

PERFLUORINATED COMPOUNDS (PFCs) IN THE SURFACE WATER FROM THE GULF OF GDAŃSK, POLAND

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Abstract

The widespread occurrence of certain perfluorinated compounds in the environment, in certain animal species, as well as in humans, has attracted great attention. In this study solid phase extraction (SPE) coupled with the HPLC-MS/MS instrumental technique were used to analyze surface water samples from the Gulf of Gdańsk, Poland. Perfluorooctanesulphonate (PFOS) and perfluorooctanoate (PFOA) were found to be dominant compounds in all samples with range from 296 to 959 pg/L and 341 to 625 pg/L, respectively. Further study to investigate sources and fate of PFCs in the Gulf of Gdańsk is necessary.

Introduction

Perfluorinated compounds are a group of chemicals that have been manufactured for over 50 years due to unique repelling properties have been used as surfactants and surface protectors in many products. Although these substances have probably been present in the environment and in biota as contaminants for a few decades, their environmental and biological effects have been realized only recently¹. In 2000, the largest global perfluorinated chemical producer, 3M, announced it would voluntarily phase out perfluorooctanesulfonyl fluoride production because of health effects caused by this compound and its derivatives. That caused many reports of occurrence of perfluorinated compounds in biological matrices with fewer reports in abiotic matrices. In this study we analyzed PFCs in surface water samples collected in the Gulf of Gdańsk in the southern part of the Baltic Sea.

Materials and methods

Chemicals and standards. The perfluorooctanesulphonate (PFOS), perfluorohexanesulphonate (PFHxS), perfluorobutanesulphonate (PFBS), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA) perfluorooctanoate (PFOA), perfluoronanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorotetradecanoate (PFTeDA), perfluorohexadecanoate (PFHxDA), perfluorooctadecanoate (PFOcDA) were purchased from different commercial suppliers as described earlier². Methanol, ammonium acetate and acetic acid were purchased from the Wako Pure Chemicals Industries, Ltd. (Osaka, Japan). Milli-Q water was obtained from Milli-Q Gradient A-10 (Millipore).

Collection of samples Surface water samples were collected in several locations around the Gulf of Gdańsk (Figure 1) during the cruise of S/Y "Oceania" research vessel in May 2005. All samples were collected into clean 1L polypropylene bottles with narrow mouths and screwed caps using pre – cleaned (methanol followed by Milli – Q water) stainless steel sampler. All samples were returned to the laboratory and stored in refrigerators at the temperature of 4 °C until extraction.

Extraction and purification The analytical procedure for the extraction of water samples was similar to that described earlier². Prior to the extraction of individual PFCs from water samples the OASIS WAX cartridge was preconditioned by eluting with 4 mL of 0.1 % NH₄OH/MeOH and followed by 4 mL of MeOH and 4 mL of Milli-Q water, respectively. Water samples were then passed through preconditioned cartridges at a rate 1 drop/s. The cartridges were prevented from drying at all times during sample loading. They were then washed by 4 mL 25 mM acetate buffer solution (pH 4) and discarded. The target analytes were eluted into two fractions. The first fraction (F1) and second fraction (F2) were eluted by 4 mL methanol and 4 mL 0.1 % ammonium/methanol, respectively. The eluant was concentrated to 0.5 mL under a gentle stream of high purity nitrogen.

Instrumental analysis Concentrations of PFCs in surface water samples were analyzed by the use of high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). Separation of the analytes was performed by an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) operated in electro-spray mode. A 10 μ L aliquot of seawater extract was injected onto a Keystone Betasil C₁₈ column (2.1 mm i.d. x 50 mm length, 5 μ m, 100 \AA pore size, endcapped) with 2 mM ammonium acetate and methanol as the mobile phases. Instrumental conditions were reported elsewhere².

Results and discussion

QA/QC To ensure quality of collection of samples and whole analytical procedure field blank and recovery tests as well as procedural blank and recovery tests were performed. Blank sample bottles were prepared by filling up sampling bottles with Milli-Q water. Recovery bottles were prepared by filling up with Milli-Q water and each 1ng of PFOS, PFHxS, PFBS, PFHxA, PFHpA, PFUnDA, PFTeDA, PFHxDA, PFOcDA was spiked into the bottle. Limit of quantification (LOQ) was calculated as 62.5 pg/L for PFOS, PFOA, PFHxA, PFHpA, PFHxDA, as 12.5 pg/L for PFBS, PFNA, PFDA and PFTeDA and for PFOcDA as 250 pg/L. Results of field and procedural blank remained below LOQ. Recoveries are as follow (results of field recovery are presented in brackets): PFOS; 94 % (89 %); PFHxS; 96 % (92 %), PFBS; 92 % (89 %), PFOcDA; 90 % (87 %), PFHxDA; 87 % (85 %); PFDoDA; 102 % (90 %); PFUnDA; 92 % (89 %); PFDA; 97 % (92 %); PFNA; 97 % (88 %), PFOA; 86 % (80 %); PFHxA; 100 % (88 %), PFHpA; 91 % (85 %).

Concentrations of individual PFCs in surface water from the Gulf of Gdańsk. PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA, PFDA were detected and quantified in analyzed samples (Table 1). PFUnDA, PFTeDA, PFHxDA, and PFOcDA were analyzed but remained below the limit of quantification. PFOS was found to be the most prevalent in the samples nos. A (35.4 %), E (40.2 %) and K (41.5 %), whereas in sample C PFOA become more dominant (28.2 %). PFBS was found in detectable concentration in the samples nos. A, C, E with contribution of 22.1 %, 22.2 % and 4.9 %, respectively (Figure 2).

