博士論文

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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Chapter 1 Introduction

In this chapter, an introduction about the background of the research that indicates some reasons for choosing this title; research purpose; literature review; and a methodology for achieving the research purpose is represented.

1.1 Research background

Perfluoroalkylated substances (PFAS) is the collective name for a vast group of fluorinated compounds, including oligomers and polymers, which consist of neutral and anionic surface active compounds with high thermal, chemical and biological inertness. Perfluorinated compounds are generally hydrophobic but also lipophobic and will therefore not accumulate in fatty tissues, as is usually the case with other persistent halogenated compounds. An important subset is the (per) fluorinated organic surfactants, to which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) belong.

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 (OECD, 2002). 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 (OECD, 2002). Such applications have led to measurable PFAS contamination of both the indoor and outdoor environments. (UK) These chemicals have been widely detected in wildlife and humans around the world (Delinsky et al., 2010; Zhang et al., 2010). 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).

Previous research indicates that PFASs, due to their persistence, water solubility, and measurability, could represent excellent tracers of global circulation of oceanic waters (Yamashita et al., 2008). 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.

1.2 Research purpose

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.

1.3 Literature Review

1.3.1 Ambient Particle

Particle size is a major determining factor in the atmospheric behavior of aerosol particles and controls the residence time and removal mechanisms of aerosol-bound contaminants. (Bidleman, 1988; Offenberg and Baker, 1999) Although there have been no investigations on size characteristics of ambient particles that may be affected by geographical region, weather, land use where monitoring sites are located in world scale. Many researches have been done to study the spatial and temporal variation of ambient particle concentration and size distribution in their local area.

For spatial variation, previous study has proved that the difference of ambient particle mass concentration exists among different types of sampling sites. For instance, J. Yin, R.M. Harrison (2008) sampled airborne particulate matter in the PM10, PM2.5 and PM1.0 size ranges at three sites within 20 km of one another, representing urban background, urban roadside and rural locations. The results shows PM mass concentrations at the three sites rank, as might be expected, i.e. BROS (roadside)>BCCS (urban background)>CPSS (rural background).

While there are not many researches discuss about size distribution variation of ambient particle, and most existing research only use $PM_{2.5}/PM_{10}$ ration as an index to analyze the variation of size distribution. For example, by analyzing and comparing PM characteristics of seven selected regions within the European Union (EU), Querol. X et al. (2004) suggested the ratio $PM_{2.5}/PM_{10}$ is highly dependent on the type of site-- regional, urban background and curbside sites, and varied widely between different EU regions. And also, L.Y. Chan et al. (2001) conducted roadside particulate sampling to measure the TSP, PM_{10} and $PM_{2.5}$ mass concentration in 11 urbanized and densely populated districts in Hong Kong. This study suggest that PM ratios in metropolitan Hong Kong significantly fluctuated from site-to-site and over time, the mean $PM_{2.5}/PM_{10}$ mass ratios were high at sites with higher traffic flow.

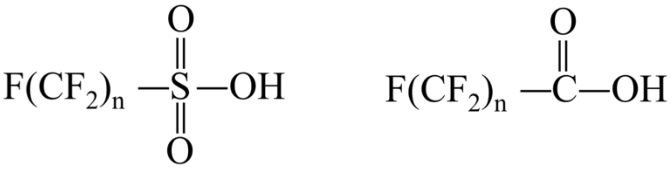
As to temporal variation, previous research has indicated that size distributions are strongly affected by weather conditions (e.g., relative humidity or wind direction) and the solar radiation (photochemistry). Consequently, in many areas, the seasonal variations of ambient particle mass concentration are reported. Y. Cheng et al. (2006) measured PM1.0, $PM_{2.5}$ and PM_{10} at 24-hour intervals near a high-traffic road in Hong Kong, suggested that the particulate masses showed notable seasonal patterns with high concentrations in cold seasons and low in warm seasons, especially high concentrations of $PM_{2.5-10}$ during the cold seasons.

However, for size distribution, most existing research only use $PM_{2.5}/PM_{10}$ ration as an index to analyze the variation. For instance, by measuring hourly average concentrations of PM_{10} and $PM_{2.5}$ simultaneously at a site within Birmingham U.K., Harrison et al. (1997) suggested that a marked difference between summer and winter periods, $PM_{2.5}$ particles contribute around 80% of PM_{10} in winter and 50% in summer time.

1.3.2 Physicochemical properties of PFASs

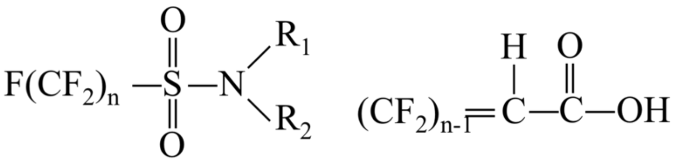
PFASs are characterized by varying lengths of carbon chains in which all hydrogen atoms are substituted by fluorine atoms. All PFASs found in the environment are anthropogenic; they have been manufactured and used for more than 60 years. Because of their unique properties, they have been widely used in a variety of commercial and industrial products. Currently concerned PFASs can be divided into two main groups: (i) perfluoroalkyl sulfonates (PFSAs), and (ii) perfluoroalkyl carboxylates (PFCAs). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which has both eight-carbon chain lengths, are the representatives for the two groups respectively.

Apart from manufacturing, PFSAs and PFCAs seem to be the degradation products of their corresponding precursors. Perfluoroactyl sulfonamides (FOSA) are one of the potential precursors for PFSAs, while fluorotelomer alcohol (FTOHs) can finally degrade and yield PFCAs (Ellis DA et al., 2004; Wallington TJ et al., 2006). Chemical structures of PFSAs, PFCAs, FOSA and FTUCA have been shown in Figure 1.



PFSAs: Perfluoroalkane sulfonic acids
e.g. PFOS (n=8), PFHxS (n=6)

PFCAs: Perfluoroalkyl carboxylic acids
e.g. PFOA (n=8), PFHxA (n=6)



FOSA: Perfluoroalkyl sulfonamides

n:2 FTCUA: (n:2) Fluorotelomer unsaturated carboxylic acids

Figure 1 chemical structure of four groups target PFASs

Because of (i) high electronegativity of fluorine atom (4.0), (ii) high energy of C–F bond (approx. 466 kJ mol^{-1}), (iii) small diameter of the fluorine atom and (iv) three pairs of negatively charged electrons in its outer shell that are not involved in bonding with other atoms, rendering PFASs chemically and thermally stable and strongly resistant to hydrolysis, photolysis, microbial degradation and metabolism by vertebrates (Giesy JP and Kannan K, 2002; Lewandowski G, 2006). The oleophobic and hydrophobic perfluorinated chains when adding to a hydrophilic charged moiety such as sulfonic acid or carboxylic acid can create the surfactant properties of PFASs. These molecules have both polar (charged moieties) and non-polar (perfluorinated chains) domains that can lessen water surface tension than hydrocarbon-based surfactants, and therefore more powerful wetting agents. These oleophobic and hydrophobic perfluorinated chains also enable the functionalized fluorochemicals water, oil and fat resistant (Giesy JP and Kannan K, 2002; Kissa E, 2001). The physicochemical properties of target PFASs in this study are shown in Table 1. Owing to the high water solubility and low vapor pressure of PFASs, aquatic ecosystem is thought to be a major sink for these compounds.

Unlike other persistent organic pollutants (POPs) that accumulated in the fatty tissues, PFASs such as PFOA and PFOS are ionic and polar surfactants, they supposed to bind to blood proteins and accumulate in liver and gall bladder. Hence, they are also bioaccumulative (Renner R, 2001). Properties of PFASs enable them to be globally distributed in both abiotic and biotic matrices. Concentrations of PFASs had been detected in human blood (Kannan K et al., 2004; Yeung LWY et al., 2006), breast milk (So MK et al., 2006B), seafood (Taniyasu S et al., 2003; Gulkowska A et al., 2006; So MK et al., 2006A), wildlife (Giesy JP and Kannan K, 2001; Li XM et al., 2008A and B) and many different water bodies (So MK et al., 2004; *Mak YL et al., 2009)*.

Table 1 Physichemical properties of target PFASs in this study.

Acronym	Formula	CAS#	Boiling point [℃]	Melting point [℃]	Vapor pressure at 20℃ [Pa]	Water solubility [mg L^{-1}]	pKa	Henry's Law constant [atm m^3 mol^{-1}]	Particulate-air constant, Kpa
PFEtS	$F(CF_2)_2SO_3H$	354-88-1							
PFPrS	$F(CF_2)_3SO_3H$	423-41-6							
PFBS	$F(CF_2)_4SO_3H$	375-73-5							
PFHxS	$F(CF_2)_6SO_3H$	355-46-4							
PFOS	$F(CF_2)_8SO_3H$	1763-23-1	149[i]	70-100[i]					
PFDS	$F(CF_2)_{10}SO_3H$	335-77-3							
FOSA	$F(CF_2)_8SO_2NH_2$	754-91-6							
N-EtFOSA	$F(CF_2)_8SO_2N(C_2H_5)H$	4151-50-2	~110[f]	~90[f]	0.2[f]				
N-EtFOSAA	$F(CF_2)_8SO_2N(C_2H_5)CH_2COOH$	2991-50-6							
PFPrA	$F(CF_2)_2COOH$	422-64-0							
PFBA	$F(CF_2)_3COOH$	375-22-4	120[b]	-19.5[b]	586[j]		0.4[l]		
PFPeA	$F(CF_2)_4COOH$	2706-90-3	127[b]						
PFHxA	$F(CF_2)_5COOH$	307-24-4	157[b]	12-14[b]			0.7[l]		>2.18E-03[m] >3.6E-02[m]
PFHpA	$F(CF_2)_5COOH$	307-85-9	175-177[b]	54 in CCl_4[b]	6E-03[k]		1.3[l]		>1.2E-02[m] >4.8E-02[m]
PFOA	$F(CF_2)_7COOH$	335-67-1	189-192[g]	55[b,g]	2.2[c]	3400[g]	2.5[g]	4.6×10^{-6} [a]	>3.1E-02[m] >9.7E-01[m]
PFNA	$F(CF_2)_8COOH$	375-95-1	203.4[c]	71-77[b]			2.1[l]		>2.0E-02[m] >1.7[m]
PFDA	$F(CF_2)_9COOH$	335-76-2	218[b]	83-85[b]	0.1[c]		2.6[l]		>1.6E-02[m] >3.9[m]
PFUnDA	$F(CF_2)_{10}COOH$	2058-94-8	160[b]	96-101[b]			2.6[l]		>1.9E-02[m]
PFDoDA	$F(CF_2)_{11}COOH$	307-55-1	245[b]	107-109[b]	3E-03[c]		3.1[l]		
PFTrDA	$F(CF_2)_{12}COOH$	72629-94-8		117.5-122[d]					
PFTeDA	$F(CF_2)_{14}COOH$	376-06-7		130[e]					
PFHxDA	$F(CF_2)_{16}COOH$	67905-19-5							
PFOcDA	$F(CF_2)_{18}COOH$								
8:2FTCUA	$F(CF_2)_7CF{=}CHCOOH$	70887-84-2		105[h]		64[h]			

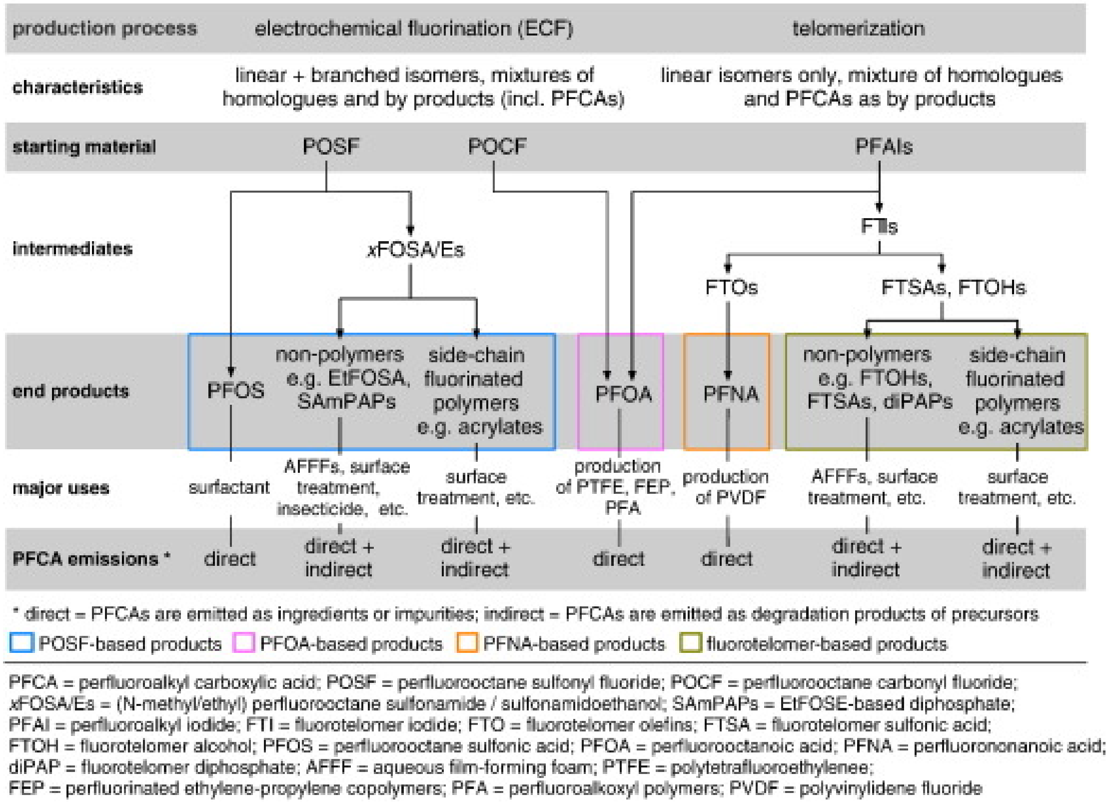
Data from a: Hekster FM et al., 2003; b: FluorochemicalManufacturesGroup, 2002; c: Kaiser MA et al., 2005; d: Kunieda H and Shinoda K, 1976; e: Ellis DA et al., 2004; f: USEPA, 2000; g: USEPA, 2002; h: Fischer-Drowos SG et al., 2007; i: http://www.jemco-mmc.co.jp/products/products033.html; j:Steele WV, 2002B; k: Steele WV, 2002B; l: Moroi Y et al., 2001; m: Barber JL et al., 2007.

1.3.3 Application and usage amount of PFASs

Due to the concern, the 3M Company, the major global manufacturer of POSF, announced the phase-out of POSF-based materials in 2000, butyl-based substances were used as a replacement. The synthesis of PFASs is based on either obtaining the perfluoroalkyl chain or the introduction of functional groups into fluorinated chain. The perfluoroalkyl chain can be obtained by two common methods: (i) electrochemical fluorination (ECF) and (ii) telomerization fluorination process.

Figure 2 summarizes general information on the production and uses of perfluorooctanoic acid (PFOA)-, perfluorononanoic acid (PFNA)-, perfluorooctane sulfonyl fluoride (POSF)- and fluorotelomer-based products as well as their relevance to the emissions of C_4–C_{14} PFCAs. (Wang Z et al., 2014). The work by Prevedouros et al. (2006) highlighted the significance of historical direct sources to the overall presence of PFCAs in the environment, in particular from production of certain fluoropolymers where PFOA- or PFNA-based products have been used as processing aids (Prevedouros et al., 2006).

The 3M company employed the ECF to produce PFASs since 1950 (3M, 1999). In brief, all the hydrogen atoms of a hydrocarbon were replaced by fluorine atoms under electric current (Kissa E, 2001). PFASs were used widely in inks, varnishes, waxes, fire-fighting foam formulation, metal plating and cleaning, lubricant, water and oil repellents for textile, paper as well as leather (3M, 1999; 3M, 2000A). PFCAs (e.g. PFOA) were also produced in 1947 using the ECF (3M, 1995). This process yields about 35 - 40% straight-chain POSF and a mixture of by-products and waste of unknown and variable composition such as branched-chain, straight-chain or cyclic perfluoroalkylsulfonyl fluorides with various chain lengths with 8-9 fluorinated carbon as major constituents (3M, 1999; 3M, 2000A). PFOA was mainly manufactured as ammonium salt (APFO), the primary worldwide production of APFO using ECF ceased by 2002, though a limited number of small manufacturers was still in production in Europe and Asia. Telomerization (e.g. fluorotelomer iodide (FTI) oxidation, fluorotelomer olefin (FTO) oxidation, and fluorotelomer iodide (FTI) carboxylation) is another important manufacturing process in producing PFASs (Kissa E, 2001). Dupont uses the telomerization process, which yields linear, even-numbered perfluorocarbon chains (Kissa E, 2001). Commercial products manufactured through the telomerization process are generally mixtures of polyfluorinated straight-chain compounds with ranges of even carbon numbers (USEPA, 2000). Ammonium perfluoronanoate (APFN) in manufactured in Japan by oxidation of a mixture of linear fluorotelomer olefin (mainly 8:2 FTOs) oxidation to the corresponding odd-numbered of PFCAs (Asahi Glass Co., 1975; Daikin Industries, 1998).



* direct = PFCAs are emitted as ingredients or impurities; indirect = PFCAs are emitted as degradation products of precursors

PFCA = perfluoroalkyl carboxylic acid; POSF = perfluorooctane sulfonyl fluoride; POCF = perfluorooctane carbonyl fluoride; xFOSA/Es = (N-methyl/ethyl) perfluorooctane sulfonamide / sulfonamidoethanol; SAmPAPs = EtFOSE-based diphosphate; PFAI = perfluoroalkyl iodide; FTI = fluorotelomer iodide; FTO = fluorotelomer olefins; FTSA = fluorotelomer sulfonic acid; FTOH = fluorotelomer alcohol; PFOS = perfluorooctane sulfonic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; diPAP = fluorotelomer diphosphate; AFFF = aqueous film-forming foam; PTFE = polytetrafluoroethylenee; FEP = perfluorinated ethylene-propylene copolymers; PFA = perfluoroalkoxyl polymers; PVDF = polyvinylidene fluoride

Figure 2 General information on the production and uses of perfluorooctanoic acid (PFOA)-, perfluorononanoic acid (PFNA)-, perfluorooctane sulfonyl fluoride (POSF)- and fluorotelomer-based products as well as their relevance to the emissions of C_4–C_{14} PFCAs. (Wang Z et al., 2014)

Figure 3 summarized main usage of PFASs products. Following introduced several typical PFASs:

PFBS (Perfluorobutane sulfonate) is an active ingredient in 3M's new Scotchgard (old formulation was phased out in 2000 over health concerns).

PFHxS (Perfluorohexanesulfonate) is in fire fighting foams and carpet treatments. Phased out of consumer products by 3M in 2000 over health concerns.

PFOS (Perfluorooctanesulfonate) is an active ingredient in Scotchgard prior to 2000. Phase out forced by EPA because concentrations in human blood close to levels that harm lab animals.

PFBA (Perfluorobutyric acid) is breakdown product of stain- and grease-proof coatings on food packaging, couches, and carpets.

PFHxA (Perfluorohexanoic acid) is breakdown product of stain- and grease-proof coatings on food packaging and household products.

PFOA (Perfluorooctanoic acid) is used to make Teflon pan coatings; breakdown product of stain- and grease-proof coatings.

PFNA (Perfluorononanoic acid) is breakdown product of stain- and grease-proof coatings on food packaging, couches, and carpets.

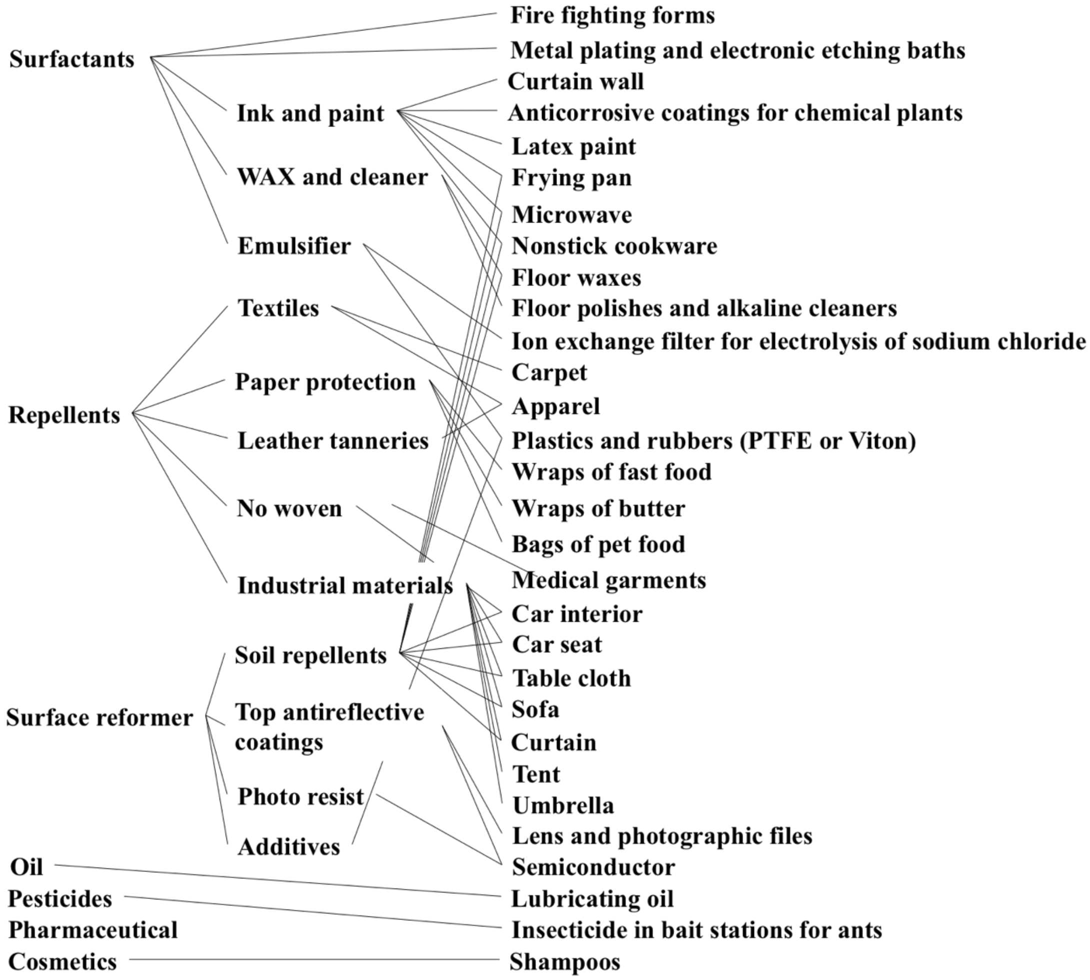


Figure 3 Applications of PFASs

1.3.4 Sources of PFASs

There are two major sources of PFCA emission to the environment: (i) direct and (ii) indirect. Direct sources might be resulting from the manufacturing and processing process of PFCA, ammonium perfluorooctanoate (APFO) and fluoropolymer, water soluble PFCA salts might be expected to enter the local aquatic environment directly (Figure 2). Secondly, the releases of AFFFs and other consumer and industrial products were also another direct source.

PFCAs present as chemical impurities and degradation of fluorotelomer-based products could be categorized as the indirect sources in the environment. (Prevedouros K, 2006)

Volatile FTOHs, have an atmospheric lifetime of 20 days, are supposed to be the possible precursors of PFCAs. The worldwide production of FTOHs was approximately 12 x 106 kg per year. FTOHs, with fluorinated carbons of 6, 8, 10 were found in air masses of Japan (Oono S et al., 2008), Asian and Western USA (Piekarz AM et al., 2007). Hydroxyl (OH) radical present in the atmospheric environment would initiate the oxidation of FTOHs and yield PFCAs (Ellis DA et al., 2004). Some studies had simulated the atmospheric conditions using chlorine (Cl) radicals to replace OH radicals in a smog chamber, 8:2 FTOH reacted and degraded to perfluorinated aldehydes (FTALs) and fluorotelomer carboxylic acids (FTCAs) and finally yielded the entire suite of PFCAs ranging from trifluoroacetic acid (TFA) to perfluorononanoic acid (PFNA) (Figure 4) (Ellis DA et al., 2004; Wallington TJ et al., 2006). The atmospheric concentrations of FTOHs decreased with increasing chain lengths, leading to a decreasing trend of longer chain length PFCA concentrations in the environment (Ellis DA et al., 2004).

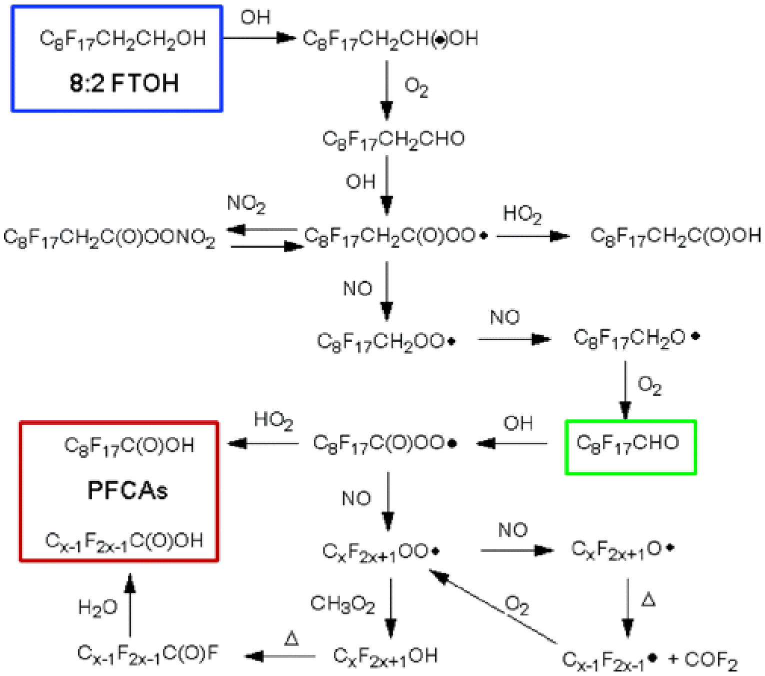


Figure 4 Proposed mechanisms for the atmospheric degradation of 8:2 FTOH (Wallington TJ et al., 2006)

Figure 5 estimated annual releases of PFCAs from PFOA production sites (top) and fluoropolymer production sites (bottom) in the United States (US), Western Europe and Japan (purple) as well as in China, Russia, Poland and India (orange). The pie charts show fract. (Wang Z et al., 2014) A trend in the geographical distribution of major industrial sites is that production of PFCAs, fluoropolymers and other PFAS products has shifted from Japan, Western Europe and the US to the emerging economies in continental Asia (e.g., China and

India), suggesting that the proportion of global PFCA emissions originating from continental Asia has increased.

