Human Health Impacts of Perfluoroalkyl Substances, Micro- and Nanoplastics Contamination of Drinking Water

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Abstract
PFAS are organic compounds made up of carbon and fluorne atoms, often characterized by a carbon backbone with fluorne atoms attached. The key feature is the presence of perfluoroalkyl groups, where all hydrogen atoms on the carbon chain are replaced by fluorne atoms. PFAS are considered persistent and bioaccumulative, meaning they do not break down easily in the environment and can accumulate in organisms over time. Long-term exposure to PFAS has been associated with potential health risks, including liver damage, immune system effects, developmental issues, and an increased risk of certain cancers. Microplastics and nanoplastics (MNPs) pose significant environmental and potential health risks. They can be ingested by humans on consumption of contaminated water potentially causing harm. MNPs have been found in drinking water sources, soil, and aquatic life including fish, shellfish, and plankton. These particles can accumulate in the tissues of plants and animals and can enter the human food chain. Due to these environmental and health concerns, efforts are being made to regulate and reduce the use of PFAS in various applications, reduce plastic pollution, improve waste management, and develop sustainable alternatives to mitigate the impacts of MNPs on the environment and human health.

1. Introduction
Water is an essential resource for human health, and the quality of drinking water is of paramount importance. Water gets to the sea through continual movement of the water cycle such as evaporation, transpiration, condensation, precipitation, and runoff. Water plays a vital role in the economic growth of any country. Transportation of agricultural products from one country to the other is mostly done using boats or ships through the seas, rivers, and oceans. Without the existence of water fishing and other agricultural activities would not be possible. Water is used in industrial processes due to its excellent solvents for a variety of substances both minerals and organic. Water is used for entertainment and sports such as swimming, boat racing, diving, etc. All these uses of water will not be possible if the water is contaminated. However, in recent years, concerns have arisen regarding the presence of emerging contaminants such as perfluoroalkyl substances (PFAS), micro- and nanoplastics (MNPs) in drinking water sources. PFAS are synthetic chemicals known for their persistence and potential adverse effects on human health, while micro- and nanoplastics have raised environmental and health concerns due to their widespread occurrence and potential toxicity. PFAS and MNPs are discharged from either domestic activities or industrial waste from power generation, manufacturing operations, and mineral extractions. As water is life to both plants and animals, it is also detrimental when contaminated. Many chemicals from the industries find their way into the water bodies causing problems to the aquatic animals and humans on ingestion. Industrialization and urbanization is the major culprit of water pollution and contamination. Many scholars are in agreement that PFAS and MNPs are among the Contaminants of Emerging Concerns (CECs) which are potentially harmful pollutants for which concern for their effects is relatively recent and are generally not regulated in present-day environmental laws (Murnyak et al., 2011). CECs when discharged as waste in the environment have the ability to enter into water cycles through the process of water runoff finding its way to the river, ocean, and or lakes by effluent discharge and eventually going to the public water supply. CECs are known for their cancer-causing and endocrine-disrupting abilities (Sauve et al., 2014). They can bio-accumulate the food web thereby causing detrimental health effects to humans when contaminated fish is ingested. The rising trends of emerging contaminants do not only impair the quality of water, air, and or soil but could also find their way to the food chain and affect human and animal health. PFASs are synthetic organofluorine chemical compounds that are composed of multiple fluorne atoms connected together with an alkyl chain. In 2021, the Organization for Economic Co-operation and Development (OECD) defined PFAS to be a fluorinated substance that contains at least one fully fluorinated methyl or methylene carbon atom without any hydrogen, chlorine, iodine, or bromine atom attached or connected to it. That is, any chemical compounds with at least one fully fluorinated methyl group (CF₃) or fluorinated methylene group (CF₂) are regarded to be PFAS (Wang et al., 2021). All PFAS incorporates

