

## PERFLUORINATED ALKYLATED SUBSTANCES (PFAS) IN SEDIMENTS FROM THE GULF OF GDAŃSK, POLAND

Rostkowski P<sup>1,3</sup>, Wei S<sup>2,3</sup>, Wong VYY<sup>2,3</sup>, Taniyasu S<sup>3</sup>, Miyake Y<sup>3</sup>, Yeung LWY<sup>2,3</sup>, Lam PKS<sup>2</sup>, Falandysz J<sup>1</sup>, Yamashita N<sup>3</sup>

<sup>1</sup>Department of Environmental Chemistry and Ecotoxicology, University of Gdańsk, Gdańsk, Sobieskiego 18, Poland; <sup>2</sup>Centre for Coastal Pollution and Conservation, Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, Peoples Republic of China; <sup>3</sup>National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki, Japan

### Abstract

In this study, a new method for the analysis of PFAS in sediment was developed. Liquid-liquid extraction combined with solid phase extraction and Envi-Carb cleanup coupled with the HPLC-MS/MS instrumental technique were used to analyze surface sediment samples from the Gulf of Gdańsk, Poland. Perfluorooctanesulphonate (PFOS), perfluorohexanesulphonate (PFHxS), perfluorodecanoate (PFDA), perfluoronanoate (PFNA), perfluorooctanoate (PFOA), perfluoroheptanoate (PFHpA), and perfluoroundecanoate (PFUnDA) were at detectable levels in all of the samples. PFOS and PFHxS were found to be the dominant compounds, with concentration ranges of 31 to 896 pg/g d.w. and 54 to 326 pg/g d.w., respectively. In contrast, PFOA had was found at a significantly lower concentration, ranging from 8 to 51 pg/g d.w. Further study to investigate the sources of PFAS in the Gulf of Gdańsk is necessary.

### Introduction

Perfluorinated alkylated substances (PFAS) consist of a perfluorinated carbon chain and functional end groups such sulfonate or carboxylate. The huge production and wide use of these compounds over the last half-century has led to their occurrence in wildlife and humans across the globe. PFAS have been used in a wide variety of applications, including coatings for textiles and paper packaging products, fire fighting foams, insecticides, and surface coatings.<sup>1</sup> Although a preliminary understanding of the global abundance of PFAS is emerging, little attention has been paid to the possible presence of this class of compounds in solid environmental matrices. Some data are available that indicate minimal losses of perfluorooctanesulphonate (PFOS) and perfluorooctanoate (PFOA) in rivers due to volatilization or sorption to sediment,<sup>2</sup> and other data suggest the sorption of PFOS to sediment and sludge.<sup>3</sup> It has also been suggested that the aqueous phase may be a major sink of perfluorinated compounds.<sup>4</sup> In view of this, a new method for the analysis of PFAS in sediment was developed and applied in a pilot study to evaluate the degree of PFC contamination in the Gulf of Gdańsk, Poland.

### Materials and methods

**Chemicals and standards** PFOS, perfluorohexanesulphonate (PFHxS), perfluorobutanesulphonate (PFBS), perfluorodecanoate (PFDA), perfluoronanoate (PFNA), PFOA, perfluoroheptanoate (PFHpA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), and perfluorohexanoate (PFHxA) were

purchased from various commercial suppliers, as described earlier.<sup>5</sup>  $^{13}\text{C}_4$ -PFOS and  $^{13}\text{C}_4$ -PFOA were purchased from Wellington laboratories (Guelph, ON, Canada), and the methanol, ammonium acetate, and acetic acid were purchased from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan). The Oasis®WAX was purchased from Waters (Milford, MA), the Milli-Q water was obtained from Milli-Q Gradient A-10 (Millipore), and the Envi-Carb sorbent was purchased from Supelco (Bellefonte, PA).

**Sample collection** Surface sediment samples from six locations around the area of the Gulf of Gdańsk (Figure 1) were collected by a Van Veen bottom grab during the research cruise of the S/Y "Oceania" research vessel in May 2005. The sampler was rinsed with methanol and Milli-Q water before each use. The samples were stored in clean polypropylene bags and kept frozen. After transportation to the laboratory, the samples were freeze-dried and stored at 4 °C until analysis.