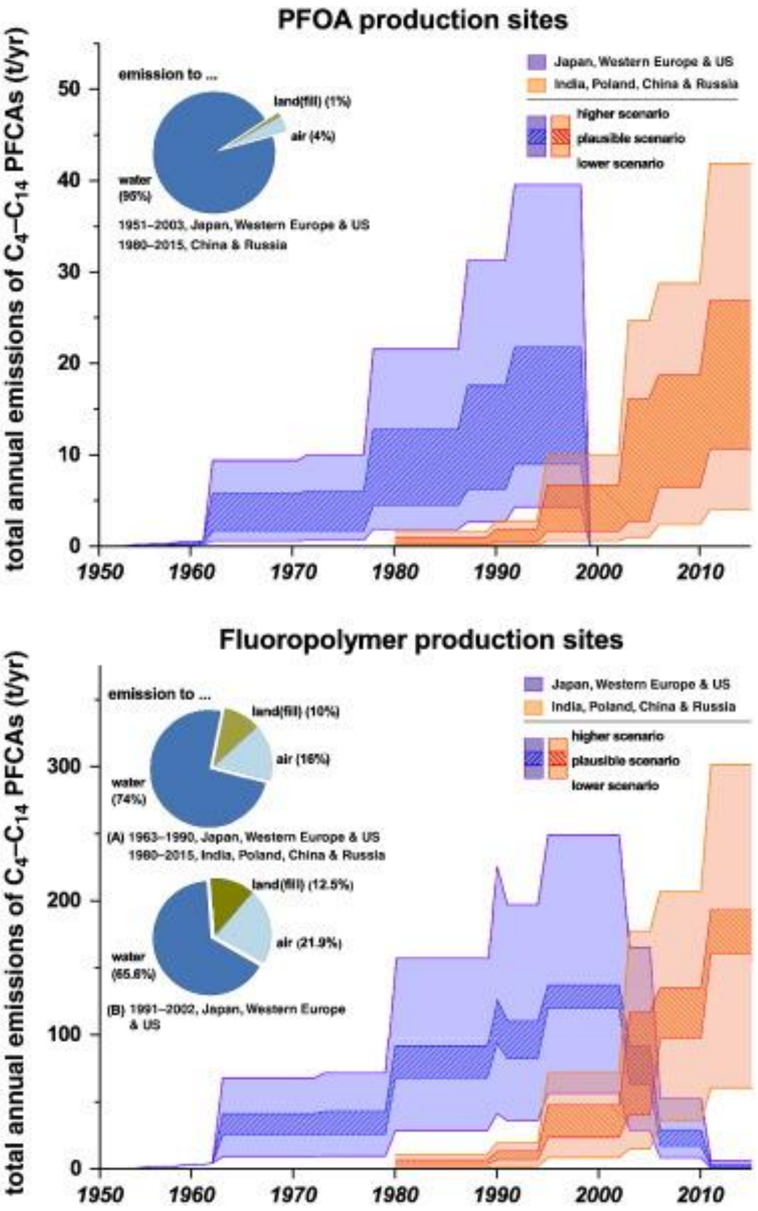


Figure 5 Estimated annual releases of PFCAs from PFOA production sites (top) and fluoropolymer production sites (bottom) in the United States (US), Western Europe and Japan (purple) as well as in China, Russia, Poland and India (orange). The pie charts show fract. (Wang Z et al., 2014)

Figure 6 shows the distribution of PFOS use amounts used in metal plating, fire-fighting foams and sulfluramid applications in 31 provinces of China. (Zhang L et al., 2012). In this study, field survey consists sampling sites from low production district (Yunnan), medium size production district (Henan) to high production district (Beijing and Hong Kong).

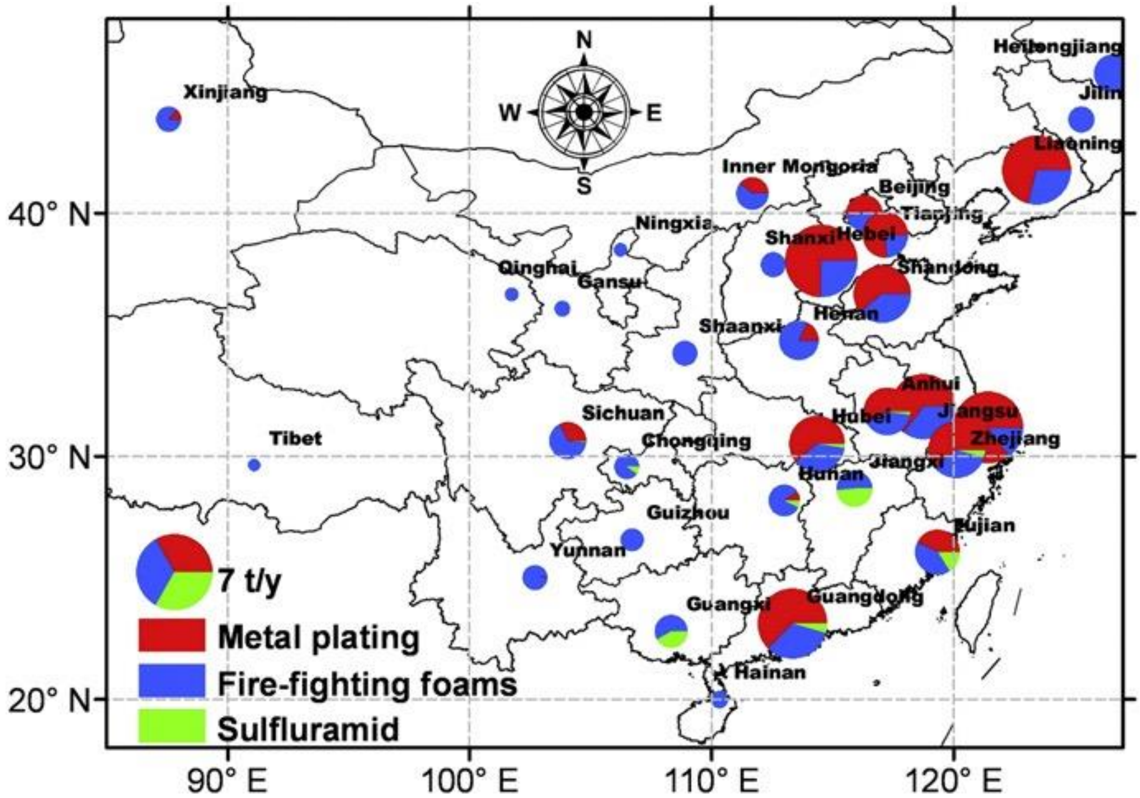


Figure 6 The distribution of PFOS use amounts used in metal plating, fire-fighting foams and sulfluramid applications in 31 provinces of China. (Zhang L et al., 2012)

1.4 Approach

Capability of the new sampler was evaluated using both indoor air and ambient air. The former was carried out at air-conditioned room and the latter was along roadside, and both investigations were carried out through a year and evaluated seasonal change.

After above verification, international field survey using the tool was carried out. Totally thirty-eight samples were collected from eleven locations in four countries, Japan, India, China and USA. Additionally, some open ocean samples were also investigated. These sample analyses provided useful information about environmental behaviour of PFASs in atmosphere, not only in particulate matter but also in gas phase under different climate conditions. This is the first research investigating both the gas and size distribution analysis of PFASs to our knowledge.

1.5 Thesis Organization

The rest of this dissertation is organized as following:

Chapter 2 introduces the methodology of this study, mainly contains three parts: 1) air sampling including instruments introduction and sample collection procedure; 2) chemical analysis including extraction method and instrumental analysis; and 3) quality assurance and quality control.

Chapter 3 showed the result about establishing sampling method by blank check and recovery sampling test.

In chapter 4 and 5, filed samples and cruise samples' results are shown.

And lastly, chapter 5 concludes the research.

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Chapter 2 Methodology

The methodology of this research mainly contains three parts: 1) air sampling, including instruments introduction and sample collection procedure; 2) chemical analysis including extraction method and instrumental analysis; and 3) quality assurance and quality control.

2.1 Air sampling

2.1.1 Instruments

In order to collect air samples, total three samplers have been involved in this study. Two of them were cascade impactors, which were used for get particulate matter samples; one of them is cryogenic moisture sampler, which can be used to get bulk air samples or gas phase samples.

2.1.1.1 Cascade impactor

A) Nanosampler

Nanosampler (NS40), operated at 40L min^{-1}, was used for size selective collection of particles in atmosphere. The inlet and filter stages allowed collection of particles in six size fractions including particle diameter (dp) greater than 10μm and less than 0.1μm (specifically, >10, 10–2.5, 2.5–1, 1–0.5, 0.5–0.1, and < 0.1 μm, respectively).

B) Portable Cascade impactor

Portable cascade impactor (NS20), operated at 20L min^{-1}, was also used for size selective collection of particles in atmosphere. The inlet and filter stages allowed collection of particles in four size fractions including particle diameter (dp) greater than 10μm and less than 1μm (specifically, >10, 10–2.5, 2.5–1 and <1μm, respectively).

Schematic diagram of samplers (NS40 and NS20) and sampler system (using NS40 as demonstration) have been shown in Figure 7 and Figure 8.

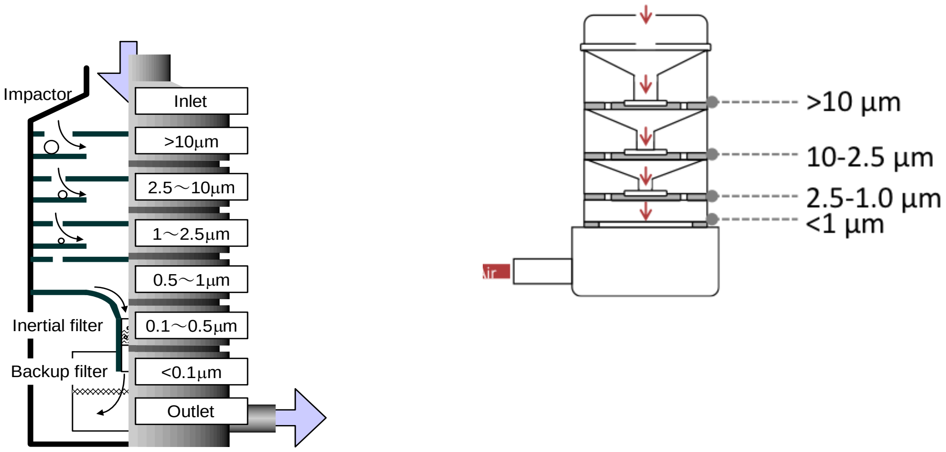

Figure 7 Schematic diagrams of NS40 (left-side) and NS20 (right-side).

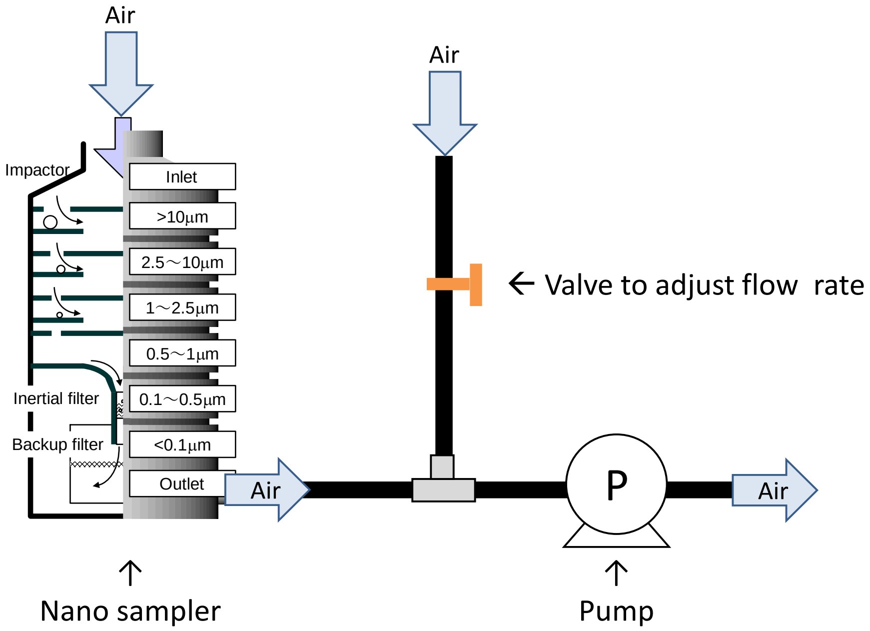

Figure 8 Schematic diagram of NS40 sampling system (using NS40 as a demonstration)

2.1.1.2 Cryogenic moisture sampler

Cryogenic moisture sampler (CMS; prototype type 5th which was developed by AIST and SIBATA Co), operated with a flow rate of 20 L min^{-1}, was used to take air sample (Yamazaki et al., 2011). The sampler could comprehensively collect all chemicals in atmosphere by rapid cooling (-6° C to -15° C). It is applicable to all PFASs with a wide range of boiling points (120° C to 250° C; Steele WV et al., 2011; Kaiser MA et al., 2005). Gas and particle phase of PFASs in atmosphere were collected into bubbler solvent consisted of methanol in Milli-Q water by bubbling and then trapped into cold trap by cooling with -4 °C. Schematic diagram of CMS sampler has been shown in Figure 9.

Not only CMS can be used individually as an air sampler to take bulk air samples, but also it can be connected with NS20 with inlet, by which system NS20 captured particle phase while CMS trap gas phase simultaneously.

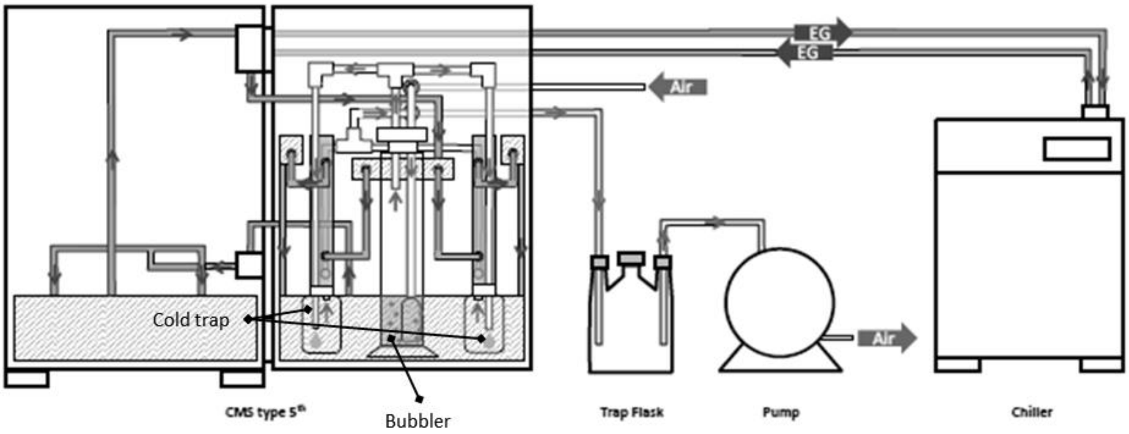

Figure 9 Schematic diagram of CMS type 5th system.

2.1.2 Sample preparation

2.1.2.1 Cascade impactor sample

Ambient particles were collected on quartz fiber filters (QFF, Pallflex, 2500QAT- UP) set to each stage of sampler. QFF were pre-baked at 350 ℃ for 3 hours to remove possible contamination. All filters were conditioned in a weighing chamber with a controlled temperature (21±1 ℃) and relative humidity (35±2% RH) for 48 hours and the weight was measured using a microbalance (readability to 1 μg) before and after the sampling. Figure 10 shows the chart flow for filter weighting procedure. After got particle weight, QFF were wrapped using aluminium foil, stored in clean polypropylene bags and kept frozen at below -20 ℃ until analysis.

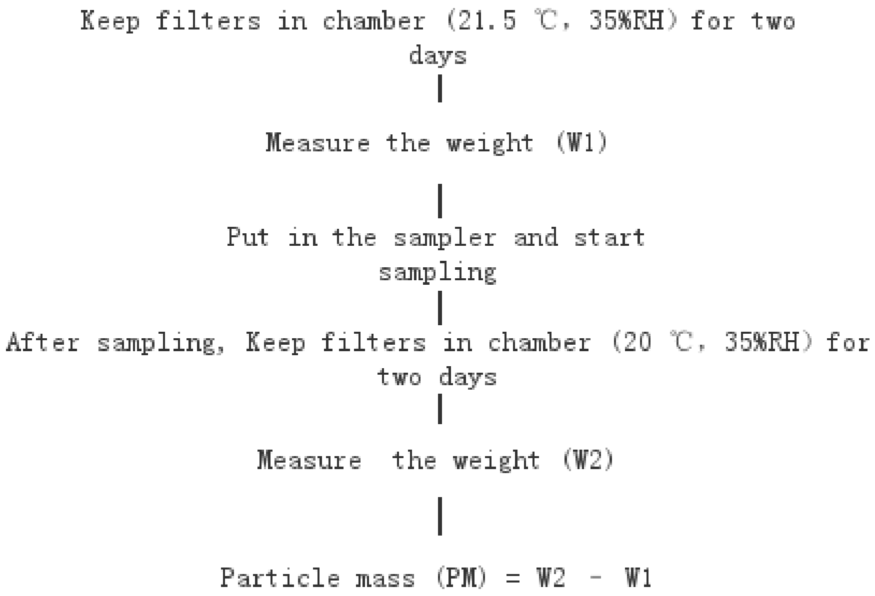

Figure 10 Chart flow for filter weighting procedure

2.1.2.2 Cryogenic moisture sampler' sample

Sample preparation and collecting method of CMS were described by Yamazaki et al. (2011). After sampling, these samples were collected and stored in clean polypropylene bottles and kept frozen at below -20 ℃ until analysis.

2.1.3 Sampling information

2.1.3.1 Meeting room and Roadside air sampling in Tsukuba

Sample collections were carried out in the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba west campus from September 2014 to February 2016. The experiment was designed for two purposes, one is to establish a method of PM sampling for measurement of PFSAs and PFCAs and the other is to validate the method.

The first experiment was carried out in an air-conditioned meeting room with controlled temperature (25℃) and relative humidity (45±10%) to avoid variability because of weather condition. This experiment was also considered as potential Meeting room air pollution by PFASs. The latter experiment was carried out at the entrance gate of AIST close to car road with heavy traffic, which representing roadside environment.

Two Nanosampers (Furuuchi et al., 2010), located 1.5 m above ground level, operated at 40L min^{-1}, were used for sample collection in duplicate, in general. The inlet and filter stages allowed collection of particles in five size fractions including particle diameter (dp) greater than 10μm and less than 0.5μm (specifically, >10, 10–2.5, 2.5–1, 1–0.5, and < 0.5

μm, respectively). These air experiments were conducted both summer and winter time, total ten sets of Meeting room samples and ten sets of roadside samples have been collected.

In parallel, two CMS connected with NS20 in the inlet also used in this experiment. By this sampling unit, particulate matters have been collected in NS20 and gas phase chemicals passed through the NS20 and captured in CMS.

In order to investigate recovery of target chemicals throughout whole procedure of sampling and analysis in laboratory, filters on the first stage of sampler were spiked with 100 μL of surrogate chemicals, namely 13C-labeled internal standards (10 ng ml^{-1}) prior to air sampling (13C2-PFBA, 13C4-PFOA, 13C5-PFNA, 13C2-PFDA and 13C4-PFOS).

Detail information of sampling campaigns was shown in Table 2.

Table 2 List of samples collected in meeting rooms (representing indoor air) and main gate AIST (representing roadside air).

	Sample I.D.	**Season**	**Sampling period**			**Duplicate or single analysis**	**Filter Weight**	**Weather condition**	
			Start date	**End date**	**Total sampling time (h)**			Temp. (℃)	Weather
Meeting Room	**MR1**	Summer	14/09/26	14/09/28	44	Single	×	14-26	Sunny
	MR2	Fall	14/10/16	14/10/19	66.4	Single	×	6-23	Sunny
	MR3	Summer	15/07/17	15/07/19	40	Duplicate	○	23-34	Cloudy
	MR4	Summer	15/07/17	15/07/19	40		○		
	MR5	Summer	15/07/19	15/07/21	42.4	Duplicate	○	23-34	Sunny
	MR6	Summer	15/07/19	15/07/21	42.4		○		
	MR7	Summer	15/08/07	15/08/10	63.9	Duplicate	○	23-33	Sunny
	MR8	Summer	15/08/07	15/08/10	63.9		○		
	MR9	Winter	16/02/19	16/02/22	65.2	Duplicate	○	-1-17	Sunny
	MR10	Winter	16/02/19	16/02/22	65.2		○		
Roadside	**RS1**	Summer	15/07/21	15/07/22	24.8	Duplicate	○	23-34	Sunny
	RS2	Summer	15/07/21	15/07/22	24.8		○		
	RS3	Summer	15/08/06	15/08/07	27.6	Duplicate	○	24-36	Sunny
	RS4	Summer	15/08/06	15/08/07	27.6		○		
	RS5	Summer	15/08/10	15/08/11	27.8	Duplicate	○	23-32	Sunny
	RS6	Summer	15/08/10	15/08/11	27.8		○		
	RS7	Winter	16/02/18	16/02/19	25.6	Duplicate	○	-4-17	Cloudy, Sunny
	RS8	Winter	16/02/18	16/02/19	25.6		○		
	RS9	Winter	16/02/22	16/02/24	45.8	Duplicate	○	2-9	Cloudy, Rainy
	RS10	Winter	16/02/22	16/02/24	45.8		○		

A) International field sampling

2.1.3.2 International field sampling

By using NS40 and NS20, international field survey was carried out from 2012 to 2016. Totally thirty-five samples were collected from eleven locations in four countries, Japan, India, China and USA. The detail monitoring site information is described below and map of sampling site is shown in Figure 11.

a) Kanazawa, Japan: Kanazawa is the capital city of Ishikawa Prefecture, Japan, with a population of 400,000. Kanazawa monitoring site is located in campus of Kanazawa University, a mountainous area without notable emission sources.

b) Okinawa, Japan: Okinawa Island is the largest of the Okinawa Islands and the Ryukyu (Nansei) Islands of Japan, located roughly 640 kilometres (400 mi) south of the rest of Japan, Okinawa monitoring site is located in a peaceful residential area, 3km from seashore.

c) Mt.Fuji, Japan: Mount Fuji, located on Honshu Island, is the highest mountain peak in Japan at 3,776.24 m. The monitoring site was located in Mount Fuji Weather Station at the summit of Mt.Fuji.

d) Hawaii, USA: The Hawaiian archipelago, in the central Pacific Ocean, is located 3,200 km southwest of the continental United States. One sample was taken in subaru telscope at Mt Mauna Kea, Hawaii,

e) Hawaii, USA: the other sample was taken in subaru Telescope Hawaii observation center.

f) India: Chennai sampling site is in Madras University campus, only 1km from seashore.

g) Hong Kong, China: Hong Kong is ranked as the fourth highest population density city in the world. Kowloon sampling site is on one building rooftop of City University of Hong Kong, surrounded by high population density residential area combined with heavy traffic.

h) Yuxi, Yunan, China: Yuxi is a prefecture-level city in the Yunnan province of the People's Republic of China, which located in south west part of China and is a part of Yunnan-Guizhou Plateau. This city is with low population density and no major industrial pollution emission source. The monitoring site is located on a rooftop of a four-floor building in Yuxi Normal Univisity campus.

i) Mt. Jiaozi, Yunnan, China: Mount Jiaozi, located in Kunming city, is the highest mountain peak in Yunan at 4223 m. the monitoring site was located in the middle of the mountain at 3115m.

j) Zhengzhou, China: Zhengzhou is a Chinese city and the provincial capital of Henan Province in east-central China, with a population of over eight million. The monitoring site was located on a rooftop of a six floor building in a residential area in suburbs. This area was mainly surrounded by campus.

k) Beijing, China: Beijing, located in northern China, is the capital of the People's Republic of China and the world's third most populous city proper. By corporation with Chinese Academy of Geological Sciences (CAGS), the monitoring site was located on the rooftop of CAGS research institute, downtown area of Beijing with high population density.

Table 3 list of international field sampling information.

Location		ID	Sampler Type	flow rate	Sampling time		Total volume
City/Country	detail			(L min^{-1})	Start date	End date	(m^3)
Kanazawa	K Univ. 6F	KN1	NS40	40	2012/1/11	2012/1/18	406.8
		KN2	NS40	40	2012/4/18	2012/4/25	400.8
		KN3	NS40	40	2012/5/16	2012/5/23	391.2
	K Univ. 6F	KN4	NS40	40	2014/4/16	2014/4/23	402.0
		KN5	NS40	40	2014/4/23	2014/4/30	401.2
Okinawa	Residental area, 10km from seashore	OK1	NS40	40	2014/4/5	2014/4/12	408.0
		OK2	NS40	40	2014/4/13	2014/4/20	408.0
Hawaii	subaru telscope at Mt Mauna Kea, Hawaii	HW1	NS40	37	2014/2/5	2014/2/6	58.7
	subaru Telescope Hawaii observation center	HW2	NS40	40	2014/2/7	2014/2/7	19.2
HongKong	City U, rooftop	HK1	NS40	40	2014/7/6	2014/7/10	229.0
		HK2	NS40	40	2014/7/10	2014/7/13	169.2
	City U, rooftop	HK3	NS40	40	2014/10/27	2014/10/28	55.4
		HK4	NS40	40	2014/10/28	2014/10/29	63.5
		HK5	NS40	40	2014/10/29	2014/10/31	95.3
India	3F, Madras Univ.	IN1	NS40	40	2014/5/25	2014/5/27	115.2
		IN2	NS40	39.5	2014/5/27	2014/5/29	113.8
Yunnan, China	Jiaozi Mt., Yunnan	JZ1	NS40	36	2015/6/20	2015/6/22	91.3
	Jiaozi Mt., Yunnan	JZ2	NS20	20	2015/6/20	2015/6/22	50.7
	Yuxi, Yunnan	YX1	NS20	21	2015/6/23	2015/6/26	93.7
	Yuxi, Yunnan	YX2	NS20	20	2015/7/14	2015/7/17	94.8
	Yuxi, Yunnan	YX3	NS20	20	2015/8/4	2015/8/7	95.6
	Yuxi, Yunnan	YX4	NS20	20	2015/8/25	2015/8/28	95.4
	Yuxi, Yunnan	YX5	NS20	20	2015/9/15	2015/9/18	94.2
	Yuxi, Yunnan	YX6	NS20	20	2015/10/6	2015/10/9	90.2
	Yuxi, Yunnan	YX7	NS20	20	2015/10/27	2015/10/30	93.2
	Yuxi, Yunnan	YX8	NS20	20	2015/11/14	2015/11/17	92.2
	Yuxi, Yunnan	YX9	NS20	20	2015/12/24	2015/12/27	91.8
	Yuxi, Yunnan	YX10	NS20	20	2016/1/22	2016/1/26	113.0
	Yuxi, Yunnan	YX11	NS20	20	2016/2/21	2016/2/24	91.8
Mt.Fuji	Mt.Fuji	FJ1	NS40	30	2015/7/29	2015/8/7	383.4
	Mt.Fuji	FJ2	NS40	20	2015/8/7	2015/8/21	402.2
Zhengzhou, China	Rooftop of residental area	ZZ1	NS20	20	2015/12/28	2015/12/29	13.0
		ZZ2	NS20	20	2015/12/29	2015/12/30	9.8
		ZZ3	NS20	20	2015/12/31	2015/12/31	10.6
		ZZ4	NS20	20	2016/1/2	2016/1/2	13.0
		ZZ5	NS20	20	2016/1/3	2016/1/3	9.0
Beijing	Rooftop of residental area	BJ1	NS20	20	2015/12/25	2015/12/26	15.0

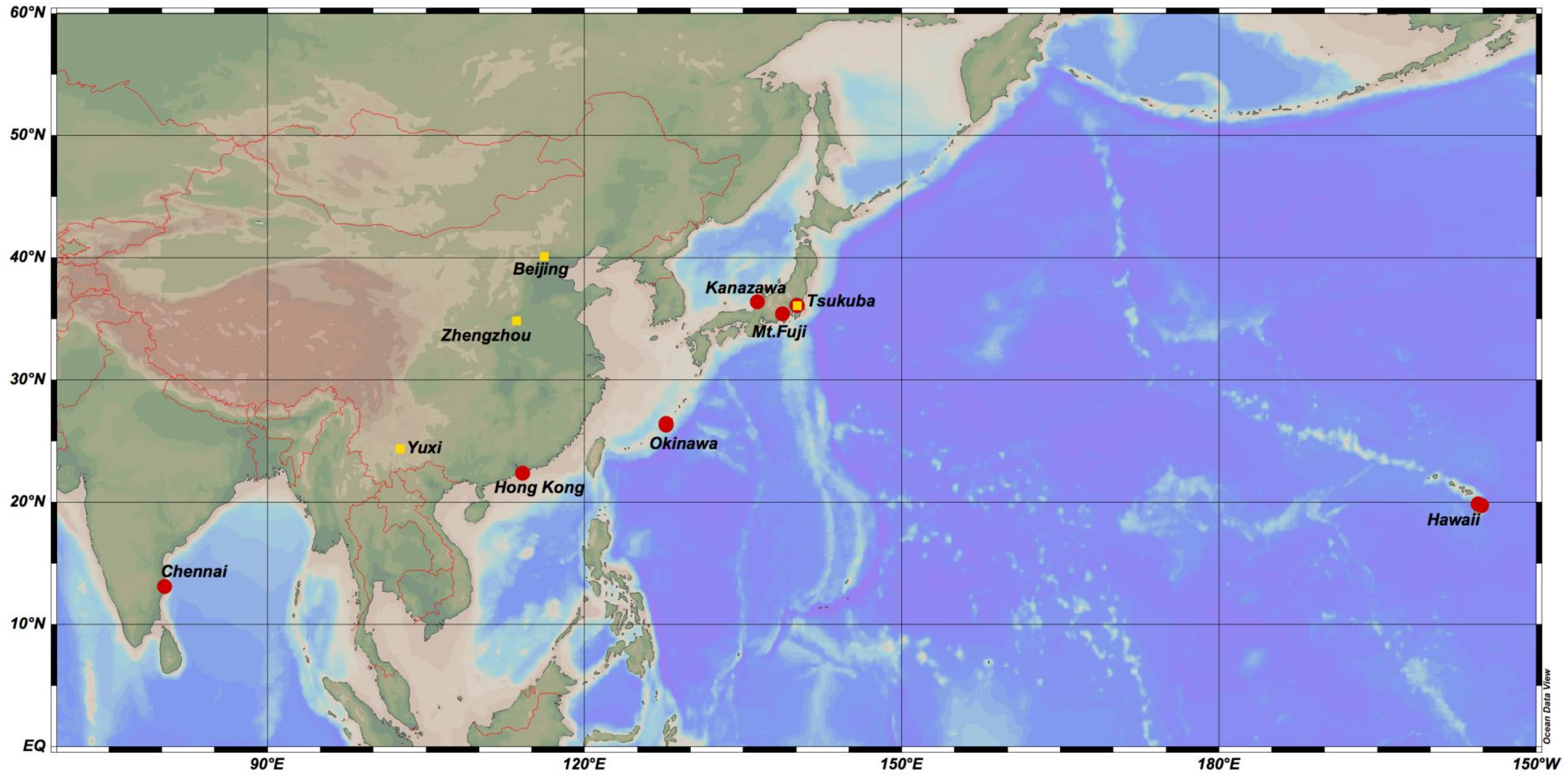

Figure 11 Map of sampling site. Red dot represent samples collected using NS40; Yellow Square represent samples collected using NS20.

