Atmospheric concentrations and trends of poly- and perfluoroalkyl substances (PFAS) and volatile methyl siloxanes (VMS) over 7 years of sampling in the Global Atmospheric Passive Sampling (GAPS) network[☆]

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ABSTRACT

Poly- and per-fluoroalkyl substances (PFAS) and volatile methyl siloxanes (VMS) were monitored at 21 sites in the Global Atmospheric Passive Sampling (GAPS) Network. Atmospheric concentrations previously reported from 2009 were compared to concentrations measured at these sites in 2013 and 2015, to assess trends over 7 years of monitoring. Concentrations of the fluorotelomer alcohols (FTOHs) and fluorinated sulfonamides and sulfonamidoethanols (FOSAs and FOSEs) were stable at these sites from 2009 to 2015 with no significant difference ($p > 0.05$) in concentrations. Elevated concentrations of all the neutral PFAS were detected at the urban sites as compared to the polar/background sites. The perfluorosulfonic acids (PFSAs), meanwhile, saw a significant increase ($p < 0.001$) in concentrations from 2009 to 2015. The perfluorocarboxylic acids (PFCAs) had elevated concentrations in 2015, however, the difference was not statistically significant ($p > 0.05$). Concentrations of the PFSAs and the PFCAs were similar at all location types, showing the global reach of these persistent compounds. Concentrations of the cyclic VMS (cVMS) were at least an order of magnitude higher than the linear VMS (lVMS) and the PFAS. Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) saw a weak significant increase in concentrations from 2009 to 2013 ($p < 0.05$), however, hexamethylcyclotrisiloxane (D3) had a strong significant decrease in concentrations from 2009 to 2015 ($p < 0.01$).

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1. Introduction

Two classes of chemicals that have seen increasing attention due to concerns over environmental fate are the poly- and perfluoroalkyl substances (PFAS) and the volatile methyl siloxanes (VMS). The PFAS have been widely used since the 1950s in numerous industrial and commercial applications (Kannan, 2011). These uses include in textile stain repellants and grease-proof paper; in fluoropolymer manufacture; coatings and aqueous film-forming foams (Buck et al., 2011). The perfluoroalkyl acids (PFAAs), in particular the perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs), are of concern due to their widespread persistence in the environment and humans, and tendency

to induce toxic effects (Butt et al., 2010). As such, perfluorooctane sulfonate (PFOS), its salts and precursor compound (perfluorooctane sulfonyl fluoride), were added to the Stockholm Convention on persistent organic pollutants (POPs) in 2009 for restriction of production and use with specific exemptions (UNEP, 2017a). Furthermore, perfluorohexane sulfonate (PFHxS) and perfluorooctanoic acid (PFOA) are currently under review for addition to the Stockholm Convention (UNEP, 2017b). Also of concern are a range of neutral PFAS (n-PFAS) which are also applied in the manufacture of polymers. These include the fluorotelomer alcohols (FTOHs) and fluorinated sulfonamides and sulfonamidoethanols (FOSAs and FOSEs). As well as being regularly detected in the environment, the n-PFAS also degrade in the atmosphere to form the more stable, and toxic, PFAAs (Wang et al., 2017).

The VMS have been produced commercially since the 1940s and are classed as high production volume chemicals, with tens of thousands of tons produced per year (Gallego et al., 2017). They are

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used industrially as intermediates in the manufacture of silicone polymers and copolymers; as surfactants in pesticides; and as defoamers, lubricants, cleaning products, sealants, waxes and polishes. They are also used in a wide range of personal care products including hair/skin products, deodorants and in pharmaceuticals (Government of Canada, 2012; Wang et al., 2013). As a result of the high production and use of these chemicals, elevated concentrations are detected regularly in the environment (Wang et al., 2013; Shoeib et al., 2016). The cyclic VMS have various direct and indirect toxic effects (Want et al., 2013) and concerns arise over environmental toxicity, including toxicity to aquatic organisms with "a need for continued environmental monitoring" (Government of Canada, 2012). The long range transport properties of both the PFAS and VMS have been shown and they are routinely detected in remote locations such as the Arctic (Butt et al., 2010; Ahrens et al., 2011; Bossi et al., 2016; Wong et al., 2018; Wang et al., 2013; Genualdi et al., 2011; Krogseth et al., 2013a). As such, continued environmental monitoring is required to further assess the environmental fate of these chemicals.

The Global Atmospheric Passive Sampling (GAPS) Network has been monitoring the PFAS and VMS since 2009 (Genualdi et al., 2010, 2011). The GAPS Network is an atmospheric monitoring program run by Environment and Climate Change Canada and regularly deploys passive air samplers (PAS) at over 50 global locations (Pozo et al., 2006). The GAPS program provides global atmospheric data on POPs, emerging POPs and other chemicals of concern, to domestic monitoring initiatives in Canada such as the Chemicals Management Plan (CMP), and to international programs including the Global Monitoring Plan (GMP) of the Stockholm Convention on POPs. The data provided by the GAPS program is used to assess the effectiveness of implemented control measures on chemicals of concern and provide new information on levels and trends of chemicals of emerging concern, supporting the development of risk assessments.

Sorbent impregnated polyurethane foam PAS (SIP-PAS) have been deployed in the GAPS Network every two years, since 2009, to monitor the PFAS and VMS. The SIP-PAS are deployed at 21 sites, with 20 sites in the United Nations region of "Western Europe and Others Group" (WEOG) and one site in the Central and Eastern Europe (CEE) region. The results from the 2009 deployment have previously been published (Genualdi et al., 2010, 2011) and the aim of this study is to provide further data from consecutive years of sampling, and to investigate trends in atmospheric concentrations of PFAS and VMS from 2009 to 2015.

