



PFAS per- and polyfluoroalkyl new compounds in the Drinking Water Directive – screening studies of surface and underground water resources

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ABSTRACT

To ensure an adequate quality and safe water supply, the new Drinking Water Directive 2021/2084-DWD introduced the obligation to carry out a risk assessment throughout the water supply chain to the consumer. In addition, it is mandatory to test water quality from the water supply area to the consumer's tap. Sound management of natural resources to reduce the load of pollutants entering water bodies from urban water treatment plants will be required. New water pollutants have been added to the directive, which should be determined in drinking water. These include per- and polyfluoroalkyl compounds. They are listed in the directive as "Total PFAS" or "Sum of PFAS", and the recommended allowable concentrations in drinking water are 500 and 100 ng/L, respectively. A screening study was carried out to determine the level of contamination of the water source water serving the Jaworzno population by testing both surface water and groundwater. In addition, the concentrations of these compounds were determined in the treated urban wastewater. Several compounds belonging to the perfluoric acid group and several compounds belonging to the sulfonic acid group were quantitatively identified in the water, and treated wastewater was analyzed. The total concentrations determined and the estimated maximum concentrations resulting from the analytical performance of these compounds did not exceed the parametric values indicated in the Drinking Water Directive. Therefore, water abstraction from these sources does not currently pose a consumer risk. Given the numerous sources of pollution, mainly industrial, and the need to ensure risk assessment rules in line with the new Drinking Water Directive, it will be essential to monitor the concentrations of these compounds in water and treated wastewater in the future.

Keywords: Perfluoroalkyl substances; Water supply system; Water resources; Monitoring

1. Introduction

In 2020, the European Commission issued a staff working document on poly- and perfluoroalkyl substances (PFASs) to accompany the 'Chemical Strategy for Sustainable Development Towards a Toxin-Free Environment' [1]. In 2021, perfluorohexanesulfonic acid and its salts (PFHxS)

were added to the REACH candidate list of substances of very high concern as a 'very persistent and very bio-accumulative substance' [2]. It is proposed to align the classification of compounds classified as PFAS with the OECD60 definition and set a limit of 100 ng/L for individual PFAS and 500 ng/L for the PFAS group. The presence of perfluorinated compounds in the environment comes mainly from

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anthropogenic sources. These compounds are widely used in industry as surfactants, repellants, paint additives [3], pesticides, fertilizers [4], transformers and in many other household products [5]. Consequently, human exposure to these compounds is relatively high. This is important for human health, as these compounds can penetrate the body, accumulate in tissues and adversely affect the body's functioning in many ways [6,7]. The presence of these compounds in common household products (fabric coverings, carpets, food packaging, floor care products, insecticides, hygiene products and others) results in their presence in municipal wastewater. However, conventional treatment processes do not adequately remove them, so sewage treatment plant effluents are also a source of poly- and perfluoroalkyl surfactants in surface waters. It is therefore important to develop new or modified known wastewater treatment methods to effectively reduce the release of these pollutants into the environment. As surface water is also a source of drinking water, the presence of PFAS in drinking water sources is a topical and important problem to identify. This problem has been addressed in new legislation such as the Drinking Water Directive 2020/2184 [8].

The group of compounds referred to by the acronym PFAS comprises 4730 synthetic compounds. These are aliphatic hydrocarbons in which fluorine, sulfur, phosphorus or nitrogen is attached in place of the hydrogen atoms in the carbon chain (straight or branched). The PFAS group primarily includes perfluorooctanesulfonic acids (PFOS), perfluorooctanoic acid (PFOA), perfluoroalkyl acid (PFAA), ammonium pentadecafluorooctanoate (APFO), perfluorononanoic acid (PFNA) and its sodium and ammonium salts, nonadecafluorodecanoic acid (PFDA) and its sodium and ammonium salts, and perfluoroheptanoic acid [9,10]. Per and polyfluorinated compounds exhibit both hydrophilic and hydrophobic properties, reduce the surface tension of water and are therefore used as surfactants. The ability of these compounds to accumulate in the body is important for human health. 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 above-ground plant tissues (shoots, leaves and fruit). Therefore, growing plants on soils heavily contaminated with short-chain PFAAs may pose a risk to humans. PFOS and PFOA have been classified as endocrine-disrupting compounds (EDCs). In addition, PFOA has been classified as Group 2B, according to the IARC Cancer Research Agency. This means it is undoubtedly carcinogenic to animals and is likely to have such effects in humans [11].

