

POLYFLUORINATED COMPOUNDS IN AIR SAMPLES OF THE GERMAN BIGHT AND HAMBURG

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Introduction

Perfluorocarboxylic acids (PFCA) and -sulfonic acids (PFSA) such as PFOA and PFOS belong to the group of polyfluorinated organic compounds that have been distributed globally in the past due to extensive industrial application and consumer use¹⁻⁵. Beneath their transport within the water phase⁶⁻⁸, atmospheric transport and subsequent degradation of volatile and semi-volatile precursor compounds like fluorotelomer alcohols (FTOH), perfluorinated sulfonamides (FASA) and perfluorinated sulfonamido ethanols (FASE) to the persistent acids, is assumed to be a main transport mechanism^{9,10}. Only few studies described the distribution of polyfluorinated compounds in air^{2,11}. Jahnke et al.² found decreasing concentration levels of FTOH, FASA, and FASE towards the southern hemisphere along a north south transect from Bremerhaven to Cape Town. Shoeib et al.¹¹ determined FTOH and FASE in air masses of northern Canada and the North Atlantic. Concentrations of these (semi-)volatile polyfluorinated substances have also been determined at some selected locations in North America, Japan, Germany, and the UK¹²⁻¹⁶. In this study, we show the regional distribution of gas-phase and particle-bound polyfluorinated compounds in the German Bight (North Sea) and Hamburg, Germany.

Materials and Methods

Daily air samples were taken onboard the German research vessel VWFS Atair during a cruise from Hamburg to the German Bight, North Sea from 30th October to 06th November 2007 (Atair 155, figure 1). Samples were taken in parallel using two High Volume Air Samplers located at the observation deck of the ship approximately 16 m above sea level. The air samplers were controlled by a computer connected to the ship's meteorological system avoiding that sampling was occurring with relative winds from aft. In general, 350 m³ of air were sampled. Cartridges filled with a sandwich of polyurethane foam (PUF) and Amberlite XAD-2 resin and glass fibre filters were used to collect gaseous and particle-bound polyfluorinated compounds. After the sampling, samples were sealed air tight and stored at -20 °C until analysis in the laboratory. During the cruise, field blanks were taken and treated the same way as real samples.

All cartridges were extracted thrice with acetone:MTBE 1:1. For the extraction, the solvent was allowed to soak into the adsorption material for 1hr (extraction step 1 and 2) and ½ hr (extraction step 3). The solvent was evaporated with ethyl acetate as keeper using rotary evaporators and nitrogen. Filters were extracted using fluidized bed extraction. Filters of sampler A were extracted with acetone:MTBE 1:1 to determine the neutral volatile polyfluorinated compounds. Filters of sampler B were extracted with methanol to determine ionic perfluorinated carboxylic and sulfonic acids. During sampling and analyses, mass labeled compounds were used as internal and injection standard to correct for variations. Quantification of neutral compounds was performed by gas chromatography/mass spectrometry with positive chemical ionization (PCI) using the selected ion monitoring (SIM) mode. Quantification of ionic compounds (perfluoro carboxylic acids (PFCA), perfluoro sulfonic acids (PFSA), perfluoro sulfinates (PFSI)) occurred on an HPLC-ESI-MS/MS. Compounds were classified as not detected (n.d.) with signal/noise below 3 and not quantified (n.q.) with signal/noise below 10. In addition to field blanks, solvent blanks (for gaseous samples) and filter blanks (for particle samples) were taken with each set of samples that was extracted. Since some compounds were detected in blank samples occasionally, all concentrations reported were blank-corrected.

Results and Discussion

PFC were almost exclusively detected in the gas phase. These concentrations are presented in table 1. Regional differences of PFC concentrations in air samples could be observed in the German Bight, North Sea. In general, low PFC concentrations were observed in samples of the German Bight whenever air masses of marine origin were sampled. In this study, highest concentrations were found in the port of Hamburg (sample 7). This is

probably due to local sources since air mass back trajectories point at northern air masses having been sampled (figure 2). Elevated PFC concentrations of sample 2 might be explained by air masses that have been passed the industrialized areas of the UK and the Netherlands (figure2).