2. Materials and methods

2.1. SIP-PAS deployment, extraction and analysis

SIP-PAS were deployed in double-dome sampling chambers at a sub-set of sites operated under the GAPS Network, with a focus on the WEOG region (Fig. 1). The chamber consisted of two stainless steel domes that allow air to circulate over the SIP-PAS surface, as described further in Pozo et al. (2004). SIP disk sample preparation and deployment followed methods that have been previously described (Shoeib et al., 2016). In 2009, 2015, SIP-PAS were deployed during the second sampling quarter of the year (Q2), i.e. April to July, and in 2013 SIP-PAS were deployed for all 4 sampling quarters (Q1, Q2, Q3 and Q4). At Mount Revelstoke one SIP-PAS was deployed for the entire year (September to September) in both 2013 and 2015 due to difficulties accessing this remote site. The locations covered three different location types: polar ($n = 3$), background ($n = 15$) and urban ($n = 3$). Site details and deployment information are listed in Tables S1 to S4 in the Supporting Information (SI). The SIP-PAS were extracted following previously described methods

(Shoeib et al., 2016). Details on target analyte names, acronyms and supplier details are provided in Tables S5 and S6 and include 18 PFAAs, 7 n-PFAS and 7 VMS. Briefly, the extraction method consisted of spiking the SIP-PAS with surrogates: 2 µg of labelled VMS, 25 ng of labelled n-PFAS and 0.5 ng of labelled PFAAs, Table S5 and S6. SIP-PAS were then extracted with accelerated solvent extraction (ASE, ASE 350, Dionex Corporation, Sunnyvale, CA, USA). Each SIP-PAS was extracted twice, once with petroleum ether/acetone (85/15, v/v, 3 cycles) to extract the more volatile n-PFAS and VMS, then a second time with acetonitrile (3 cycles) to extract the PFAAs. Fraction 1 (containing the VMS and n-PFAS) was volume reduced to 0.5 mL, using rotary evaporation and nitrogen blowdown, using isooctane as a keeper. Fraction 2 (containing the PFAAs) was volume reduced to 0.5 mL using TurboVap (Biotage, Charlotte, NC, USA) and nitrogen blowdown. All fractions were further purified with activated carbon columns containing 100 mg of ENVI-Carb (100−400 mesh, Supelco, St. Louis, MO). Fraction 1 was eluted from the carbon column using 4 mL of dichloromethane/hexane (1/4, v/v) before final solvent exchange to isooctane and volume reduction to 0.5 mL. Fraction 2 was eluted using 4 mL of acetonitrile before final solvent exchange to methanol and volume reduction to 0.5 mL. Prior to instrumental analysis, Fraction 1 was spiked with 5 ng of N,N-dimethyl perfluoro-1-octane sulfonamide (N,N-Me$_2$FOSA) and 100 ng of d_{10} fluorene for use as injection standards. Fraction 2 was spiked with 0.5 ng of $^{13}C_8$ PFOA and $^{13}C_8$ PFOS for use as injection standards. Injection standards were used to quantify the surrogates and calculate surrogate recoveries. The separation and detection of the VMS and n-PFAS were performed using gas chromatography mass spectrometry (GC-MS) and the PFAAs with ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS), following previously published methods (Shoeib et al., 2016).

2.2. Quality assurance/quality control

Air concentrations (pg/m^3 or ng/m^3) of target analytes were derived from the mass of the chemical collected on the SIP-PAS divided by an effective air sampling volume. This air volume was determined using the GAPS template (Harner, 2017), using the average temperature during the deployment period, octanol-air partition coefficients for each target chemical and site specific sampling rates determined by Genualdi et al. (2010). The sampling rates are based on depuration compounds spiked onto co-located PUF disk samplers (Table S3). We note that due to the much greater sorptive capacity of SIP disks compared to PUF disks, the depuration compound approach for assessing site-specific sampling rates cannot be used for SIP disks. However, because the geometries are identical, sampling rates derived for PUF disks can be applied to co-located SIP disks. For Mount Revelstoke a site specific sampling rate has not been reported and 4 m^3/day was used. Site specific sampling rates were used instead of the average rate of 4 m^3/day (Ahrens et al., 2013), to improve the accuracy of calculated air concentrations. For future studies, an alternative to the depuration method for determining site specific sampling rates may be to use site specific sampling rates calculated by models that are being developed, such as the model recently reported by Herkert et al. (2017).

Field blanks (a second prepared SIP-PAS) were sent to all sites to assess background contamination from shipping, handling, or extraction and analysis of samples. All samples were blank corrected by subtracting the mean mass determined in field blanks (ng) from the mass in the sample. Concentrations (ng/sample) detected in field blanks are listed in Tables S7 to S10. In 2015, unusually high concentrations of the PFCAs were detected in field blanks (Table S8). As every field blank saw elevated concentrations
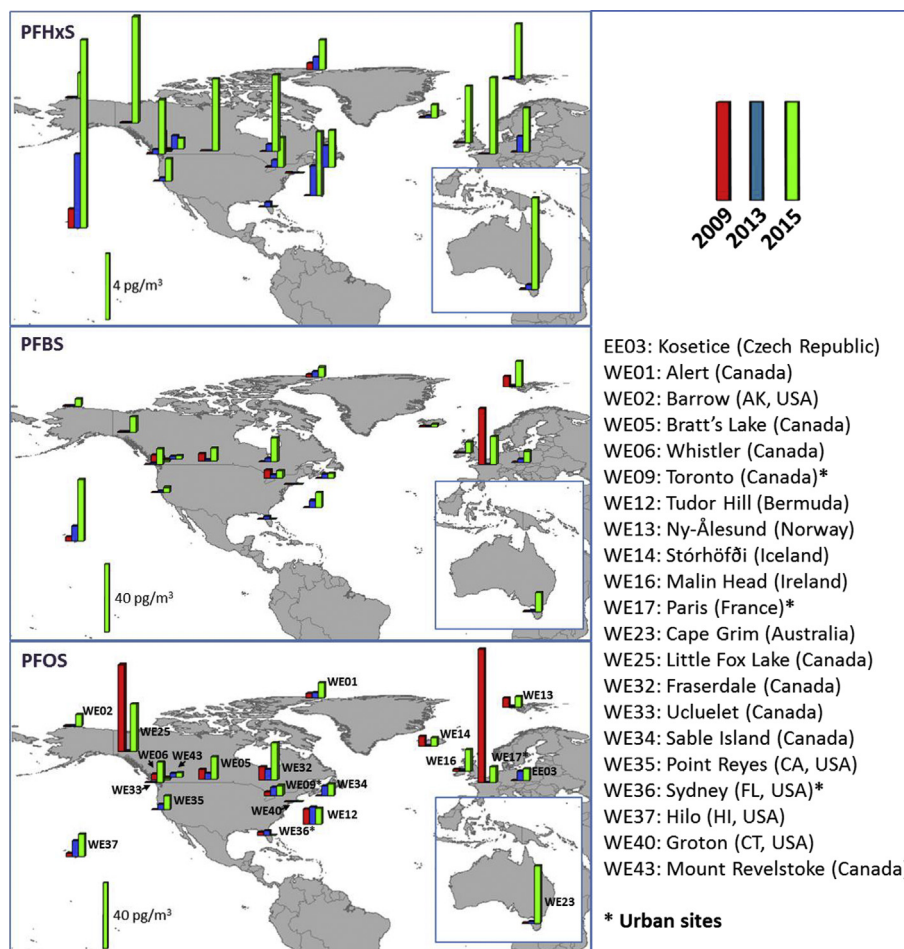
Fig. 1. Concentrations (pg/m^3) of PFHxS, PFBS and PFOS at 21 GAPS sites in 2009, 2013 and 2015. All samples were collected in quarter 2 (April—June) of their respective sampling years. Note the scale of PFHxS is 10 times lower than PFOS and PFBS.

