

Neutral poly- and perfluoroalkyl substances in air and seawater of the North Sea

Zhiyong Xie · Zhen Zhao · Axel Möller ·
Hendrik Wolschke · Lutz Ahrens · Renate Sturm ·
Ralf Ebinghaus

Received: 30 November 2012 / Accepted: 18 April 2013 / Published online: 2 May 2013
© Springer-Verlag Berlin Heidelberg 2013

Abstract Concentrations of neutral poly- and perfluoroalkyl substances (PFASs), such as fluorotelomer alcohols (FTOHs), perfluoroalkane sulfonamides (FASAs), perfluoroalkane sulfonamidoethanols (FASEs), and fluorotelomer acrylates (FTACs), have been simultaneously determined in surface seawater and the atmosphere of the North Sea. Seawater and air samples were taken aboard the German research vessel *Heincke* on the cruise 303 from 15 to 24 May 2009. The concentrations of FTOHs, FASAs, FASEs, and FTACs in the dissolved phase were 2.6–74, <0.1–19, <0.1–63, and <1.0–9.0 pg L⁻¹, respectively. The highest concentrations were determined in the estuary of the Weser and Elbe rivers and a decreasing concentration profile appeared with increasing distance from the coast toward the central part of the North Sea. Gaseous FTOHs, FASAs, FASEs, and FTACs were in the range of 36–126, 3.1–26, 3.7–19, and 0.8–5.6 pg m⁻³, which were consistent with the concentrations determined in 2007 in the North Sea, and approximately five times lower than those reported for an urban area of Northern Germany. These results suggested continuous continental emissions of neutral PFASs followed by transport toward the marine environment.

Air–seawater gas exchanges of neutral PFASs were estimated using fugacity ratios and the two-film resistance model based upon paired air–seawater concentrations and estimated Henry's law constant values. Volatilization dominated for all neutral PFASs in the North Sea. The air–seawater gas exchange fluxes were in the range of 2.5×10^3 – 3.6×10^5 pg m⁻² for FTOHs, 1.8×10^2 – 1.0×10^5 pg m⁻² for FASAs, 1.1×10^2 – 3.0×10^5 pg m⁻² for FASEs and 6.3×10^2 – 2.0×10^4 pg m⁻² for FTACs, respectively. These results suggest that the air–seawater gas exchange is an important process that intervenes in the transport and fate for neutral PFASs in the marine environment.

Keywords Neutral poly- and perfluoroalkyl substances (PFASs) · Air–seawater gas exchange · Flux · North Sea

Introduction

Poly- and perfluoroalkyl substances (PFASs) have been produced and applied worldwide in high volumes for several decades as polymerization aids and stain repellents in carpets, textiles, and leather and paper products. The term “PFAS” is used to describe a wide range of chemicals containing fluorinated carbon atoms of varying chain lengths (CF₃[CF₂]_n–) (Kissa 2001). Perfluoroalkyl acids, e.g., perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are the most widely known PFASs due to their presence in the global environment both in source regions and remote areas (Dietz et al. 2008; Giesy and Kannan 2001; Shoeib et al. 2006). Some toxicological effects have been attributed to these compounds based on recent laboratory studies (Lau et al. 2007).

PFASs have been synthesized either via electrochemical fluorination or telomerization (Schultz et al. 2003).

Responsible editor: Constantini Samara

Z. Xie (✉) · Z. Zhao · A. Möller · H. Wolschke · R. Sturm ·
R. Ebinghaus

Centre for Materials and Coastal Research, Institute of Coastal
Research, Department for Environmental Chemistry,
Helmholtz-Zentrum Geesthacht, Geesthacht, Germany
e-mail: zhiyong.xie@hzg.de

Z. Zhao
Key Laboratory of Coastal Zone Environmental Processes, Yantai
Institute of Coastal Zone Research, CAS, Yantai 264003, People's
Republic of China

L. Ahrens
Department of Aquatic Sciences and Assessment, Swedish
University of Agricultural Sciences, SE-750 07 Uppsala, Sweden

Commercial production of PFOS is based on the electrochemical fluorination with perfluorooctanesulfonyl fluoride (POSF) as the basic unit of the group of perfluoroalkyl sulfonate derivatives. The “telomerization process” is used to produce perfluoroalkyl carboxylic acids (PFCAs) and fluorotelomer alcohols (FTOHs). The annual global production of PFASs was estimated to be 4,400–8,000 t year⁻¹ between 1975 and 2004 (Prevedouros et al. 2006).

PFOA and PFOS may directly enter the environment during their production, processing and dispersion of fluoropolymers, production and use of fire fighting foams, and emission from commercial products (Schultz et al. 2003). Indirect sources of PFOA and PFOS are photo- and microbial degradation of neutral precursors such as perfluorosulfonamides (FOSA), perfluorosulfonamidoethanols (FOSE), and FTOHs (D'Eon et al. 2006; Ellis et al. 2004; Wang et al. 2005a; Wang et al. 2005b). Because of their slow reaction process with hydroxyl radicals, atmospheric lifetimes were estimated ~10–20 days for FTOH and ~20–50 days for perfluoroalkane sulphonamide (FASA) in smog chamber studies (Ellis et al. 2004; Martin et al. 2006) and atmospheric residence time of more than 50 days for FTOHs in field studies (Piekarczyk et al. 2007), which suggest they are subject to regional and long-range atmospheric transport, e.g., the Arctic and Antarctic (Dreyer et al. 2009b; Stock et al. 2007; Jahnke et al. 2007b). Degradation of these precursors may account for the presence of PFOA and PFOS in remote regions (Andersen et al. 2005; D'Eon et al. 2006; Ellis et al. 2004; Martin et al. 2006; Zhao et al. 2012). Apart from atmospheric reaction, degradation of FTOHs and FTSEs/FOSAs in the aquatic phase can be an additional source for PFCAs and PFASs, especially in the remote oceans (Armitage et al. 2006, 2009; Cousins et al. 2011). Therefore, it would be very interesting to study neutral PFASs in the aquatic environment.

In the present study, FTOHs, perfluoroalkane sulfonamidoethanol (FASE)/As, and fluorotelomer acrylates (FTACs) have been simultaneously determined in the atmosphere and seawater in the North Sea. Measured concentrations and metrological parameters were incorporated into the two-film model to estimate the direction and magnitude of air–seawater gas exchange fluxes. This work adds a novel data set for modeling environmental fate and long-range transport of PFASs.

Materials and methods

Sampling cruise

Nine air samples and 15 seawater samples were taken in the North Sea aboard the German research vessel *Heincke* (cruise no. 303) from 15 to 24 May 2009. Integrated 1-day air samples (130–423 m³) were taken via a high-volume air

sampler placed in the front of the ship's upper deck (12 m) using glass fiber filter ([GFF], GF/F, pore size: 0.7 µm) to trap airborne particles followed by a self-packed PUF/XAD-2 glass column for the gaseous phase. Both air column and filters were stored at –20 °C until analysis. Seawater samples (23–218 L) were taken via the ship's seawater intake system (depth: 5.5 m) and the seawater was passed through a GFF (GF/C, 1.2 µm) for the suspended particulate matter followed by a glass column packed with SERDOLIT® PAD III (SERVA Electrophoresis) to trap gaseous PFAS. Sampling parameters including date, mean position, temperature, wind speed, and salinity are summarized in Tables 2 and 3, respectively.

Chemicals

All solvents (methanol, acetone, dichloromethane, and *n*-hexane) were of residue grade and additionally distilled in a full glass unit prior to use. The details of analytical standards of FTOHs (6:2, 8:2, 10:2, and 12:2 FTOH), FTACs (6:2 and 8:2 FTAC), methyl and ethyl perfluorooctane sulfonamide (Me– and EtFOSA), methyl and ethyl perfluorooctane sulfonamidoethanol (Me– and EtFOSE), methyl perfluorobutane sulfonamide (MeFBSA), and methyl perfluorobutane sulfonamidoethanol (MeFBSE), and mass-labeled internal standards are summarized in Table 1.

Sample preparation and instrumental analysis

Samples were spiked with 2.5 ng of mass-labeled surrogate standards (6:2, 8:2, and 10:2 FTOH (M+5), MeFOSA D3, EtFOSA D5, MeFOSE D7, and EtFOSE D9) prior to extraction. Air and seawater columns and filters were extracted using a MX extractor for 16 h using dichloromethane. Extracts were evaporated to 1–2 mL using hexane as keeper and then passed over 3 g Na₂SO₄ to remove residual water. The extracts were further concentrated down to 150 µL and spiked with 10 µL of 100 pg µL⁻¹ FTOH 9:1 as recovery standard.

