

PERFLUORINATED CHEMICALS IN BLOOD OF FISH AND WATERFOWL FROM GULF OF GDANSK, BALTIC SEA

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ABSTRACT

Occurrence of perfluorooctane sulfonate (PFOS) in the tissues of humans and wildlife is well documented. In this study, concentrations and distribution of PFOS, perfluorohexane sulfonate (PFHxS), perfluorooctanoic acid (PFOA), perfluorooctane sulfonamide (PFOSA) and perfluoronanoic acid (PFNA) were determined. PFCs were measured in 65 samples of blood from 5 species of fish-eating water birds and 18 samples of cod collected from Gulf of Gdańsk. Quantifiable concentrations of all PFCs were found in all samples analyzed. Based on the concentrations of PFOS in water and fish tissues, bioconcentration factors were calculated to range from 6,500 to 100,000.

MATERIALS & METHODS

A total of 65 samples from 5 species of waterfowl such as razorbill (*Alca torda*), red-throated loon (*Gavia stellata*), black scoter (*Melanitta nigra*), long-tailed duck (*Clangula hyemalis*) and common eider (*Somateria mollissima*), and 18 samples of cod (*Gadus morhua*) have been examined. C6 to C9 of PFCs in blood samples were analyzed by the ion pair extraction method as a quick screening tool³. Concentrations of PFCs were determined by the use of high-performance liquid chromatography coupled with electrospray tandem mass spectrometry (HPLC-ESI MS/MS). Data quality assurance and quality control protocols included matrix spikes, procedural blanks, and continuing calibration verification. Matrix spikes were analyzed for each species. Blanks and procedural recovery were analyzed with each set of blood samples. Blanks did not contain any interference from instrumental and procedural contamination. Recoveries were measured for a wide range of PFCs and ranged from 64 to 102 %.

Table 1. Concentrations of PFCs in whole blood (ng/mL) of waterfowl and fish from the Gulf of Gdańsk

Species	Compound	PFOS		PFHxS		PFOSA		PFNA		PFOA	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Birds	Common scoter (n = 5)	9.0	4.5 - 14.4	2.6	0.9 - 4.6	0.3	0.1 - 0.7	1.0	0.4 - 2.1	0.2	0.09 - 0.6
	Eider duck (n = 16)	21.8	11.8 - 37.5	1.1	0.4 - 2.9	0.5	0.1 - 0.8	0.4	0.3 - 0.9	0.1	0.06 - 0.1
	Red-throated loon (n = 7)	71.5	40.2 - 198	0.7	0.4 - 1.2	3.8	0.7 - 6.0	1.1	0.3 - 2.0	0.5	0.2 - 0.9
	Razorbill (n = 9)	32.9	22.5 - 39.5	0.3	0.08 - 0.5	0.5	0.2 - 0.9	0.3	0.2 - 0.4	0.1	0.05 - 0.3
	Longtailed duck (n = 10)	20.1	6.0 - 53.9	2.2	1.2 - 2.9	1.8	0.9 - 3.4	0.6	0.3 - 1.7	0.6	0.3 - 1.8
Fish	Cod (n = 18)	17.0	6.1 - 51.9	0.1	0.05 - 0.8	5.7	1.2 - 13.1	1.2	0.1 - 2.1	0.2	0.05 - 0.7