this is likely an analytical issue in the laboratory and was accounted for with higher method detection limits (MDLs) assigned for the 2015 samples. MDLs were determined as the mean of the concentrations from field blanks plus three times the standard deviation and instrument detection limits (IDLs) were calculated as the concentration (ng) of a peak providing a signal:noise ratio of 3:1. To convert IDLs and MDLs to pg/m^3 an average sampling volume (m^3) from all samples deployed in that year was applied. All analytes were surrogate recovery corrected and surrogate recoveries (mean $\pm$ standard deviation) ranged from 48 ± 18 to $51 \pm 15\%$ for the VMS, 43 ± 27 to $108 \pm 28\%$ for the PFAAs and 28 ± 11 to $136 \pm 33\%$ for the n-PFAS. All statistical analyses were conducted with Microsoft Excel 2010.

The 2009 samples were previously analysed for PFAAs using high performance (HP)LC-MS/MS (Genualdi et al., 2010), whereas the 2013 and 2015 samples were analysed with UPLC-MS/MS. To check comparability between the two methods the 2009 extracts were rerun using UPLC-MS/MS, and good agreement was seen with the concentrations reported in Genualdi et al. (2010). Concentrations from both analyses are listed in Tables S11-S12 in the Supporting Information. The improved instrument detection limits of the UPLC-MS/MS method also saw detection of the PFAAs in more samples than previously reported (Table S11). The largest discrepancy was with PFOS, as the linear and branched isomers were not separated with the HPLC-MS/MS method and total PFOS was reported in 2009. With the UPLC-MS/MS method, the isomers were

separated and only the concentration of the linear isomer is reported as analytical standards of the branched isomers were not included in the analysis method. For comparisons of PFAAs between the sampling years, the 2009 concentrations determined from the rerun with UPLC-MS/MS were used. For the n-PFAS, the 2009 concentrations reported by Genualdi et al. (2010) were used for comparisons between sampling years and for the VMS the 2009 results reported by Genualdi et al. (2011) were used for comparisons.

3. Results and discussion

Concentrations of PFAS (pg/m^3) and VMS (ng/m^3) from each deployed SIP-PAS are listed in Tables S13-S20 in the SI.

PFBA and PFPeA are reported for the SIP-PAS collected in 2013 and 2015 in Tables S15 and S16, respectively, and 2009 in Table S11, however, as only one ion transition is monitored for both these compounds (i.e. no qualification trace), the analysis has a greater level of uncertainty. The authors also note that the concentrations of PFBA are highly elevated compared to previously reported atmospheric concentrations (Wong et al., 2018). For these reasons the results of PFBA and PFPeA are included, however, they are listed in a qualitative manner and are not used in comparisons and trends analysis further in this study. To overcome this quality assurance issue in the future, it is suggested that complementary methods be used (such as high resolution mass spectrometry) to confirm the

presence of PFBA and PFPeA.

3.1. n-PFAS

The majority of the FOSA/FOSEs had low detection frequencies in both 2013 and 2015, except for EtFOSA with detection frequencies of 63 and 47% in 2013 and 2015, respectively. The FTOHs generally had higher detection frequencies with >68% detection of 8:2 FTOH and 10:2 FTOH. Concentrations of the FTOHs, and EtFOSA at each site were generally within a factor of two between the three years, and there were no significant differences in concentrations between the sampling years (paired *t*-test, p > 0.05). The other FOSA/Es were not assessed due to low detection frequencies in each year (<25%) of these analytes. This is suggesting that atmospheric concentrations of at least the FTOHs and EtFOSA have remained relatively constant at these WEOG sites from 2009 to 2015. Fig. 2 depicts box and whisker plots of the concentrations of the FTOHs and EtFOSA in each sampling year.

At every site, the FTOHs dominated the profiles with highest concentrations of the 6:2 FTOH and 8:2 FTOH. In all three sampling years, FTOH concentrations were elevated at the three urban sites of Paris (France), Toronto (Canada) and Sydney (Florida). The FOSAs were detected more frequently than the FOSEs and again concentrations were generally higher at the three urban sites. As there are a reduced number of sites in the urban and polar locations in 2013 and 2015 (n = 2 or 3), meaningful statistical comparisons between the location types cannot be made. However, we are observing a tendency for elevated concentrations at the urban locations and similar concentrations between the polar and background locations. Concentration ranges of total FTOHs and total FOSA/FOSEs at the three location types (polar, background and urban) are listed in Table S21, as well as concentration ranges from other reported studies in these regions.

