Occurrence of Perfluorinated Organic Acids in the Water of the North Sea

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Introduction

Perfluorinated organic acids (PFC) and their derivatives are industrially produced since many years in very large quantities and are used for many purposes [1]: Perfluoroalkyl sulfonates are applied, e.g., as surfactants and surface protectors to carpets, leather, paper, fabrics and many more. In addition, some sulfonated and carboxylated PFCs have been utilized in or as fire fighting foams, alkaline cleaners, shampoos, and insecticide formulations. Due to the large production quantities and the persistence in the environment, perfluorinated compounds are meanwhile globally distributed. Perfluorooctanesulfonic acid (PFOS) and other long chain perfluorinated chemicals have been detected in blood of ringed seals, in polar bears, arctic foxes, mink, birds, and fishes collected in the USA, at the coasts of the Baltic and Mediterranean Sea and in the Arctic[1,2,3,4,5,6]. Because of the findings of perfluorinated compounds in Arctic biota samples, it is of special interest to investigate their long range transport. Due to their high polarity, a transport by the water phase is likely. However up till now, only few studies report on the occurrence in surface or ground water and none in sea water [7]. The aim of this work was, therefore, to develop a method for the determination of perfluorinated organic acids in seawater and to study their occurrence and distribution in the North Sea.

Methods and Materials

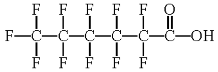
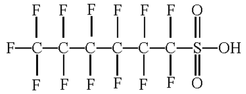
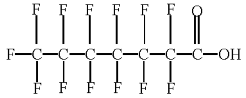
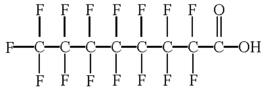
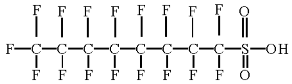
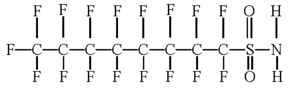
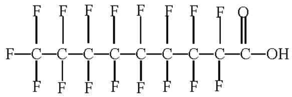
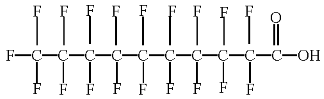
Water samples were collected in 10 L glass bowls in 5 m water depth on cruises with RV "Gauss" in March and August 2003 [8]. The water was acidified with 10 mL of hydrochloric acid (25 %) to a pH of 2 to 3, and a solution of deuterated internal standards (d_6-diuron and d_3-mecoprop) is added. 9 L of this sample are pumped over a cartridge filled with 4 g of Chromabond HR-P resin (Macherey-Nagel, Düren, Germany) [9]. After washing with pure water and drying in a stream of nitrogen, the cartridges are eluted with 100 mL of methanol in the reversed direction. After concentrating the extract to 200 µL(rotary evaporator, then N_2-stream) 8 µL of this solution are injected into the HPLC-MS-MS system. (Agilent 1100 Series autosampler, binary pump, column oven (23°C) and Applied Biosystems API 2000 LC-MS-MS system, ESI source). A Synergi Hydro-RP phase column (Phenomenex) is used (2mm, 7.5 cm). Eluent A consists of water with 10 mM ammonium acetate and 10 mM acetic acid, pH 4.5, eluent B is methanol with the same concentrations of buffering compounds.

Table 1: HPLC gradient conditions

Time [min]	-15	0	0.1	6	13	23	36	46
Flowrate [µL/min]	170	170	170	190	220	220	220	220
Composition of mobile Phase [%B]	20	20	20	40	55	70	95	95

Mass spectrometric parameters, and their detection response are summarised in the table below.

Table 2: Mass spectrometric parameters

Compound		Precursor Ion	DP	Fragment Ion	CE	S/ N for 500 pg abs.
PFHxA		313	-16	268,4	-8	389
PFHxS		398,9	-86	79,6	-60	1530
PFHpA		362,9	-21	318,7	-10	949
PFOA		412,9	-21	368,5	-12	888
PFOS		498,8	-91	79,8	-74	742
PFOSA		498	-91	77,6	-60	1250
PFNoA		462,9	-21	418,8	-12	557
PFDeA		512,9	-16	468,7	-14	482

