Cod: 2.1005

DETERMINATION OF PERFLUORINATED ORGANIC COMPOUNDS IN BALTIC SEA FISH

I. Wójcik[1], A. Grochowalski[2], W. Krzymiński[3], M. Rybka[3], T. Kalicki[1]

[1]Institute of Geography, Jan Kochanowski University in Kielce, Poland

[2]Department of Chemical Engineering and Technology, Krakow University of Technology

[3]Department of Oceanography and Baltic Sea Monitoring, IMGW-PIB, Gdynia, Poland

Introduction

The name perfluorinated organic compounds (PFOC) is used to determine the group of aliphatic compounds in which zhydrogen atoms bound to carbon in the alkyl chain have been replaced by fluorine and have polar functional groups.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 persistent organic pollutants (POPs) 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, impregnants.

PFOC are detected in all types of environmental samples: surface water, groundwater, soil, air, plant and animal tissues (Post et al. 2012; Yamashita et al. 2005; Zareitalabad et al. 2013).

Materials and methods

Within the framework of the State Environmental Monitoring, in the years 2014 - 2015 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.

Table 1. Information of Baltic Sea fish samples.

Fig.1. The area of fishing in the Baltic Sea.

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).

After collection, all samples were stored at -20 Celsius. After defrosting, the samples were pulverized. Samples were subjected to extraction assisted by ultrasonication for 30 min. Chromatographic separation was made in the 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.

The determination of: PFBA, PFHxA, PFOA, PFNA, PFDA, PFHxS, and PFOS were performed using the ID-LC-MS/MS isotopic dilution technique. However, PFPA, PFHpA and PFBS were determined using the external standard method.

Results and discussion:

PFOC were present in all the analysed samples collected in 2014 and 2015 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 and 4 show the average content of PFAA (Fig. 2) and PFAS (Fig. 4).
For the Vistula Lagoon (Fig. 3), 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 PFAA in muscle tissue of Baltic fish.

Fig. 3. The content of PFAA in muscle tissue of fish from the Vistula Lagoon in 2015.

Fig. 4. The average content of PFAS in muscle tissue of Baltic fish.

The content of PFAS acids in samples of muscle tissue of fish from the Szczecin Lagoon from 2015 was three times lower than in samples from 2014. Tissues samples of fish in the same age were analysed. Much higher concentrations, especially PFNA, in samples from 2014 may testify that water pollution with PFOC in the Szczecin Lagoon has decreased. The content of PFAS in samples from 2015 is almost twice less than in 2014.
In the case of the Gulf of Pomerania, both in 2014 and in 2015 samples of four-year fish were analysed. In both cases, the concentrations of PFAA and PFAS in samples of muscle tissue of fish were at the same level, which indicates that in 2010-2015 water pollution with PFOC in the Gulf of Pomerania has not changed.
The content of PFAA and PFAS in samples from the Darłowo-Kołobrzeg fishery in 2015 was at the same level as in 2014. Since in 2015 the analysis included samples of four-year fish, and in 2014 of two-year fish, similar contents of PFOC may suggest that fish exposure to these compounds in the last two years has reduced.
In the case of the Władysławowo fishery, in 2014 two-year fish were analysed, and in 2015 three-year fish. The content of PFAA in both series of samples was at the same level, indicating a decrease in fish exposure to these compounds. The situation is different in the case of PFAS, as their content in samples from 2015 is twice of that from 2014, which means that in 2015 fish were subjected to as much PFAS as in two previous years in total.
In the case of fish from the Gulf of Gdańsk, the series of samples from both years analysed samples of muscle tissue of four-year fish. The content of PFAA in samples from 2015 was twice less than in 2014, whereas the content of PFAS increased by 250%. This shows the growing exposure of fish to PFAA and PFAS in the last year.
The content of PFOC in samples of muscle tissue of fish from the Vistula Lagoon from 2015 was 40% lower than in samples from 2014. Since in both years the analysed samples were taken from four-year fish it can be concluded that the exposure of fish to these compounds has been reduced.
The ichthyologic analysis of fish showed that most of perch, both in 2014 and in 2015, was ready to breed, although in the sampling period gonads of fish should be at rest. Tissues of the fish showed the highest concentration of PFOC.
Acknowledgements:
The results of the PFOC determination were obtained as part of the State Environmen-tal Monitoring programme.

