

LONGITUDINAL AND LATITUDINAL DISTRIBUTION OF POLYFLUORINATED COMPOUNDS IN SURFACE WATER IN THE ATLANTIC OCEAN

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Introduction

Per- and polyfluorinated compounds (PFCs) are widely used in a lots of consumer products such as polymerization aids, stain repellents on carpets, textiles, leather, and paper products because of their unique physicochemical properties. PFCs are persistent in the environment and they have been found in water, wildlife and human tissues around the globe¹. But little is known about their aqueous transport to remote areas. The perfluorinated acids have high water solubilities, low pK_a values and are therefore dissociated at environmentally relevant pH values. The perfluorosulfonamides are neutral compounds and consequently not as water-soluble as the acids and also more volatile. It is assumed that they are transformed to perfluorinated sulfonic acids (PFSAs) in the atmosphere, while fluorotelomer alcohols (FTOHs) are degraded over the intermediates fluorotelomer acids (FTCAs), unsaturated telomer acids (FTUCAs) to perfluorocarboxylic acids (PFCAs). PFCs have been detected in precipitation², surface³, ocean⁴, and tap water⁵. Detected concentrations are usually around some hundreds of pg L⁻¹ to a few tens of ng L⁻¹, depending on the location and the compound. The aim of this study was to investigate the longitudinal and latitudinal gradient of PFCs in surface water in the Atlantic Ocean.

Materials and Methods

In this study 40 PFCs were determined from the following groups: one fluorotelomer sulfonate, seven perfluorosulfonates, three perfluorosulfonates, sixteen perfluorocarboxylic acids, three fluorotelomer acids, three unsaturated telomer acids, four perfluorosulfonamides and three perfluorosulfonamidoethanols. In addition 20 mass-labelled standards were used as internal standards (IS). The water samples were collected in the Atlantic Ocean with the research vehicle *Maria S. Merian* (Leibniz Institute for Baltic Sea Research (IOW) Warnemünde) and *Polarstern* (Alfred-Wegener-Institut (AWI) Bremerhaven) from the 14th to 30th of April (cruise "MSM05") and 29th October to 22nd November (cruise "ANT XXIV-1") 2007, respectively. The first cruise with the RV *Maria S. Merian* was performed along the longitudinal gradient from 15°W to 52°W and the second cruise was performed along the latitudinal gradient from 46°N to 26°S (Figure 1). Two litre water samples were taken in brown glass bottles via a ship intake system at approximately 11 m below the surface, or were dropped under water by a sampler at 2 m or directly at the surface. The samples were filtered through a glass fibre filter (GFF, Whatman, ø 47 mm) on the same day; the water phase was stored at 4°C and the GFF at -20 °C. The water phase and the GFF were spiked with 100 µL IS-mix (10 ng absolute) separately. The filtrate was spiked with the IS and extracted by solid phase extraction (SPE) with Waters WAX cartridges. After the precondition with 5 mL methanol and Millipore water the cartridge was loaded with the two litres sample with approximately 4 drops sec⁻¹. Then the cartridge was washed with 5 mL 0.1% formic acid in Millipore water and dried for 30 min. After the loading and drying on the ship, the cartridges were stored at -20 °C and eluted in a clean lab at GKSS. In the clean lab the elution was divided into two parts; the sulfonamides were eluted by 14 mL acetonitrile; thereafter the acids were eluted by 5 mL 0.1% ammonium hydroxide in methanol. The extract was reduced to 200 µL under a nitrogen stream and spiked with an injection standard (InjS). The particulate matter (> 1.2 µm) was analysed by sonication. The GFF was placed into a glass fibre thimble in a beaker and sonicated with methanol for one hour. This was done twice and the two fractions were combined, evaporated and filtered. Then it was reduced to 200 µL and spiked with the InjS like the dissolved phase extract. Finally both extracts were analysed with high performance liquid chromatography-negative electrospray ionisation-tandem mass spectrometry (HPLC-(-)ESI-MS/MS).