In the polar region, concentrations of n-PFAS at the GAPS sites were generally in line with concentrations previously reported for this region. Concentrations of the sum of the three FTOHs (ΣFTOHs) at the three polar sites in the GAPS study (<0.4−21 pg/m^3) were in line with those previously reported from the Canadian Arctic in 2004 of <1.5−35 pg/m^3 (Stock et al., 2007), in 2005 of 7.0−55 pg/m^3 (Shoeib et al., 2006) and North Greenland during 2008−2013 of <0.2−48 pg/m^3 (Bossi et al., 2016). Concentrations at Alert (Canada) in the GAPS study, were also in line with an active air study at Alert from 2006 to 2014 (Wong et al., 2018). However, FTOHs at the GAPS sites were lower than those reported from monitoring studies over the seas of the Canadian Arctic in 2007−2008 of 20−138 pg/m^3 (Ahrens et al., 2011) and the Arctic Ocean in 2010 of 98−195 pg/m^3 (Cai et al., 2012). Of the FOSA/FOSEs, only EtFOSA was detected in the polar GAPS locations and concentrations were an order of magnitude lower than previously reported in the Arctic (Bossi et al., 2016; Ahrens et al., 2011). However, concentrations were in line with levels over the Arctic Ocean in 2010 (Cai et al., 2012) and at Alert during 2006−2014 (Wong et al., 2018). The mixed comparisons of EtFOSA may be in part due to the low detection of this compound. At the background locations in the GAPS study, concentrations of both the ΣFTOHs (<0.4−90 pg/m^3) and ΣFOSA/FOSEs (<0.04−7.5 pg/m^3) were in line with levels reported from background sites in Europe. Active air studies from Germany in 2011−2012 (Wang et al., 2014), Switzerland in 2010 (Müller et al., 2012), over the North Sea in 2007 (Dreyer and Ebinghaus, 2009) and the North Sea in 2009 (Xie et al., 2013) all saw similar concentrations to the GAPS background locations with FTOHs ranging 2.5−172 pg/m^3 and FOSA/Es ranging 0.6−41 pg/m^3.

Concentrations of the ΣFTOHs at the urban sites in the three GAPS years were mostly in line with levels previously reported from urban locations in Canada and Europe. The urban GAPS sites

(40−238 pg/m^3) were in line with those from 2007 at semi-rural sites in Germany of 30−200 pg/m^3 (Dreyer and Ebinghaus, 2009). Active air samples collected in 2010 in Toronto, Canada (Ahrens et al., 2012) were also in line with the GAPS samples at Toronto. However, concentrations at the GAPS sites were lower than reported at Manchester (UK) in 2005 of 268−801 pg/m^3 (Barber et al., 2007) and at Zurich (Switzerland) in 2010 of 950 pg/m^3 (Müller et al., 2012). For the ΣFOSAs/FOSEs, the levels in the GAPS samples were also in line with levels reported at Germany of 1.7−12 pg/m^3 (Dreyer and Ebinghaus, 2009) but higher than at Toronto in 2010 (Ahrens et al., 2012). Again, Zurich (Müller et al., 2012), Manchester (Barber et al., 2007) and also Birmingham (UK) in 2008−2009 (Goosey and Harrad, 2012) had higher concentrations than the GAPS samples (3.4−460 pg/m^3), suggesting greater inputs of localized sources are being captured at these urban areas, than at the GAPS locations.

Temporal trends of the n-PFAS have been investigated in previous studies. Wong et al. (2018) reported slow increasing trends of the FTOHs at Alert from 2006 to 2014, and an expected doubling time of 5 and 10 years for 8:2 FTOH and 10:2 FTOH, respectively (Wong et al., 2018). Bossi et al. (2016), meanwhile, did not observe changes in concentrations of the FTOHs at North Greenland from 2008 to 2013. Global trends have also been investigated by Gawor et al. (2013), at up to 46 GAPS sites from 2006 to 2011 (note: these data were reported as ng/sampler and not converted to air concentrations). The FOSA/FOSEs had a decreasing trend over the 6 years, whereas the FTOHs had an initial decrease and more stable levels from 2009 to 2011. The same stable concentrations were seen in this GAPS study (21 sites) for the FTOHs from 2009 to 2015. The variable trends reported in different studies show that further monitoring is required to provide more information on global atmospheric trends of the n-PFAS.

Previous studies have investigated the ratios of the individual FTOHs to provide information on sources to the air mass sampled. As the 8:2 FTOH has the longest atmospheric residence time of the FTOHs (Bossi et al., 2016; Wang et al., 2014), a higher ratio of the 8:2 FTOH to the other FTOHs indicates that long range atmospheric transport is a primary source to the region. A lower 8:2 FTOH ratio indicates direct emissions from localised sources in the area are contributing (Wang et al., 2014). In the Arctic region, ratios of 6:2 to 8:2 to 10:2 FTOH have been reported at 1.7: 3.1: 1.8 (Bossi et al., 2016); 1.0: 9.6: 2.1 (Ahrens et al., 2011); 1.0: 5.6: 2.5 (Xie et al., 2013) and 1.0: 58: 9.6 (Cai et al., 2012). Furthermore, in background locations such as over the North China Sea ratios of 1.0: 9.6: 2.1 were reported (Lai et al., 2016). In more urbanised regions (with contributing localised sources) lower ratios have been reported of 4.2: 3.7: 1.0 in Toronto, Canada (Ahrens et al., 2012, 2013) and 1.3: 3.1: 1.0 at Hamburg, Germany (Dreyer and Ebinghaus, 2009).

The ratios of the FTOHs were investigated in this study and showed similar trends. At the polar and background sites in 2013 and 2015, a higher proportion of 8:2 FTOH was seen, as compared to the urban sites suggesting atmospheric transport contributed to these regions. The 2009 samples had low detection frequencies of all the n-PFAS so ratios were not determined for this year. Košetice (Czech Republic), Tudor Hill (Bermuda) and Malin Head (Ireland) had ratios similar to the urban sites, suggesting there may be a combination of sources contributing to these areas. Calculated ratios from the 2013 and 2015 samples are listed in Table S22.