References:
1. Post G. B., Cohn P. D., Cooper K. R. (2012) Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: A critical review of recent literature, Environmental Research 116, 93–117.
2. Yamashita N., Kannan K., Taniyasu S., Horii Y., Petrick G., Gamo T. (2005) A global survey of perfluorinated acids in oceans, Marine Pollution Bulletin, 51, 658–668.
3. Zareitalabad P., Siemens J., Hamer M., Amelung W. (2013) Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients, Chemosphere 91, 725–732.

Table 1. Information of Baltic Sea fish samples.

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

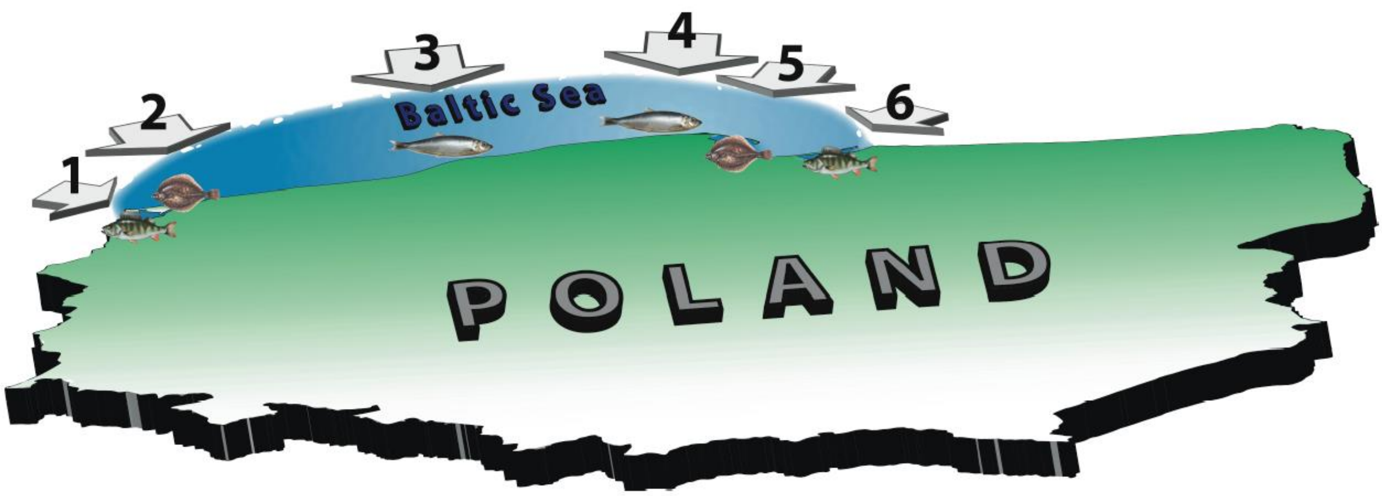

Fig.1. The area of fishing in the Baltic Sea.

