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Synthetic micropollutants in the water supply infrastructure of the City of Krakow, Poland

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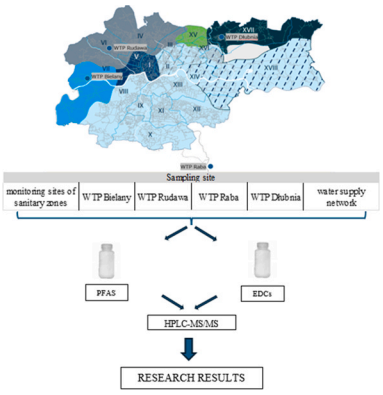
GRAPHICAL ABSTRACT



Abbreviations: PFAS, synthetic per- and polyfluoroalkyl substances; PFBA, perfluorobutanoic acid; PFPA, perfluoropentanoic acid; PFHxA, perfluorohexanoic acid; PFHpA, perfluoroheptanoic acid; PFOA, perfluorooctanoic acid; PFNA, perfluorononanoic acid; PFDA, perfluorodecanoic acid; PFUnDA, perfluoroundecanoic acid; PFDoDA, perfluorododecanoic acid; PFTrDA, perfluorotridecanoic acid; PFBS, perfluorobutanesulfonic acid; PFPS, perfluoropentanesulfonic acid; PFHxS, perfluorohexanesulfonic acid; PFHpS, perfluoroheptanesulfonic acid; PFOS, perfluorooctane sulfonic acid; PFNS, perfluorodecanonanesulfonic acid; PFDS, perfluorodecane sulfonic acid; PFUnDS, perfluoroundecanesulfonic acid; PFDoDS, perfluorododecane sulfonic acid; PFTrDS, perfluorotridecane sulfonic acid; EDCs, endocrine active compounds; HAA, haloacetic acids; THM, trihalomethanes; MRL, maximum residue limit; EU, European Union; WHO, World Health Organization; BPA, Bisphenol A; KCW, Krakow City Waterworks; WTP, water treatment plants; WWTP, wastewater treatment plants; LC-MS, liquid chromatograph-mass spectrometry; UHPLC, ultra-high performance liquid chromatograph; SPE, solid-phase extraction; MS, mass spectrometry; EPA, Environmental Protection Agency; pH, potential of Hydrogen; HD, high definition; LOQ, limit of quantification; TFA, trifluoroacetic acid; TFSA, trifluoromethanesulfonic acid; 4NP, 4 Nonylophenol; BPE, 1,1-Bis4-hydroxyphenylethane; BPS, 4,4′-Sulfonyldiphenol; DBPs, disinfection by-products; HAN, haloacetonitrile; HK, haloketones; CH, chloral hydrate; HNM, halonitromethanes.

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ABSTRACT

The paper analyzes both raw and drinking water for the presence of synthetic per- and polyfluoroalkyl substances (PFAS), endocrine active compounds (EDC), i.e. 17ß-estradiol, bisphenol A and 4-nonylphenol. A series of tests for the presence of PFAS, EDC, were performed at four water treatment plants in Krakow. The total concentration of all fluoroalkyl compounds was below the parametric value of 0.1 μg/l. There was also no positive response for endocrine disrupting compounds (EDC). Samples from water intake basins were analyzed for the presence of selected PFAS and EDC. The tests will be continued at three-month intervals to capture any changes in water parameters as well as a possible risk of higher concentrations occurring during hydrological drought. The results obtained for all samples did not show exceedances of concentration in accordance with the Water Directive of 2020 for PFAS and EDC. It should be remembered that the compounds such as PFAS and EDC, despite of their low concentrations, may pose a threat to human health and life, and therefore testing for micropollutants has not only an environmental, but also a health and socio-economic aspect.

1. Introduction

A dynamic civilizational development, including population growth, intensive exploitation and degradation of the environment and extreme weather phenomena (climate change) hinder access to clean drinking water. In addition, the development of industry, pharmacology and animal breeding increase a risk of pollution of rivers and water reservoirs, that serve as a source of drinking water, as well as worsen the quality of wastewater discharged to wastewater treatment plants. Progressive urbanization accompanied by people's awareness and their higher expectations with respect to a life quality and our common good, i.e. water [1], impose new requirements on water and wastewater companies.

In accordance with the new Directive of the European Parliament and of the Council (EU) 2020/2184 of 16 December 2020 on the quality of water intended for human consumption (OJ EU L 435 of 23 December 2020) [2,3], the obligation of entities supplying water is, among others, to improve the health safety of water and ensure its appropriate quality. Higher parametric requirements, in relation to the assumptions of Council Directive 98/83/EC of 3 November 1998 [4], come from a recent state of knowledge and scientific and technological achievements, including new more accurate methods and the need to add in previously abandoned pollutants.

The assumptions of the new EU law also include modification of water quality monitoring and control of a compliance with quality requirements [5]. Water quality standards and limits for many of the listed pollutants were also established by organizations such as the World Health Organization (WHO) and national and regional environmental protection agencies. In Poland, the applicable implementing act is the Regulation of the Minister of Health of December 7, 2017 on the quality of water intended for human consumption (Journal of Laws 2017, item 2294) [6].

Micropollutants, i.e. substances that even at small quantities can upset ecosystem and harm the environment have become a new challenge for water treatment processes. From the perspective of protection of public health and resources, a reduction of micropollutant emissions into the environment has become a serious problem.

Endocrine disrupting compounds (EDCs) such as hormones and pharmaceuticals can affect human and animal endocrine systems. Micropollutants in closed-loop systems pose a technological challenge and therefore understanding of their cycle within urban water infrastructure is essential for developing effective methods of their elimination. This matter is particularly important since the present water infrastructure, in most cities worldwide, does not include processes that effectively remove these pollutants. Standard water treatment methods such as conventional filtration, coagulation and sedimentation may not be effective. Therefore, water and wastewater utilities should modernize their water and wastewater infrastructure with both commercially used processes (e.g. adsorption on activated carbon, ion exchange, ozonation) and innovative research methods (e.g. advanced oxidation processes - AOPs, reduction processes, membrane filtration or thermal degradation). On the other hand, if such technology has already been employed (mostly in larger urban agglomerations), there would be a need to introduce continuous monitoring procedures – " from intake to tap" - as mandated by the new EU law [7]. It is worth noting that many countries have not yet adopted new regulations on the permissible concentrations of micropollutants in both drinking water and treated wastewater. In summary, studies on micropollutants in water infrastructure pose an innovative analytical challenge (complex procedures, operation of the specialized equipment, reliability and reproducibility of results, meeting international standards) but also introduce a fresh approach to water treatment technology. Therefore, the proposed research topic can be placed among the most important issues and challenges of modern environmental management, related to water quality.

