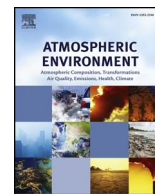




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## Assessing temporal trends and source regions of per- and polyfluoroalkyl substances (PFASs) in air under the Arctic Monitoring and Assessment Programme (AMAP)



Fiona Wong<sup>a</sup>, Mahiba Shoeib<sup>a</sup>, Athanasios Katsoyiannis<sup>b</sup>, Sabine Eckhardt<sup>c</sup>, Andreas Stohl<sup>c</sup>, Pernilla Bohlin-Nizzetto<sup>c</sup>, Henrik Li<sup>d</sup>, Phil Fellin<sup>d</sup>, Yushan Su<sup>a,e</sup>, Hayley Hung<sup>a,\*</sup>

<sup>a</sup> Air Quality Processes Research Section, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

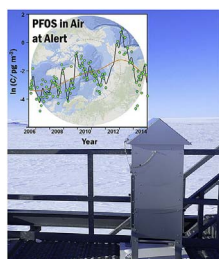
<sup>b</sup> Norwegian Institute for Air Research (NILU), FRAM - High North Research Centre for Climate and the Environment, Hjalmar Johanssens Gt 14, NO-9296 Tromsø, Norway

<sup>c</sup> Norwegian Institute for Air Research (NILU), PO Box 100, 2027 Kjeller, Norway

<sup>d</sup> Airzone One Ltd., 222, Matheson Blvd. E., Mississauga, Ontario L4Z 1X1, Canada

<sup>e</sup> Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment and Climate Change, 125 Resources Road, West Wing, Etobicoke, Ontario M9P 3V6, Canada

### GRAPHICAL ABSTRACT



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### ABSTRACT

Long-term Arctic air monitoring of per- and polyfluoroalkyl substances (PFASs) is essential in assessing their long-range transport and for evaluating the effectiveness of chemical control initiatives. We report for the first time temporal trends of neutral and ionic PFASs in air from three arctic stations: Alert (Canada, 2006–2014); Zeppelin (Svalbard, Norway, 2006–2014) and Andøya (Norway, 2010–2014). The most abundant PFASs were the perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorobutanoic acid (PFBA), and fluorotelomer alcohols (FTOHs). All of these chemicals exhibited increasing trends at Alert with doubling times ( $t_2$ ) of 3.7 years (y) for PFOA, 2.9 y for PFOS, 2.5 y for PFBA, 5.0 y for 8:2 FTOH and 7.0 y for 10:2 FTOH. In contrast, declining or non-changing trends, were observed for PFOA and PFOS at Zeppelin (PFOA, half-life,  $t_{1/2} = 7.2$  y; PFOS  $t_{1/2} = 67$  y), and Andøya (PFOA  $t_{1/2} = 1.9$  y; PFOS  $t_{1/2} = 11$  y). The differences in air concentrations and in time trends between the three sites may reflect the differences in regional regulations and source regions. We investigate the source region for particle associated compounds using the Lagrangian particle dispersion model FLEXPART. Model results showed that PFOA and PFOS are impacted by air masses originating from the ocean or land. For instance, PFOA at Alert and PFOS at Zeppelin were dominated by oceanic air masses whereas, PFOS at Alert and PFOA at Zeppelin were influenced by air masses transported from land.

\* Corresponding author.

E-mail address: [hayley.hung@canada.ca](mailto:hayley.hung@canada.ca) (H. Hung).

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been applied in a wide variety of consumer and industrial products such as oil and liquid repellents (Begley et al., 2005), firefighting foams (Ahrens et al., 2015), pesticides (Schnellmann, 1990), and food packaging materials (Gebbinck et al., 2013). PFASs are ubiquitous in environmental media, such as air (Shoeib et al., 2006; Dreyer et al., 2009; Genualdi et al., 2010; Xie et al., 2013, 2015; Gawor et al., 2014; Bossi et al., 2016), snow (Kirchgeorg et al., 2013), and water (Ahrens and Bundschuh, 2014). They are also found in humans (Kato et al., 2011; Gebbinck et al., 2015) and wildlife (Giesy and Kannan, 2001; Riget et al., 2010; Braune and Letcher, 2013). Among the entire chemical family of PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have received the most attention to date due to their environmental persistence, bioaccumulation and potential adverse effects on humans and wildlife.

PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF), have been listed under Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2017a) as well as in the amendment of the Aarhus protocol on POPs under the Convention on Long-range Transboundary Air Pollution (CLRTAP) (UNECE, 2015). In 2002, 3M, the main global manufacturer of PFOS at that time, voluntarily phased out the production of the chemical. PFOA, its salts and C<sub>9</sub> to C<sub>14</sub>-based perfluoroalkyl carboxylic acids (PFCAs), are listed in the Candidate List of Substances of Very High Concern in Europe under Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (ECHA, 2012, 2015, 2017). PFOA is being proposed for listing under the Stockholm Convention (UNEP, 2017b). In Canada and US, PFOA is restricted to specific use (Government of Canada, 2016a, b; USEPA, 2016).

PFASs are known to undergo long-range transport to remote environments, such as the Arctic, via oceanic or atmospheric transport, though the mechanism is not clear. Neutral PFASs, such as fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamidoethanols (FOSEs) and perfluorooctane sulfonamides (FOSAs), are more volatile than perfluoroalkyl acids (PFAAs) and are susceptible to long-range atmospheric transport (LRAT) to the Arctic (Shoeib et al., 2006; Young et al., 2007; Schenker et al., 2008; Ahrens et al., 2011a). Neutral PFASs can be degraded in the atmosphere to form PFAAs and subsequently deposit via wet or dry atmospheric deposition (Ellis et al., 2004; Hurley et al., 2004; Martin et al., 2006; Schenker et al., 2008). PFAAs, also referred to as the ionic PFASs, are more water soluble and less volatile than neutral PFASs. Early modelling studies indicated that PFAAs are more likely to be transported via oceanic currents than the atmosphere (Armitage et al., 2006; Wania, 2007) but recent study by Yeung et al. (2017) suggested that atmospheric input accounts for the majority of measured PFOA in the Arctic Ocean.

The atmosphere is the medium with the fastest response to changes in emissions, hence the temporal variation of contaminants in remote Arctic air may indicate the effectiveness of chemical control regulations and changes in usage pattern. Here, we provide the first overview of measured concentrations and time trends of PFASs in Arctic air. We analyzed long-term atmospheric monitoring data of PFASs at three Arctic stations, namely Alert (Canada) from 2006 to 2014, Zeppelin (Svalbard, Norway) from 2006 to 2014, and Andøya (Norway) from 2010 to 2014. The occurrences, relative abundances, and distribution of the different groups of PFASs (neutral PFASs and PFAAs), their seasonal and long-term variations, source regions, and temperature dependence are discussed. This work is a joint effort by Canada's Northern Contaminants Programme (NCP) and the national Norwegian Pollutant Monitoring Program (SFT) in collaboration under the Arctic Council's Arctic Monitoring and Assessment Programme (AMAP). Data presented here are produced by two national long-term air monitoring programs for organic pollutants initiated in the 1990s. Each program follows its own established protocol for sample collection, chemical analysis, data management, quality assurance and control (QA/QC).