Results and Discussion

All Teflon parts were removed from the HPLC system, after these modifications no blank contamination of the instrument was detected. All the method blank contaminations were below the lowest calibration point (1 pg

absolute). Method detection limits (MDLs) were calculated for substances that were found in real samples using the signal to noise of 3 or three times the standard deviation of the average blank signal, if blank contaminations exist. The MDLs were in low ppq level for the two litre water samples.

7 of 40 analysed PFCs were found in the dissolved phase in the Atlantic Ocean (i.e. perfluorobutanesulfonate (PFBS), perfluorooctanesulfonate (PFOS), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorooctane sulfonamide (PFOSA)). All concentrations in the particle phase were below the MDLs. In this study was observed for the first time PFHxA, PFHpA and PFOSA in surface water in the Atlantic Ocean. At five sampling locations water samples were taken at 2 m depth and directly at the surface. No connection between sampling depth and concentration level was observed. For control of the repeatability and blank contamination of the ship inlet system five samples were taken parallel with the outboard sampler and with the ship inlet system. Higher concentrations were found for PFOS in two samples taken with the ship inlet system; for all detected PFCs no significant differences were observed.

The longitudinal and latitudinal Σ PFCs concentration in the Atlantic Ocean is given in Figure 1. The highest Σ PFCs concentration (1.1 ng L^{-1}) was found close to the coast of Spain and Portugal. A gradient was observed towards the Canary Islands where the mean Σ PFCs concentration dropped down at a factor of 6 to 0.2 ng L^{-1} . The Σ PFCs concentrations remained relatively constant towards the south down to 10°N . In the equator area the concentration decreased by a factor of 4 and southern of 4°S no PFCs were detected. An explanation for this gradient could be the influence of the ocean current. The Canary Current comes from the north and crosses in the equator area the Equatorial Counter Current and the Benguela Current, which is the biggest current in this area. The Benguela Current comes from Antarctic water with low PFCs loading and resulting in Σ PFCs concentrations under the MDLs. The west to east transect in the North Atlantic showed a different behaviour. The Σ PFCs concentrations east of 40°W and one sampling point directly at the coast from Canada was by a factor of 2 higher than from the samples close to the Labrador Sea. These results imply that the eastern samples were possibly influenced by the low PFCs contaminated Labrador Current whose origin is the Arctic Ocean.

The pattern of individual PFCs changed depending on the sampling area. In the north-east of the Atlantic Ocean close to Spain and Portugal all seven PFCs were detected. The concentration ranged from several ten pg L^{-1} (PFBS, PFHxA, PFHpA and PFNA) to a few hundreds of pg L^{-1} (PFOS, PFOA and PFOSA). The concentration of the both PFSA, PFOS and PFBS, dropped down under the MDLs south of 32°N and 25°N , respectively. The detection of the PFCAs towards the south depended on their chain length. The longer the chain length of the PFCAs, the more southwards they were detected. The reason could be the higher persistence of the longer chained compounds. PFOSA was found more southerly than all the other detected PFCs, down to 4°S . Along the west-east transect PFOS, PFHpA and PFOA dominated with a range of several ten pg L^{-1} to a little over one hundred pg L^{-1} .

The results described can be compared with open oceans water samples presented from Yamashita *et al.*⁴. They took samples in the North and the Mid Atlantic Ocean in 2002 to 2004 with a concentration level of several tens pg L^{-1} for perfluorohexanesulfonate (PFHxS), PFOS and PFNS to a few hundreds pg L^{-1} for PFOA. This was in the same range as in this study, except for PFHxS, which could not be found here. In another study of Yamashita *et al.*⁶ they took vertical profiles samples in the Labrador Sea, Mid Atlantic Ocean, South Pacific Ocean and Japan Sea to use PFCs as chemical tracers for the global circulation of ocean waters. The surface water concentrations in the north-west Atlantic Ocean of PFOA and PFOS were comparable with this study, but in addition PFHpA and PFNA could be detected and PFBS could not in this study. In comparison to this study the concentration of PFOS, PFHxS and PFNA in the Pacific Ocean were lower with up to a few pg L^{-1} . Otherwise the concentration of PFOA is only a little under the concentration level as in this study.