A novelty in the conducted research, apart from the use of new, verified analytical procedures, is also the performance of the first, comprehensive study of all water sources for an agglomeration of over a million people, in terms of the occurrence of selected micropollutants originating from human activity.

1.1. Origin and types of micropollutants in drinking water

The new Directive's watchlist includes endocrine disruptors, pharmaceuticals and microplastics. These substances of various origin are present in tap water at very low concentrations and can be harmful to both human health and the environment.

Micropollutants include many compounds, both hydrophobic and hydrophilic [8]. Typical micropollutants found in tap water include pharmaceuticals, endocrine disrupting compounds, personal hygiene products, pesticides, heavy metals, microplastics, per- and polyfluoroalkyl substances, aromatic hydrocarbons, organic halogenated compounds, and water treatment by-products [9,10]. Micropollutants can enter drinking water from various sources, both anthropogenic (caused by human activity) and natural. Anthropological sources include industrial or municipal wastewater, including households sewage, carrying various chemicals, such as pharmaceuticals, personal hygiene products, detergents, and cleaning agents. These compounds may also migrate from agriculture and landfills [10]. Endocrine disrupting compounds and pharmaceuticals enter water along with domestic and hospital sewage. These include antibiotics, painkillers, hormones, antidepressants, as well as bisphenol A, used in production of plastics and resins, and nonylphenol from chemical, paper, and clothing industries. Per- and polyfluoroalkyl substances (PFAS), i.e. synthetic chemicals, are used in many industrial and consumer products, such as food packaging, waterproof clothing, and fire extinguishing agents. Particular attention is paid to so-called PFAS precursors, i.e. compounds that are not persistent PFAS themselves but can be transformed into such end products e.g. perfluorooctanoic acid (PFOA) or perfluorooctane sulfonic acid (PFOS) [11]. Often PFAS precursors are difficult to determine by conventional methods and therefore their presence is

underestimated in the overall environmental impact caused by PFAS. Their presence in surface water, groundwater and drinking water poses a serious challenge since they can evolve to more persistent forms in the environment and during water treatment processes.

By-products of water treatment with chlorine compounds include trihalomethanes (THM), haloacetic acids, bromates, and chlorites and chlorates; all of them are mutagenic and may cause cancer.

Metals in drinking water cause a serious health risk. They can originate from various sources, like environmental factors related to a geological structure of the Krakow agglomeration, as well as typical human factors, e.g. a discharge of sewage to rivers upstream of water intakes [10]. They all can penetrate to surface and groundwater, if not fully removed at wastewater treatment plants [12]. It is therefore critical to monitor water quality and use proper treatment technologies to minimize the risk associated with micropollutants in drinking water. The chemical, pharmaceutical, textile and metallurgical industries discharge various micropollutants, such as: heavy metals, organic solvents, chemical substances, including BPA or 4-nonylphenol or by-products of production processes [13]. BPA production has been constantly growing since the 1950s; in 2008 it was 5.2 million tons, in 2016 it was already 8 million tons, while in 2022 the global production was 10.6 million tons [14]. Also poorly protected waste landfills can release micropollutants e.g. heavy metals and organic compounds into groundwater, due to their leakage and leaching [15]. Old, corroded pipes and leaking fuel tanks may become a source of pollution of drinking water. Additionally, micropollutants may also appear as a result of natural processes, such as: soil and rocks erosion, volcanic eruptions and geothermal emissions [16]. During such activities heavy metals, radionuclides and a number of other substances are released to both surface and groundwater [17].

1.2. Effects on humans

Micropollutants in water may pose danger for human health. Some pharmaceuticals, hormones, and other endocrine disrupting substances, such as EDCs, as mentioned above, affect a human endocrine system. This can lead to developmental disorders, fertility problems, and other health problems. PFAS disrupt the immune and endocrine systems, leading to a higher risk of cancer and metabolic problems [18]. Haloacetic acids (HAA) are potential carcinogens. They are formed during water disinfection, where residual chlorine reacts with organic compounds and disinfection by-products appear. Also some components of personal care products, e.g. triclosan, may be carcinogenic and toxic to humans, if present in drinking water [19]. Pesticides may have neurotoxic effects, i.e. be harmful to a nervous system, especially in case of children who are more susceptible to their effects [20]. Heavy metals, such as lead and mercury, may damage kidneys, liver, and brain; a chronic exposure to these metals is associated with numerous long-lasting diseases [21]. Microplastics carry various toxic substances that, if ingested, may affect the digestive system and are generally harmful to humans [22].

1.3. Micropollutants in Poland

In Poland, micropollutants in water require integrated actions, including monitoring their quality to identify and track their levels in water as well as advanced treatment of water and wastewater. A modern approach to the problem involves raising a public awareness and endorsing responsible ways of handling and disposal of pharmaceuticals and chemicals. In general, micropollutants in water are becoming more and more obvious and pose a challenge to environmental protection and public health. Studies across the country have exposed the presence of various micropollutants, such as pharmaceuticals, pesticides, personal hygiene products, heavy metals and per- and polyfluoroalkyl substances (PFAS) both in surface and groundwater [23].

2. Scope

The presence of micropollutants in Krakow's water has been the subject of research and monitoring. Krakow, as a large city with an established industrial infrastructure and a continuously growing number of inhabitants, faces numerous challenges related to providing a good water quality. Studies have disclosed pharmaceuticals e.g. antibiotics, painkillers and hormones in Krakow's surface waters; their presence results from their poor removal at traditional wastewater treatment plants located ahead of the water intakes [24,25]. Pesticides may pose another problem for a water supply infrastructure as they penetrate into surface and groundwater through surface runoff and soil infiltration. Farming activity close to Krakow may trigger the presence of insecticides, herbicides and other plant protection products in water and therefore they should be monitored. Also, mining industry in the upper Vistula river basins [26,27] is the main source of heavy metals, such as lead, cadmium and mercury, which contaminate waters in Krakow. Additionally, different sectors of industry and municipal services in Krakow as well as atmospheric pollution resulting from these activities contribute to the presence of heavy metals in surface and ground water.

In the research, the authors determined micropollutants in raw water and at the water intakes and then follow their possible residues in a drinking water. The scope of the research included analysis of the following groups of substances and their selected representatives: synthetic per and polyfluoroalkyl substances (PFAS) - all twenty listed in Directive 2020/2184; endocrine-active compounds (EDCs), i.e. 17ß-estradiol, bisphenol A, 4-nonylphenol. Currently, the Krakow City Waterworks Laboratory does not have UHPLC-MS/MS equipment with high resolution necessary to perform sample analysis in Fullscan mode, therefore monitoring has not been extended to identify precursors and other PFAS not listed in the Directive.