Detailed analysis methods have been described elsewhere (Dreyer et al. 2008). In brief, analysis was performed using gas chromatography–mass spectrometry (GC/MS) in selective ion monitoring (SIM) mode using positive chemical ionization (PCI). The monitored mass-to-charge ratios are summarized in Table 1. The response factors were derived from the calibration curves (six points) based on the ratio between target compounds (0–0.25 ng µL⁻¹) and the corresponding surrogate (0.05 ng µL⁻¹).

Quality assurance and quality control

All resin columns were precleaned with organic solvents (methanol, acetone, and hexane/acetone, in turn, for 96 h) and GFFs were baked at 450 °C for 12 h prior to their usage.

Table 1 Full names, acronyms, formulas, Chemical Abstract System (CAS) numbers of perfluoroalkylated substances (PFASs). The physical–chemical properties are calculated using Advanced ChemistryDevelopment (ACD/Labs) Software V11.02 (© 1994–2012 ACD/Labs) (<https://www.cas.org/products/scifinder>)

Neutral PFAS	Abbreviation	CAS number	Ion (<i>m/z</i>)	MW	MV	Sw (mg L ⁻¹)	Vp (pa)	<i>H</i> (Pa m ³ mol ⁻¹)	Δ_{vap} (kJ mol ⁻¹)
6:2 Fluorotelomer alcohol	6:2 FTOH	647-42-7	365, 327	364.10	229.2	58.0	50.9	320	47.79
8:2 Fluorotelomer alcohol	8:2 FTOH	678-39-7	465, 427	464.12	284.1	3.00	22.7	3,506	49.36
10:2 Fluorotelomer alcohol	10:2 FTOH	865-86-1	565, 527	564.13	339.0	0.17	2.8	9,202	53.36
12:2 Fluorotelomer alcohol	12:2 FTOH	39239-77-5	665, 627	664.15	393.9	0.010	0.3	23,111	57.16
<i>N</i> -methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8	514, 515	513.17	299.9	0.000092	10.4	58,005,747	46.39
<i>N</i> -ethyl perfluorooctane sulfonamide	EtFOSA	4151-50-2	528, 529	527.2	316.4	0.00004	3.6	47,268,376	48.37
<i>N</i> -methyl perfluorobutane sulfonamide	MeFBSA	68298-12-4	314, 315	313.14	190.1	1.6	337.3	66,015	39.58
<i>N</i> -methyl perfluorooctane sulfonamidoethanol	MeFOSE	24448-09-7	540, 558	557.22	328.8	0.000067	0.015	128,621	62.61
<i>N</i> -ethyl perfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2	554, 572	571.25	345.4	0.00003	0.005	86,061	64.7
<i>N</i> -methyl perfluorobutane sulfonamidoethanol	MeFBSE	34454-97-2	340, 358	357.19	219	0.68	0.6	298	56.28
6:2 Fluorotelomer acrylate	6:2 FTAC	17527-29-6	419, 447	418.15	279.7	4.10	44.3	4,514	43.62
8:2 Fluorotelomer acrylate	8:2 FTAC	27905-45-9	519, 547	518.17	334.6	0.24	7.5	16,091	47.0

MW molecular weight, *MV* molar volume, *SW* solubility in water (25 °C), *Vp* vapor pressure, *H* Henry's law constant, Δ_{vap} enthalpy of vaporization

Na₂SO₄ was cleaned with dichloromethane for 12 h and baked at 450 °C for 12 h prior to usage. The air columns were protected against UV–sunlight during sampling using aluminum foil in order to avoid degradation of the target compounds on the column. Breakthrough of the sampling methods has been checked previously at land base station (for air) and on board (for seawater) using two columns connected in series. The upper column was spiked with 20 μL of the internal standard mixture (0.05 ng μL^{-1}). The recoveries ($C_{\text{upper}}/(C_{\text{upper}}+C_{\text{lower}}) \times 100\%$) of mass-labeled 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, MeFOSA, EtFOSA, MeFOSE, and EtFOSE were 91, 82, 85, 86, 80, 88, and 87 % for air (sample volume: 1,500 m³) and 95, 89, 84, 84, 86, 84, and 84 % for seawater (sample volume: 200 L), respectively. Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation (σ) (for compounds showing no blanks and peak area of 50 was adopted as background response), which ranged from 0.1 (MeFBSA/E) to 1.5 pg m⁻³ (8:2 FTOH) in the gaseous phase and from 0.1 (MeFBSA/E) to 1.0 pg L⁻¹ (6:2 FTAC) in the dissolved phase.

Air mass back trajectories

Air mass origins along the cruise segments of the individual air samples were calculated using NOAA's HYSPLIT model (http://www.arl.noaa.gov/HYSPLIT_info.php) Air mass back trajectories (BTs) were calculated in 6-h steps tracing back the air masses for 5 days using the sampling height of 20 m as arrival height.

Results and discussion

PFASs in the gaseous phase

PFASs were detected in the gaseous phase of the air samples, and concentrations are shown in Fig. 1 and summarized in Table 2. The ΣPFAS concentration varied between 44 and 180 pg m⁻³, which is consistent with concentrations determined in the North Sea on a cruise conducted in November 2007 (Dreyer and Ebinghaus 2009), indicating a “background” level of neutral PFSA in European marine atmosphere (Table 3). Air mass back trajectories (Fig. 2) showed that the air masses mainly originated from northern and northeastern Europe for A1 to A4 and changed to southwestern and western Europe for A5 and A9. Therefore, the neutral PFASs found in these air samples should mainly originate from local emission sources. For instance, the concentrations of neutral PFASs were 40–244 pg m⁻³ in land-based sites around Hamburg (Dreyer et al. 2009a) and 84–706 pg m⁻³ over landfill fields in Germany (Weinberg et al. 2010), which are approximately two to five times higher than those determined in the North Sea. It is interesting to note that neutral PFASs showed different atmospheric transport potential from land to the marine environment.

Generally, the ΣFTOH concentrations were 9, 11, and 36 times higher than ΣFASA , ΣFASE , and ΣFTAC concentrations. Like in the previous study, 8:2 FTOH was the dominant FTOH (ranging from 23 to 75 pg m⁻³, median: 43 pg m⁻³), which accounts for ~50 % of neutral PFASs, followed by 10:2 FTOH (6.8–50 pg m⁻³, median:

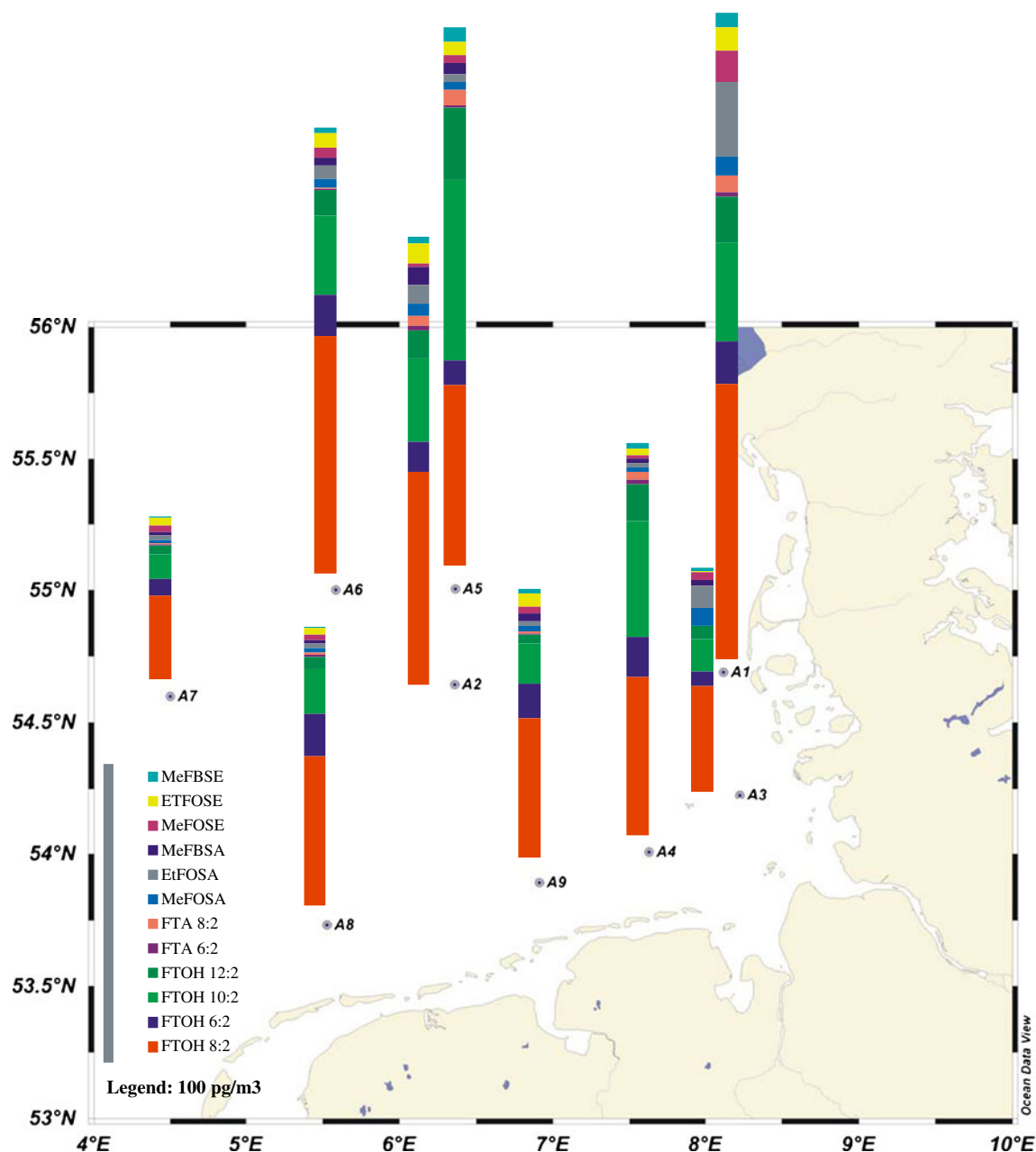


Fig. 1 Concentrations of PFASs in air of the North Sea

22 pg m^{-3}), 6:2 FTOH (4.0–12 pg m^{-3} , median: 9.5 pg m^{-3}), and 12:2 FTOH (2.3–20 pg m^{-3} , median: 6.9 pg m^{-3}). The chemical pattern of FTOHs in this study was in the order 8:2 FTOH > 10:2 FTOH > 6:2 FTOH \approx 12:2 FTOH, with average ratios of 5.6:2.5:1.0:0.9 for 8:2 FTOH to 10:2 FTOH to 6:2 FTOH to 12:2 FTOH. This result well agrees with the ratios found in previous studies, e.g., in the Canadian Arctic (Ahrens et al. 2011), Mount Bachelor Observatory (Piekartz et al. 2007), and in the North Sea (Dreyer and Ebinghaus 2009). However, the ratios of 8:2 FTOH to 10:2 FTOH to 6:2 FTOH in urban areas, e.g., in Hamburg (Germany) in 2005 (Jahnke et al. 2007) and 2007–2008

(Dreyer et al. 2009a) and in Toronto (Shoeib et al. 2006) showed a higher proportion of 6:2 FTOH. This variation is consistent with the estimated atmospheric residence times of FTOHs of 80, 70, and 50 days for 8:2 FTOH, 10:2 FTOH, and 6:2 FTOH, respectively (Piekartz et al. 2007). Gaseous FTOHs reported in Asia and the Pacific regions (Li et al. 2011) were generally higher than those determined in the European continent and marine environment (Dreyer and Ebinghaus 2009; Jahnke et al. 2007) as well as in this work. It should be noted that the ratios of 8:2 FTOH to 10:2 FTOH to 6:2 FTOH reported in Asia and the Pacific region (8.0:1.3:0.2) (Li et al. 2011) are much

Table 2 Detailed information on air sampling in the North Sea (15–24. 05. 2009, Cruise Heincke 303). Latitude and longitude are mean sampling stations. Air temperature and wind speed represents the mean values during sampling

Sample	Date	Latitude (°N)	Longitude (°E)	Volume (m ³)	Air temperature (°C)	Wind speed (m s ⁻¹)
A1	15/05/09	54.689	9.186	130	13.0	8.5
A2	16/05/09	54.643	6.360	201	11.0	7.2
A3	17/05/09	54.226	8.226	227	10.3	7.1
A4	18/05/09	54.007	7.634	400	10.8	7.1
A5	19/05/09	55.004	6.365	322	10.4	7.4
A6	20/05/09	55.001	5.585	396	10.7	7.4
A7	21/05/09	54.598	4.500	423	10.5	8.9
A8	22/05/09	53.732	5.528	403	12.0	6.7
A9	23–24/05/09	53.892	6.912	400	12.7	6.0

higher than those in this study and the European atmosphere (Dreyer et al. 2009a).

For FASE/As, Σ FASA (3.1–26 pg m⁻³, median: 7.5 pg m⁻³) and Σ FASE (3.2–19 pg m⁻³, median: 6.9 pg m⁻³) were comparable in this work. The median concentration profile was EtFOSE>EtFOSA>MeFOSA>MeFOSE>MeFBSA>MeFBSE (Table 4). It is different from the findings in 2007 (e.g., EtFOSE: ~0.1 pg m⁻³, MeFBSA: 4.7 pg m⁻³) (Dreyer and Ebinghaus 2009). It is probable that sampling and analytical differences may account for some of this variation, though it can be caused by various sources. In principle, gaseous FASEs likely react with OH radicals resulting in various products, including FASAs. It was reported that the atmospheric lifetime of MeFBSE is approximately 2 days, and MeFBSA has an atmospheric lifetime of >20 days (D'Eon et al. 2006). In this work, we did not find a significant change of composition

between FASAs and FASEs as compared to the data determined in an urban area of Hamburg (Germany) (Dreyer and Ebinghaus 2009). Although production of perfluorooctane sulfonamidoethanol and perfluorooctane sulfonamide (FOSE/A) was phased out in 2002 (Paul et al. 2008) and these compounds have widely been replaced with four carbon equivalents, concentrations of FOSE/FOSA and MeFBSE/A stayed at a similar level. The major emission source of FASE/As in European marine environment can be addressed to the products containing POSF-based chemicals in use. However, it should be noted that increased FBSA/FBSE concentrations have been observed in Asia and the Pacific regions (Li et al. 2011), and in the Southern Ocean (Del Vento et al. 2012) due to the geographical shift of production and increasing use of perfluorobutane sulfonyl compounds.

Unlike FTOHs, FTACs have just been reported in a few studies. In this work, two fluorotelomer acrylates, 8:2 FTAC

Table 3 Detailed information on water sampling in the North Sea (15–24. 05. 2009, Cruise Heincke 303). Latitude and longitude are mean sampling stations. Water temperature and salinity represent the mean values during sampling

Water	Date	Latitude (°N)	Longitude (°E)	Volume (L)	Water temperature (°C)	Salinity (PSU)	Wind speed (m s ⁻¹)
W1	15/05/09	53.724	8.278	61	13.1	29.8	13.6
W2	16/05/09	54.682	8.119	23	12	29.8	5.7
W3	17/05/09	55.060	7.500	188	9.2	33.6	6.6
W4	18/05/09	54.199	7.630	108	9.9	30.1	8.2
W5	18/05/09	54.174	7.894	110	9.7	33.2	7.6
W6	19/05/09	53.883	6.599	208	11.1	31.9	3.9
W7	19/05/09	54.227	6.361	115	12.3	32.4	5.7
W8	20/05/09	55.195	7.294	201	10.3	32.4	8.4
W9	20/05/09	54.724	8.064	172	10.7	34.2	6.0
W10	21/05/09	54.851	5.328	218	11.2	32.5	5.3
W11	21/05/09	55.296	4.844	198	10.4	34.4	9.0
W12	22/05/09	54.866	4.493	196	10.2	34.5	7.3
W13	22/05/09	54.425	4.500	204	10.5	34.5	8.9
W14	23/05/09	53.686	5.269	168	11.8	34.3	2.4
W15	24/05/09	53.950	7.096	203	10.7	32.7	7.1