The new DWD on drinking water quality [8] provides a list of compounds needed to be controlled in water whose effects on human health are of public or scientific concern. A new group of contaminants in water intended for human consumption whose testing is mandatory under the aforementioned directive are anthropogenic compounds and by-products of water treatment processes. These include bisphenol A, chlorates, halogenoacetic acids, microcystin, and per- and polyfluoroalkyl organic compounds PFAS [8]. The new CPD mentions two terms: "Total PFAS" and "Sum of PFAS", which mean, respectively: the total of all per- and polyfluoroalkyl substances and the sum of per- and

polyfluoroalkyl substances that belong to PFAS but contain a perfluoroalkyl moiety with at least three carbon atoms – $C F_{n2n}$ – (where $n \geq 3$) or a perfluoroalkyl ether moiety with at least two carbon atoms – $C F_{n2n} O C F_{m2m}$ – (where n and $m \geq 1$). Concentrations of these compounds will be monitored when it is evident from the risk assessment and risk management in the recharge areas that they may be present at water points. The adopted parametric value for "Total PFAS" is 500 ng/L, and for "Sum of PFAS" is 100 ng/L. Article 13, paragraph 7 of the DWD obliges the European Commission by 12 January 2024 to establish technical guidance on analysis methods for monitoring per- and polyfluoroalkyl substances as "Total PFAS" and "Sum of PFAS", including the setting of detection limits and sampling frequency. In addition, according to Article 25 DWD, Member States should, by 12 January 2026, take the necessary measures to ensure that water intended for human consumption meets the parametric values set out in Annex I, Part B of the directive for "Total PFAS" and "Sum of PFAS". On the other hand, water suppliers will, according to the provisions of the new DWD (Article 25, paragraph 2), be required to monitor PFAS in water from January 2026. This applies where risk assessments in supply areas for water points carried out in accordance with Article 8 indicate that these substances may be present in a given water supply. Guidance on acceptable levels of PFAS in drinking water varies among global regulatory agencies. For example, considering health risks, the US Environmental Protection Agency indicates that the sum concentration of PFOA and PFOS in drinking water should not exceed 70 ng/L. The permissible concentrations in various North American states are 20 or 70 ng/L. In Sweden, 11 different PFASs are included in the 90 ng/L limit; above this level, no water is recommended for consumption [9]. Given the presence of PFAS in natural water supplies, as confirmed by the above studies, and the high health risk to consumers, it is necessary to apply techniques to remove these compounds from water intended for human consumption. As the risk of occurrence of PFAS in natural water resources under the new directive 2020/2184 is not known in Poland.

As work is ongoing to transpose the directive into Polish law, it was considered appropriate to carry out preliminary studies to identify these compounds in exemplary drinking water sources. The study was expected to cover surface and groundwater sources in a heavily industrialized area of southern Poland. Therefore, a site with a mixed supply source (groundwater, surface water) was selected, and, in addition, PFAS concentrations were determined in treated municipal wastewater from this area. The studies in wastewater aimed to identify the potential threat of PFAS contamination of surface water resources, which closely affects groundwater quality in this area.

2. Materials and methods

2.1. Study subject

Jaworzno is a medium-sized city in southern Poland (Fig. 1A), in the eastern part of the Silesian Province (Fig. 1B). Jaworzno is a highly urbanized region of Poland, which in the past was dominated by lead and zinc ore mines and now by coal mining. The leading industries in the area are chemicals, glass, sand mining and energy.

The water supply system (WSS) in Jaworzno consists of a water production subsystem (WPSs – including water intake and treatment) and a water distribution subsystem (WDSs). Water prepared for consumption comes from 5 independent water supply systems (IWSS) operating based on surface water resources as well as groundwater in a comparable proportion (Table 1).

The groundwater resources exploited by WSS in Jaworzno are fracture-karst-pore aquifer complexes. Inter-connection and mixing of waters between aquifers are of sedimentary, tectonic and erosional type. Such geological structure of the aquifer and substantial anthropogenic degradation of the environment increases the risk of contamination of the abstracted waters with micropollutants, including