3. Materials and methods

The Krakow's water supply infrastructure is a very modern one; the city has an excellent technological background and resources that deliver a high-quality water to the residents. The Krakow Water (KW) is responsible for managing the water supply in Krakow.

Four water treatment plants (WTP) supply drinking water to the Krakow agglomeration, they are: WTP Rudawa (from the Rudawa river), WTP Bielany (from the Sanka river), WTP Dłubnia (from the Dłubnia river, serving the eastern part of Krakow), WTP Raba (from the Raba river, located outside the city).

The series of tests were run in 2023 and then in the first half of 2024 in these facilities. The water samples were also taken at monitoring sites, located within the water intake protection zones. These are tributaries, that before discharging water to larger rivers serving as a water source, pass by smaller towns and their sewage treatment plants; such journey may significantly alter a raw water quality in Krakow. Over the year, two sampling periods were selected: late February to March (a wet season) and August (a dry season). The number of repetitive samples has been insufficient to observe the seasonal changes in the obtained results. Therefore, more samples in different seasons of the year will be collected in the next research study, to determine the possible impact of seasons on the final test results. The extreme weather phenomena observed in recent years, as the result of climate change, require that the studies have to be extended over several years, e.g. from 3 to 5 years, to be reliable.

The sample collection points have been marked in the map [28] (Fig. 1).

Fig. 2 presents water supply zones, attributed to individual WTP in Krakow [28], together with raw and treated water collection points.

In 2023 and 2024, more than 51 water samples were collected and analyzed:

Fig. 1. Water supply system in the urban agglomeration of Krakow, including monitoring sites of sanitary zones.

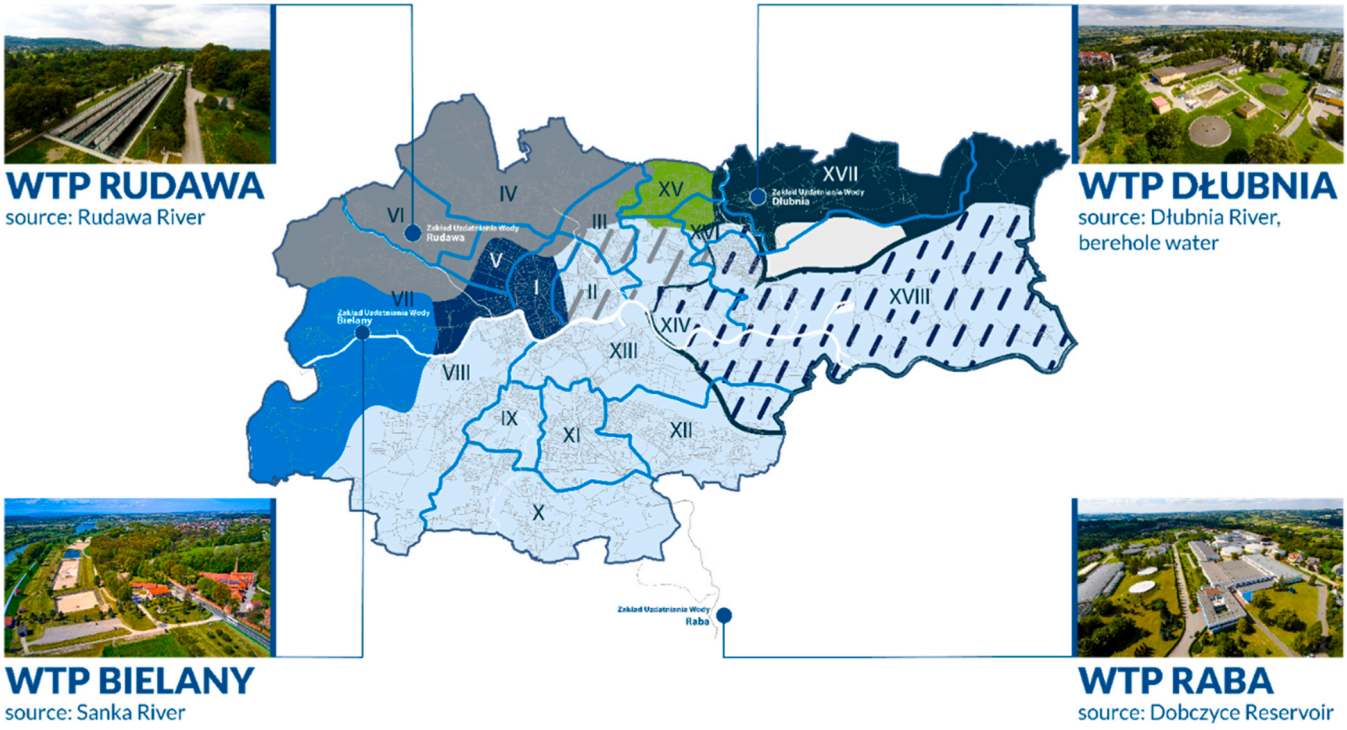

Fig. 2. Water supply zones for Krakow residents.

PFAS, EDCs compounds were tested in samples of raw and treated water as well as in water from the water supply network and the intake protection zones.

The analyses were carried out using chromatographic techniques. All methods were validated for repeatability and precision of analytical methods. Advanced analytical methods were used to accurately identify and quantify micropollutants in water. The necessary reagents and solvents used in the experiments were purchased from different manufacturers and had the required purity for LC-MS/MS analyses, confirmed by the certificate. Certified reference materials were used in each series:

PFAS: Wellington Laboratories
EDC: CPAchem

Laboratory analyses were performed with highly specialized

measuring instruments: PFAS, EDCs - UHPLC Agilent 1290 Infinity II liquid chromatograph with LC-MS/MS 6470B tandem mass detector;

PFAS, EDCs - SPE-03 automatic extraction and concentration station by Promochrom.

3.1. Analyzed compounds

The groups of compounds were studied using methods appropriate for individual substances and following the global analytical standards. Analysis of micropollutants in water is a complicated process that requires advanced analytical techniques. Since sampling and preparation of samples is very important it is critical to ensure a sample integrity to avoid its contamination. Some analyses require a solid phase extraction and purification (SPE). In general, they require: high sensitivity and precision of analytical equipment, selectivity, high efficiency while analyzing low molecular weight compounds and a possibility to perform a trace analysis.

Laboratory tests for PFAS and EDCs analysis comprised the following stages: sampling into 250 ml polypropylene bottles, transport at a temperature below 4°C, sample preparation with liquid-solid extraction in the SPE-03 automatic extraction and concentration station manufactured by Promochrom. Sample analysis was carried out using the liquid chromatography technique with mass spectrometry detection, using the Agilent 1290 Infinity II UHPLC Chromatograph with the MS/MS 6470B tandem mass detector. The method development process consisted of selecting appropriate standards and internal standards and then calibration and validation of the analytical methods. In both analyses a delay column was used to eliminate contamination of the tested analytes from the apparatus. The additional SPE On-line module was used for better sensitivity of the method.