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a series of carbon atoms bonded to fluorine atoms. PFASs include the following: Perfluorooctane Sulfuric Acid (PFOS), Perfluorooctanoic Acid (PFOA), Perfluorononanoic Acid (PFNA), Perfluorodecanoic Acid (PFDA), Perfluorooctane Sulfonamide (PFOSA) among others. MNPs are emerging contaminants globally whose attention was drawn as a result of their potential threats to humans and the environment. The potential treatment of MNPs is due to their persistence and bioaccumulation. NPs are non-biodegradable, biologically incompatible, and can be found in air, water, soil, and or food. Due to the miniaturizing nature of NPs and their chemical diversification, it can infiltrate wastewater treatment processes. Micro- and nanoplastics (MNPs) are fragments of any kind of plastic that are less than 5 mm and 1mm in size respectively (Colligno et al., 2014). They contaminate natural ecosystems from sources like cosmetics, clothing, food packaging, and commercial processes. There are two classifications of MNPs which include primary and secondary MNPs. Primary MNPs consist of any plastic fragments or particles that are intentionally manufactured like nanofibers for clothing, nanobeads for cosmetics, and plastic pellets (Cole et al., 2013). Secondary nanoplastics emanate as a result degradation (breakdown) of large plastic products via natural weathering processes after getting into the environment. Sources of secondary MNPs include the degradation of water bottles, fishing nets, plastic bags, microwave containers, tea bags, and tire wear (Conkle et al., 2018). Both classes of MNPs persist in the environment at excessive levels, particularly in aquatic and marine ecosystems. Additionally, MNPs accumulate in the air and terrestrial ecosystems and have an excessive chance of ingestion, incorporation into, and accumulation in the bodies and tissues of many organisms (Chamas et al., 2020, Klein et al., 2018).

2. Perfluoroalkyl substances (PFASs)

Perfluoroalkyl Substances (PFASs) refer to synthetic organofluorine chemical compounds that are composed of multiple fluorine atoms connected together with an alkyl chain. In early 2011, PFASs were said to contain at least one perfluoroalkyl moiety \(-\text{CF}_n\text{F}_{2n+1}\) (Buck et al., 2011; Ritscher et al., 2018). In 2021, the Organization for Economic Co-operation and Development (OECD) defined PFAS to be a fluorinated substance that contains at least one fully fluorinated methyl or methylene carbon atom without any hydrogen, chlorine, iodine, or bromine atom attached or connected to it. That is, any chemical compounds with at least perfluorinated methyl group (FCF) or perfluorinated methylene group (CF2) are regarded to be PFAS (Wang et al., 2021). All PFAS have chains of carbon atoms bonded to fluorine atoms. Some of the PFAS have functional groups attached at the end of the chain. These different structures entail the bias for the different chemical names and chemical properties of PFAS. In Perfluoroalkyl Substances all carbon atoms are attached to fluorine atoms except the last carbon atom which is attached to the functional group (Buck et al., 2011) as indicated in the skeletal structure of Perfluorooctane Sulfuric Acid (PFOSA) in Figure 1. Some scholars describe PFAS as forever chemicals because they remain in the environment for a very long period of time. According to the National Academies of Sciences, Engineering, and Medicine, PFAS exposure is associated with an increased risk of hypercholesterolemia (abnormally high cholesterol), reduction of infant and fetal growth, and as well high rate of kidney cancer. Many of the products and materials such as Teflon and aqueous film foaming foam were used in mid 20th century as a result of their enhanced water-resistant properties but their environmental and human health impacts were not known as of then till of recently when more researchers embarked deeply on the study of the impacts and toxicity of
cholesterol, changes to liver function, reduction of immune response, thyroid disease, and increased kidney and testicular cancer. PFOA is utilized in numerous commercial applications, inclusive of carpeting, upholstery, apparel, ground wax, textiles, fire-preventing foam, and sealants. PFOA serves as a surfactant in the emulsion polymerization of fluoropolymers and as a building block for the synthesis of perfluoroalkyl-substituted compounds, polymers, and polymeric materials. PFOA has been manufactured since the 1940s in industrial quantities Linstrom et al. (2011).

The chemical structure of PFOA is depicted in Figure 2 above with the chemical formula of \( C_8H_{15}O_2 \) and a molar mass of 414 g/mol.

