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Longitudinal and Latitudinal Distribution of Perfluoroalkyl Compounds in the Surface Water of the Atlantic Ocean

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Perfluoroalkyl compounds (PFCs) were determined in 2 L surface water samples collected in the Atlantic Ocean onboard the research vessels *Maria S. Merian* along the longitudinal gradient from Las Palmas (Spain) to St. Johns (Canada) (15° W to 52° W) and *Polarstern* along the latitudinal gradient from the Bay of Biscay to the South Atlantic Ocean (46° N to 26° S) in spring and fall 2007, respectively. After filtration the dissolved and particulate phases were extracted separately, and PFC concentrations were determined using high-performance liquid chromatography interfaced to tandem mass spectrometry. No PFCs were detected in the particulate phase. This study provides the first concentration data of perfluorooctanesulfonamide (FOSA), perfluorohexanoic acid, and perfluoroheptanoic acid from the Atlantic Ocean. Results indicate that trans-Atlantic Ocean currents caused the decreasing concentration gradient from the Bay of Biscay to the South Atlantic Ocean and the concentration drop-off close to the Labrador Sea. Maximum concentrations were found for FOSA, perfluorooctanesulfonate, and perfluorooctanoic acid at 302, 291, and 229 pg L⁻¹, respectively. However, the concentration of each single compound was usually in the tens of picograms per liter range. South of the equator only FOSA and below 4° S no PFCs could be detected.

Introduction

Perfluoroalkyl compounds (PFCs) are persistent against the typical environmental degradation processes and have been found in water, wildlife, and human tissues around the globe (1–3). Because of their unique physicochemical properties due to their combination of lipophilic and

hydrophilic characteristics, PFCs have been widely used in a lot of consumer products such as polymerization aids and stain repellents on carpets, textiles, leather, and paper products for over 50 years (4). From the production and use of these products, PFCs can be released into the environment. PFCs could be bioaccumulative (5) and have toxic effects in biota (6, 7). The transportation pathways of PFCs to remote regions have not been conclusively characterized to date. Two main hypotheses were proposed for the global transportation of PFCs. First, neutral, volatile precursor compounds could undergo long-range atmospheric transport and be degraded in remote regions (8), or second, ionic PFCs could be transported directly by oceanic currents or by means of sea spray (9, 10).

The first hypothesis is supported by the determination of precursor compounds, such as fluorotelomer alcohols (FTOHs), perfluoroalkanesulfonamidoethanols, in the Arctic atmosphere (11). The second hypothesis is supported by the fact that ionic PFCs such as the perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs) have high water solubilities and low pK_a values and are therefore dissociated at environmentally relevant pH values (4). The ocean currents were calculated by Prevedouros and co-workers to be the major transportation pathway for PFCAs in comparison to atmospheric transportation (12). However, irrespective of the transportation pathway involved, high concentrations of PFCs have been found in biota from the Canadian Arctic, especially in marine mammals which are top predators in the marine ecosystem (13).

The global occurrence of PFCs in open-ocean water was described first by Yamashita et al. (1). Further investigations of PFCs in the Indian Ocean and close to Antarctica were described subsequently (14). Detected concentrations are usually around some tens to hundreds of picograms per liter, depending on the location and the compound. It was hypothesized that PFCs could be transported globally with the thermohaline circulation system (15), with the open-ocean water acting as a final sink for perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) (1). However, ocean measurements are very limited and essential for the validation of models as well as quantifying inputs of PFCs to remote environments such as the Arctic. Further, seawater measurements of PFCs are very useful for determining the dominant transportation pathway, either oceanic currents or atmospheric transport of precursors.

The aim of this study was to investigate the longitudinal and latitudinal gradient of PFCs in surface water in the Atlantic Ocean. Sixty water samples were collected during cruises on the research vessels *Maria S. Merian*, from Las Palmas (Spain) to St. Johns (Canada) (15° W to 52° W), and *Polarstern*, from the Bay of Biscay to the South Atlantic Ocean (46° N to 26° S), in spring and fall 2007, respectively. Concentrations of various PFCs, including perfluorobutanesulfonate (PFBS), PFOS, perfluorooctanesulfonamide (FOSA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, and perfluorononanoic acid (PFNA), were quantified in open-ocean water samples. The observed distribution, characterized by increasing and decreasing concentration gradients of PFCs, can be explained by the pattern of ocean water currents. A comparison with open-ocean water PFC data from Yamashita et al. (1, 15) and Wei et al. (14) is given. This study provides the first evidence for the presence of FOSA, PFHxA, and PFHpA in the Atlantic Ocean.

