

TIME TRENDS OF PERFLUORINATED COMPOUNDS IN THE SEDIMENT CORE OF TOKYO BAY, JAPAN (1950s-2004)

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Abstract

The time trend of perfluorinated compounds (PFCs) was determined in sediment core samples collected in Tokyo Bay. The core sample deposited during 1950s-2004 was divided into two- to three-year intervals. Perfluorocalboxylates (PFCAs), perfluoroalkylsulfonates (PFASs), perfluorooctane sulfonamidoacetic acids (FOSAAAs), fluorotelomer calboxylates (FTCAs), fluorotelomer unsaturated carboxylates (FTUCAs), branched isomers of PFCs, and other compounds were measured. Perfluorooctane sulfonate (PFOS) decreased gradually from the early 1990s while N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA) and N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA) decreased rapidly in the late 1990s. Perfluorooctanoic acid (PFOA) increased during 1990s. The observed trends were regarded as a reflection of the shift from perfluorooctyl sulfonyl fluoride (POSF)-based products to telomer-based products after 2001 due to the phase out of POSF-based products. Several other characteristics of the PFC trend were obtained: “rapid increase after the early 1970s” for long-chain PFCA (C11 - C13); “gradual increase from the 1950s” for middle-chain PFCA (C9 - C10); and others. This study revealed that the sediment core can serve as a tool to reconstruct the past pollution trend of PFCs with longer than eight-carbon chain and provides interesting evidence concerning their environmental dynamics.

Introduction

Perfluorinated compounds (PFCs) have been used since the 1950s in multiple industries and in the development of consumer products. Many studies have been conducted since the first report of worldwide contamination by PFCs. Also, regulations concerning the manufacture, transport and use of PFCs, especially perfluorooctane sulfonate (PFOS) and perfluorooctyl sulfonyl fluoride (POSF), have been established^{1,2}. 3M, the dominant producer of POSF, which degrades to PFOS and related compounds, phased out the production of POSF and its related compounds during 2000 and 2002³. DuPont, which is a perfluorooctanoic acid (PFOA) producer, planned to reduce emission of such products by more than 85% by 2007 based on the production volume in 1999⁴. However, PFCs are still detected in various environmental media, such as humans, biota, air,

water, and sediment in many areas of the world. In most of the reports, the increasing trends of perfluoroalkylsulfonate (PFSA) and/or perfluorocalboxylates (PFCA) levels from the 1970s to the 1990s or their recent decrease after 2000 were observed⁵⁻⁸. However, most of studies could not reveal the detail picture of historical trend of PFCs because of limitations, such as limited time span of observation, long time intervals between measurements, or use of samples affected by various environmental factors. Thus, further research is required, which assessed from a different way, to reveal the detail of historical trend and to evaluate past environmental release, transport and fate of PFCs. In the present study, as many as 24 kinds of PFCs, including precursor compounds, in the sediment core covering approximately fifty-year period were analyzed with frequent time intervals.

Material and Method

Sampling Locations and Collection

Tokyo Bay is located adjacent to Tokyo Metropolis, which is the most industrialized, urbanized and populated area in Japan. The total area of its basin is 9,261 km² and it has a population of 29 million people (Fig. 1).

The sediment core of Tokyo Bay was obtained using an acrylic core pipe in February 2004. The sample was sliced at 2 cm intervals, and the separated samples were homogenized. The homogenized samples were refrigerated at -30 °C and subsequently freeze-dried for water removal. Coarse particles were removed by use of a 2 mm stainless mesh. The samples were stored in brown bottles and refrigerated at below -20 °C until analysis.

Sediment Dating

Sediment dating was conducted using the ¹³⁷Cs and ²¹⁰Pb dating techniques⁹. ¹³⁷Cs and ²¹⁰Pb contained in sediment core samples were analyzed using a well-type Ge semi-conductor detector (Ortec GWL-120230-S)

Extraction and analysis

A sliced sediment sample spiked with labeled internal standards was extracted with 10 mL of ethanol and 1 mL of 0.5 M Tetrabutyl ammonium hydrogen sulfate. The mixture was shaken at 300 rpm for 20 min, followed

