

PERFLUOROCTANE SULFONATE (PFOS) AND PERFLUOROCTANOIC ACID (PFOA) LEVELS IN URBAN AIRBORNE PARTICLES LONG-TERM TRENDS IN TOKYO IN THE 1980s, 1990s AND 2000s

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Introduction

Perfluorooctane sulfonate (PFOS) is a perfluorinated compound (PFC) which has been manufactured for more than 50 years and widely used as a surfactant and surface protector for carpets, leather, paper, food containers, fabric, upholstery and as performance chemicals in products such as fire-fighting foams, floor polishes and shampoos. These compounds have recently been detected in both the environment and in animals, as well as in human serum. Even though the environmental fate of PFOS is not fully understood, the 3M Co., one of the largest producers of PFCs, ceased most of its production of PFOS in 2000 due to the widespread prevalence and potential toxicities of PFCs. In order to estimate human exposure to these chemicals, it is important to measure the annual trends regarding the environmental concentrations of these compounds. Although there are a few reports on the levels of airborne PFOS in some cities such as Kyoto and Morioka^{1,2}, no reports on the long-term trends of PFC levels in large Japanese cities are known. The present study examines PFOS and the related compound, perfluorooctanoic acid (PFOA), in airborne particles which were collected in the center of Tokyo between 1982 and 2003. Characteristic trends in the levels of PFOS and PFOA were determined over a period of two decades.

Materials and Methods

Reagents: Methanol (pesticide residue analysis grade) and distilled water (HPLC grade) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Perfluorooctane sulfonate potassium salt was purchased from Strem Chemicals (MA, USA). Perfluorooctanoic acid was purchased from Acros Organics (NJ, USA).

Airborne particle samples: Several samples from a specimen bank which had been collected and stored at the National Institute of Public Health (NIPH) were used in the present study. Airborne particles were collected on a quartz fiber filter (20 cm x 25 cm, Pallflex Products Co., U.S.A.) using high volume air samplers (Kimoto Electric Co., Japan or Shibata Scientific Technology Ltd., Japan) placed on the rooftop of the former NIPH building located in Shirokanedai, Tokyo, for a continuous period of over 20 years (1980-2004). After gravimetric analysis, samples were placed in deep-freezer (-80 °C) storage.

Extraction: Filter samples were cut into small pieces and placed into 200 mL Erlenmeyer flasks. 100 mL methanol was added and then sonicated twice for 20 minutes. After extraction, solutions were passed through a nylon membrane filter cartridge (Iwaki, pore size 0.2 µm) to remove suspended materials and insoluble particles. After removing the solvent by evaporation at room temperature under a weak nitrogen gas flow, the extracts were dissolved in 500 µL methanol for LC/MS analysis.

Analysis and Quantification: Analysis of PFOS and PFOA was performed by an HPLC tandem mass spectrometer, comprising an Agilent HP1100 LC system interfaced with a Micromass QII API tandem mass spectrometer operated in the electrospray negative ionization mode. The analytical methodology was followed according to that previously reported³.

Results and Discussion

Good separation was observed for both PFOS and PFOA. Product ions $m/z=98.7$ and 368.8 were used for the determination of PFOS and PFOA, respectively. Extraction recoveries were 90% for PFOS and 81% for PFOA when 11.9 ng of chemicals were applied to 1/2 of a blank filter. The coefficient variations (CV) for the filter samples were 13% for PFOS and 15% for PFOA with 4 repeated extractions and determinations.