The data was assessed further by comparing concentrations with the latitude of the sampling site, to investigate evidence of atmospheric degradation as the air mass moves away from source (urban) regions. There were no significant correlations (p > 0.05) between concentrations of the FTOHs at the northern hemisphere background/polar sites with latitude in either 2013 or 2015. This is suggesting that in this study, there are no observable decreases in
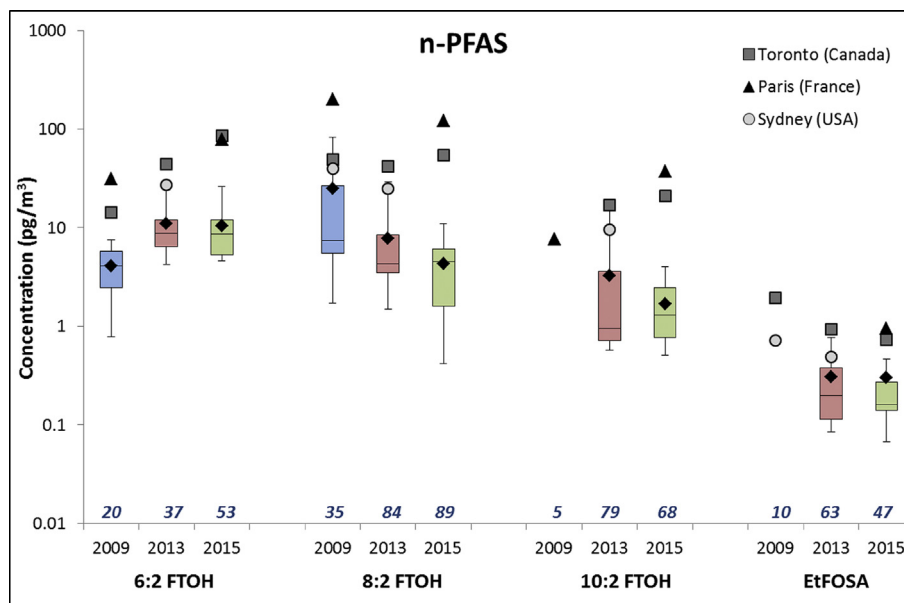
Fig. 2. Box and whisker plots of concentrations (pg/m^3) of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH and EtFOSA detected at background and polar sites in 2009, 2013 and 2015. The boxes show median concentrations and the 25th and 75th percentiles, minimum and maximum concentrations are indicated by the whiskers. Mean concentrations are indicated by the diamond. Where an analyte was below detection limits the sample was not included and detection frequencies are listed below the plots. Concentrations (pg/m^3) determined at the three urban sites are indicated separately by the triangles, squares and circle icons. Note only Paris (France) saw detection of 10:2 FTOH above detection limits in 2009 and only Toronto (Canada) and Sydney (USA) saw detection of EtFOSA above detection limits in 2009.

FTOH atmospheric concentrations as the air mass moves away from the source (urban) regions, and similar concentrations are observed in the polar and the background sites. All correlations are shown in Figure S1.

3.2. PFAAs

The PFSAs had similar concentrations between 2009 and 2013, and the levels were not significantly different ($p > 0.05$), although PFSAs were only detected in 65% of samples in 2009. In 2015, however, the concentrations were significantly higher for all detected PFSAs ($p < 0.006$). This may be indicating that atmospheric concentrations are increasing at these WEOG sites but future monitoring is needed to determine a trend. The PFCAs had similar concentrations between the three sampling years and there were no significant differences in concentrations ($p > 0.05$), although detection frequencies were low in 2009 at 50%. Fig. 3 depicts box and whisker plots of the concentrations of (a) PFSAs and (b) PFCAs in each sampling year.

The PFSAs were detected more frequently than the PFCAs, and PFBS, PFHxS and PFOS were detected regularly at all sites with PFDS below detection limits. In all three sampling years PFOS and PFBS dominated the profiles and there were no discernable differences in concentrations between location types. Fig. 1 maps concentrations of PFBS, PFHxS and PFOS at the 21 GAPS sites in all three sampling years. Of the PFCAs, the 6 to 10 carbon chain compounds were detected the most frequently. In 2013 concentrations were similar at all location types, however, in 2015 concentrations were elevated at the urban locations ($n = 2$) by at least a factor of 2. The higher levels at urban sites in 2015, as compared to 2013, are substantial and likely attributed to new sources/emissions of these compounds. Concentration ranges of total PFSAs, PFCAs and the commonly monitored PFOS and PFOA at the three location types are listed in Table S23, as well as concentration ranges from other reported studies in these regions.

The PFAAs have been reported previously at polar locations, from three Arctic monitoring stations during 2006–2014 (Wong et al., 2018). The concentrations of the PFSAs at these monitoring sites (<0.006–4.9 pg/m^3) were in line with the polar GAPS sites in 2009 (<0.02–7.6 pg/m^3) and 2013 (0.16–2.1 pg/m^3), but were 3–4 times lower than the elevated levels observed at the GAPS sites in 2015 (8.5–16 pg/m^3). The PFCAs at these monitoring sites (<0.006–4.2 pg/m^3) were also in line with levels at the GAPS sites in 2009 (<0.1–6.2 pg/m^3) and 2013 (3.9–11 pg/m^3), but lower than the GAPS levels in 2015 (5.9–21 pg/m^3). Even though PFCA concentrations in the GAPS study were not significantly different between 2013 and 2015, this may be indicating levels are increasing in the Arctic region. At the background locations, levels of both PFCAs and PFSAs in the 2009 and 2013 GAPS samples were in line with levels in Switzerland in 2010 of 23 and 1.7 pg/m^3, for the PFCAs and PFSAs respectively (Müller et al., 2012). The PFSAs in 2009 (<0.02–7.6 pg/m^3) and 2013 (0.41–4.7 pg/m^3) were also in line with concentrations over the North Sea in 2007 of $<$MDL-9.1 pg/m^3 (Dreyer and Ebinghaus, 2009). The PFCAs meanwhile, were higher in the GAPS study (in all sampling years) than reported over the North Sea.