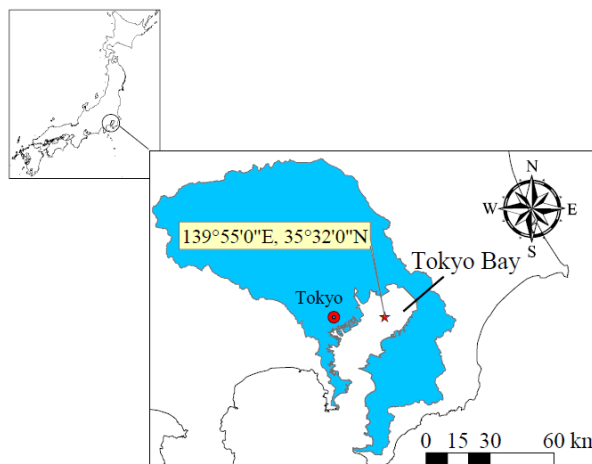


Fig. 1 Location of the sediment core sampling point. Shaded area is the basin of the Tokyo Bay.

by sonication for 20 min. The extraction was repeated twice, and the combined extract was concentrated under a gentle stream of nitrogen gas. Then, 10 mL of 10% ethanol and 20 μ L of 4 M HCl were added and the mixture was loaded onto Oasis WAX extraction cartridges (150 mg/6 cc) (Waters). Prior to solid phase extraction, the cartridge was preconditioned by loading of 5 mL of methanol followed by 5 mL of distilled water. The loaded cartridge was washed with 5 mL of 2% formic acid and 5 mL of 40% methanol. The cartridge was then dried and washed with 7 mL of methanol. Target compounds were eluted with 7 mL of 1% ammonium methanol solution. Finally, the eluate was passed through an envi-carb cartridge (100 mg/1 cc) (Supelco), dried under a gentle stream of nitrogen gas, and dissolved in 200 μ L of methanol. It was then transferred to a polypropylene vial for PFC analysis after being passed through a nylon membrane Millex filter unit (pore diameter 0.2 μ m, Millipore).

The ignition loss and the total organic carbon (TOC) in the sediment sample were also measured.

Instrumental Analysis

The PFC concentrations in the sediment samples were analyzed by use of a high-performance liquid chromatograph (Agilent 1100LC) interfaced with a tandem mass spectrometer (Micromass Quattro). The sum of the branched chain isomers of PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and Perfluorotridecanoic acid (PFTrDA) (iso-PFOA, iso-PFNA, iso-PFDA, iso-PFUnDA and iso-PFTrDA, respectively) was analyzed using the ratio of the peak area between PFNA and isopropyl PFNA. Also, the branched isomers of PFOS were separated into two peaks by HPLC and quantified using a PFOS standard whose linear and branched isomer content ratio was predetermined. The resolutions (R_s) of the isomer separation for PFOA/iso-PFOA, PFNA/iso-PFNA, PFDA/iso-PFDA, PFUnDA/iso-PFUnDA, PFTrDA/iso-PFTrDA and PFOS/iso-PFOS were 0.94, not calculated (NA), NA, 1.20, 1.49 and 1.24, respectively.

QA/QC

The limit of quantitation (LOQ) was estimated based on the S/N ratio of 10:1 in the measurement of each sediment sample. The recoveries of the PFCs were examined by spiking 1 ng of native standard into 2 g of the sediment sample prior to extraction and spiking 1 ng of internal standard into the final aliquots after extraction. Due to their unsatisfactory recoveries (< 50%), the results of some kind of PFCs are not reported in this paper.

The method blank value ($n=4$) was 0.12 ± 0.01 ng/g for PFOA, and below the LOQ for the other compounds. Although the blank value of PFOA was subtracted from the measured values, the blank value was relatively high compared with PFOA concentration in sediment samples (0.21 - 0.52 ng/g). Thus, the results of PFOA contain analytical variability.

Results and Discussion

Time trend of TOC and Characteristics of the sediment core

The ignition loss and TOC in each slice of the sediment are shown in Fig. 2.

These values peaked around the 1960s, gradually decreased until the early 1980s, and then increased again.

We have no clear explanation for this time trend. An unexpected shift was also observed for the values of ^{210}Pb and ^{137}Cs in deep sediment samples (late 1950s - 1960s) (data not shown). Changes in the sedimentary condition might have occurred due to accidental pollution, and/or deposition of large volumes of sediment by flood.