Concentrations of gas-phase FTOH, FASA, and FASE were in about the same ranges as in other authors' studies^{2,11,12,17}. High PFC concentrations found in sample 7 (Hamburg) were consistent with concentrations determined in this and other urban regions^{11,12,14}. The low concentrations of volatile polyfluorinated compounds were similar those determined for marine regions^{2,11}. Partly in contrast to other studies^{11,17}, (semi-)volatile polyfluorinated compounds (FASA, FASE) were detected only occasionally in low concentrations in the particulate phase. Particle-bound PFCA (C4-C10) and PFSA (C4-C8) were determined in low concentrations only. Maximum concentrations were observed for PFOS and PFOA. PFOS and PFOA concentrations in the port of Hamburg (1.4 pg m⁻³ and 3.7 pg m⁻³, respectively) were lower than those of sample 2 (2.7 pg m⁻³ and 8.3 pg m⁻³, respectively).

As observed in other European studies^{2,12,17}, FTOH were the dominating class of compounds with 8:2 FTOH in maximum concentrations. An increase of neutral PFC concentrations was mainly due to the FTOH; proportions of FASA, FASE, and FTA usually remained below 5 to 10 %.

Acknowledgements

Annekatriin Dreyer was funded by the scholarship program of the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU). We thank Norbert Theobald and Wolfgang Gerwinski from the Federal Maritime and Hydrographic Agency of Germany (BSH) for the organization of and the possibility to take part in this cruise. Thanks to the crew of VWFS Atair for their valuable help throughout the entire sampling campaign.

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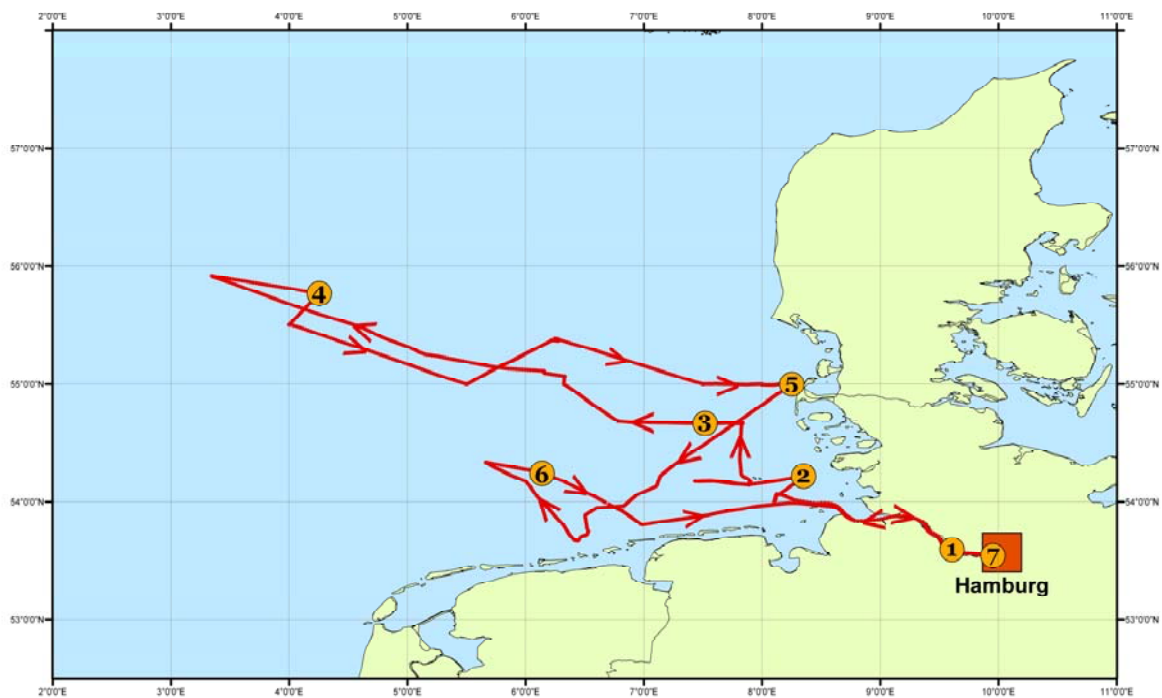


Figure 1: Track of VWFS Atair in the German Bight. The numbered dots mark the location of sample input. Samples were taken in between this and the following location. Sample 7 was taken in the port of Hamburg.

