Persistent Organic Pollutants and Chemicals of Emerging Concern in Canadian Arctic Air

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Introduction

The Canadian Northern Contaminants Program (NCP) monitors for persistent organic pollutants (POPs) and other priority organic pollutants in Arctic air at the High Arctic station of Alert, Nunavut (82°30'N, 62°20'W) since 1992. Air samples were screened for emerging contaminants, including halogenated flame retardants (HFRs), neutral and ionic per- and polyfluoroalkyl substances (PFASs) and short-chain chlorinated paraffins (SCCPs), to assess the long-range transport potential (LRTP) of these compounds in support of national and international control initiatives. This study will provide an update on the time trends and air concentrations of POPs and emerging contaminants found at Alert to better understand and evaluate the effectiveness of control measures.

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 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

At Alert, weekly air samples were collected 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]. Air monitoring for polybrominated diphenyl ethers (PBDEs) started at this location in 2002. Screening for HFRs started in 2007. In 2006, a new PS-1 high-volume air sampler was setup at Alert to capture PFASs. Sampling generally occurred once a month from October to February and once every other week from March to September. 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. Air samples were extracted with an accelerated solvent extractor (ASE). GFF and PUF/XAD/PUF were extracted with hexane followed by methanol.

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.

Site names and number of PUF-PAS (*n*) analyzed were: Fort Resolution (*n* = 4), Inuvik (*n* = 4), Iqaluit (*n* = 3), Kuujjuaq (*n* = 2), and Nain (*n* = 3), Downsview (*n* = 4). Downsview is the urban site. Two XAD-PAS were extracted at each site, and the extracts were combined for analysis. The PUF-PAS and XAD-PAS samples were extracted using Acelerated Solvent Extraction (ASE) with petroleum ether/acetone (5:1) and hexane/acetone (1:1) respectively. The PUF-PASs and XAD-PASs were analysed for 26 organochlorines (OCs), 17 HFRs, 14 PBDEs, 2 brominated anisoles (BA), and 10 neutral PFASs. PAS results are presented in units of $pg \cdot m^{-3}$ by assuming linear uptake of chemicals by the PUF- and XAD-PAS. The sampling rate of PUF-PAS was assumed to be 4 $m^3 \cdot day^{-1}$ for all sites [2], and XAD-PAS was 0.59 $m^3 \cdot day^{-1}$ for the Arctic sites and 1.85 $m^3 \cdot day^{-1}$ for the urban site [3].

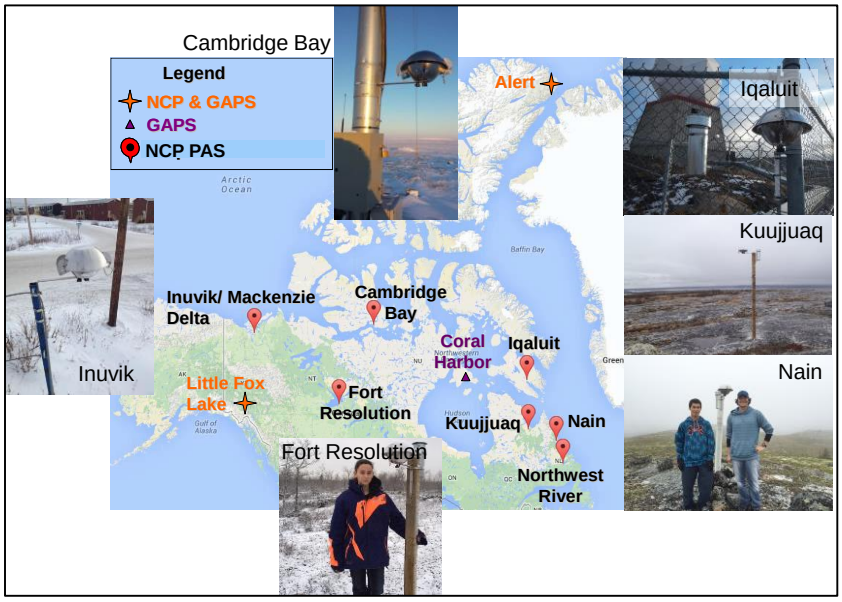

Figure 1 Air Monitoring Site Map (Sites in orange and purple fonts are existing air monitoring sites under the NCP and the Global Atmospheric Passive Sampling (GAPS) network.

Results and discussion

According to the last assessment of temporal trends of POPs in Arctic air under the Arctic Monitoring and Assessment Programme (AMAP)[1], most legacy POPs are declining reflecting the effectiveness of national and international control initiatives such as the Stockholm Convention. With two additional years of data collected from Alert since the last assessment, endosulfan I which has not shown any significant decline up to 2010 is now showing a clear declining trend up to 2014 with a half-life of 14 years. In addition, PBDEs which were not declining in air at Alert up to 2012 in the last assessment, in contrast to declining trends in European Arctic air, are now showing slow declining trends between 2012 and 2014 with half-lives of 15 and 10 years for BDE 47 and 99, respectively. Monitoring needs to continue to confirm such declining trends.

