

Polycyclic Aromatic Hydrocarbons Not Declining in Arctic Air Despite Global Emission Reduction

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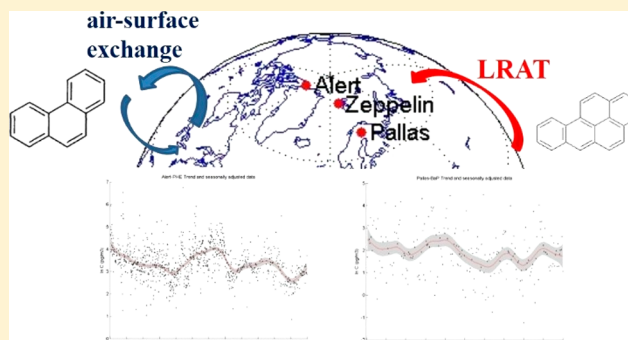
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Supporting Information

ABSTRACT: Two decades of atmospheric measurements of polycyclic aromatic hydrocarbons (PAHs) were conducted at three Arctic sites, i.e., Alert, Canada; Zeppelin, Svalbard; and Pallas, Finland. PAH concentrations decrease with increasing latitude in the order of Pallas > Zeppelin > Alert. Forest fire was identified as an important contributing source. Three representative PAHs, phenanthrene (PHE), pyrene (PYR), and benzo[*a*]pyrene (BaP) were selected for the assessment of their long-term trends. Significant decline of these PAHs was not observed contradicting the expected decline due to PAH emission reductions. A global 3-D transport model was employed to simulate the concentrations of these three PAHs at the three sites. The model predicted that warming in the Arctic would cause the air concentrations of PHE and PYR to increase in the Arctic atmosphere, while that of BaP, which tends to be particle-bound, is less affected by temperature. The expected decline due to the reduction of global PAH emissions is offset by the increment of volatilization caused by warming. This work shows that this phenomenon may affect the environmental occurrence of other anthropogenic substances, such as more volatile flame retardants and pesticides.



INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic pollutants released into the environment primarily through incomplete combustion of fossil fuels and biomass. They are of great public concern due to their toxicity and potential carcinogenicity. PAHs can undergo long-range atmospheric transport (LRAT) to remote locations and are listed for regulation under the United Nations Economic Commission for Europe (UNECE) Aarhus Protocol on Persistent Organic Pollutants (POPs) in the Convention on Long Range Transboundary Air Pollution (CLRTAP).^{1–3} Due to their tendency to travel over long distances, PAHs are regularly detected in very remote areas, far away from primary

sources. As such, PAHs are ubiquitous in the Arctic environment. Levels of most regulated POPs are declining over time in the Arctic environment, reflecting the effectiveness of national and international emission control initiatives such as CLRTAP and the Stockholm Convention on POPs.^{4,5} However, temporal trends of PAHs measured in various Arctic media did not show consistent declining trends,^{6–8} despite the estimated reduction in global PAH emissions from 592000 to

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499000 tons between 1995 and 2008.⁹ Studies have shown that PAHs measured in Arctic marine waters and sediments mainly originate from natural underwater hydrocarbon seeps,^{10–12} while those measured in air originate from atmospherically derived sources, making the air the most suitable medium for PAH monitoring to verify the outcome of regulations on PAH emissions. In addition, their occurrence in the Arctic atmosphere is of particular importance because what is detected is the combined result of LRAT, continuous regional emissions (heating, industrial activities), and temporary local emissions due to commercial and other activities (maritime traffic, coal mining etc.). In a warming Arctic, PAH emissions due to increased human activities within the Arctic may also increase.

PAHs are characterized as “seasonal contaminants” as space heating is one of the most important sources, suggesting that their concentrations in winter are much higher than their respective levels during the warmer months. In addition, some PAHs are subject to photodegradation. With the extended winter darkness in the Arctic, PAHs can behave differently in the Arctic atmosphere than regions that experience a regular diurnal cycle of daylight.¹³ For some of the above reasons, PAHs have been identified as emerging contaminants in the Arctic.⁶

The Arctic Monitoring and Assessment Programme (AMAP) investigated the occurrence of POPs in the Arctic atmosphere for three decades.^{4,14} Here, we use long-term measurement data sets (~20 years) of PAHs in Arctic air collected at three AMAP sites, i.e., Alert, Canada; Zeppelin, Svalbard; and Pallas, Finland, to assess sources, transport pathways, and cycling of PAHs in Arctic air, and from their temporal trends, try to evaluate the outcome of reduction in PAH global emissions.