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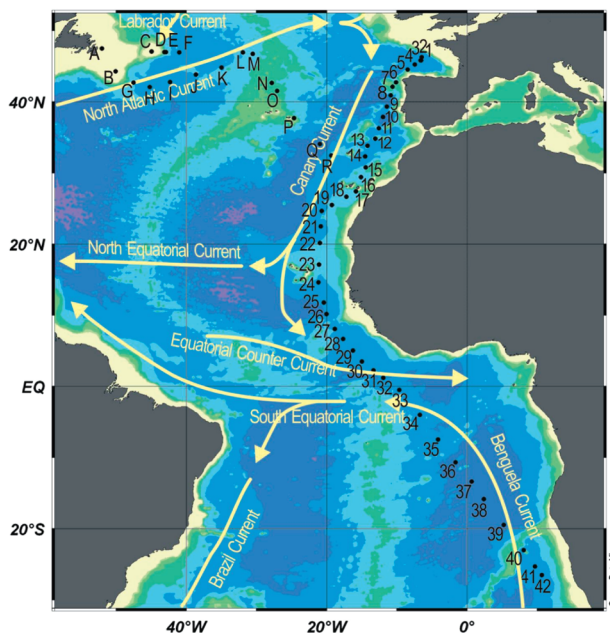


FIGURE 1. Map showing the sampling stations of the *Maria S. Merian* (15° W to 52° W, A–R) and *Polarstern* (46° N to 26° S, 1–42) cruises in 2007. The yellow arrows display the main surface currents in the Atlantic Ocean.

Experimental Section

Chemicals. The target analytes include 33 ionic PFCs (PFCAs, PFASs, perfluorinated sulfonates (PFSAs), fluorotelomer carboxylic acids (FTCAs), and unsaturated fluorotelomer carboxylic acids (FTUCAs)) as well as 7 neutral PFC precursor compounds (perfluoroalkanesulfonamides, perfluoroalkanesulfonamidoethanols) (for details, see Table S2 in the Supporting Information). Methanol (SupraSolv), acetonitrile (LiChrosolv), ammonium hydroxide (25% for analysis), formic acid (98–100% suprapure), and ammonium acetate were purchased from Merck (Darmstadt, Germany).

Sampling Campaign. Surface water samples were collected with the research vessels *Maria S. Merian* (Leibniz Institute for Baltic Sea Research (IOW), Warnemünde) and *Polarstern* (Alfred-Wegener-Institut (AWI), Bremerhaven) from April 14 to April 30 (cruise “MSM05”) and Oct 29 to Nov 22 (cruise “ANT XXIV-1”), 2007, respectively. The first cruise with the R/V *Maria S. Merian* was performed along the longitudinal gradient from 15° W to 52° W, and the second cruise with the R/V *Polarstern* was performed along the latitudinal gradient from 46° N to 26° S (Figure 1, Table S1 in the Supporting Information). Water samples (62 L) were collected in brown glass bottles via the ships’ intake systems at approximately 11 m below the surface at sampling stations 1–42 (46° N to 26° S) and A–R (15° W to 52° W). In addition, at sampling stations J, K, L, O, and R water samples were collected at 2 m depth and directly at the water surface by an external sampler in a brown glass bottle, and at sampling station L two deep-water samples were taken at depths of 200 and 3800 m with a rosette-type sampler (Seabird SBE-32 carousel water sampler equipped with 24 10 L Hydrobios-Freeflow bottles) to examine concentration differences between different water layers. The different sampling techniques, ship intake systems, rosette-type sampler, and outboard sampler using 2 L brown glass bottles were tested to evaluate for possible background contamination during sampling.