Several HFRs, e.g. hexabromocyclododecane (HBCD), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromophthalate (BEHTBP), 2,3,5,6-tetrabromo-p-xylene (TBX) and pentabromobenzene (PBBz), were frequently detectable in air at Alert. However, the concentrations were very low and seasonal variations were not consistent for most compounds. Despite the fact that 7 years of data are now available (2008-2014), it is not possible to estimate temporal trends for these compounds because blank levels were relatively high in certain years for different HFRs. Efforts are being made to ensure that field and lab blank levels remain as low as possible in order to derive time trends in the future.

Neutral and ionic PFASs were being analyzed in air samples from Alert. Perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorobutanoic acid (PFBA) and perfluorobutane sulfonic acid (PFBS) showed increasing trends at Alert, with doubling times of 3.7 y, 2.9 y, 2.5 y and 2.6 y, respectively. Increasing trends of PFBA and PFBS may reflect the shift from long to short chain fluorochemical production.

The HFRs, PBDEs, and neutral PFASs were rarely found in the Arctic sites and the concentrations were close to the detection limits. OCs/BAs, e.g. hexachlorobutadiene (HCBD), hexachlorobenzene, (HCB), pentachloronitrobenzene (PCNB), pentachloroanisole (PCA), 2, 4-dibromoanisole (DBA), and 2, 4, 6-tribromoanisole (TBA), were frequently detected in the samples.

The overall means and ranges ($pg \cdot m^{-3}$) of chemicals in the PUF-PAS from the 5 Arctic sites were: HCBD = 10 (4.3-21), HCB = 130 (30-280), PCNB = 77 (18-150), PCA = 8.0 (1.7-13), DBA = 17 (8.1-28), TBA = 98 (20-205). For the urban site, Downsview, which is used as a reference here: HCBD = 2.4 (0.8-5.1), HCB = 26 (9.2-54), PCNB = 15 (5.2-32), PCA = 8.0 (5.7-11), DBA = 3.5 (2.1-5.5), TBA = 14 (3.4-24).

The concentrations and ranges ($pg \cdot m^{-3}$) of chemicals in the XAD-PAS from the 5 Arctic sties were HCBD = 770, HCB = 110 (510-1230), PCNB = 42 (31-62), PCA =6.7 (3.9-13), DBA =35 (17-70), TBA = 150 (71-300). For the urban site, Downsview: HCBD =67, HCB = 25, PCNB = 8.4, PCA = 10, DBA =4.1, TBA = 22.

Among the Arctic sites, Iqaluit, which is the most populated among all 5 sites, has the highest concentration in HCBD, HCB, PCNB, PCA and DBA, and TBA, while Fort Resolution has the lowest concentration in all of the above mentioned OCs/BAs. The levels of most OCs/BAs, except PCA, at the urban site, Downsview, were lower than the Arctic sites. There is no clear seasonality observed in the PUF-PASs which were deployed in different seasons. Mean concentration of HCBD in XAD-PASs was 80 times higher than PUF-PASs but concentrations of other chemicals in the XAD- and PUF-PASs agreed well, varying within a factor of two. Class and Ballschmiter [4] reported that HCBD at 18 background stations in Europe and North Atlantic Ocean, ranged from 210 to 3200 $pg \cdot m^{-3}$, with geometric mean of 1800 $pg \cdot m^{-3}$. The literature value is higher than our mean PUF-PAS concentrations at the Arctic sites (i.e. 10 $pg \cdot m^{-3}$). However, mean HCBD concentration in the XAD-PASs was 770 $pg \cdot m^{-3}$, which is 80 times higher than that found in the PUF-PASs, but within the range to those reported by Ref. [4]. HCBD has a relatively high vapour pressure (20 *Pa at 20°C* [5]). It is possible that the chemical has reached equilibrium during the 3-month deployment period of the PUF-PAS, thus sampling volume of the PUF-PAS was over-estimated, resulting in a lower concentration. The assumption of linear uptake for PUF-PAS may not be valid. XAD-PAS has a high uptake capacity and uptake of HCBD should be linear, thus providing a better estimation of air concentration [3].

Bromoanisoles (BAs) are transformation products of bromophenols (BPs) by microorganisms. BPs are

manufactured as fumigants, wood preservatives, and intermediates for the production of high-molecular weight flame retardants. They are also naturally produced by marine organism. Wong et al. [6] reported that levels of DBA and TBA in Canadian Archipelago in 2008 were 16 and 23 $pg \cdot m^{-3}$ in marine air respectively. Recent measurements of DBA and TBA in the Baltic in 2012-2013 were 21 and 43 $pg \cdot m^{-3}$ respectively [7]. Our measurements of the BAs were within the range of the literature values.

Initial PAS results indicate that the volatile OCs/BAs were commonly found in our Arctic sites. PUF- and XAD-PAS provided good means in capturing the volatile organic chemicals in Arctic air.

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