

LONG TERM AIR MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN THE CANADIAN ARCTIC AND GREAT LAKES

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are environmental contaminants of concern released as a result of incomplete combustion of organic material such as fossil fuel and biomass. PAHs are carcinogenic and may have genotoxic effects in humans. In 1992, Environment and Climate Change Canada (ECCC) has initiated long-term air monitoring of PAHs at the Canadian High Arctic Station of Alert (Nunavut) under the Northern Contaminants Program (NCP). In 1997, air monitoring of PAHs in the Great Lakes Basin (GLB) began to provide scientific information in support of the Canada/U.S. Great Lakes Water Quality Agreement. The purpose of both programs are to assess long-range transport of PAHs to sensitive ecosystems, to provide insight in the sources of these substances in the Canadian environment and to develop long-term time trends of PAHs to assess effectiveness in emission control strategies. In this study, we will explore the spatial and temporal differences in PAH concentrations observed in air in the Canadian Arctic and the Great Lakes.

Materials and methods

Air Sampling

Locations for air monitoring of PAHs are shown in Figure 1. At the Canadian High Arctic Station of Alert (Nunavut), weekly air samples are collected using a custom-made super high-volume air sampler, with one 20 cm glass fiber filter (GFF) and two polyurethane foam (PUF) (20 cm diameter, 4 cm thickness) to capture particle and gas phase compounds separately in ~13000 m³ of air over 7 days from 1992 to 2015. In the Great Lakes, air samples were collected at Burnt Island (BNT), Egbert (EGB), and Point Petre (PPT) from January 1997 to March 2013, from January 1997 to March 2006 and from January 1997 to December 2015, respectively. Samples were taken on a PS-1 high-volume sampler. Samples were collected at a variety of intervals (every 6 days, every 12 days, every 36 days) for a 24-hour period. The sample canister consists of a 102-mm diameter round GFF, followed by a PUF.

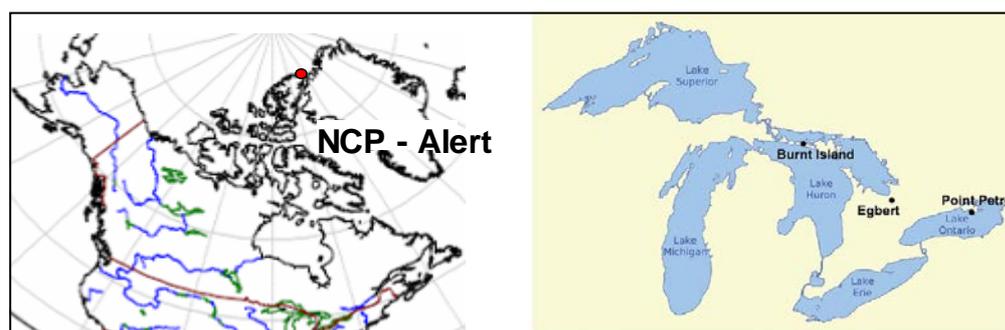


Figure 1. Air Monitoring Stations in the Canadian Arctic and Great Lakes

Sample extraction and analysis

Samples collected from Alert were extracted by Soxhlet for 24 h using dichloromethane and hexane for GFFs and PUFs, respectively. Samples were split into two portions, one is archived and the other was analyzed for various persistent organic pollutants, including PAHs. Each GFF and PUF extract was cleaned up with an alumina/silica gel column and fractionated into a hexane and a 1:1 hexane:dichloromethane fraction before quantification with external calibration. PAH analysis was performed using gas chromatography-mass spectrometry (GC-MS). Analytical details can be found in Halsall et al.¹.

For the Great Lakes samples, the PUFs and GFFs were extracted in hexane by Soxhlet and in hexane/acetone (70/30, V/V) using an accelerated solvent extractor, respectively. The extract for PUF and GFF was volume reduced by Turbovap, blow-down using nitrogen and solvent-exchange to iso-octane. The extract was then cleaned up using silica Solid-Phase Extraction, elution by dichloromethane, volume reduction by Turbovap, nitrogen blowdown, and finally solvent exchange to iso-octane and then acetonitrile. The analysis of PAHs was performed by high-performance liquid chromatography - wavelength-programmed fluorescence and UV detection.