Some PFCs, such as PFOA, PFNA, PFOS, N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA), and N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA), had high concentrations during the late 1950s - 1960s, and seem to have been affected by the higher organic content in the sediment. Higgins et al. reported that the partitioning of PFC in the sediment was dominantly affected by the amount of organic carbon¹⁰. The sediment-water partitioning coefficient (K_d) increased with the organic carbon content in the sediment. Thus, the trends of PFCs were recalculated based on the organic carbon content (ng/g-OC). The peak of PFNA and PFOS observed during the late 1950s -1960s were normalized by the organic carbon based correction, though those peaks of PFOA, N-EtFOSAA and N-MeFOSAA remained.

Time trend of organic carbon-based PFC concentrations

The time trends of PFCs in the organic carbon base are shown in Fig. 3. Most of the PFCs increased with time, especially after the early 1970s. PFOS decreased gradually after the early 1990s, while N-EtFOSAA and N-MeFOSAA decreased rapidly in the late 1990s. Their rapid decrease could be the reflection of the phase out of POSF-based product production by 3M³. Although PFOA result contains analytical problem (See material and method), it is safe to say that the rapid increase in PFOA from the late 1990s to 2004 (60% increase) was notable. It might be due to the shift from POSF-based products toward telomer-based products^{4, 11}.

The observed trends were regarded as a reflection of the shift from POSF-based products to telomer-based products after 2001 due to the phase out of POSF-based products. Several other characteristics of the PFC trend were obtained: “rapid increase after the early 1970s” for long-chain PFCA (C11 - C13); “gradual increase from the 1950s” for middle-chain PFCA (C9 - C10); and others. Some compounds did not show any distinct trend (isomers of PFCA/PFOS, fluorotelomer calboxylates (FTCAs), fluorotelomer unsaturated carboxylates

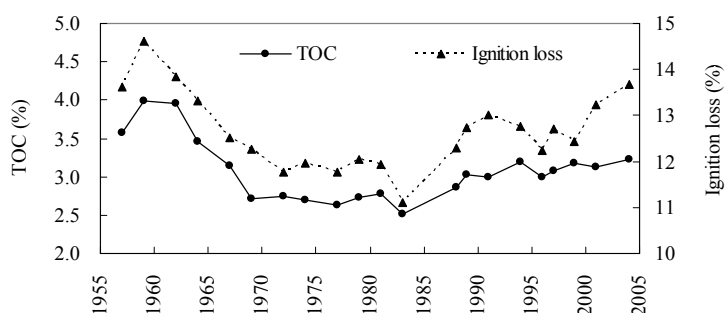


Fig. 2 Time trend of ignition loss and TOC in the sediment samples.

(FTUCAs), and 1H,1H,2H,2H-tetrahydroperfluorooctanesulfonate (THPFOS); most of these data were below the LOQ).

Comparison of PFC concentrations in sediment

The concentrations of linear chain PFCs (dry solid base) in 2004 were ranked as follows: PFOS (1.7 ng/g), PFTrDA (1.2 ng/g) and N-EtFOSAA (1.0 ng/g) > PFUnDA (0.55 ng/g), PFNA (0.50 ng/g) and PFOA (0.45 ng/g) > PFDoDA (0.29 ng/g) > PFDA (0.15 ng/g), N-MeFOSAA (0.13 ng/g), perfluoroheptanoic acid (PFHpA) (0.08 ng/g) > perfluorohexanoic acid (PFHxA), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), FTCAs, FTUCAs and THPFOS (< LOQ). PFOS and PFOA concentration in the sediment, which deposited in 2004, were similar level with their concentration detected in sediment samples of the San Francisco Bay area in 2004 (N.D. - 3.1

and N.D. - 0.63 ng/g d.w. for PFOS and PFOA, respectively)¹². PFOS and PFOA were also detected in Kyushu area, Japan in 2004 with respective ranges of 0.09 - 0.14 and 0.84 - 1.1 ng/g d.w.¹³. Most of short chain PFCs (C 6-7) were not detected in the current study. Among the PFCAs, PFTrDA was the predominant compound in the sediment in this report. It could be considered that PFTrDA have been the most abundant within PFCAs in the sediment due to its high K_{oc} value.

