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Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water

Lutz Ahrens [a,b,*], Wolfgang Gerwinski [c], Norbert Theobald [c], Ralf Ebinghaus [a]

[a] GKSS Research Centre Geesthacht, Department for Environmental Chemistry, Institute for Coastal Research, DE-21502 Geesthacht, Germany
[b] Leuphana University of Lüneburg, Institute for Ecology and Environmental Chemistry, Faculty of Environment and Technique, DE-21335 Lüneburg, Germany
[c] Federal Maritime and Hydrographic Agency (BSH), DE-20359 Hamburg, Germany

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ABSTRACT

The spatial distribution of 15 polyfluoroalkyl compounds (PFCs) in surface water was investigated in the North Sea, Baltic Sea and Norwegian Sea. In addition, an interlaboratory comparison of the sampling techniques and analysis was conducted. Highest concentration in the North Sea was found near the coast, whereas the ∑PFC concentration decreased rapidly from 18.4 to 0.07 ng l^{-1} towards the open North Sea. The river Elbe could identify as a local input source for PFCs into the North Sea, whereas perfluorobutanoic acid (PFBA) was transported into the sampling area with the easterly current. In contrast to the North Sea, the distribution of PFCs in the Baltic Sea was relatively homogenous, where diffuse sources dominated. In general, the composition profile was influenced from local sources caused by human activities, whereas atmospheric depositions of here analysed PFCs were negligible, but it could have possibly an influence on low contaminated sites like the open North Sea or Norwegian Sea.

1. Introduction

Polyfluoroalkyl compounds (PFCs) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are man-made chemicals which are found ubiquitously in water (Yamashita et al., 2005), sediment (Higgins and Luthy, 2006), wildlife (Giesy and Kannan, 2001) and humans (Yeung et al., 2006), and are persistent against the typical environmental degradation processes (Kissa, 2001). The longer-chained PFCs are known to be bioaccumulative (Martin et al., 2003) and have possible adverse effects on human and wildlife (Austin et al., 2003; Goecke-Flora and Reo, 1996).

The perfluorinated acids have a high water solubility, low pK_a values and are therefore dissociated at environmentally relevant pH values (Kissa, 2001). They can be found mostly in water or can bind to particles, sediments and soil (Higgins and Luthy, 2006). Neutral PFCs as perfluoroalkyl sulfonamides (FASAs), perfluoroalkyl sulfonamido ethanols (FASEs) and fluorotelomer alcohols (FTOHs) are not as water-soluble as the perfluoroalkyl acids and also more volatile. They can degrade in the atmosphere (Ellis et al., 2004; Martin et al., 2006) as well as under aerobic conditions in activated sludge (Rhoads et al., 2008) to perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs). Because of their unique characteristics they are widely used as processing additives during fluoropolymer production and as surfactants in consumer applications, including surface coatings for carpets, furniture and paper products over the past 50 years (Kissa, 2001; Prevedouros et al., 2006). From the production and use of these products, PFCs can be released into the environment. Known pathways of PFCs in the aqueous environment are effluents from waste water treatment plants (WWTPs) (Schultz et al., 2006), landfills (Kallenborn et al., 2004), precipitation (Scott et al., 2006), runoff from contaminated soil by precipitation (Skutlarek et al., 2006) or after the usage of aqueous film forming foams (AFFFs) (Moody and Field, 2000). The PFCs can further transport directly or via rivers to the coastal environment, but data on the transport and distribution of PFCs in the coastal area are scarce. Sinks and reservoirs of PFCs could be the sediment and deep ocean waters (Higgins and Luthy, 2006; Prevedouros et al., 2006; Yamashita et al., 2008).

The aim of this study was to investigate the occurrence and spatial distribution of PFCs in surface water close to industrial areas and far away from these potential anthropogenic sources. Samples were taken in the North Sea, Baltic Sea and Norwegian Sea, where we compared the concentration profiles between river estuaries, coastal waters, in brackish as well as salt water, and open sea water. In addition, the dissolved phase and particulate phase were extracted separately to investigate the partitioning behaviour of PFCs. Finally, the performance of the sampling and analysis was examined by an interlaboratory comparison study between the GKSS Research Centre Geesthacht GmbH (GKSS) and the Federal Maritime and Hydrographic Agency (BSH) at 19 sampling stations in the North Sea.