3.1.1. PFAS

The studies included all PFAS listed in Directive (EU) 2020/2184 of the European Parliament and of the Council. i.e.: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorobutanesulfonic acid (PFBS), perfluoropentanesulfonic acid (PFPS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanesulfonic acid (PFHpS), perfluorooctane sulfonic acid (PFOS), perfluorodecanonanesulfonic acid (PFNS), perfluorodecane sulfonic acid (PFDS) perfluoroundecanesulfonic acid (PFUnDS), perfluorododecane sulfonic acid (PFDoDS) and perfluorotridecane sulfonic acid (PFTrDS); then their sum was calculated, as the value standardized by the regulations of the Directive. The compounds were analyzed in samples of raw and treated water as well as in water from intake protection zones and from the water supply network. Laboratory tests for PFAS analysis were conducted in accordance with the EPA533 method [29], and comprised the following steps: collection of samples into special containers, preservation, transport and storage, preparation of samples using the liquid-solid extraction technique, optimization of the method, selection of specific internal standards, calibration and validation of analytical methods. The method applies to samples with concentrations ranging from 0.0015 μg/l to 0.2 μg/l, for each compound. Native and internal standards in the PFAS analysis included 20 and per- and polyfluoroalkyl substances with a concentration of 2000 μg/l.

The analytical standards were supplied by Wellington Laboratories. Working standard solutions were prepared by diluting the initial solutions with distilled water using the 20 % methanol solution. Between the series, the samples were stored at a temperature of 4 °C, in the dark, for a month.

In the next step, the sample volume was determined. The real and control samples had the same volume. The pH range of the sample with 1 g/l of ammonium acetate was between 6.0 and 8.0. Samples with a volume of 250 ml were enriched with isotope-labeled analogues of the analytes of the method, acting as standards for diluting isotopes. The samples passed through the SPE cartridge with polystyrene divinylbenzene and a positively charged diamine ligand to extract method analytes and isotopic dilution analogues. The cartridges were rinsed sequentially with the aqueous solution of ammonium acetate, methanol and then with phosphate buffer. Phosphate buffer with a concentration of 0.1 M and pH 7 is a standard conditioner for WAX-type SPE cartridges used in methods of PFAS analysis. Conditioning of the column prepares the sorbent before loading the sample, ensures full phase hydration and sets appropriate pH and ionic conditions. The buffer maintains a neutral environment (pH ~ 7) to keep WAX functional groups positively charged and maintain the appropriate ionic form of PFAS analytes. Additionally, the conditioning buffer washes out potential non-polar-ionic contaminants from the sorbent and fills the pores with an aqueous solution of known ionic strength. An accurate ionic strength (0.1 M) prevents matrix effects associated with a rapid change of the environment from a purely organic (methanol) to an aqueous one [30].

In the next step, the compounds were eluted from the sorbent in the solid phase with methanol and ammonium hydroxide [31]. The extracts were dry concentrated with nitrogen in a heated water bath. The volume of extracts was brought to 1.0 ml with methanol 20 % solution in water (v/v). The instrument was pre-set according to the User's Manual [32]. The phases were prepared for PFAS analysis: the aqueous phase contained 5 mM ammonium acetate in water while methanol was used as the organic phase. A 20 % solution of reagent water in methanol was used to rinse the injection port. The injection volume was 100 μl, at a pre-set flow of 0.04 ml/min in the binary pump.

A Zorbax Eclipse Plus C18 Rapid Resolution HD 2.1 × 50 mm 1.8-Micron liquid chromatography column was used in combination with a Zorbax Eclipse Plus C18 2.1 × 5 mm 1.8-Micron UHPLC Guard precolumn. The analysis was performed in Dynamic MRM mode, setting the retention time for each indicator as well as both masses of precursor and product ions. Calibration was performed with standard solutions at five levels. At the beginning and in the middle of the sequence, blank tests were performed every 10 samples to control the possible contamination of the system with PFAS. In each sequence, control tests on standards as well as repeated tests with standard recovery were performed to examine the entire analytical procedure.

3.1.2. EDCs

An analysis of bisphenol A, nonylphenol and 17-β estradiol was carried out in samples of raw and treated water as well as in samples collected at the intake protection zones and in the water distribution mains. The methodology was developed based on the Agilent Technologies application note, "Determination of hormones in drinking water by the LC/MS/MS method using the Agilent InfinityLab Poroshell HPH column (EPA 539)". The method applies to samples with concentrations ranging from 0.5 ng/l to 320 ng/l, for each component. The InfinityLab Poroshell 120 EC-C18 2.1 × 50 mm 1.9-Micron liquid chromatography column was used in combination with the InfinityLab Poroshell 120 EC-C18 2.1 × 5 mm 1.9-Micron UHPLC Guard precolumn. The samples were prepared using the SPE extraction technique, with SPE C18 cartridges. The cartridges were activated with methanol, rinsed with water and, eluted with methanol after the test. The extracts were concentrated to dryness with nitrogen in a heated water bath. The volume of the extracts was adjusted to 1.0 ml with 30 % acetonitrile in water (v/v). The HPLC instrument was pre-set according to the User's Manual [30]. The appropriate phases were prepared: eluent A – 0.5 mM solution of ammonium fluoride in water and eluent B – acetonitrile 100 %. The injection volume was 400 μl, with a pre-set flow of 0.04 ml/min in the binary pump. The analysis was performed in the MRM mode, defining ion collection segments for subsequent indicators. In the EDCs analysis, analytical standards were provided by CPAChem. The certified standards were used for calibration to ensure measurement consistency. Individual working standard solutions were obtained by diluting the

initial solutions with distilled water. Calibration was performed on standard solutions at five levels. In each sequence, blank tests, standard controls and repeat tests with standard recovery were also performed during the test procedure. Between the series, the standards and extracts were stored at 4 °C, in the dark, for a month.

4. Results and discussion

The study presents the results for the groups of PFAS and EDCs compounds analyzed in the following water samples: water collected at the intake protection zones, raw water (water intakes), treated water (drinking water) and water from the water supply system (distribution).

