Temporal Trends of Persistent Organic Pollutants and Chemicals of Emerging Arctic Concern in Arctic Air

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Introduction

Air monitoring of Persistent Organic Pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEAC) is conducted under Canada's Northern Contaminants Program (NCP) and Chemicals Management Plan (CMP). Air monitoring of POPs started at the Canadian High Arctic station of Alert, Nunavut (82°30'N, 62°20'W) since 1992. CEAC, including neutral and ionic per- and polyfluoroalkyl substances (PFASs), halogenated flame retardants (HFRs) and organophosphate esters (OPEs), are screened for in air samples collected to assess the long-range transport potential (LRTP) of these compounds in support of national and international chemical control initiatives. This study will provide an update on the temporal trends and air concentrations of polycyclic aromatic hydrocarbons (PAHs), PFASs and OPEs found at Alert to better understand and evaluate the effectiveness of control measures.

Air sampling for POPs and CEAC was also conducted on-board the Amundsen Icebreaker from 2007-2016 under ArcticNet. In this study, we report OPE measurements from the cruises in comparison with land-base measurements from Alert.

To expand the geographic coverage of the air monitoring program, 7 new passive air sampling stations have been planned since 2014 (Figure 1). Here, analytical results of polychlorinated biphenyls (PCBs) measured in the passive air samplers (PAS) collected in 2015 from 5 Arctic sites are reported in comparison with results from one urban site in Downsview, Ontario.

Materials and methods

Weekly air samples were collected at Alert with a custom-made super-high volume air sampler. Each air sample represents approximately 13000 m^3 of air sampled over 7 days. A 20 cm glass fibre filter (GFF) and two polyurethane foam (PUF) plugs (4 cm×20 cm diameter), were used to collect the respective particle and vapour fractions. Collected samples were extracted by Soxhlet for 24 h using dichloromethane and hexane for GFFs and PUFs, respectively. Details of sampling and analysis can be found elsewhere[1]. These samples were analyzed for PAHs, organochlorine pesticides, PCBs and HFRs. A new PS-1 high-volume air sampler was setup at Alert in 2006 to capture PFASs. The PS-1 sampler was equipped with a GFF to sample particles and a sandwich cartridge of PUF/XAD-2/PUF to trap gaseous species. Particle-phase OPEs monitoring started in 2015 with samples taken with a PS-1 high volume air sampler using a GFF/QFF only. Sampling for both PFASs and OPEs generally occurred once a month from October to February and once every other week from March to September. Air samples for PFASs were extracted with an accelerated solvent extractor (ASE). GFF and PUF/XAD/PUF were extracted with hexane followed by methanol. Filters for OPEs were soxhlet extracted overnight in dichloromethane. Air samples collected while on board the Amundsen were collected by drawing

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[6].

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^3/day for the Arctic sites and 1.85 m^3/day for the urban site[2].

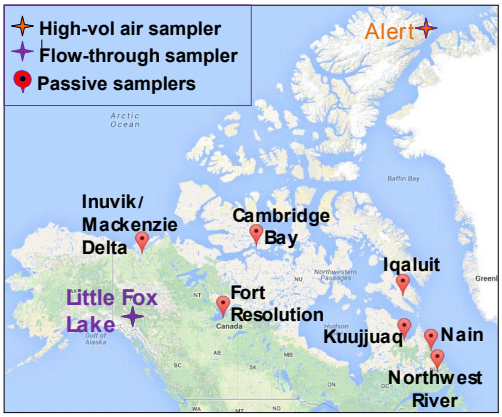

Figure 1. Air Monitoring Site Map showing different types of samplers used.

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 Σ8PAHs [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 pg/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[1] (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[4] 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[5]. 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.

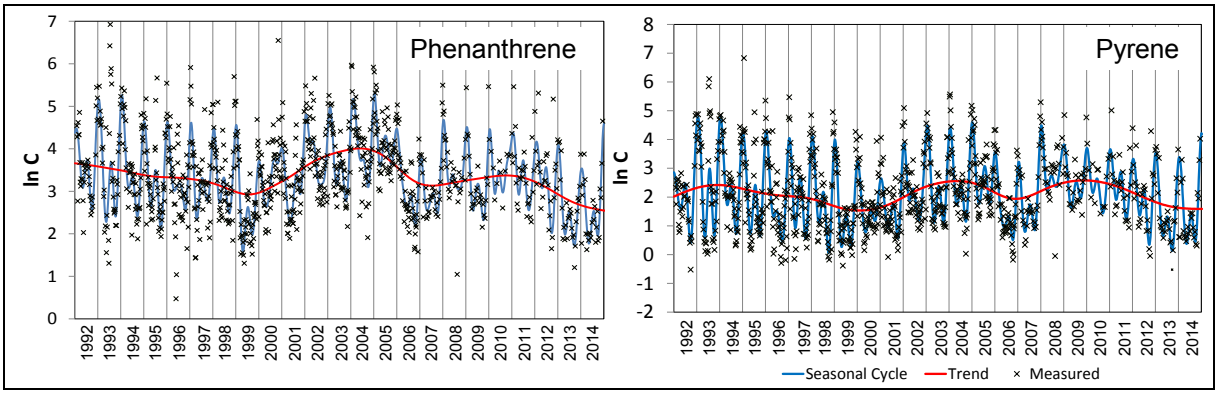

Figure 2. Temporal trends of PHE and PYR at Alert derived with DF

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[6].

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[6]. 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-live 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), Kuujjuaq (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^3) > NA (7.1 pg/m^3) > IN (2.2 pg/m^3) > FR (1.4 pg/m^3) > KU (0.0014 pg/m^3) > IQ (0.0008 pg/m^3).

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 (Pozo 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^3, ranging from non-detect to 3.7 pg/m3. The sum of 7 PCBs (i.e. 28, 52, 101, 105, 118, 153, 180) in Alert was 1.7 pg/m^3 in 2012 (data available at ebas.nilu.no). In air in Finland during 2011, the sum of 7 PCBs in Råo was 12.5 ± 7.5 pg/m^3 and in Pallas was 4.1 ± 3.4 pg/m3 (Anttila et al., 2016). In air in Norway, the sum of 7 PCBs in 2015 ranged from 1.8-2.8 pg/m3 for the three sites: Andøya, Zepplein 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.

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