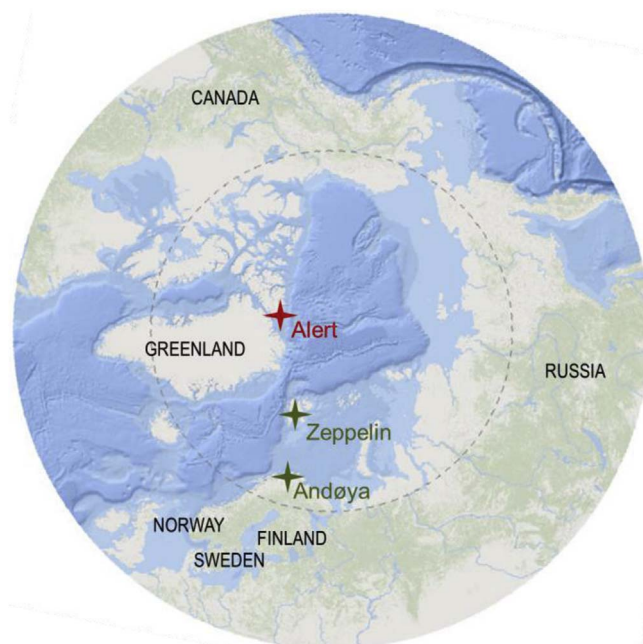


Fig. 1. Map of sampling sites.

## 2. Material and methods

### 2.1. Sampling sites and method

Air sampling was carried out at the Canadian High Arctic station of Alert, Nunavut, Canada (82° 30' N 62° 20' W) and the Norwegian-operated stations of Zeppelin, Svalbard, Norway (78° 54' N 11° 53' E) and Andøya, Norway (62° 16' N 16° 0' E). Fig. 1 shows the locations of the three sampling sites. Samples from the Canadian site, Alert, were analyzed by Environment and Climate Change Canada (ECCC) and those from the Norwegian sites were analyzed by the Norwegian Institute for Air Research (NILU). Data for the Norwegian sites are extracted from the European Monitoring and Evaluation Programme (EMEP) Website (<http://ebas.nilu.no/>).

At Alert, air samples ( $n = 169$ ) were collected from August 2006 to February 2015 using a Tisch PS-1 high-volume active air sampler (HV-AAS) (Tisch Environmental, Cleves, OH) made of stainless steel (volatile methyl siloxane (VMS)-free sealing in the HV-AAS sampling head). Each sample represents  $\sim 2000 \text{ m}^3$  of air sampled over 7 days. Sampling occurred once per month from October to February and once every other week between March and September. Each sample comprised of a glass fiber filter (GFF, TE-G653, TISCH Environmental Inc.), and a cartridge containing two polyurethane foams (PUF,  $2 \times 2.5$  inch diameter and  $1 \times 2.5$  inch diameter, Tisch Environmental Inc.), and 15 g of XAD-2 (Supelpak™-2, 20–60 mesh, pre-cleaned, Sigma Aldrich). Hence, both gas- and particle phase PFASs were collected.

At Zeppelin, air samples ( $n = 383$ ) were collected from September 2006 to December 2014, while at Andøya, air samples ( $n = 249$ ) were collected from November 2009 to December 2014. The Norwegian air samples were taken with a Digital (DH77) HV-AAS using only a GFF. This results in sampling of solely the particle-phase PFASs. Sampling at the Norwegian sites occurred on a weekly basis, with one sample over 48 h collecting an air volume of  $\sim 1200 \text{ m}^3$ . Exceptions to these sampling procedures were that at Zeppelin in 2007, air samples were collected every second week, and at Andøya the sampling duration was 24 h instead of 48 h from November 2009 to September 2010. Details of the sampling protocol for the Norwegian sites are described elsewhere (Nizzetto and Aas, 2016).

The targeted PFASs for air samples from Alert included i) neutral PFASs: 6:2, 8:2, 10:2 FTOHs, 6:2, 8:2, 10:2 fluorotelomer acrylates

(FTAs), methyl and ethyl perfluorooctane sulfonamides (Me- and EtFOSA), and methyl and ethyl perfluorooctane sulfonamidoethanols (Me- and EtFOSE) and ii) PFAAs, which included C<sub>4-14</sub>, C<sub>16</sub>, C<sub>18</sub> PFCAs and C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> perfluoroalkyl sulfonic acids (PFSAs). The targeted PFASs for air samples from the Norwegian sites included perfluorooctane sulfonamide (PFOSA), 6:2 fluorotelomer sulfonate (FTS), PFAAs, which included C<sub>6-11</sub> PFCAs, and C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> PFSAs. The full list of targeted chemicals is reported in Tables S1 and S2.

## 2.2. Sample preparation and analysis

Details of sample preparation and analytical procedures are presented in S1 and briefly described here. The Alert samples were extracted using a pressurized liquid extraction system (Accelerated Solvent Extraction System from Dionex Corporation, Sunnyvale, CA, USA). An internal standard (IS) mixture containing mass-labelled PFAS surrogates was added to the samples prior to extraction. Injection standards (InjS) were added to the extract prior to instrumental analysis.

The separation and detection of the neutral PFASs was performed using gas chromatography–mass spectrometry (Agilent 5975C; Agilent Technologies, Palo Alto, CA, USA) (GC/MS) in selective ion monitoring (SIM) mode using positive chemical ionization mode (PCI). The target and qualifier ion, and the allocation of internal and injection standards for the neutral PFASs are provided in Table S1. The separation and detection of PFAAs was performed using an Acquity I-class Ultra-Performance Liquid Chromatography (UPLC) system coupled with Xevo TQ-S triple quadrupole mass spectrometer (MS/MS) (Waters Corporation). Allocation of internal and injection standards for PFAAs is given in Table S2. For the Alert air samples that were collected prior to October 2012, no mass-labelled PFAAs internal standards were added prior to extraction, and quantification was achieved by using the injection standards only. Isotope dilution method was used for quantification of neutral PFASs and PFAAs.

The air samples from the Norwegian sites were extracted using ultra-sonication for 3 × 10 min in methanol. An internal standard mixture containing mass-labelled PFAS surrogates was added to the samples prior to extraction. The separation, identification and quantification of all the target analytes was performed using Acquity UPLC coupled to a LCT Premier XE orthogonal-acceleration time-of-flight (TOF) mass spectrometer (MS) equipped with a Z-spray electrospray ion source operated in a negative-ionization mode (Waters Corporation).