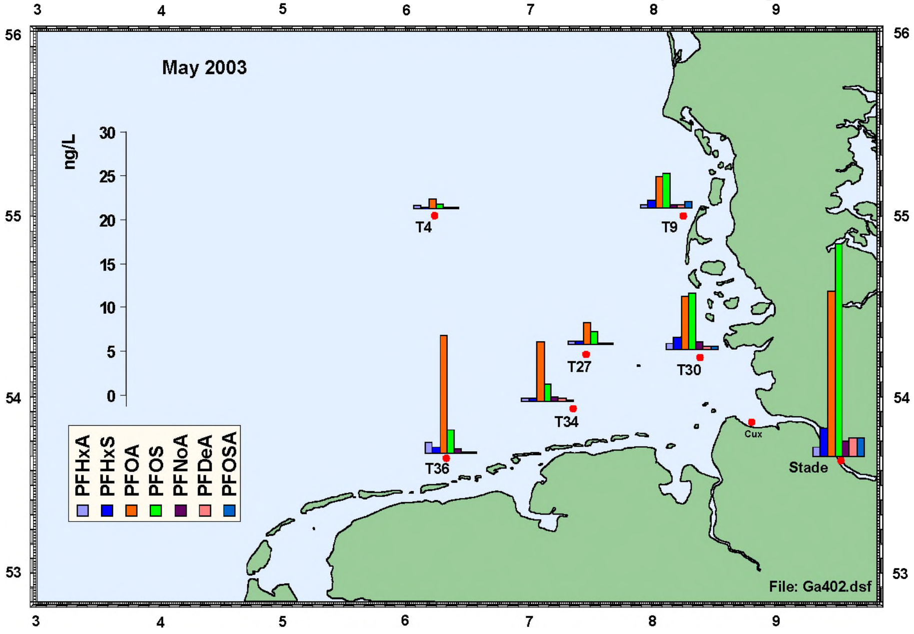
The mass spectrometric determination is carried out by neg. electrospray ionisation (ESI) in the multi reaction mode (MRM). The precursor ions are always the $(M-1)^-$ -ions; for the sulfonic acids the fragmentation to the SO_3^- -ion is observed, while for carboxylic acids the loss of CO_2 is monitored.

Results and Discussion

Performance of the developed method: The presented method consisting of SPE extraction/ enrichment and HPLC-neg.-ESI-MS-MS enables the selective and sensitive determination of a number of perfluorinated organic acids in river, coastal and marine water samples. The limits of determination (S/N= 10) range between 0.05 and 0.5 ng/L. For a further improvement of the sensitivity an additional cleanup-step might be necessary. Special care has to be taken for blank control and prevention of contamination. Especially the perfluorinated carboxylic acids are susceptible to contamination, e.g., by Teflon^{R}, and Viton materials, while for the sulfonic acids less contamination problems have been observed. The selection of internal standards could not yet be solved to our full satisfaction. The availability of stable isotope marked analogues would optimise the procedure considerably.