2.1.3.3 Cruise air sampling

Air sampling experiment was conducted under field condition during KH14-06 cruise and MR15-03 cruise. One CMS, one NS20 and two NS40 were used during these two cruise sampling. Experiment was carried out in the Pacific Ocean and Antarctic Ocean from Dec.2nd 2014 to Feb.14th 2015 during KH14-06 and in the Pacific Ocean and Arctic Ocean from Aug.24th to Oct.22th 2015 during MR15-03. Total fourteen sets of air samples were collected with each sampler during KH14-06 and MR15-03 cruise. Figure 18 and Figure 19 shows track of RV Hakuho-maru during the cruise KH14-06 and track of RV Mirai during the cruise MR15-03. Cruise information is listed in Table 4. Detail sampling information has been listed in Table 5 and Table 6.

In order to avoid contamination from exhaust gas from ship, samples were collected during underway and CTD operation. Meanwhile, wind select unit was used to control power supply of NS40 pump. Relative wind direction condition was set between 110~250° and relative wind speed condition was set between 7m/s to 100m/s. Only if both wind direction and speed conditions were satisfied, the power switch would turn on and enable NS40 sampling system working. Figure 12 demonstrates sampling system on board.

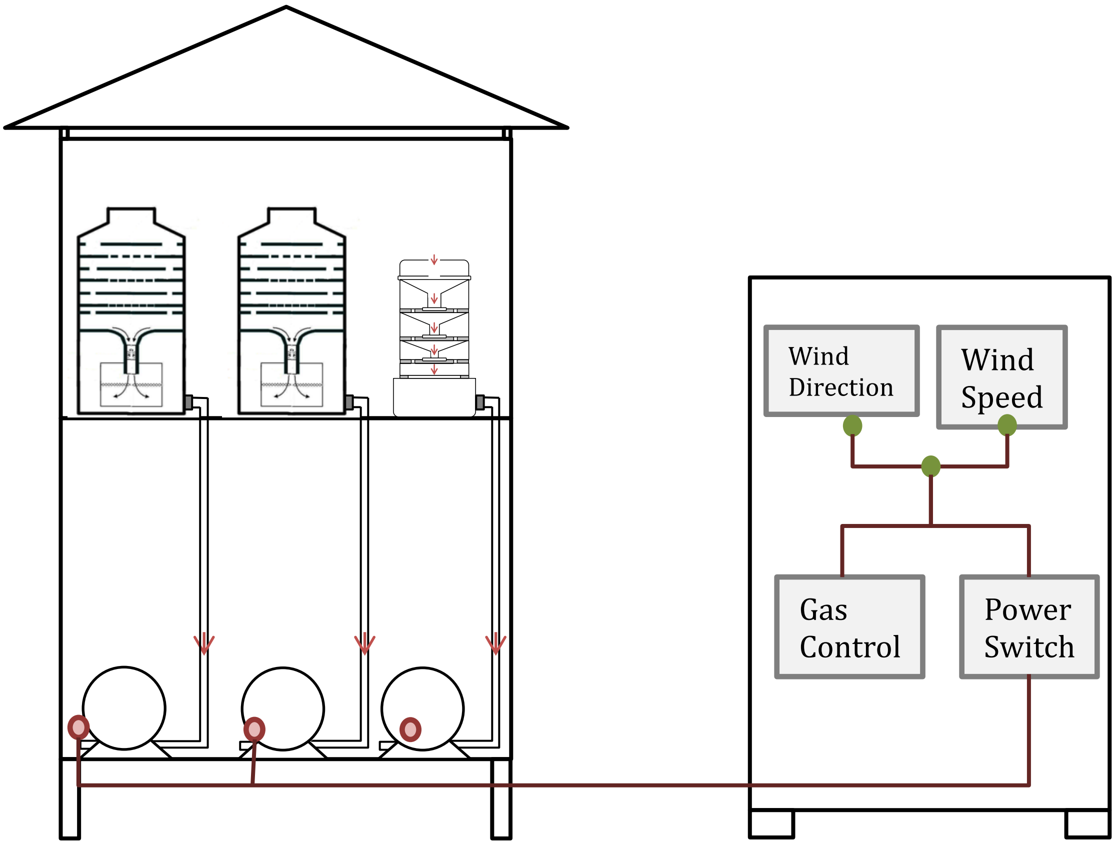

Figure 12 Schematic diagram of air sampling system on board

Air samples were wrapped using aluminum foil, stored in clean polypropylene bags and kept frozen at below -20 ℃ until analysis.

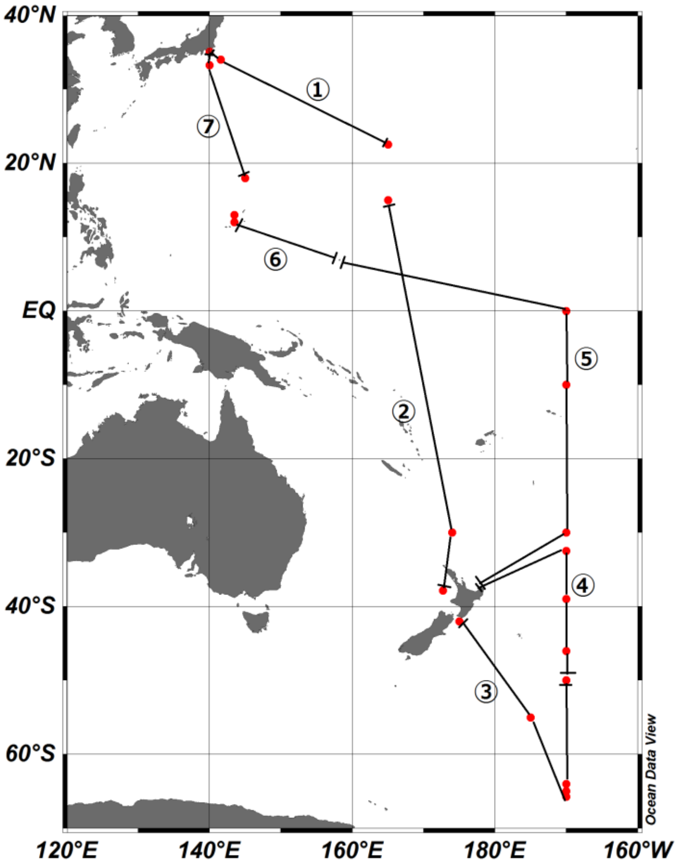

Figure 13 Track of RV Hakuho-maru during the cruise KH14-06. Separatrices mark the start and end points of each sample during the cruise. Samples were taken in between this and the following location. Red dots mark seawater-sampling locations.

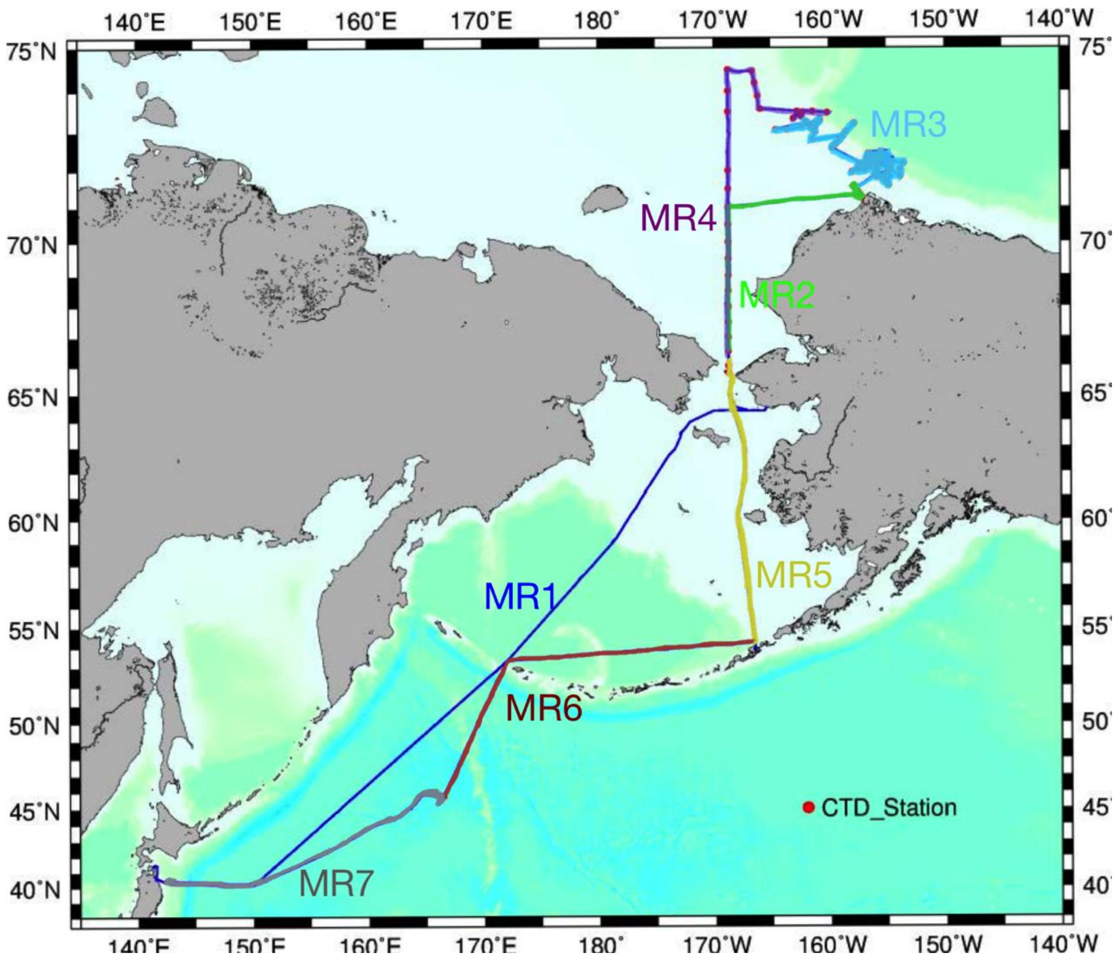

Figure 14 Track of RV Mirai during the cruise MR15-03. Colors distinguish each sample during the cruise. Samples were taken in between this and the following location.

Table 4 Research cruise information of KH14-06 and MR15-03

Research Cruise information		
Ship name	R/V Hakuho (*Tokyo Univ.*)	R/V Mirai (*JAMSTEC*)
Cruise name	KH14-06	MR15-03
Cruise date	December 2014 - February 2015	August 2015 – October 2015
Sampling area	North Pacific Ocean - Antarctic Ocean	North Pacific Ocean - Arctic Ocean
Sampler	NS40*2, NS20, CMS	NS40*2, NS20, CMS

Table 5 Samples list for air samples on KH14-06 cruise

Sample ID		Sampling time						Latitude			Longitude			Total sampling time	Total sampling volume	Note
NS20	CMS		yyyy	MM	dd	HH:mm		deg	min	N/S	deg	min	E/W	(hrs)	m^3	
KH 1	KH-C1	start	2014	12	4	6:55	UTC	34	15.57	N	141	22.19	E	103.67	124.40	North Pacific
		stop	2014	12	8	4:00	UTC	23	05.64	N	164	01.87	E			
KH 2	KH-C2	start	2014	12	11	10:30	UTC	15	08.63	N	165	00.76	E	110.97	133.16	Pacific
		stop	2014	12	21	23:00	UTC	34	51.27	S	171	55.76	E			
KH 3	KH-C3	start	2014	12	27	21:55	UTC	46	07.35	S	176	37.50	E	133.12	159.75	Pacific & Antarctic
		stop	2015	1	7	23:00	UTC	51	12.64	S	170	00.35	W			
KH 4	KH-C4	start	2015	1	9	2:00	UTC	49	59.94	S	170	00.03	W	148.45	178.14	Pacific & Antarctic
		stop	2015	1	18	23:00	UTC	35	57.54	S	179	34.35	E			
KH 5	KH-C5	start	2015	1	24	19:00	UTC	34	48.86	S	179	11.36	E	91.00	109.21	Pacific
		stop	2015	2	10	4:30	UTC	6	28.53	N	174	01.34	E			
KH 6	KH-C6	start	2015	2	14	5:00	UTC	7	15.69	N	171	00.84	E	87.99	105.58	North Pacific
		stop	2015	2	18	19:00	UTC	12	37.31	N	143	56.53	E			
KH 7	KH-C7	start	2015	2	22	8:50	UTC	21	34.72	N	144	00.50	E	41.09	49.30	North Pacific
		stop	2015	2	24	23:25	UTC	34	31.74	N	139	51.49	E			

Table 6 Samples list for air samples on MR15-03 cruise

Sample ID		Sampling time						Latitude			Longitude			Total sampling time	Total sampling volume	Note
NS20	CMS		yyyy	MM	dd	HH:mm		deg	min	N/S	deg	min	E/W	(hrs)	m^3	
MR 1	MR-C1	start	2015	8	26	11:18	UTC	40	28.23	N	142	00.71	E	102.44	122.93	North Pacific
		stop	2015	9	6	3:55	UTC	65	28.26	N	168	31.59	W			
MR 2		start	2015	9	6	22:32	UTC	67	44.65	N	168	45.31	W	150.17	180.21	Arctic
		stop	2015	9	15	4:40	UTC	72	20.26	N	156	10.55	W			
MR 3		start	2015	9	18	1:35	UTC	72	17.76	N	155	15.39	W	57.11	68.53	Arctic
		stop	2015	9	27	2:30	UTC	73	18.04	N	160	47.07	W			
MR 4	MR-C2	start	2015	9	27	4:50	UTC	73	18.04	N	160	47.07	W	98.02	117.63	Arctic
		stop	2015	10	3	21:22	UTC	65	21.31	N	168	33.27	W			
MR 5	MR-C3	start	2015	10	3	22:55	UTC	65	04.11	N	168	38.80	W	64.12	76.94	Arctic
		stop	2015	10	6	17:05	UTC	50	01.99	N	166	30.10	W			
MR 6	MR-C4	start	2015	10	9	22:57	UTC	54	13.76	N	164	09.76	W	142.47	170.96	North Pacific
		stop	2015	10	16	22:37	UTC	43	54.46	N	160	11.19	E			
MR 7	MR-C5	start	2015	10	17	0:08	UTC	43	48.08	N	159	58.10	E	65.30	78.36	North Pacific
		stop	2015	10	20	21:05	UTC	40	40.01	N	141	37.69	E			

2.2 Chemical analysis

2.2.1 Chemicals

All chemicals, standard compounds were of high quality and purity. Information of targets and their abbreviations are as follows. The sodium salts of perfluorohexanesulfonate (PFHxS), perfluoroheptanesulfonate (PFHpS), perfluorooctanesulfonate (PFOS), perfluorodecanesulfonate (PFDS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and ^{13}C-labled $^{13}C_4$ -PFOS, $^{13}C_2$ -PFDA, $^{13}C_5$ -PFNA $^{13}C_4$ -PFOA, and $^{13}C_4$ –PFBA were a purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Perfluoroetyl sulfonate (PFEtS) and perfluoropropyle sulfonate (PFPrS) was donated by JEMCO Inc. (Akita, Japan). Perfluorobutane sulfonate (PFBS) was from Chiron AS (Trondheim, Norway). N-ethyl perfluorooctane sulfonamide (N-EtFOSA), N-ethyl perfluorooctanesulfonamido acetate (N-EtFOSAA), N-methyl perfluorooctanesulfonamidoethanol (N-MeFOSE) and N-ethyl perfluorooctanesulfonamidoethanol (N-EtFOSE) were donated by the 3M Company (St. Paul, MN). Perfluorobutyric acid (PFBA) was supplied by Avocado Research Chemicals, Ltd. (Lancashire, UK). Perfluorohexanoic acid (PFHxA) was from Wako Pure Chemical Industries (Osaka, Japan). Perfluoropentanoic acid (PFPeA), perfluoroheptanoic acid (PFHpA), PFDA, perfluoroundecanoic acid (PFUnDA) and perfluorododecanoic acid (PFDoDA) and perfluorooctanesulphonyl fluoride (PFOSF) were supplied by Fluorochem Ltd. (Derbyshire, UK). Perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were supplied by SynQuest Lab Inc. (Alachua, FL). Trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), 8:2FTOH were purchased from Daikin Industries Ltd (Osaka, Japan).

2.2.2 Extraction method

A) Samples collected by cascade impactor

After collection, each QFF was put into a polypropylene (PP) tube (15ml) and extracted by 4ml of methanol in a sonication water bath (40℃) for 10 min, three times. The supernatant was collected in a new PP tube and concentrated to 1mL using nitrogen gas then injected in to HPLC MS/MS.

If the extract was highly influenced by large amount of particle matter and filter fiber, Envi-carb was involved in extraction procedure. The extract was applied to Supelclean ENVI-Carb cartridges (100 mg, 1 mL, 100-400 mesh, Supelco, U.S.A.) to remove interferences. The conditioning of the cartridges was carried out three times with 1 mL of methanol. Afterward, the sample extract was applied and then 1 mL of methanol was added to the cartridge and directly collected in another PP tube. This procedure was repeated for three times. Finally, the extract was concentrated to 1 mL under a nitrogen stream and transferred into a vial for determination using high performance liquid chromatograph coupled with tandem mass spectrometer (HPLC-MSMS).

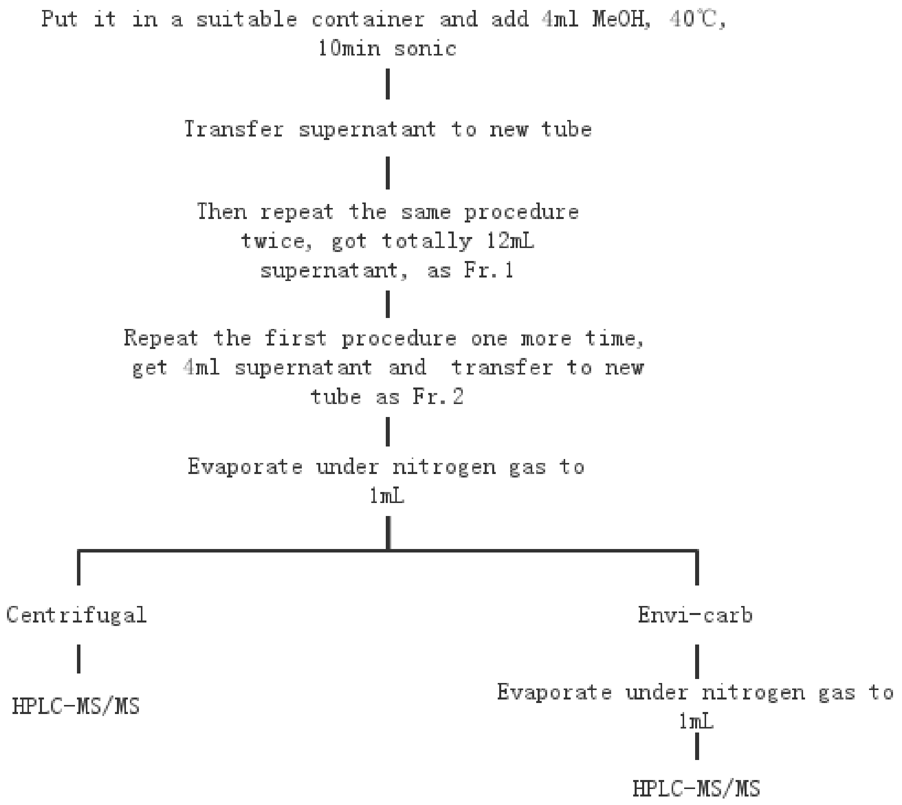

Figure 15 Chart flow of chemical extraction procedure for samples collected by cascade impactor.

B) Samples collected by CMS

CMS Samples were kept frozen for storage and thawed at room temperature one-day priory to analysis. Analysis of PFASs was performed using a solid phase extraction (SPE) method using Oasis®WAX cartridge (150 mg, 30 μm) (Waters Co.). Briefly, after preconditioning by passage of 4 mL of 0.1% ammonia/methanol, 4 mL of methanol, and 4 mL of Milli-Q-water, the cartridges were loaded water samples at approximately 1 drop sec-1. CMS samples were spiked surrogate standard (1 ng of each compound) before sample loading. The cartridges were then washed with Milli-Q water and then 25 mM ammonium acetate buffer (pH 4) in Milli-Q water and dried by centrifugation. The elution was then divided into two fractions. The first fraction was carried out with methanol and the second with 0.1% ammoniumhydroxide in methanol. Both fractions were reduced to 1 mL under a nitrogen stream and analyzed separately. Figure 16 is a demonstration of chemical extraction procedure for samples collected by CMS.

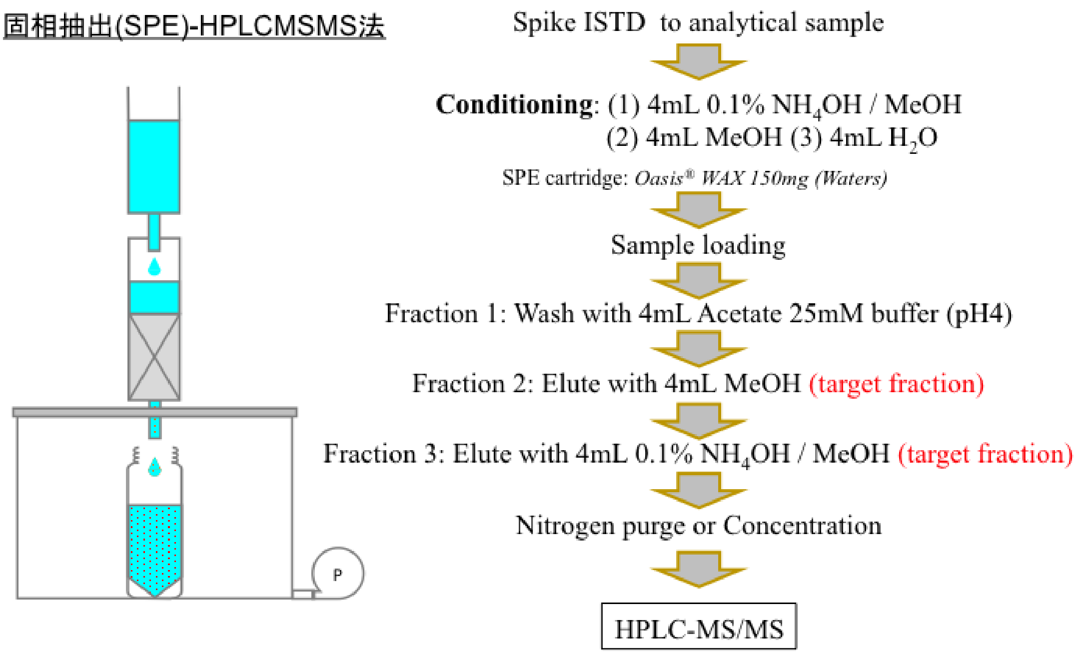

Figure 16 Demonstration of chemical extraction procedure for samples collected by CMS.

2.2.3 Instrumental analysis

Separation and quantification of the analytes was performed by an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro Ultima Pt Mass Spectrometer (Waters Corp., Milford, MA) operated in the electrospray negative ionization mode. A 10 μL aliquot of the extract was injected onto 2 different analytical columns. One of the columns was a Keystone Betasil C18- column (2.1 mm i.d. × 50 mm length, 5 μm, 100Å pore size, endcapped; Termo Hypersil-Keystone, Bellefonte, PA) with 2 mM ammonium acetate and methanol as the mobile phase for the quantification of C6-C18 PFASs. Another column was ion exchange column, RSpak JJ-50 2D (2.0 mm i.d. × 150 mm length; Shodex, Showa Denko K.K., Kawasaki, Japan) with 50 mM ammonium acetate and methanol as the mobile phase and was employed for the quantification of C3-C5 PFASs. The PFAS concentrations (C6-C18) determined by these two stationary phases were checked against each other for confirmation. The variations in PFAS concentrations determined between these two columns should be less than 10%. If more than 10% difference between duplicate analysis using two stationary phases, sample were re- analyzed. This procedure enable high accuracy analysis of PFCAs and PFASs.

The capillary is held at 1.2 kV. Cone-gas and desolvation-gas flows are kept at 60 and 650 L/h, respectively. Source and desolvation temperatures were kept at 120 and 420 ℃ respectively. The collision energies, cone voltages and MS/MS parameters for the instrument were optimized for individual analytes, and were similar to those reported elsewhere (2-5).

By using HPLC-MS/MS, total 20 chemicals (7 PFSAs and 13 PFCAs) have been analyzed.

2.3 Quality assurance and quality control

Data quality assurance and quality control (QA/QC) protocols included laboratory blanks and recoveries, surrogate spikes and continuing calibration verification.

Laboratory blanks and recoveries were analyzed with each set of QFF extraction and SPE as a check for possible laboratory contamination and interferences. Blanks did not contain any interference. Overall recovery of PFCAs and PFASs using the specified analytical procedure ranged from 81% to 104%. Overall recovery of FOSA, N-EtFOSA, N-EtFOSAA, 8:2FTCA, 8:2 FTUCA were 82%, 85%, 81%, 125% and 98% respectively.

Reported PFOS concentrations were not corrected for recovery.