The samples were filtered directly after sampling onboard using glass fiber filters (GFF, GC/C, Whatman, Ø 47 mm, >1.2 µm). The dissolved-phase samples were stored at 4 °C prior to solid-phase extraction (SPE) onboard ship on the

same or following days, whereas the GFFs were stored in sealed test tubes in a freezer at –20 °C and extracted after the end of the sampling cruise in a clean laboratory (class 10 000) within a few days of arrival at the laboratory.

Field blanks (FBs) were taken every 10th sample for the filtrate and GFF to test for possible blank contamination. For the dissolved-phase FB, 100 mL of Millipore water (Millipore Elix 5 and Millipore Milli Q Plus) was added to a 2 L brown glass bottle and then put through SPE extraction. The sources of blank contamination are mostly caused by sampling, the extraction process, and instrument analysis (1), which indicates that the amount of contamination is independent of the volume of Millipore water extracted. FB GFFs were prepared by placing them on the filtration equipment for 1 min. Both types of field blanks were then stored and extracted in the same manner as “real” samples.

Sample Extraction and Instrumental Analysis. The filtrate and the GFF were separately spiked with 10 ng absolute of an internal standard (IS) mix (i.e., [¹³C₂]PFHxA, [¹³C₄]PFOA, [¹³C₄]PFNA, [¹³C₄]PFDA, [¹³C₂]PFUnDA, [¹³C₂]PFDoDA, [¹⁸O₂]PFHxS, [¹³C₄]PFOS, [¹³C₄]PFOSi, *d*₃-MeFOSA, *d*₅-EtFOSA, *d*₇-MeFOSE, *d*₉-EtFOSE, [¹³C₂]FHEA, [¹³C₂]FOEA, [¹³C₂]FDEA, [¹³C₂]FHUEA, [¹³C₂]FOUEA, [¹³C₂]FDUEA, 100 µL of a 0.1 µg mL^{–1} solution; see Table S1 in the Supporting Information). The filtrate was spiked with the IS mix and extracted by SPE with Oasis WAX cartridges (Waters, 150 mg, 6 cm³, 30 µm), as described elsewhere (16) with some modifications. Briefly, after being preconditioned with 5 mL of methanol and Millipore water, the cartridge was loaded with the 2 L sample at approximately 4 drops s^{–1} (~0.1 mL min^{–1}). The cartridge was then washed with 5 mL of 0.1% formic acid in Millipore water and dried for 30 min under vacuum. After the loading and drying steps onboard the ships, the cartridges were stored in a freezer at –20 °C. The cartridges were eluted after the end of the sampling cruise in a clean laboratory (class 10 000) within a few days of arrival at the laboratory. The elution was divided into two parts: The sulfonamides were eluted with 14 mL of acetonitrile; thereafter the acids were eluted with 5 mL of 0.1% ammonium hydroxide in methanol. The combined extract was reduced to 150 µL under a nitrogen stream and spiked with 20 ng absolute of the injection standard *d*₅-EtFOSAA (InjS, 50 µL of a 0.4 µg mL^{–1} solution; see Table S1).

The particulate matter (>1.2 µm) was analyzed by sonication as described elsewhere (17) with some modifications. The GFF was spiked with the same IS mix as the filtrate and sonicated with 100 mL of methanol for 1 h. This extraction was performed twice, and the two fractions were combined, evaporated by rotary evaporation, and filtered. The extract was reduced to 150 µL under a nitrogen stream and spiked with 20 ng of the InjS (see above). Finally, the extracts from the dissolved- and particulate-phase samples were analyzed 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 µ Hydro RP Mercury (20 × 2 mm, 2 µm). The triple-quadrupole mass spectrometer, supplied by Applied Biosystems/MDS SCIEX (API 3000), used an electrospray ionization (ESI) interface in negative ionization mode (for details see ref 18).

