

Size Specific Distribution Analysis of Perfluoroalkyl Substances In Atmosphere -Development and Verification

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journal or publication title	博士論文要旨Abstract
学位授与番号	13301甲第4481号
学位名	博士(學術)
学位授与年月日	2016-09-26
URL	http://hdl.handle.net/2297/46584



博 士 論 文 要 旨

大気中ペルフルオロアルキル化合物の粒子
サイズ別分析法の開発と検証

**Size Specific Distribution Analysis of
Perfluoroalkyl Substances In Atmosphere -
Development and Verification**

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Abstract

The international regulation of persistent organic pollutants (POPs) according to the Stockholm convention started in May 2001, to regulate production and use of hazardous chemicals in global scale. Perfluoro octane sulfonate was one of newly listed as emerging POPs and only one of huge group of perfluoroalkyl substances (PFASs), it was known as “super set” of chemical tracers including more than ninety related chemicals. Comprehensive monitoring of PFASs is necessary to make reliable understanding of environmental kinetics. However, atmospheric pollution by PFASs is still unclear because their existence condition was not fully understood yet. This is a motivation to develop new sampling tool to investigate PFASs in atmosphere in this study. Capability of new sampler was evaluated using the both indoor air and ambient air. The former was carried out in air-condition room and the latter was on roadside, both investigation were carried out through a year. After above verification, international field survey using the tool was carried out. Totally thirty-eight samples was collected from eleven locations from four countries, Japan, India, China and USA. Additionally, some open ocean samples were also investigated. These sample analyses provided useful information about environmental kinetics of PFASs in atmosphere, not only in particulate matter but also in gas phase under different climate conditions. This is the first research to investigated PFASs by both gas and size distribution analysis to our knowledge.

要旨

Perfluoroalkyl substances (PFASs), which known as “super set” of chemical tracers including more than 90 related chemicals, are used in a variety of industrial and commercial applications, including surfactants in pesticides, surface protectors in textiles, furnishings and food packaging. Perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs), typically dominated by the eight-carbon members perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are two main groups of PFASs. PFASs in the environment arise from their widespread use in industrial applications like metal plating, surfactants, hydraulic fluids for aircraft, polymers in semiconductor manufacturing, and aqueous fire fighting foams. Consumer applications include stain-proof coatings on drapery and fabrics, oil resistant coatings on food contact paper, and non-stick coatings on kitchen utensils and water. Such applications have led to measurable PFAS contamination of both the indoor and outdoor environments. These chemicals have been widely detected in wildlife and humans around the world. Starting from May 2001, to regulate the production and use of hazardous chemicals at the global scale, and protect nature from inconsiderate discharges of chemicals, a

total of 164 countries and the European Union made agreement conclude with this rule. Considering the recent situation of worldwide use of new hazardous chemicals, the previous list was updated and new chemicals were added recently. PFOS (its salts) and perfluorooctane sulfonyl fluoride (POSF) were newly listed as an emerging persistent organic pollutant (POP) and as the only member of the large group of perfluoroalkyl substances (PFASs).

There is some uncertainty regarding the fate and exposure pathways of humans to PFOS and PFOA. Exposure may occur through a number of mechanisms including (i) directly, due to the manufacture and use of PFOS and PFOA in commercial products;¹⁰⁻¹³ (ii) abiotic breakdown (to PFOS and/or PFOA) of “precursor” compounds that are also released during PFC production and/or from commercial products (examples include fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), and perfluorooctane sulfonamidoethanols (FOSEs) that degrade to PFOS and/or PFOA);^{14,15} and (iii) metabolic transformation of precursors that have already been absorbed into the body.^{16,17}

Previous research indicates that PFASs, due to their persistence, water solubility, and measurability, could represent excellent tracers of global circulation of oceanic waters. Comprehensive monitoring of PFASs is necessary to enable reliable understanding of environmental kinetics. However, atmospheric pollution by PFASs is still unclear because their existence condition is not fully understood yet. Hence, reliable analytical method to measure exact residue of PFASs in particles is needed.

