

# Fundamental study on analytical methods for Perfluoroalkylsulfonates and Perfluorocarboxylicacids (PFASs/PFCAs) in ambient air

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## Introduction

PFOS is extremely persistent and has substantial bioaccumulating<sup>1)</sup> and biomagnifying properties<sup>2)</sup>, although it does not follow the classic pattern of other persistent organic pollutants (POPs) by partitioning into fatty tissues but instead binds to proteins in the blood<sup>3)4)</sup> and the liver<sup>5)</sup>. At its fourth meeting held May 2009, the Conference of the Parties (COP) of the Stockholm Convention decided to amend Annex B (restriction) to list it as POPs<sup>6)</sup>. In addition, PFOA was also found in human blood in the general population, and has been aimed at EPA's "2010/15 PFOA Stewardship Program"<sup>7)</sup>. In this way, the reduction of these substances has been begun by international efforts.

Historically, commercial PFAS/PFCA products were mixtures containing linear eight-carbon substances (PFOS/PFOA) as their major component. Depending upon the synthesis route and raw material, the PFAS/PFCA products also contained the homologues ranging from four to thirteen carbons<sup>8)</sup>.

There are a number of reports about concentrations, distribution, and transport of the volatile polyfluorinated alkyl substances such as perfluoroalkylsulfonamides (PFASs) and fluorotelomer alcohols (FTOHs) in ambient air<sup>9)10)</sup>. However, only limited data is currently available on PFASs/PFCAs including PFOS/PFOA<sup>11)</sup>.

In this study, we examined a highly selective and sensitive analytical method for the simultaneous analysis of PFASs/PFCAs in ambient air.

## Material and Methods

(Recovery experiments)

Air samples were collected using high-volume air sampler (HV-700F (Sibata Scientific Technology Ltd.)) equipped with a quartz fiber filter (QFF; QR-100 (Toyo Roshi Kaisha Ltd.)) to collect the particle phase. Environmental air samples were taken in June 2009 at Osaka City Institute of Public Health and Environmental Sciences in Osaka City, Japan. The flow rates were adjusted to approximate of 700L/min for 24 hours, leading to average sample volumes of 1000m<sup>3</sup>. After sampling, QFFs were sealed in alumina-coated PP bags, and stored at <-20°C until extraction.

The QFF was spiked with 2ng of two isotope-labelled C<sub>6,8</sub>PFASs and seven isotope-labelled C<sub>4,6,8-12</sub>PFCAs(MPFAC-MXA(Wellington Laboratories Inc.)) after sampling. Spiked nine isotope-labelled PFASs/PFCAs were extracted from QFFs by soxhlet (24hours) or ultrasonic extraction (30min × 2) with aqueous solution containing 10% methanol (soxhlet: 300mL, ultrasonic: 150mL) as the extraction solvent. After the extraction step, samples were passed through a membrane filter and solid phase cartridge (OASIS HLB (Waters)) for clean-up. The eluate was spiked with injection standard (Inj.S, <sup>13</sup>C<sub>8</sub>PFOA (CIL) and SDS-d25(C/D/N ISOTOPES)) before being reduced to a final volume for injection. Nine isotope-labelled PFASs/PFCAs were analysed by LC / (-) ESI-MS/MS (API2000; Applied Biosystems)(Table1), and recoveries were calculated respectively.

(Breakthrough Experiments)

To examine the collection efficiencies of target analyte and the extent of sample blowoff, several breakthrough experiments were conducted under field conditions.

The QFF was spiked with 2ng of two isotope-labelled C<sub>6,8</sub>PFASs and seven isotope-labelled C<sub>4,6,8-12</sub>PFCAs before sampling. Then, air samples were taken from June to July (summer) and December (winter) 2009 in Osaka City, Japan. These tests were also performed without the spiking before or after sampling.