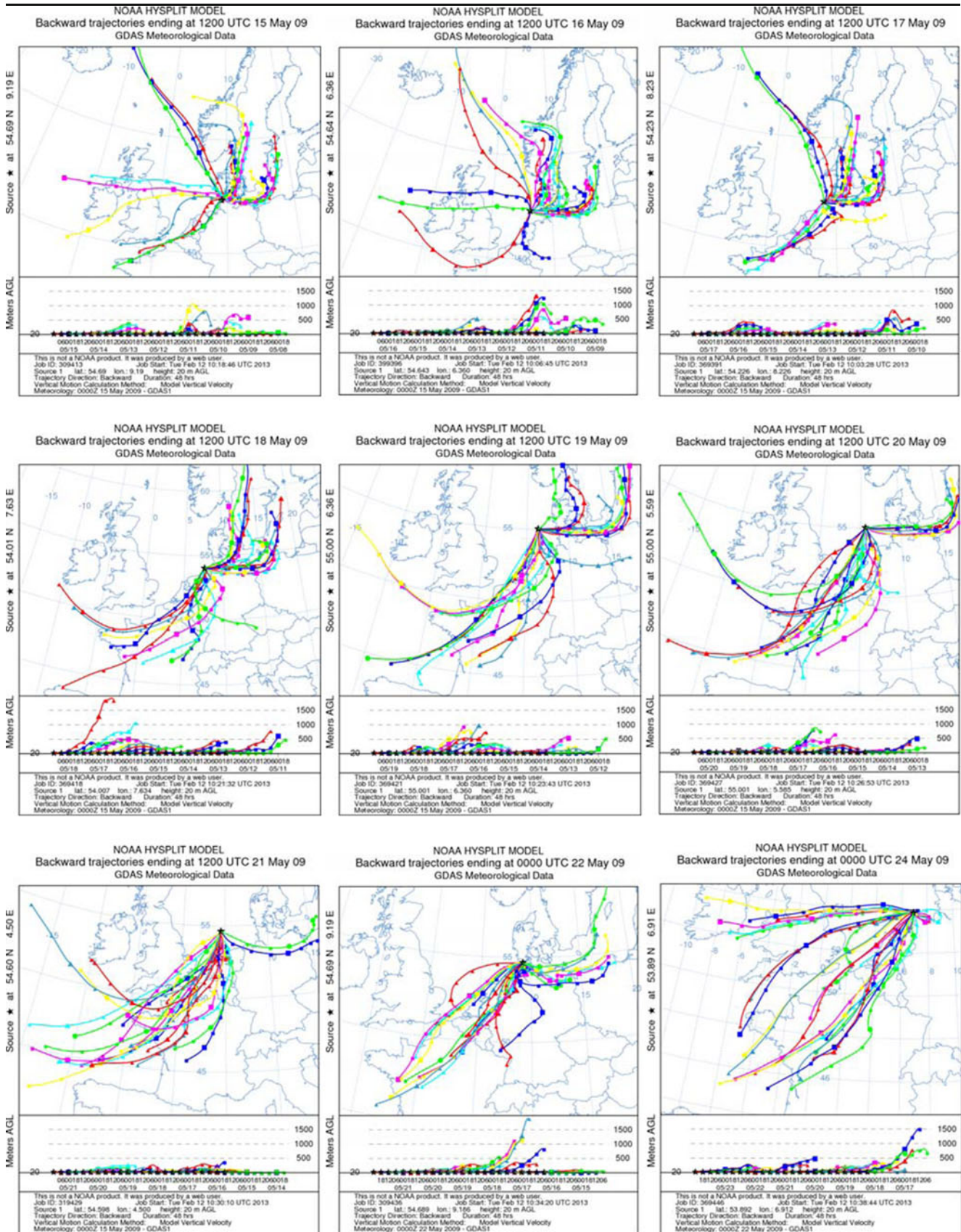


Fig. 2 Air mass back trajectories for air sampling on the North Sea. Trajectories were recalculated every 6 h and calculated 5 days backwards

Table 4 Concentrations of neutral PFASs in air (pg m^{-3}) and seawater (pg L^{-1}) of the North Sea

PFAS	FTOH 8:2	FTOH 6:2	FTOH 10:2	FTOH 12:2	Σ FTOH	MeFOSA	EtFOSA	MeFBSA	Σ FASA	MeFOSE	EtFOSE	MeFBSE	Σ FASE	FTAC 6:2	FTAC 8:2	Σ FTAC	Σ PFAS
Air (pg m^{-3})																	
MDL	1.5	0.1	1.0	1.0	3.5	0.1	0.4	0.0	0.4	0.8	0.1	0.1	0.9	0.9	0.2	1.1	5.5
A1	75	12	27	13	127	5.1	21	0	26	8.6	6.2	4.1	19	1.2	4.4	5.6	177
A2	58	8	23	7.6	97	3.5	5.2	4.6	13	1	5.5	2	8.5	1.2	2.6	3.8	122
A3	29	4	8.9	3.5	45	4.8	6.3	1.6	13	2	0.3	0.9	3.2	<0.9	<0.2	0.1	61
A4	44	11	32	10	96	1.3	1.1	1.1	3.6	1.0	2.0	1.2	4.1	1.1	2.3	3.4	107
A5	50	6.5	50	20	125	2.1	2.4	3	7.5	2.1	3.5	3.9	9.5	0.7	4.2	4.9	147
A6	65	11	22	6.9	105	2.3	3.9	2.1	8.2	2.8	3.9	1.6	8.2	0.4	0.4	0.8	122
A7	23	4.6	6.8	2.4	37	1	1.2	0.8	3.1	1.7	2.3	0.2	4.2	0.4	0.3	0.6	44
A8	41	12	12	3.3	68	1.2	1.2	1	3.4	1.4	1.8	0.5	3.7	0.5	0.7	1.2	76
A9	38	9.5	11	2.3	61	1.6	1.1	2	4.8	1.9	3.7	1.3	6.9	0.3	0.6	0.9	73
Mean	47	8.6	21	7.6	84	2.6	4.8	1.8	9.1	2.5	3.2	1.7	7.5	0.6	1.7	2.4	103
Median	44	9.5	22	6.9	96	2.1	2.4	1.6	7.5	1.9	3.5	1.3	6.9	0.5	0.7	1.2	107
Seawater (pg L^{-1})																	
MDL	0.2	0.2	0.3	0.5	1.1	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.3	1.0	0.2	1.2	2.8
W1	27	3.6	24	19	74	2.6	5.1	12	19	35	17	11	63	3.3	0.6	3.9	160
W2	18	3.7	19	12	52	0.3	2.2	6.2	8.7	23	14	10	47	7.8	1.2	9.0	117
W3	3.3	0.3	3.4	2.9	10	<0.1	<0.1	1.5	1.7	1.9	1.5	3.1	6.4	1.1	<0.2	1.3	20
W4	7.7	0.5	5.3	2.1	16	0.2	0.2	2.8	3.2	2.5	2.8	3.0	8.3	2.2	1.8	4.1	31
W5	2.4	0.8	2.8	1.4	7.4	0.6	<0.1	3.7	4.4	1.2	1.7	3.6	6.4	1.5	<0.2	1.6	20
W6	2.5	0.7	1.8	1.8	6.9	0.7	0.4	5.9	7.0	1.5	0.8	3.5	5.8	<1.0	<0.2	<1.2	21
W7	3.4	0.6	2.1	1.0	7.2	1.0	<0.1	4.8	5.9	1.1	1.3	3.5	5.9	1.6	<0.2	1.7	21
W8	1.7	0.4	1.0	<0.5	3.7	0.5	<0.1	1.6	2.2	0.9	<0.2	3.1	4.1	<1.0	<0.2	<1.2	11
W9	1.1	0.5	1.1	0.7	3.5	<0.1	<0.1	1.3	1.5	<0.1	<0.2	1.9	2.0	<1.0	<0.2	1.3	8.2
W10	0.5	0.3	0.9	0.7	2.4	0.2	0.3	<0.1	0.4	0.2	0.3	<0.1	0.5	<1.0	<0.2	<1.2	4.6
W11	1.1	0.4	0.9	1.0	3.4	<0.1	<0.1	0.6	0.7	<0.1	<0.2	1.4	1.5	<1.0	<0.2	<1.2	6.7
W12	1.2	0.6	0.6	<0.5	2.6	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	<0.1	<0.3	<1.0	<0.2	<1.2	3.7
W13	0.8	0.6	1.5	1.2	4.2	0.2	0.2	<0.1	0.4	<0.1	<0.2	<0.1	0.3	1.5	0.3	1.8	6.6
W14	2.8	2.3	4.9	4.0	14	0.2	0.3	<0.1	0.5	<0.1	<0.2	<0.1	0.3	1.9	0.6	2.5	17
W15	1.3	0.5	1.1	<0.5	3.2	<0.1	<0.1	4.6	4.8	<0.1	<0.2	3.1	3.3	<1.0	<0.2	<1.2	12
Mean	5.0	1.0	4.2	2.9	13	0.4	0.6	2.7	3.7	4.0	2.3	2.8	9.2	1.7	0.4	2.1	28
Median	2.4	0.6	1.8	1.2	6.9	0.2	<0.1	1.6	2.2	0.9	0.3	3.1	4.1	1.1	<0.2	1.3	15

and 6:2 FTAC, were determined at relatively low levels with ranges of <0.2 – 4.4 and <0.9 – 1.2 pg m^{-3} , respectively. These results are two to five times lower than those reported in the North Sea and at an urban site of Hamburg (Dreyer and Ebinghaus 2009) and in the Asia-Pacific region (Li et al. 2011), and 3 orders of magnitude lower than those reported in Japan (Oono et al. 2008). FTACs are monomers used in the manufacturing of fluorotelomer-based polymers. Residuals of FTACs can be definitely released to the atmosphere from production and application of fluorotelomer-based polymer products in a similar manner to that of FTOHs. However, an atmospheric chemistry study of 4:2 FTAC showed that FTACs can react with OH radicals and O_3 leading to a short atmospheric lifetime on a time scale of approximately 1 day (Butt et al. 2009) and may suggest FTACs are not subject to long-range atmosphere transport.

