

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

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Introduction

Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) have homologues and isomers with the shape of the molecule depending on the numbers and structures of the carbon chains. Those compounds are called Perfluoroalkylsulfonates (PFASs) and Perfluorocarboxylicacids (PFCAs), respectively. PFASs and PFCAs such as PFOS and PFOA have been found to be persistent, bioaccumulative, and entailing toxic properties¹⁻⁵).

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 carbons⁶).

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 air⁷⁾⁸⁾. However, only limited data are currently available on PFASs/PFCAs including PFOS/PFOA⁹⁾.

In previous study¹⁰⁾, we reported the results of recovery and breakthrough experiments using a quartz fiber filter (QFF) as collecting material for PFASs/PFCAs in ambient air. The results suggest that the breakthrough efficiency of PFASs/PFCAs were significantly affected by variations of air temperature during sampling. Therefore, it was presumed that the sampling method using only QFF cannot estimate accurately the concentrations of PFASs/PFCAs in ambient air at the time and areas of high temperature (>20°C).

By the results, we examined an analytical method applied QFF with Polyurethane form (PUF) using to collect gaseous POPs such as low chlorinated PCDD/Fs and PCBs¹¹⁾.

Material and Methods

This study was conducted while the hot season (from June to July) in Osaka City Institute of Public Health and Environmental Sciences in Osaka City, Japan because of the high breakthrough efficiencies of PFASs/PFCAs were relatively caused at the time of high temperature.

The QFF (QR-100:Toyo Roshi Kaisha Ltd.) was spiked with 2ng of two isotope-labelled C_{6,8}PFASs and seven isotope-labelled C_{4,6,8-12}PFCAs(MPFAC-MXA:Wellington Laboratories Inc.) before sampling. Then, air samples were collected using high-volume air sampler (HV-700F:Sibata Scientific Technology Ltd.) equipped with QFF and PUF(PUF for DXN analysis:Sibata Scientific Technology Ltd.) . The flow rates were adjusted to approximate of 700L/min for 24 hours, leading to average sample volumes of 1000m³. After sampling, QFFs and PUFs were sealed in alumina-coated PP bags, and stored at <-20°C until extraction.

Spiked nine isotope-labelled PFASs/PFCAs were extracted from QFFs by ultrasonic extraction (30min × 2) with aqueous solution containing 10% methanol (150mL) as the extraction solvent. After the extraction step, samples were passed through a membrane filter and solid phase cartridge (OASIS WAX:Waters) for clean-up. The cartridges were eluted with 4mL of 28% ammonia solution/methanol (1/999). The eluate was spiked with injection standard (¹³C₈PFOS(Wellington) and ¹³C₈PFOA (CIL)) before that was concentrated under nitrogen gas flow to a final volume (1mL) for analysis. Nine isotope-labelled PFASs/PFCAs were analyzed by LC / (-) ESI-MS/MS (Xevo TQ MS:Waters), and recoveries were calculated respectively.

On the other hand, nine labelled compounds were extracted from PUFs by ultrasonic extraction (30min × 3) with 28% ammonia solution/methanol (1/999 100mL) as the extraction solvent. The extracts were concentrated by rotary vacuum evaporator to 5mL and samples were passed through a membrane filter and solid phase cartridge (OASIS WAX:Waters) for clean-up. Subsequent steps were also performed that of QFFs.

Results and Discussion

The results of this study (breakthrough experiments) are shown in Figure 1. Recoveries efficiencies (≐ the rate of retained on QFF+PUF) of the nine isotope-labelled PFASs/PFCAs ranged from 4.8-76%. MPFHxA, MPFOA, MPFNA, MPFDA and MPFHxS showed good recoveries (50-76%). The recovery efficiencies of MPFOS and MPFUdA were low slightly (46 and 48% respectively). MPFBA (4.8%) and MPFDoA (12%) had too lower recoveries. These two compounds have the longest- and shortest-carbon chain length in this target analyte (nine isotope-labelled PFASs/PFCAs). It is necessary to improve the analytical method further in order to analyze PFBA and PFDDoA with PFOS / PFOA.