Branched chain isomers of PFSA and PFCAs

The concentration ratios of PFUnDA/iso-PFUnDA, PFTrDA/iso-PFTrDA and PFOS/iso-PFOS are shown in Fig. 4. Although the data were limited because many samples were below the LOQ, the obtained data indicate that the ratios for PFOS and PFUnDA did not change much over time. On the other hand, the ratio for PFTrDA

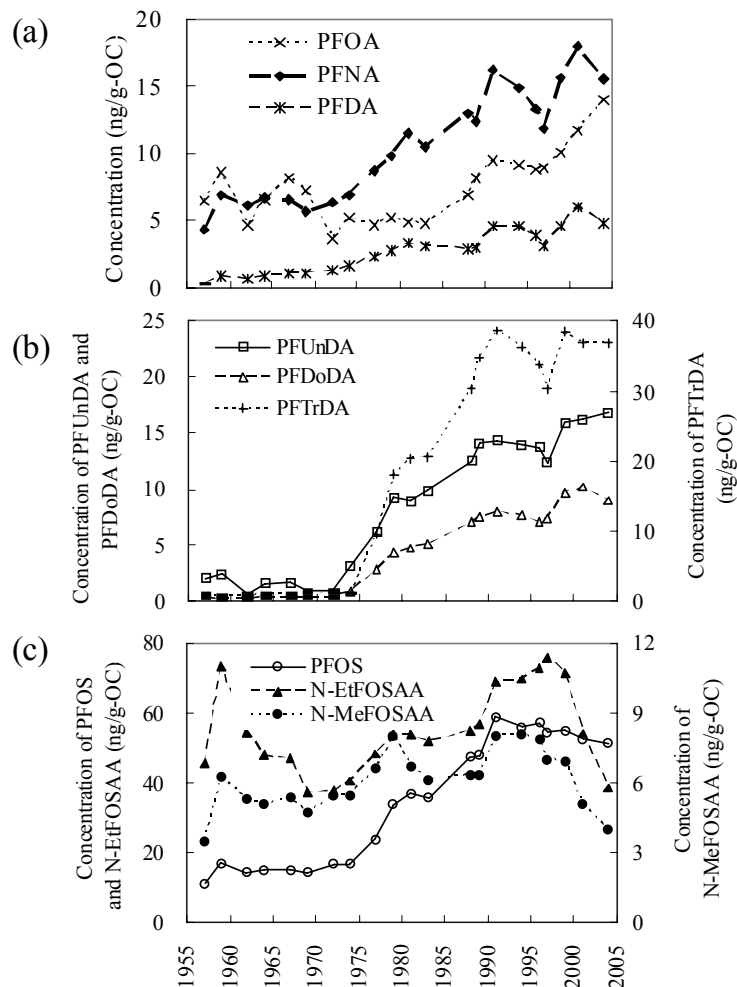


Fig. 3 Time trend of organic carbon-based PFC concentrations in the sediment. (-) means below LOQ.

gradually decreased with time. Even for long-chain PFCA, branched chain isomers were synthesized by telomerization using branched telogen, and it was reported that the ratios of linear chain to branched chain of PUnDA and PTrDA gradually increased after 1980 in lake trout collected in Lake Ontario¹⁴. The authors mentioned that the results indicated the possibility of an alternative source of these isomers in the Great Lakes environment,

particularly for products produced by telomerization of branched telogens. By contrast, the results obtained in the present study indicate a decrease in the telomerization process with linear telogen and/or an increase of telomerization with a branched telogen.

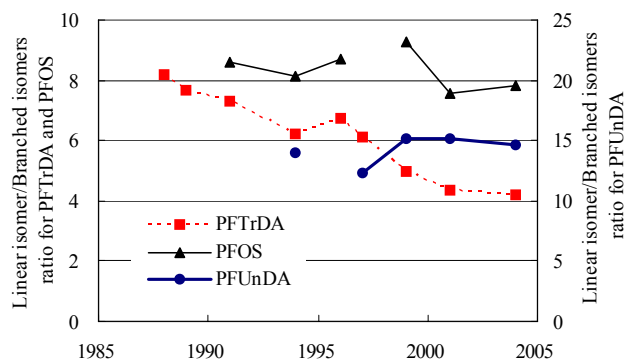


Fig. 4 Ratio of branched-isomer/linear-isomer concentrations for PFUnDA, PTrDA and PFOS in the sediment.

Acknowledgements

This study was supported by the Global COE program “Global Eco-Risk Management from Asian Viewpoints”, JSPS Research Fellowships for Young Scientists, and the ESPEC Foundation for Global Environment Research and Technology (Charitable Trust). The presenting author received financial support from Kurita Water and Environment Foundation for attending this conference.

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