Trend analysis technique

For developing trends of PAHs found at Alert, the dynamic harmonic regression (DHR) method, which can handle extreme values and time series breaks, was used². DHR was chosen because the winter time air concentrations of PAHs found at Alert were much higher than those found in the summer time. In the summer, PAHs were mostly non-detectable in arctic air, resulting in breaks in time series. On the other hand, for air measurements of PAHs observed in the Great Lakes, the digital filtration (DF) technique was used for developing the temporal trends and seasonal cycles. Although winter time concentrations of PAHs were also higher than in the summer in the Great Lakes Basin, the differences between summer and winter concentrations were not as large as those observed at Alert. Venier et al.³ compared four commonly-used time series models for developing long-term time trends for persistent organic pollutants and found that DF and DHR methods provide comparable results in time trends and both can capture smaller scale interannual variations in long-term trends.

The Seasonal Kendall test was further performed for all time trends observed at Alert and in the Great Lakes to test the statistical significance of the trends. Negative Z_{sk} values mean a decline and positive Z_{sk} values mean an increase and p-values are used to confirm if the trends were statistically significant.

Results and discussion:

PAH concentration distributions and profiles

Total air concentrations (gas + particle phases) of 8 PAHs [Σ 8PAH, including phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz-a-anthracene (BaA), benzo-e-pyrene (BaP), indeno-1,2,3-c,d-pyrene (IcdP), and benzo-g,h,i-pyrene (BghiP)] measured in the Great Lakes fluctuated between 24 and 12000 pg/m^3 for the three sampling sites. The median air concentrations of Σ 8PAH were 380, 1700 and 890 pg/m^3 for BNT, EGB and PPT, respectively. The median air concentration of Σ 8PAH found at the Arctic site of Alert was 48 pg/m^3 which is much lower⁴. This is reasonable due to the remoteness of the site. PAH concentrations were dominated by PHE in both the Great Lakes and at Alert; with the concentrations ranging from 6.6 to 7000 pg/m^3 at the three Great Lakes sites and PHE concentrations ranged from 1.60 to 1600 pg/m^3 at Alert⁴. Other dominant PAHs were fluorene (FLU), FLA, and PYR with the average concentrations in the ranges of 130-460, 80-360, and 50-240 pg/m^3 at the Great Lakes sites of BNT, EGB, and PPT, respectively. These compounds also dominate the PAH profile at Alert with average concentrations of FLU 125 pg/m^3 ; FLA 30.2 pg/m^3 ; and PYR 22.1 pg/m^3 , which are also much lower than those observed in the Great Lakes region⁴.

In general, Σ 8PAH concentrations decreased from the most populated site (EGB) to less populated site (PPT) to background site (BNT), then to the remote Arctic site of Alert. This trend was found for most of the PAHs which is probably due to the influence of human settlements, as EGB is close to the city of Toronto while the other two Great Lake sites are further away from human settlements and the Alert site is most remote. This finding was consistent with the previous study which found that higher PAHs levels in the atmosphere of the Great Lakes basin tend to be found at locations surrounded by more people⁵.

Seasonality

To assess the seasonality of PAHs, the sampling periods in the Great Lakes were separated into four seasons from December to February, March to May, June to August, September to November. In general, the highest concentrations of PAHs were found in the coldest season between December to February. For PPT, the average concentration of Σ PAH was found in the coldest season (2800 pg/m^3), while the lowest concentration was detected in the hottest season between June to August (1200 pg/m^3). This difference suggested that the sources of PAHs in the air samples were significantly affected by seasonal variations of the fuel burning and the space heating system in the wintertime.

For the Arctic site, the sampling periods were separated into two seasons, i.e. warm, sunny season from May to October and the cold, dark season from November to April. The concentrations and detection frequencies of

PAHs during the cold, dark seasons were much higher than those in warm sunny seasons as mentioned above. Back trajectory analysis suggests that air arriving at Alert during the coldest months of December to February includes more air masses from Russia than in other months⁴.

