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Original Research Article

PFAS - PERFLUORINATED ORGANIC COMPOUNDS IN VIEW OF THE NEW WATER DIRECTIVE

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A b s t r a c t

The purpose of the work was to review the literature and characterize organic micropollutants from the group of perfluorinated surfactants - PFAS. It is a result of the proposal to include these compounds in the new Water Directive on the list of compounds which control in drinking water will be required and subject to inspection. The group of these organic bonds includes several thousand compounds in which fluorine is linked to the (straight or branched) chain of aliphatic hydrocarbons instead of hydrogen. The article describes the permissible concentrations of PFAS in waters, the properties of these compounds, their potential impact on organisms, concentrations identified in waters, and indicates the need to limit the emissions of these compounds to surface waters. This is an important problem from the point of view of these compounds' impact on organisms and the fact that such waters are often a source of water supply for the national economy, including consumption by the population.

Keywords: PFAS perfluorinated compounds, water environment, water directive

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1. INTRODUCTION

In 2004, the Stockholm Convention defining persistent organic compounds for the aquatic environment was approved by the European Parliament and Council. Persistent organic pollutants include 8 chemical compounds from the group of polychlorinated hydrocarbons, polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). There are 7 dioxin congeners, 10 compounds count among the furans, and 7 congeners are the most common among PCBs. Based on this convention, Regulation EC No. 850/2004 and the amendment to Directive 79/117 /EEC [5, 20] were created. In this regulation, the group of persistent pollutants also includes polycyclic aromatic hydrocarbons (PAH), linear alkylbenzene sulphonate (LAS), phthalic acid esters (DEHP) and many other combinations of organic compounds with various substituents. Due to the fact that the list of POPs published in the Stockholm Convention is open, another 11 compounds were included in this group of pollutants in 2009. These are: hexabromobiphenyl HBB, tetra-, hexa-, hepta-, octa- and pentabromodiphenyl ethers, α, β, γ - hexachlorocyclohexanes, chlordecone, pentachlorobenzene, perfluorooctanesulfonic acid and its salts, and perfluorooctanesulfonyl fluoride. In 2020, the European Commission issued a Commission staff working document on poly- and perfluoroalkyl substances (PFAS) accompanying the "Chemical Strategy for Sustainability Towards a Toxin-Free Environment" [1]. In 2021, perfluorohexanesulphonic acid and its salts (PFHxS) were added to the REACH Candidate List for the list of substances of very high concern as "very persistent and very bioaccumulative substances" [17]. It is proposed to normalize the classification of PFAS compounds with the OECD60 definition and to establish a limit value of 0.1 μg/l for a single PFAS and 0.5 μg/l for the PFAS group in total.

The interest in these relationships among scientists and the expansion of legal acts arises from their identification in the environment. This in turn is the result of civilizational and industrial development, and urbanization as anthropogenic sources play the most important role in the emission of these xenobiotics. These compounds are widely used in industry as surfactants, impregnants, paint additives [10], pesticides, fertilizers [19], in transformers and many other household products [6]. Therefore, human exposure to contact with these compounds is relatively high. It is important from the point of view of human health since these compounds can penetrate the body, accumulate in tissues and adversely affect its functioning in many ways [14, 20]. Because the source of poly- and perfluoroalkyl surfactants in the environment are the effluents from wastewater treatment plants, it is important to develop new or modify known methods of wastewater treatment enabling an effective reduction of the emission of these pollutants to the environment. Further taking into account the fact that surface waters are the source of drinking water supply, the problem becomes a current one.

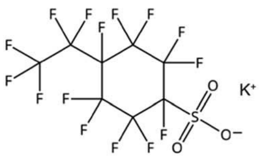
The aim of the article was to present, based on the available literature, the properties of these compounds, their potential impact on organisms, methods of determination and denotation of the level of water contamination with these micropollutants.

2. CHARACTERYSTIC OF PFAS

The group of compounds abbreviated to PFAS includes synthetic per- and polyfluoroalkyl compounds (4730 compounds). They are aliphatic hydrocarbons in which fluorine is linked in place of the hydrogen atoms in the (straight or branched) carbon chain. In addition to the basic perfluorine compounds, there are also those containing sulfur, phosphorus or nitrogen atoms in the particle. The PFAS group includes, primarily, perfluorosulfonic acids (e.g. perfluorooctanesulfonic acid - PFOS), perfluorocarboxylic acids (e.g. perfluorooctanoic acid - PFOA), perfluoroalkyl acid PFAA, Ammonium pentadecafluorooctanoate (APFO), perfluorononan-1-oic acid (PFNA) and its sodium and ammonium salts, nonadecafluorodecanoic acid (PFDA) and its sodium and ammonium salts, and perfluoroheptanoic acid [2, 7].