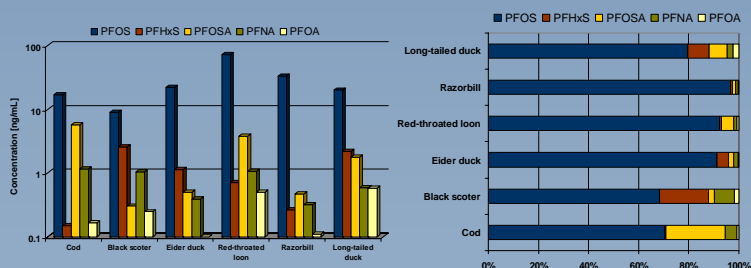


Figure 1. PFCs concentration in blood of water birds and fish from Poland

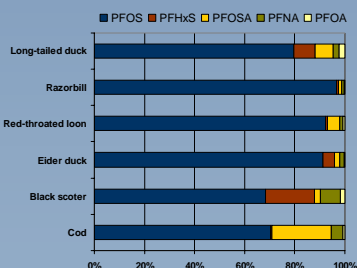


Figure 2. PFCs concentration profile in animal blood from Poland

INTRODUCTION

Worldwide pollution by perfluorooctane sulfonate (PFOS) in wild animals have resulted in the increased monitoring effort being carried out in the US and several developed countries for the last five years^{1,3}. However, they reported very little on eastern Europe except for human exposure studies². It also appeared that PFOS is only one member of related perfluorinated compounds (PFCs) instead of global concern about PFOS itself. In this study, a preliminary screening of several PFCs was performed in whole blood samples of fish and waterfowl. Cod (*Gadus morhua*) from the Gulf of Gdańsk and birds collected by near shore fishermen as by-catch during fishing in the Gulf of Gdańsk, were collected during wintering season of 2002 and 2003.

RESULTS & DISCUSSIONS

The results (arithmetic mean and range) of 65 whole blood samples are presented in Table 1. In the present study, PFOS was the predominant fluorochemical found in blood of the biota examined (Fig. 1). The highest body burden of PFOS (40-198 ng/mL) was found in the fish-eating red-throated loon. The concentration profile of PFOS and four other fluorochemicals (PFOSA, PFHxS, PFNA and PFOA) was largely similar between all 5 bird species and their concentrations in descending order were as follow: PFOS > PFHxS ≈ PFOSA > PFNA > PFOA (Fig. 2). Cod samples displayed a similar concentration profile of PFCs to that of waterfowl, however, PFHxS was significantly lower than PFOSA and somehow comparable with PFOA concentration. PFOS, PFOSA, PFNA, PFOA and PFHxS concentrations in cod blood ranged from 6 to 52, 1.0 to 13, 0.1 to 2.0, <LOQ (0.05) to 0.73, and <LOQ (0.05) to 0.83 ng/mL, respectively. We have tried to estimate bioconcentration factor (BCF) of PFCs in cod, corresponding with water analyzed from the same location (Fig. 3). The estimated average value was 34,000 (ranged 6,500 to 100,000). This is comparable to the highest BCF (21200) observed from our previous study in Tokyo Bay, Japan in 2002¹. Although all these birds species were migratory birds, biomagnification factors were calculated corresponding with cod analyzed in this study (Fig. 4). The PFCs bioconcentrate in cod as follows: PFOSA > PFOS > PFNA > PFHxS > PFOA, whereas biomagnify in birds in the order: PFHxS > PFOS > PFOA > PFNA > PFOSA. The difference between BCF and BMF pattern, especially for PFOSA and PFHxS indicates on the different metabolic capabilities among various species. In general, perfluorooctanesulfonates (PFASs) are characterized by greater tendency to biomagnify than perfluorocarboxylic acids (PFCAs). This is the first report, when BCF and BMF were calculated for PFHxS, PFOSA, and PFNA.

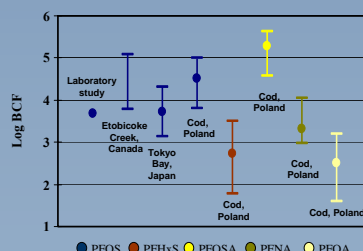


Figure 3. Bioconcentration Factor (BCF) of PFCs in cod in comparison with literature data^{1,4}

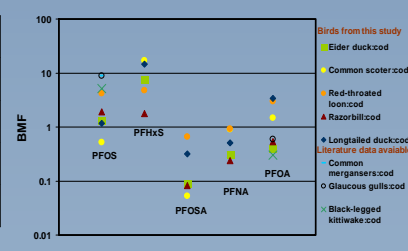


Figure 4. Biomagnification Factor (BMF) of birds from this study in comparison with previous data⁵

CONCLUSIONS

In general, results of this study suggested that fish-feeding birds including red-throated loon and razorbill showed higher PFC concentrations than birds feeding on amphipods. Interspecies differences in PFC concentrations exist in seabirds. These differences were likely to be related to their diet habits, migration habitats, exposure, and differences in metabolic capabilities. A striking finding was that one of five bird species examined showed lower concentration of PFCs in blood than cod, which occupies the lowest trophic level of all organisms surveyed. The pattern of bioaccumulation of PFCs is complicated and varies among the different compounds. Despite these difficulties, it is clear that perfluorosulfonates biomagnify in sea birds. This is the first report about PFC bioaccumulation including C4 to C9 carboxylic acids in wild animals in Poland.

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