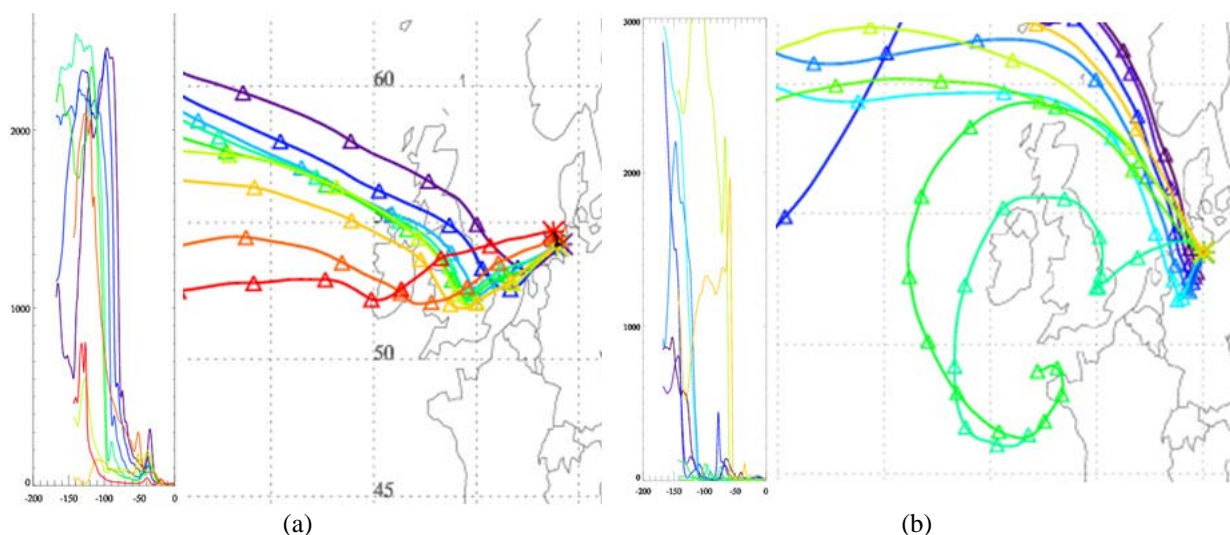


Figure 2: Details of seven days air mass back trajectories calculated for 3 hours intervals as generated by Hysplit 4.0 using GDAS data (<http://www.arl.noaa.gov/ready/hysplit4.html>) for (a) sample 2 and (b) sample 7. Triangles mark the position of the air parcel in 12 hours intervals.

Table 1: Gas phase concentrations (pg m^{-3}) of neutral polyfluorinated compounds.

pg/m^3	1	2	3	4	5	6	7
4:2 FTOH	1.4	n.d.	n.d.	2.3	1.8	1.4	n.d.
6:2 FTOH	4.9	8.5	5.8	5.7	3.3	14.8	12.3
8:2 FTOH	10.3	55.7	13.6	16.0	8.2	28.0	128.6
10:2 FTOH	2.7	14.5	3.6	5.7	2.1	6.7	28.6
12:2 FTOH	1.6	3.1	1.3	1.3	1.5	2.3	7.9
ΣFTOH	21.0	81.8	24.2	31.1	17.0	53.2	177.4
6:2 FTA	n.d.	5.7	n.d.	n.d.	n.d.	n.d.	4.2
8:2 FTA	2.2	3.2	1.9	1.7	1.8	3.6	14.8
10:2 FTA	0.9	1.3	0.9	1.2	0.8	1.2	6.5
ΣFTA	3.0	10.2	2.8	3.0	2.6	4.8	25.5
MeFBSA	7.0	5.8	3.1	3.4	6.0	4.7	3.4
MeFOSA	3.7	1.5	2.5	3.3	3.9	3.1	2.4
Me2FOSA	n.d.	0.4	n.d.	1.5	0.5	0.7	0.5
EtFOSA	1.6	0.8	0.4	1.4	1.6	1.1	0.5
PFOSA	2.5	1.9	3.4	2.9	n.q.	n.d.	7.2
ΣFASA	14.8	10.5	9.5	12.5	11.9	9.7	14.0
MeFBSE	0.6	1.4	1.0	1.3	0.6	1.0	2.5
MeFOSE	1.3	0.9	2.0	2.6	2.2	1.2	1.4
EtFOSE	n.d.	0.1	n.d.	0.3	0.3	n.d.	n.d.
ΣFASE	1.9	2.4	3.0	4.2	3.2	2.2	3.8
ΣFTOH+FTA	24.0	92.0	27.0	34.1	19.6	58.1	202.9
ΣFASA+FASE	16.6	12.9	12.6	16.7	15.1	11.9	17.9
Σtotal	40.6	104.9	39.6	50.7	34.8	69.9	220.7