Levels of PFOS and the other perfluorinated organic compounds in Polish inland waters and Baltic Sea coastal waters

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Introduction

The name perfluorinated organic compounds (PFOC) is used to determine the group of aliphatic compounds in which hydrogen atoms bound to carbon in the alkyl chain have been replaced by fluorine and have polar functional groups. Due to the structure these compounds have specific properties, are characterized by high chemical and thermal stability, and are not biodegradable.

Due to the presence of polar functional groups they exhibit hydrophilic properties, and contrary to other POPs (persistent organic pollutants) they dissolve in water relatively well. This makes them highly mobile in the natural environment.

PFOC are widely used in industry as flame-retardants, refrigerants, substances that modify properties of paper, extinguishing agents, etc. They are constituents of paints, detergents, impregnates.

PFOC are detected in all types of environmental samples: surface water, groundwater, soil, air, plant and animal tissues [1, 3, 4].

Materials and metod

Within the framework of the State Environmental Monitoring, in the years 2014 - 2016 research on the content of PFOC in muscle tissue of fish was carried out.

Three species of fish from 6 fisheries were subject to the research.

The analysis included females only.

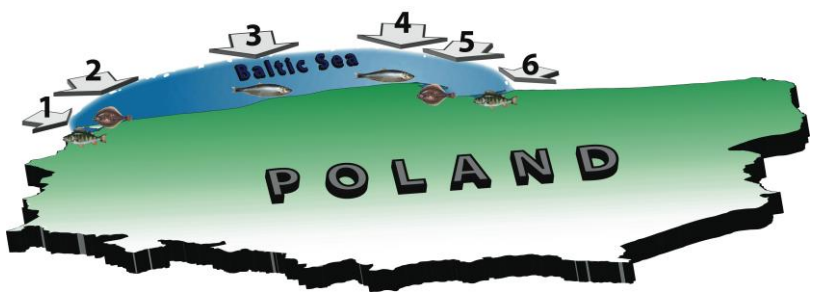

Fig.1. Fishing spot for Baltic fish

Table 1: Data for fishing in Baltic Sea coastal waters.

No.	Fishing area	Fish	Well. of samples	age of fish (years)		
				2014	2015	2016
1	the Szczecin Lagoon	perch (Perca fluviatilis)	10	3 - 4	3	3
2	the Gulf of Pomerania	flounder *(Platychtys flesus)*	10	3 - 5	3 - 5	4
3	Fishery Kołobrzeg-Darłowo	herring (Clupea harengus)	12	2	3 - 4	3 - 4
4	Fishery Władysławowo	herring (Clupea harengus)	12	2	3 - 4	3
5	the Gulf of Gdańsk 2014, 2015 – Orłowo, 2016 – Hel	flounder *(Platychtys flesus)*	10	4	4	4
6	the Vistula Lagoon	perch (Perca fluviatilis)	10	4	3 - 4	4 - 5

Seven compounds from the group of perfluoroalkyl acids (PFAA) were determined in the samples of muscle tissue of Baltic fish: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic (PFDA), and three compounds from the group of perfluoroalkylsulfonic acids (PFAS): perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS).
Samples of fish were obtained from anglers all over the country. Samples of fish muscle tissue were used for the study: 15 perch samples, 30 bream samples, 100 roach samples.
Samples were lyophilized and stored at -25°C. After the sample was shredded, ultrasonically assisted extraction was performed and purified by SPE. Chromatographic separation was performed using gradient system on a Kinetex 2.6 µm XB C18 100A column, 100 x 2.1 mm Phenomenex with a SecurityGuard Ultra cartridges C18 pre-column. To eliminate the interference caused by the presence of perfluorinated compounds, the solvents used as the mobile phase included an additional Kromasil C18 pre-column before the autosampler.
Determination of perfluorinated compounds was made using the LC-MS/MS technique with a triple quadrupole analyser and a QTRAP AB 3200 Sciex appartus. Electrospray ionisation (ESI) was used.

Results

PFOC were present in all the analysed samples collected in 2014, 2015 [2] and 2016 years. All the samples showed the presence of the following compounds: PFBA, PFOA, PFNA, PFDA, and PFOS. Least frequently detected were PFHxA, PFHpA, and PFBS. Figures 2 show the average content of PFAA (Fig. 2a) and PFAS (Fig. 2b). For the Vistula Lagoon the average PFOC content in 2015 was calculated from 9 samples since the concentrations of three PFAA in one sample were several dozen higher than in other samples in this fishery and amounted to: PFOA - 7.73 ng/g. PFNA - 12.39 ng/g and PFDA - 6.42 ng/g.