Results and Discussion

Quality Assurance. The analytical quality of the laboratory has been approved in interlaboratory studies (19). As standard procedure, FBs, method detection limits (MDLs), method quantification limits (MQLs) (see Table 1), and recoveries of spiked samples were examined (see Table S3 in the Supporting Information). Matrix spike recoveries of the target

TABLE 1. MDLs and MQLs for the Dissolved Phase and Field Blank Concentrations (Dissolved and Particulate Phases) for Cruises Onboard the Research Vessels *Maria S. Merian* (FB 15° W to 52° W, $n = 4 + 4$) and *Polarstern* (FB 46° N to 26° S, $n = 6 + 6$) in the Atlantic Ocean (pg L^{-1})^a

analyte	MDL ^b	MQL ^b	dissolved-phase FB		particulate-phase FB	
			R/V <i>Maria S. Merian</i>	R/V <i>Polarstern</i>	R/V <i>Maria S. Merian</i>	R/V <i>Polarstern</i>
PFBS	0.49	1.6	<1.6	<1.6	nd	nd
PFOS	3.1	10	<10	<10–25	nd	nd
FOSA	5.1	17	<17	<17	nd	nd
PFHxA	1.7	5.7	<5.7	<5.7–9.2	nd	nd
PFHpA	1.8	5.9	<5.9	<5.9–9.7	nd	nd
PFOA	1.2	4.0	<4.0–15	<4.0–28	nd	nd
PFNA	1.5	5.1	<5.1	<5.1	nd	nd

^a Blank levels were calculated from a sample volume of 100 mL of Millipore water. One FB sample from the R/V *Maria S. Merian* cruise and two FB samples from the *Polarstern* cruise showed a blank contamination. Details are given in the text. nd = not detected. < x = below the respective MQL. ^b MDL and MQL (ng L^{-1}) at 3 and 10 times the signal-to-noise ratio in natural samples ($n = 4$), respectively.

analytes ranged from 77% to 131% for the dissolved phase and from 72% to 113% for the particulate phase.

A variety of laboratory products contain fluoropolymers such as polytetrafluoroethylene (PTFE) (20). All fluorinated materials which could come in contact with the sample during the sampling (including SPE block), sample preparation, and instrumental analysis were removed (for details see ref 1). After the removal of all PTFE parts from the HPLC system, no instrument blank was detected. All procedure blanks, using 1 L of Millipore water, which were extracted in the same manner as the samples, were below the MQL. No background contamination was detected in the FB for the particulate phase. For the dissolved phase, the FBs from both sampling cruises were usually below the MQL, but in three FBs contamination levels of a few picograms per liter up to 28 pg L^{-1} (PFOA) were quantified (see Figure S1 in the Supporting Information). For control of the repeatability and blank contamination of the ship inlet system at stations J, K, L, O, and R, five samples were taken in parallel using the outboard sampler and the ship inlet system; for all detected PFCs no significant differences were observed (Mann–Whitney U -test [$p < 0.01$]). MDLs and MQLs were calculated for substances that were found in real samples using signal-to-noise ratios of 3 and 10, respectively. The MDLs were in the low picogram per liter range for the 2 L water samples. Matrix spike recoveries of the IS at two different spike levels (5 and 20 ng L^{-1}) ranged from 23% (d_3 -MeFOSA) to 90% ($[^{13}\text{C}_2]$ FHUEA) for the dissolved phase and from 50% (d_3 -MeFOSA) to 124% ($[^{13}\text{C}_2]$ PFHxA) for the particulate phase.

Concentrations of PFCs in the Atlantic Ocean. In this study, 40 PFCs (see Table S2 in the Supporting Information) were measured in the water samples. PFBS, PFOS, FOSA, PFHxA, PFHpA, PFOA, and PFNA could be quantified in the dissolved phase of the marine water samples in a concentration range of <MQL to 1115 pg L^{-1} ; all other PFCs were below the corresponding MDLs. PFCs were not detectable in the particulate phase. The low particle mass in the 2 L water samples could be responsible for the not detectable PFC concentration in the particulate phase in the Atlantic Ocean; however, the partitioning behavior of PFCs is an important future research field to evaluate their physical state and bioavailability. To the authors' knowledge, this is the first report of quantifiable concentrations of PFHxA, PFHpA, and FOSA in surface water in the Atlantic Ocean. At five sampling locations, water samples were taken in parallel at 11 and 2 m

