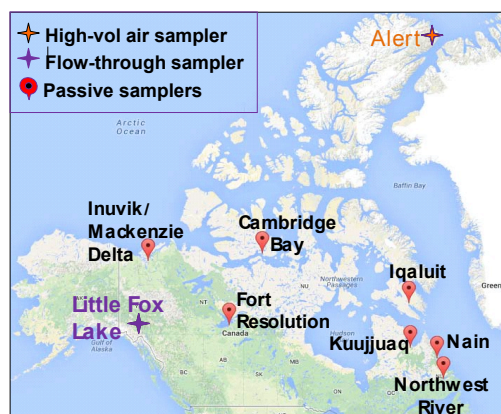




air through a GFF followed by a sampling train consisting of a PUF/XAD/PUF sandwich. GFFs and PUF/XAD/PUF were Soxhlet extracted in DCM and 50:50 acetone-petroleum ether, respectively<sup>6</sup>.

At each of the passive air sampling station, a polyurethane foam (PUF)-disk based passive air sampler (PAS) and a XAD-based PAS (refer to as PUF-PAS and XAD-PAS hereafter) collects time-integrated samples for 3 months and 1 year, respectively. Here, PCBs measured in the XAD-PAS collected in 2015 at 5 sites are presented. The sampling rate of XAD-PAS was 0.59 m<sup>3</sup>/day for the Arctic sites and 1.85 m<sup>3</sup>/day for the urban site<sup>2</sup>.

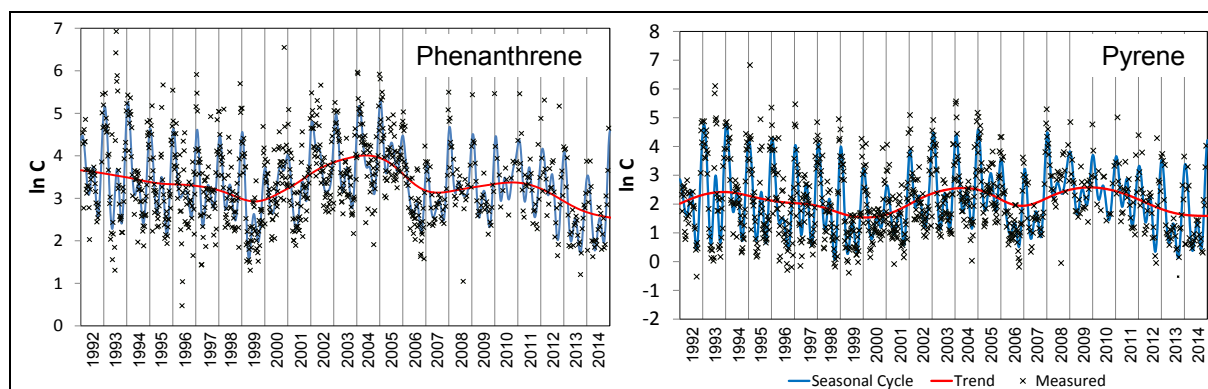


**Figure 1.** Air Monitoring Site Map showing different types of samplers used.

## Results and discussion:

**Levels and Temporal Trends of PAHs at Alert** Air monitoring results for PAHs are available from 1992 to 2014. The annual mean concentrations of  $\Sigma 8$ PAHs [sum of phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR), anthracene (ANT), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IcdP), and benzo(g,h,i)perylene (BghiP)] ranged from 51.0 to 296  $\mu\text{g}/\text{m}^3$ . PHE, FLA and PYR were the most abundant PAHs found. PAH air concentrations were much higher in colder months than warmer months. This observation can be attributed to increased PAH emissions due to space heating in winter and reduced photodegradation during the extended Arctic winter darkness.