Concentrations of the PFAAs at the urban locations in all three sampling years were generally in line with previously reported levels from urban sites in North America/Europe. Concentrations of both PFSAs and PFCAs in Albany (USA) in 2006 of 1.4–4.6 and 2.7–10.7 pg/m^3 respectively (Kim and Kannan, 2007) were in line with the urban GAPS sites in 2009 and 2013 (1.2–76 and < 0.1–17 pg/m^3 for the PFSAs and PFCAs respectively) but lower than the elevated levels of both the PFSAs and PFCAs seen in 2015 (2.1–21 and 64–72 pg/m^3). At Toronto (Canada) levels of PFSAs from an active air sampling campaign in 2010 of 0.38–3.12 pg/m^3 (Ahrens et al., 2012) were in line with levels at this GAPS site in 2009 (4.6 pg/m^3) and 2013 (0.29–4.69 pg/m^3), but lower than the levels seen in 2015 (8.1 pg/m^3). These results are in line with the significant increase in concentrations ($p < 0.05$) of the PFSAs determined in this GAPS study from 2013 to 2015 and suggest PFCA concentrations may also be increasing at Toronto (and the other
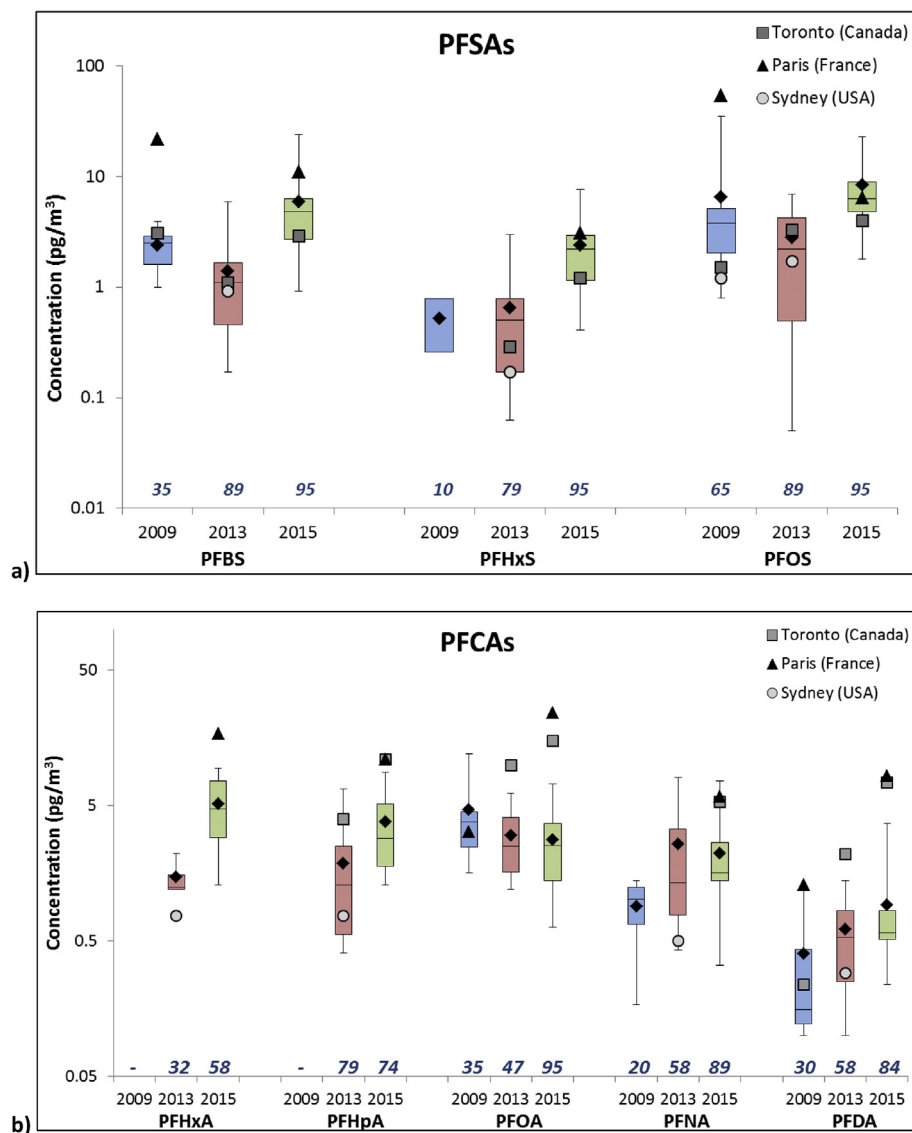
Fig. 3. Box and whisker plots of concentrations (pg/m³) of a) PFSAs and b) PFCAs detected at background and polar sites in 2009, 2013 and 2015. PFHxA and PFHpA were not detected above MDLs in 2009. The boxes show median concentrations and the 25th and 75th percentiles, minimum and maximum concentrations are indicated by the whiskers. Mean concentrations are indicated by the diamond. Where an analyte was below detection limits the sample was not included and detection frequencies are listed below the plots. Concentrations (pg/m³) determined at the three urban sites are indicated separately by the triangles, squares and circles.

urban sites). Active air campaigns at Birmingham (UK) in 2008—2009 (Goosey and Harrad, 2012), semi-rural sites in Germany in 2007 (Dreyer and Ebinghaus, 2009) and at Zurich (Switzerland) in 2010 (Müller et al., 2012) also had levels similar to the 2009 and 2013 GAPS samples (<1—36 and < 1.9—20 pg/m³ for PFSAs and PFCAs respectively). Again, levels in these studies were lower than the elevated concentrations at the GAPS sites in 2015. However, concentrations in all GAPS sampling years were up to an order of magnitude lower than levels reported at Manchester (UK) in 2005 of 44—55 and 231—472 pg/m³ for the PFSAs and PFCAs (Barber et al., 2007). Elevated levels of the n-PFAS (as compared to the GAPS study) were also reported at Manchester, suggesting the Manchester study is collecting a larger input of localized sources than the GAPS urban sites.

Temporal trends of the PFAAs have been previously investigated by Wong et al. (2018) with increasing concentration trends

observed at Alert. Doubling times of the PFAAs ranged 2.5—3.7 years, with high year to year variability in levels. Declining or non-changing trends were seen for PFOS and PFOA at the two Norwegian sites in the study. In the GAPS study, increasing concentrations were observed for the PFSAs at both Alert and Ny-Ålesund (Norway). Generally higher concentrations of the PFCAs were also observed at the polar sites in the 2015 GAPS samples, than in 2009 and 2013. This is in line with the trends determined at Alert by Wong et al. (2018).