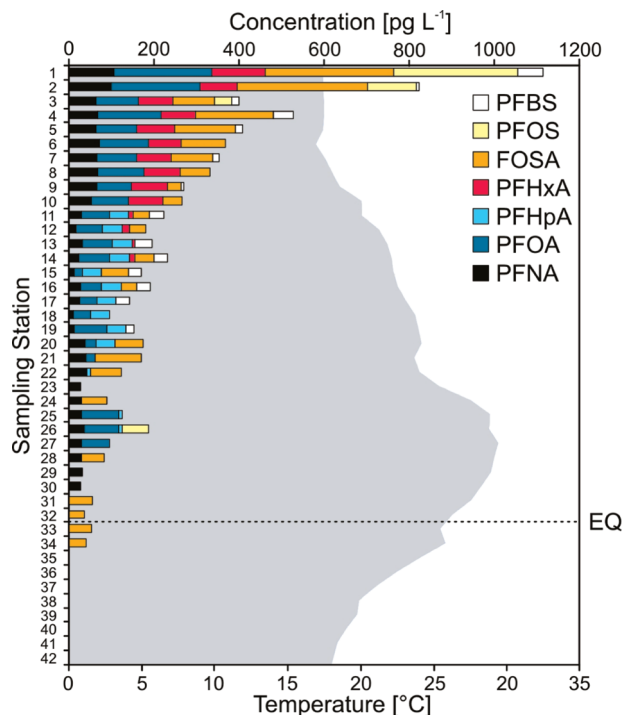


FIGURE 2. Individual PFC concentrations (pg L^{-1}) and ambient temperature from the *Polarstern* cruise (46° N to 26° S, 1–42) in 2007.

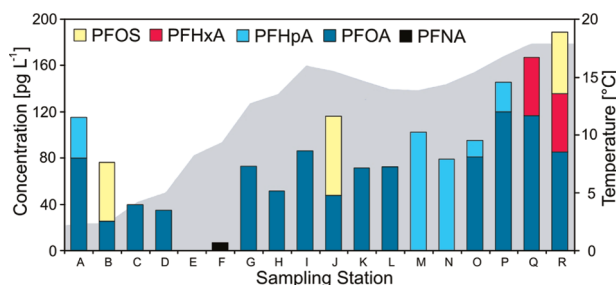


FIGURE 3. Individual PFC concentrations (pg L^{-1}) and ambient temperature from the *Maria S. Merian* cruise (15° W to 52° W, A–R) in 2007.

depths and directly at the surface. No correlation between sampling depth and concentration levels was observed, which indicates that there is a well-mixed zone between the surface and 11 m water depth in open-ocean waters. Ju et al. found at three near-shore sites that the surface microlayer (50 μL thickness) had by a factor of 24–109 higher PFOS concentration than the subsurface water (>30 cm depth) (21); however, the results are not comparable because of the different sampling techniques. Concentrations of PFCs at location L in the two deep-water samples at 200 and 3800 m were below the MDL. Yamashita et al. investigated vertical profiles in the Labrador Sea, Middle Atlantic Ocean, South Pacific Ocean, and Japan Sea, where they detected relatively constant concentration levels of PFOS, PFOA, and PFBS down to 2000 m in the Labrador Sea and a decreasing concentration gradient with water depth in the other areas. They suggested that the global circulation system has an influence on the occurrence of PFCs in deep water (15). Our deep-water samples were taken far away from downwelling currents, which explains why no PFCs were detected.

The longitudinal and latitudinal distribution of ΣPFC concentrations in the Atlantic Ocean is shown in Figures 2 and 3 and Table S4 in the Supporting Information. The highest ΣPFC concentration (1115 pg L^{-1}) was found in the Bay of Biscay close to the European source area. A decreasing north

to south latitudinal gradient was observed toward the Canary Islands where the mean Σ PFC concentration declined by a factor of 6 to 142–191 pg L⁻¹ (sampling stations 16 and 17). The Σ PFC concentrations remained relatively constant toward the south from the Canary Islands down to 10° N. In the equator area, the Σ PFC concentrations decreased by a factor of 4, relative to those of the Canary Islands down to 10° N, with only FOSA quantifiable at 37–53 pg L⁻¹ (sampling stations 31–34). South of 4° S, no PFCs were detected. The west to east transect in the North Atlantic showed a different pattern of concentrations. The Σ PFC concentrations east of 25° W (sampling stations G–R) and at sampling points A and B at the coast from Canada ranged from 52 to 117 pg L⁻¹ and were on average a factor of 2 higher than those of samples C–F, clustered north of the main transect close to the Labrador Sea (nd to 40 pg L⁻¹). The increasing concentrations, observed from sampling station L to sampling station R, could be influenced by latitudinal as well as longitudinal trends.