## 2.3. Quality assurance and quality control (QA/QC)

Data presented here are produced by ECCC and NILU. Both agencies have taken strict QA/QC measures to ensure data consistency and comparability. Such measures include regular participation in AMAP/NCP inter-laboratory studies, upkeep of thorough documentation about the sampling, analytical procedures and data management. Details about the interlaboratory studies are presented in S2. The QA/QC procedures are briefly described here.

At all three sites, field blanks were prepared, transported and analyzed the same way as the samples, except that the blanks were collected by placing the sample cartridge on the HV-AAS, exposed for 1 min without turning the pump on. Laboratory blanks were obtained by taking equivalent amount of solvent through extraction, cleanup and analysis.

For Alert, one field blank was taken every third sampling period and one laboratory blank was taken for every batch of sample extraction. During this reporting period, 57 field blanks and 29 laboratory blanks were taken. For the Norwegian sites, one field blank was obtained every third to fourth month, representing one field blank in every 15 samples. In total, 40 field blanks and 70 laboratory blanks were taken for both Zeppelin and Andøya. Both the Alert and Norwegian data were not blank corrected. Range concentrations of PFASs in the blanks are given

in Tables S3 and S4.

For Alert, recovery of the internal standards that were spiked prior to extraction ranged from 65 to 109% for the six neutral mass-labelled PFASs (i.e. <sup>13</sup>C<sub>2</sub>-8:2 FTOH, <sup>13</sup>C<sub>2</sub>-10:2 FTOH, d<sub>3</sub>-MeFOSA, d<sub>5</sub>-EtFOSA, d<sub>7</sub>-MeFOSE and d<sub>9</sub>-EtFOSE), except that <sup>13</sup>C<sub>2</sub>-6:2 FTOH has the lowest recovery with 29 ± 13%. Recoveries for the nine mass-labelled PFAAs (i.e. <sup>13</sup>C<sub>4</sub>, <sup>13</sup>C<sub>6</sub>, <sup>13</sup>C<sub>8-12</sub>-PFCAs, and <sup>13</sup>C<sub>6</sub>, <sup>13</sup>C<sub>8</sub>-PFSAs) ranged from 71 to 99%. As the recoveries of the nine mass-labelled PFAAs were satisfactory, data obtained prior to October 2012, should be comparable to those obtained after October 2012. Hence, the effect of recovery correction to the overall trend of PFAAs observed at Alert is expected to be negligible. The recoveries of the internal standards for PFAAs (i.e. i.e. <sup>13</sup>C<sub>6-11</sub>-PFCAs, <sup>13</sup>C<sub>6</sub>, <sup>13</sup>C<sub>8</sub>-PFSAs, <sup>13</sup>C<sub>8</sub>-PFOSA, <sup>13</sup>C<sub>2</sub>-6:2 FTS) in samples from Zeppelin and Andøya were 20–70%. For both the Alert and Norwegian data, recoveries that were below 15% were considered below the quality criteria and the data were not included.

According to the data analysis protocol of the responsible laboratory, the Alert data were screened by the instrumental detection limit (IDL), while the Norwegian data were screened by the method detection limit (MDL). Data below the respective detection limit were considered non-detects and they were replaced with 2/3 of the detection limit when performing statistical analysis. Definitions of the IDL and MDL established by the ECCC and NILU data analysis protocol are given in S3.

## 2.4. Trend development, half-lives, doubling time, source identification and statistical method

To develop temporal trends and seasonal cycles, a statistical fitting method called Digital Filtration technique is used and described in S4 (Hung et al., 2005). First order half-life ( $t_{1/2}$ ) or doubling time ( $t_2$ ) which refers to the time required for the air concentration of a chemical to decline to half or increase to double its original value was estimated by  $\ln 2/k$ .  $k$  was defined as the linear regression slope of the Digital Filtration-derived concentration ( $\ln C$ ) vs. time (year). If  $k$  is positive, it indicates the chemical is increasing and the doubling time is reported, whereas if  $k$  is negative, the chemical is declining and half-life is estimated. Statistical analysis was performed using OriginPro 2015. Only data that are above the screening criteria (i.e. IDL for the Alert samples, MDL for the Norwegian samples) were subject to trend analysis.  $F$ -test was used to assess the significance of the coefficient of determination ( $r^2$ ) between the trend derived by the Digital Filtration model and the measured data (S5).

To identify the source regions of PFOA and PFOS, we employed the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005) and a statistical analysis of the model output. FLEXPART was run 20 days backward in time for every measurement (i.e., from the sampling location and during the time period of the measurement) using meteorological input data from the European Centre for Medium Range Weather Forecasts (ECMWF). The model output consists of an emission sensitivity function  $S$  (in units of  $\text{s m}^{-3}$ ), which is proportional to the particle residence time. We use this emission sensitivity, the so-called footprint (i.e., the emission sensitivity near the surface where emissions are expected to occur) for a statistical analysis described in Hirdman et al. (2010), and a brief description is provided in S6. Basically, the analysis considers where air is coming from for the highest 20% of the measured data, compared to the average transport for all the data.

## 3. Results

### 3.1. Air concentrations of PFASs

The descriptive statistics of all targeted chemicals are presented in Table S5. The reported air concentrations from Alert represent the sum of chemicals on the filter and the PUF/XAD/PUF sandwich, while chemicals on the filters are reported for the Norwegian sites, Zeppelin

and Andøya.

Fig. 2 shows the box-whisker plots for selected PFASs at Alert, Zeppelin and Andøya. The detection frequency is the percentage of samples that were above the detection limit and it is presented in the bottom of Fig. 2.

### 3.1.1. Alert, Canadian Arctic

The fluorotelomer alcohols, FTOHs (sum of 6:2, 8:2 and 10:2 FTOHs) accounted for 52% of total PFASs (neutral PFASs and PFAAs). The concentration of FTOHs in Alert ranged from below detection limit < 0.17–30 pg m<sup>-3</sup> with a median of 3.8 pg m<sup>-3</sup>. Among the FTOHs, 8:2 FTOH was the highest in concentration followed by 10:2 and 6:2 FTOH (medians of 2.5, 0.67, 0.057 pg m<sup>-3</sup> respectively). The mean fractions of 6:2, 8:2 and 10:2 FTOH relative to ΣFTOHs were 9%, 67%, 24% respectively. The detection frequencies of FOSEs (Me- and Et-FOSE) ranged from 60 to 89%, FOSAs (Me- and Et-FOSA) ranged from 81 to 93%. FTAs showed the lowest DF, ranging from 20 to 35%. The levels of FOSEs at Alert were higher than FOSAs with median and range concentrations of 0.49 (< 0.10–4.8) pg m<sup>-3</sup> and 0.13 (< 0.014–0.82) pg m<sup>-3</sup>, respectively. The median and range for FTAs was 0.24 (< 0.19–1.4) pg m<sup>-3</sup>, which is ~16 times lower than FTOHs.