The purpose of this study aims at establishing a systematic method to evaluate capability of new sampler by using the both indoor air and ambient air. Then by carrying out international field survey in eleven locations from four countries to test performance of sampling system and investigate PFASs existence in land atmosphere. Moreover, by applying this system in research vessel, PFASs existence in oceanic atmosphere has been also studied.

In this study, in order to investigate PFASs in atmospheric particles including PM_{2.5}, performance of new sampling equipment was testified by sampling in a stable indoor environment multiple times. Meanwhile, by sampling simultaneously at a roadside environment, PFASs characters in two different types of air environment have been compared. This experiment confirmed the reliability and stability of air sampling and chemical analysis for study atmospheric PFASs concentration, provided new information about size segregated PFASs concentration information and compared two typical indoor and outdoor environment. Moreover, by using CMS connected with NS20, PFASs partitioning in gas phase and particle phase has been studied. Figure 1 shows average concentrations (pg m⁻³) of PFASs in particle phase (NS40) and gas phase(CMS) in meeting room (n=10) and roadside(n=9) air (error bar = standard deviation). In meeting room air, PFASs concentration was dominated by neutral

PFASs, especially FOSA, while in roadside air, PFASs concentration was dominated by ionic PFCAs, especially shorter chain PFBA, PFPeA and PFHxA. Moreover, in meeting room, gas phase and particle phase PFASs concentration is comparable while in roadside air, PFASs mainly existed in gas phase. This is the first research to investigated PFASs by both gas and size distribution analysis to our knowledge