* Corresponding author. Address: GKSS Research Centre Geesthacht, Department for Environmental Chemistry, Institute for Coastal Research, DE-21502 Geesthacht, Germany. Tel.: +49 4152 87 2353; fax: +49 4152 87 2366.
E-mail address: lutz.ahrens@gkss.de (L. Ahrens).

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2. Materials and methods

2.1. Sampling campaign

Surface water samples were taken at 6 stations in the North Sea/Norwegian Sea (sampling stations I–VI), 22 stations in the North Sea/German coast (sampling stations 1–22) and 18 stations in the Baltic Sea (sampling stations A–R) in 2007 (Fig. 1). Details of the sampling and the water temperature and salinity are presented in Table S1 in the Supplementary material. Two litre water samples were collected in brown glass bottles via the ships' intake systems at ~5 m below the surface. At 14 sampling stations in the North Sea were collected duplicate samples for quality control. In addition, at sampling stations 1–8, 10, 11 and 13–21 water samples were collected in 10 l glass bowls at the same water depth as the 2 l water samples, in order to compare the two different sampling and analysis techniques. The standards used in this study are listed in Table S2 in the Supplementary material. Methanol (SupraSolv), acetonitrile (LiChrosolv), ammonium hydroxide (25% for analysis), formic acid (98–100% suprapure) and ammonium acetate were purchased from Merck (Darmstadt, Germany).

The 2 l water samples were filtered directly after sampling onboard or the following days using glass fibre filters (GFF, GC/C, Whatman, ø 47 mm, >1.2 μm). The dissolved phase samples were stored at 4 °C while the GFF were sealed in test-tubes and stored at −20 °C in a freezer until the sample extraction. Field blanks (FB) were taken every tenth sample for the filtrate and GFF to test for possible blank contamination (for details see Ahrens et al., 2009). The 10 l water samples were filtrated before solid phase extraction (SPE) by a glass wool bed.

2.2. Sample analysis

2.2.1. PFC analysis of the 2 l water samples from the North Sea, Baltic Sea and Norwegian Sea

The filtrate was extracted by SPE with Oasis WAX cartridges (Waters, 150 mg, 6 cc, 30 μm) and the suspended particulate matter (SPM, >1.2 μm) on the GFF was extracted by sonication (for details see Ahrens et al. (2009)).

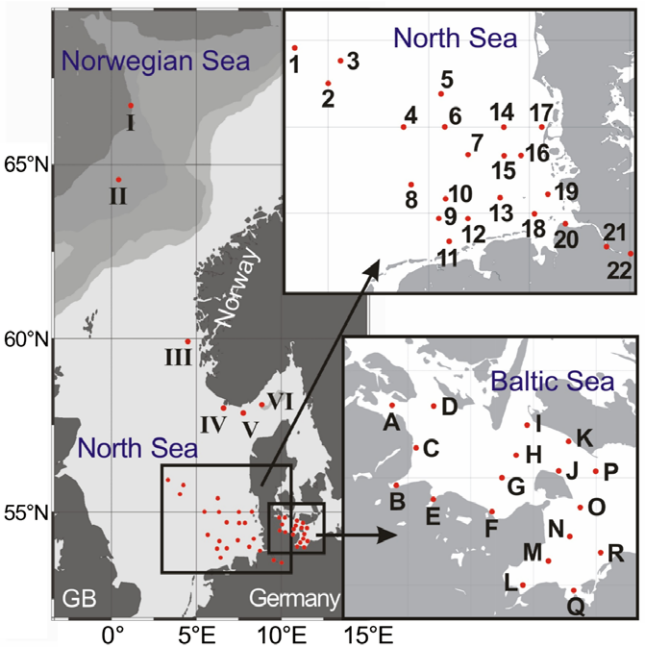

Fig. 1. Geographic locations of the water sampling sites in the North Sea, Norwegian Sea and Baltic Sea.