The most detected PFAA was PFBA with 99% detection frequency. The median concentration of PFBA in air at Alert was 1.7 pg m<sup>-3</sup>, being the second most abundant PFAS measured after 8:2 FTOH. PFOA and PFOS were also frequently detected in 89% and 96% of the samples respectively. Median concentrations and ranges were 0.097 (< 0.0063–1.3) pg m<sup>-3</sup> for PFOA and 0.070 (< 0.0063–2.8) pg m<sup>-3</sup> for PFOS. Other PFAAs that were detected in more than 50% of the samples were PFDA (87%, 0.030 pg m<sup>-3</sup>), PFBS (66%, 0.013 pg m<sup>-3</sup>), PFHpA (57%, 0.018 pg m<sup>-3</sup>), and PFNA (54%, 0.022 pg m<sup>-3</sup>).

### 3.1.2. Zeppelin and Andøya, Norwegian Arctic

PFOSA was routinely found in the samples from Zeppelin with detection frequency of 56%, but rarely found at Andøya where the detection frequency was only 9.3%. The median concentration and range for PFOSA at Zeppelin was 0.12 (< 0.086–4.9) pg m<sup>-3</sup>. 6:2 FTS was rarely found in the Zeppelin and Andøya samples with detection frequencies of 1.1 and 4.0%, respectively.

PFOA was detected in 59% and 48% of the Zeppelin and Andøya samples, respectively. The median concentration and range of PFOA at Zeppelin was 0.33 (< 0.12–4.0) pg m<sup>-3</sup> and at Andøya was 0.24 (< 0.12–5.5) pg m<sup>-3</sup> (Fig. 2). PFOS was detected in 50% and 48% of the samples collected at Zeppelin and Andøya, respectively. The median and range of PFOS at Zeppelin was 0.050 (< 0.037–2.2) pg m<sup>-3</sup> and at Andøya was 0.072 (< 0.043–0.43) pg m<sup>-3</sup>. Other PFASs were found with low detection frequency at Zeppelin and Andøya.

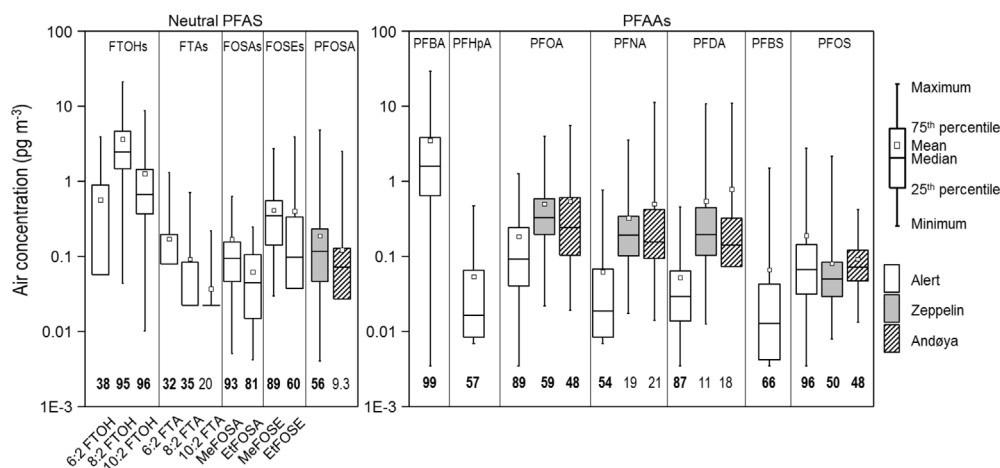


Fig. 2. Box-whisker plots of concentration of PFASs in air at Alert (2006–2014), Zeppelin (2006–2014) and Andøya (2010–2014). Non-detects was substituted with 2/3 of the detection limit when performing the statistical calculations. Detection frequencies (DF, %) are shown in the bottom of the plot. DF > 30% are shown in bold. Note that when DF < 30%, medians and means are biased towards the detection limit.

## 3.2. Temporal trends

The temporal trends of PFASs were derived for selected compounds. PFASs with detection frequency less than 50% or close to the detection limit were not subjected to this exercise. At Alert, only two samples were obtained in 2015 and hence they were not included in the trend analysis. At Andøya, since only few data were available during 2009, we developed the trends for 2010–2014 only. At Alert (2006–2014), 8:2 and 10:2 FTOHs showed slow increasing trends with doubling times ( $t_2$ ) of 5.0 and 7.0 years (y), respectively. Similarly, increasing trends were observed for PFAAs, including: PFBA ( $t_2 = 2.5$  y), PFOA ( $t_2 = 3.7$  y), PFBS ( $t_2 = 2.6$  y), and PFOS ( $t_2 = 2.9$  y) at Alert. At Zeppelin (2006–2014), PFOSA, a precursor for PFOS, exhibited non-changing trend (half-life,  $t_{1/2} = 63$  y). This is consistent with PFOS at Zeppelin, which also showed an extremely long half-life ( $t_{1/2} = 67$  y), and PFOA was declining ( $t_{1/2} = 7.2$  y). At Andøya (2010–2014), PFOS ( $t_{1/2} = 11$  y) and PFOA ( $t_{1/2} = 1.9$  y) were decreasing.

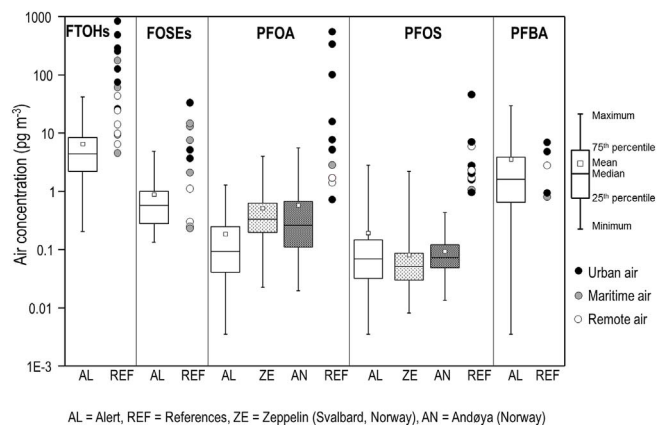
## 4. Discussion

### 4.1. Comparison of PFASs in air in Alert, Zeppelin and Andøya with other studies

Fig. 3 compares the air concentrations of the most frequently detected PFASs measured in this study and the literature. The literature values were grouped according to the nature of the sampling location.