The structure of these compounds includes a fluorinated hydrophobic alkyl "tail" and a hydrophilic "head", which makes them both hydrophilic and hydrophobic. Therefore, they effectively reduce the water surface tension, i.e. they have surfactant properties. These properties depend on the length of the carbon chain in direct proportion: the properties of surfactants are better the longer the carbon chain and the greater the number of carbon-fluorine bonds. From the perspective of human health, the ability of these compounds to accumulate in the body is important. These are compounds that contain at least six perfluorinated carbons in their structure. These properties (bioaccumulation) have not been confirmed for short-chain PFAAs in animals, but it has been shown that they can accumulate in terrestrial plant tissues (shoots, leaves and fruits). Therefore, growing plants in soils heavily contaminated with short-chain PFAAs can pose a threat to humans. Figure 1 shows selected perfluorine compounds for which the bioaccumulation ability in organisms has been confirmed. An important characteristic of PFAS compounds is their effect on organisms. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are included in the group of endocrinically active EDCs. Moreover, the results of toxicology studies were the basis for classifying PFOA to Group 2B *"possibly carcinogenic to humans"* according to the International Agency for Research on Cancer (IARC). This is equivalent to the fact that this compound is undoubtedly carcinogenic to animals and probably has the same effect on humans. Due to the use of these compounds in many household products (fabric coatings, carpets, food packaging, firefighting foam, floor care products, insecticides, hygiene products and others), human exposure to them is high. PFAS are pfluorosurfactants and have unique properties.

PFAS are both hydrophobic and oleophobic compounds. They have low surface tension, and thermal stability, versatility, strength, resilience and durability. They are persistent, bioaccumulative and toxic and, due to their persistence in the environment can be transported long distances. They are grease and water resistance, heat, chemical and abrasion resistance.



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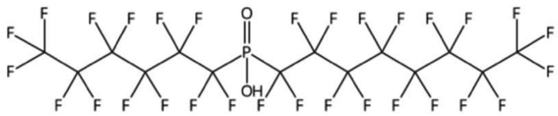

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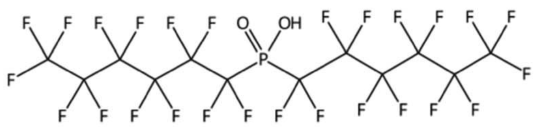
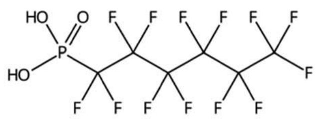


Bis(perfluorohexyl) phosphinic acid (CAS No.40143-77-9)



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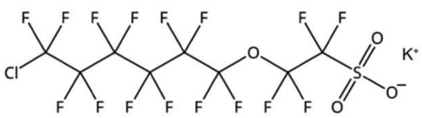
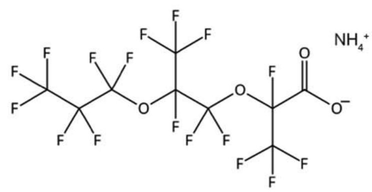
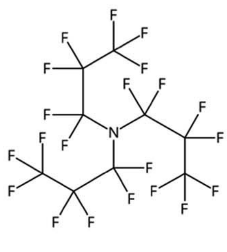


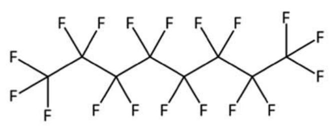
6:2 Cl-PFAES (CAS No. 73606-19-6)



Ammonium perfluoro-2-[(propoxy)propoxy]-1-propanoate (CAS No. 13043-05-5)



Perfluorotripropyl amine (CAS No. 338-83-0)



Perfluorooctane (CAS No. 307-34-6)

Fig. 1. The structure of selected PFAS [2]