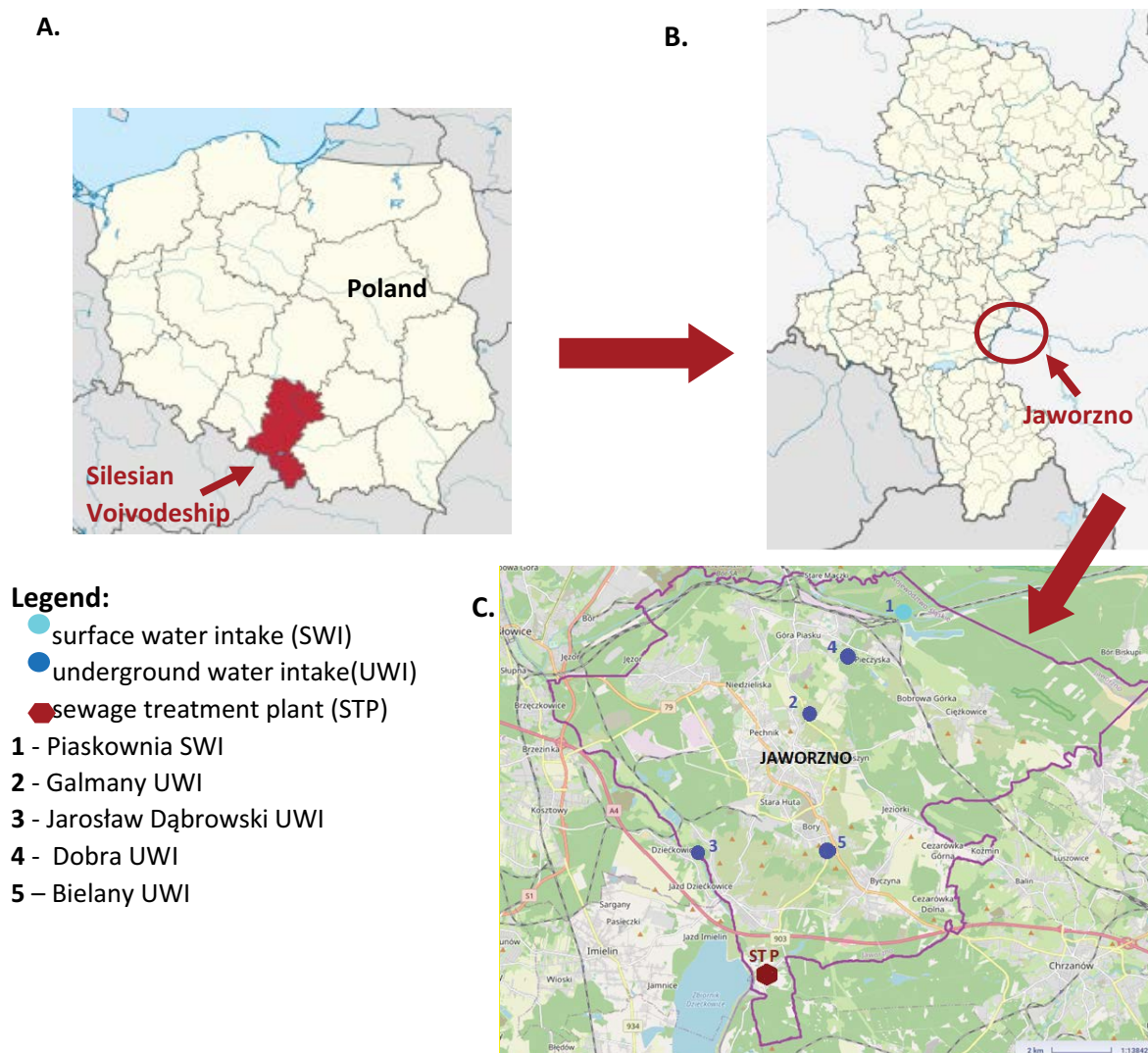


Fig. 1. Water intakes and sewage treatment plant in Jaworzno City.

Table 1
 Characteristics of the water supply system Jaworzno

	Water supply system	Water resources	Type of shot	Daily water production [m ³ /d] (%)
1	Piaskownia	Surface waters	Shoreline intake	7,182 (51.2%)
2	Galmany		3 wells	5,376 (38.4%)
3	Jarosław Dąbrowski	Groundwater – quaternary, Triassic and carboniferous aquifers	Mineshaft	807 (5.8%)
4	Dobra		2 wells	513 (3.7%)
5	Bielany		1 well	132 (0.9%)

perfluorinated compounds (PFAS). The largest Piaskownia IWWS is located in the northeastern part of the city (Fig. 1C, Site 1) and is fed by surface water. This plant meets more than 50% of the city's water demand. The second largest supply system is the Galmany IWWS, located in the north-eastern part of the city (Fig. 1C, facility no. 2), from which almost 39% of the city's water demand is covered (Table 1). The water supply system of IWWS Jarosław Dąbrowski is located in the southwestern part of the town (Fig. 1C, object no. 3). The intake is a mine shaft with a depth of 102.0 m. IWWS Dobra operates the oldest water intake in the city. It is located in the northeastern part of the town (Fig. 1C, object no. 4). The intake consists of two depths of 101.0 and 88.0 m. The Bielany intake is located in the southeastern part of the town (Fig. 1C, object no. 5). The intake consists of one deep well with a depth of 74.0 m. Municipal wastewater from the town is discharged via the general sewer network to the wastewater treatment plant located on the southwestern outskirts of the town (Fig. 1C). The Jaworzno wastewater treatment plant is located on the city's southern outskirts, with the Przemsza River flows from the west, which is the recipient of treated wastewater. The sewage treatment plant is a mechanical-biological treatment plant with enhanced nutrient removal. The daily sewage flow is 16,000 m³/d.

2.2. Study method

The research was conducted in two stages. Stage I was a screening study in the treated wastewater stream and the raw water of selected feed systems. In this study stage, raw water directed to two treatment stations from different feed sources was analyzed. This was the surface water intake SUW Piaskownia, as the largest source of supply for the residents of Jaworzno (51.2%, Table 1). SUW Jarosław Dąbrowski, supplied with groundwater, was selected as the second facility for the study. The choice of this facility was dictated by the facility's foundation in an area heavily exploited industrially, which may impact the quality of the abstracted water. The second stage of the study analyzed PFAS content in waters from the same measurement points, that is, the surface water intake (Piaskownia) and the groundwater intake (Dąbrowski). In addition, these compounds were determined in water from the Galmany intake, the second largest supply source to the Jaworzno water supply system. The total volume of water abstracted from these three intakes exceeds 95% of the city's water demand (Table 1).