The limit of quantification (LOQ) for each analyte was defined as the smallest mass of the compound injected that resulted in a reproducible measurement of the peak areas, on the basis of the calibration curve. The limit of quantification (LOQ) varied depending on the compound, and ranged from 0.02 to 0.50 ng L^{-1} for injected samples. Sample concentration factors and a signal-to-noise ratio of 10 were applied in the calculation of LOQ.

Matrix spikes were analyzed for each sample type and species.

Instrumental blank concentrations (pg mL^{-1}) with methanol injections were confirmed to check influence from instrument to samples. Meanwhile, standard solutions as Quality control (QC) were injected to check stabilities of instrumental analysis.

Reliability of analysis was confirmed by blank test, recovery test, reproducibility test and matrix spike recovery test by triplicate analysis. Further information regarding the QAQC from the inter-laboratory trial were reported elsewhere.

Table 7 Limit of quantification information

LOQ (pg m^{-3})	Meeting Room Sample (n=10)		Roadside sample (n=10)	
	MAX	MIN	MAX	MIN
PFEtS	0.49	0.06	0.84	0.09
PFPrS	0.48	0.06	0.17	0.09
PFBS	0.10	0.01	0.17	0.03
PFHxS	0.10	0.01	0.04	0.02
PFOS	0.10	0.01	0.18	0.02
PFDS	0.10	0.01	0.18	0.02
FOSA	0.10	0.01	0.17	0.03
N-EtFOSA	0.10	0.01	0.04	0.02
N-EtFOSAA	0.10	0.01	0.18	0.02
PFPrA	0.32	0.06	0.84	0.15
PFBA	0.48	0.01	0.84	0.03
PFPeA	0.48	0.01	0.17	0.03
PFHxA	0.10	0.01	0.18	0.02
PFHpA	0.10	0.01	0.04	0.02
PFOA	0.10	0.01	0.18	0.02
PFNA	0.10	0.01	0.18	0.02
PFDA	0.10	0.01	0.18	0.09
PFUnDA	0.10	0.06	0.18	0.09
PFDoDA	0.10	0.01	0.18	0.02
PFTrDA	0.10	0.01	0.18	0.02
PFTeDA	0.10	0.01	0.18	0.02
PFHxDA	0.10	0.01	0.18	0.02
PFOcDA	0.10	0.01	0.18	0.02
8:2FTCUA	0.06	0.01	0.17	0.03

Reference

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Yamazaki, E.; Taniyasu, T.; Shimamura, K.; Sasaki, S.; Yamashita, N. Development of solid phase extraction method for trace analysis of perfluoroalkyl substances in open ocean water. Bunseki Kagaku, 2015. (in press, accepted July 5)

Chapter 3 Sampling method establishment

To establish sampling method for cascade impactors, two experiments have to be finished before publish reliable air sampling results. One is to check blank about sampler parts and filters to exclude potential possibility of contamination from sampler and filter materials. The other is to confirm chemical recovery rates after sampling and chemical extraction by repeatable air sampling.

3.1 Blank check

As a preliminary work to investigate atmospheric pollution of PFASs, this experiment is to elucidate possible contamination of target chemicals during sampling procedure since widely used fluoropolymers in sampling apparatus could be source of contamination. Sampler parts

In order to avoid contamination from every possible parts of sampler, sampler has been disassemble into 22 pieces and numbered, then were separated into 14 groups and washed with MeOH.

Method 1 (for small parts):

a. Put it in a suitable container and add 10ml MeOH, 10min sonic

b. Transfer supernatant to new tube as Fr.1

c. Add another 10ml MeOH, 10min sonic

d. Transfer supernatant to new tube as Fr.2

Method 2 (for large parts):

a. Wash only inlet and outlet of airflow place with 10mL MeOH, collected as Fr.1

b. Wash the same place again with 10mL MeOH, collected as Fr.2

1) Inject after extraction

Classify 14 groups into 4 categories according to material as plastic, metal, membrane filter and rubber.

Extract Fr.1 and Fr.2 from 10ml to 1ml. then inject samples into LC-MS/MS according to possible concentration from low to high.

2) **Result**

Most data is zero or below LOQ, other relatively high concentration is belonging to fraction one, indicating environment contamination.

Most high concentrations become below LOQ in Fr.2, indicating that washing is an efficient method to remove contamination.

Fr.1 of membrane filter (12) is below LOQ, means it can be used without washing.

3) **Conclusion**

Blank were detected from without washing (as Fraction 1) parts. However blank levels decreased after washing (as Fraction 2). It means washing procedure (as Fraction 1) is useful to reduction of blank levels for PFASs.

Fr.1 of membrane filter shows it can be use without pretreatment

3.2 QA/QC establishment

3.2.1 Sample collection

3.2.2 QA/QC result

Table 8 shows the recovery of surrogate standards those were spiked on the first stage filters of Nanosampler before air sampling. Overall, average recovery rate of total eight 13C-labeled surrogate standards are from 60% to 100%, with standard deviation less than 30%. For Meeting room samples, averages recovery rates for each surrogate standards ranges from 82 to 103% with the standard deviation less than 21%. For roadside samples, averages recovery rates for each surrogate standards ranges from 60 to 95% with the standard deviation less than 30%. Table 9 shows the recovery of surrogate standards those were spiked on the first stage filters of Nanosampler before air sampling. Overall, average recovery rate of total eight 13C-labeled surrogate standards are from 76% to 101%, with standard deviation less than 27%. For Meeting room samples, averages recovery rates for each surrogate standards ranges from 91 to 101% with the standard deviation less than 14%. For roadside samples, averages recovery rates for each surrogate standards ranges from 76 to 97% with the standard deviation less than 27%. This result indicates most PFASs would remain on collected filters and no obvious chemical re-suspension occurred along with sampling flow rate. Also, no significant loss of target chemicals occurred during extraction procedure.

Relative standard deviation (RSD) of each duplicate of air mass concentration (µg m^{-3}) and selected chemical concentration (pg m^{-3}) was shown in **Table 10**. Overall average RSD for single chemicals were varying from 5% to 24%, indicating a stable and reliable sampler performance and chemical analyzing procedure.

Figure 17 shows correlation between NS40 and NS20 result about PFASs concentration in total particle phase. High correlation was found between NS40 and NS20 result about PFASs concentration in total particle phase, indicating comparable results between two samplers.

Table 8 **Recovery of surrogate standards that spiked on the first stage filters of NS40 before air sampling.**

	NS40	$^{18}O_2$-PFHxS	$^{13}C_4$-PFOS	$^{13}C_2$-PFBA	$^{13}C_3$-PFPeA	$^{13}C_2$-PFHxA	$^{13}C_4$-PFOA	$^{13}C_5$-PFNA	$^{13}C_2$-PFDA	$^{13}C_2$-PFUnDA	$^{13}C_2$-PFDoDA
Meeting Room	AVE	100%	98%	82%	87%	99%	97%	103%	103%	97%	100%
	Median	98%	94%	77%	87%	104%	91%	103%	102%	97%	105%
	Min	79%	75%	70%	68%	71%	73%	76%	72%	72%	74%
	Max	118%	124%	104%	116%	117%	126%	126%	138%	139%	129%
	SV	12%	14%	12%	14%	17%	20%	14%	21%	20%	16%
Roadside	AVE	95%	94%	60%	72%	78%	78%	88%	92%	84%	90%
	Median	90%	95%	60%	72%	76%	74%	94%	90%	86%	89%
	Min	75%	75%	4%	23%	48%	57%	62%	81%	60%	72%
	Max	115%	109%	106%	106%	107%	98%	110%	105%	107%	108%
	SV	15%	13%	30%	24%	19%	13%	17%	8%	16%	12%

Table 9 **Recovery of surrogate standards that spiked on the first stage filters of NS20 before air sampling.**

	NS20	$^{18}O_2$-PFHxS	$^{13}C_4$-PFOS	$^{13}C_2$-PFBA	$^{13}C_3$-PFPeA	$^{13}C_2$-PFHxA	$^{13}C_4$-PFOA	$^{13}C_5$-PFNA	$^{13}C_2$-PFDA	$^{13}C_2$-PFUnDA	$^{13}C_2$-PFDoDA
Meeting Room	AVE	99%	101%	91%	91%	94%	95%	94%	97%	98%	99%
	Median	100%	101%	93%	87%	94%	92%	92%	98%	99%	99%
	Min	84%	87%	73%	79%	82%	82%	85%	79%	81%	82%
	Max	118%	117%	113%	112%	108%	112%	111%	120%	118%	111%
	SV	11%	10%	14%	12%	11%	10%	8%	13%	14%	10%
Roadside	AVE	97%	97%	76%	83%	89%	90%	95%	93%	94%	95%
	Median	98%	98%	81%	88%	93%	91%	96%	94%	95%	96%
	Min	78%	82%	19%	35%	57%	75%	79%	76%	83%	80%
	Max	115%	110%	106%	110%	108%	104%	108%	107%	102%	104%
	SV	11%	9%	27%	22%	18%	11%	11%	10%	7%	7%

Table 10 Relative standard deviation of each duplicates of air mass concentration (μg m^{-3}) and selected chemical concentration (pg m^{-3}).

		PM	PFHxS	PFOS	FOSA	N-EtFOSA	N-EtFOSAA	PFHxA	PFHpA	PFOA	PFNA
Meeting room	Mean	18%	16%	9%	5%	8%	9%	7%	13%	10%	14%
	Median	15%	14%	8%	4%	6%	7%	6%	10%	8%	6%
	Max	59%	39%	25%	19%	21%	21%	28%	51%	24%	72%
	Min	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Roadside	Mean	14%	4%	12%	24%	16%	16%	11%	16%	12%	19%
	Median	9%	4%	16%	14%	19%	13%	7%	16%	13%	11%
	Max	41%	4%	22%	29%	32%	22%	50%	93%	51%	37%
	Min	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

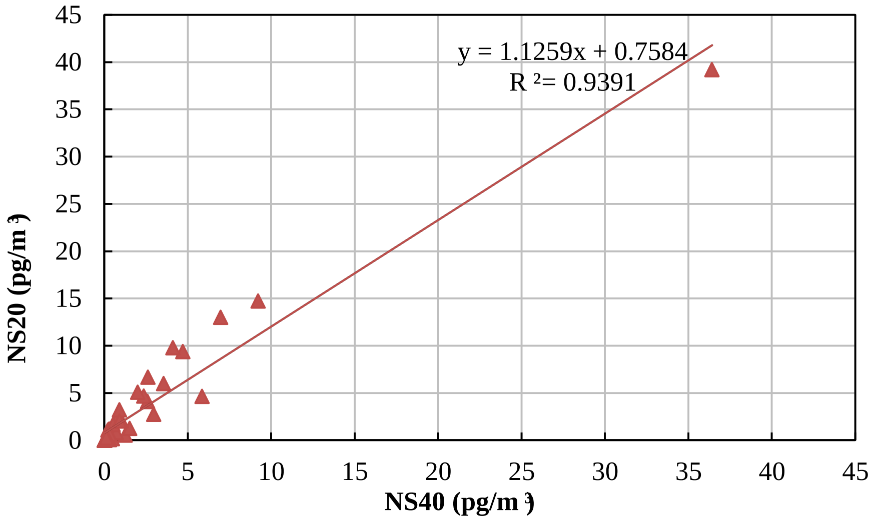


Figure 17 Correlation among NS40 and NS20 result about PFASs concentration in total particle phase.

Chapter 4 PFASs in Atmosphere

4.1 Meeting Room and Roadside air sampling

4.1.1 Particulate matter (PM) concentration

Results of particle matter concentration (µg m^{-3}) of meeting room samples and roadside samples have been shown in **Figure 18**. The average air mass concentration in roadside air is 46µg m^{-3}, about 2 times comparing with that of Meeting room air (27µg m^{-3}). The size distributions in Meeting room and roadside air were different. In Meeting room air, the air mass concentration is gradually decreased along with the increase of particle size. While in roadside air mass concentration shows a bi-model distribution, with main peak appeared at 2.5~10µm and second peak appeared at 0.5~1µm. The first peak indicated a natural source while the second peak indicates a human source, generally automobile exhaust.

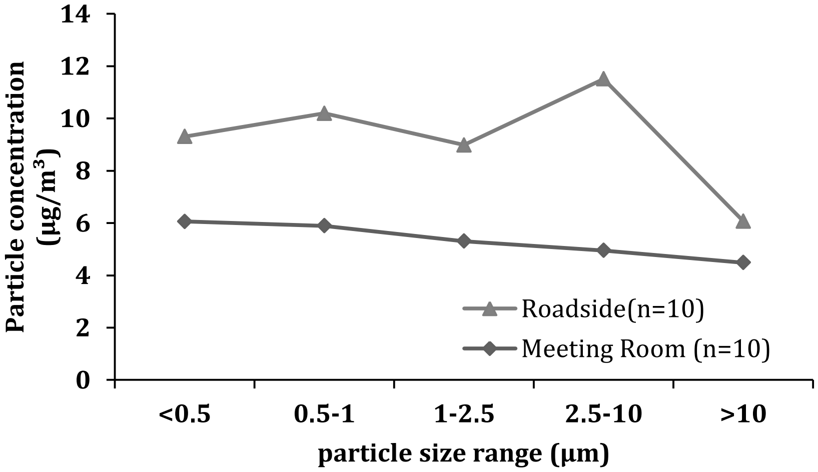


Figure 18 Particle matter concentration (µg m^{-3}) of meeting room samples (n=10) and roadside samples (n=10)

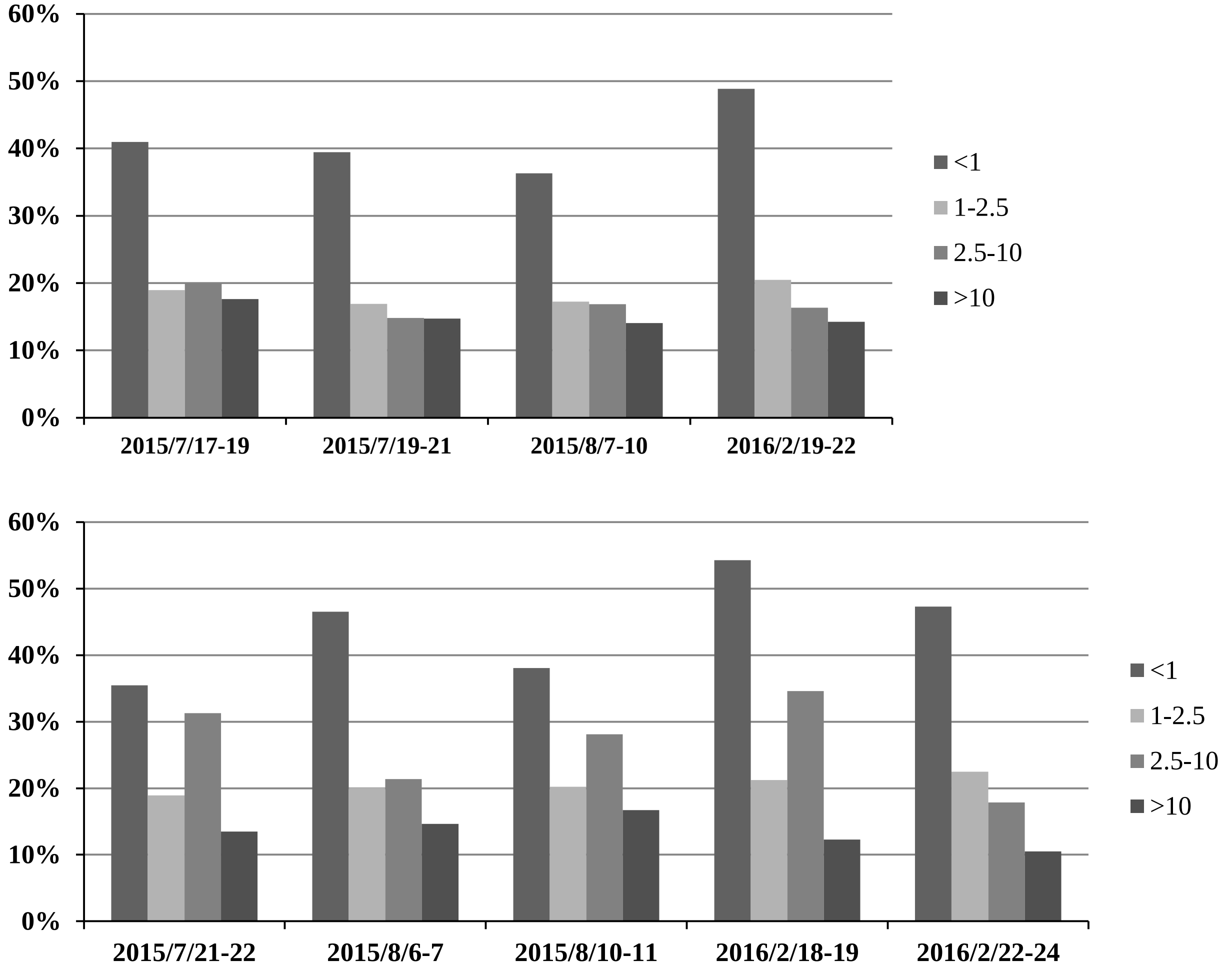


Figure 19 Size fraction of each sample (upper: meeting room samples, bottom: roadside samples).

4.1.2 PFASs concentration in particle phase

A) PFASs concentration in total particle

Figure 20 shows average concentrations (pg m^{-3}) of PFASs in air samples collected from meeting room and roadside (all stages combined). The LOQ for each chemical were varied from 0.01 to 0.84 pg m^{-3} depending on chemical and sample variation, detail information were listed in supporting information Table S3.

The meeting room air profile was mainly dominated by neutral PFASs -- FOSA (5.7 pg m^{-3}), N-EtFOSAA (4.7 pg m^{-3}), N-EtFOSA (3.0 pg m^{-3}) and one ionic PFASs (PFNA, 4.1 pg m^{-3}), while the roadside air profile was dominated by ionic PFCAs – PFHxA (7.3 pg m^{-3}), PFHpA (3.7 pg m^{-3}), PFOA (3.1 pg m^{-3}) and PFNA (2.6 pg m^{-3}). The concentrations of three neutral PFASs (FOSA, N-EtFOSA, N-EtFOSAA) in meeting room exceed substantially those of roadside air. The meeting room/roadside ratios of these three compounds were 10, 11, 5, respectably, highlighting the importance of the indoor exposure pathway. Similar monitoring result was reported in 2011 (Shoeib et al., 2011). In both meeting room and roadside air, PFCAs concentrations were significantly higher than those of PFSAs. Harada et al. also reported 7~50 times differential between PFOA and PFOS in Fukushima sampling (Harada et al., 2006). Concentration of PFOA and PFHxA were about 3, 10 times of those of PFOS and PFHxS in both meeting room air and roadside air. As a representative ionic PFCA, PFOA concentration in indoor air were reported by other studies (Goosey and Harrad, 2012; Shoeib et al., 2011), while report about concentration of other ionic PFCAs is limited. In this study, the dominant PFCAs is PFNA, about 2 times comparing with PFOA. Generally, there are two emission sources for PFNA, one is indirect input, degradation product from FTOs. e.g. 8:2 FTOH (C8F17C2H4OH) can degrade into C5–C9 PFCAs through OH radical oxidation (Ellis et al., 2004). The other is direct input, Prevedouros et al. report that PFNA production is primarily in Japan and that 14 of the world's 33 fluoropolymer production sites are in east Asia (Prevedouros et al., 2006). Same wise, a higher ratio of PFNA/PFOA in the Western Arctic than in the Eastern Arctic is reported, which is consistent with the manufacture and use of PFNA/APFN in Eastern Asia. (Polar bear)

Moreover, the concentrations of carboxylate (C4-C8) in Roadside air were increased comparing with those of Meeting room particles. The Meeting room/ Roadside ratios of these compounds varied from 0.26 (PFHpA) to 0.76 (PFOA). Considering the result that Meeting room/ Roadside air mass concentration is about 0.5, this result suggest that other than indoor emissions are driving roadside contamination (), for the roadside environment, there maybe exists other contamination source that is responsible for concentrations of carboxylate PFASs in particles. Also, both in the Meeting room and roadside air, average concentration of PFHxA exceeded that of PFOA, which is consistent with the hypothesis that PFHxA use is increasing in response to restrictions on the use of PFOA( ).

Table 11 summarized of concentrations (pg m^{-3}) of PFASs in meeting room (representing indoor environment) and roadside (representing outdoor environment) air samples (this study), and in indoor and outdoor samples from different cities in selected other studies. Indoor air concentration in Canada (Shoeib et al., 2011) and United Kindom (Goosey and Harrad, 2012) were more than an order of magnitude higher than roadside concentrations and then indoor air was considered a source to ambient air. While given the differences in concentrations and compounds profile between indoor and roadside samples observed in this study, Meeting room air in Tsukuba city seemed not to be the only main contributor to roadside air level. The similar observation in Korea cities was also reported (Kim et al., 2012).

Also, Study in Kyoto area, Japan also reported 3~20 times high concentration of PFOS and PFOA in busy traffic national route comparing with local road, indicating contribution from automobile exhaust (Harada et al., 2006). Further studies are necessary to elucidate the presence of PFAS emission sources in the outside air.

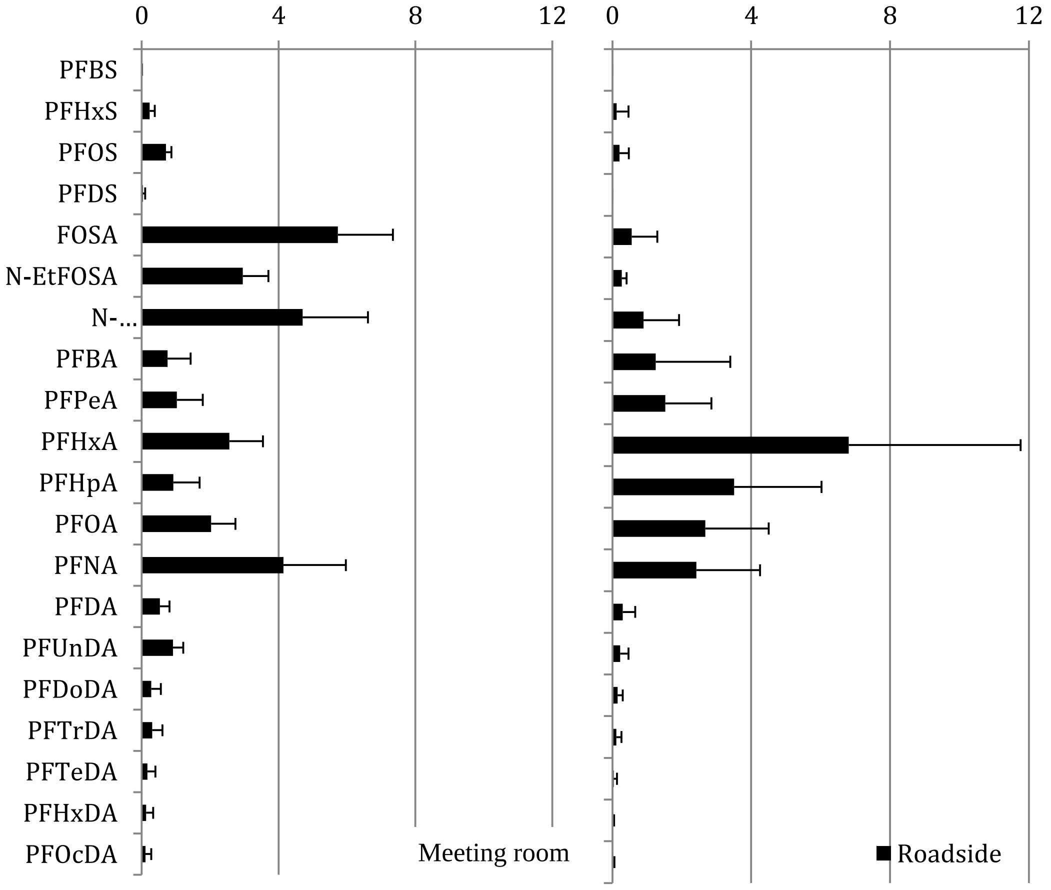


Figure 20 Average concentrations (pg m^{-3}) of PFASs in Total suspended particles (TSP) in indoor (n=10) and roadside(n=9) air (error bar = standard deviation).

B) Size segregated PFASs concentration (pg m^{-3})

Figure 21 shows size segregated chemical concentrations (pg m^{-3}) of selected PFASs and mass air concentration (μg m^{-3}) in Meeting room and roadside air, representing the first size segregated PFASs concentrations reported, except for PFOA and PFOS which were reported by Harada et.al (Harada et al., 2006). Detail information was listed in Table S6.

Size segregated PFASs concentrations FOSA were enriched in particles which size less than 0.5 μm in Meeting room air, while enriched in particles which size between 2.5~10μm and 0.5~1μm in roadside air. Both these two size distribution pattern is highly consist with that of air mass. As to ionic PFCA, in Meeting room air, PFHxA and PFHpA concentration was dominated by <0.5μm stage, 34% and 38% respectably. As to PFOA and PFNA, the proportion of <0.5 μm stage was decrease to 28% and 19%. On the other hand, 1~10 μm proportion is increasing from 36%, 39% of PFHxA, PFHpA to 44%, 51% of PFOA and PFNA.

In roadside air, PFHxA, PFHpA, PFOA and PFNA shows similar pattern from particle size 0.5μm to >10μm, which decreased from 2.5~10μm, 1~2.5μm, >10μm and 0.5~1μm. Especially 1μm to >10μm, which is also consist with air mass pattern. As to <0.5μm stage, proportions were gradually increased along with carbon chain length, 15%, 20%, 25% and 32%, respectably.

C) PFASs concentration in Meeting room and Roadside particulate (ng g^{-1})

Figure 22 shows PFNA and PFOA particulate concentration (ng g^{-1}) in Meeting room and roadside air. In this discussion, due to lack of particle weight information, two 2014 samples were not included in discussion, thus 8 meeting room samples and 9 roadside samples were used for this part. Detail information was listed in Table S7. In general, PFNA and PFOA particulate concentration in Meeting room air is ~4 times higher than that of roadside air. PFOA and PFNA were significantly positive correlated(r>0.88, p<0.01) for all stages in Meeting room particles. PFOA and PFNA is positively correlated in <0.5μm stage (r>0.92, p<0.01) in roadside particles.

In Meeting room environment, PFNA concentration reached to ~800ng g^{-1} in particle size <0.5μm, 1~2.5 μm and >10μm, two times higher than that of particle size between 0.5~1 μm and 2.5~10 μm, which reached to 350ng g^{-1}. PFOA concentration reached to ~350ng g^{-1} in particle size <0.5μm, 1~2.5 μm and >10μm, two times higher than that of particle size between 0.5~1 μm and 2.5~10 μm, which reached to 150ng g^{-1}. PFNA/PFOA ratio varied from 1.8 to 3.5, indicating similar emission source, especially particle size larger than 0.5μm that PFNA concentration was about 3 times higher than PFOA. While in roadside environment, PFOA and PFNA concentration in each stage do not exist significant variation, reached to 100ng g^{-1} except <0.5μm stage, which reached to 200ng g^{-1}. Also PFOA/PFNA ratio (1.5) is similar with Meeting room air (1.8), indicating similar emission source for these two chemicals in Meeting room and roadside environment.

As to other stages (except >10μm), R-value is decreasing and PFOA/PFNA ratios (around 1) also significantly differ from Meeting room air (3~3.5), indicating multiple chemical sources in larger size particles. Hypothesis : Pathway for Ionic PFASs from Meeting room to outside is particle phase, especially through fine particles. Since the doors and windows were barely open during daily use and kept close during sampling time, the main air exchange between meeting room to outside is air ventilation system with filters. Infiltration could remove most of the coarse particles in this process. Thus, this explained the high correlation in PM<0.5 and low correlation of larger particles.