**Extraction and purification** An improved extraction and cleanup method was developed based on earlier work<sup>5,6</sup> with some modifications. In brief, 5 g of freeze-dried surface sediment sample was transferred into a disposable polypropylene tube, and 1 ng of internal standard ( $^{13}\text{C}_4$  – PFOS and  $^{13}\text{C}_4$  – PFOA) was spiked directly into the sediment sample. Liquid-liquid extraction with methanol was performed followed by another liquid-liquid extraction with acetonitrile. The extract was reduced under a gentle stream of nitrogen gas, and the supernatant was shaken with the Envi-Carb sorbent to remove any pigments and decrease the matrix suppression and enhancement. Following the Envi-Carb cleanup, the solution was then subjected to further purification by solid phase extraction using an Oasis®WAX cartridge in accordance with the procedures that are described in detail elsewhere.<sup>5</sup> The extract was then subjected to a further cleanup with 25 mg of Envi-Carb cleanup. After removing the sorbent from the mixture, the volume was reduced to 0.5 mL, and 100 µL of the aliquot was injected into HPLC–MS/MS for quantification (Figure 2).

**Instrumental analysis** The concentrations of PFCs in the surface sediment samples were analyzed through high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). The separation of the analytes was performed with an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) that was interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) and operated in the electro-spray mode. The details of the instrumental parameters are reported elsewhere.<sup>5</sup>

## Results and discussion

**QA/QC** To evaluate the extraction efficiency of the method, two kinds of recovery tests were performed. During the first step, 1 ng of internal standard ( $^{13}\text{C}_4$  – PFOS and  $^{13}\text{C}_4$  – PFOA) was spiked directly into each sample. Although the recovery of  $^{13}\text{C}_4$ -PFOS (in the range of 60 to 121%) was acceptable, the recovery of  $^{13}\text{C}_4$ -PFOA was relatively low (22 to 96%). For the second recovery test, one of the samples was duplicated and was spiked with 1 ng each of PFOS, PFHxS, PFBS, PFDA, PFNA, PFOA, PFHpA, PFUnDA, PFDoDA, and PFHxA so that a matrix-spike recovery test could be performed. The recovery levels of the native standards with subtracted background values are as follows. PFOS: 104%, PFHxS: 52%, PFDoDA: 65%, PFUnDA: 68%, PFDA: 103%, PFNA: 101%, PFOA: 102%, PFHpA: 108%, and PFHxA: 114%. The limit of quantification (LOQ) was calculated as 2 pg/g for all of the chemicals.

**Concentrations of PFAS in surface sediment from the Gulf of Gdańsk.** PFOS, PFHxS, PFUnDA, PFDA, PFNA, and PFOA were found to be above the LOQ in all of the samples (Table 1). PFOS and PFHxS were found

to be the dominant compounds in all of the samples, with the greatest concentration of 896 pg/g for the former occurring in location C (PFOS) and 326 pg/g for the latter occurring in location I (PFHxS). PFOS was found to be most prevalent in samples B, C, and D (63%, 74%, 69%, respectively), whereas PFHxS was found to be dominant in samples I, J, and N, accounting for 45%, 58%, and 43%, respectively, of the total PFCs (Figure 3). The mean concentration of PFOS in these samples was within the range of concentrations that is reported in the literature, but the concentration of PFOA was lower than that reported for Tokyo Bay<sup>9</sup> and the Ariake Sea<sup>4</sup>, Japan and coastal areas of the Netherlands.<sup>7</sup> Further study is needed to investigate the sources of PFAS in the Gulf of Gdańsk.

Table 1. Concentrations of PFAS in surface sediment samples from the Gulf of Gdańsk, Poland (pg/g, d.w.)