FTOHs in Alert (< 0.17–30 pg m<sup>-3</sup>) were similar to those reported in remote (6.4–44 pg m<sup>-3</sup>) (Piekarz et al., 2007; Genualdi et al., 2010; Wang et al., 2015; Xie et al., 2015; Bossi et al., 2016) and maritime air (4.6–178 pg m<sup>-3</sup>) (Shoeib et al., 2006; Dreyer and Ebinghaus, 2009; Ahrens et al., 2011a, b; Cai et al., 2012; Wang et al., 2015) but were lower than urban air (75–950 pg m<sup>-3</sup>) (Barber et al., 2007; Jahnke et al., 2007; Dreyer and Ebinghaus, 2009; Müller et al., 2012; Ahrens et al., 2013). For FOSEs, air concentrations at Alert (< 0.10–4.8 pg m<sup>-3</sup>) and at other remote sites (0.25–1.1 pg m<sup>-3</sup>) (Wang et al., 2015; Xie et al., 2015; Bossi et al., 2016) were similar, but lower than those at urban sites (3.7–33 pg m<sup>-3</sup>) (Barber et al., 2007; Dreyer and Ebinghaus, 2009; Ahrens et al., 2013) and in maritime air (0.24–15 pg m<sup>-3</sup>) (Shoeib et al., 2006; Dreyer and Ebinghaus, 2009; Ahrens et al., 2011a, b; Cai et al., 2012; Wang et al., 2015).

PFOA concentrations in air at Alert (< 0.0063–1.3 pg m<sup>-3</sup>), Zeppelin (< 0.12–4.0 pg m<sup>-3</sup>) and Andøya (< 0.12–5.5 pg m<sup>-3</sup>) were lower than those reported in urban and maritime air. PFOA in air at Alert (median ± SD: 0.097 ± 0.24 pg m<sup>-3</sup>) was significantly ( $p < 0.05$ ) lower than Zeppelin (median 0.33 ± 0.54 pg m<sup>-3</sup>) and Andøya (median 0.24 ± 0.79 pg m<sup>-3</sup>). As PFOA is water soluble and reported to burst to the atmosphere (McMurdo et al., 2008; Reth et al.,



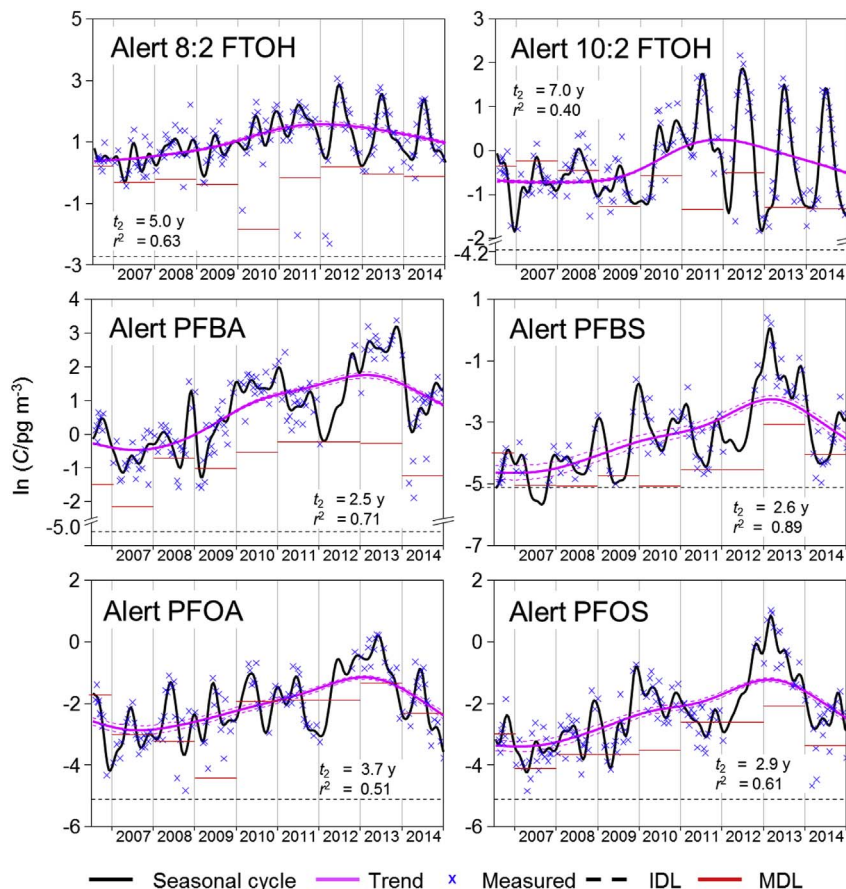
**Fig. 3.** FTOHs, FOSEs, PFOA, PFOS and PFBA in air at Alert (AL), Zeppelin (ZE) and Andøya (AN). Reference data are shown as dots: urban air (black), maritime air (grey) and remote air (white). Remote air refers to samples from rural, background and/or polar region (Piekarz et al., 2007; Stock et al., 2007; Genualdi et al., 2010; Müller et al., 2012; Wang et al., 2015; Xie et al., 2015; Bossi et al., 2016). Maritime air refers to samples collected over water surfaces during scientific cruises (Shoeib et al., 2006; Dreyer and Ebinghaus, 2009; Ahrens et al. 2011a, b; Cai et al., 2012; Wang et al., 2015). Urban air samples were obtained from populated or industrialized areas that are considered as primary source-impacted regions (Barber et al., 2007; Jahnke et al., 2007; Kim and Kannan, 2007; Dreyer and Ebinghaus, 2009; Müller et al., 2012; Ahrens et al., 2013).

2011), the relatively elevated PFOA air concentrations at the Norwegian sites could be due to different distances from the open ocean. Alert is located at the northeastern tip of the Ellesmere Island where it is surrounded by land, and approximately 4 km from water. The water surrounding the land is covered by sea ice for most of the year. Zeppelin is located on a mountain about 2 km from the ocean, and Andøya is within 100 m to water. There has been open water year round since

2006 in proximity to both of these sites (Prop et al., 2015). Hence, it is speculated that the Norwegian sites may receive additional PFOA from sea spray aerosol compared to Alert (McMurdo et al., 2008; Reth et al., 2011).

There was no significant difference ( $p < 0.05$ ) in air concentrations of PFOS at Alert (median  $\pm$  SD:  $0.070 \pm 0.42 \text{ pg m}^{-3}$ ), Zeppelin ( $0.050 \pm 0.14 \text{ pg m}^{-3}$ ) and Andøya ( $0.072 \pm 0.067 \text{ pg m}^{-3}$ ). Thus, PFOS reported here may reflect the background PFOS level in the Arctic. Higher air concentrations of PFOS at remote Arctic sites ( $2 \text{ pg m}^{-3}$  in Alert and  $5.9 \text{ pg m}^{-3}$  at Cornwallis Island, Nunavut, Canada) have been reported by Genualdi et al. (2010) in which air samples were collected in 2009 using sorbent impregnated passive air samplers. These differences may be due to the use of different sampling methodology. PFOS observed in this study was substantially lower than air concentrations reported from urban ( $0.96\text{--}46 \text{ pg m}^{-3}$ ) (Barber et al., 2007; Kim and Kannan, 2007; Dreyer and Ebinghaus, 2009; Müller et al., 2012; Ahrens et al., 2013), and maritime sites ( $1.1 \text{ pg m}^{-3}$ ) (Dreyer and Ebinghaus, 2009).