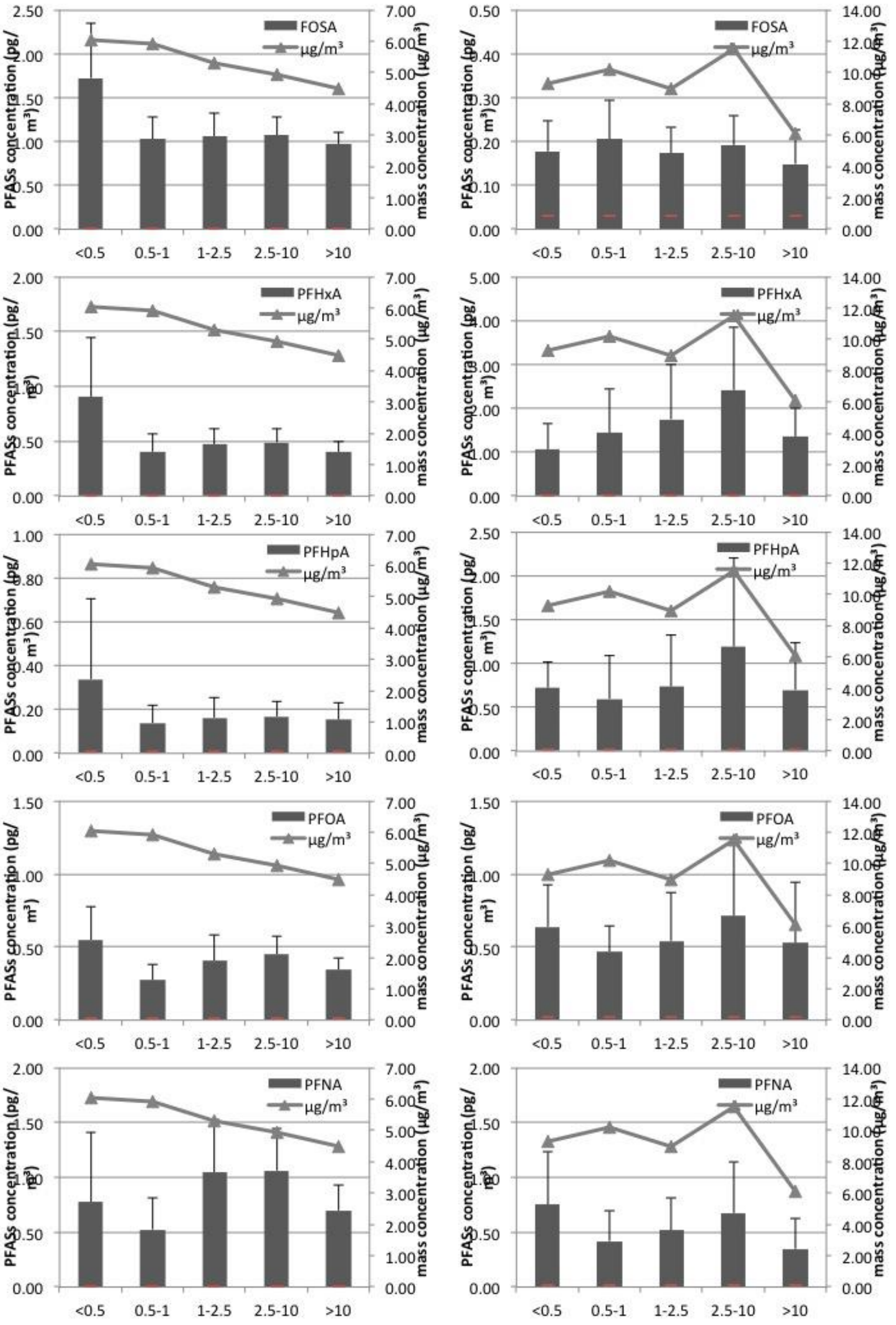


Figure 21 Size segregated concentrations (pg m^{-3}) of selected PFASs and mass air concentration (µg m^{-3}) in particulate matters from meeting room (left side, n=10) and

roadside air (right side, n=9).

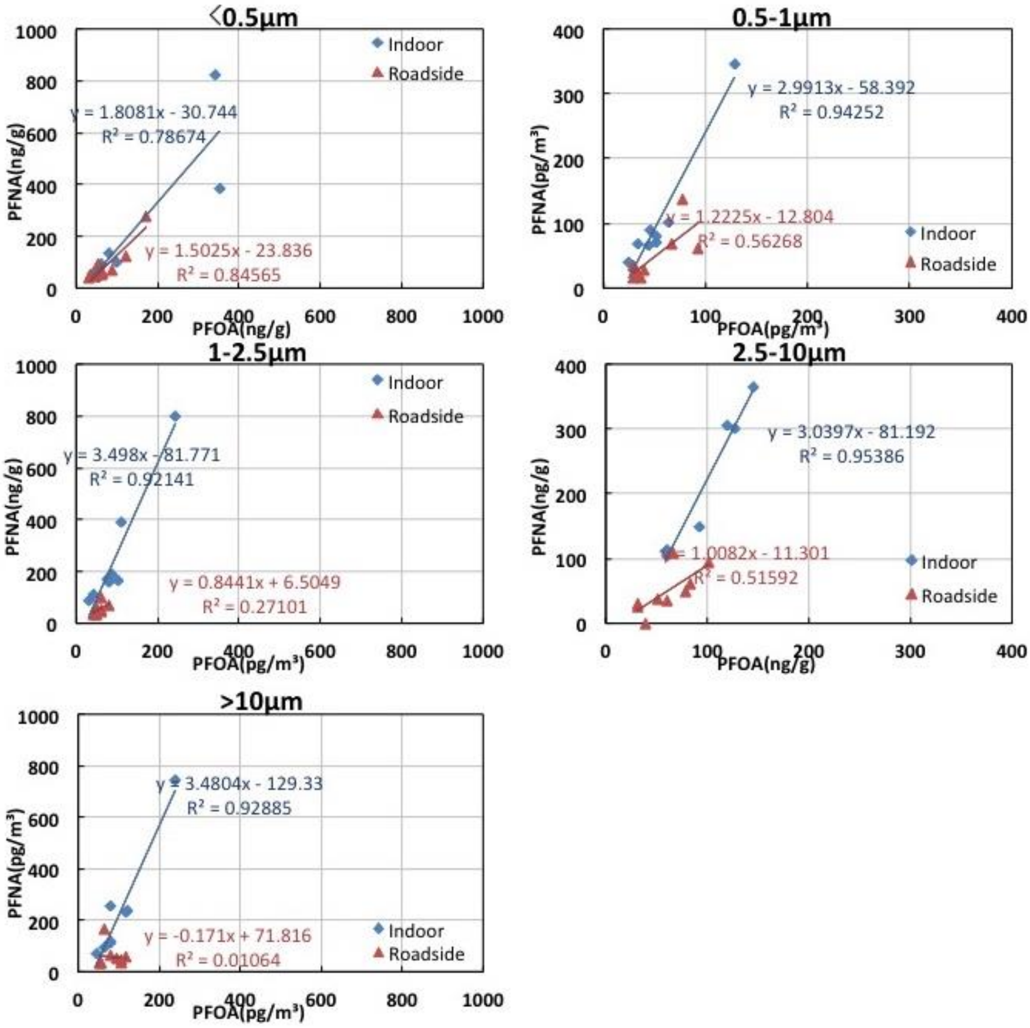


Figure 22 Correlation among concentrations (ng g^{-1}) of PFOA and PFNA in each particle size. Blue dot: indoor samles(n=8); red dot: roadside samples(n=9).

Table 11. Summary of concentrations (pg m^{-3}) of PFASs in meeting room (representing indoor environment) and roadside (representing outdoor environment) air samples (this study), and in indoor and outdoor samples from different cities in selected other studies.

	Location(# samples). Reference	Parameter	PFHxS	PFOS	FOSA	PFHxA	PFHpA	PFOA	PFNA
Indoor	Meeting Room Tsukuba, Japan(n = 10). This study	Average	0.2	0.8	5.9	2.7	0.9	2.0	4.1
		Median	0.2	0.8	6.2	2.6	0.5	1.9	3.5
		Range	0.1-0.5	0.3-0.9	3.7-7.5	1.4-4.2	0.4-2.2	1.3-3.2	2.8-8.7
	Homes. Birmingham. UK(n = 20). (Goosey and Harrad, 2012)	Average (range)	36 (< 1.1-220)	38 (< 1.0-400)	152 (16-1300)	-	-	52 (< 1.9-440)	-
	Offices. Birmingham. UK(n = 12). (Goosey and Harrad, 2012)	Average (range)	94 (< 1.1-330)	56 (12-89)	74 (4-310)	-	-	58 (< 1.9-200)	-
	Homes. Catalonia. Spain(n = 10). (Ericson Jogsten et al., 2012)	Range	-	< DL-69	-	-	-	-	-
	Vancouver. Canada (homes)(n = 59. except for PFOS and PFOA n = 39). (Shoeib et al., 2011)	Average (range)	-	< 0.02	-	-	-	113 (3.4-2600)	-
Outdoor	Roadside Tsukuba, Japan(n = 9). This study	Average	0.14	0.25	0.54	6.98	3.95	2.89	2.63
		Median	<0.02	0.18	0.56	7.36	3.34	2.74	2.02
		Range	<0.02-1.09	<0.02-0.63	<0.03-1.51	<0.02-15.17	1.92-7.79	1.18-5.45	0.99-5.83
	Birmingham UK(n = 10). (Goosey and Harrad, 2012)	Average (range)	7 (< 1.1-30)	2.3 (< 1.0-6.1)	13 (< 1.8-27)			3.5 (< 1.9-20)	
	Paris. France(n = 1). (Genualdi et al., 2010)	Average	60	150	-			4.5	
	Manchester. UK(n = 2). (Barber et al., 2007)	Average	1	46	< 1.6			341	
	Hazelrigg. UK(n = 10). (Barber et al., 2007)	Average	0.04	1.6	0.2			101	
	Vancouver. Canada(n = 6). (Shoeib et al., 2011)	Average (range)		< 0.02				2.5 (< 0.47-9.2)	
	Hamburg. Germany(Barbüttel. n = 117). (Dreyer et al., 2009)	Average		1.3	1			0.3	
	Hamburg. Germany(GKSS. n = 121). (Dreyer et al., 2009)	Average		0.6	0.8			0.2	

4.1.3 PFASs concentration in gas phase

Figure 23 shows average concentrations (pg m^{-3}) of PFASs in air samples collected from meeting room and roadside using CMS. The LOQ for each chemical were varied from 0.01 to 0.84 pg m^{-3}depending on chemical and sample variation.

The meeting room air profile was mainly dominated by neutral PFASs -- FOSA, while the roadside air profile was dominated by ionic PFCAs – PFBA, PFPeA, PFHpA and followed by PFHpA and PFOA. Unlike PFASs concentration in particle phase, PFASs concentration of shorter chain (C4-C5) was significant increased. Also, the concentration variation between PFSA and PFCA of same carbon chain length was decreased both in meeting room and roadside air.

Moreover, the concentrations of carboxylate (C4-C8) in Roadside air were increased comparing with those of Meeting room particles. The Roadside / Meeting room ratios of these compounds variedabout 6-10. Considering the result that Roadside / Meeting room air mass concentration is about 2, this result suggest that other than indoor emissions are driving roadside contamination, for the roadside environment, there maybe exists other contamination source that is responsible for concentrations of carboxylate PFASs in particles.

Figure 24 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 PFSAs, 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 were mainly existing in gas phase.

Figure 25 shows logK$_{PG}$ value calculated using 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). （LogK$_{PG}$= Log (C$_{particle}$ / C$_{gas}$)). Results shows LogK$_{PG}$ values of meeting room samples is higher than roadside sample, indicating PFASs concentration in particle phase contributed more than gas phase in meeting room. In both meeting room and roadside samples, logK$_{PG}$ increase along with carbon chain (C3-C9). Moreover, logK$_{PG}$ of ionic PFSAs (PFHxS and PFOS) were below 0 indicating PFASs concentration in particle phase is larger than gas phase.

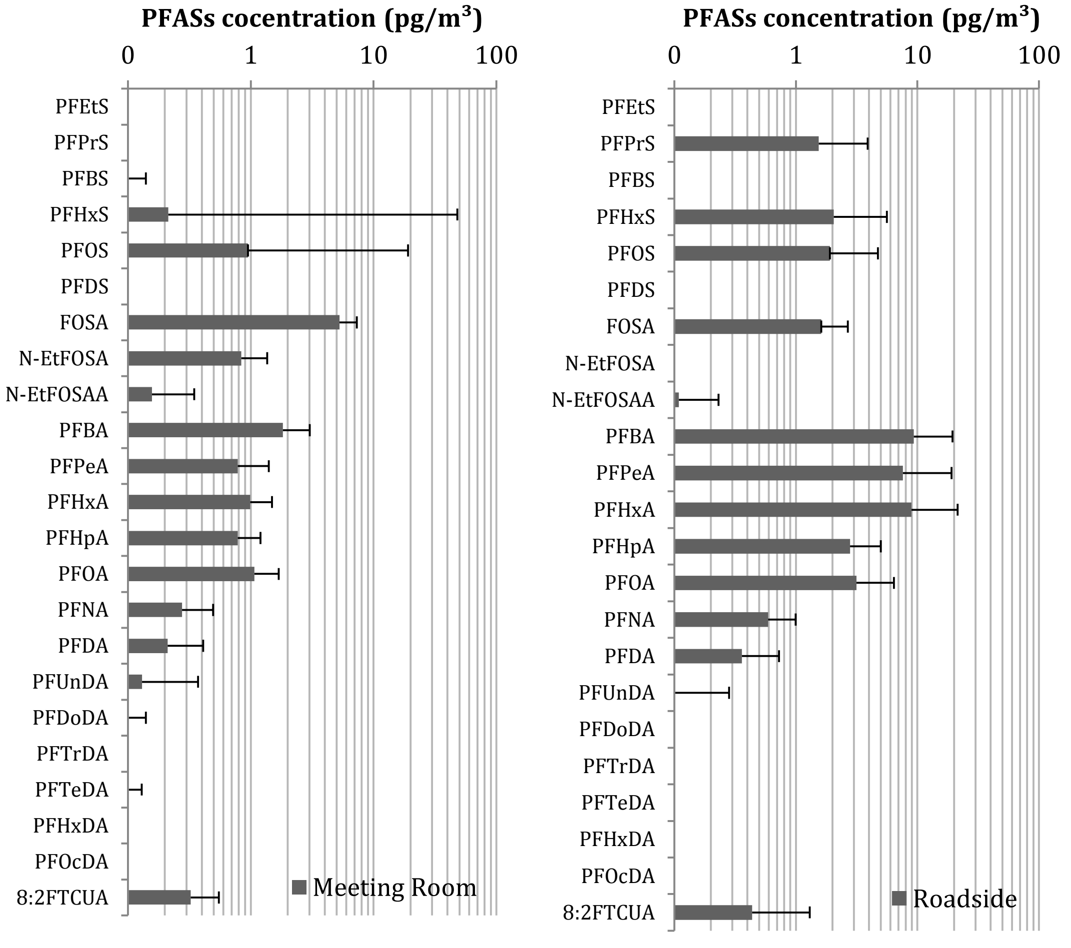


Figure 23 Average concentrations (pg m^{-3}) of PFASs in gas phase(CMS） in meeting room (n=10) and roadside(n=9) air (error bar = standard deviation)

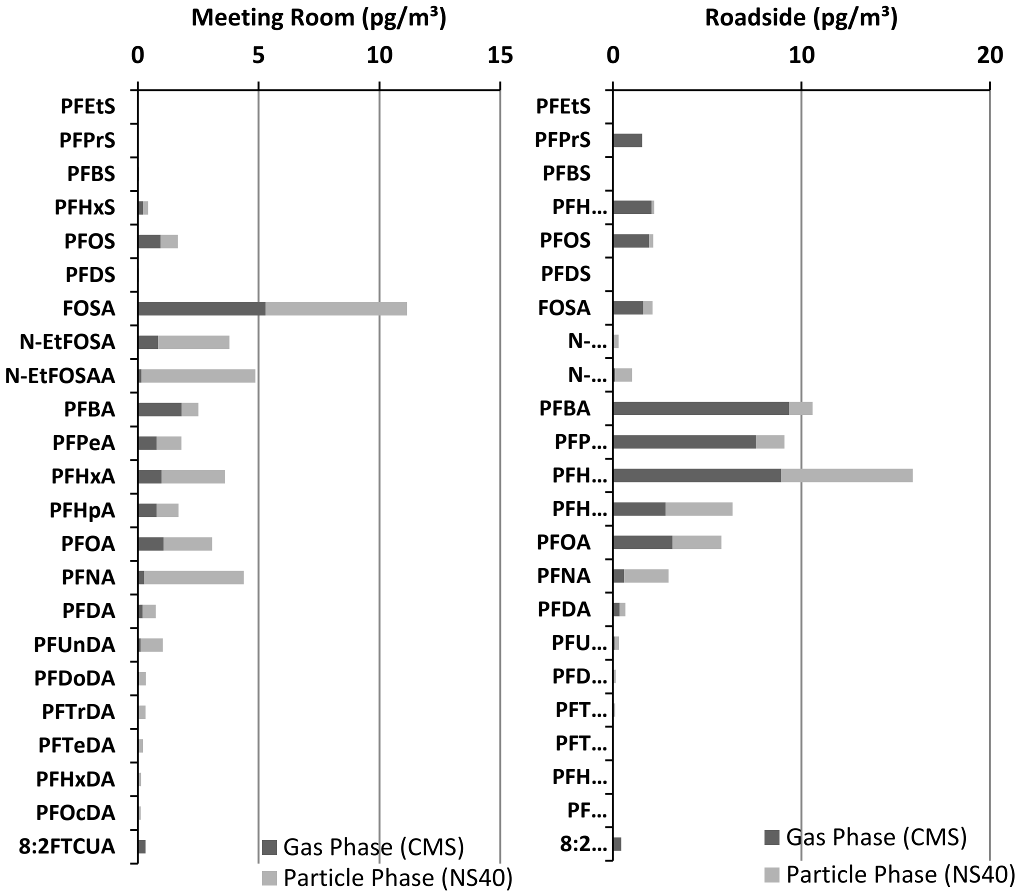


Figure 24 Average concentrations (pg m^{-3}) of PFASs in particle phase (NS40) and gas phase (CMS) in meeting room (n=10) and roadside(n=9) air (error bar = standard deviation)

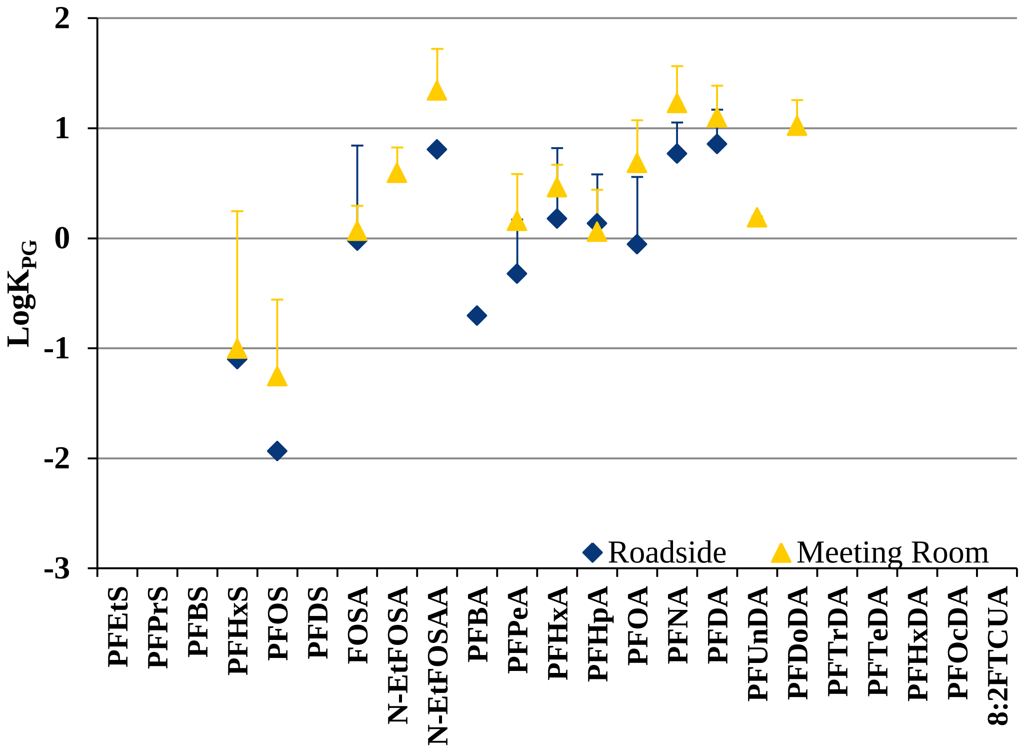


Figure 25 LogK$_{PG}$ value calculated using average concentrations (pg m^{-3}) of PFASs in particle phase(NS40) and gas phase(CMS) in meeting room (n=10) and roadside(n=9) air (error bar = standard deviation). LogK$_{PG}$= Log (C$_{particle}$ / C$_{gas}$)

4.2 International field sample

4.2.1 Particulate matter (PM) concentration

TSP, PM_{10}, $PM_{2.5}$ and PM_1 concentration were listed in **Table 12** and Figure 27. The highest mass concentration was witnessed at two Chinese city in northen part, Zhengzhou and Beijing (PM_{10} varied from 160 to over 400 µg m^{-3}), followed by Hong Kong, India, Hawaii and Okinawa, Moutain Fuji in Japan. Figure 26 shows average concentration (µg m^{-3}) of total suspended particle of each location, including NS40 and NS20 result.

Table 13 listed WHO (World Health Organization) air quality guidelines and interim targets for particulate matter: 24-hour concentrations (WHO, 2005). According to this guideline, air quality of all three sampling locations in Japan (Kanazawa University, Okinawa, Mt. Fuji) has reached to AQR level. The following are samples collected in Yunnan, China. Based on our result, the air quality of Yunnan varies from AQR to IT-3. For India, the air quality is about IT-3 level according to the sample results. For Hong Kong, the air quality varies from AQR level (July, 2014) to IT-2 (October 2014). The worst air quality was observed in China, 1-5 times comparing to IT-1. These samples were collected during December.2015 and January.2016, which is a heating season that released huge amount of pollutants to air.

Table 12 list of particle concentration (μg m^{-3}) of each sample.

Location	ID	Sampler Type	Sampling time		Total volume	Calculation			
City/Country			Start date	End date	(m^3)	TSP	PM_{10}	$PM_{2.5}$	PM_1
Kanazawa	KN1	NS40	2012/01/11	2012/01/18	406.8	12.0	10.6	9.4	6.0
	KN2	NS40	2012/04/18	2012/04/25	400.8	34.7	31.5	23.5	10.5
	KN3	NS40	2012/05/16	2012/05/23	391.2	35.6	31.2	22.9	13.0
	KN4	NS40	2014/04/16	2014/04/23	402.0	31.4	28.4	20.7	13.1
	KN5	NS40	2014/04/23	2014/04/30	401.2	19.3	17.9	14.2	11.1
Okinawa	OK1	NS40	2014/04/05	2014/04/12	408.0	33.3	26.8	15.4	11.4
	OK2	NS40	2014/04/13	2014/04/20	408.0	31.5	24.6	11.9	8.0
Hawaii	HW1	NS40	2014/02/05	2014/02/06	58.7	69.1	60.1	38.2	25.5
	HW2	NS40	2014/02/07	2014/02/07	19.2	96.4	85.4	61.2	43.3
Hong Kong	HK1	NS40	2014/07/06	2014/07/10	229.0	50.5	43.8	31.8	22.6
	HK2	NS40	2014/07/10	2014/07/13	169.2	36.9	30.1	18.9	12.9
	HK3	NS40	2014/10/27	2014/10/28	55.4	157.4	128.6	90.6	62.0
	HK4	NS40	2014/10/28	2014/10/29	63.5	139.1	112.2	71.8	48.2
	HK5	NS40	2014/10/29	2014/10/31	95.3	89.2	71.3	42.5	41.0
India	ID1	NS40	2014/05/25	2014/05/27	115.2	85.8	68.3	31.8	24.9
	ID2	NS40	2014/05/27	2014/05/29	113.8	78.1	63.0	36.6	24.7
Yunnan, China	YX1	NS20	2015/06/23	2015/6/26	93.7	24.7	24.7	17.7	9.8
	YX2	NS20	2015/07/14	2015/07/17	94.8	47.0	43.2	30.9	16.5
	YX3	NS20	2015/08/04	2015/08/07	95.6	13.4	11.8	6.2	0.0[a]
	YX4	NS20	2015/08/25	2015/08/28	95.4	19.9	18.5	12.9	7.1
	YX5	NS20	2015/09/15	2015/09/18	94.2	20.5	18.6	11.7	0.0[a]
	YX6	NS20	2015/10/06	2015/10/09	90.2	31.9	28.9	21.5	10.7
	YX7	NS20	2015/10/27	2015/10/30	93.2	46.6	43.4	31.8	20.0
	YX8	NS20	2015/11/14	2015/11/17	92.2	35.4	32.7	24.9	15.8
	YX9	NS20	2015/12/24	2015/12/27	91.8	60.2	56.3	44.0	20.5
	YX10	NS20	2016/01/22	2016/01/26	113.0	63.4	60.4	49.5	24.9
Mt.Fuji	FJ1	NS40	2015/07/29	2015/08/07	383.4	13.6	12.1	7.0	4.9
	FJ2	NS40	2015/08/07	2015/08/21	402.2	30.6	28.0	16.4	12.5
Zhengzhou, China	ZZ1	NS20	2015/12/28	2015/12/29	13.0	448.8	425.3	287.6	152.3
	ZZ2	NS20	2015/12/29	2015/12/30	9.8	227.9	220.4	177.4	124.1
	ZZ3	NS20	2015/12/31	2015/12/31	10.6	170.5	161.6	125.3	85.4
	ZZ4	NS20	2016/01/02	2016/01/02	13.0	400.6	375.3	267.9	167.5
	ZZ5	NS20	2016/01/03	2016/01/03	9.0	739.6	728.4	592.4	285.3
Beijing	BJ1[b]	NS20	2015/12/01	2015/12/03	58.9	-	-	-	-
	BJ2[b]	NS20	2015/12/07	2015/12/09	52.1	-	-	-	-
	BJ3[b]	NS20	2015/12/12	2015/12/15	68.5	-	-	-	-
	BJ4	NS20	2015/12/25	2015/12/26	15.5	387.9	380.9	317.5	262.4

a: QFF was broken during filter weighting operation after filed sampling. b: particulate mass concentration data is invalid.

Table 13 WHO air quality guidelines and interim targets for particulate matter: 24-hour concentrations[a]. (WTO, 2005)

	PM10 ($\mu g\ m^{-3}$)	PM2.5 ($\mu g\ m^{-3}$)	Basis for the selected level
Interim target-1 (IT-1)	150	75	Based on published risk coefficients from multi-centre studies and meta-analyses (about 5% increase of shortterm mortality over the AQG value).
Interim target-2 (IT-2)	100	50	Based on published risk coefficients from multi-centre studies and meta-analyses (about 2.5% increase of shortterm mortality over the AQG value).
Interim target-3 (IT-3)*	75	37.5	Based on published risk coefficients from multi-centre studies and meta-analyses (about 1.2% increase in short-term mortality over the AQG value).
Air quality guideline (AQG)	50	25	Based on relationship between 24-hour and annual PM levels.

[a] 99th percentile (3 days/year).