The concentrations of the individual PFAAs were regressed against latitude with no significant correlations (p > 0.05) in either 2013 or 2015 (Figure S2). This is perhaps not surprising given the environmental persistence and high water solubility leading to long range transport properties of the PFAAs, as well as constant additional sources of breakdown of the neutral precursors in the atmosphere. All these factors lead to the similar global

concentrations of the PFAAs observed in this study.

3.3. VMS

The individual VMS had a mix of increasing or decreasing tendencies between the sampling years. D4, D5 and D6 had a weak significant increase in concentrations from 2009 to 2013 ($p < 0.05$) with no significant difference ($p > 0.05$) between 2013 and 2015. D3, however, had a strong significant decrease in concentrations from 2013 to 2015 ($p < 0.01$). As concentrations of the D3 at these sites are decreasing while the other cVMS are remaining similar or increasing, this is suggesting that the use of D3 may be reducing with a shift towards the use of the other cVMS. Fig. 4 depicts box and whisker plots of the concentrations of the cVMS in each sampling year. The lVMS are not depicted due to the low detection frequencies (<25%) of these analytes.

The concentrations of the cVMS were at least an order of magnitude higher than the lVMS at all sites. The lVMS were only detected regularly at the urban sites, and the highest concentrations were at Toronto (Canada). The cVMS had similar concentrations at all sites in 2013, regardless of location type. In 2015, however, elevated concentrations of D5 and D6 were detected at the urban sites. D3 and D4 did not show this trend in 2015, with similar concentrations at all location types. Concentration ranges of the sum of the cVMS and lVMS at the three location types (polar, background and urban) are listed in Table S24, as well as concentration ranges from other reported studies in these regions.

At the polar sites, only the cVMS were detected and concentrations (1.6–120 pg/m^3) were higher (by a factor of ~6) than previously reported from active air samples at Zeppelin (Ny-Ålesund, Norway) in 2011 of 0.2–6.5 pg/m^3 (Krogseth et al., 2013a). At the background sites, meanwhile, the concentrations of the cVMS (<0.001–169 pg/m^3) were in line with levels from a rural site in Iowa in 2011 (Yucuis et al., 2013), at Uetliberg (Switzerland) in 2011 (Buser et al., 2013) and Sweden in 2011 (Kierkegaard and McLachlan, 2013) of 8.3–177 pg/m^3. However, concentrations were not in line with a previous study in Portugal in 2014 (Ratola et al., 2016), where concentrations were at least an order of

magnitude lower than in the GAPS study (0.6–1.3 pg/m^3). The variations between studies and the limited atmospheric data available in the polar and background regions show that more environmental monitoring is needed of the VMS.

At the urban sites in the GAPS study, the cVMS and lVMS were generally in line with previously reported studies. The lVMS have been reported at Toronto in 2010–2011 (Ahrens et al., 2014) and 2012 (Krogseth et al., 2013b) with concentrations in both studies (0.78–15 ng/m^3) in line with levels at this site in the GAPS study (1.2–8.1 ng/m^3). The cVMS at Toronto in the GAPS study were also in line with the levels in 2010–2011 and 2012, except for D3. The concentrations of D3 in 2010–2011, of 0.7–2.9 ng/m^3 (Ahrens et al., 2014), are in line with the decrease in concentrations observed at this site from 2009 to 2015, as concentrations of 18, 1.4 and 0.54 ng/m^3 were observed in 2009, 2013 and 2015 respectively. The cVMS have also been reported at urban sites in the USA in 2011 (Yucuis et al., 2013) where concentrations were elevated compared to the GAPS sites at 123–1340 pg/m^3. However, concentrations at the suburban and rural areas reported by Yucuis et al. (2013) were in line with the levels seen at the urban GAPS sites. It is likely that the urban sites in the USA study are capturing higher inputs of localized sources than the GAPS sites. The study by Yucuis et al. (2013) also observed a general trend of increasing atmospheric concentrations with increasing population density. This was also observed for D5 and D6 in the GAPS study, with higher concentrations detected at the urban sites.

Previous studies have investigated the ratio of D5/D4 to provide information on atmospheric sources to a sampling location (Yucis et al., 2013). Due to the different half-lives of the two chemicals (11 days for D4 and 7 days for D5, Yucis et al., 2013) the ratio should be highest around localized emission (sources) and decrease as the air mass moves away from urbanized areas, as the D5 degrades at a faster rate. Ratios of 4.5, 3.1 and 2.1 have been reported for urban, suburban and rural areas respectively (Yucis et al., 2013). In the GAPS study, higher ratios were also seen at the urban sites in all three years (1.0–15). Ratios at the polar sites and the majority of background sites were lower with ratios of <2.0, suggesting atmospheric transport is contributing to these areas. Košetice (Czech
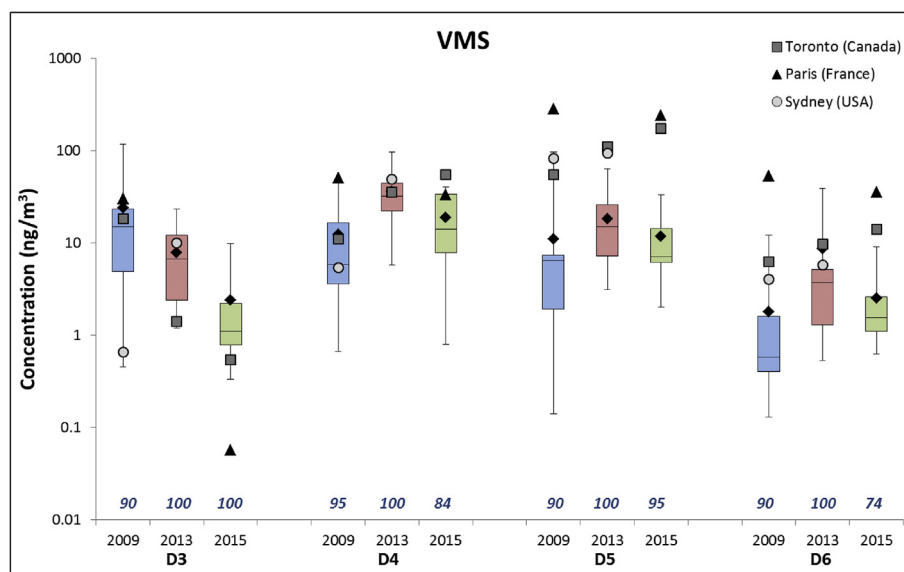
Fig. 4. Box and whisker plots of concentrations (ng/m^3) of D3, D4, D5 and D6 detected at background and polar sites in 2009, 2013 and 2015. The boxes show median concentrations and the 25th and 75th percentiles, minimum and maximum concentrations are indicated by the whiskers. Mean concentrations are indicated by the diamond. Where an analyte was below detection limits the sample was not included and detection frequencies are listed below the plots. Concentrations (ng/m^3) determined at the three urban sites are indicated separately by the triangles, squares and circles.