Temporal trends of PAHs were assessed with the Digital Filtration (DF) technique which has been successfully used to derive time trends of POPs in Arctic air<sup>1</sup> (trends derived for PYR and PHE are shown in Figure 2). PHE and PYR declined from 1992 to 1999, then increased again from 2001 to 2005. This increase could be associated with the relatively more frequent wildfire events during these years<sup>4</sup> resulting in greater emissions of PAHs. Overall, no significant decline in trends was observed for the PAHs in air at Alert. Global emission of PAHs was estimated to have declined significantly from 1992 to 2015<sup>5</sup>. However, this decline in PAH emissions was not reflected in the temporal trends of PAHs observed in Arctic air. This could be due to increased human activities in the Arctic resulting in greater local emissions or increasing biomass burning due to warming. Continued monitoring is required to confirm the estimated decline in global emissions.



**Figure 2.** Temporal trends of PHE and PYR at Alert derived with DF

**OPEs concentrations** Many OPEs, including tris(2-ethylhexyl) phosphate (TEHP); 2-ethylhexyl diphenyl phosphate (EHDPP); triphenyl phosphate (TPhP); tris(2,3-dichloropropyl) phosphate (TDCPP); tris(2-chloroisopropyl)phosphate (TCPP); tris(2-chloroethyl) phosphate (TCEP); tri-n-butyl phosphate (TnBP), were widely found in Arctic air collected from land- and ship-based air sampling campaigns during 2007-2016<sup>6</sup>.

TCEP dominated the composition of OPEs in most of the sampling years, except 2013. TCEP and to a lesser extent TCPP are volatile and have characteristic travel distances that allow long range transport to occur<sup>6</sup>. Highest OPE levels were found in 2013 where TPhP was the dominating OPE, although TPhP is quite variable and maybe the result of episodic transport events. TnBP was highest at land based stations probably due to the use of aircraft hydraulic fluids that are composed of 50% TnBP.

**PFAS trend update** Data collected from February 2015 to March 2017 at Alert were analyzed for neutral and ionic PFASs. The time trends of 8:2 fluorotelomer alcohol (FTOH), 10:2 FTOH, perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS) in Alert air from 2006 to 2017 were derived using the digital filtration (DF) method. Atmospheric levels of 8:2 FTOH showed an overall increasing trend from 2006 to 2017, with a very long doubling time ( $t_2$ ) of 24 year (y). 10:2 FTOH exhibited a decreasing trend with half-life ( $t_{1/2}$ ) of 19 y. 8:2 and 10:2 FTOH levels peaked in 2012, and both compounds have been decreasing since then. Indeed, half-lives derived from the 2012-2017 data for 8:2 FTOH  $t_{1/2} = 3.5$  y; 10:2 FTOH,  $t_{1/2} = 2.0$  y.

Atmospheric levels of PFOS showed an overall increasing trend from 2006 to 2017 with  $t_2 = 4.9$  y. Similar to the FTOHs, PFOS appeared to have peaked in 2013. The half-life derived from the 2013-2017 data for PFOS was 2.0 y.

PFOA, PFBA and PFBS levels in air exhibited increasing trends from 2006 to 2017. The doubling times were: PFOA = 4.8 y, PFBA = 3.6 y; PFBS = 3.4 y.

**PCBs in XAD-based Passive Samples (PAS) in 2015** We have analysed the XAS-PAS collected in 2015 for 27 PCB congeners. The target PCB congeners were: 11, 18, 28+31, 44, 52, 70, 77, 100, 101, 105, 110, 114, 118, 119, 126, 131, 138+163, 153, 156, 170, 171, 172, 180, 199 and 202. XAD-PAS were one-year integrated sample and designed to capture gas-phase compounds only. There was one field blank analyzed for each site. Trace levels of PCBs were found in the field blanks. Data presented here were blank corrected according to the field blank obtained at the specific site.

The names of the Arctic sites and abbreviations used in the following discussion were: Fort Resolution (FR), Inuvik (IN), Iqaluit (IQ), Kuujuaq (KU), Nain (NA). Downsview (DV) is the urban site.