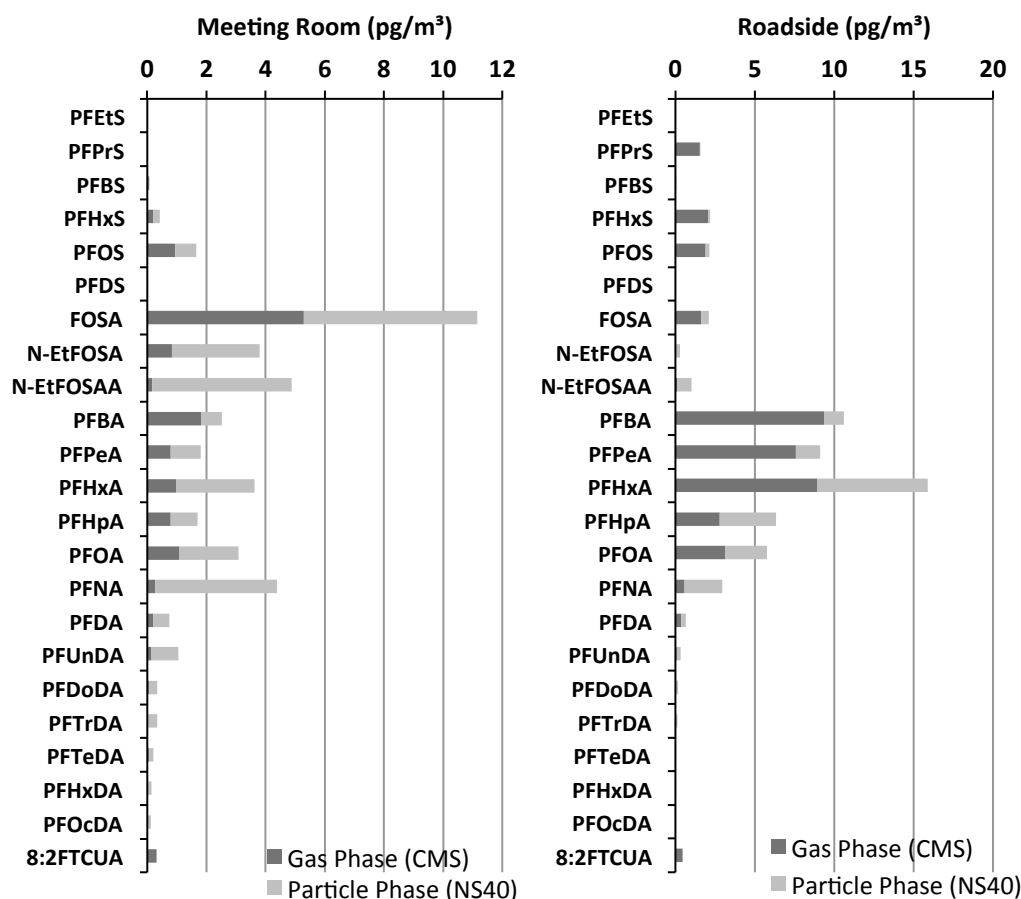


Figure 1 Average concentrations (pg/m³) of PFASs in particle phase(NS40) and gas phase(CMS) in meeting room (n=10) and roadside(n=9) air (error bar = standard deviation)

After above verification, international field survey using the tool was carried out. Totally thirty-eight samples was collected from eleven locations from four countries, Japan, India, China and USA. PFASs existence in atmosphere have been investigated and size segregated PFASs concentration has been reported. **Figure 2** shows average PFOA concentrations (pg/m³) in total particles of each sampling location, including NS40 and NS20 result. Differ from particle matter concentration, the highest PFOA concentration were observed in Hong Kong, followed by Zhengzhou, Beijing, India, Tsukuba, Kanazawa, Okinawa, Mt.Fuji. The lowest concentration is observed in Yunnan, China. Considering the fact that average PM concentration in Zhengzhou and Beijing are about 6 times higher than

that of Hong Kong, the PFOA concentration in particulate (ng/g) in Hong Kong is over 10 times higher than those two places in China.

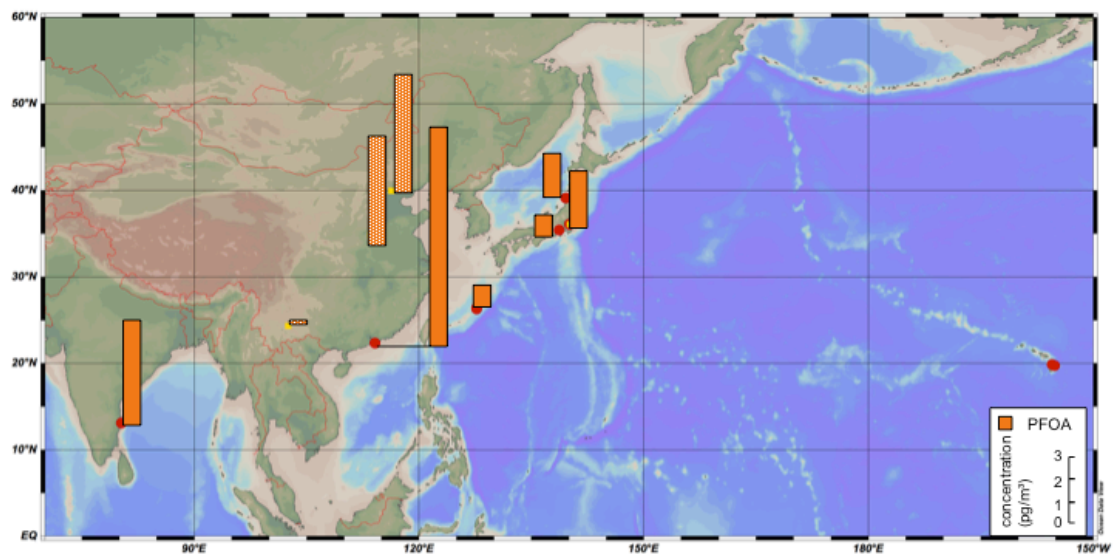


Figure 2 Average PFOA concentrations in total particles of each sampling location, including NS40 and NS20 result.