Table1 Analytical Method for PFASs/PFCAs

HPLC			MS/MS	
Instrument	Agilent 1100		Instrument	API 2000
Column	TOSOH ODS-100S		Ionization	ESI
Mobile phase	A: 2mM NH <sub>4</sub> HCO <sub>3</sub> H <sub>2</sub> O B: 2mM NH <sub>4</sub> HCO <sub>3</sub> MeOH		Polarity mode	Negative
Flow rate	200 μL/min		Scan type	MRM
Column oven temp.	40°C		Heater Temp.	500°C
Injection volume	5 μL		Nebulizer Gas	60 psi
Gradient	time / min	A / %	Heater Gas	80 psi
	0	90		
	5	90		
	12	30		
	24	0		
	28	0		
	Reequilibration time	5min		

## Results and Discussion

(Recovery experiments)

Each method of extraction, clean-up, and instrumental measurement were examined for analysis of PFASs/PFCAs in air. In extraction process, recovery rate of C<sub>10-11</sub>PFCAs with Soxhlet extraction was lower than that of ultrasonic extraction. As compared with ultrasonic, Soxhlet was taken longer time in extraction, suggesting that longer carbon chain length PFCAs were adsorbed on the surface of glass vessel. To perform measurements of high sensitivity and selectivity, selection of monitored ions was very important in instrumental measurement. Furthermore, for separation of isomers, LC column selection will be important.

The results of the recovery experiments are shown in Figure 1. Recoveries of the nine isotope-labelled PFASs/PFCAs ranged from 0-130%. PFOS/PFOA, PFHxA, PFNA, and PFDA showed good recoveries (80-110%). PFHxS had too high recovery efficiency (130%) and PFUdA showed very low (47%). PFBA and PFDaA were not recovered.

These reasons were not clear at present, but pointing out the importance of appropriate isotope-labelled IS or Inj.S for each individual analyte.

#### (Breakthrough Experiments)

Recovery efficiencies ( $\hat{=}$  the rate of retained on QFF) of isotope-labelled PFOA from breakthrough experiment ranged from 20-74%. Average of recovery efficiencies during summer (n=2) and winter (n=3) sampling period were 26% and 61%, respectively. The

comparison of average air temperature and recovery efficiency of PFOA is shown in Figure 2. Average dairy temperatures in the field during breakthrough experiments were between 5.1 and 25 °C. The figure shows that the recovery efficiency had a significant inverse relationship with temperature. PFOS was also indicated similar tendency. These results suggest that the variability of concentrations of PFASs/PFCAs including PFOS and PFOA in air were significantly affected by air temperature variations during sampling.

The results from our preliminary experiments have to be further supported by extended study. Study is in progress in order to establish the analytical method of PFASs /PFCAs in air.

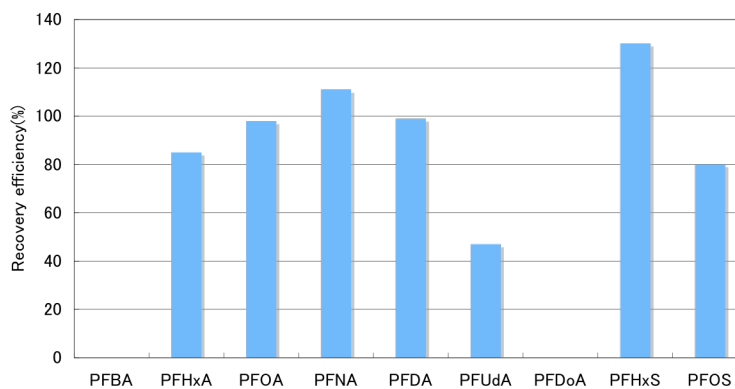


Fig.1 Results of recovery experiment for PFASs/PFCAs in ambient air samples

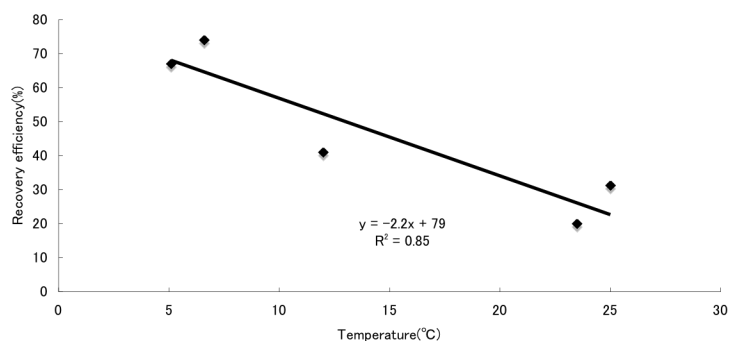


Fig.2 Relationship between average air temperature and recovery efficiency of PFOA from breakthrough experiment

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