3. PERMISSIBLE PFAS CONCENTRATIONS IN DRINKING WATER

The new Directive on the quality of drinking water, expected to enter into force in 2022, proposes an updated list of compounds necessary for water control, which impact on human health is of social or scientific concern. The plans include, among other things, introduction of permissible concentrations of perfluorinated organic compounds. The Position of the European Council No. 14/2020 published in the Official Journal of the European Union C 410/1 of 27/11/2020 concerns the quality of water intended for human consumption and the new list also includes perfluorinated surfactants [8]. Two terms are used in this document: "Total PFAS" and "Sum of PFAS". The explanation of these terms indicates that "Total PFAS" means the total content of all per- and polyfluoroalkyl substances, while "Sum of PFAS" means the sum of per- and polyfluoroalkyl substances that belong to the PFAS but contain a perfluoroalkyl part with at least three carbon atoms -C_nF_{2n}–, where n ≥ 3 or part of a perfluoroalkyl ether with at least two carbon atoms –$C_nF_{2n}OC_mF_{2m}$–, where n and m ≥ 1. This group includes 20 acids such as: perfluorobutanoic (PFBA), perfluoropentane (PFPA), perfluorohexane (PFHxA), perfluoroheptanoic (PFHpA), perfluorooctane (PFOA), perfluorononane (PFNA), perfluorononane (PFNA), perfluorodecane (PFDA), perfluoroundecane (PFUnDA), perfluorododecane (PFDoDA), perfluorotridecan (PFTrDA), perfluorobutanesulfone (PFBS), perfluoropentanesulfone (PFPS), perfluorohexanesulfonic (PFHxS), perfluoroheptanesulfonic (PFHpS), perfluorooctane sulfone (PFOS), perfluoronanesulfonic (PFNS), perfluorodecanesulfone (PFDS), perfluoroundecanesulfone, perfluorododecanesulfone, and perfluorotridecanesulfone. These substances will be monitored when it appears from the risk assessment and risk management in the supply areas that they may be present at the water supply points.

The proposed cut-off point is 500 ng/L for "Total PFAS" and 100 ng/L for "Sum of PFAS". European Union Member States will be able to decide and introduce into their legal regulations the "Total PFAS", the "Sum of PFAS" or both indicators simultaneously. The document also indicates that the method of analysis of per- and polyfluoroalkyl substances referred to as "total PFAS" and "sum of PFAS", including detection limits, parametric values, sampling frequency, will be developed three years after the Directive's entry into force. Global regulatory agencies have developed guidelines or recommendations for acceptable PFAS levels in drinking water. Due to the numerous group and the diverse structure and properties of perfluorinated compounds, the data from toxicological tests are not complete and only a few or over a dozen combinations are mentioned in the regulations. Therefore, acceptable concentrations have been developed for selected groups in most cases. Table 1 shows the established limits for various groups of these compounds. For example, the U.S. Environmental Protection Agency indicates that the total concentration of PFOA and PFOS in drinking water should not exceed 70 ng/L [2], taking into account health risks. In various states of North America, the acceptable concentration is 20 ng/L or 70 ng/L. In Sweden, 11 different PFASs are within the limits of 90 ng/L and water consumption above this level is not recommended.

Table 1. Permissible PFAS concentrations in drinking water in differend countries [μg/L [2, 16]

Country/ies	Unit, ng/ L	Basis for the development of limit value
European Union	– 100 for sum of 20 PFAS (C4–C13 PFSAs and C4–C13 PFCAs) – 500 for 'PFAS Total' – the total of all PFAS	prophylactic aspect
Denmark	-100 for C4–C10 PFCAs (perfluorocarboxylic acids), PFBS, PFHxS, PFOS, PFOSA and 6:2 FTS (6:2 Fluorotelomer sulfonic acid)	12 compounds with similar toxicity to PFOS
Sweden	-90 for C4–C10 PFCAs, PFBS, PFHxS, PFOS and 6:2 FTS	11 compounds similar in toxicity to PFOS
Canada	- 200 for PFOA and - 600 for PFOS	cumulative toxicity of PFOA and PFOS occurring simultaneously
Australia	-70 for PFOS and PFHxS	additive toxicity of PFH_xS and PFOS are similar
USA EPA	-70 for PFOA and PFOS	toxicity
USA	- 20/70 PFHpA, PFOA, PFNA (Perfluorononanoic acid), PFHxS and PFOS	Sum of five PFAS, similar toxicity to PFOS and PFOA