PFASs in seawater

The total concentrations of PFASs in seawater are shown in Fig. 3 and the individual PFAS concentrations are summarized in Table 2. Only dissolved phase concentrations are presented and no PFASs were detectable in the particle phase in this work.

Figure 2 shows that elevated concentrations occurred in the seawater samples that were collected near the estuaries of the discharging rivers and an obviously declining spatial distribution profile from the coast to the open sea. This distribution pattern is consistent with ionic PFASs as well as other organic contaminants (Ahrens et al. 2009), e.g., alkylphenols (Xie et al. 2006) and phthalates (Xie et al. 2005) in the North Sea. PFASs showed the highest concentrations at station W1 collected in the mouth of the River Weser (ΣPFAS : 160 pg L^{-1}), followed by W2 (ΣPFAS : 120 pg L^{-1}) that is located within the plume of the River Elbe, and decreased down to 3.7 – 31 pg L^{-1} in offshore seawater.

FTOHs were detected in all seawater samples ranging from 0.5 to 27 pg L^{-1} for 8:2 FTOH, 0.3 to 3.6 pg L^{-1} for 6:2 FTOH, 1.0 to 24 pg L^{-1} for 10:2 FTOH, and <0.5 to 19 pg L^{-1} for 12:2 FTOH, respectively. Data of neutral PFASs in the aquatic environment are hardly available. So far, only 8:2 FTOH, 6:2 FTOH, and 10:2 FTOH have been reported in an urban area of Japan (Mahmoud et al. 2009). Mean concentrations of 8:2 FTOH and 10:2 FTOH were 1.97 and 0.82 ng L^{-1} in rainwater, 1.4 and 1.18 ng L^{-1} in river water (Keihan area, Japan), and 17.4 and 5.08 ng L^{-1} in WWTP effluent (Mahmoud et al. 2009), which are 3 orders of magnitude higher than those determined in seawater of the North Sea (8:2 FTOH: 5.0 , 10:2 FTOH 4.2 pg L^{-1}). To our knowledge, 6:2 FTOH and 12:2 FTOH were determined in the aquatic environment for the first time, ranging from 0.3 to 3.6 pg L^{-1} and from <0.5 to 19 pg L^{-1} , respectively. Concentrations of 12:2 FTOH were comparable to 10:2 FTOH, which were two

times lower than those of 8:2 FTOH and approximately two to five times higher than those of 6:2 FTOH. Although there are no data available for FTOHs in the European aquatic environment, it is reasonable to expect that FTOHs can be released into surface water by WWTPs and transported into the North Sea via discharging rivers, such as the rivers Rhine, Elbe, and Weser.

The composition of FTOHs in seawater is obviously different from the composition in air (Fig. 4). For instance, 8:2 FTOH and 12:2 FTOH accounted for ~ 45 and 7 % in air, which changed to 16 and 11 % in seawater, respectively. These variations might be caused by (1) different sources of FTOHs for air and water, (2) diverse degradation processes of FTOHs in air and water, and (3) air–seawater gas exchange. FTOHs are raw materials intensively used to manufacture FTOH-based polymeric and surfactant products, e.g., in textiles, papers, carpet, paint, and lubricating oil. Historically, FTOHs with a carbon chain length ≥ 10 were the major FTOHs used in FTOH-based products (Kissa 2001). As 8:2 FTOH can be transformed to PFOA in various environmental processes, recently, 4:2 FTOH and 6:2 FTOH have been introduced to replace 8:2 FTOH to eliminate the potential formation of long-chain PFCA in the environment (Kissa 2001; Prevedouros et al. 2006). Release of 6:2 FTOH from production application may steadily increase and, thus, become a predominant FTOH in the environment (Ritter 2010). A study of 6:2 FTOH biotransformation in an aerobic river sediment system has revealed that the primary biotransformation of 6:2 FTOH was rapid with a half-life time of <2 days and formed polyfluorinated acids after 100 days (Zhao et al. 2013). Seawater concentrations determined in this work may suggest that FTOHs are mainly released from old FTOH-based ($C \geq 10$) products in use in Europe. However, the occurrence of 6:2 FTOH in seawater implied that 6:2 FTOH-based products exist and may become predominant in the future (Sun et al. 2012; Wang et al. 2012). Actually, increased short-chain PFCA concentration have been observed in surface water along the River Rhine watershed to the North Sea in 2008 (Möller et al. 2010).

In seawater, ΣFASes and ΣFASAs ranged from <0.3 to 63 pg L^{-1} and <0.2 to 19 pg L^{-1} , respectively. The composition was $\text{MeFOSE} > \text{EtFOSE} > \text{MeFBSE} > \text{MeFBSA} > \text{EtFOSA} > \text{MeFOSA}$ in W1 and W2 and then changed to $\text{MeFBSE} > \text{MeFBSA} > \text{EtFOSE} > \text{MeFOSE} > \text{MeFOSA} > \text{EtFOSA}$ in other seawater samples (Fig. 4). Ahrens et al. (2009) reported MeFBSE and MeFBSA to be lower than 0.75 ng L^{-1} in seawater of the North Sea in 2007 based on LC-MS/MS measurement. Möller et al. (2010) measured MeFBSE (0.66 ng L^{-1}) and MeFBSA (1.01 – 3.37 ng L^{-1}) in river water of the Rhine, which are 2 to 3 orders of magnitude higher than those determined in this work. The estimated water solubilities of MeFBSE (0.6 mg L^{-1}) and MeFBSA (337.3 mg L^{-1}) are 5 to 7 orders of magnitude