Two-thirds of the water samples contained quantifiable concentrations of PFOA, which was the most abundant compound in the water samples from the Atlantic Ocean, with a mean contribution of 37% to the Σ PFCs and a concentration range from <4.0 to 229 pg L⁻¹. PFNA was detected in 52% of the water samples at concentrations greater than the LOQ, but the concentrations from <5.1 to 107 pg L⁻¹ were less than those of PFOA. Concentrations of the other PFCs ranged from <17 to 307 pg L⁻¹ for FOSA, from <10 to 291 pg L⁻¹ for PFOS, from <5.7 to 127 pg L⁻¹ for PFHxA, from <5.9 to 104 pg L⁻¹ for PFHpA, and from <1.6 to 60 pg L⁻¹ for PFBS; however, the concentrations were below the MQL in more than half of the samples.

Comparison with Other Ocean Water PFC Measurements. Minimum and maximum PFC concentrations in surface open-ocean water from the Atlantic, Pacific, and Indian Oceans are shown in Table 2. In previous studies, the highest concentrations of PFOA and PFOS were found in the North and Mid Atlantic Ocean and the Western Pacific Ocean, while the lowest concentrations were observed in the Central and Southern Pacific and the Indian Ocean (1, 14, 15, 22). The results presented here can be compared with open ocean water samples presented from Yamashita et al. (1). They collected samples from the North and Middle Atlantic Ocean in 2002–2004 and found concentration levels of several tens of picograms per liter for perfluorohexanesulfonate (PFHxS), PFOS, and PFNA to a few hundreds of picograms per liter for PFOA. A similar study from Theobald et al. (22) was carried out from 53° N to 30° S in the Atlantic Ocean in 2005. The concentrations of PFOA and PFOS were in a range of a few tens of picograms per liter with a maximum concentration of 170 pg L⁻¹ for PFOS. Both studies (1, 22) reported concentrations in the same range as in this study, except for PFHxS, which was found in the first study, but could not be detected by us.

Concentrations of PFOS and PFOA reported in the West Pacific Ocean are in the same range as found in the Atlantic in this study, with concentrations of PFOS and PFOA in the Central and South Pacific and Indian Oceans about 1 magnitude lower than in the North Atlantic Ocean. PFBS and PFNA were also found in the Central to East Pacific Ocean and the Antarctic region, respectively, but the concentrations were less than those found in the Atlantic Ocean. The global distribution of PFBS might originate from the increasing production of *n*-methylperfluorobutanesulfonamidoethanol (MeFBSE) and related products with four perfluorinated carbons, which was introduced after the voluntary phase-out of perfluorooctanesulfonyl fluoride (POSF) by the 3M Co. in 2000 (23, 24). In comparison to this study, FOSA, PFHxA, and PFHpA could not be detected or were not analyzed in the Pacific and Indian Oceans, respectively. Conversely, PFHxS and PFDODA were detected in the Indian Ocean and

TABLE 2. Comparison of Minimum and Maximum PFC Concentrations in Surface Open-Ocean Water with Literature Data (pg L⁻¹)^a

	location	PFBS	PFHxS	PFOS	FOSA	PFHxA	PFHpA	PFOA	PFNA	PFDODA
Yamashita et al.(1)	North Atlantic Ocean (n = 9)	na	4.1–6.1	8.6–36	na	na	na	160–338	15–36	na
	Middle Atlantic Ocean (n = 7)	na	2.6–12	37–73	na	na	na	100–439	na	na
	West Pacific Ocean (n = 2)	na	2.2–2.8	54–78	na	na	na	136–142	na	na
	Central to East Pacific Ocean (n = 12)	na	0.1–1.6	1.1–20	na	na	na	15–62	1.0–16	na
Theobald et al.(22)	North to South Atlantic Ocean (n = 22)	na	na	<14–170	na	na	na	<17–90	na	na
	South Pacific Ocean (n = 5)	na	<5–11	<5–21	<5	na	na	<5–11	na	na
	Central and South Pacific Ocean (n = 9)	<25	<5	<5–8.6	<5	<5	<5	<5–7.0	<5	<1
	Indian Ocean (n = 7)	<5	<5	<5–22.6	na	<5	<5	<5–11	<5	<1–1.4
this study	Antarctic region (n = 5)	<1(5)–2.9	<1(5)	5.1–22.6	na	<5	<5	<5	<5	<1–1.1
	North Atlantic Ocean (n = 40)	<1.6–60	nd	<10–291	<17–307	<5.7–127	<5.9–104	<4.0–229	<5.1–107	nd
	Middle Atlantic Ocean (n = 10)	<1.6	nd	<10–60	<17–60	<5.7	<5.9–9.7	<4.0–87	<5.1–35	nd
	South Atlantic Ocean (n = 10)	<1.6	nd	<10	<17–53	<5.7	<5.9	<4.0	<5.1	nd