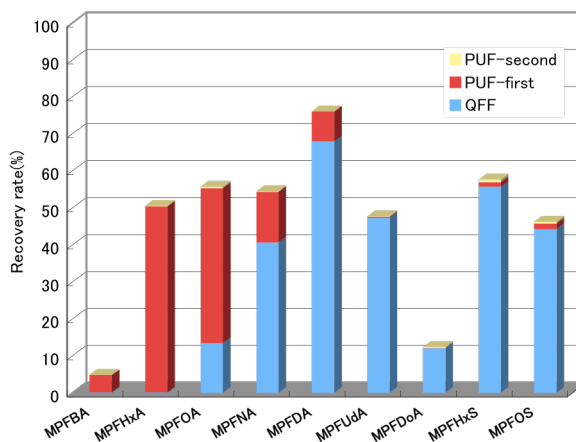


Fig.1 Results of breakthrough experiment for PFASs/PFCAs in ambient air samples (n=2)

In the distribution between QFF and PUF of PFASs /PFCAs in ambient air, although the breakthrough from QFF had caused for the sampling period (average temperature 26.6 °C), PUF could effectively collect the analyte relatively had short-carbon chain length. Thus, this method using PUF with QFF was effective to estimate the concentrations of gaseous and particle bound PFASs /PFCAs (for short-carbon chain compounds in particular).

In addition, figure 2 shows recoveries of isotope-labelled PFASs /PFCAs from extraction and clean-up steps (recovery experiments). The recoveries of these compounds in QFF and PUF were in a wide range of 31 to 100% and 76 to 170%, respectively.

MPFOS/MPFOA, MPFHxA, MPFNA and MPFDA in both QFF and PUF showed good recoveries (74-100%). MPFBA (82%) and MPFHxS (100%) in QFF were good recoveries, while those in PUF have high recovery rates (170%, 130%), respectively. PFUdA and

PFDoA in PUF showed a good recovery (77% and 120% respectively), whereas low recoveries for QFF (45%, 31%).

These reasons are not clear at present, it was possible that longer carbon-chain length PFASs/PFCAs such as PFUdA and PFDoA could not be extracted adequately by aqueous solution containing 10% methanol. In case of PFOS/PFOA to its homologues as well as to target, these compounds have physical properties comprehensively. To perform the simultaneous analysis of PFOS/PFOA and its homologues, it may be necessary to separate samples and change methods of extraction and clean-up steps for each long- and short-carbon chain length compounds.

Furthermore, although two compounds ($^{13}\text{C}_8\text{PFOS}$ for PFASs and $^{13}\text{C}_8\text{PFOA}$ for PFCAs) were used to calculate the recoveries in this study, it is possible to improve the recoveries by using appropriately labelled compounds for each analyte as injection standard.

Acknowledgements

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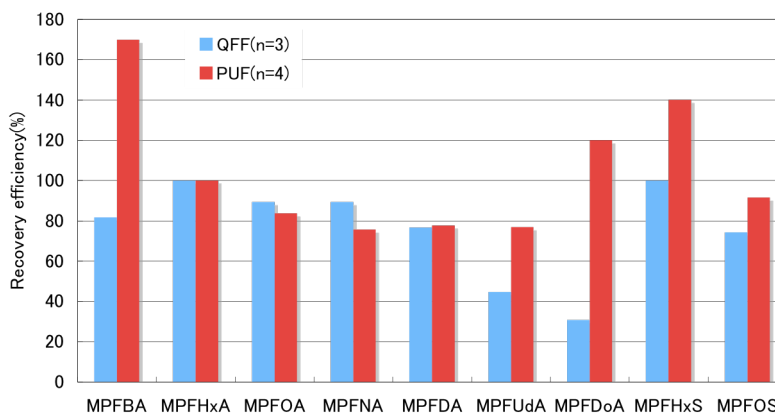


Fig2. Results of Recovery Experiment for PFASs/PFCAs in QFF and PUF

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