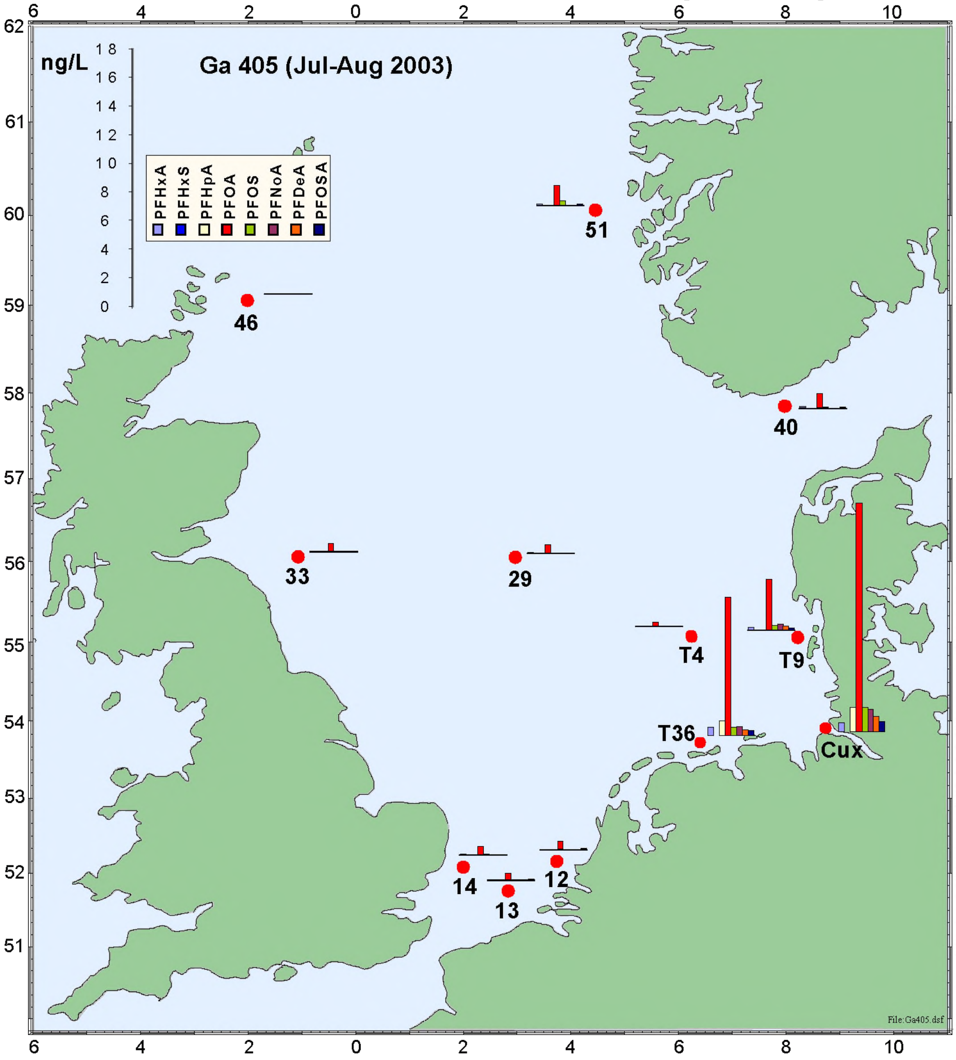
Occurrence of perfluorinated acids in the water of the North Sea: Up till now environmental concentrations of the PFC have been described mainly for biota and only few for surface water samples. The presence in river water on the one side and the widespread occurrence in marine fish and mammals render it highly likely that these PFC are found in marine waters as well. Because of the high polarity of the acids a transport route by the water phase might be of great importance.

Figure 1: Concentrations of PFCs in surface-near water (5 m) in May 2003 [ng/L]



The investigations started in the estuary of the river Elbe – one of the most important sources for pollutants entering the German Bight and the southern and eastern North Sea - and continued to the open sea. The distribution of the concentrations of 7 PFCs is shown in Fig.1 for the German Bight in May 2003. The highest concentrations were observed for PFOA and PFOS. At the mouth of the river Elbe values of ca. 20 ng/L were encountered, while the other compounds range from 1 to 3 ng/L. Along the Elbe plume towards the north concentrations of the major compounds decrease to 3 to 6 ng/L (at a salinity of 28 to 30), while to the open sea they drop to 0.5 to 1.2 ng/L at station T4 (salinity 34.4). In the southern German Bight at station T34 and T36 (salinity: 32) a different pattern with higher PFOA but low PFOS was observed, indicating a different source. In August 2003 the investigation were extended into the whole North Sea (Fig. 2). The distribution of PFOA

Figure 2: Concentrations of PFC in surface-near water (5 m) in August 2003 [ng/L]



was very similar to that of the May survey, again there was observed a high value at station T36. However, the PFOS concentrations this time were much lower. At most stations of the open sea only PFOA could be detected at concentrations of ca. 0.5 ng/L, all other target compounds were below the present detection limits. The concentrations near the mouth of the river Rhine (stations 12 and 13) were not elevated, but the salinity of 34.4 of the samples indicates that there was almost no riverine freshwater present at these sampling stations. At the Norwegian coast (stations 40, 51), however, slightly higher values of ca. 1 ng/L were found which could be attributed to the outflow of Baltic sea water (salinity 28 to 30).

The occurrence of PFC in the North Sea has not been described before. The concentrations of the major occurring PFOA and PFOS determined on the two cruises are within a similar range as other polar pollutants such as phenylurea, triazine or phenoxyacetic acid herbicides. They are present in part well above classical contaminants like chlorinated hydrocarbons (HCH, DDT group, PCB) [10].

The investigations demonstrated, that the developed method is suitable for the study of the distribution of perfluorinated organic acids in the coastal and open sea water. For extended studies into more remote areas, however, some improvements concerning the LOD are necessary.

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