^a nd = not detected. na = not analyzed. <x = below the respective MQL.

Arctic region in the few picograms per liter range, whereas both compounds could not be detected in this study.

Yamashita et al. have studied vertical profiles of several PFCs in the Labrador Sea, Middle Atlantic Ocean, South Pacific Ocean, and Japan Sea in 2004 and 2005 (15). The surface water concentrations of PFOA and PFOS in the Northwest Atlantic Ocean were comparable with those from this study, but in addition in this study, PFHpA and PFNA were detected and PFBS was not detected in this area.

Impact of the Ocean Currents on the PFC Pattern and Concentration Level. The occurrence of elevated PFC levels in the Arctic ecosystem (25) raises the question about the global transportation and fate of PFCs. In addition to the atmosphere, the ocean currents could be an important global transport pathway for transport of PFCs from industrial to remote areas (1). This study examined the impact of environmental factors, such as ocean currents, on the distribution of PFCs in the Atlantic Ocean. The PFC concentration distribution along the latitudinal gradient will be influenced by the Canary, Equatorial Counter, and Benguela Currents (see Figures 1 and 2). The Canary Current comes from the north from the European Continent source region and crosses the Equatorial Counter Current and the Benguela Current in the equator area. The Benguela Current has for its origin Antarctic water with low PFC loading (14), and the influence of this water body resulted in a rapid decrease of Σ PFC concentrations to below the MDLs. The presence of cold surface water from the Benguela Current was confirmed by the drop-off of the water temperature from the equator region to the south. Furthermore, the West African coast seemed to have no impact on the concentration level, which suggests lack of sources (e.g., river discharge) from this area in contrast to the industrial European area. It is probable that PFC-laden water from the Canary Current was transported to the west and northwest by the North and South Equatorial Currents and possibly further south along the coast of Brazil by the Brazil Current. The decreasing latitudinal gradient is consistent with the decreasing gradient of PFOA and PFOS on airborne particles described by Jahnke et al. (26). What it is not known, however, is whether the airborne particle-bound fraction originated from sea spray or atmospheric degradation of volatile precursor compounds, i.e., whether the ocean was the source or sink for this airborne contamination. It is noteworthy that the pattern of importance of individual PFCs changed depending on the sampling area. In the northeast of the Atlantic Ocean in the Bay of Biscay, all PFCs, except for PFHpA, were detected, with the latter detected for the first time at 37° N. The concentration ranged from several tens of picograms per liter (PFBS, PFHxA, and PFNA) to a few hundreds of picograms per liter (PFOS, PFOA, and FOSA). The concentration of PFSA, PFOS, and PFBS dropped below the MDLs south of 32° N and 25° N, respectively. The occurrence of PFCs toward the south depended on their chain length, with the longer the chain length of the PFCs (C_6 to C_9), the further southward they were detected. The reason for this behavior could be different physicochemical characteristics (e.g., vapor pressure, partition coefficient) and/or input from atmospheric sources (17, 8). The increasing Σ PFC concentration at sampling stations 24–28, attended by an increasing water temperature, could be caused by higher rainfall in this area, leading to increased deposition of PFCs from the atmosphere (27). Of all detected PFCs, FOSA was found furthest south, down to 4° S, possibly as a result of its higher vapor pressure increasing the importance of atmospheric transport.

