecological and human health risks. Microplastics are primarily vectors and indicators of contamination, not strongly biomagnifying themselves, but their chemical and particle interactions pose an unresolved exposure risk. From the public health perspective, PFAS and co-occurring hydrophobic ECs are most highly exposed through seafood, especially predatory species, and pose the greatest risk to populations highly dependent on this seafood (Wang *et al.*, 2019; McIlwraith *et al.*, 2021). This knowledge has to be poured into policy through the harmonization of methods, biologically relevant metrics, and contextually sensitive, culturally, and nutritionally relevant advisories. Future risk reduction efforts rely on the risk prevention strategy of substituting persistent chemicals, preventing their release into the environment, the modernization of wastewater and feed systems, and open data pipelines between monitoring researchers, health departments, and affected populations (Hu *et al.*, 2023). Bioaccumulation in the aquatic environment can transform from an endpoint of contamination to a monitoring system for chemical stewardship, aligning bioaccumulation studies with precautionary management (Savoca and Pace, 2021).

Conclusion

To conclude, there is enough and growing evidence to show that the bioaccumulation and trophic transfer of emerging contaminants are chemically selective and context dependent. Among

the persistent, protein-affinitive class of compounds, long-chain PFAS continue to show the strongest and most policy-relevant biomagnification signals across aquatic food webs. In contrast, numerous pharmaceuticals, UV filters, and newer flame retardants are less persistent, yet, because of mixture effects, they should continue to be monitored. For subsistence and high-intake populations, seafood consumption remains the most credible pathway for important human exposures. Consequently, the incorporation of harmonized bioaccumulation indicators, mixture-toxicology, and socio-ecological risk assessments will be crucial to connect the environmental surveillance and health-guarding aspects of the bioaccumulation problem. Increased synergy between scientists, regulators, and the public can enable bioaccumulation research to inform preventive chemical management and just food safety policies, thus protecting the integrity of the ecosystem and the health of the population.

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