

THE LONG RANGE TRANSPORTATION OF PFOS AND PFOA BY GLOBAL SCALE WATER CURRENT

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Abstract

Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are global environmental contaminants. The physicochemical properties of perfluorinated acids (PFAs) are unique in that they have high water solubilities despite the low reactivity of carbon-fluorine bond, which also imparts high stability in the environment. Because of the high water solubilities, the open-ocean water column is suggested to be the final sink for PFOS and PFOA. However, very little is known on the distribution of these compounds in the oceans around the world. Here we describe the horizontal (spatial) and vertical distribution of PFOS and PFOA in ocean waters worldwide. The results provide evidence that concentrations and profiles of PFOS and PFOA in the oceans adhere to a pattern consistent with the global "Broecker's Conveyor Belt" theory of open ocean water circulation, and provide an insight of new research field of high resolution hydrodynamics to understand both the local scale kinetics by wet deposition and global scale by ocean water circulations.

Introduction

The international joint research between AIST, Ocean Research Institute of Tokyo University and Leibniz Institute of Marine Science from 2002 conducted a joint study by collecting water samples from oceans worldwide for the analysis of PFAs and the results were reported in 2005¹. Earlier results of the monitoring survey revealed that there were remarkably higher concentrations of PFOS and PFOA in surface water from the northern and middle Atlantic Ocean compared to those from the southern Pacific Ocean. No reasonable hypothesis, including the traditional long range atmospheric transportation, could be possible to explain such global distribution of these compounds in the open ocean. It is known that the oceans are a three-dimensional compartments and the results of surface water analysis show only limited information of hydrodynamics of PFAs. In this study, we performed ultra-trace level analysis of PFOA and PFOA in five water columns upto a depth of 5500 m (3500 – 5500 m) collected from the middle Atlantic Ocean and the South Pacific Ocean.

Materials and Methods

Open ocean and offshore surface and subsurface water samples were collected between 2002 and 2006 from 62 locations around the world¹. Five water-column samples, at several depths of up to 5500 m, were collected from the Mid Atlantic Ocean and the South Pacific Ocean. Seawater were collected by rosette-type sampler equipped with Go-Flo or Niskin bottles during several international ocean research cruises by the Leibniz-Institute of Marine Sciences (Germany), the Ocean Research Institute (ORI) of Tokyo University (Japan), and Ibaraki University (Japan). Water samples were stored in clean 1-L polypropylene bottles and were kept frozen until analysis. Detailed analytical procedure reported elsewhere^{2,3}. Quality assurance and quality control (QA/QC) protocols were based on participation in a round-robin test of the International Organization for Standardization (ISO/TC147/SC2/WG56, PFOS and PFOA; protocol number CD25101).

Results and Discussion

The vertical profile of PFOS and PFOA in the Mid-Atlantic Ocean (AO3, AO4, AO5) seems to be typical of the profiles found for coastal and off-shore regions of the industrialized countries (Figure 1). PFOS and PFOA discharged into the surface waters in the Mid-Atlantic Ocean seemed to have long residence times due to the isolation of the surface waters from the deep waters, and due also to the circulation of the water mass by the Gulf Stream and the North Atlantic Drift. These factors provide an explanation for the highest concentrations found in the Mid-Atlantic Ocean.

The vertical profiles of PFOS and PFOA in two water columns, PO1 and PO2 from the South Pacific Ocean were completely different from the middle Atlantic Ocean. Concentrations of PFAs were consistently low (<10 pg/L) or below the limit of detection, from surface to bottom. These water columns are samplings of ocean currents that are more than 1000 years old, in terms of global circulation, as well as surface coastal streams derived from Antarctic circumpolar waters. Despite the fact that PO1 and PO2 are different masses of water, concentration profiles were constant throughout both columns. Negligible level of PFOS and PFOA in the water columns of the South Pacific Ocean showed that there is no direct input to this remote region. Thus, the open ocean water in the South Pacific is less contaminated by PFOS and PFOA than the water masses in the middle Atlantic Ocean.

The results presented above provide evidence that PFOS and PFOA concentrations and profiles in the oceans adhere to a pattern consistent with the global "Broecker's Conveyor Belt" theory of open ocean water circulation⁴, as described in Figure 2. Striking differences in the vertical and spatial distribution of PFAs, depending on the oceans, suggest that these persistent acids can serve as useful chemical tracers to allow us to study oceanic transportation by major water currents.

Acknowledgements

We thank the staff of ORI, Leibniz-Institute of Marine Sciences in Germany, Ibaraki University in Japan, City University of Hong Kong, and Dr. Yuichi Horii at the Wadsworth Center in the USA, for sample collection. We also thank Prof. Douglas Wallace and Dr. Toste Tanhua at the Leibniz-Institute of Marine Sciences for their critical comments.