The location of the Labrador, North Atlantic, and Canary Currents will similarly affect the distribution of PFCs along the longitudinal transect (see Figures 1 and 3). PFC concentrations dropped off in sampling stations C–F. These results imply that the northeastern samples were influenced

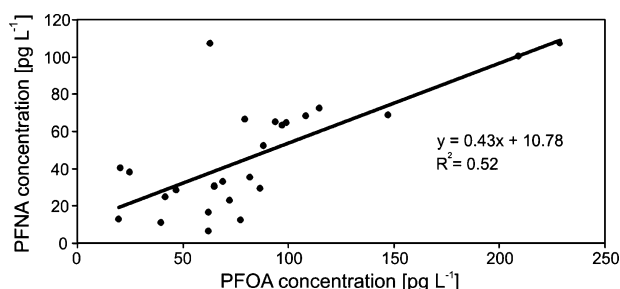


FIGURE 4. Correlations between PFNA and PFOA concentrations in surface water in the Atlantic Ocean.

by the Labrador Current, whose origin is the Arctic Ocean and is relatively “clean” (15), and the low ocean temperatures in this area support this hypothesis. In contrast, sampling stations A and B had elevated concentrations and were probably influenced by inputs from the Canadian coast and North Atlantic Current, respectively. In the area of the North Atlantic Current, PFOS, PFHpA, and PFOA dominated, with sum concentrations of 52–117 pg L^{-1} (sampling stations G–O). This is twice the concentration found at sampling stations C–F influenced by the Labrador Current. The warm temperature of the North Atlantic Current became noticeable at sampling stations L and M, which were at latitudes similar to those of stations C–F, but with surface water temperatures much higher than those close to the Labrador Sea. The highest concentrations were found at sampling stations P–R, which could be induced by the Canary Current carrying PFCs from the European Continent source region.

The concentrations of PFNA and PFOA were positively correlated ($r^2 = 0.52$; see Figure 4), which indicates that the sources of both compounds are related (28). Young et al. found a positive correlation with a gradient of ~ 1 in snow on remote ice caps that were contaminated atmospherically by precursors, in this case 8:2 FTOH (28). The gradient in the Atlantic Ocean is ~ 0.4 , and it is possible that the degradation of perfluoroalkanesulfonamides could lead to a higher amount of PFOA relative to PFNA (29). Plots of PFHxA, PFOA, and PFNA concentrations versus PFOS concentrations are also correlated for the Atlantic Ocean, but the significance is lower because the calculations are based on only a few data points (Figure S2 in the Supporting Information). Young et al. found no correlation among PFHxA, PFNA, and PFOS on the ice cap, which further supported the source there being the atmospheric pathway (28). Concentrations of PFHpA and PFOA were negatively correlated in the Atlantic Ocean ($r^2 = 0.32$, see Figure S2), probably as a consequence of the patchy distribution of PFHpA. Simcik et al. found that the ratio of PFHpA to PFOA increased with increasing distance from nonatmospheric sources and suggested that a high ratio would be a good tracer of atmospheric deposition (30). In this study, only a few stations (15, 20, M, and N) had PFHpA/PFOA ratios greater than 1, which suggests that direct releases are important determinants of open Atlantic Ocean surface water concentrations.

Several reasons for the distribution pattern of PFCs in the Atlantic Ocean have been suggested, but for each location several factors could be responsible for the occurrence of the PFCs. Ocean currents and related dilution effects have a crucial influence on PFC distribution (15). The spatial distribution data obtained in this study are useful for global transportation models (31), in which industrial areas are considered as source of PFCs, and ocean waters and the atmosphere are important as sinks and for transportation of these compounds. This transportation to remote regions could have adverse effects in top predators here, because of the high bioaccumulation potential for PFOS and longer chained PFCs in the marine food web (32). Further investigations of the biochemical cycle of PFCs in ocean

waters are necessary for understanding the transportation and fate of PFCs in the marine environment.

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Note Added after ASAP Publication

Reference 18 was modified in the version of this paper published March 30, 2009; the corrected version published ASAP April 6, 2009.

Supporting Information Available

Additional information about the location of the sampling sites, target analytes, and method recovery rates, overview of PFC concentrations in the Atlantic Ocean, chromatograms of a real sample and a blank sample, and correlations between PFC concentrations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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