The extracts from the dissolved and particulate phase samples were analysed using high performance liquid chromatography coupled with tandem mass spectrometry (HPLC–MS/MS). An HP 1100 HPLC-system (Agilent Technologies) was used with a Synergi Hydro RP 80A column (150 × 2 mm, 4 μm) by Phenomenex, combined with a suitable guard column: Synergi 2 μm Hydro RP Mercury (20 × 2 mm, 2 μm). Millipore water and methanol were used as mobile phases, both with 10 mM ammonium acetate as an ionisation aid. The flow rate was set to 200 μl min^{-1} and 10 μl of the sample was injected. The triple-quadrupole mass spectrometer, supplied by Applied Biosystems/MDS SCIEX (API 3000), used an electrospray ionisation (ESI) interface in negative ion mode (for details see Ahrens et al. (2009)).

2.2.2. PFC analysis of the 10 l water samples from the North Sea

A solution of IS mix (i.e., [$^{13}C_2$]-PFOA and [$^{13}C_4$]-PFOS, 1000 μl of a 0.01 μg ml^{-1} solution) was added. The water samples were extracted with an half-automated extraction system (APOS, Automated Extraction System for Organic Substances) using a 12 ml polypropylene cartridge filled with 1.7 g glass fibre cotton for the separation of the particles and 1.7 g of Chromabond HR-P resin (Macherey–Nagel, Düren, Germany) for the enrichment of the target compounds. After preconditioning with 200 ml methanol and 100 ml Millipore water the 10 l of the sample was pumped over the cartridge with a loading rate of approximately 100 ml min^{-1}. After washing with 50 ml Millipore water and drying in a stream of nitrogen, the cartridges were eluted with 60 ml of 2.5 mM acetic acid and 5 mM ammonium acetate in methanol (pH 6) in the reversed direction without the glass fibre cotton. Finally, the extracts were reduced to 250 μl using rotary evaporation and under a nitrogen stream.

An HP 1100 HPLC-system (Agilent Technologies) was used with a Synergi Polar RP (50 × 2 mm, 4 micron) coupled with a Synergi Hydro RP (75 × 2 mm, 4 μm) by Phenomenex. Millipore water and methanol were used as mobile phases, both with 10 mM ammonium acetate and 10 mM acetic acid (pH 4.5). The gradient flow rate was set from 200 to 220 μl min^{-1} and 7 μl of the sample was injected. The triple-quadrupole mass spectrometer, supplied by Applied Biosystems/MDS SCIEX (API 2000), used an ESI interface in negative ionisation mode.

2.3. Quality control

The analytical quality of the laboratory has been approved in interlaboratory studies (van Leeuwen et al., 2009). As standard procedure, FB, method quantification limits (MQLs), recoveries of spiked samples and duplicate samples were examined in the dissolved and particulate phase for the 2 l water samples (GKSS) (see Table 1). In addition, the method performance of the FB, MQL and recoveries for the analysis of PFCs in the dissolved phase was compared between the 2 l (GKSS) and 10 l water sampling (BSH) (Table 1).

All fluorinated materials which could come in contact with the sample during the sampling, sample preparation and instrumental analysis were removed (Yamashita et al., 2004). All FB, using 1 l Millipore water, which were extracted in the same manner as the samples, were usually below the MQL, but in some FB contamination levels for PFOA (n.d.–0.046) and PFDA (n.d.–0.016) were quantified. The FB for the 10 l water samples were all not detected. One explanation for the lower blank contamination could be the higher sampling volume of 10 l in comparison to 2 l for the GKSS which result in lower blank contamination per litre water sample. No background contamination was detected in the FB for the particulate phase. MQLs were calculated for substances that were found in real samples using the signal to noise ratios of 10. The MQLs were in low ppq level for both methods. Recoveries for the