** For management purposes. Based on annual average guideline values; precise number to be determined on basis of local frequency distribution of daily means. The frequency distribution of daily PM2.5 or PM10 values usually approximates to a log-normal distribution.*

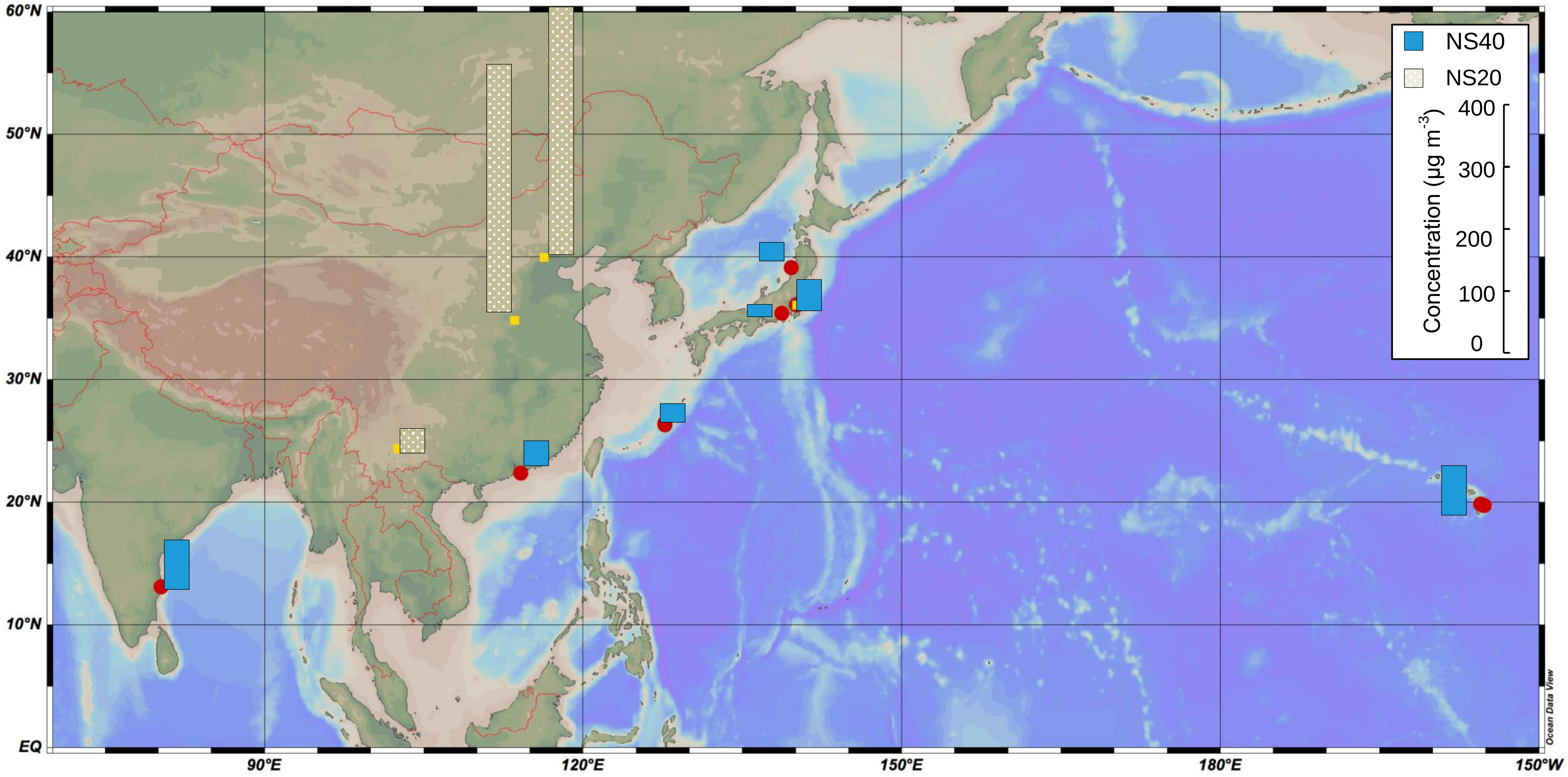


Figure 26 Total particle concentration (µg m^{-3}) of each location, including NS40 and NS20 result.

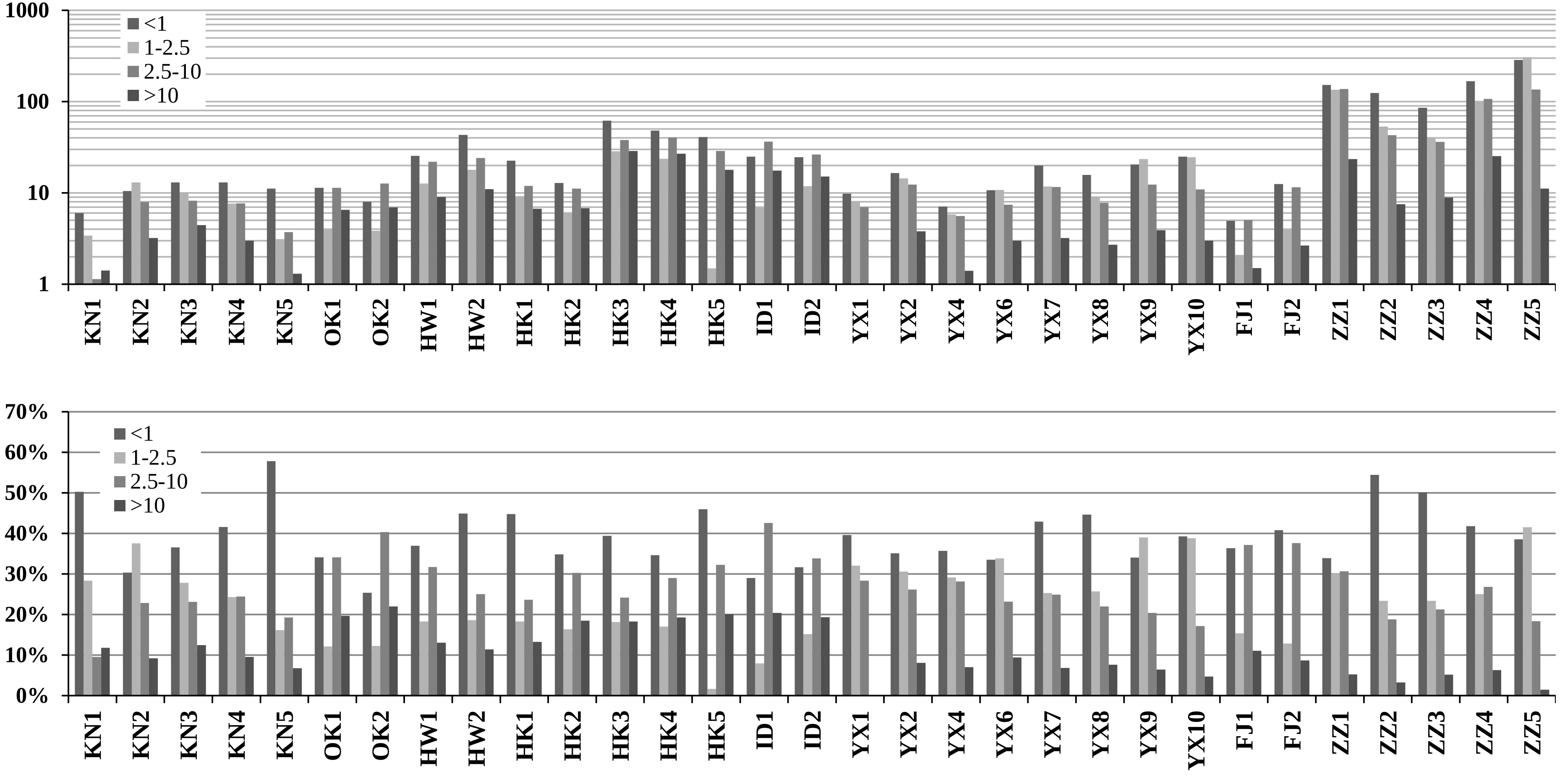


Figure 27 Size segregated particle concentration (μg m^{-3}, upper) and fraction (%, bottom) of each sample.

4.2.2 PFASs concentration in atmosphere (pg m^{-3})

Figure 28 shows average PFOA concentrations (pg m^{-3}) 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^{-1}) in Hong Kong is over 10 times higher than those two places in China.

Figure 30 shows size segregated PFASs concentrations in the atmosphere with PFOS, PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFTrDA, PFTeDA and PFHxDA in selected locations. Each compounds' concentration is shown according to six aerosol size fractions (specifically, >10, 10–2.5, 2.5–1, 1–0.5, 0.5–0.1, and < 0.1 μm, respectively). In general, relatively high PFOA concentrations were detected, followed by PFNA, PFDA and PFHpA. PFASs concentration in Hong Kong is highest among these samples, followed by Indai, Kanazawa and Okinawa.

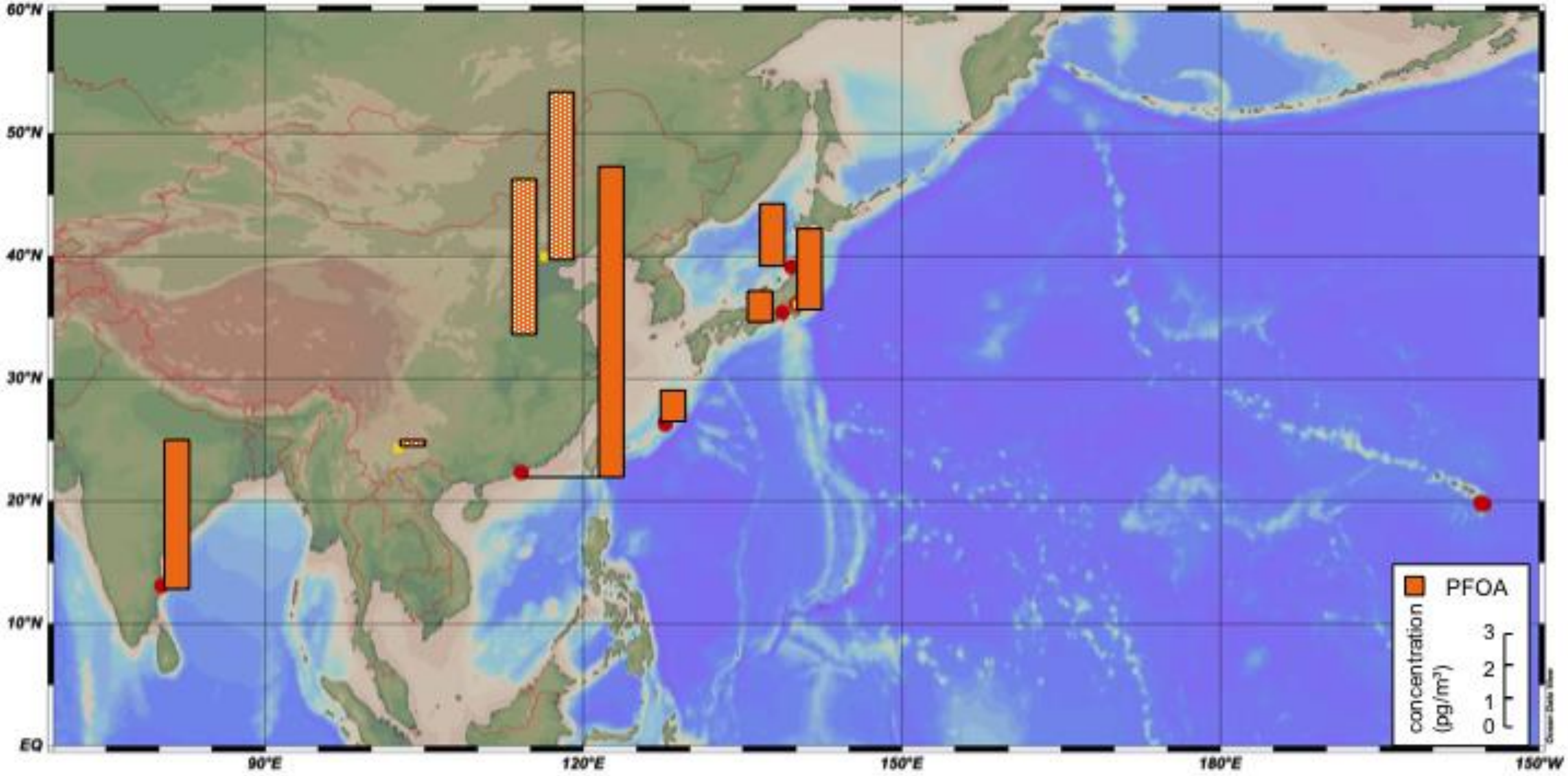
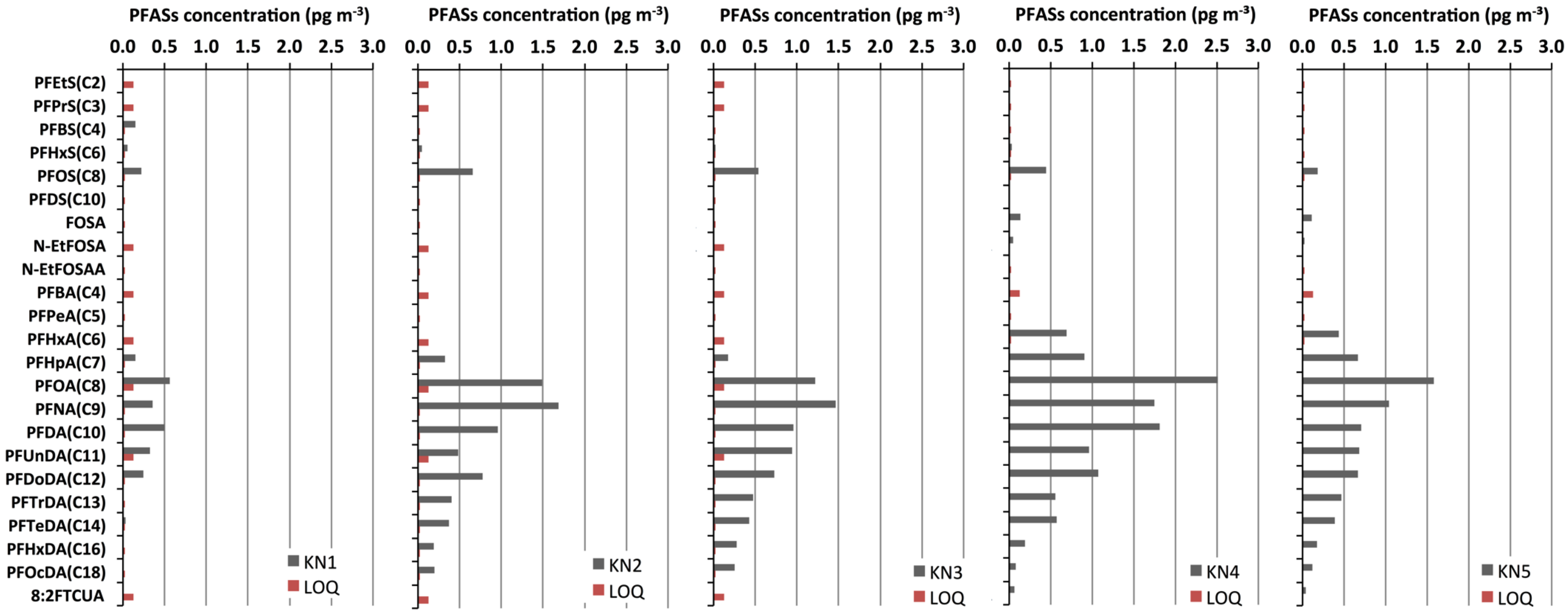


Figure 28 Average PFOA concentrations in total particles of each sampling location, including NS40 and NS20 result.


PFASs concentration (pg m-3)
0.0 0.5 1.0 1.5 2.0 2.5 3.0
PFEtS(C2)
PFPrS(C3)
PFBS(C4)
PFHxS(C6)
PFOS(C8)
PFDS(C10)
FOSA
N-EtFOSA
N-EtFOSAA
PFBA(C4)
PFPeA(C5)
PFHxA(C6)
PFHpA(C7)
PFOA(C8)
PFNA(C9)
PFDA(C10)
PFUnDA(C11)
PFDoDA(C12)
PFTrDA(C13)
PFTeDA(C14)
PFHxDA(C16)
PFOcDA(C18)
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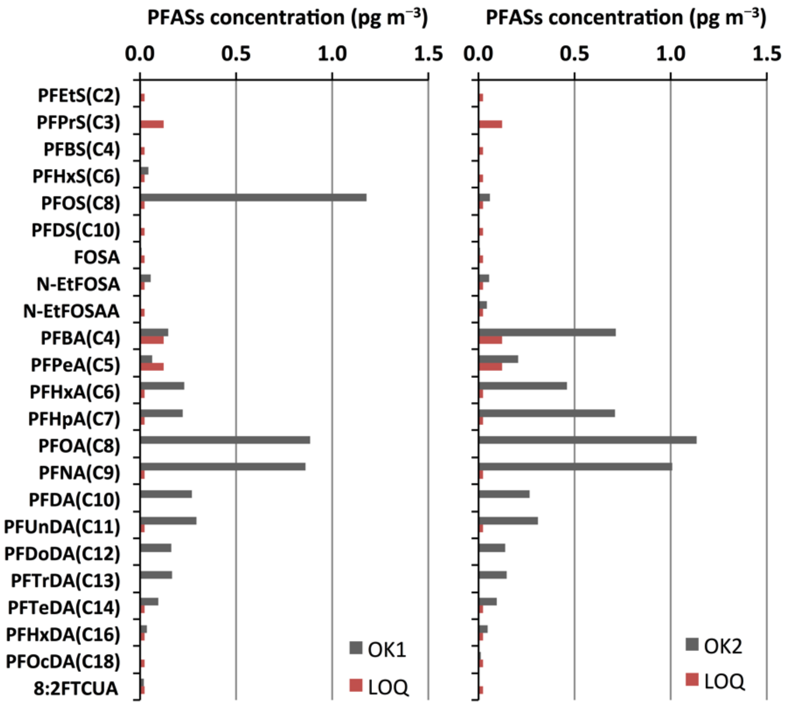
LOQ
KN2
LOQ
KN3
LOQ
KN4
LOQ
KN5
LOQ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N-EtFOSA
N-EtFOSAA
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PFHxA(C6)
PFHpA(C7)
PFOA(C8)
PFNA(C9)
PFDA(C10)
PFUnDA(C11)
PFDoDA(C12)
PFTrDA(C13)
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LOQ
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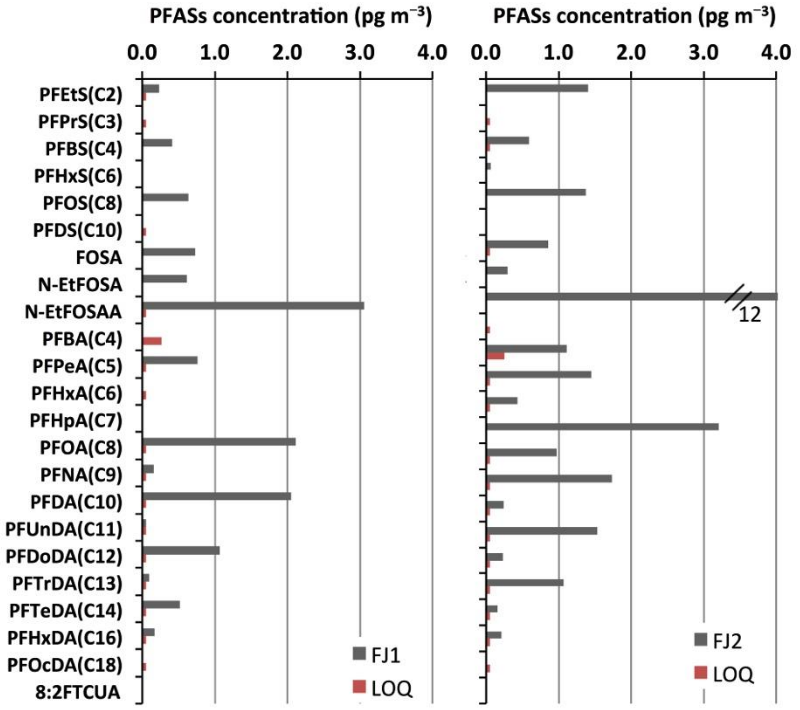
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PFDA(C10)
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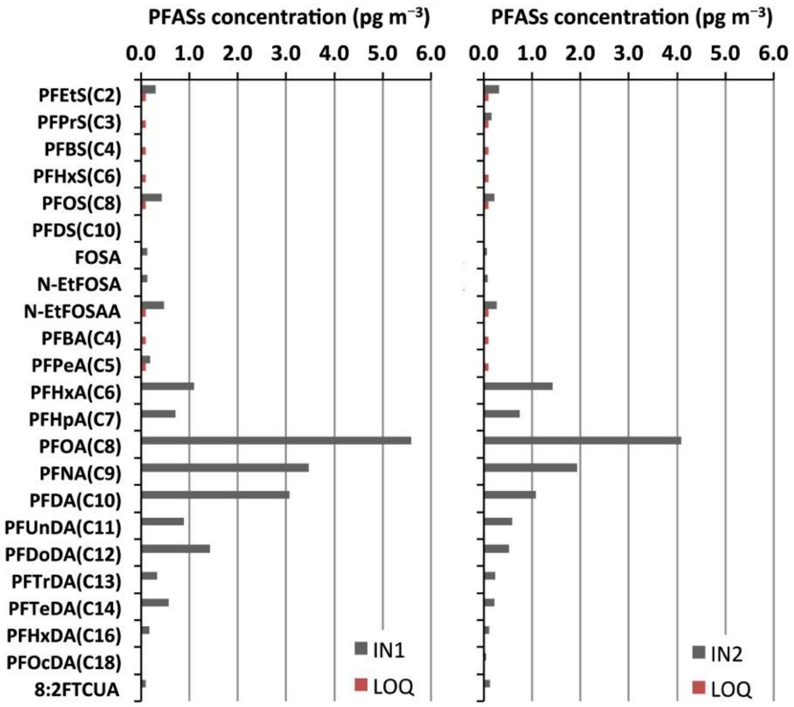
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PFHxS(C6)
PFOS(C8)
PFDS(C10)
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N-EtFOSA
N-EtFOSAA
PFBA(C4)
PFPeA(C5)
PFHxA(C6)
PFHpA(C7)
PFOA(C8)
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PFDA(C10)
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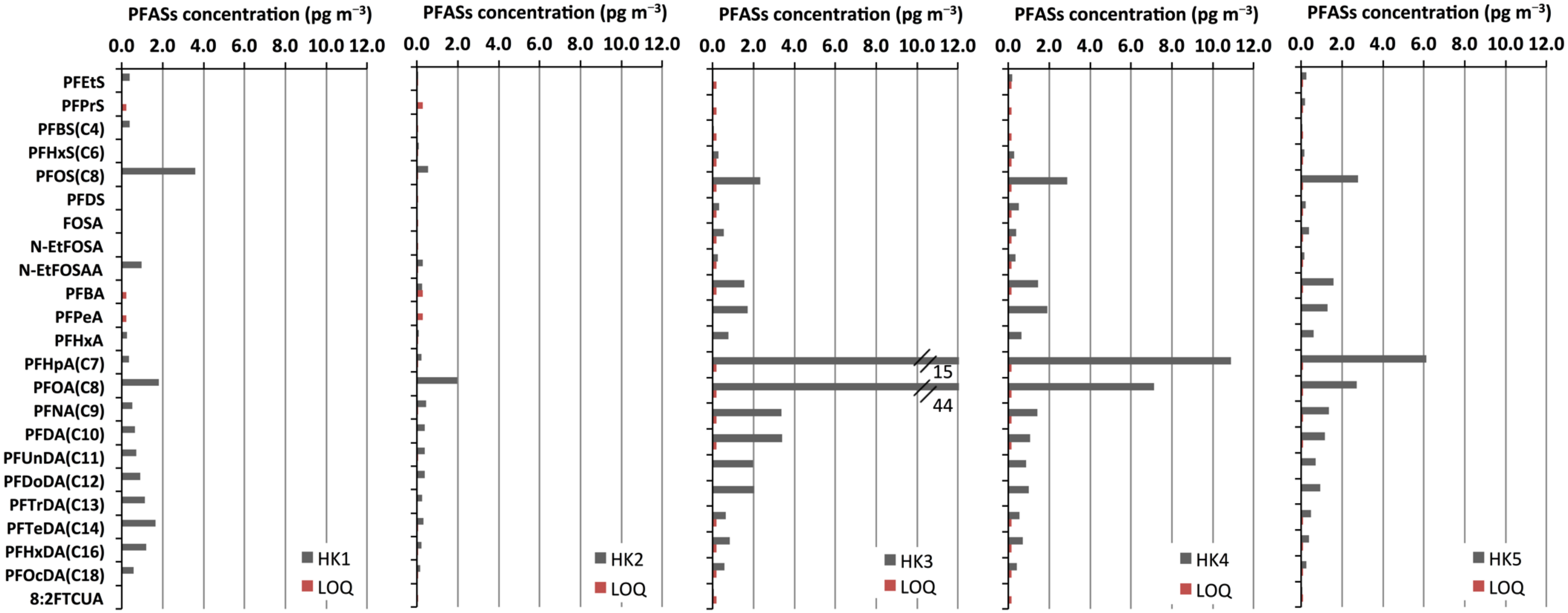
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PFDS
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N-EtFOSAA
PFBA
PFPeA
PFHxA
PFHpA(C7)
PFOA(C8)
PFNA(C9)
PFDA(C10)
PFUnDA(C11)
PFDoDA(C12)
PFTrDA(C13)
PFTeDA(C14)
PFHxDA(C16)
PFOcDA(C18)
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HK2
LOQ
HK3
LOQ
15
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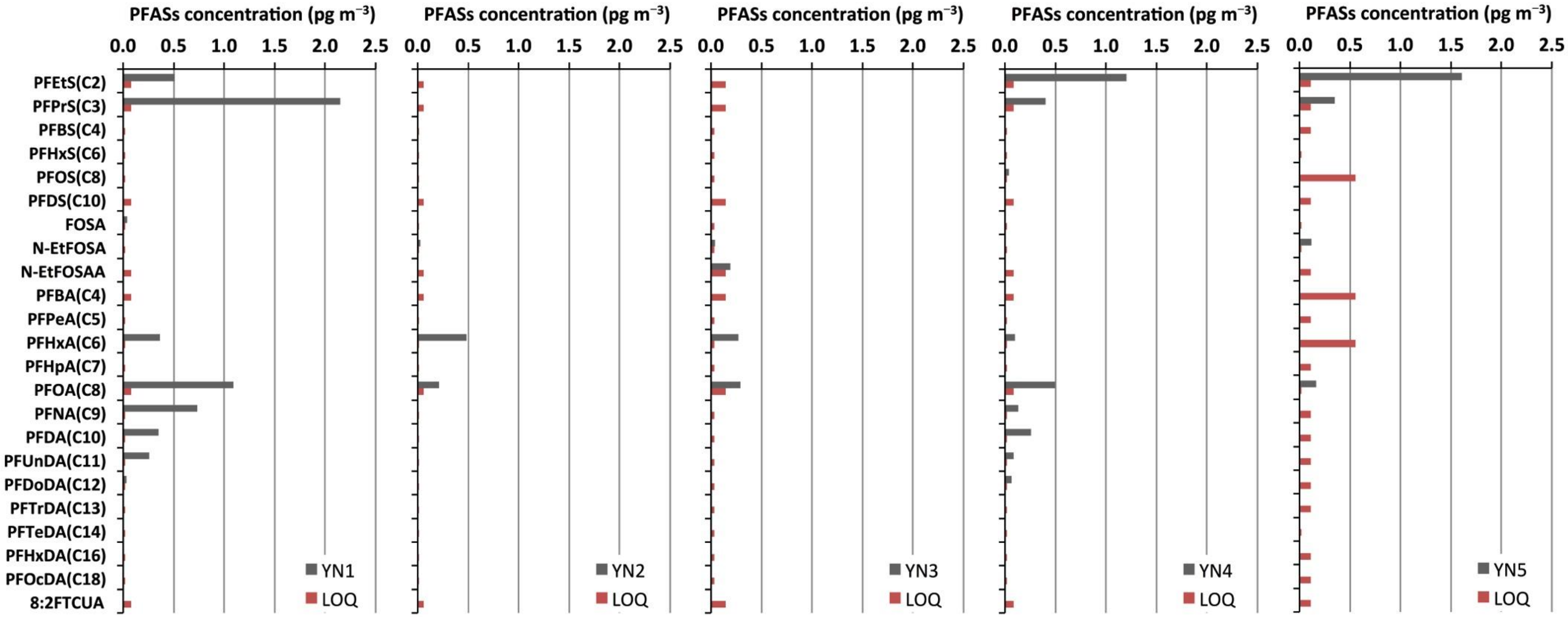
HK4
LOQ
HK5
LOQ