The measurement range was set between the highest and lowest values that will be useful with respect to the 2020 Directive and can be determined using a given measurement method with the assumed precision, accuracy and linearity. Correlation coefficients above 0.995 were obtained for all the coefficients. The detection limit was determined at the analyte concentration corresponding to three times the standard deviation of the sample series with a concentration close to the detection limit. The concentration limits for all PFAS were obtained below 0.0015 μg/l and this value was adopted, while for endocrine active compounds, values below 0.5 ng/l were obtained and this level was assumed as the method's quantification limit. The basis for the Type A uncertainty analysis process was to indicate and then assess the standard uncertainty of each of the identified sources of uncertainty. The key to assessing the uncertainty of any source was to determine the standard deviation associated with it. While assessing the combined uncertainty of the test results, the following sources related to standard uncertainty were considered: sampling, calibration curve, recovery by standard addition, recovery by interlaboratory study and precision. The highest contribution of all sources of uncertainty identified during the validation process for both PFAS and EDCs was from intermediate precision from the lower control charts (uncertainty ranged between 27 % and 43 %.)

4.1. PFAS

The presence of PFAS was observed in water collected at the intake protection zones for Krakow.

Fig. 3 shows that the highest concentrations (2.0511 μg/l) were found in the Dłubnia river, at the intake point of Minożka: Iwanowice Dworskie. At other intake zones, the highest values were: 1.4615 μg/l (the Rudawa river, Krzeszowice), 0.2679 μg/l (the Raba river, Myślenice, upstream of the treatment plant) and 0.0146 μg/l (the Sanka river, Liszki).

A comparative analysis of PFAS concentrations in raw and treated water at 4 water treatment plants, including the average values in the water supply network (Fig. 4), shows small differences between the sum of these compounds before and after the treatment processes. Per and polyfluoroalkyl compounds are particularly difficult to remove in conventional water treatment processes due to their high persistence fluorine-carbon bonds. The highest number of PFAS was detected at the Bielany WTP, both in raw and drinking water. PFAS detected in drinking water stayed within the limits set in the Water Directive of 2020.

The PFAS concentrations for raw and treated water showed slight differences, they usually stayed below 10 %. Due to the structure and therefore high persistence of PFAS in the environment, standard water treatment technologies such as coagulation, flocculation, sedimentation or filtration show limited efficiency. The analyzed values of the sum of PFAS for the subsequent treatment plants were comparable and stayed one order of magnitude below the limit value of 0.1 μg/l specified in the Directive. Detailed tests for all the analyzed PFAS compounds (Table 1) showed that PFBA predominated in the treated water and its concentration at the Raba WTP was 0.00180 μg/l while at the Dłubnia WTP it was 0.00085 μg/l. At the Bielany WTP, the highest concentration of PFHxS was detected (0.00342 μg/l) while the highest concentration of PFOA (0.00151 μg/l) was found at the Rudawa WTP. On the other hand, the highest PFBA (0.00141 μg/l) was observed in the water from the water supply network. In case of two water treatment plants: Raba and Dłubnia, the concerns were caused by PFBA both in raw and drinking water. The highest concentrations of PFAS compounds in raw water were recorded for PFOA in the Raba river (0.001282 μg/l) and in the Rudawa river (0.001434 μg/l). At the Bielany WTP, the PFHxS concentration in the Sanka river was 0.003197 μg/l, while the PFTrDA concentration of at the Dłubnia WTP was 0.002783 μg/l (Tables 1 and 2).

Similar studies were carried out for the Odra river, Poland. They showed the presence of fourteen PFAS and their total concentrations ranged from 0.0076 to 0.068 μg/l. The main compounds were short-chain analogues and PFBA was the predominant one; it accounted for about one-third of all PFAS detected. The only exception was the Gliwice canal, where mainly 4,8-dioxa-3H-perfluorononanoic acid was found. PFAS in the Odra river most likely came from domestic and agricultural

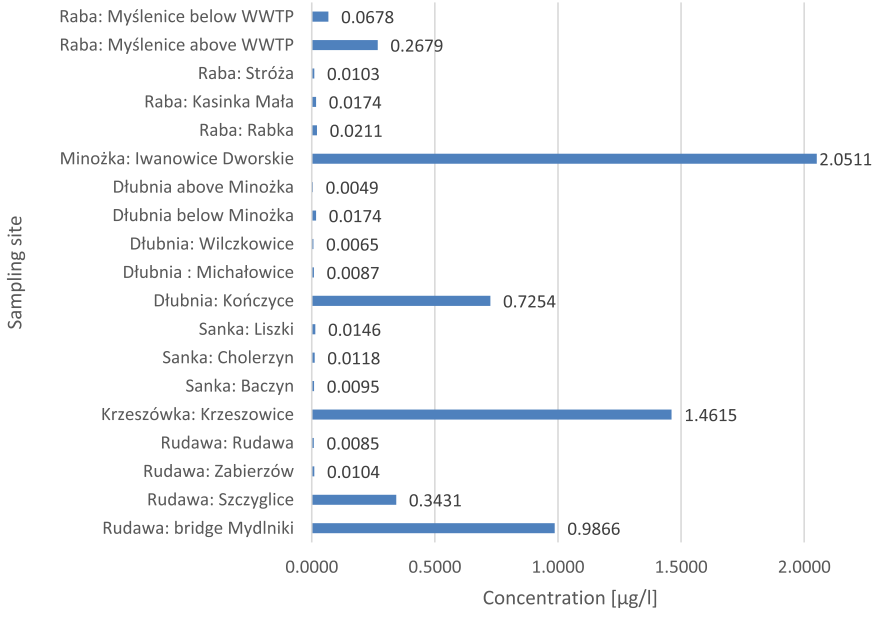

Fig. 3. PFAS concentrations in water from intake protection zones for Krakow.

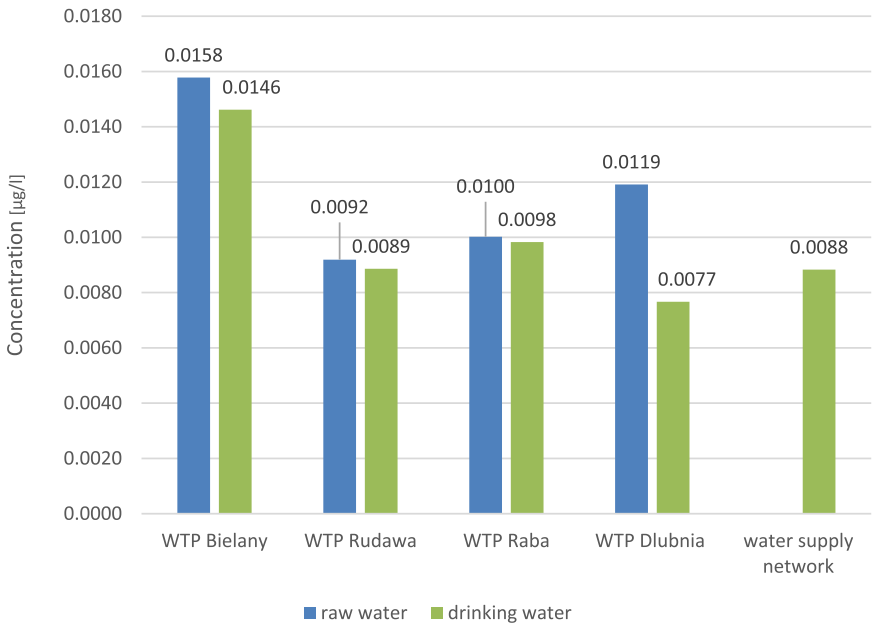

Fig. 4. Sum of PFAS in drinking water at four water intakes for Krakow.