Air concentrations of PFBA in Alert (median  $1.7 \text{ pg m}^{-3}$ ,  $< 0.0063\text{--}29 \text{ pg m}^{-3}$ ) were within the same range as the urban ( $0.93\text{--}7.0 \text{ pg m}^{-3}$ ) (Dreyer and Ebinghaus, 2009; Müller et al., 2012; Ahrens et al., 2013) and remote air ( $2.8 \text{ pg m}^{-3}$ ) (Müller et al., 2012), which suggests that PFBA is uniformly distributed in the global atmosphere. PFBA was mainly detected in the gas phase in this study unlike other PFAAs that are mainly present in the particle phase (Ahrens et al., 2011b). The vapor pressure of PFBA is higher than that of other long chain PFAAs, thus PFBA may be more susceptible to LRAT (Bhatarai and Gramatica, 2011). Another plausible reason could be atmospheric transformation of certain volatile hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) to PFBA, which have been demonstrated in laboratory studies under zero or low NO<sub>x</sub> conditions (Bravo et al., 2010; Wang et al., 2014b). It should be noted that the



**Fig. 4.** Seasonal cycles and trends of neutral PFASs and PFAAs in Alert. Doubling times ( $t_2$ ) or half-lives ( $t_{1/2}$ ) are shown in units of years (y). Measured data are shown as blue crosses, the black line is the seasonal cycle, and the pink line is the trend derived from the Digital Filtration model. Dash pink lines indicate the lower and upper 95% confidence limits of the trend.  $r^2$  indicates the correlation coefficient between the trend and measured data.  $r^2$  is only shown for statistically significant correlations at 95% confidence (see S5). IDL and MDL are shown as dash black and red lines respectively.

early literature-reported values of PFBA may have been under-estimated due to the sampling methodologies applied (Dreyer and Ebinghaus, 2009; Müller et al., 2012; Ahrens et al., 2013). For some of the previous studies, samples were only collected using a filter which most likely was not capturing the gas-phase PFAAs. These differences may render literature data not directly comparable to our measurements, as the total PFBA in the filter and the PUF/XAD/PUF is reported here.

## 4.2. Temporal trends and seasonal variations

### 4.2.1. Alert

Fig. 4 shows the trend analysis of PFAAs in Alert. The neutral PFAAs, 8:2 and 10:2 FTOHs showed slow increasing trends with doubling times ( $t_2$ ) of 5.0 and 7.0 years (y), respectively. Although the overall trends (i.e. 2006–2014) of 8:2 and 10:2 FTOH were increasing, they appeared to be declining from 2012, which may indicate a slow-down in the emission of these substances. It is noted that 8:2 and 10:2 FTOH concentrations were not statistically significantly different ( $p > 0.05$ ) between years of 2012, 2013 and 2014. Hence this potential decline in trend needs to be confirmed with continual measurements to extend the time series for future trend assessments. Different global trends of FTOHs were reported previously. For instance, 8:2 and 10:2 FTOH are reported to decline 60–70% in mass per passive air sampler between 2006 and 2011 by the Global Air Passive Sampling (GAPS) study (Gawor et al., 2014). However, Bossi et al. (2016) found no significant trend for neutral PFAAs in air collected from 2008 to 2013 in Northern Greenland.

PFBA, PFOA, PFBS, and PFOS were increasing with doubling times ranging from 2.5 to 3.7 y at Alert. This is not surprising as many of these substances are still being used, stored in stockpiles or are slowly being released from products after disposal. Wang et al. (2014a) estimated that the global annual emissions of PFCAs steadily rose from 1951 to 2002, followed by a decline and a subsequent increase from mid-2000s to 2012. The first decline was due to the phase-out of PFCAs in North America and Europe, while the intermediate increase in mid-2000s was due to the production of PFCAs in Asia, especially in China, which is reported to be the world's largest industrial contributor of PFOA (Wang et al., 2014a; Li et al., 2015). Another possibility is that there could be a

time-lag for remote sites in response to the removal of chemicals from its source region. If the presence of PFAAs in remote sites is due to long-range oceanic transport (Wania, 2007), it will take many years for the atmospheric concentration to decline since ocean-mixing is a very slow process. The ocean could be considered as a reservoir for these substances.

Furthermore, the shift from the long to short chain fluorochemical production, may lead to the increasing trends of PFBA and PFBS in air at Alert (Wang et al., 2013). Kirchgeorg et al. (2013) reported that there was an increasing proportion of PFBA to the overall PFAAs in firn cores from the European Alps dated 1996–2008. Significant increasing proportion of PFBS to PFOS has been reported in dolphin liver samples from the South China Sea during 2002–2014 (Lam et al., 2016). Caution is advised when interpreting the trends of PFAAs in Alert, given the small number of data available in 2012 and the high concentrations of PFAAs measured in 2013, which is discussed later.

Although the half-lives or doubling times of FOSEs and FOSAs were not estimated because of their values being close to the MDL, visual inspection of the trend plots showed that these chemicals were declining (Fig. S1). Such observation is consistent with the global decline of FOSEs and FOSAs in air from 2006 to 2011 reported under the GAPS program (Gawor et al., 2014), and may reflect the phase-out of the production of PFOS-related products in North America and Europe.

In terms of seasonality, summer maxima were observed for FTOHs (Fig. 4) at Alert which may be related to volatilization due to higher temperatures. Summer maxima have also been reported for FTOHs in air at Greenland (Bossi et al., 2016). No consistent seasonality was observed for PFBA and PFOS. PFBS appears to show winter maxima which may be due to the stagnant atmospheric condition during the winter months in which contaminants coming into the Arctic from southerly regions are trapped in the Arctic (Gregor et al., 1998). PFOA seems to exhibit summer maxima which may be due to the increase in atmospheric oxidation of precursors, as it has been shown that concentration of precursors are higher in the summer, or the increased contribution of sea spray aerosols under open water condition in the summer.