In general, the sum of 27 PCBs for all sites, from highest to lowest concentrations were: DV (8.6 pg/m<sup>3</sup>) > NA (7.1 pg/m<sup>3</sup>) > IN (2.2 pg/m<sup>3</sup>) > FR (1.4 pg/m<sup>3</sup>) > KU (0.0014 pg/m<sup>3</sup>) > IQ (0.0008 pg/m<sup>3</sup>).

PCB concentrations in air in the urban site, DV, were higher than in the Arctic sites. This is expected as PCBs consumptions and storage are mostly in urban/industrial areas. Previous studies have reported higher atmospheric PCB levels were associated with urban sites (Poza et al., 2009; Silva-Barni et al., 2018). However, it is interesting to observe that levels of PCBs in air from NA were only slightly lower than those in DV. This may suggest local point sources (such as waste burning, PCB-containing transformers) of PCBs at NA near the sampling site.

PCB levels were within the same range as those reported in air in Alert and other Arctic sites. The mean sum of 8 PCBs (i.e. 28+31, 52, 101, 105, 118, 153, 180) in the 5 Arctic sites was 1.1 pg/m<sup>3</sup>, ranging from non-detect to 3.7 pg/m<sup>3</sup>. The sum of 7 PCBs (i.e. 28, 52, 101, 105, 118, 153, 180) in Alert was 1.7 pg/m<sup>3</sup> in 2012 (data available at ebas.nilu.no). In air in Finland during 2011, the sum of 7 PCBs in Råö was 12.5 ± 7.5 pg/m<sup>3</sup> and in Pallas was 4.1 ± 3.4 pg/m<sup>3</sup> (Anttila et al., 2016). In air in Norway, the sum of 7 PCBs in 2015 ranged from 1.8-2.8 pg/m<sup>3</sup> for the three sites: Andøya, Zeppelin and Birkenes (NEA 2016).

In conclusion, our initial results indicate that PCBs were found in our Arctic passive air sampling sites. Our measurements were consistent with previous reports. We will further investigate the sources and transport of these chemicals to the Arctic and performance of the XAD-PAS.

#### **Acknowledgements:**

The team would like to acknowledge NCP (Indigenous and Northern Affairs Canada) for funding. The analysis of emerging chemicals at Alert is co-funded by Environment and Climate Change Canada's Chemicals Management Plan (CMP). The sampling and analysis for samples collected on-board the Amundsen Icebreaker is co-funding by ArcticNet and NCP. The continued support of the 5 Regional Contaminants Committees, northern community members and associations of the passive air sampling initiative is greatly appreciated. We would also like to thank all volunteers/agencies which provided sample change service for the PASs.

#### **References:**

1. Hung H, Katsoyiannis AA, Brorström-Lundén E, Olafsdottir K, Aas W, Breivik K, Bohlin-Nizzetto P, Sigurdsson A, Hakola H, Bossi R, Skov H, Sverko E, Barresi E, Fellin P, Wilson S (2016) *Environ. Pollut.*, 217: 52-61.
2. Hayward SJ, Gouin T, Wania F (2010) *Environ. Sci. Technol.* 44: 3410-3416.
3. Becker S, Halsall CJ, Tych W, Hung H, Attewell S, Blanchard P, Li H, Fellin P, Stern G, Billeck B, Friesen S (2006) *Environ. Sci. Technol.* 40: 3217-3222.
4. MODIS Active Fire Product <http://modis-fire.umd.edu/pages/ActiveFire.php> (data downloaded March 10, 2018)
5. Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W, Liu J, Tao S (2013) Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions, *Environ. Sci. Technol.* 47: 6415-6424.
6. Sührling R, Diamond ML, Scheringer M, Wong F, Pučko M, Stern G, Burt A, Hung H, Fellin P, Li H, Jantunen LM (2016) *Environ. Sci. Technol.*, 50: 7409-7415.
7. Wania F, Shen L, Lei YD, Teixeira, C, Muir, DCG(2003) *Environ. Sci. Technol.* 37: 1352-1359.