Table 1
Parameters of methods used in research.

Analyzed group of compounds	Analysis method	Chromatograph sensitivity	Accuracy of the method [%]	Precision of the method [%]	Uncertainty of the method [%]
PFAS	HPLC-MS/MS	in mode ESI MRM S/	0.51–21	12–17	28–43
EDCs	HPLC-MS/MS	N > 350000:1	12–20	15–21	< 40

Table 2
PFAS concentrations in drinking water at four water plants in Krakow.

	drinking water					**raw water**			
	WTP Bielany	WTP Rudawa	WTP Raba	WTP Dłubnia	water supply network	WTP Bielany	WTP Rudawa	WTP Raba	WTP Dłubnia
PFBA	0.00182	0.00054	0.00147	0.00067	0.00141	0.00166	0.00096	0.00180	0.00085
PFPeA	0.00100	0.00053	0.00072	0.00019	0.00034	0.00105	0.00029	0.00080	0.00044
PFBS	0.00138	0.00069	0.00085	0.00046	0.00060	0.00130	0.00054	0.00081	0.00049
PFHxA	0.00130	0.00066	0.00124	0.00040	0.00049	0.00101	0.00057	0.00070	0.00040
PFPeS	0.00073	0.00027	0.00024	0.00025	0.00025	0.00025	0.00027	0.00026	0.00029
PFHpA	0.00061	0.00032	0.00065	0.00026	0.00035	0.00048	0.00037	0.00045	0.00029
PFHxS	0.00320	0.00059	0.00028	0.00026	0.00050	0.00342	0.00041	0.00024	0.00018
PFOA	0.00111	0.00143	0.00124	0.00088	0.00068	0.00139	0.00151	0.00091	0.00078
PFHpS	0.00020	0.00019	0.00018	0.00018	0.00020	0.00026	0.00019	0.00019	0.00019
PFNA	0.00040	0.00035	0.00045	0.00032	0.00033	0.00041	0.00029	0.00031	0.00030
PFOS	0.00050	0.00042	0.00026	0.00091	0.00086	0.00065	0.00063	0.00042	0.00062
PFDA	0.00027	0.00040	0.00037	0.00037	0.00038	0.00038	0.00036	0.00040	0.00039
PFNS	0.00020	0.00020	0.00020	0.00019	0.00026	0.00026	0.00026	0.00026	0.00027
PFDS	0.00015	0.00015	0.00015	0.00014	0.00016	0.00016	0.00016	0.00016	0.00016
PFUnDA	0.00030	0.00029	0.00040	0.00051	0.00035	0.00036	0.00036	0.00038	0.00036
PFUnDS	0.00027	0.00027	0.00049	0.00029	0.00037	0.00038	0.00038	0.00048	0.00037
PFDoDA	0.00113	0.00036	0.01341	0.00135	0.00046	0.00040	0.00042	0.00043	0.00042
PFDoDAS	0.00050	0.00030	0.00366	0.00078	0.00036	0.00033	0.00033	0.00034	0.00034
PFTrDA	0.00054	0.00025	0.00715	0.00278	0.00025	0.00026	0.00033	0.00027	0.00030
PFTrDS	0.00018	0.00017	0.00662	0.00071	0.00024	0.00022	0.00023	0.00022	0.00023

sewage, as well as from the chemical industry discharges. However, the PFAS concentrations in both the Odra river and the rivers of the Krakow agglomeration are low and stay below the limits set out in the Directive [33].

Completely different PFAS compounds were detected in experiments conducted in other European countries, e.g. in the Mur river in Austria. Upstream from the wastewater treatment plant only PFPA was found, while PFHxA and PFPS were found in samples taken downstream from the plant. The other samples, i.e. all river water samples taken upstream and downstream of the wastewater treatment plant, showed values below the limit of quantification (LOQ) [34]. In Spain, short- and ultra-short-chain PFASs have been found to be abundant in the Barcelona area, with the highest concentrations detected for perfluorobutanesulfonic acid (PFBS), trifluoroacetic acid (TFA) and trifluoromethanesulfonic acid (TFSA). Long-chain PFAS and new PFAS were found at very low concentrations (< 50 ng/l) [35].

4.2. EDC

Water taken from smaller tributaries of the rivers serving as sources of drinking water for Krakow was tested for EDC (Fig. 5). It was found that the highest concentrations of bisphenol A were observed at the Sanka Baczyn point (0.0173 μg/l), Raba Rabka (0.0129 μg/l), Rudawa, Mydlniki bridge (0.0074 μg/l) and Dłubnia Michałowice (0.0012 μg/l), respectively. The highest concentration of nonylphenol was observed at: Raba Kasinka Mała (0.0160 μg/l), Dłubnia, Minożka Iwanowice Dworskie (0.0046 μg/l), Sanka Cholerzyn (0.0056 μg/l) and Rudawa Zabierzów (0.0065 μg/l), respectively.

According to the Fig. 6, the highest concentration of 17-Beta Estradiol in the protection zones of tributaries to Krakow water intakes was observed for Kasinka Mała, the Raba river (3.68×10^{-5} μg/l). In other zones and subsequent intake points the highest values were: 3.19×10^{-6} μg/l (Kończyce, the Dłubnia river), 1.99×10^{-5} μg/l (Baczyn, the Sanka river) and 2.91×10^{-5}μg/l (Szczyglice, the Rudawa river).

Raw and drinking water was analyzed at all Kraków water treatment plants (Fig. 7). The EDCs concentrations were detected in raw water. These values are below the maximum permissible concentration for BPA (2.5 μg/l for Bisphenol A), according to the guidelines of the Drinking Water Directive. In this document, the precautionary levels for 17β-Estradiol and Nonylphenol are 0.001 μg/l and 0.3 μg/l, respectively, and have not been exceeded either. The values below the detection limits results from the removal of endocrine active compounds during water treatment processes.