This study examined the distribution and the transport of PFCs in the Atlantic Ocean. A PFCs transport from north to south was determined with the Canary Current through the equator. Due to the Benguela Current at the equator the PFCs concentration decreased rapidly up to the MDLs. Probably the PFCs loading were transported further with the South Equatorial Current to the west and along the coast of Brazil to the south with the Brazil

Current. In the north-west Atlantic the Labrador Current could be responsible for the drop-off of the PFC concentrations. Further investigations of the distribution and fate of PFCs in open water are necessary for understanding of the origin of PFCs in the marine environment in rural areas.

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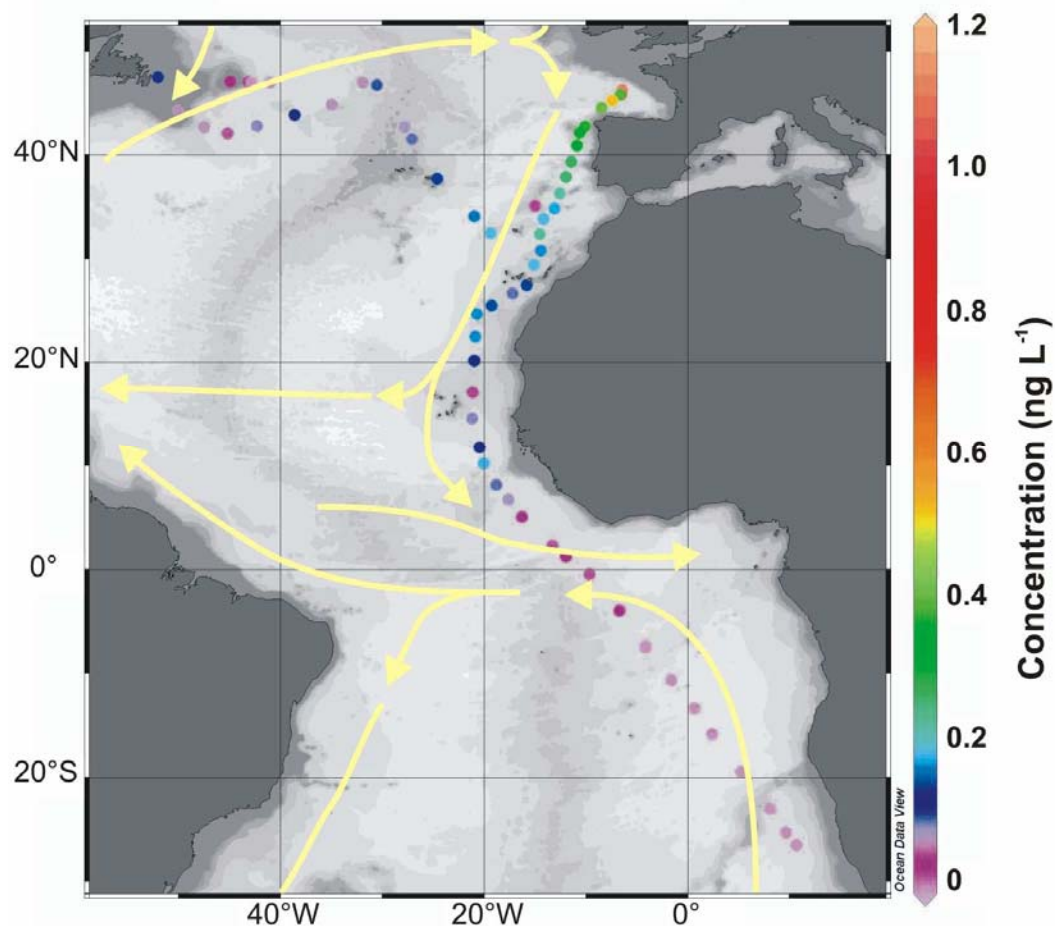


Figure 1: Concentrations of Σ PFCs in the Atlantic Ocean (ng L^{-1}). The yellow arrows show the main ocean currents.