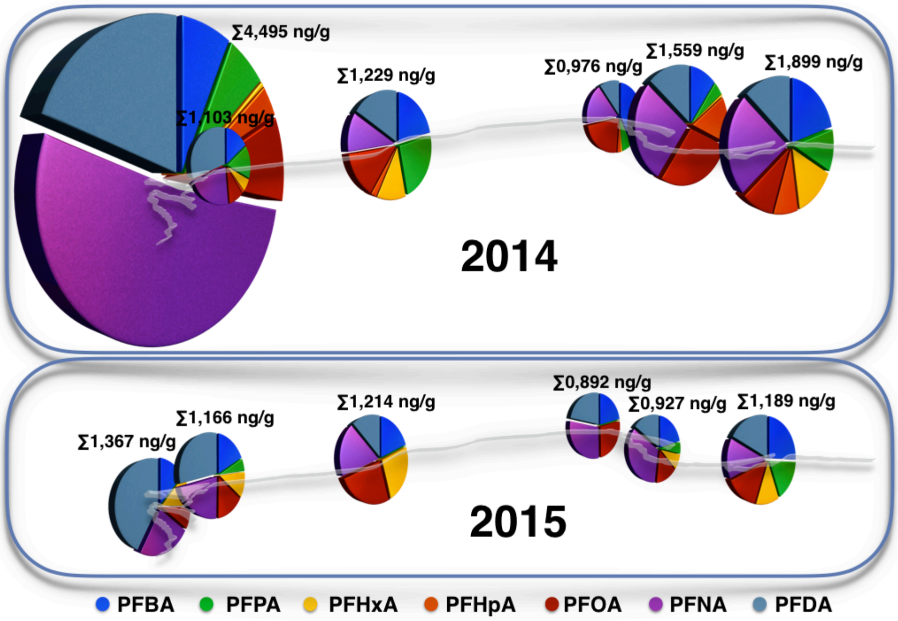

Fig. 2. The average content of PFAA in muscle tissue of Baltic fish.

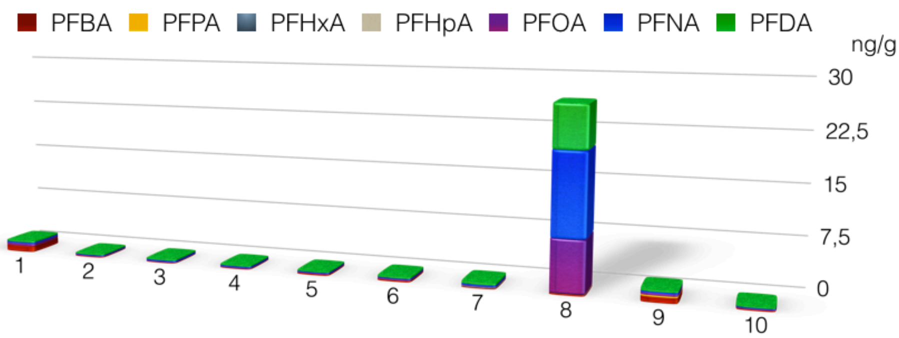

Fig. 3. The content of PFAA in muscle tissue of fish from the Vistula Lagoon in 2015.

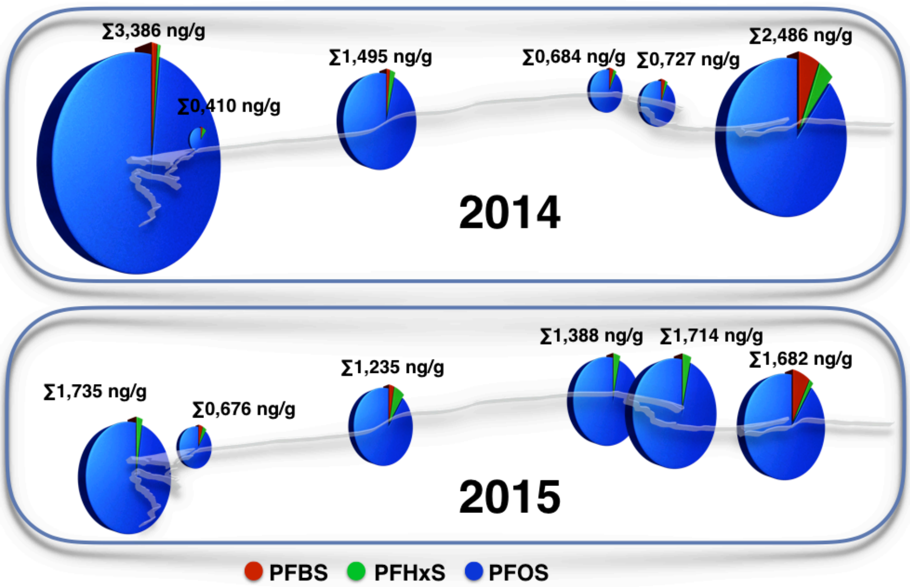

Fig. 4. The average content of PFAS in muscle tissue of Baltic fish.