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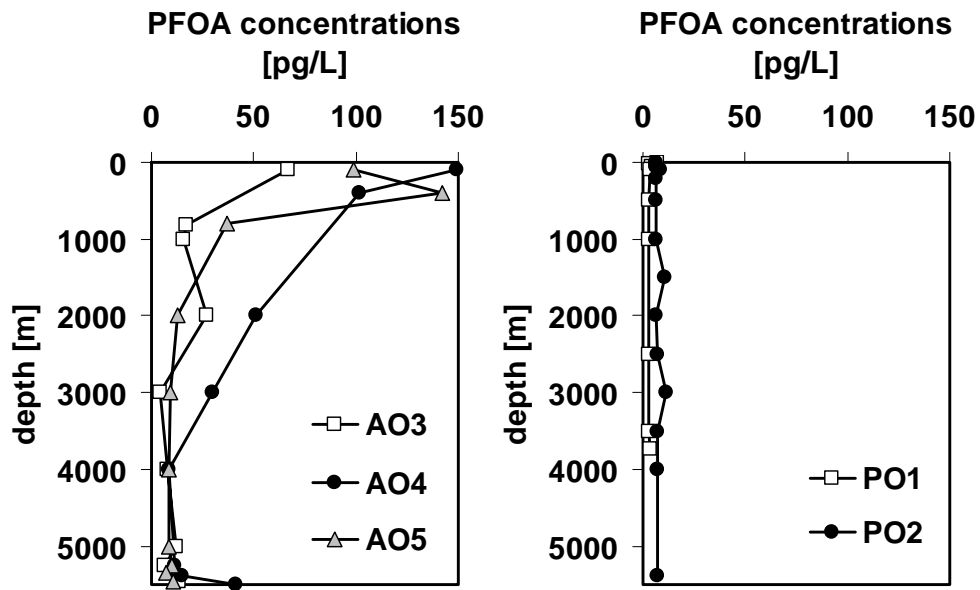


Figure 1. Vertical profiles of PFOA in water column in the Middle Atlantic Ocean (AO3, AO4, AO5) and the South Pacific Ocean (PO1, PO2).

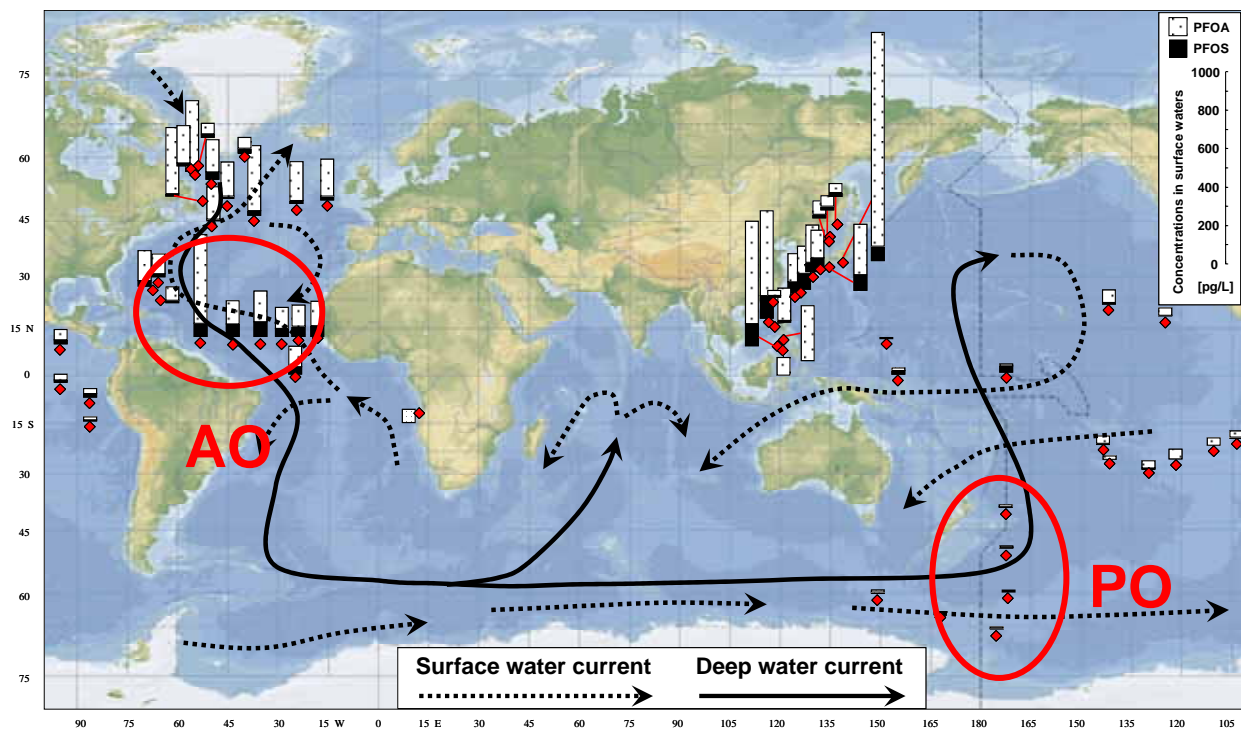


Figure 2. Global monitoring survey of PFOS and PFOA in surface water - possible long range transportation by global scale water current (modified from Broecker's conveyor belt).