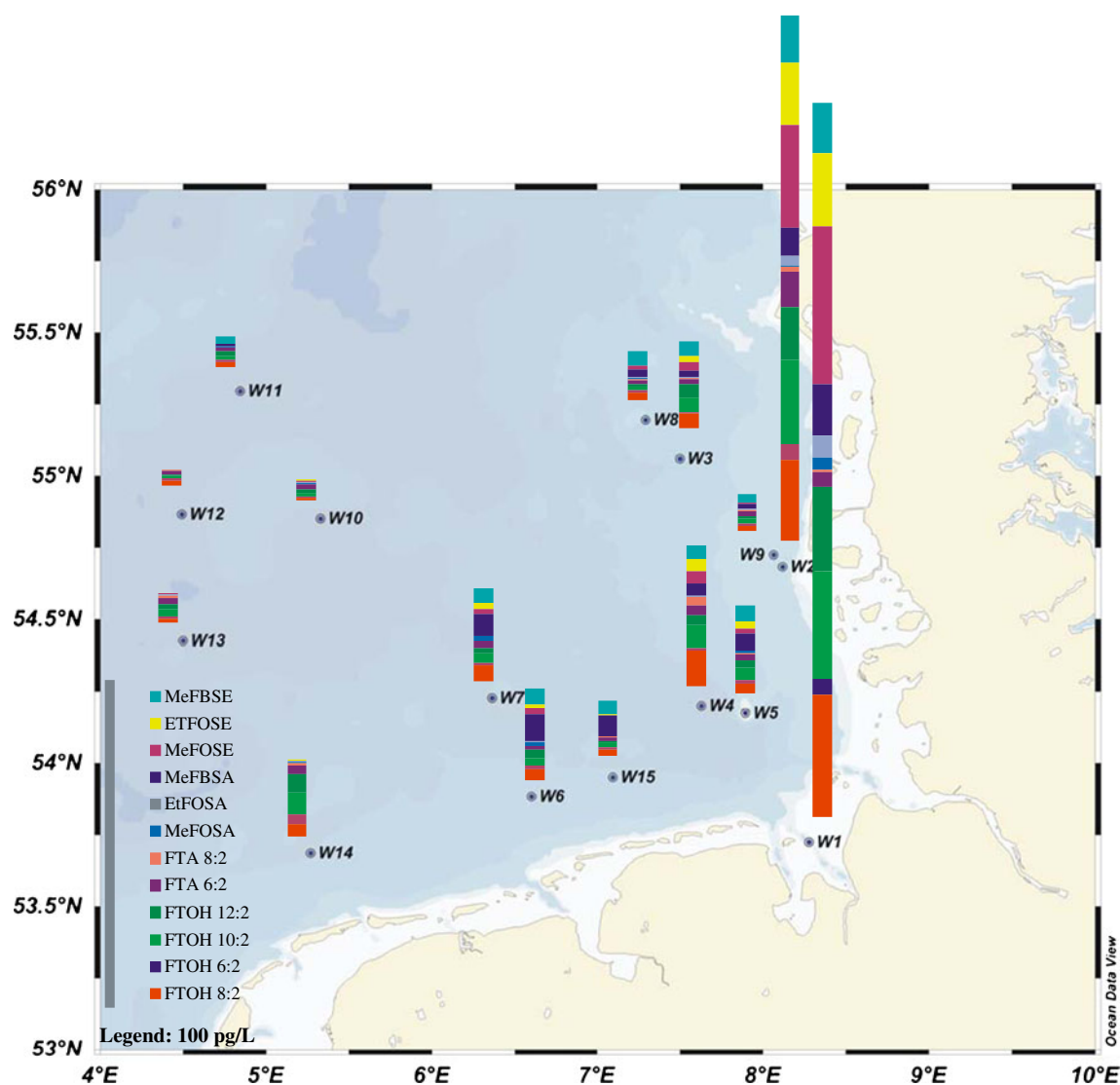


Fig. 3 Concentrations of neutral PFASs in seawater of the North Sea

higher than those of MeFOSE, EtFOSE, MeFOSA, and EtFOSA (Table 1). This indicates that MeFBSE and MeFBSA likely partition into the dissolved phase and have higher bioaccumulation ability to biota. In general, EtFOSE, MeFOSE, and MeFBSE may transfer to EtFOSA, MeFOSA, MeFBSA, and PFCA under photolysis and OH-initiated oxidations (Plumlee et al. 2009; Benskin et al. 2013). Aerobic biotransformation study for EtFOSE in activated sludge has shown that EtFOSE can be degraded to *N*-ethyl perfluorooctane sulfonamido acetic acid (NEtFOSAA) with an observed first-order rate of $0.99 \pm 0.08 \text{ day}^{-1}$ and then further transferred to EtFOSA at a slower rate, with the final transformation product being PFOS. No PFOA was observed in this study (Rhoads et al. 2008). 6:2 FTAC and 8:2 FTAC have been detected in seawater as well, with concentrations ranging from <1.0 to 7.8 pg L^{-1} and <0.2 to 1.8 pg L^{-1} , respectively. Concentrations

of 6:2 FTAC were generally higher than those of 8:2 FTAC, which corresponds to their water solubility (6:2 FTAC: 4.1 mg L^{-1} , 8:2 FTAC 0.24 mg L^{-1}).

Air–water gas exchange of PFASs in the North Sea

The gas exchange direction (or equilibrium status) was estimated based on the fugacity ratio f_A/f_W (FR) (Fig. 5), and the exchange fluxes were calculated using the two-film model that have been applied in Lohmann et al. (2009) and Xie et al. (2011). Briefly, the fugacity ratio was calculated using Eq. 1:

$$\frac{f_A}{f_W} = \frac{C_A R T_A}{C_W H} \quad (1)$$

where f_W and f_A are the fugacities in water and air, C_W and C_A are the dissolved and gaseous concentrations in water

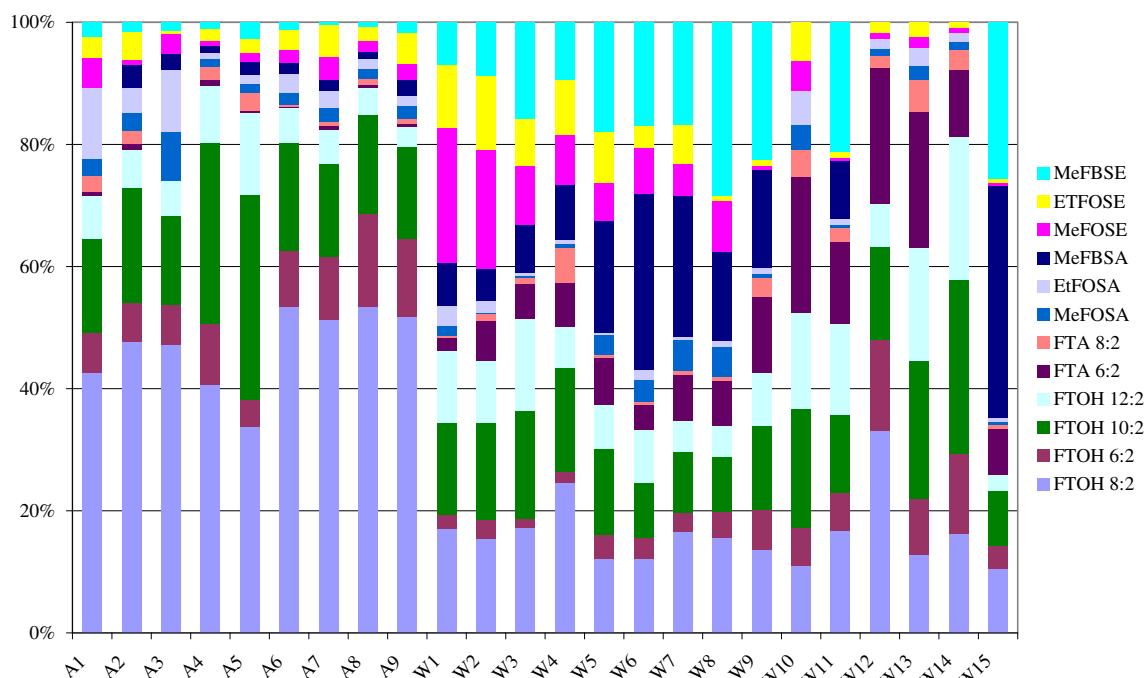


Fig. 4 Composition profiles of neutral PFASs in air and water of the North Sea

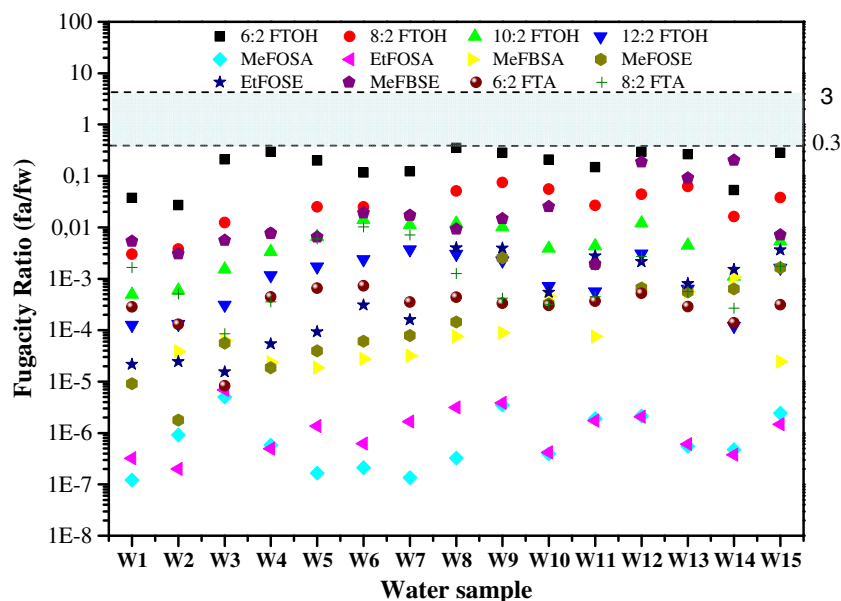
(picograms per cubic meter) and air (picograms per cubic meter), H is the Henry's Law constant (pascal per cubic meter per mole) at the given water temperature and corrected by the salinity according to ref (Schwarzenbach et al. 2003), R is the gas constant ($8.31 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$), and T_A is the air temperature (Kelvin). The Henry's law constants of PFASs were estimated from their vapor pressure and solubility (see Table 1, summarized from <http://www.cas.org/products/scifinder>). Generally, a fugacity ratio $f_A/f_W=1$ means a system at equilibrium, whereas $f_A/f_W>1$

and $f_A/f_W<1$ indicates deposition and volatilization, respectively. Due to uncertainties of the estimated Henry's law constant, a significant deviation from equilibrium cannot be assessed within a factor of 3 around a fugacity ratio of 1 (Bruhn et al. 2003; Lohmann et al. 2009).

The air–seawater gas exchange was calculated based on Eq. 2 (Bidleman and McConnell 1995; Liss and Slater 1974):

$$F_{AW} = K_{OL} \left(C_W - \frac{C_A}{H'_{salt,T}} \right) \quad (2)$$

Fig. 5 Fugacity ratios (FR) calculated with water/air pair concentrations of PFASs. Generally, a fugacity ratio $f_A/f_W=1$ means a system at equilibrium, $f_A/f_W>3$ and $f_A/f_W<0.3$ indicates deposition and volatilization, respectively



$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'} \quad (3)$$

where $H'_{\text{salt}, T}$ is the dimensionless temperature and salinity (C_s , 0.5 mol L⁻¹) corrected Henry's law constant defined as $H' = H/RT$ (R = gas constant, T = temperature). K_{OL} (meters per hour) is the overall air–water mass transfer coefficient compromising the resistances to mass transfer in both water (K_W , meters per hour) and air (K_A , meters per hour) (Hornbuckle et al. 1994).

