Occurrence of Perfluorinated Organic Acids in the Water of the North Sea and Arctic North Atlantic

C. Caliebe, W. Gerwinski, N. Theobald and H. Hühnerfuss

Introduction

In recent years, perfluorinated organic acids (PFCs) and their derivatives have attracted large attention as a new group of environmental pollutants because they are industrially produced in large quantities and proved to be very persistent in the environment. Perfluorooctyl sulfonates and carboxylic acids are applied, e.g., as surfactants and surface protectors to carpets, leather, paper, fabrics and many more. Further, PFCs are used 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. Up till now, only few studies report on the occurrence in seawater and to study their occurrence and distribution in the North Sea and adjacent sea areas.

Methods and Materials

Analytical scheme for sea water samples

Sampling of sea water (10 L glass sphere water sampler; 5 m depth)

Acidifying with 5 mL HCl (25 %)

Addition of internal standards (D1-Mecoprop)

Solid phase extraction 2 g Chromatix HR-P adsorbent; NEPOS-Workstation

Drying the adsorbent with nitrogen (flow rate 7 L/h)

Elution of 40 mL methanol containing acetate buffer (flow rate 5 mL/min, reverse to the extraction direction)

Concentrating to 250 µL

HPLC-ESI-MS-MS

Liquid Chromatography - Mass Spectrometry

HPLC-System: Agilent 1100 Series (autosampler, binary pump, column oven: 35°C)

Column: Syngene Hydro-RP (Phenomenex), (2 mm, 7.5 cm)

Eluent A: water with 10 mM ammonium acetate + 10 mM acetic acid pH 4.5

Eluent B: methanol with 10 mM ammonium acetate + 10 mM acetic acid

HPLC-Gradient Program

Quality Control

Recovery %

Limits of Determination [pg/L]

Concentration pg/L Seawater

Results and Discussion

The presented method enables the selective and sensitive determination of a number of perfluorinated organic acids in water samples. In comparison to our first report,1 the limits of determination (S/N = 10) were improved by a factor of 10 and range between 5 and 20 pg/L. The limits of determination for PFDA and PFNoA is limited by blanks and is for both compounds 30 pg/L.

The investigations started in 2003 in the German Bight, a subregion of the North Sea, and were continued and expanded in 2004 (Arctic North Atlantic, s.b.) and 2005 (Baltic Sea, North Sea). In addition, 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 - was included in the studies. The distribution of the concentrations of 8 PFCs is shown in Fig. 2 for the German Bight in May 2004.

The highest concentrations were observed for PFDA and PFOS. At the mouth of the river Elbe values of ca. 7 ng/L were encountered, while the other compounds ranged from 0.3 to 2 ng/L. Along the Elbe plume towards the north, concentrations of the major compounds decreased to ca. 1 ng/L, while to the open sea they dropped to 0.5 and 1.2 ng/L at station NSB2.

In June 2004 the investigations were extended into the Arctic (Fig. 3). The developed method proved to be sensitive enough to detect most of the PFCs, PFOS and PFDA were present in all samples with concentrations ranging between 20 and 120 pg/L. The C4 acids ranged between 10 and 40 pg/L. A slight gradient was observed with a minimum for all compounds in the center of the Greenland Sea.

The results show that PFCs are widely distributed in marine waters. A distinct gradient from sources from the European continent into the North Sea could be observed. Low level "background concentrations" in a remote area could be found as well.

References


Acknowledgments

This work was supported by the German Environmental Agency (Umweltbundesamt, Berlin) by the project No. 202 202 213.

Contact: www.buh.de / christina.caliebe@buh.de