Perfluorononanoic Acid (PFNA)

Perfluorononanoic acid (PFNA) is a fluoroalkanoic acid. That is a nonanoic acid in which all the hydrogen in the alkyl chain is replaced with fluorines. Perfluorononanoic acid is a persistent organic pollutant, a xenobiotic, and a surfactant. Its functional group is related to nonanoic acid. It is a synthetic perfluorinated carboxylic acid and fluorosurfactant. It is an environmental contaminant found in both humans and wildlife. PFNA is the most important perfluorinated carboxylic acid surfactant. Fluorocarbon derivatives with terminal carbohydrates are only surfactants when they possess five to nine carbons. Fluorosurfactants lessen the surface tension of water up to half of what hydrocarbon surfactants can, by concentrating at the liquid-air interface due to the lipophilicity of fluorocarbons Salager, Chen Li et al., (2001). PFNA is very stable and is not known to degrade in the environment by oxidative processes due to the strength of the carbon-fluorine bond and the electronegativity of fluorine. The chemical structure of PFNA is represented in Figure 3 below with a molecular formula of \( C_9H_{17}O_2 \) and a molar mass of 464 g/mol.

Perfluorodecanoic Acid (PFDA)

Perfluorodecanoic acid (PFDA) is a perfluoroalkyl acid (PFAA). PFDA has been frequently detected in the environment, plants, fish, and animals. It is a fluorosurfactant and has been used in industry with applications as a wetting agent and flame retardant Reich et al., (1987). It is a breakdown product of stain- and grease-proof coatings on food packaging, couches, and carpets. Like many PFAAs, it is persistent and bio-accumulative. PFDA are said to be endocrine disruptors. Many are known toxicants and carcinogens. PFDA has been used in the manufacture of such prominent consumer goods as Teflon and Gore-Tex. It has been proposed as a chemical probe to study peroxisome proliferation Chen Li et al. (2001). The chemical structure of PFDA is depicted in Figure 4 with a molecular formula of \( C_{10}H_{17}O_2S \) and an atomic mass of 514 g/mol.

Perfluoroctane Sulfonamide (PFOS)

Perfluoroctane sulfonamide (PFOS) is a synthetic organofluorine compound. It is a derivative of fluorocarbons and perfluorinated compounds composed of eight carbon chains and a terminal sulfonamide functional group. PFOS is a persistent organic pollutant (Stephen K., 2006, Boulanger et al., 2005). From 1956 till 2003, PFOS was primarily used as a grease and water repellent in food packaging (Fromme et al., 2009). PFOS can be synthesized from perfluorooctanesulfonyl halids by reaction with liquid ammonia (Lehmler, 2005) or by a step reaction via an azide followed by reduction with zinc and hydrochloric acid Lehmler et al., (2007). The chemical structure of PFOS is represented in Figure 5 below with a molecular formula of \( C_8H_2F_{17}NO_2S \) and a molar mass of 499.14 g/mol.

Figure 6 is a tree diagram showing the different kinds of perfluoroalkyl substances present in the environment as a result of its release from industrial sources.
3. Uses of PFAS

Glüge et al. (2020) gave a complete summary of the main historical and modern-day uses of PFAS. Based on this paper and an OECD database on PFAS (OECD, 2018), PFAS are used globally in a wide variety of industries which consist of:

- Fire-fighting (fire suppressants)
- Chemical manufacturing
- Building and construction
- Cabling and wiring
- Metal finishing and plating
- Hydraulic fluids
- Fluoropolymer manufacturing
- Paper products and packaging
- Semiconductor Manufacturing
- Textiles, leather, and apparel (such as carpets and furniture)
- Cleaning products (such as industrial surfactants)
- Refrigeration
- Refrigeration

4. Sources and pathways of PFAS

Globally, the main sources of PFAS in the environment are as follows:

- Industrial facilities that produce PFAS, facilities that use PFAS chemical compounds or products in production or other activities.
- Areas in which fluorine-containing fire-preventing substances are or have been stored, used, or released.
- Waste control facilities including landfills.
- Wastewater treatment residuals and areas of biosolids manufacturing and application, with greater considerable impacts related to industrial wastewater discharges.
- Diffuse sources can even contribute to the general environmental load. Examples consist of use in consumer products and subsequent release via washing and general wear and tear of textiles (Commission for Environmental Cooperation, 2017), and coatings including anti-graffiti paints (Scheeder et al., 2005).
- Historic use that has caused legacy contamination also contributes to the environmental burden due to the lifespan of the products containing them in addition to their intrinsic persistence.