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1.5
2.0
2.5
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PFBS(C4)
PFHxS(C6)
PFOS(C8)
PFDS(C10)
FOSA
N-EtFOSA
N-EtFOSAA
PFBA(C4)
PFPeA(C5)
PFHxA(C6)
PFHpA(C7)
PFOA(C8)
PFNA(C9)
PFDA(C10)
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PFDoDA(C12)
PFTrDA(C13)
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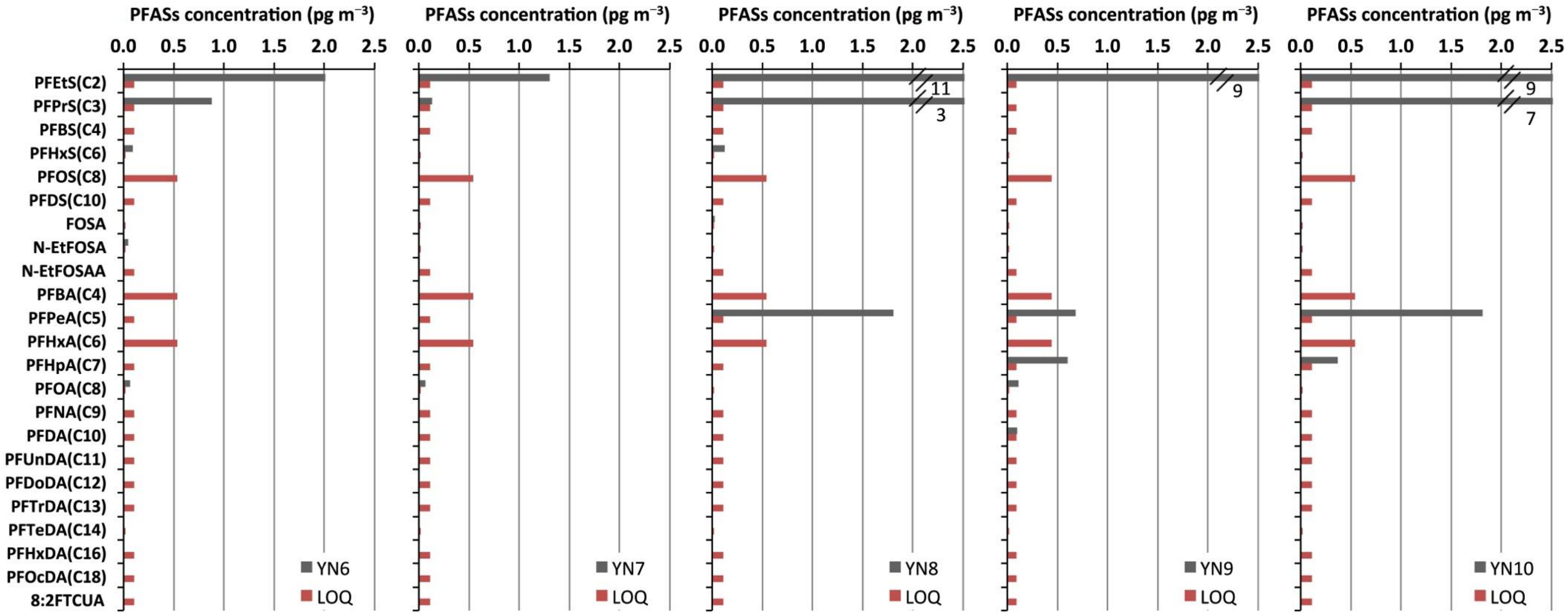
YN2
YN3
YN4
YN5
LOQ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PFBS(C4)
PFHxS(C6)
PFOS(C8)
PFDS(C10)
FOSA
N-EtFOSA
N-EtFOSAA
PFBA(C4)
PFPeA(C5)
PFHxA(C6)
PFHpA(C7)
PFOA(C8)
PFNA(C9)
PFDA(C10)
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LOQ
9
7
YN10
LOQ

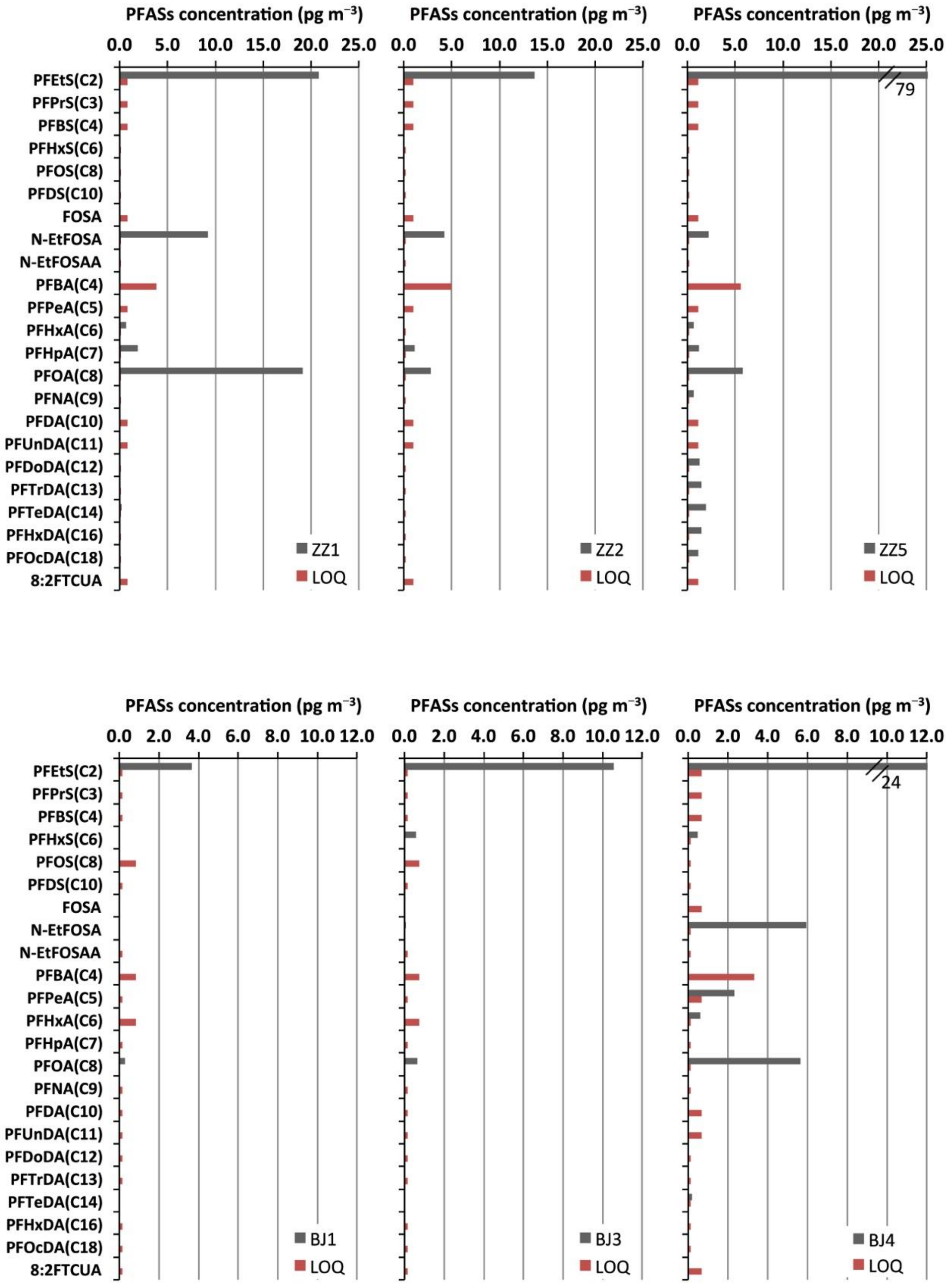

Figure 29 PFASs concentration in total particles (pg m^{-3}) for each sample.

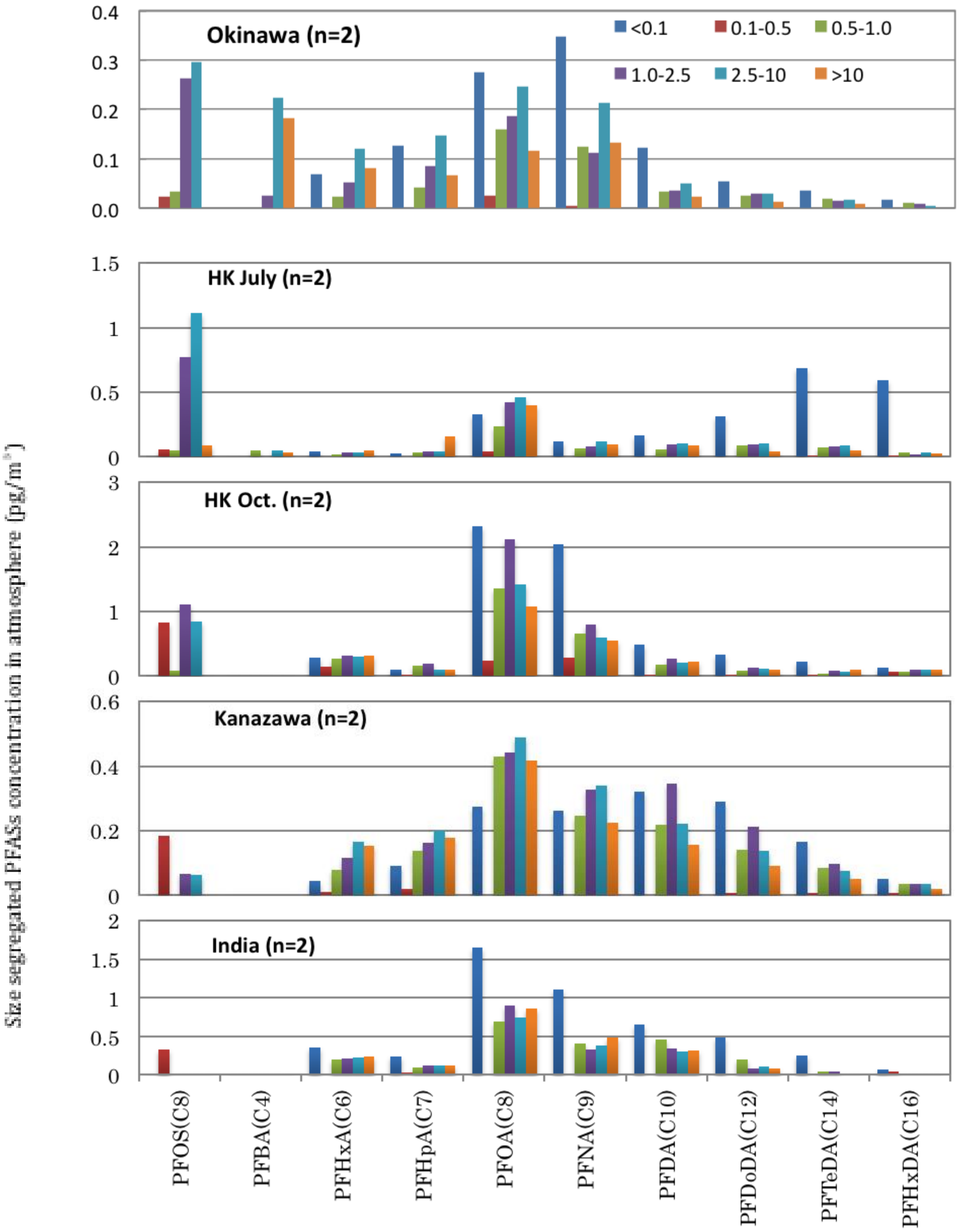

Figure 30 Size segregated PFASs concentration in atmosphere (pg m^{-3})

4.2.3 Time series analysis

By continuously sampling in Yuxi for over eight monthes, the sample can be used for time series analysis. Sampling location and detail sampling information have been described in previous text. Particulate mass concentration results (μg m^{-3}) of samples in Yunnan, China have been shown in **Table 12** and percentage of particulate concentration in each stage of samples has been shown in **Figure 31**. Since PM$_1$ QFF weight were invalid in samples of 2015/8/4 and 2015/9/15, the PM result of these two samples were not involved in discussion of this part. According to **Figure 31**, PM$_1$ have been contributes most among all stages (35-45%), followed by PM$_{1\text{-}2.5}$ (20-35%), PM$_{2.5\text{-}10}$ (20-28%), PM$_{>10}$ (5-12%). PM$_{2.5}$ was varied from 65% to 78%, attributes two of third of total particles. From July 2015 to Feb 2016, along with the decreasing of temperature, the attribution of PM$_{2.5}$ is gradually increasing for 65% to 78%.

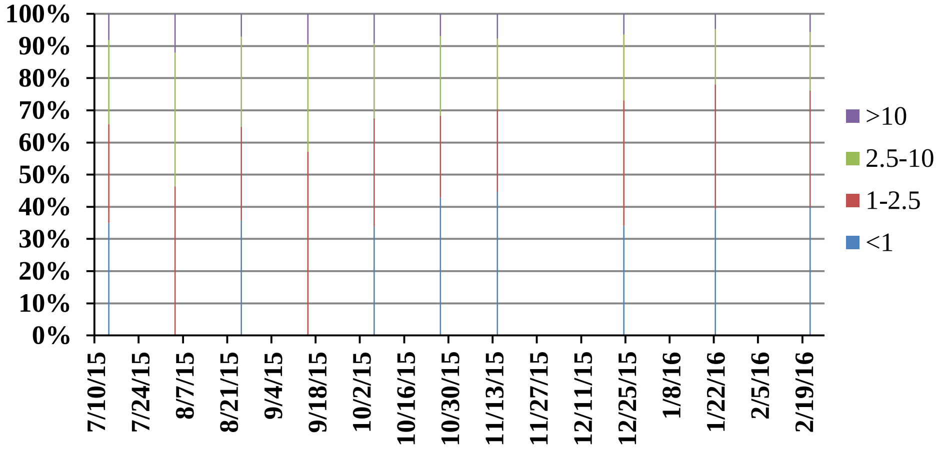

Figure 31 Percentage of particulate concentration in each stage of samples

Figure 32 shows the time series of PFASs concentration (pg m^{-3}; primary y-axis) and total particle concentration (μg m^{-3}; secondary y-axis). Left side is total PFASs concentration while right side is PFOA as a representable PFCA. ΣPFAS concentration is positive correlated with particle concentration. While for PFOA, there is no obvious correlation between PFOA concentration and particle concentration.

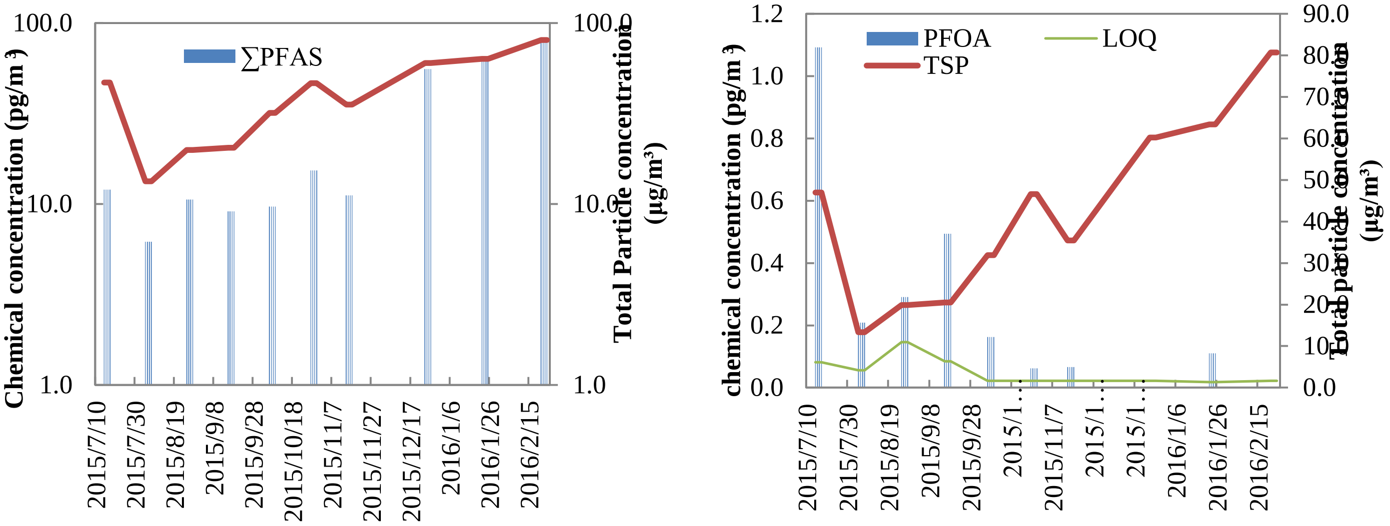

Figure 32 Time series of PFASs concentration (pg m^{-3}, primary y-axis) and total particle concentration (µg m^{-3}, secondary y-axis).

Table 14 Concentrations of selected PFASs (pg m^{-3}) in Yuxi samples.

	Sample ID	**YN1**	**YN2**	**YN3**	**YN4**	**YN5**	**YN6**	**YN7**	**YN8**	**YN9**	**YN10**
PFEtS	*LOQ*	*0.08*	*0.06*	*0.15*	*0.09*	*0.11*	*0.11*	*0.11*	*0.11*	*0.09*	*0.11*
	<1	0.51	n.d.	n.d.	0.48	0.80	1.10	0.88	2.84	2.40	3.25
	1-2.5	n.d.	n.d.	n.d.	0.72	0.62	0.73	0.43	6.92	5.04	4.38
	2.5-10	n.d.	n.d.	n.d.	n.d.	0.19	0.18	n.d.	1.02	0.93	0.83
	>10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.25	0.24	0.17
PFOS	*LOQ*	*0.02*	*0.01*	*0.03*	*0.02*	*0.55*	*0.54*	*0.54*	*0.54*	*0.44*	*0.54*
	<1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	1-2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2.5-10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	>10	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPrA	*LOQ*	*0.41*	*0.28*	*0.73*	*0.43*	*0.55*	*0.54*	*0.54*	*0.54*	*0.44*	*0.54*
	<1	2.88	3.39	6.10	1.74	3.23	5.17	3.47	16.76	24.73	27.25
	1-2.5	1.61	1.63	3.72	1.87	2.33	3.64	2.67	11.62	16.85	21.22
	2.5-10	1.16	n.d.	n.d.	1.79	0.89	1.69	1.66	7.44	6.97	9.89
	>10	0.82	0.46	n.d.	0.95	1.01	1.73	1.88	3.85	2.93	4.70
PFHxA	*LOQ*	*0.02*	*0.01*	*0.03*	*0.02*	*0.55*	*0.54*	*0.54*	*0.54*	*0.44*	*0.54*
	<1	n.d.	0.34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	1-2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2.5-10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	>10	0.36	0.14	0.27	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	*LOQ*	*0.08*	*0.06*	*0.15*	*0.09*	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*
	<1	0.47	0.21	0.29	0.33	0.05	0.02	n.d.	n.d.	0.05	n.d.
	1-2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.
	2.5-10	0.18	n.d.	n.d.	n.d.	0.03	n.d.	0.07	n.d.	n.d.	n.d.
	>10	0.44	n.d.	n.d.	0.16	0.08	0.04	n.d.	n.d.	n.d.	n.d.

n.d.: not detected, data< LOQ.

4.3 Cruise sample

Cruise sample information has been described in 2.1.3. In this part, particulate samples was discussed using NS20 sample and CMS sample

4.3.1 QA/QC control

	KH14-06					MR15-03				
	I-LOQ	Blank	Rec.	LOQ		I-LOQ	Blank	Rec.	LOQ	
				Max	Min				Max	Min
PFEtS	10-50	n.d.	105%	4.06	0.09	10	n.d.	101%	0.15	0.06
PFPrS	10-50	n.d.	115%	0.47	0.20	10	n.d.	101%	0.15	0.06
PFBS	2-10	n.d.	104%	0.20	0.06	2	n.d.	98%	0.03	0.01
PFHxS	2-10	n.d.	107%	0.20	0.06	2	n.d.	103%	0.03	0.01
PFOS	10	n.d.	97%	0.20	0.06	2	n.d.	97%	0.03	0.01
PFDS	10	n.d.	100%	1.01	0.06	10	n.d.	98%	0.15	0.06
FOSA	2-10	n.d.	98%	0.20	0.06	2	n.d.	96%	0.03	0.01
N-EtFOSA	2-10	n.d.	83%	0.20	0.01	2	n.d.	90%	0.03	0.01
N-EtFOSAA	2-10	n.d.	108%	1.01	0.01	10	n.d.	99%	0.15	0.06
PFPrA	10-50	n.d.	192%	1.01	0.28	50	n.d.	69%	0.73	0.28
PFBA	10-50	n.d.	97%	0.40	0.09	10	n.d.	99%	0.15	0.06
PFPeA	10	n.d.	116%	0.20	0.06	2	n.d.	97%	0.03	0.01
PFHxA	2-10	n.d.	89%	0.20	0.02	2	n.d.	101%	0.03	0.01
PFHpA	2	n.d.	91%	0.04	0.01	2	n.d.	97%	0.03	0.01
PFOA	2-10	n.d.	89%	0.20	0.02	10	n.d.	92%	0.15	0.06
PFNA	10	n.d.	111%	0.20	0.06	2	n.d.	98%	0.03	0.01
PFDA	10	n.d.	123%	0.20	0.06	2	n.d.	93%	0.03	0.01
PFUnDA	10	n.d.	108%	0.20	0.06	2	n.d.	96%	0.03	0.01
PFDoDA	10	n.d.	117%	0.20	0.06	2	n.d.	94%	0.03	0.01
PFTrDA	2-10	n.d.	124%	1.01	0.01	2	n.d.	91%	0.03	0.01
PFTeDA	2-10	n.d.	107%	1.01	0.01	2	n.d.	90%	0.03	0.01
PFHxDA	2-10	n.d.	70%	1.01	0.01	2	n.d.	80%	0.03	0.01
PFOcDA	10	n.d.	91%	1.01	0.06	2	21.4	85%	0.03	0.01
8:2FTCUA	2-10	n.d.	119%	0.20	0.02	10	n.d.	92%	0.15	0.06

4.3.2 Particulate phase samples

4.3.2.1 Particulate matter (PM) concentration

Table 15 listed Particle matter concentration (μg m^{-3}) of samples from KH14-06 and MR15-03. The TSP of these fourteen samples varied from 2~30 μg m^{-3}. PM_{10} concentration of samples collected from Arctic ocean is about 9~18 μg m^{-3}(MR15-03, Set 2,3,4), while PM_{10} concentration of samples collected from Antarctic ocean is about 6~15 μg m^{-3}(KH14-06, Set 2,3,4). In KH14-06, $PM_{1-2.5}$ contributed the most to PM concentration while in MR15-03, the PM concentration peaks were highly observed in PM_1 and $PM_{2.5-10}$. In KH14-06 and MR15-03 samples, the highest PM concentration were both observed in last sample, which collect near Japan and the wind direction is from land to ocean, indicating the influence from land.

Table 15 Particle matter concentration (μg m^{-3}) of samples from KH14-06 and MR15-03

	d_p (μm)	**<1**	**1-2.5**	**2.5-10**	**>10**	**TSP**	**PM_{10}**	**$PM_{2.5}$**	**PM_1**
KH14-06	KH1	0.2	1.3	0.4	0.0	2.0	2.0	1.5	0.2
	KH2	1.2	10.7	2.8	0.0	14.7	14.7	11.9	1.2
	KH3	1.4	9.6	3.8	0.2	14.9	14.8	11.0	1.4
	KH4	0.7	4.3	1.2	0.2	6.5	6.3	5.1	0.7
	KH5	0.8	1.5	0.7	1.4	4.3	2.9	2.3	0.8
	KH6	0.4	8.0	2.8	2.9	14.1	11.2	8.4	0.4
	KH7	2.8	11.3	6.8	9.5	30.3	20.8	14.0	2.8
MR15-03	MR1	6.4	3.3	7.5	2.3	19.5	17.2	9.7	6.4
	MR2	3.3	1.9	4.1	1.7	11.1	9.4	5.2	3.3
	MR3	10.0	3.4	5.3	3.5	22.2	18.7	13.4	10.0
	MR4	5.5	3.5	8.0	3.5	20.6	17.1	9.1	5.5
	MR5	6.6	5.6	11.6	3.5	27.3	23.8	12.2	6.6
	MR6	4.0	3.9	11.0	4.1	22.9	18.8	7.9	4.0
	MR7	10.3	5.2	9.6	5.0	30.1	25.2	15.6	10.3

4.3.2.2 PFASs concentration

Due to the low concentration in oceanic atmosphere, only limited PFASs can be detected in these samples. PFOA and PFHxA were two of the most representative and widely detected PFASs. Figure 33 and Figure 34 shows the PFOA/ PFHxA concentration (pg m^{-3}) in air from NS20 sample respectably. (Land sample in Japan is average PFOA/PFHxA concentration in roadside samples from Tsukuba (n=10). In general, PFHxA concentration is higher than PFOA, which may due to the increasing production of PFHxA related products as a substitute of PFOA. For both PFOA and PFHxA, relatively high concentration is observed in Parcific Ocean, gradually decreasing when close to polar region. Meanwhile, PFOA and PFHxA concentration in Arctic Ocean is about two times higher comparing with that in Antarctic Ocean, which is a result of more human activity near Arctic region comparing with Antarctic region.

Besides PFOA and PFHxA, other PFCAs like PFHpA, PFNA and PFDA were also occasionally detected. On the contrast, PFSAs were barely detected in these samples.