To explore the influence of detection limit on the trend analysis, trends were derived from data above the MDL for the Alert samples. We found that the overall trend (i.e. increasing or decreasing) derived from

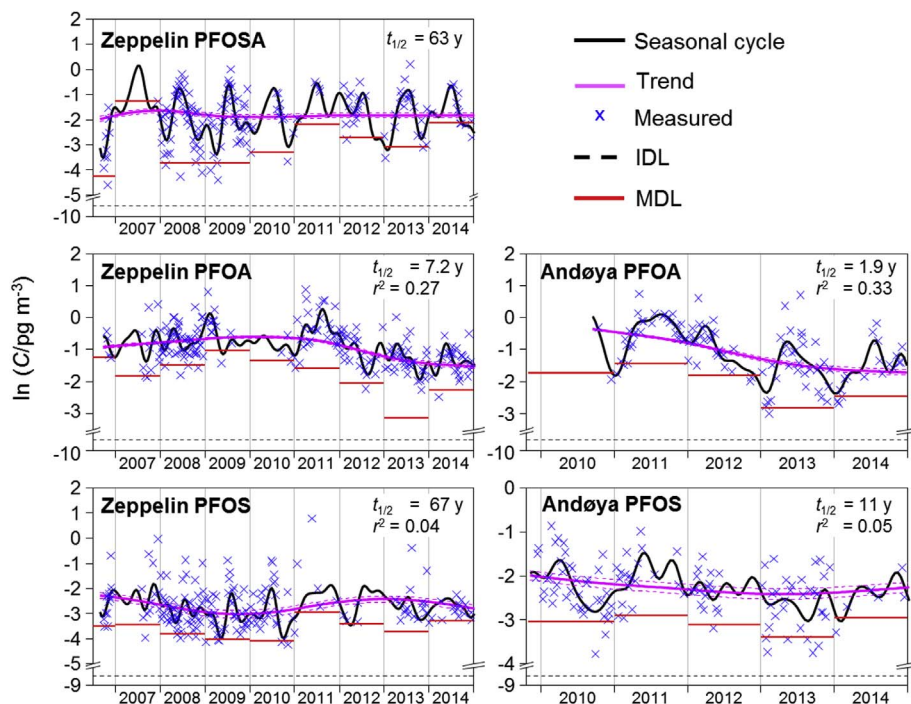


Fig. 5. Seasonal cycles and trends of PFOSA at Zeppelin, PFOS and PFOA at Zeppelin and Andøya. Doubling times ( $t_2$ ) or half-lives ( $t_{1/2}$ ) are shown in units of years (y). Measured data are shown as blue crosses, the black line is the seasonal cycle, and the pink line is the trend derived from the Digital Filtration technique. Dash pink lines indicate the lower and upper 95% confidence limits of the trend.  $r^2$  indicates the correlation coefficient between the trend and measured data.  $r^2$  is only shown for statistically significant correlations at 95% confidence (see S5). IDL and MDL are shown as dash black line and red line respectively.

the data above IDL, and MDL were the same. The difference in  $t_2$  calculated from the two datasets ranged from 0.1 to 0.5 years for 8:2 FTOH, PFBA, PFBS and PFOS, while the difference was the greatest for 10:2 FTOH with 1.5 years and PFOA with 1.1 years (Table S6).

#### 4.2.2. Zeppelin and Andøya

Fig. 5 presents the trend analysis for PFOSA, PFOA and PFOS from the Norwegian samples. PFOSA, a precursor for PFOS, at Zeppelin exhibited non-changing trend (half-life,  $t_{1/2} = 63$  y). This is consistent with PFOS at Zeppelin, which also showed an extremely long half-life of 67 y. PFOS at Andøya was slowly decreasing with a  $t_{1/2}$  of 11 y. PFOA exhibited declining trends with  $t_{1/2} = 7.2$  y at Zeppelin and 1.9 y at Andøya. This is in contrast to the findings at Alert. The different findings might be due to different regulations on the regional level. In Canada, there was a voluntary phase out of products containing PFOA from 2010 to 2015. To-date (i.e. 2017), the use of PFOA, its salts and precursors is restricted to photo media coatings and aqueous film-forming foams used in firefighting applications (Government of Canada, 2016a, b). In Norway, a legislation which bans the manufacture, import, export of PFOA in consumer goods and textiles was implemented in 2014, but exemptions were made for medical equipment. The use of PFOA and related substances in photographic coatings for film, paper, or printing plate, adhesive, foil or tape in semiconductors was allowed until 2016 (Norwegian Pollution Control Authority, 2007; Norwegian Environment Agency, 2013).

In terms of seasonality, PFOSA appears to show summer maxima in Zeppelin. PFOA and PFOS showed no consistent seasonality at Zeppelin and Andøya because these substances are likely bounded on particulate matter and thus are not expected to be influenced by volatilization.

#### 4.3. Source identification of PFOA, PFOS and PFOSA

The relative emission sensitivity fields ( $R_p$ ) of the highest 20% ( $P = 80^{\text{th}}$  percentile) measurements of PFOA and PFOS were plotted to explore the potential source regions. Data from 2013 at Alert are not included in the analysis due to the anomalous PFOA and PFOS measurements, which are analyzed separately and discussed later.

Figure 6 illustrates the  $R_{80}$  fields for PFOS and PFOA at Alert, Zeppelin and Andøya. At Alert, the highest PFOS data (Fig. 6a) are associated with continental air masses transported from North America, north-central, and western region of Russia. The highest PFOA data at Alert (Fig. 6b) are associated with air mass transport over the water, i.e., the Canadian Archipelago, Baffin Bay, Labrador Sea and Greenland Sea. At Zeppelin, the highest PFOA data (Fig. 6c) are associated with transport from Europe. On the contrary, highest PFOS data at Zeppelin (Fig. 6d) are associated with air mass coming from the Atlantic Ocean, Arctic Ocean and Bering Sea. At Andøya, similar transport patterns were found for PFOA and PFOS (Fig. 6e and f), with frequent arrival of high concentrations from Eastern Europe. PFOSA at Zeppelin (Fig. S2) was mostly associated with oceanic air mass transported from the Atlantic Ocean, Bering Sea and North Pacific Ocean. It has been hypothesized that PFOA is transported by oceanic currents (Wania, 2007), and subsequently the chemical may be transferred from ocean to air via sea spray aerosols (McMurdo et al., 2008; Reth et al., 2011). A mix of continental and oceanic air masses associated with high concentrations of PFOA is seen in the current study. Note that the trajectory analysis does not account for the contribution of the many known precursors, such as the FTOHs, FOSEs, FOSAs, hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs). These precursors may undergo atmospheric degradation and contribute to the overall concentrations of PFOA or PFOS (Wang et al., 2014a, b).