Additionally, some open ocean samples were also investigated. These sample analyses provided useful information about environmental kinetics of PFASs in atmosphere, not only in particulate matter but also in gas phase under different climate conditions. This result provides the information about PFASs existence in open Ocean Atmosphere, especially polar region like Arctic Ocean and Antarctic Ocean. **Figure 3** shows the PFOA concentration (pg/m^3) in air from NS20 sample. (Land sample in Japan is average PFOA concentration in roadside samples from Tsukuba ($n=10$)). For PFOA, relatively high concentration is observed in Pacific Ocean ($0.2\sim 0.7 \text{ pg}/\text{m}^3$), gradually decreasing when close to polar region ($< \text{LOQ}$). The open ocean atmospheric PFOA concentration is about one or two magnitude lower than land samples (e.g. Roadside samples from Tsukuba).

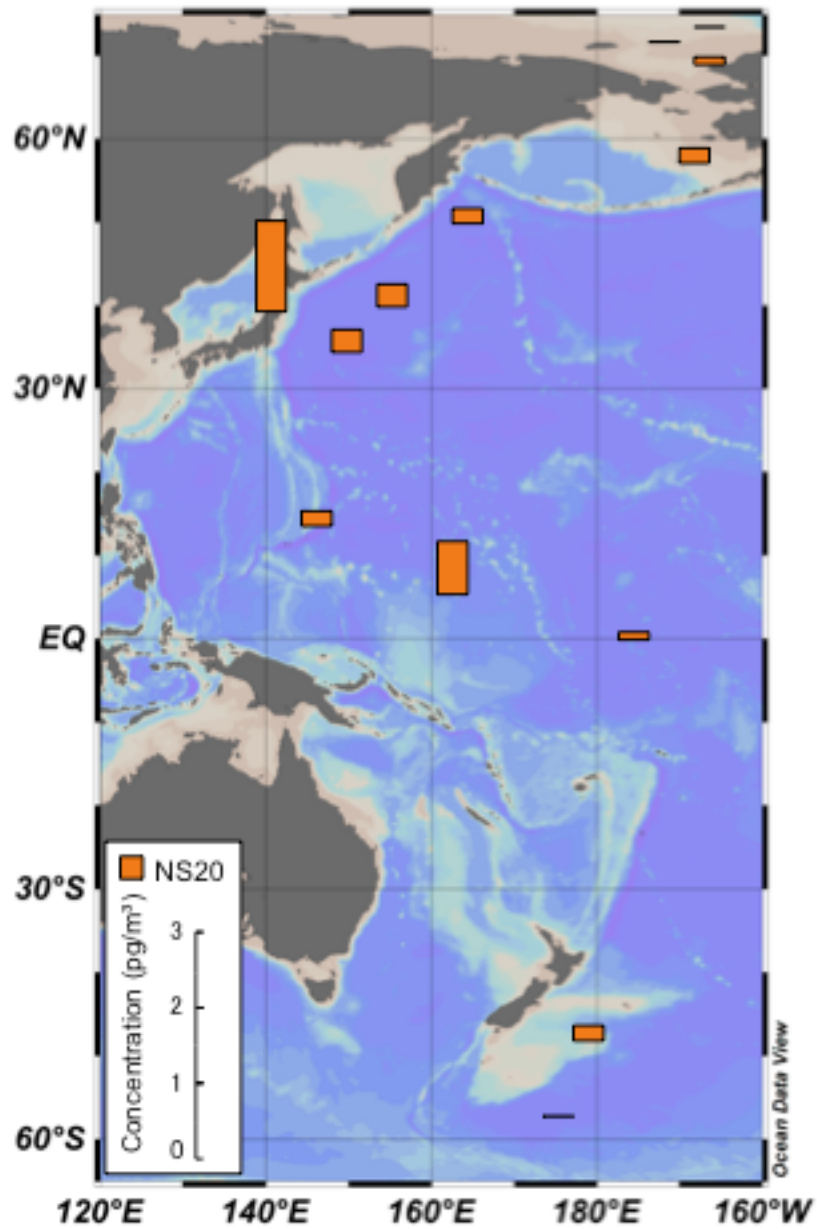


Figure 3 PFOA concentration (pg/m^3) in air from NS20 sample. (Land sample in Japan is average PFOA concentration in roadside samples from Tsukuba ($n=10$)).