5. Classification of PFAS

PFAS compounds may be categorized into polymeric and non-polymeric PFAS based on their molecular structure and composition Henry et al. (2018), Buck et al. (2011)

(a) Non-Polymeric PFAS: Non-polymeric PFAS are individual molecules that don’t have a repeating polymer structure. They commonly include a fluorinated carbon chain connected to a functional group. Examples of non-polymeric PFAS include:
- Perfluoroalkyl acids (PFAAs): These consist of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), which have been extensively utilized in industrial and consumer applications.
- Perfluorooctane sulfonamide (PFOSA): Another compound associated with PFOS, used in numerous applications like firefighting foams.
- Perfluorobutanesulfonic acid (PFBS): A shorter-chain PFAS used as a substitute for longer-chain compounds because of issues about their persistence and potential toxicity.

(b) Polymeric PFAS: Polymeric PFAS are PFAS compounds that have a polymer-like structure, often consisting of repeating units of smaller molecules. These polymers may also contain perfluorinated or partially fluorinated segments. An example of a polymeric PFAS is polytetrafluoroethylene (PTFE) which is used in non-stick coatings (e.g., Teflon) and different applications because of its low friction properties and excessive thermal stability. It's essential to note that each non-polymeric and polymeric PFAS has raised environmental and health issues because of their persistence, potential bioaccumulation, and possible detrimental effects on human and environmental health. Efforts are being made to phase out using PFAS and to better understand their effects on the environment and public health. Figure 7 below shows the classifications and sub-classifications of PFAS found in the environment.
6. Micro- and nano-plastics (MNPs)

Plastics are synthetic or semi-synthetic materials that use polymers as a key ingredient. Their plasticity makes it feasible for plastics to be molded, extruded, or pressed into strong items of numerous shapes. This adaptability, plus a huge variety of different properties, including being lightweight, durable, flexible, and cheaper to produce, has brought about its vast use. Plastics commonly are made via human industrial systems. Most present-day plastics are derived from fossil fuel-based chemical compounds like natural gas or Petroleum. However, modern-day commercial strategies use editions crafted from renewable substances, inclusive of corn and cotton derivatives. Micro/Nanoplastics (MNPs) are emerging contaminants globally whose attention was drawn as a result of their potential threats to humans and the environment. The potential treatment of NPs is due to their persistence and bioaccumulation. NPs are non-biodegradable, biologically incompatible, and can be found in air, water, soil, and or food. Due to the miniaturizing nature of NPs and their chemical diversification, they can infiltrate wastewater treatment processes. Micro/Nanoplastics (MNPs) are fragments of any kind of plastic that are less than 5 mm in size (Collignon et al., 2014). They cause pollutants by getting into natural ecosystems from a number of sources, together with cosmetics, clothing, food packaging, and commercial processes. There are two classifications of microplastics which include primary and secondary microplastics. Primary microplastics consist of any plastic fragments or particles that are already 5.0 mm in size or less before getting into the environment. These consist of microfibers from clothing, microbeads, and plastic pellets (Cole et al., 2013). Secondary microplastics emanate as a result of the degradation (breakdown) of large plastic products via natural weathering processes after getting into the environment. Such sources of secondary microplastics consist of water and soda bottles, fishing nets, plastic bags, microwave containers, tea bags, and tire wear (Conkle et al., 2018). Both classes of microplastics are said to persist in the environment at excessive levels, particularly in aquatic and marine ecosystems, in which they cause water pollutants. However, microplastics additionally accumulate in the air and terrestrial ecosystems. Because plastics degrade slowly, and have an excessive chance of ingestion, incorporation into, and accumulation in the bodies and tissues of many organisms (Chamas et al., 2020, Klein et al., 2018). The poisonous chemical substances that come from each of the classes in the sea and runoff water can biomagnify up the food chain.