It is noted that episodes of high PFOA and PFOS measurements at Alert occurred in 2013. Indeed the maximum concentrations of the entire studied period were measured during these episodes. Fig. S3 plots the average sensitivity fields ( $S_T$ ) for year 2013 relative to the average  $S_T$  of the overall Alert data. The red region indicates the area

where the air masses passed through more frequently in 2013 relative to the entire study period. Particularly, more air masses travelled across the Hudson Bay of Canada in 2013 than in other years, indicating that the Hudson Bay could be a source for these substances as it has a large watershed extending over five Canadian provinces, three territories and four US states with drainage from major streams (the Nelson, Saskatchewan and Churchill rivers) passing through cities (e.g. Edmonton and Winnipeg) (Zhang et al., 2017). High concentrations of PFASs have been reported in surface waters from lakes, rivers, and estuaries near urban areas which could be due to river discharge (Filipovic et al., 2013; Zhang et al., 2016).

#### 4.4. Temperature dependence

The correlations between selected PFASs and temperature were investigated by plotting the natural logarithm of the PFAS concentration ( $\ln C$ ) against inverse temperature ( $1/T$ ). Significant ( $p < 0.05$ ) correlation indicates re-volatilization from local surfaces. Data below detection limit are not used for this analysis.

Fig. S4 shows  $\ln C$  vs.  $1/T$  for 8:2, 10:2 FTOHs, Me- and EtFOSE at

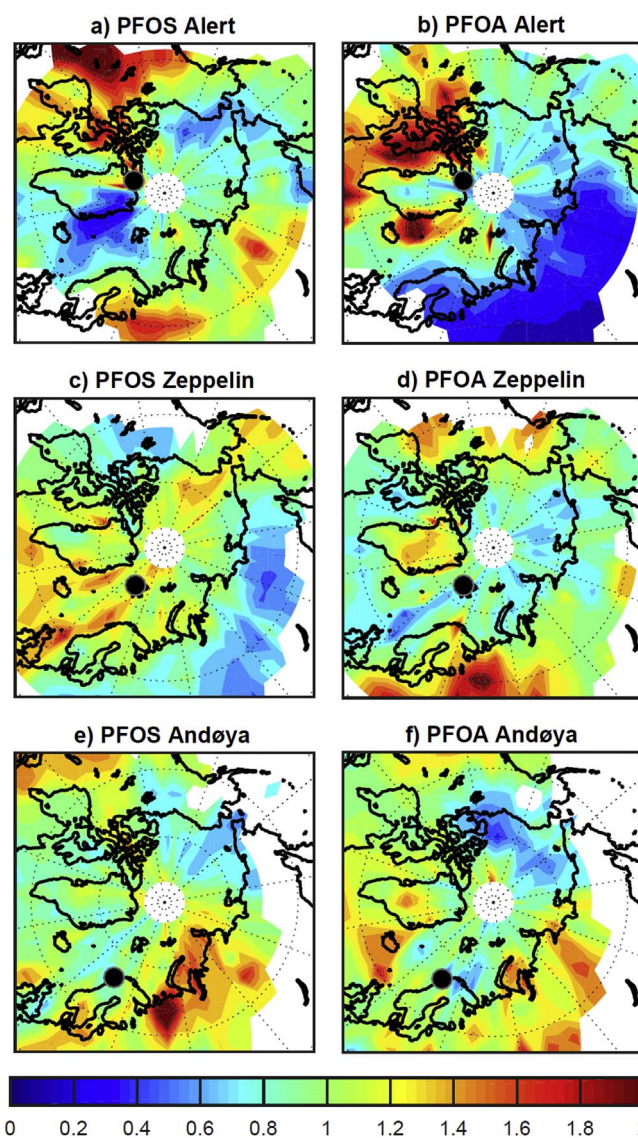


Fig. 6. Fields of  $R_{80}$  for the highest 20% of all measured PFOS (left panels) and PFOA (right panels) concentrations for Alert (a, b), Zeppelin (c, d) and Andøya (e, f). The data used for Alert from 2006 to 2012 and 2014, for Zeppelin from 2006 to 2014 and Andøya are from the years 2010–2014.

Alert. Significant correlations ( $p < 0.01$ ) were observed for 8:2, 10:2 FTOHs and MeFOSE, with higher concentrations observed in the warm season. However, large scatter of the data ( $r^2$  ranging from 0.09 to 0.24) implies that the presence of these compounds in Arctic air is probably due to both atmospheric long-range transport and volatilization from snow or ocean. Net volatilization of FTOHs from snow and ocean to air has been demonstrated in the North Sea (Xie et al., 2013), and from snow in Antarctica (Xie et al., 2015) and Ny-Ålesund (Wang et al., 2015).

For the PFAAs at Alert, analysis is only performed for the years 2013 and 2014 due to the high detection frequencies. Fig. S5 shows that PFBA, PFOA, and PFOS at Alert were not correlated with temperature. This is probably a result of primary emission followed by advection, which are not dependent on temperature. The PFAAs, unlike legacy POPs, have high water solubility and low vapor pressure. Hence, they can be transferred from the ocean to the air through aerosol ejection associated with bursting bubbles and waves (McMurdo et al., 2008; Reth et al., 2011). Other plausible pathways include atmospheric oxidation of precursor compounds, volatilization from snow or land surfaces. PFBS was positively correlated with  $1/T$  (Fig. S5). The cause of low PFBS concentration during the summertime is not clear since these chemicals are known to be very persistent in both aerobic and anaerobic conditions, and persistency of 180 days in air is reported (Gamez Grijalva, 2009). Elevated concentrations in winter may be associated with the generally higher aerosol concentrations in the Arctic in winter, known as Arctic Haze (Law and Stohl, 2007).

At Zeppelin, concentrations of PFOSA were negatively correlated with  $1/T$  (Fig. S6), suggesting volatilization from ocean is a source of this compound to the atmosphere. This observation is consistent to the FLEXPART analysis discussed previously that PFOSA is influenced by oceanic air mass. No temperature dependence was observed for PFOA and PFOS at Zeppelin (Fig. S7). At Andøya, negative and weak correlation was observed for PFOA (Fig. S7). Although these chemicals tend to be higher in concentrations during the warmer months, the weak correlations suggest that atmospheric processes other than volatilization are important.

In conclusion, we report for the first time temporal trends and source region analysis of neutral and ionic PFASs in air (2006–2014) from three arctic stations: Alert (Canada), Zeppelin (Svalbard, Norway) and Andøya (Norway). PFOA, PFOS, PFBA exhibited increasing trends at Alert. Neutral precursor compounds such as the 8:2 and 10:2 FTOHs also showed slow increasing trends. In contrary, declining or non-changing trends were observed for PFOA and PFOS at Zeppelin and Andøya. Lagrangian particle dispersion model FLEXPART has shown that PFOA and PFOS are impacted by air masses originating from the ocean, or land, depending on the studied site. Specifically, PFOA at Alert and PFOS at Zeppelin were dominated by oceanic air masses whereas, PFOS at Alert and PFOA at Zeppelin were influenced by air masses transported from land. The differences in air concentrations and in time trends between the three sites may reflect the differences in regional regulations and source regions.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.10.028>.

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