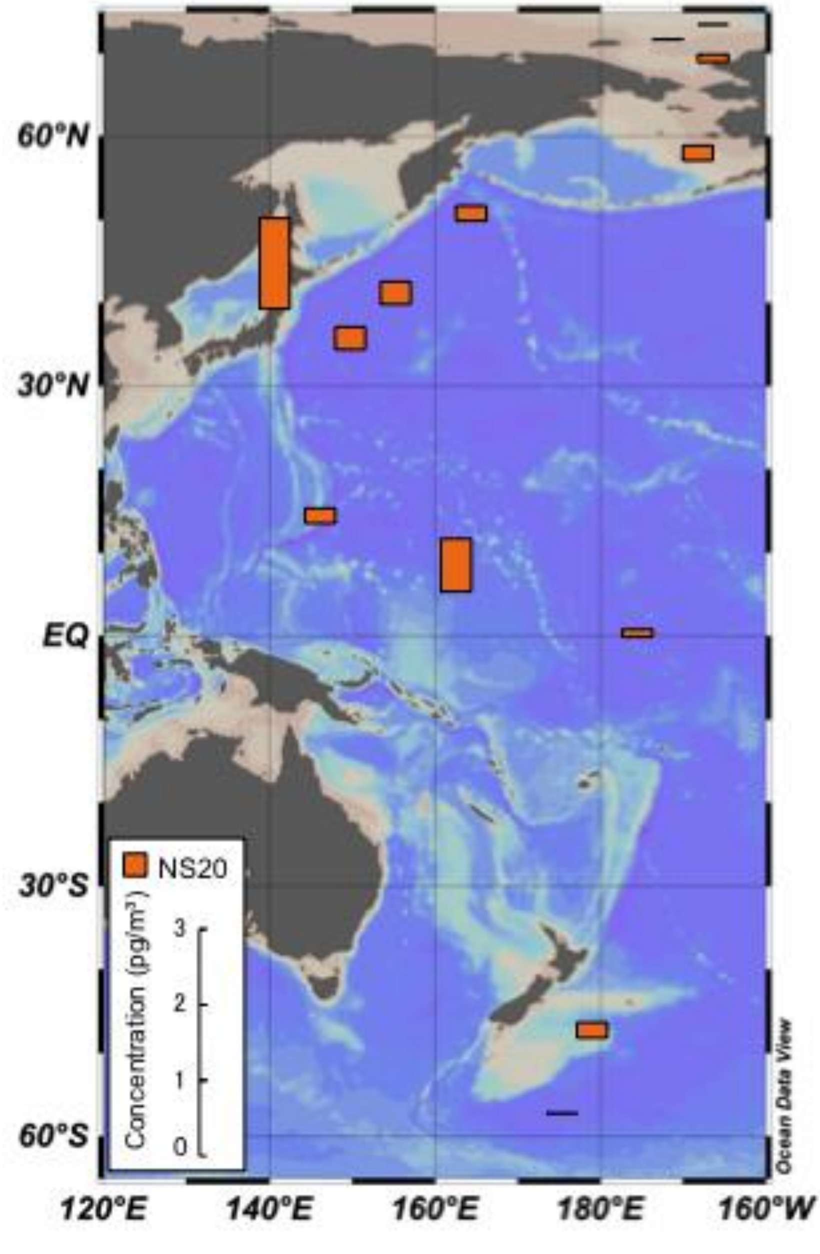

Figure 33 PFOA concentration (pg m^{-3}) in air from NS20 sample. (Land sample in Japan is average PFOA concentration in roadside samples from Tsukuba (n=10).

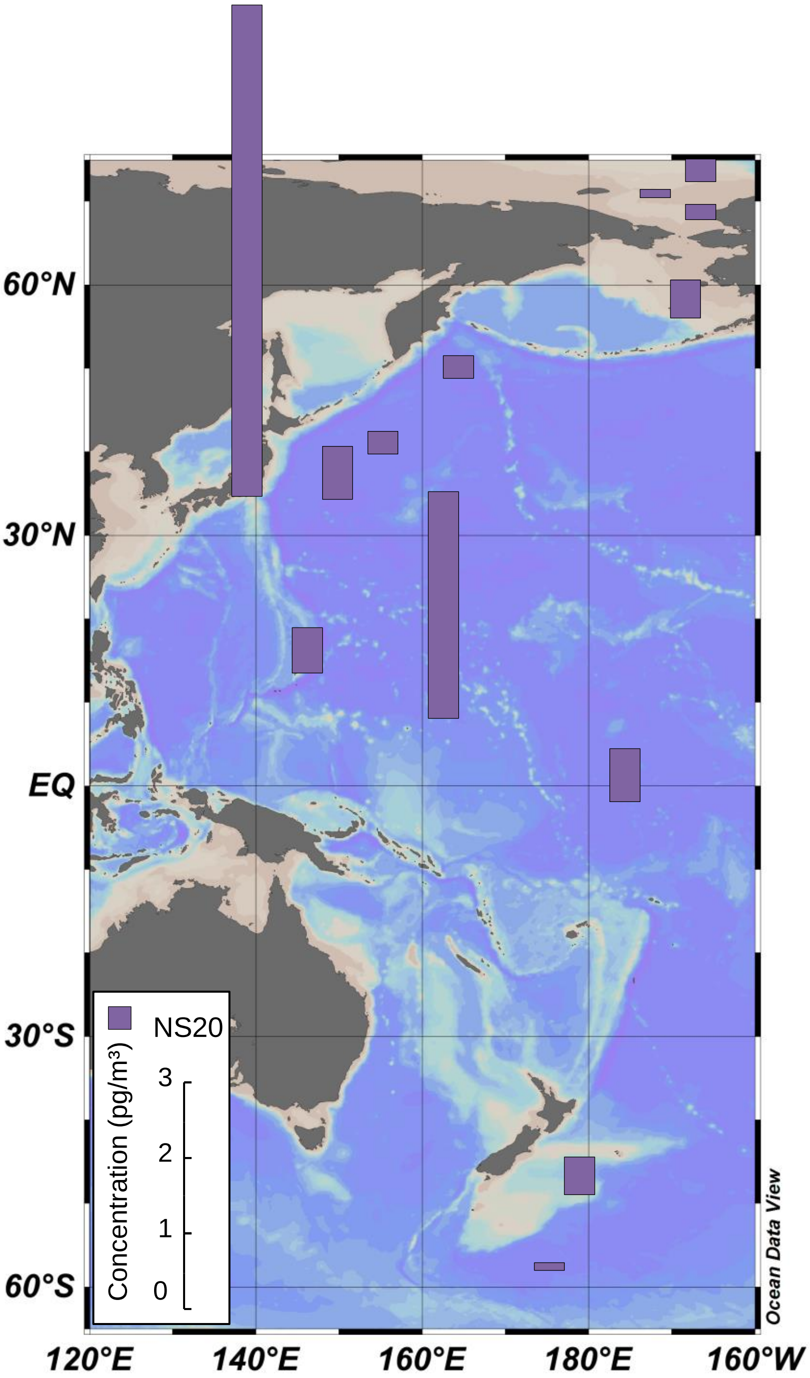

Figure 34 PFHxA concentration (pg m^{-3}) in air from NS20 sample. (Land sample in Japan is average PFOA concentration in roadside samples from Tsukuba (n=10)

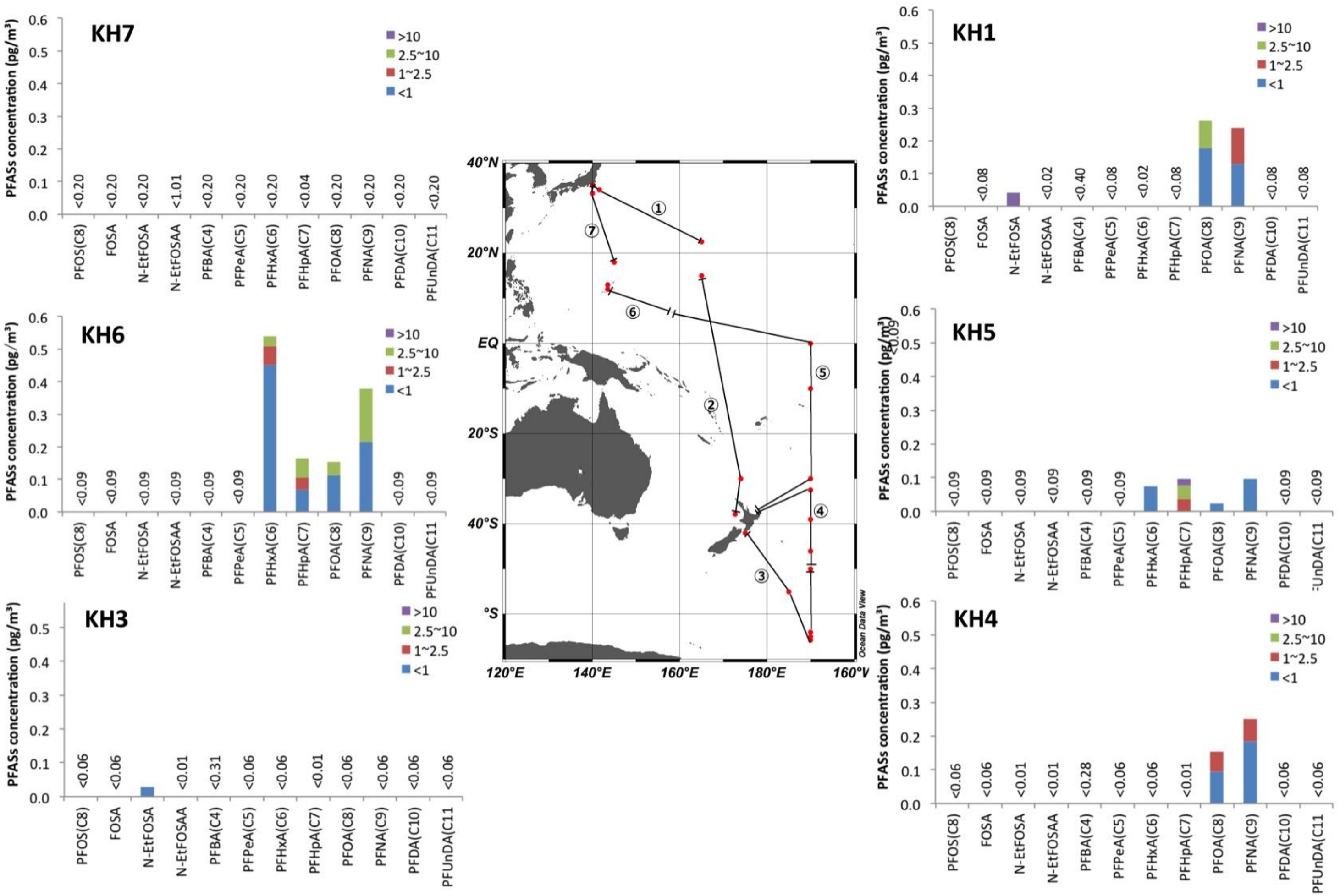

Figure 35 Selected PFASs concentration (pg m^{-3}) in air from NS20 sample collected during cruise KH14-06.

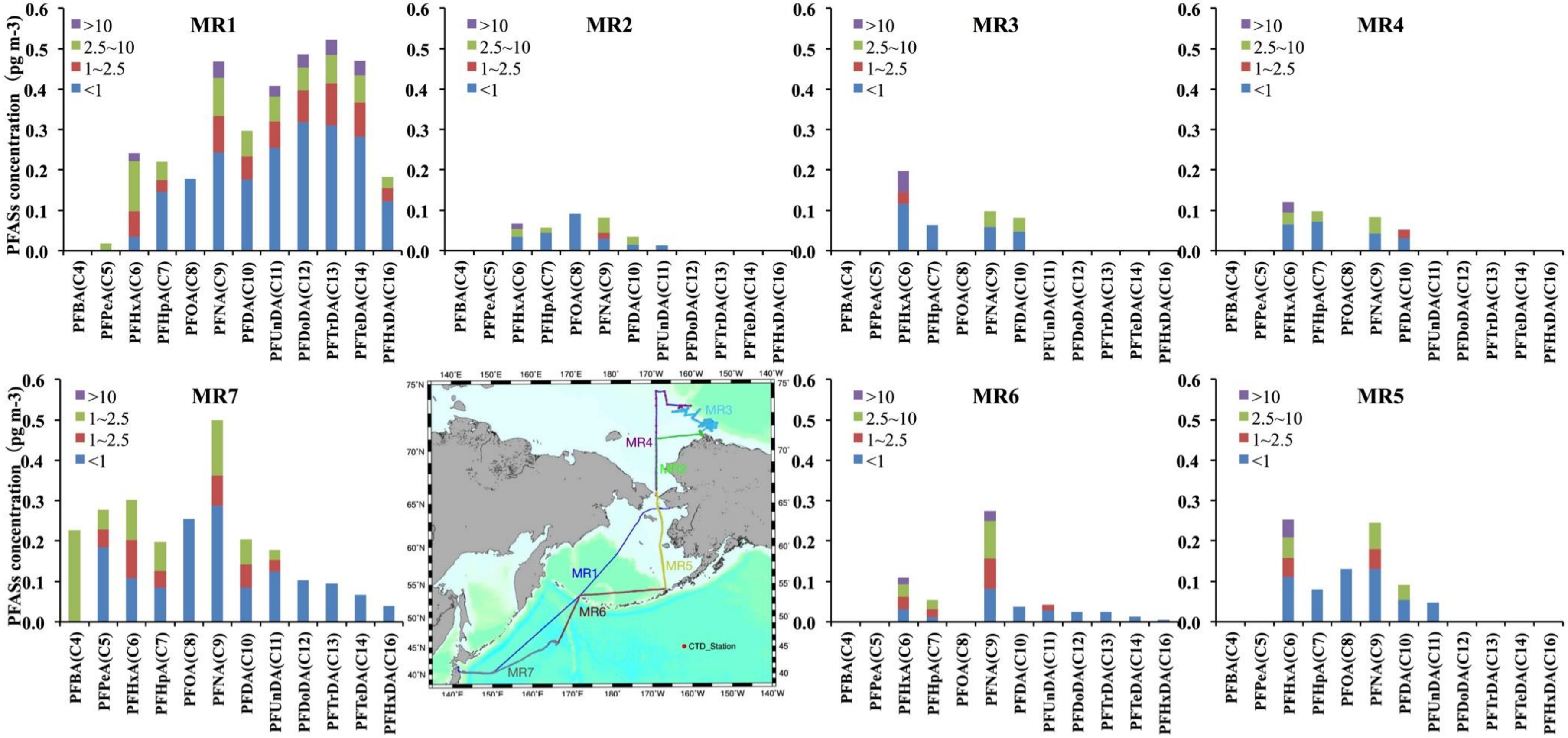

Figure 36 Selected PFASs concentration (pg m^{-3}) in air from NS20 sample collected during cruise MR15-03.

4.3.3 Gas phase samples

Similar to NS20 samples, due to the low concentration in oceanic atmosphere, only limited PFASs can be detected in these CMS samples. PFOA and PFHxA were two of the most representative and widely detected PFASs. Figure 39 and Figure 40 shows the PFOA/ PFHxA concentration (pg m^{-3}) in air from CMS sample respectably. (Land sample in Japan is average PFOA/PFHxA concentration in roadside samples from Tsukuba (n=10). In general, PFHxA concentration is higher than PFOA, which may due to the increasing production of PFHxA related products as a substitute of PFOA. For both PFOA and PFHxA, relatively high concentration is observed in Parcific Ocean, gradually decreasing when close to polar region. Meanwhile, PFOA and PFHxA concentration in Arctic Ocean is about two times higher comparing with that in Antarctic Ocean, which is a result of more human activity near Arctic region comparing with Antarctic region.

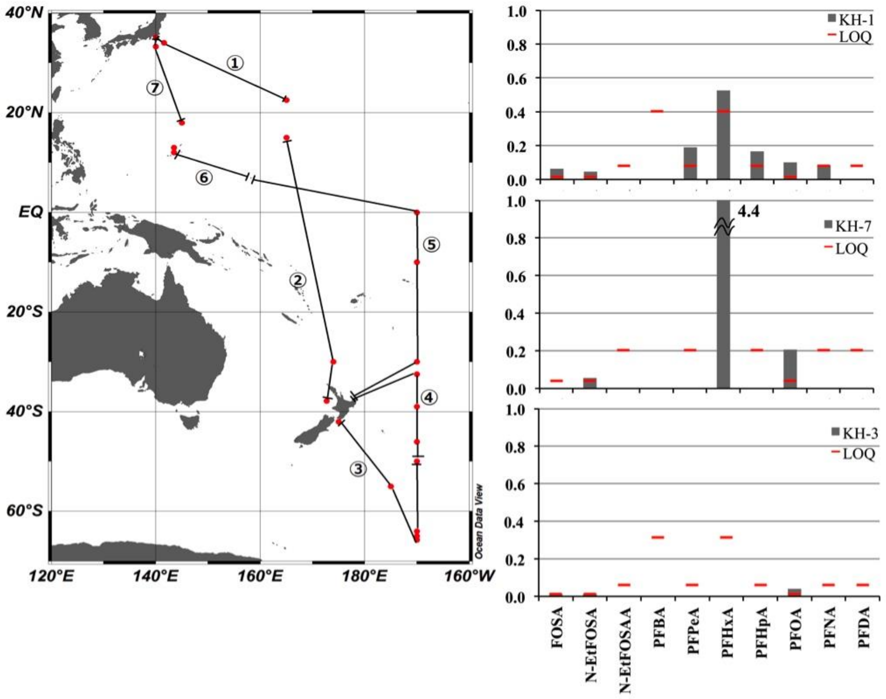

Figure 37 Selected PFASs concentration (pg m^{-3}) in air from CMS sample collected during cruise KH14-06.

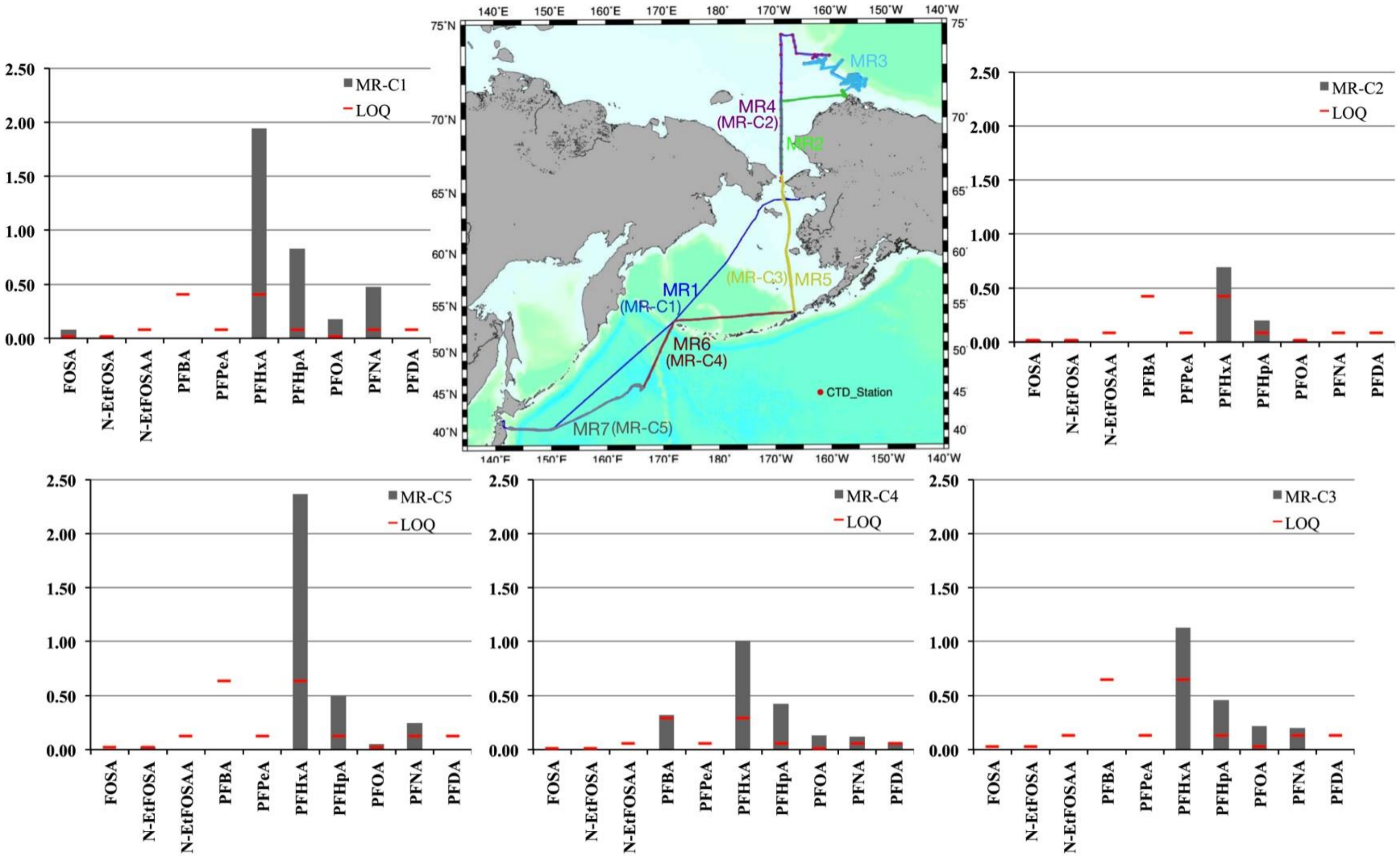

Figure 38 Selected PFASs concentration (pg m^{-3}) in air from CMS sample collected during cruise MR15-03.

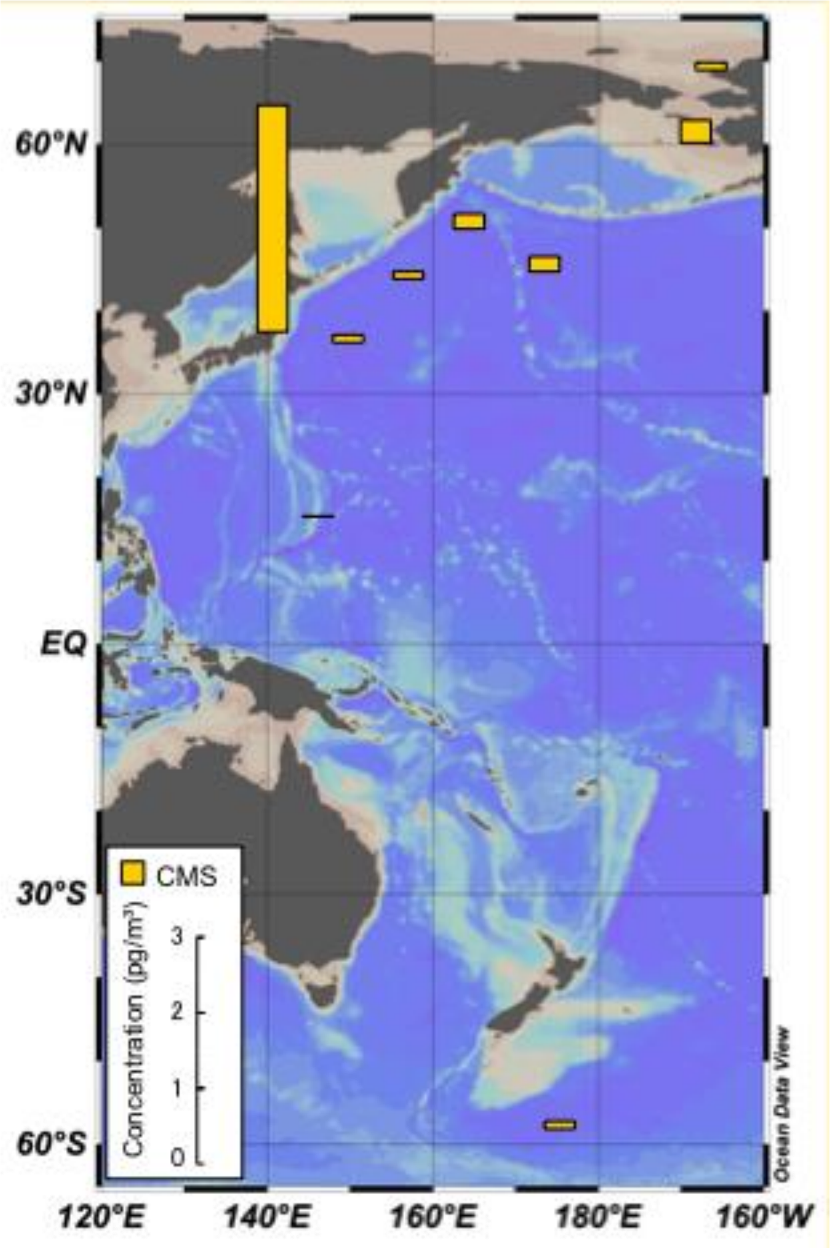

Figure 39 PFOA concentration (pg m^{-3}) in air from CMS sample. (Land sample in Japan is average PFOA concentration in roadside samples from Tsukuba (n=10)

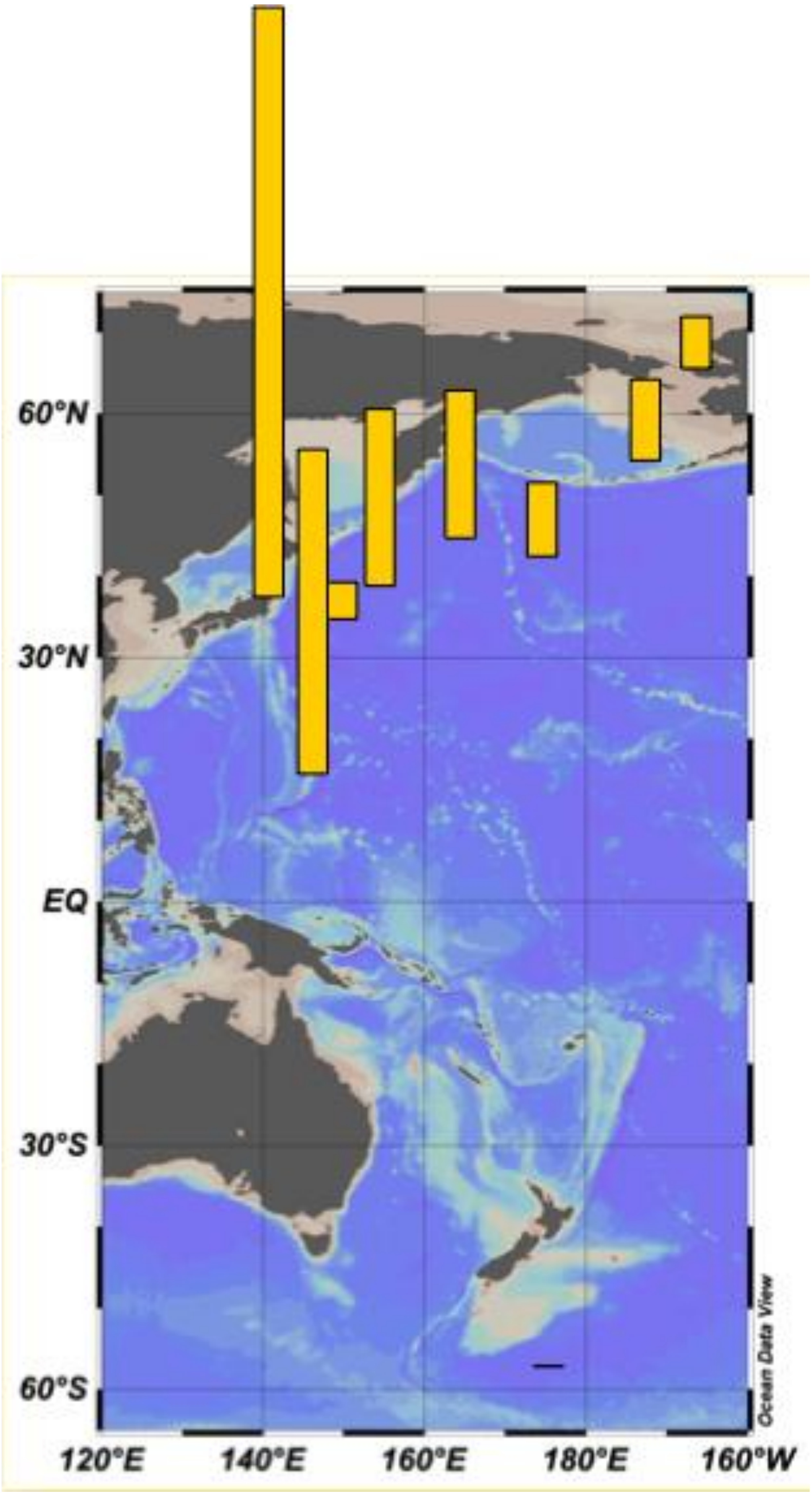

Figure 40 PFHxA concentration (pg m^{-3}) in air from CMS sample. (Land sample in Japan is average PFOA concentration in roadside samples from Tsukuba (n=10)

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Chapter 5 Conclusion

This study 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.

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 investiged and size segrageted PFASs concentration has been reported

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. This is the first research to investigated PFASs by both gas and size distribution analysis to our knowledge.

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