Sample name	Perfluorosulfonates (PFASs)			Perfluorocarboxylates (PFCAs)					
	PFOS	PFHxS	PFDODA	PUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
B	291	109	5	28	12	8	8	n.d	n.d
C	896	111	9	82	45	37	25	4	2
D	829	179	7	74	22	41	21	5	14
I	281	326	4	17	9	36	51	5	n.d
J	169	288	3	9	5	6	12	n.d	n.d
N	31	54	n.d	3	6	4	24	2	n.d

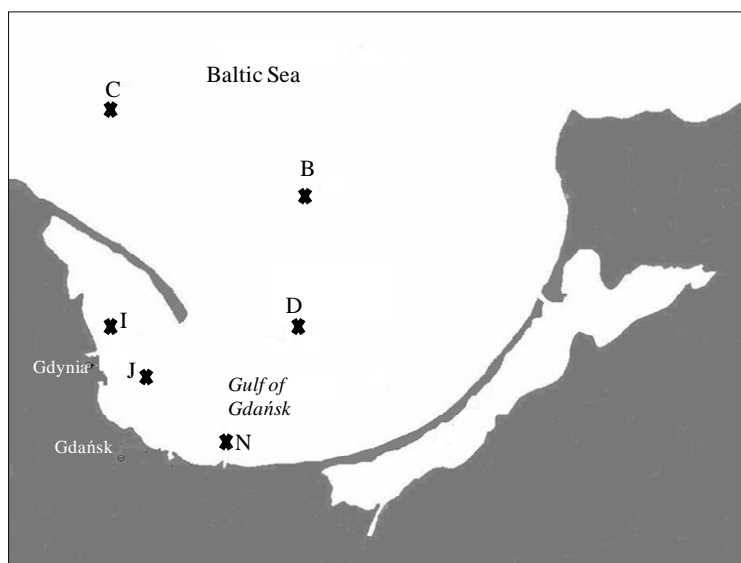


Figure 1. Map of sampling locations

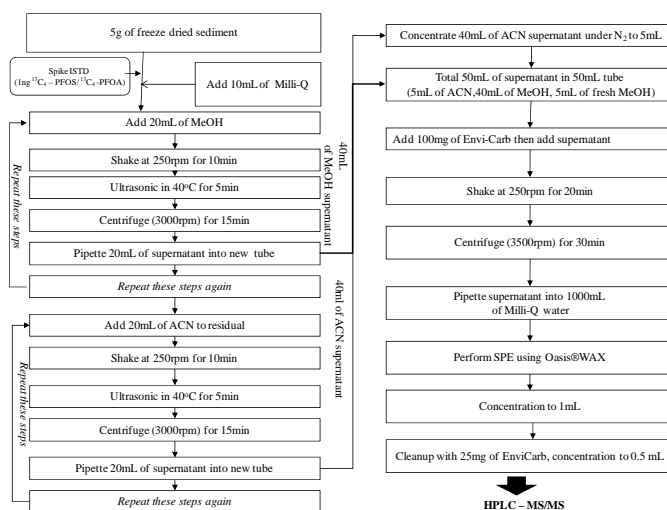


Figure 2. Schematic diagrams of the extraction procedures

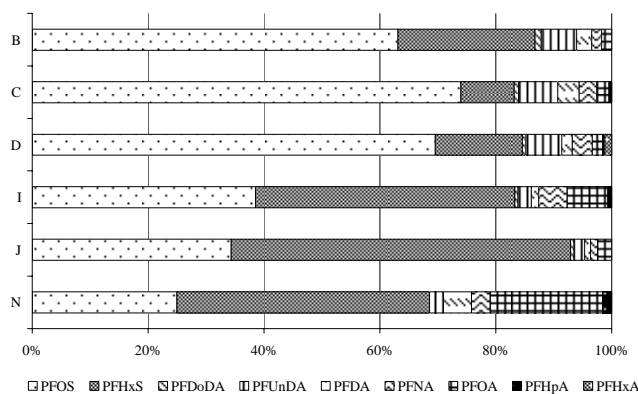


Figure 3. Composition of individual PFCs in surface sediment samples from different locations

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