Temporal trends

At Alert, PHE and PYR (Figure 2) increased significantly between 2001 and 2005 to levels similar to that found in the early 1990s. From 2006 to 2015, their concentrations increase and declined again. This complex trend can be attributed to much higher concentrations in the summers during 2003 to 2005 which may be associated with more frequent active forest fire events in Canada, Alaska and Greenland⁴. Higher PAH concentrations were also observed in the summer of 2015 coinciding with more frequent forest fire of that year. Retene (RET) which is a tracer for softwood burning showed high levels during 2003-2005 and 2015, confirming the potential contribution of forest fire events to elevated levels of PAHs observed at Alert. Overall, no apparent decline in air concentrations of lighter PAHs were observed at Alert since 2000; while declining trends in the 1990s were observed for heavier PAHs, e.g. benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbFA) and benzo(e)pyrene (BeP). This is probably because a warming Arctic results in greater volatilization of lighter PAHs from environmental sinks, e.g. open oceans, sustaining levels of lighter PAHs in air; while heavier PAHs which tend to be particle-bound were less affected by temperatures.

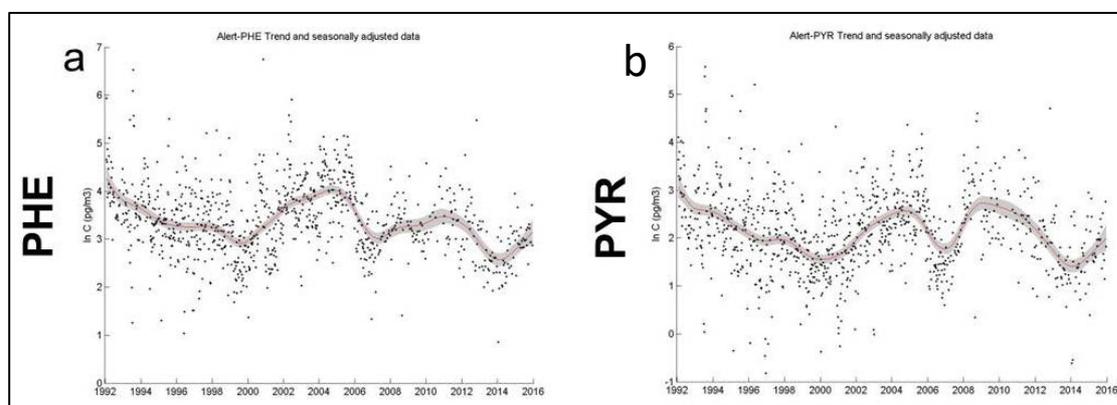


Figure 2. Temporal trends of (a) PHE and (b) PYR at Alert developed using DHR⁴

For the Great Lakes, the dominant PAH of PHE did not show significant changes in air concentrations over time at BNT and PPT. However, for most of the higher molecular weight PAHs, their concentrations at the three Great Lake sites showed decreasing trends since 1997. For BNT, 6 out of 21 PAHs showed the significantly decreasing trends with halving time ranged from 4.2-21 years ($Z_{sk} = -11$ to -2.0 , $p < 0.05$), and only 3 PAH congeners showing significantly increasing trends ($Z_{sk} = 2.2$ to 5.3 , $p < 0.05$). For EGB, 7 PAH congeners were decreasing during 1997-2006, and only three PAH congeners showing significantly increasing trends ($Z_{sk} = 2.0$ to 2.6 , $p < 0.05$). For PPT, concentrations of 17 out of 21 PAH congeners were significantly decreasing with the halving life ranged from 3.6-32 years ($Z_{sk} = -11$ to -2.4 , $p < 0.05$), while the trends for other seven PAHs were not changing over time ($p > 0.05$). The overall declining trends of PAHs measured in the Great Lakes reflect the effective control of PAH emissions in the region.

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