4. DETERMINATION OF PFAS IN AQUEOUS SOLUTIONS

Perfluorinated organic compounds are most often determined in food, food packaging and less often - in waters. Reference literature provides information on the identification of PFAS by liquid chromatography with tandem mass spectometry (LC/MS/MS). The basics of the determination in water can be found in the US EPA 537 [9, 15]. It was developed in 2009 and updated in 2018 and 2020. It concerns the determination of selected per- and polyfluorinated alkyl substances in drinking water by solid phase extraction (SPE) and liquid chromatography/tandem mass spectrometry (LC/MS/MS). However, it should be emphasized that other perfluorinated PFOA/PFOS compounds have also been produced and used since the method was developed, which may cause contamination of water, including drinking water. This procedure is recommended for the quantitative determination of sixteen selected perfluorinated alkyl acids (PFAA) as well as hexafluoropropylene oxide-dimer acid (HFPO-DA) and the ammonium salt of fluorinated ether acid in drinking water, used as GenX [15]. The preparation of the sample enriched with the internal standard is directed to solid-phase extraction (SPE) using polystyrenedivinylbenzene (SDVB). The analytes are eluted with methanol and concentration is carried out under a stream of nitrogen. An injection of 10 µl is placed onto a C18 column of the liquid chromatograph linked to MS/MS. The analytes are separated and identified by comparing the obtained mass spectra and retention times with the standard spectrum identified in the chromatograms at the right retention time.

5. OCCURRENCE OF PFAS IN THE AQUATIC ENVIRONMENT

Perfluorinated organic compounds are identified in the aquatic environment, groundwater, surface waters, including marine waters, rainwater and sewage. The sources of water pollution are leachate from landfills, surface runoff and outflows from municipal and industrial sewage treatment plants. Nonetheless, literature data in this range are not extensive and mainly concern water, sewage and drinking water outside the country. Table 2 presents exemplary information on the scope of these compounds determined in the aforementioned waters. The concentration ranges of perfluorooctanesulfonic acid PFOS and perfluorooctanoic acid PFOA were different. These concentrations did not exceed the values of 44 and 78 ng/L, respectively, in water intended for consumption. Much higher values were noted in surface waters where the PFOS concentration reached 2.709 ng/L, while the PFOA concentration was 4.534 ng/L. However, the highest concentration in sewage, reaching 15,900 ng/L, was noted in the European Union countries. This presents the problem of water pollution resulting from insufficiently treated wastewater. Due to the fact that surface waters can be a source of water for municipal purposes, there is a risk of contamination of drinking water. Additional processes are required to remove PFAS during water treatment and/or wastewater treatment. They include adsorption, membrane separation or chemical or photochemical oxidation [11, 12]. The implementation of third step of wastewater treatment is important not only for elimination of PFAS but also for removal of other persistent micropollutants. Among them hormones, pharmaceutics, retardants, preservatives, personal care products PAHs, pesticides and other organic xenobiotics can be mentioned [3,4,13,18, 20] .

Table 2. Concentration of PFAS in waters in countries [16]. (-) - below

Country	Concentration, ng/L		Country	Concentration, ng/L	
	PFOS	PFOA		PFOS	PFOA
Drinking water					
China	- 11.0	2.6-78.0	Italy	6.2-9.7	1.0-2.9
Japan	- 43.7	- 42.2	Spain	0.4-0.9	0.3-6.3
Surface water					
Austria	4.0-35.0	- 19.0	China	-394.0	- 4,534.0
Australia	7.5-21.0	4.2-6.4	France	-62.0	- 12.0
Brazil	0.4-6.7	0.4-3.3	Germany	-193.0	- 3,640.0
India	-1.8	- 0.2	Japan	- 990.0	- 1,800.0
Italy	-25.0	1-1,270	Swiss	43.0-60.0	7.0-7.6
Spain	-2,709	- 68	USA	-756.0	- 498.0
Wastewater					
Austria	1.0-66.0	2.0-73.0	China	1.0-32.0	2.0-41.0
Germany	-82.2	-78.0	Japan	14.0-635.0	10.0-68.0
Spain	-501.0	-62.0	EU	0.5-2,101	-15,900

6. CONCLUSION

Based on the review, the following conclusions can be drawn:

- The introduction of permissible concentrations of selected organic perfluorine compounds to the new Water Directive will require the adaptation of Polish regulations and the development of an analytical procedure.
- Perfluorinated organic compounds are identified in the aquatic environment in different concentration - it is important not only for water organisms because toxic properties of them but also the surface waters are often source of drinking water for human (after water treatment processes)
- In order to minimize water pollution, it will be necessary to introduce additional processes/modifications applied to water and wastewater treatment installations, and to control the PFAS concentration (and other persistence organic micropollutants) in waters and wastewater disposed to receivers.

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