2.3. Analytical methods

Twenty perfluorinated organic compounds were analyzed, categorized as 'Total PFAS', listed in Annex III, Part B, point 3 of the Drinking Water Directive 2020/2184 (Table 2).

The acids listed in Table 2 (entries 1–10) are a subset of total PFAS substances, which include compounds containing a perfluoroalkyl moiety with at least three carbon atoms (i.e., C F_{n2n} –, where $n \geq 3$) or a perfluoroalkyl ether moiety with at least two carbon atoms (i.e., C F_{n2n} OC F_{m2m} –, where n and $m \geq 1$). Among the compounds analyzed were also those containing sulfur in the form of a sulfonic group

(Table 2 – compounds No. 11–20) and two fluorotelomers sulfonic acid (Table 2: No. 21–22) and perfluorooctanesulfonamide (Table 2: No. 23). The two compounds 6:2 fluorotelomer sulfonic acid and 8:2 fluorotelomer sulfonic acid are considered as precursors of PFAS [12]. The stages of the study differed in the methodology of sample preparation for analysis, including the detection limit of the analytes (Table 2). In the first step, sample preparation was performed according to methodology 537 EPA/600/R-08/092 solid phase extraction method. According to DIN 38407-42, the second step is the determination of selected polyfluorinated compounds (PFCs) in water. The quantitative and qualitative perfluorinated compounds were determined using a liquid chromatograph kit with a quadrupole LC/MS/MS mass detector. In the first stage of the study, the limit of quantification was at the level of 10 ng/L, while in the second stage, it varied for individual compounds and took values in the range of 0.2 to 1 ng/L.

3. Results

3.1. PFAS in surface water and in treated wastewater

Concentrations of the identified compounds in surface water and treated wastewater are shown in Table 3.

PFAS concentrations in surface water obtained in the first stage of the study were below the limit of quantification, set at 10 ng/L. Thus, the total concentration of the nine identified fluorine-containing acids did not exceed 90 ng/L. The presence of eight compounds containing a sulphonic group (–SO₃H) in the structure was identified. At the high limit of quantification, no concentration value was determined for any of the detected compounds. Considering the maximum values, the total concentration of the identified compounds would not exceed 170 ng/L. The analysis performed at the lower limit of quantification allowed quantification of the concentrations of several compounds. The highest concentration of perfluorobutanoic acid was 0.95 ng/L. Of the sulphonic compounds, only perfluorohexanesulfonic acid was quantified at a 0.69 ng/L concentration. Considering the determined concentrations and the probable concentrations below the quantification limit, the analyzed compounds' total content would not exceed 9.34 ng/L.

Available literature reports show high variability in the concentrations of these compounds in surface water supplies, especially in different geographical regions as well as various forms of interpretation. Concentrations are often reported as the sum of PFOA acids and the sum of PFOS sulphonic compounds. The most commonly analyzed compounds are perfluorooctanoic acid and the form containing a sulphonic group with the same carbon chain length perfluorooctanesulfonic acid [13,14]. For example, in surface waters from European sites, PFOA concentrations were lowest in Switzerland (7.0–7.6 ng/L) not exceeding 12 ng/L in waters from France, and 19 ng/L in Austria. In waters from Italy and Germany, the determined PFOA concentrations were much higher, reaching 1,270 and 3,640 ng/L values, respectively. Published data on PFOA concentrations in surface waters from Australia did not exceed 6.4 ng/L, Japan 43.7 ng/L and China reached 4,534 ng/L. concentrations of sulphonic compounds, defined as PFOS, were also variable