Sources of Micro- and nano Plastic Emission in the Environment

Micro- and nanoplastics pollutants emanate from textiles, car tires through wear and tear, cosmetics industries, manufacturing industries, processing and shipping, and city dust. These sources account for about 80% of all micro/nanoplastics in the environment. The existence of micro/nanoplastics in the environment is obtained through aquatic studies. These include taking plankton samples, observing vertebrate and invertebrate consumption, and evaluating chemical pollutants (do Sul et al., 2014). Through the above-mentioned methods, it has been shown that there are micro/nanoplastics from multiple sources in the environment. Since perfluoroalkyl substances and micro/nanoplastics are said to be among the contaminants of emerging concern, figure 8 shows different sources through which these Contaminants enter the environment. The sources of these contaminants to the environment include industrial effluent, micro/nanoplastics, and or perfluoroalkyl substances.
Effects of MNPs on the Environment

According to a complete assessment of clinical proof posted through the European Union’s Scientific Advice Mechanism in 2019, microplastics are actually found in each part of the environment. While there may be no proof of a huge ecological chance from microplastic pollutants yet, dangers are probable to become enormous within a century if pollutants remain at their modern rate. So far, studies have particularly centered on large plastic items. This causes severe public concern. In contrast, microplastics aren’t as conspicuous, being much less than 5 mm, and are typically invisible to the bare eye. Particles of this size are available to a much broader variety of species, enter the food chain at the bottom, become embedded in animal tissue, and are then undetectable through unaided visible inspection. Furthermore, the effects of plastic degradation and pollutants released over a long time have generally been overlooked. The large quantities of plastic presently in the environment, uncovered to degradation have many extra years of deterioration and release of poisonous compounds to follow which lead to toxicity (Rillig et al., 2021). Microplastics have been detected not just in marine but also in freshwater systems which include marshes, streams, ponds, lakes, and rivers in (Europe, North America, South America, Asia, and Australia) (Helcoski et al., 2020, Eerkes-Medrano et al., 2015). Samples accrued throughout 29 Great Lakes tributaries from six states in the United States had been determined to include plastic particles, 98% of which were microplastics ranging in size from 0.355mm to 4.75mm (Baldwin et al., 2016).

PFAS and MNPs Contamination and Remediations

Perfluoroalkyl substances (PFAS) and micro/nanoplastics are two types of environmental contaminants that have gained significant attention due to their persistence and potential harm to human health and the environment. Here’s an overview of each and some potential remediation measures:

Remediation Measures for PFAS:
- **Activated Carbon Treatment**: Activated carbon can adsorb PFAS from water. It’s an effective treatment method for removing PFAS from drinking water and industrial wastewater.
- **Ion Exchange**: Ion exchange resins can replace PFAS ions in contaminated water with less harmful ions, effectively removing PFAS from the water.
- **Bioremediation**: Some microorganisms have been found to break down PFAS in soil and groundwater. Research on bioremediation methods for PFAS is ongoing.
- **Phytoremediation**: Certain plants have shown the ability to absorb PFAS from soil. Planting and managing these plants can help remediate PFAS-contaminated areas.

Remediation Measures for Micro/Nanoplastics:
- **Wastewater Treatment Upgrades**: Improving wastewater treatment plants to effectively capture and
7. Conclusion

PFASs are stated to be a set of artificial chemical compounds acknowledged for their top-notch water and oil-repellent properties. They have been used extensively in various industrial and consumer products, including firefighting foams, non-stick cookware, and waterproof textiles. However, PFAS has garnered attention due to their persistence in the environment and potential health hazards. Their resistance to degradation has led to widespread contamination of water sources, soil, and even wildlife. Research suggests that exposure to PFAS may be linked to adverse health effects, such as cancer, reproductive disorders, and immune system disruption. MNPs in water have as well become a pressing environmental issue. Microplastics are small fragments measuring less than 5 mm in size while nanoplastics are smaller at the nanometer scale. They enter water bodies through various sources, including the breakdown of larger plastics, micro-beads in personal care products, and industrial processes. Once in the water, these particles can persist for an extended period of time due to their resistance to degradation. They pose a significant threat to aquatic life, as marine organisms may ingest them, potentially leading to adverse effects on their health and the ecosystems. It's important to note that addressing both PFAS and MNPs contamination requires a multidisciplinary approach involving scientific research, policy changes, public awareness, and technological advancements in wastewater treatment and waste management. Ongoing research and collaboration are essential to effectively mitigate the impacts of these environmental contaminants.

Declaration of interest

The authors declare no conflicts of interest.

References