Fugacity ratios (FR) calculated with paired seawater and air concentrations of PFASs are shown in Fig. 3. In general, volatilization trends were dominant for all neutral PFASs in the North Sea. Water samples collected in the open sea exhibited lower volatilization potential in comparison to those close to the coast. For FTOHs, FRs of 10:2 FTOH (0.0005–0.015) and 12:2 FTOH (0.0001–0.004) were all below 0.3 indicating water to air volatilization, while FRs of 8:2 FTOH and 6:2 FTOH increased from 0.003 to 0.23 and from 0.03 to 0.82, respectively, showing dynamic air–seawater exchange conditions. 6:2 FTOH showed equilibrium conditions in the open sea area. FRs of Me/EtFOSE, Me/EtFOSA, MeFBSA, 6:2 FTAC, and 8:2 FTAC ranged from 1×10^{-7} to 7×10^{-2} , showing strong water to air volatilization potential. In contrast, FRs of MeFBSE ranged from 0.003 to 0.2, showing that equilibrium conditions can be reached in the open sea. As atmospheric concentrations of PFASs are relatively constant in the marine environment, the diversity of air–water gas exchange potential and directions should be mainly controlled by the dissolved PFASs in seawater and meteorology parameters, e.g., air and water temperature and wind speeds. Volatilization of PFAS from water to air has been observed in studies for point sources such as WWTPs (Ahrens et al. 2011; Weinberg et al. 2011).

The estimated air–seawater gas exchange fluxes of PFASs are summarized in Table 5. The net fluxes were also generally dominated by net volatilization. The highest volatilization fluxes were observed at station W1 with values of 3.6×10^5 pg m⁻² day⁻¹ for Σ FTOH, 3.0×10^5 pg m⁻² day⁻¹ for Σ FASE, 1.0×10^5 pg m⁻² day⁻¹ for Σ FASA, and 2.0×10^4 pg m⁻² day⁻¹ for Σ FTAC, respectively, which might be driven by relatively high water concentrations presented in the estuary of the River Weser. From the coastline toward the open sea, the volatilization fluxes of PFASs decreased by 1 to 3 orders of magnitude for most samples. The volatilization fluxes of FTOHs were predominant in the North Sea, indicating coastal waters can be an important source of gaseous PFASs in the marine atmosphere. Once PFASs are emitted into the atmosphere, they can be transported with air masses and be subject to removal processes, such as air to water deposition and precipitation along their transport pathway to the remote oceans.

Table 5 Air–sea gas exchange fluxes (F, pg m⁻² day⁻¹) of PFASs in the North Sea

PFAS	8:2 FTOH	6:2 FTOH	10:2 FTOH	12:2 FTOH	Σ FTOH	MeFOSA	EtFOSA	FBSA	Σ FASA	MeFOSE	EtFOSE	FBSE	Σ FASE	6:2 FTAC	8:2 FTAC	Σ FTAC
W1	140,000	18,000	120,000	86,000	360,000	13,000	25,000	65,000	100,000	170,000	78,000	56,000	300,000	17,000	2,900	20,000
W2	22,000	4,600	22,000	13,000	62,000	320	2,700	8,800	12,000	27,000	17,000	13,000	57,000	9,700	1,500	11,000
W3	5,700	390	5,600	4,600	16,000	130	160	3,000	3,300	3,100	2,400	5,400	11,000	2,000	270	2,200
W4	18,000	900	12,000	4,500	36,000	420	530	7,600	8,600	5,800	6,300	7,100	19,000	5,400	4,100	9,500
W5	4,900	1,400	5,500	2,800	15,000	1,300	170	8,700	10,000	2,400	3,300	7,600	13,000	3,200	220	3,400
W6	1,700	470	1,200	1,100	4,400	490	230	4,600	5,300	1,000	500	2,400	4,000	560	69	630
W7	4,200	730	2,500	1,200	8,600	1,300	140	6,700	8,100	1,300	1,600	4,400	7,300	1,900	170	2,100
W8	4,000	720	2,300	1,200	8,200	1,300	290	4,400	6,000	2,200	170	7,700	10,000	2,000	200	2,200
W9	1,400	550	1,500	880	4,300	65	130	2,100	2,300	66	92	2,600	2,800	1,400	330	1,800
W10	550	270	970	760	2,500	210	280	130	620	250	310	120	680	1,200	220	1,400
W11	3,000	1,000	2,300	2,500	8,800	110	180	2,000	2,300	110	160	4,000	4,300	2,500	410	2,900
W12	2,300	790	1,000	460	4,600	82	110	220	420	190	120	82	390	1,600	140	1,800
W13	2,200	1,200	3,900	3,000	10,000	430	510	310	1,200	300	410	250	960	4,000	880	4,900
W14	830	680	1,400	1,100	4,000	69	76	34	180	37	44	25	110	580	160	740
W15	2,300	630	2,000	560	5,500	92	130	9,900	10,000	98	130	6,000	6,200	1,700	160	1,900
Mean	14,000	2,100	12,000	8,200	36,000	1,300	2,000	8,200	12,000	14,000	7,400	7,800	29,000	3,600	780	4,400
Median	3,000	730	2,300	1,200	8,500	320	180	4,400	5,300	1,000	410	4,400	6,200	2,000	220	2,200

Conclusions

Neutral PFASs have been investigated simultaneously in air and seawater of the North Sea using ship-born samples. Gaseous concentrations were comparable to those determined in 2007 in the North Sea and about five times lower than those in an urban area of Northern Germany, suggesting ongoing continental input for the marine environment. Concentrations of PFASs in seawater ranged from below detection limits (0.2 pg L^{-1}) to $\sim 100 \text{ pg L}^{-1}$ and declined dramatically from the coastline to the open sea. The highest concentrations were determined in the estuary of River Elbe, where MeFBSE and MeFBSA were 2 orders of magnitude lower in comparison to those measured in the lower stream of the River Rhine. This indicates that the rivers are main input sources for neutral PFASs present in the North Sea. Fugacity ratios showed that volatilization dominated the air–seawater gas exchange of all neutral PFASs. The volatilization fluxes ranged from $2.0 \times 10^4 \text{ pg m}^{-2} \text{ day}^{-1}$ for ΣFTAC to $3.6 \times 10^5 \text{ pg m}^{-2} \text{ day}^{-1}$ for ΣFTOH , respectively. Obviously, air–seawater exchanges of neutral PFASs are controlled by the seawaterside concentrations and their Henry's law constant values. It can be expected that equilibrium will be reached in the open sea, whereas net air to seawater depositions will occur in cold winter, or cold regions, e.g., in the Arctic. Nevertheless, this study indicated that the North Sea receives dissolved PFASs via riverine discharge and acts as a potential source for atmospheric PFASs. Transformation of PFASs to PFCAs and PFASs, e.g., PFOA and PFOS can occur either in atmosphere or in water phase. Therefore, further studies will be conducted to elucidate the spatial and temporal dependences of the neutral and ionic PFASs in the coastal margins and in the open ocean.

Acknowledgments We acknowledge Alfred-Wegener-Institute for Polar and Marine Research (AWI), Bremerhaven, Germany, for the possibility of taking part in the expedition cruise. We are grateful to the captain and the crew of R/V *Heincke*. Armando Caba (HZG) is kindly acknowledged for organizing and assisting on the cruise.