Table 2
Characteristic of perfluoroalkyl compounds

	Compounds	Abbreviation	Chemical formula	Limit of detection	
				Step 1 ng/L	Step 2 ng/L
1	Perfluorobutanoic acid	PFBA	$C_3F_7CO_2H$	10	0.3
2	Perfluoropentanoic acid	PFPA	$CF_3(CF_2)_3COOH$	10	0.3
3	Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	10	0.3
4	Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	10	0.3
5	Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	10	0.3
6	Perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	10	0.3
7	Perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	10	0.3
8	Perfluoroundecanoic acid	PFUnDA	$C_{11}HF_{21}O_2$	10	0.3
9	Perfluorododecanoic acid	PFDoDA	$C_{12}HF_{23}O_2$	10	0.3
10	Perfluorotridecanoic acid	PFTTrDA	$C_{13}HF_{25}O_2$	–	1
11	Perfluorobutanesulfonic acid	PFBS	$C_4HF_9O_3S$	10	0.3
12	Perfluoropentanesulfonic acid	PFPS	$C_5HF_{11}O_3S$		0.3
13	Perfluorohexanesulfonic acid	PFHxS	$C_6HF_{13}O_3S$	10	0.3
14	Perfluoroheptanesulfonic acid	PFHpS	$C_7HF_{15}O_3S$	10	0.3
15	Perfluorooctanesulfonic acid	PFOS	$C_8HF_{17}O_3S$	10	0.2
16	Perfluorononanesulfonic acid	PFNS	$C_9HF_{19}O_3S$	–	0.3
17	Perfluorodecanesulfonic acid	PFDS	$C_{10}HF_{21}O_3S$	10	0.3
18	Perfluoroundecanesulfonic acid		$C_{11}HF_{23}O_3S$	–	1
19	Perfluorododecanesulfonic acid		$C_{12}HF_{25}O_3S$	–	1
20	Perfluorotridecanesulfonic acid		$C_{13}HF_{27}O_3S$	–	1
21	6:2 Fluorotelomer sulfonic acid	6:2 FTS	$C_8H_5F_{13}O_3S$		
22	8:2 Fluorotelomer sulfonic acid	8:2 FTS	$C_{10}H_5F_{17}O_3S$		
23	Perfluorooctanesulfonamide	FOSA	$C_8H_2F_{17}NO_2S$		
	Total PFAS				0.2

in surface waters from European countries, with values ranging from 4 ng/L (Austria) – 2,709 ng/L (Spain). Intermediate values were determined in the waters of Italy (25 ng/L), France (62 ng/L), and Germany (193 ng/L). Comparing the results obtained with data published in the literature, it can be concluded that the determined concentrations are within the range determined in other waters. Still, the hypothetical maximum concentrations not exceeding the limit of quantification are at a low level. Quoting from Xu et al. [15], Table 4 shows examples of concentrations of selected perfluorinated compounds in surface waters in selected region of China and India. PFAS monitoring in China was conducted in eight rural areas of eastern China while in India, samples for analysis were taken from the Ganges River.

A similar relationship applies to treated wastewater, where the estimated maximum total concentration determined in the study would not exceed 172.3 ng/L. Compared to concentrations in surface water, concentrations may be higher, especially of sulfonic compounds, as two of the compounds selected for analysis were quantified: perfluorohexanesulfonic acid and perfluorooctanesulfonic acid. Concentrations of perfluorinated compounds in wastewater reported in the literature were also determined over a wide range. In EU countries, PFOS concentrations in raw wastewater reached 2,101 ng/L and PFOA concentrations reached

15,900 ng/L [13,14]. According to other data, concentrations of these compounds have been reported to reach values of several hundred ng/L or several thousand ng/g dry weight in raw sewage and sludge, respectively. It should be emphasized that perfluorinated compounds are not significantly removed during conventional biological treatment processes and their concentrations in treated effluent may be higher compared to raw sewage. The specifics of the wastewater treatment system, the varying size of the settlement unit, the type and proportion of industrial wastewater and the hydrological conditions hampers the comparison. The published evidence indicates little or no biodegradation of perfluorinated compounds during wastewater treatment. The decrease in the concentration of these compounds during biological wastewater treatment is attributed to sorption onto suspended particles. This process is considered to be the main one in removing these compounds from wastewater in municipal treatment plants [16]. Based on the literature reports and the results of the studies described in this article, it can be concluded that significant amounts of perfluorinated organic compounds can be introduced into surface waters with treated wastewater. Wastewater containing PFAS is not sufficiently treated by conventional processes used in municipal treatment plants. Given the potential for water contamination resulting from inadequately

Table 3
PFAS concentration in surface water (Piaskownia) and in treated wastewater

Perfluoroalkyl compounds		Concentration of perfluoroalkyl compounds, ng/L		
		Surface water Piaskownia		Treated wastewater
		1 step	2 step	1 step
1	Perfluorobutanoic acid	<10	0.95	<10
2	Perfluoropentanoic acid	<10	<0.3	<10
3	Perfluorohexanoic acid	<10	<0.3	<10
4	Perfluoroheptanoic acid	<10	<0.3	<10
5	Perfluorooctanoic acid	<10	0.60	<10
6	Perfluorononanoic acid	<10	<0.3	<10
7	Perfluorodecanoic acid	<10	<0.3	<10
8	Perfluoroundecanoic acid	<10	<0.3	<10
9	Perfluorododecanoic acid	<10	<0.3	<10
10	Perfluorotridecanoic acid	n.d.	<1.0	n.d.
11	Perfluorobutanesulfonic acid	<10	<0.3	<10
12	Perfluoropentanesulfonic acid	n.d.	<0.3	<10
13	Perfluorohexanesulfonic acid	<10	0.69	11.0
14	Perfluoroheptanesulfonic acid	n.d.	<0.3	n.d.
15	Perfluorooctanesulfonic acid	<10	<0.3	11.3
16	Perfluorononanesulfonic acid	n.d.	<0.3	n.d.
17	Perfluorodecanesulfonic acid	<10	<0.3	<10
18	Perfluoroundecanesulfonic acid	n.d.	<0.3	n.d.
19	Perfluorododecanesulfonic acid	<10	<1.0	<10
20	Perfluorotridecanesulfonic acid	n.d.	<1.0	n.d.
21	6:2 Fluorotelomer sulfonic acid	<10	n.d.	<10
22	8:2 Fluorotelomer sulfonic acid	<10	n.d.	<10
23	Perfluorooctanesulfonamide	<10	n.d.	<10
	Total PFAS	<170*	<9.34*	<172.3*

n.d. – no detected;

* – maximum estimated value assuming the maximum concentration.

treated wastewater and the fact that surface water may be a water source for municipal purposes, there is a risk of perfluorinated compounds in drinking water [15].