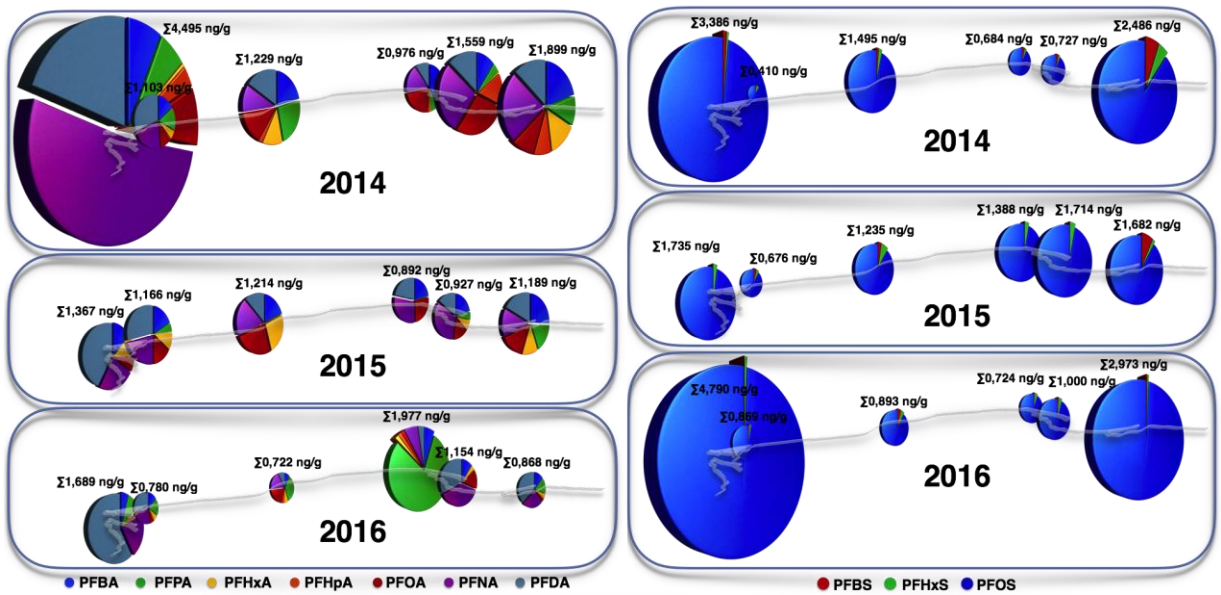

Fig. 2. The average content of PFAC in muscle tissue of Baltic fish.

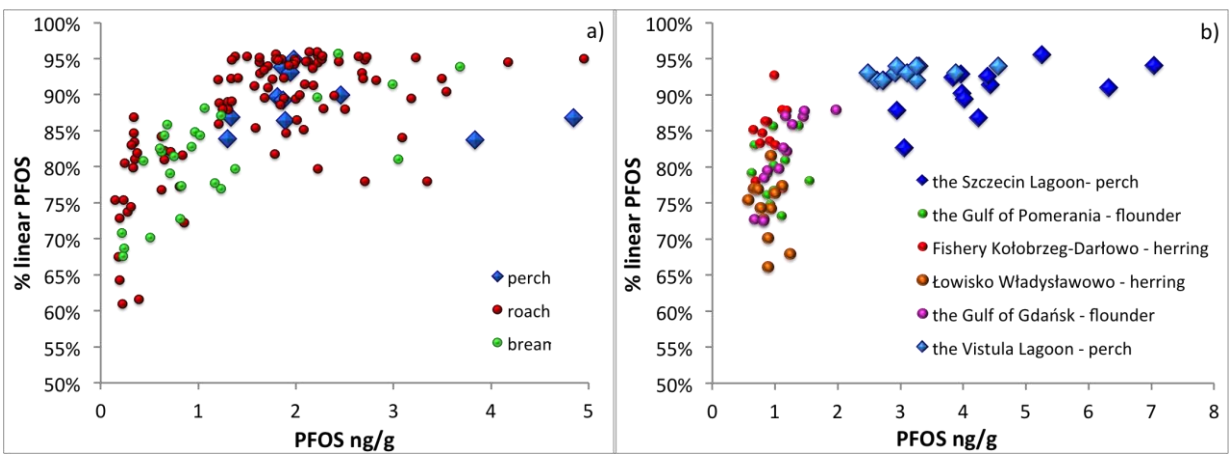

Fig. 3. Percentage share of linear form of PFOS in fish samples:
a) fish from inland waterways, b) fish from Baltic Sea

Results and discussion

PFAA and PFAS compounds were present in all samples of Baltic fish in the years 2014-2016. The largest quantities were PFOA, PFNA and PFDA except for 2016 samples from
Wladyslawowo fishing grounds. In samples from 2016, PFAA concentrations in addition to PFPA remained at similar levels as in the previous years. PFNA, which was present in only 25% of samples in 2014 at around 0.2 ng / g, was present in all 2016 samples in several times greater quantities.
Of PFAS compounds in all PFOS samples was more than 90%.
The highest concentrations of both PFAA and PFOS occurred in samples from the Szczecin Lagoon and amounted to around 5 ng / g PFAA in 2014 and almost 5 ng / g PFAS in 2016.
In fish samples from the Vistula Lagoon the PFAA concentrations did not exceed 2 ng / g, PFAS concentration was up to 3 ng / g.
In the remaining fish samples, PFAA concentrations ranged between 0.722 ng / g and 1.977 ng / g, PFAS ranged from 0.410 ng / g to 1.714 ng / g.
In samples of Baltic fish from 2016 the concentration of linear PFOS and the sum of isomers (Figure 3) was determined. The share of linear form varies between 65-95%. In fish samples from the Szczecin Lagoon and Vistula Lagoon this range is much narrower and amounts to 83-95%. Also in the case of fish from inland waters, the extent of the contribution of the linear form of PFOS is in the pearch muscle narrowed to other fish.

The results of the PFOC determination were obtained as part of the State Environmental Monitoring programme.

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