In Poland, most of the research on alkylphenols and Bisphenol A focuses on the northern areas of the Baltic Sea region. According to Staniszewska et al., the EDCs content stayed below 0.278 μg/l. The concentrations of BPA ranged from < 0.001 μg/l to 0.834 μg/l, while the concentrations of 4NP from < 0.004 μg/l to 0.229 μg/l [36,37]. In our studies, the concentrations of these compounds in rivers constituting tributaries to Kraków water intakes ranged: from < 0.0005 μg/l to 0.017 μg/l (BPA), from < 0.0005 μg/l to 0.016 μg/l (4NP) and from < 0.0005 μg/l to $3.68 \cdot 10^{-5}$ (17β-Estradiol). As reported by Urszula Kotowska [38], Bisphenol A did not exceeded the detection limit. Studies in the Krakow agglomeration showed that the analyzed compounds were found in lower or comparable concentrations to European countries. For example, in the Tagus and Douro rivers (the Iberian Peninsula) BPA concentrations ranged from 0.054 μg/l to 4.424 μg/l [39]. The average values for the Douro river were 0.0154 μg/l, while for the Tagus river 0.940 μg/l. Other studies from a similar geographical area showed lower concentrations of bisphenol. The BPA concentration of 0.880 μg/l was found in water from the Mondego estuary in Portugal [40] while the levels reaching 0.190 μg/l were detected in the Tagus estuary in the later studies [41]. BPA concentrations up to 0.272 μg/l have been found in the Körsch River in Germany [42]. In the Iberian rivers in Spain BPA concentrations reached up to 0.280 μg/l while in the Romagna region in Italy up to 0.1713 μg/l. BPB (3.3′,5.5′-tetrabromophenolsulfophthalein), BPE (1,1-Bis(4-hydroxyphenyl)ethane) and BPS(4,4′-Sulfonyldiphenol) were often detected below the LOQ. Their presence in water may be caused by replacement of BPA with other bisphenols and their subsequent release into the environment. As reported by Irene Beltrán et al., Bisphenol A was present in 100 % of samples taken from three rivers in the north of Spain (Cadagua, Deba, Urola) while nonylphenol was detected in 75 % of samples [43]. Analyses from Slovenia (water from 33 rivers upstream and downstream of the wastewater treatment plant) showed the presence of BPA in 93 % of the upstream samples (ranging from 0.00012 μg/l to 0.122 μg/l) and in 100 % of the upstream samples (ranging from 0.00012 μg/l to 0.278 μg/l. 17β-Estradiol was detected in 86 % of the upstream samples (ranging from 0.00016 μg/l to 0.0013 μg/l) and in 73 % of the downstream samples (ranging from 0.00016 μg/l to 0.0014 μg/l) [44]. In Germany, Nonylphenol concentrations have been changing from 0.0025 μg/l to 0.0138 μg/l.

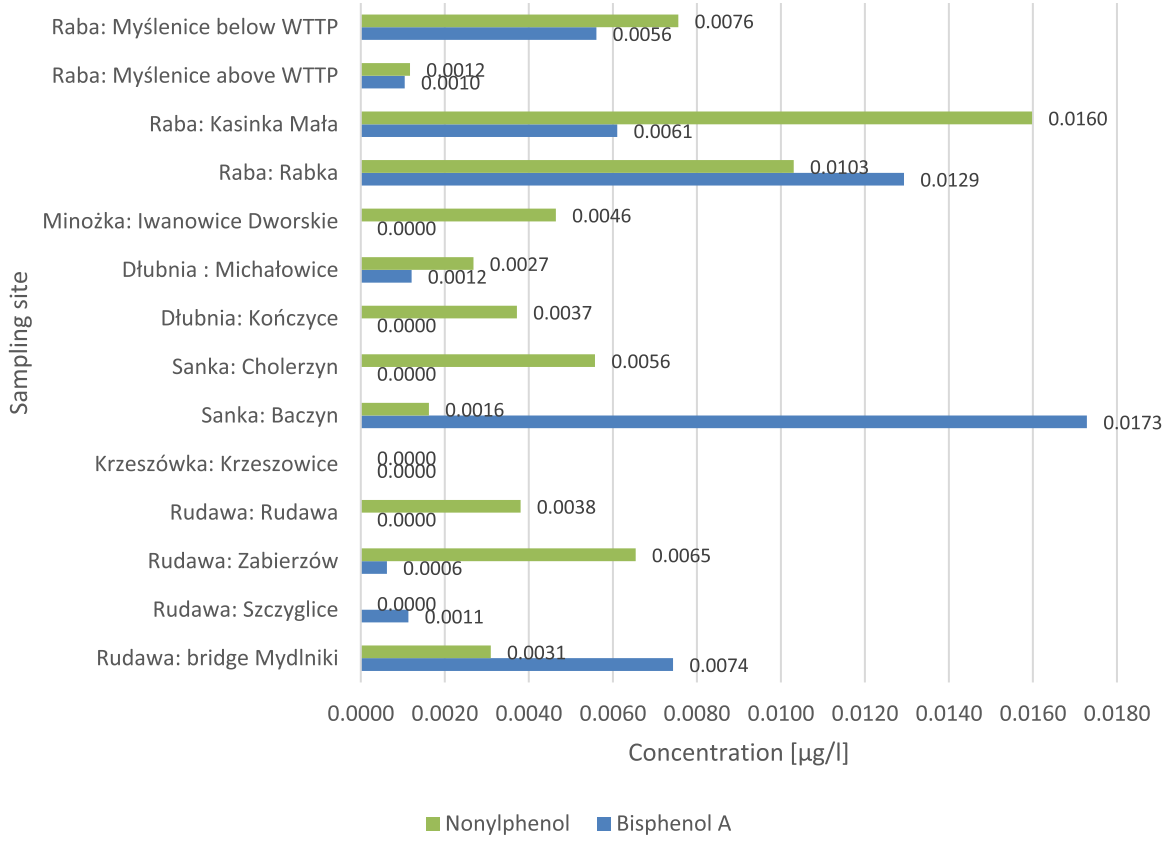

Fig. 5. EDCs concentrations in water collected at the intake protection zones in Krakow.