3.2. PFAS in groundwater

In Table 5 concentration of the determined compounds in groundwater are presented.

Concentrations of more perfluorinated compounds were quantified in groundwater collected from the selected intakes than in surface water. The concentrations of identified compounds were also higher. Perfluorooctanoic Acid was present in the highest concentration (26 ng/L) in water from the Galmany intake. This is important because this intake covers 38.4% of the water demand in the city of Jaworzno. (Table 1). In water from this intake, concentrations of four compounds that contain 4 to 7 carbon atoms in the chain (perfluorobutanoic, perfluoropentanoic, perfluorohexanoic, perfluoroheptanoic acids) were in the range of 1.6 to 1.8 ng/L. Of the sulphonic compounds, (perfluorohexane sulphonic acid and perfluorooctane sulphonic acid) were quantified as in surface water and wastewater. The concentrations of these

compounds (0.69–0.71 ng/L) were comparable to those in surface water. The occurrence of perfluorinated compounds in groundwater is most likely due to the exposure of this heavily mined area to the infiltration of anthropogenic contaminants into the aquifer due to structural disturbance. As a result of underground mining activities in this region, the hydrogeological regime of the Triassic formations has been altered. In fault zones, the effects of mining drainage are felt here at the contact with the carboniferous. Forced drainage has resulted in the unblocking of faults and micro-faulting. In contrast, surface mining has contributed to the formation of absorptive basins that strengthen the recharge of the Triassic aquifer. Hence, the groundwater resources of the Galmany intake are highly exposed to anthropogenic pollution. In the waters of the Jarosław Dąbrowski intake, two compounds belonging to the subset of total PFAS substances, which contain a perfluoroalkyl part with 4 and 8 carbon atoms, respectively, were identified (perfluorobutanoic acid 1.4 ng/L, perfluorooctanoic acid 0.57 ng/L). However, among the sulphonic compounds, perfluorohexanesulphonic acid (0.69 ng/L) and perfluorooctanesulphonic acid (0.71 ng/L) were quantified in the waters of this

Table 4
Concentration of selected perfluoroalkyl compounds in surface water in different countries

Compounds	Concentration, ng/L		Compounds	Concentration, ng/L	
	China	India		China	India
PFOA	0–224	0.1–1.2	PFOS	0–22	0–1.8
PFBA	0–99	<LOD	PFBS	0–15	0–0.03
PFNA	0–4.6	0–0.2	PFHxS	0–42	0–10.2
PFOA/Total PFAS ratio	0.14–0.56	0.11	PFOA/PFOS ratio	3.84–8.78	0.93

Table 5
PFAS concentration in groundwater

	Perfluoroalkyl compounds	Concentration of perfluoroalkyl compounds, ng/L		
		Jaroslaw Dąbrowski		Galmany
		1 step	2 step	2
1	Perfluorobutanoic acid	<10	1.4	1.7
2	Perfluoropentanoic acid	<10	<0.3	1.6
3	Perfluorohexanoic acid	<10	<0.3	1.8
4	Perfluoroheptanoic acid	<10	<0.3	1.8
5	Perfluorooctanoic acid	<10	0.57	26.0
6	Perfluorononanoic acid	<10	<0.3	<0.3
7	Perfluorodecanoic acid	<10	<0.3	<0.3
8	Perfluoroundecanoic acid	<10	<0.3	<0.3
9	Perfluorododecanoic acid	<10	<0.3	<0.3
10	Perfluorotridecanoic acid	n.d.	<1.0	n.d.
11	Perfluorobutanesulfonic acid	<10	0.61	0.52
12	Perfluoropentanesulfonic acid	n.d.	<0.3	<0.3
13	Perfluorohexanesulfonic acid	<10	0.69	<0.3
14	Perfluoroheptanesulfonic acid	n.d.	<0.3	<0.3
15	Perfluorooctanesulfonic acid	<10	0.71	0.32
16	Perfluorononanesulfonic acid	n.d.	<0.3	<0.3
17	Perfluorodecanesulfonic acid	<10	<0.3	<0.3
18	Perfluoroundecanesulfonic acid	n.d.	<1.0	<0.3
19	Perfluorododecanesulfonic acid	<10	<1.0	<1.0
20	Perfluorotridecanesulfonic acid	n.d.	<1.0	<1.0
21	6:2 Fluorotelomer sulfonic acid	<10	n.d.	n.d.
22	8:2 Fluorotelomer sulfonic acid	<10	n.d.	n.d.
23	Perfluorooctanesulfonamide	<10	n.d.	n.d.
	Total PFAS	<170*	<10.3*	<34.0*

n.d. – no detected;