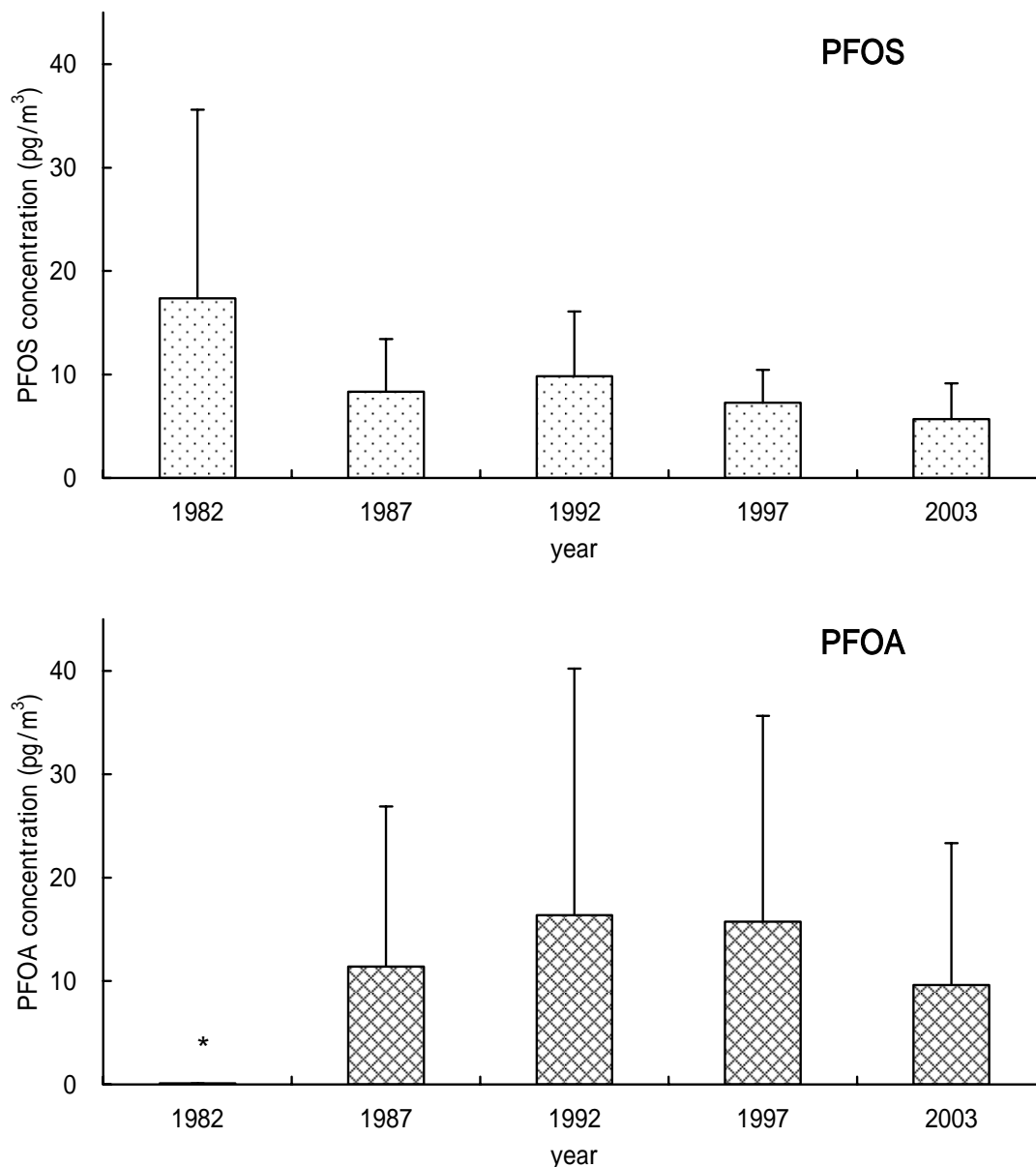


Figure 1 PFOS and PFOA concentrations of airborne particulate samples in winters of 1982, '87, '92, '97 and 2003

Bars indicate mean values with standard deviations (n = 7), except for 1992 and 2003 (n = 5).

* PFOA concentrations of all samples in 1982 were below the determination limit.

So far, several winter season samples in 1982 (n=7), 1987 (n=7), 1992 (n=5), 1997 (n=7) and 2003 (n=5) have been assayed. PFOS was determined in all samples, although some PFOA concentrations were below the determination limit. Figure 1 shows PFOS and PFOA concentrations of airborne particulate samples in the winter seasons of 1982, '87, '92, '97 and 2003. The vertical axis represents the concentration (pg/m³).

Each bar indicates mean and standard deviation. From the figure, mean concentrations of PFOS were 17.38 (SD 18.23) pg/m^3 in 1982, 8.35 (5.07) pg/m^3 in 1987, 9.85 (6.24) pg/m^3 in 1992, 7.28 (3.16) pg/m^3 in 1997, and 5.70 (3.45) pg/m^3 in 2003. Although there were slight variations, the PFOS level decreased throughout the sampling period. On the other hand, the PFOA concentrations of all samples (7/7) in 1982, 4/7 samples in 1987, 3/5 in 1992, 3/7 in 1997, and 4/5 in 2003 were below the determination limit. The mean concentrations of PFOA were 11.40 (SD 15.48) pg/m^3 in 1987, 16.38 (23.85) pg/m^3 in 1992, 15.73 (19.91) pg/m^3 in 1997, and 9.61 (13.73) pg/m^3 in 2003. Generally, CVs for PFOA were greater than those for PFOS.

Sasaki et al. (2003) reported PFOS concentrations in airborne dust which were collected every month from Apr. 2001 to Mar. 2002, in Fukuchiyama city and the town of Oyamazaki (Kyoto Pref., Japan). The annual geometric means for the air were 0.6 pg/m^3 for Fukuchiyama (rural area) and 5.3 pg/m^3 for Oyamazaki (urban area). The report also described a tendency for higher PFOS concentrations during summer (July to August) compared to winter (December to February) at both sites¹. From our results, the geometric means of PFOS concentrations were 12.21 pg/m^3 in 1982, 7.16 pg/m^3 in 1987, 8.51 pg/m^3 in 1992, 6.44 pg/m^3 in 1997, and 4.24 pg/m^3 in 2003. These levels were similar to the results from Oyamazaki.

In previous reports^{4,5}, polycyclic aromatic hydrocarbon (PAH) concentrations decreased throughout the sampling periods, especially in the late '80s, and slowly decreased from the mid 1990s. The PAH concentrations were higher in autumn and winter seasons rather than spring and summer seasons⁵. Also the TEQ of PCDDs/PCDFs decreased between 1994 and 1999, and the average concentrations were higher in winter than in summer. On the other hand, the TEQ for co-PCBs clearly showed a decrease every year since 1980, and there were no significant differences in seasonal variations⁴.

In total, the sum results discussed here suggest multiple and varied levels, trends and dynamics between PFOS and PFOA in airborne particles, as well as other airborne pollutants such as PAHs and dioxins.

Acknowledgement

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