Republic) and Groton (USA) had more variable ratios (0.5–16) suggesting there may be a combination of sources to these areas. Ratios from all samples are listed in Table S25.

The data was assessed further by comparing concentrations with latitude. There were no significant correlations ($p > 0.05$) between any of the cVMS concentrations and latitude in 2015 (even with the two elevated urban sites removed from the data set). A weak significant negative correlation ($r = 0.46$, $p = 0.023$) was determined between the concentration of D5 and latitude in 2013. The cVMS ratios (e.g. D5/D4) were also investigated with no significant correlations with latitude ($p > 0.05$). Correlations are shown in Figure S3. Even though the VMS have shorter atmospheric half-lives than the n-PFAS, a substantial decrease in concentration as the air mass moves away from source (urban) regions is not being observed in this study. The widespread distribution of the VMS are likely attributed to their relatively high volatility and numerous and constant emission sources to air. As described in the Junge relationship (MacLeod et al., 2013), a higher variability in concentrations at remote sites is also expected of the VMS, as compared to compounds with a higher atmospheric half-life such as the PFAS.

3.4. Seasonal comparison

In 2013, SIP-PAS were deployed for all four sampling quarters to investigate seasonal differences. For the n-PFAS, the urban site of Toronto (Canada) saw higher concentrations of the FTOHs and FOSA/FOSEs in spring/summer (Q2 and Q3, Apr to Oct) (Table S13). This is in line with patterns seen in Toronto from 2010 to 2011 where elevated concentrations were reported in summer (Ahrens et al., 2013). The other urban site sampled in 2013 (Sydney, USA) saw similar concentrations throughout the year with no obvious seasonal differences. Sable Island (Canada) was the only background site to show a general seasonal difference, with higher concentrations of the FTOHs and EtFOSA in Q2 and Q3 (spring/summer). Seasonal trends have been reported previously in the Arctic with elevated concentrations in summer of the FTOHs (Bossi et al., 2016; Wong et al., 2018). However, this was not seen in the GAPS study and no seasonal differences were determined at the polar sites.

Seasonal differences were not observed throughout 2013 for either the PFSAs or PFCAs (Table S15 and S17). Previous studies have reported similar results with no seasonal trends observed during 2010 at Toronto (Ahrens et al., 2013). Seasonal trends of the 4–6 carbon chain PFCAs (Yao et al., 2017) have been reported at a coastal area near the Bohai Sea (China), however, this was not observed in the GAPS samples. Seasonality was also not observed for PFOA or PFOS in a previous study at two Arctic Norwegian sites from 2006 to 2014, although at Alert (Canada) a winter maxima was seen for PFBS and a summer maxima for PFOA (Wong et al., 2018). The polar sites in this GAPS study were similar in behaviour to the Norwegian sites in 2006–2014, with no seasonal differences observed.

For the VMS, ratios of D4/D3, D5/D3 and D6/D3 were investigated to determine seasonal differences (ratios not reported, concentrations given in Table S19). At Toronto, ratios were up to three times higher in Q2 (spring) than in Q3 and Q4 (summer/autumn) which is in line with trends previously reported in urban regions (Gallego et al., 2017; Ahrens et al., 2014). However, no trend was observed at the other urban site (Sydney, USA). Higher concentrations have been reported in summer over winter at various location types in Portugal (Ratola et al., 2016), but this was not observed in the GAPS study. It has also been suggested that seasonality would be more pronounced in remote areas than in source regions (Krogseth et al., 2013b). Constant emissions in source regions should reduce the impact of seasonality from degradation by hydroxyl radicals. However, the ratios at background/polar sites in

this GAPS study were highly variable between the sampling quarters, with no obvious seasonal differences. Bratt's Lake (Canada) and Sable Island (Canada) saw higher ratios in autumn/winter; Stórhöfði (Iceland) and Malin Head (Ireland) saw higher ratios in winter and Cape Grim (Australia) saw higher ratios in summer. As SIP-PAS are deployed for 3 month periods, the time-integrated approach may average out seasonal differences at these sites for the VMS, and the PFAS.

The current study provides atmospheric concentrations of PFAS and VMS over 7 years of sampling in the GAPS Network. The elevated atmospheric concentrations of the VMS over the PFAS are highlighted, a factor of their high and continuous emission to the atmosphere. The n-PFAS saw a tendency for elevated concentrations at the urban sites, compared to the polar/background sites. Concentrations of the FTOHs and EtFOSA were not statistically different between the three sampling years, suggesting levels have remained relatively constant at these 21 sites from 2009 to 2015. The PFSAs saw a statistically significant increase in concentrations in 2015 and concentrations were similar regardless of location type. The PFCAs meanwhile, had elevated concentrations at the urban sites, and while an increase in concentrations was again observed in 2015, it was not significant. The VMS had a mix of increasing or decreasing concentration tendencies with D3 showing a strong significant decrease in concentrations, and D4, D5 and D6 a weak significant increase. D5 and D6 also had elevated concentrations at urban sites and ratios of D5/D4 decreased with population density of the location, which is in line with previous studies.

In this particular study we are yet to observe significant decreasing atmospheric concentrations of the regulated PFAS compounds and the PFAS are actually showing an increase in atmospheric concentrations in 2015. However, future planned sampling campaigns will provide more information on this tendency. As such, it is recommended that further environmental monitoring is required on all these chemicals of concern, particularly in global regions other than the WEOG that have had less attention in monitoring studies.

Appendix A. Supplementary data

Supplementary data related to this article can be found at

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