References

- Ahrens L, Felizeter S, Ebinghaus R (2009) Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. *Chemosphere* 76:179–184
- Ahrens L, Shoeib M, Hamer T, Lee SC, Guo R, Reiner EJ (2011) Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environ Sci Technol* 45:8098–8105
- Andersen MPS, Nielsen OJ, Hurley MD, Ball JC, Wallington TJ, Ellis DA, Martin JW, Mabury SA (2005) Atmospheric chemistry of 4:2 fluorotelomer alcohol (*n*-C₄F₉CH₂CH₂OH): products and mechanism of Cl atom initiated oxidation in the presence of NO_x. *J Phys Chem A* 109:1849–1856
- Armitage J, Cousins IT, Buck RC, Prevedouros K, Russell MH, MacLeod M, Korzeniowski S (2006) Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. *Environ Sci Technol* 40:6969–6975
- Armitage J, MacLeod M, Cousins I (2009) Modeling the global fate of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. *Environ Sci Technol* 43:1134–1140
- Benskin JP, Ikonomou MG, Gobas FAPC, Begley TH, Woudneh MB, Cosgrove JR (2013) Biodegradation of *N*-ethyl perfluorooctane sulfonamido ethanol (EtFOSE) and EtFOSE-based phosphate diester (SAMPAP Diester) in marine sediments. *Environ Sci Technol* 47:1381–1389
- Bidleman TF, McConnell LL (1995) A review of field experiments to determine air–water gas exchange of persistent organic pollutants. *Sci Total Environ* 159:101–117
- Bruhn R, Lakaschus S, McLachlan MS (2003) Air/sea gas exchange of PCBs in the southern Baltic Sea. *Atmos Environ* 37:3445–3454
- Butt CM, Young CJ, Mabury SA, Hurley MD, Wallington TJ (2009) Atmospheric chemistry of 4:2 fluorotelomer acrylate [C₄F₉CH₂CH₂OC(O)CH=CH₂]: kinetics, mechanisms, and products of chlorine-atom- and OH-radical-initiated oxidation. *J Phys Chem A* 113:3155–3161
- Cousins I, Kong D, Vestergren A R (2011) Reconciling measurement and modelling studies of the sources and fate of perfluorinated carboxylates. *Environ Chem* 8:339–354
- Del Vento S, Halsall C, Gioia R, Jones K, Dachs J (2012) Volatile per- and polyfluoroalkyl compounds in the remote atmosphere of the western Antarctic Peninsula: an indirect source of perfluoroalkyl acids to Antarctic waters? *Atmos Pollut Res* 3:450–455
- D'Eon JC, Hurley MD, Wallington TJ, Mabury SA (2006) Atmospheric chemistry of *N*-methyl perfluorobutane sulfonamidoethanol, C₄F₉SO₂N(CH₃)CH₂CH₂OH: kinetics and mechanism of reaction with OH. *Environ Sci Technol* 40:1862–1868
- Dietz R, Bossi R, Riget FF, Sonne C, Born EW (2008) Increasing perfluoroalkyl contaminants in east Greenland polar bears (*Ursus maritimus*): a new toxic threat to the Arctic bears. *Environ Sci Technol* 42:2701–2707
- Dreyer A, Ebinghaus R (2009) Polyfluorinated compounds in ambient air from ship- and land-based measurements in northern Germany. *Atmos Environ* 43:1527–1535
- Dreyer A, Temme C, Sturm R, Ebinghaus R (2008) Optimized method avoiding solvent-induced response enhancement in the analysis of volatile and semi-volatile polyfluorinated alkylated compounds using gas chromatography–mass spectrometry. *J Chromatogr A* 1178:199–205
- Dreyer A, Matthias V, Temme C, Ebinghaus R (2009a) Annual time series of air concentrations of polyfluorinated compounds. *Environ Sci Technol* 43:4029–4036
- Dreyer A, Weinberg I, Temme C, Ebinghaus R (2009b) Polyfluorinated compounds in the atmosphere of the Atlantic and Southern oceans: evidence for a global distribution. *Environ Sci Technol* 43:6507–6514
- Ellis DA, Martin JW, De Silva AO, Mabury SA, Hurley MD, Sulbaek Andersen MP, Wallington TJ (2004) Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ Sci Technol* 38:3316–3321
- Giesy JP, Kannan K (2001) Global distribution of perfluorooctane sulfonate in wildlife. *Environ Sci Technol* 35:1339–1342
- Hornbuckle KC, Jeremiasen JD, Sweet CW, Eisenreich SJ (1994) Seasonal variations in air–water exchange of polychlorinated biphenyls in Lake Superior. *Environ Sci Technol* 28:1491–1501
- Jahnke A, Ahrens L, Ebinghaus R, Temme C (2007) Urban versus remote air concentrations of fluorotelomer alcohols and other

- polyfluorinated alkyl substances in Germany. *Environ Sci Technol* 41:745–752
- Kissa E (ed) (2001) Fluorinated surfactants and repellents, 97. Marcel Dekker, New York
- Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J (2007) Perfluoroalkyl acids: a review of monitoring and toxicological findings. *Toxicol Sci* 99:366–394
- Li J, Del Vento S, Schuster J, Zhang G, Chakraborty P, Kobara Y, Jones KC (2011) Perfluorinated compounds in the Asian atmosphere. *Environ Sci Technol* 45:7241–7248
- Liss PS, Slater PG (1974) Flux of gases across air–sea interface. *Nature* 247:181–184
- Lohmann R, Gioia R, Jones KC, Nizzetto L, Temme C, Xie Z, Schulz-Bull D, Hand I, Morgan E, Jantunen L (2009) Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. *Environ Sci Technol* 43:5633–5639
- Mahmoud MAM, Karrman A, Oono S, Harada KH, Koizumi A (2009) Polyfluorinated telomers in precipitation and surface water in an urban area of Japan. *Chemosphere* 74:467–472
- Martin JW, Ellis DA, Mabury SA, Hurley MD, Wallington TJ (2006) Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of *N*-ethyl perfluorobutanesulfonamide. *Environ Sci Technol* 40:864–872
- Möller A, Ahrens L, Sturm R, Westerveld J, van der Wielen F, Ebinghaus R, de Voogt P (2010) Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. *Environ Pollut* 158:3243–3250
- Oono S, Matsubara E, Harada KH, Takagi S, Hamada S, Asakawa A, Inoue K, Watanabe I, Koizumi A (2008) Survey of airborne polyfluorinated telomers in Keihan area, Japan. *Bull Environ Contam Toxicol* 80:102–106
- Paul AG, Jones KC, Sweetman AJ (2008) A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environ Sci Technol* 43:386–392
- Piekarz AM, Primbs T, Field JA, Barofsky DF, Simonich S (2007) Semivolatile fluorinated organic compounds in Asian and western US air masses. *Environ Sci Technol* 41:8248–8255
- Plumlee MH, McNeill K, Reinhard M (2009) Indirect photolysis of perfluorochemicals: hydroxyl radical-initiated oxidation of *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA) and other perfluoroalkanesulfonamides. *Environ Sci Technol* 43:3662–3668
- Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH (2006) Sources, fate and transport of perfluorocarboxylates. *Environ Sci Technol* 40:32–44
- Rhoads KR, Janssen EML, Luthy RG, Criddle CS (2008) Aerobic biotransformation and fate of *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE) in activated sludge. *Environ Sci Technol* 42:2873–2878
- Ritter SK (2010) Fluorochemicals go short. *Chem Eng News* 88:12–17
- Schultz MM, Barofsky DF, Field JA (2003) Fluorinated alkyl surfactants. *Environ Eng Sci* 20:487–501
- Schwarzenbach RP, Gschwend PM, Imboden DM (2003) Environmental organic chemistry. Wiley, Hoboken
- Shoeib M, Harner T, Vlahos P (2006) Perfluorinated chemicals in the Arctic atmosphere. *Environ Sci Technol* 40:7577–7583
- Stock NL, Furdul VI, Muir DCG, Mabury SA (2007) Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination. *Environ Sci Technol* 41:3529–3536
- Sun H, Zhang X, Wang L, Zhang T, Li F, He N, Alder AC (2012) Perfluoroalkyl compounds in municipal WWTPs in Tianjin, China—concentrations, distribution and mass flow. *Environ Sci Pollut Res* 19:1405–1415
- Wang N, Szostek B, Folsom PW, Sulecki LM, Capka V, Buck RC, Berti WR, Gannon JT (2005a) Aerobic biotransformation of 14 C-labeled 8–2 telomer B alcohol by activated sludge from a domestic sewage treatment plant. *Environ Sci Technol* 39:531–538
- Wang N, Bogdan Szostek B, Buck RC, Folsom PW, Sulecki LM, Capka V, Berti WR, Gannon JT (2005b) Fluorotelomer alcohol biodegradation: direct evidence that perfluorinated carbon chains breakdown. *Environ Sci Technol* 39:7516–7528
- Wang T, Khim JS, Chen C, Naile JE, Lu Y, Kannan K, Park J, Luo W, Jiao W, Hu W, Giesy JP (2012) Perfluorinated compounds in surface waters from Northern China: comparison to level of industrialization. *Environ Int* 42:37–46
- Weinberg I, Dreyer A, Ebinghaus R (2010) Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air. *Atmos Environ* 45:935–941
- Weinberg I, Dreyer A, Ebinghaus R (2011) Waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air. *Environ Pollut* 159:125–132
- Xie Z, Ebinghaus R, Temme C, Caba A, Ruck W (2005) Atmospheric concentrations and air–sea exchanges of phthalates in the North Sea (German Bight). *Atmos Environ* 39:3209–3219
- Xie Z, Lakaschus S, Ebinghaus R, Caba A, Ruck W (2006) Atmospheric concentrations and air–sea exchanges of nonylphenol, tertiary octylphenol and nonylphenol monoethoxylate in the North Sea. *Environ Pollut* 148(142):170–180
- Xie Z, Moller A, Ahrens L, Sturm R, Ebinghaus R (2011) Brominated flame retardants in seawater and atmosphere of the Atlantic and the Southern Ocean. *Environ Sci Technol* 45:1820–1826
- Zhao Z, Xie Z, Moller A, Sturm R, Tang J, Zhang G, Ebinghaus R (2012) Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast. *Environ Pollut* 170:71–77
- Zhao L, Folsom PW, Wolstenholme BW, Sun H, Wang N, Buck RC (2013) 6:2 Fluorotelomer alcohol biotransformation in an aerobic river sediment system. *Chemosphere* 90:203–209