Concentrations of PFOS and PFOA detected in water samples from the Gulf of Gdańsk were significantly lower than those observed in freshwater of Poland^{3,4} and in freshwater and coastal environments in China, Hong Kong, Japan and Korea.^{1,2,5-8}

PFOS and PFOA were found to be dominant compounds in the surface water from the Gulf of Gdańsk whereas in sediment PFOS and PFHxS are the most prevalent compounds.⁹ Further study to investigate sources and fate of PFCs in the Gulf of Gdańsk is necessary.

Table 1 Concentrations of individual PFCs in surface water samples from the Gulf of Gdańsk [pg/L].

Sample name	Perfluorosulfonates (PFASs)			Perfluorocarboxylates (PFCAs)				
	PFBS	PFHxS	PFOS	PFHxA	PFHpA	PFOA	PFNA	PFDA
A	359	<250	575	167	117	341	50.1	12.5
C	297	<250	296	148	135	377	70.4	12.5
E	116	260	953	220	178	543	89.1	12.5
K	<12.5	250	959	197	156	625	90.4	35.2

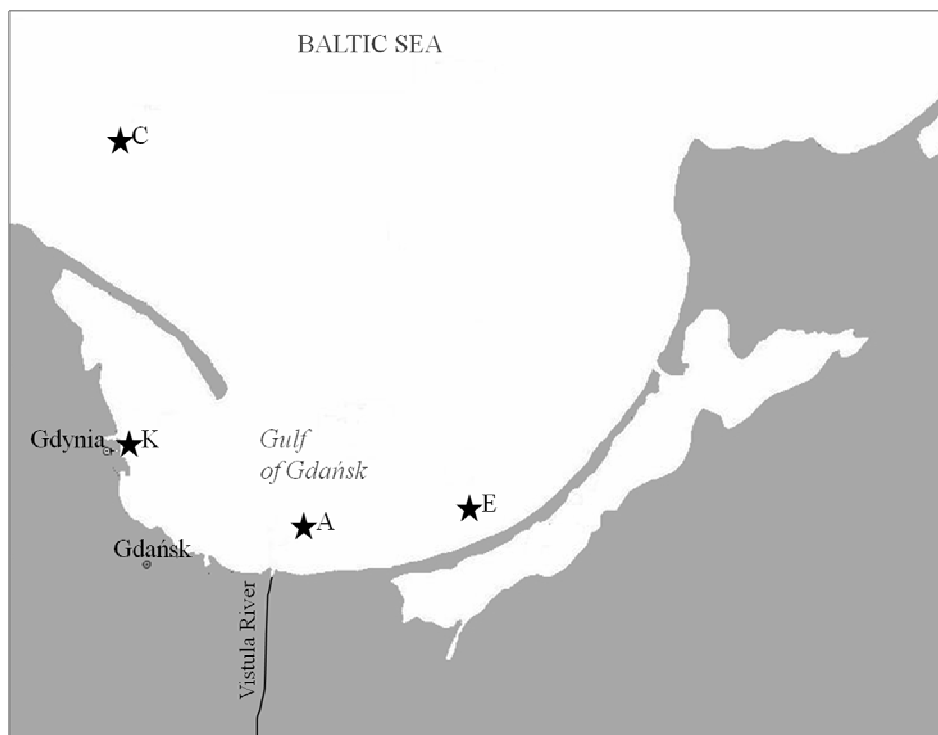


Figure 1 Map of sampling locations.

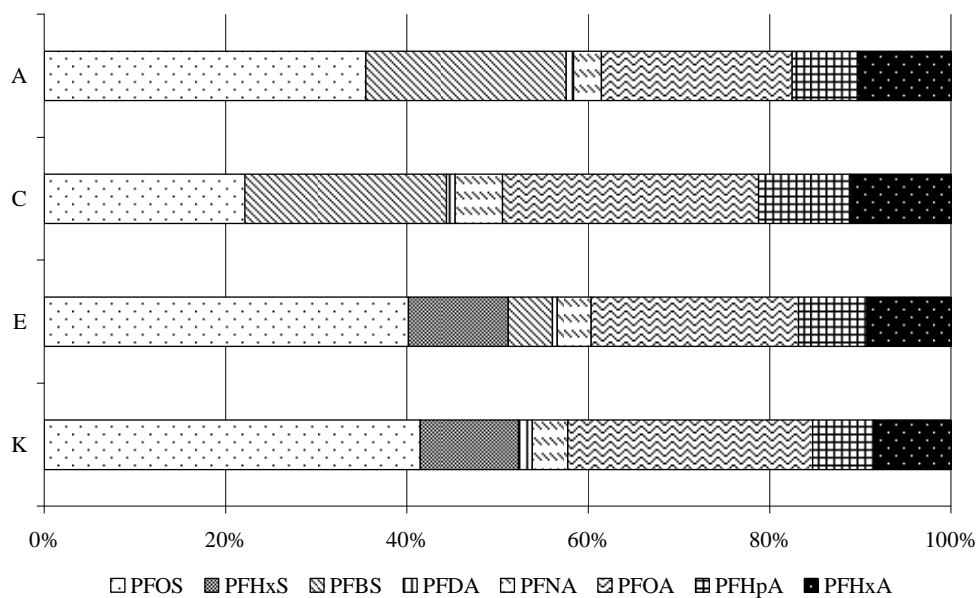


Figure 2 Contribution of individual PFCs in surface water samples from the Gulf of Gdańsk

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