* – the maximum estimated value assuming the maximum concentration.

intake. The study showed that in the surface water intake, total PFAS levels were more than 3.5 times lower than in the groundwater of the Galmany intake. Quoting from Xu et al. [15] Table 6 shows examples of concentrations of selected perfluorinated compounds in groundwater in China, India and Australia (water taken from a landfill-impacted area). Other data indicate that PFOA, perfluorobutanoic acid, PFOS and perfluorobutanesulfonic acid were present in groundwater from an area influenced by the fluorochemical industry in China at concentrations as high as 21,200 ng/L.

A study by McMahon et al. to assess the prevalence of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in groundwater used as a source of drinking water in the eastern United States confirmed the presence of 14 PFAS compounds out of 24 analyzed. Water from 60% of public supply wells was found to contain at least one compound from perfluorinated compounds. Waters collected from domestic supply wells were contaminated with PFAS to a lesser extent, as these compounds were detected in 20% of the sites studied. Based on the relationships between 57 variable selected

Table 6
Concentration of selected perfluoroalkyl compounds in groundwater in different countries

Compounds	Concentration, ng/L			Compounds	Concentration, ng/L		
	China	India	Australia		China	India	Australia
PFOA	7–175	0–0.08	1.7–74	PFOS	<37	0–1.2	1.3–4,800
PFBA	<59	0–9.2	<2.2	PFBS	<1.5	0–0.1	2.6–280
PFNA	<22	0–0.2	<49	PFHxS	<7.4	0–4.9	2.0–31.0
PFOA/Total PFAS ratio	0.3–0.6	0.3	0.06	PFOA/PFOS ratio	4.71–4.73	2.88	0.08

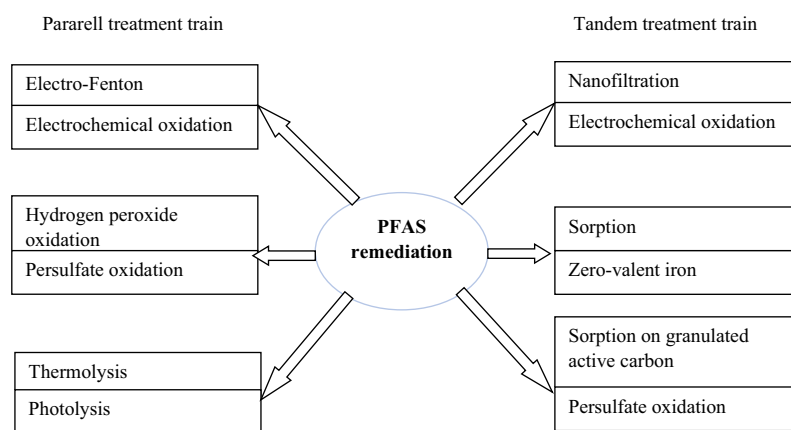


Fig. 2. Parallel and Tandem treatment methods dedicate for PFAS remediation [based on Lu et al. 21].

water quality indicators and environmental conditions, the most important predictors of PFAS in groundwater were found to be tritium concentration, distance to fire training areas, land use and concentrations of other organic compounds (including volatile compounds as VOCs). Therefore, it was concluded that hydrological, geochemical and land use conditions are the main factors for the occurrence of PFAS in groundwater [17]. A screening study of PFAS concentrations in groundwater of the intake of the water supply system of Jaworzno also confirmed this conclusion. Additional processes will be required to remove per- and polyfluorinated compounds from water intended for human consumption. These include remediation and PFAS degradation processes as well as integrated processes. Remediation processes include sorption [18], membrane separation and ion exchange, while processes providing PFAS degradation include chemical, photochemical, or photocatalytic or electrochemical oxidation, thermolysis or a sonochemical process. Fig. 2 shows schematically the unit processes, which can be used in parallel or as integrated systems [19–21]. Taking into account the economic and environmental considerations enabling in situ remediation, a system consisting of nanofiltration, electrochemical anodic oxidation and electro-Fenton degradation is proposed [19].

4. Conclusion and perspectives

Based on preliminary screening studies involving the determination of perfluorinated organic compounds in waters from selected water intakes and treated wastewater, it can be concluded that

- For the quantification of PFAS in water, it is essential to use a technique with as low a limit of quantification as possible,
- concentrations of perfluorinated compounds in surface water did not exceed 10 ng/L (IWWS Piaskownia) and groundwater 34 ng/L (IWWS Galmany) and were lower than in other regions of the world,
- Based on the limit of quantification, the maximum concentrations of perfluorinated compounds in treated effluent did not exceed 173 ng/L, so their discharge into surface water may pose a risk of water pollution,
- Given the confirmed and potential toxic effects on humans, monitoring the concentrations of perfluorinated compounds in municipal water supply sources is necessary.