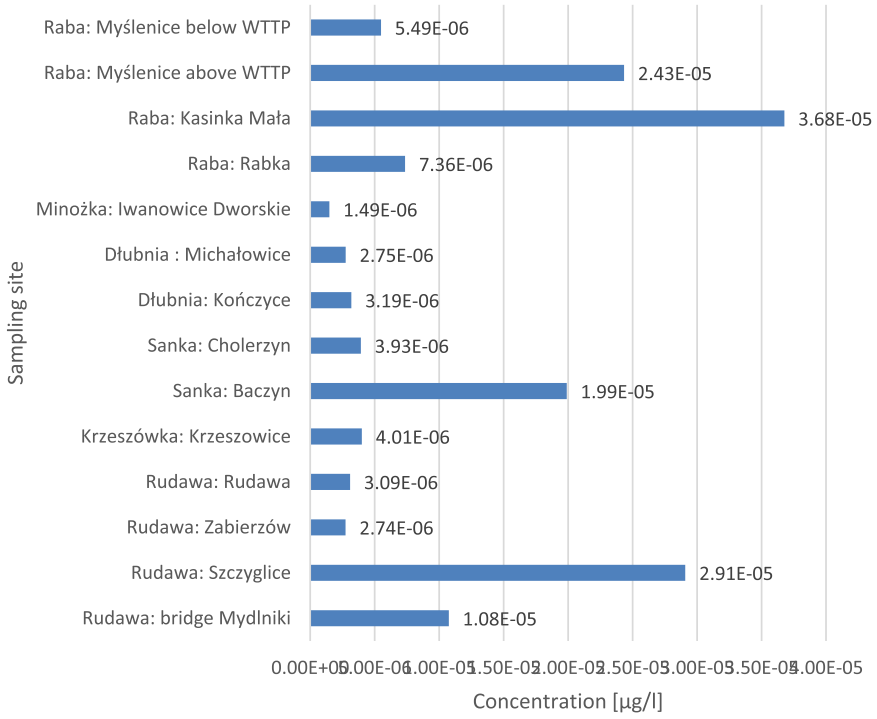

Fig. 6. Concentrations of 17-Beta Estradiol in water from intake protection zones in Krakow.

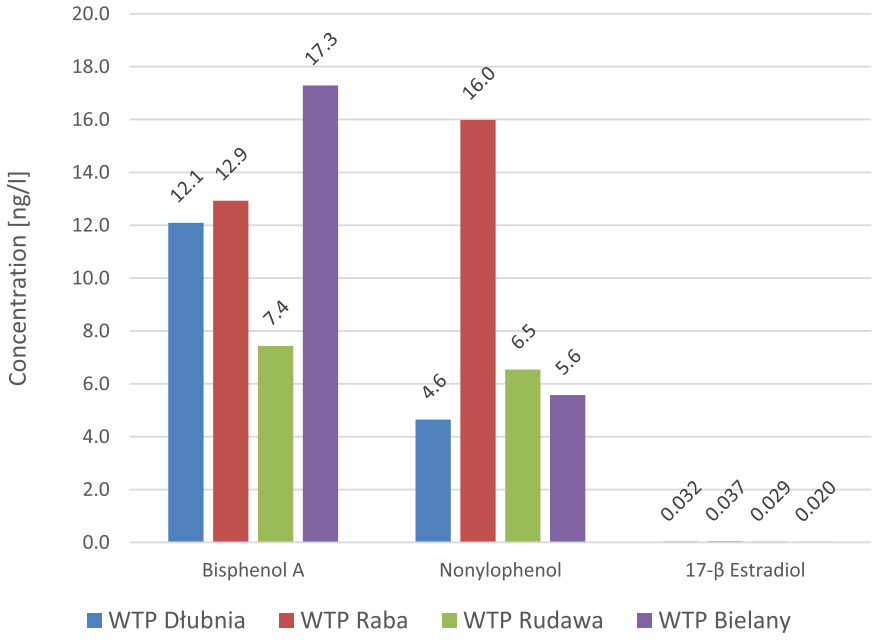

Fig. 7. Concentrations of 17-Beta Estradiol in raw water at four water treatment plants in Krakow.

In Poland, which is considered as a low-industrialized country, selected endocrine compounds stay below the standards set out in Directive (EU) 2020/2184 of the European Parliament and of the Council. However, their presence in surface waters should be controlled due to their negative effects on humans.

5. Summary and conclusions

The Directive (EU) 2020/2184 of the European Parliament and of the Council requires introduction of analytical methods for monitoring of newly emerging pollutants. The Krakow Waterworks have initiated a research to identify synthetic per- and polyfluoroalkyl compounds and selected endocrine active compounds.

Raw and treated water were analyzed at four Kraków water treatment plants (WTP): Bielany, Rudawa, Raba and Dłubnia. Micropollutants were analyzed following the guidelines of Directive (EU) 2020/2184 of the European Parliament and of the Council as well as the Regulation of the Minister of Health of 2017 on the quality of water intended for drinking. The samples were collected at intake protection zones, treatment plants and from the water supply system. The research included more than 50 water samples collected between 2023 and 2024. Advanced chromatographic methods (LC-MS/MS, GC-MS) and

extraction techniques (SPE, HeadSpace) were used in the research. In summary of this research, several most important conclusions can be identified:

1. Low concentrations of total PFAS were observed in samples collected at the intake protection zones, with the highest concentrations recorded in the Dłubnia river (2.0511 μg/l). Bisphenol A was detected in surface waters, with the maximum value of 0.0173 μg/l observed in the Sanka river, as well as nonylphenol, whose highest concentration of 0.0160 μg/l was found in the Raba river.
2. The highest concentration of 17β-estradiol was recorded in the Raba River (3.68×10^{-5} μg/l). PFAS were detected in raw and drinking water at comparable concentrations, due to their poor removal in technological processes, but they still remained below the limit value of 0.1 μg/l. Short-chain PFAS, such as PFBA and PFHxS, predominated in the samples. Endocrine compounds such as Bisphenol A (BPA), Nonylphenol and 17β-estradiol were detected in raw water, but as they were effectively removed during the treatment processes, their concentrations in drinking water fell below the detection limits.
3. The study confirmed that the quality of drinking water in Krakow meets all the standards set out in the Water Directive 2020/2184. The micropollutants, such as PFAS, EDC, although found in raw water, are effectively reduced during technological processes, with the exception of PFAS compounds, which are difficult to remove.
4. The authors checked also whether the analyzed micropollutants were present in the tributaries of the rivers serving as drinking water sources for Krakow. They found that the micropollutants concentrations remained below the limits set by the Directive. The drinking water was free of EDCs while fluorinated compounds remained in similar concentrations as for raw water, i.e. well below the allowable standards.
5. The studies indicate a need for further water quality monitoring, especially now when an intensive growth of industrial activities is observed. They also highlight the need for investment in education and advanced water treatment technologies. The studies on water quality in the intake protection zones will be continued every few months to monitor seasonal changes of water quality and look at possible risks that higher concentrations may occur during hydrological droughts. Raw water, drinking water and water from the water supply network will also be tested on a monthly basis to observe any changes and dependencies that may be attributed to the analyzed compounds.

CRediT authorship contribution statement

Cimochowicz-Rybicka Małgorzata: Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Ochmańska Monika:** Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Łomińska-Płatek Dominika:** Writing – review & editing, Writing – original draft, Visualization, Resources, Data curation, Conceptualization. **Bochnia Tadeusz:** Writing – review & editing, Validation, Resources, Methodology, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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