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References

- [1] Commission Staff Working Document Poly- and Perfluoroalkyl Substances (PFAS). Available at: <https://op.europa.eu/en/publication-detail/-/publication/2614f1f2-0f02-11eb-bc07-01aa75ed71a1/language-en>
- [2] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 on the Registration, Evaluation, Authorization and Restriction of Chemicals

- (REACH) and Establishing a European Chemicals Agency, Amending Directive 1999/45/EC and Repealing Council Regulation (EEC) No. 793/93 and Commission Regulation (EC) No. 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.
- [3] E. Kissa, *Pfluorinated Surfactants and Repellents*, Marcel Dekker, New York, 2005.
- [4] A. Staszowska, *Sources and Levels of Perfluorinated Compounds in the Indoor Environment*, Environmental Engineering Committee Monograph, Vol. 100, Part II, M. Dudzińska, A. Pawłowski, Ed., Lublin, 2012 (in Polish).
- [5] J.P. Giesy, K. Kannan, Perfluorochemical surfactants in the environment, *Environ. Sci. Technol.*, 36 (2002) 146–152.
- [6] N. Kudo, M. Katakura, Y. Sato, Y. Kawashima, Sex hormone-regulated renal transport of perfluorooctanoic acid, *Chem. Biol. Interact.*, 139 (2002) 301–316.
- [7] C.J. Weschler, W.W. Nazaroff, Semivolatile organic compounds in indoor environments, *Atmos. Environ.*, 42 (2008) 9018–9040.
- [8] Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the Quality of Water Intended for Human Consumption (Recast), OJ L 435, 23.12.2020, pp. 1–62
- [9] I.T. Cousins, J.C. DeWitt, J. Glüge, G. Goldenman, D. Herzke, R. Lohmann, M. Miller, C.A. Ng, M. Scheringer, L. Vierke, Z. Wang, Strategies for grouping per- and polyfluoroalkyl substances (PFAS) to protect human and environmental health, *Environ. Sci. Processes Impacts*, 22 (2020) 1444–1460.
- [10] <https://echa.europa.eu/pl/hot-topics/perfluoroalkyl-chemicals-pfas>
- [11] <https://monographs.iarc.who.int/wp-content/uploads/2018/06/mono110-01.pdf>, IARC Monograph, 110.
- [12] R. Mao, Y. Lu, M. Zhang, C. Wang, B. Sun, Y. Shi, S. Song, P. Wang, J. Yuan, J. Zhao, Distribution of legacy and novel per- and polyfluoroalkyl substances in surface and groundwater affected by irrigation in an arid region, *Sci. Total Environ.*, 858 (2023) 159693, doi: 10.1016/j.scitotenv.2022.159693.
- [13] B.K. Pramanik, Occurrence of perfluoroalkyl and polyfluoroalkyl substances in the water environment and their removal in a water treatment process, *J. Water Reuse Desal.*, 5 (2015) 196–210.
- [14] M. Włodarczyk-Makula, PFAS - perfluorinated organic compounds in view of the new water directive, *Civ. Environ. Eng. Rep.*, 32 (2022) 191–200.
- [15] B. Xu, S. Liu, J.L. Zhou, C. Zheng, B. Chen, T. Zhang, W. Qiu, PFAS and their substitutes in groundwater: occurrence, transformation and remediation, *J. Hazard. Mater.*, 412 (2021) 125159, doi: 10.1016/j.jhazmat.2021.125159.
- [16] O.S. Arvaniti, A.S. Stasinakis, Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment, *Sci. Total Environ.*, 524–525 (2015) 81–92.
- [17] P.B. McMahon, A.K. Tokranov, L.M. Bexfield, B.D. Lindsey, T.D. Johnson, M.A. Lombard, E. Watson, Perfluoroalkyl and polyfluoroalkyl substances in groundwater used as a source of drinking water in the Eastern United States, *Environ. Sci. Technol.*, 56 (2022) 2279–2288.
- [18] Z. Du, S. Deng, Y. Bei, Q. Huang, B. Wang, J. Huang, G. Yu, Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—a review, *J. Hazard. Mater.*, 274 (2014) 443–454.
- [19] T.P. Knepper, F.T. Lange, Ed., *Polyfluorinated Chemicals and Transformation Products*, The Handbook of Environmental Chemistry, Springer, 2012.
- [20] S. Książek, M. Kida, P. Koszelnik, Occurrence of perfluorinated organic compounds in the environment and physicochemical methods of removing them from aqueous solutions, *J. Civ. Eng.*, 62 (2015) 221–238.
- [21] D. Lu, S. Sha, J. Luo, Z. Huang, X.Z. Jackie, Treatment train approaches for the remediation of per- and polyfluoroalkyl substances (PFAS): a critical review, *J. Hazard. Mater.*, 386 (2020) 121963, doi: 10.1016/j.jhazmat.2019.121963.