The Arctic is recognized as a key area for studying climate effect on pollutants due to its sensitivity to climate change. Climate change-driven processes, e.g., temperature, precipitations, and winds, may affect the LRAT and temporal trends of POPs in the Arctic atmosphere.^{15,16} One approach to test the relationship between climate change and the variation of POPs is by comparing modeling results and long-term monitoring data.^{17,18} These large data sets may help to provide greater insight on the influence of climate change on temporal trends of PAHs.

METHODS

Sampling. The locations of the sampling sites are shown in Figure S1. A super high-volume air sampler (SHV) was employed to collect air samples at the Alert Global Atmosphere Watch Observatory, Nunavut, Canada (82.50°N, 62.33°W, 200 m a.s.l.) from 1992 to 2015. One 20 cm glass fiber filter (GFF) and two polyurethane foam (PUF) plugs (20 cm diameter, 4 cm thickness) were used to trap the particle and gas phase compounds separately in approximately 13500 m³ of air over a 7-day sampling period. In the Norwegian-operated Zeppelin Observatory, Ny-Ålesund, Svalbard (78.91° N, 11.88° E, 478 m a.s.l.), a high-volume air sampler (HV) was employed to sample from 1994 to 2015. Two-day integrated weekly samples with a total sample volume of about 1200 m³ of air were collected every week with one 11 cm GFF and two PUFs (11 cm in diameter and 5 cm in height). In Pallas, Finland (68.0°N, 24.24°E, 340 m a.s.l.), 7-day integrated samples (1996–2008) with a volume of ~4000 m³ and 30-day integrated samples (composite of 4 weekly samples) (2009–

2015) with a volume of ~16000 m³ air were collected with a HV. One 14 cm GFF and three PUFs (11 cm diameter, 4.5 cm thickness) were used to collect the particle and gaseous substances. The sampling frequency and extraction strategy may vary in different years (Table S1), subject to availability of funds. The details about the analytical procedure and breakthrough can be found in the Supporting Information.

Data and Analysis. PAH concentrations of Alert are entered into the Research Data Management and Quality Control (RDMQ) system which is a software system written in SAS for data management that includes an extensive flagging system to highlight anomalies and to perform data quality checks. Data from all three sites were reported to the EBAS database (ebas.nilu.no). To ensure data quality, two large-scale interlaboratory comparison studies were conducted for the analysis of trace organic chemicals in Arctic air and an air sample was shared among all participating laboratories.^{19,20}

A Positive Matrix Factorization (PMF, version 5.0) model recommended by the USEPA was used to quantify the contribution of various emission sources to PAHs in the Arctic. For all PAH congeners, the specificity of unknown sources is excluded, and the congeners with weak signal-to-noise ratio and poor linear relationship were removed based on the PMF guideline.²¹ PMF analysis was repeatedly run 20 times with 2–6 factors and then the results at the lowest Q value were output for analysis. The details about the PMF model can be found in the Supporting Information.

Venier et al.²² compared four time series models: a modified Clausius–Clapeyron equation, a multiple linear regression, digital filtration, and dynamic harmonic regression (DHR). Of these, the DHR model exhibited the best performance in fitting the data in the long term time trends. Moreover, DHR can handle extreme values and time series breaks,²³ e.g., the concentrations of PAHs in summer are much lower than those in winter. Therefore, DHR was applied to derive time trends here. A detailed description of the DHR can be found in the Supporting Information.

Model Description. A Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP) was used to simulate the transport, deposition, and degradation of air pollutants from the surface up to 11 km, which successfully simulated the transport of PAHs²⁴ and pesticides.^{25,26} The model is driven by assimilated Canadian Meteorological Centre (CMC) meteorological data, using a time step length of 30 min, spatial resolution of 1° latitude × 1° longitude, and 14 vertical levels to simulate daily mean concentrations of selected PAHs from 1992 to 2015. Estimated global atmospheric emissions of PAHs for 2004 were employed for the simulations.²⁷ By using an emission inventory (from 2004) in the middle of the time period between 1992 and 2015, we can eliminate any bias, which may be introduced by a changing emission that is unknown/uncertain for an individual PAH, and focus on the influence of climate change. The details about the CanMETOP, including air–surface flux and sensitivity analysis, can be found in the Supporting Information.

RESULTS AND DISCUSSION

Air Concentrations of PAHs. Details and data availability of PAHs at each site are provided in Table S2. The concentration ranges and detection frequencies of PAHs at the three Arctic sites are summarized in Table S3. In general, concentrations of most PAHs decreased from the most southerly site of Pallas to the most northerly site of Alert in

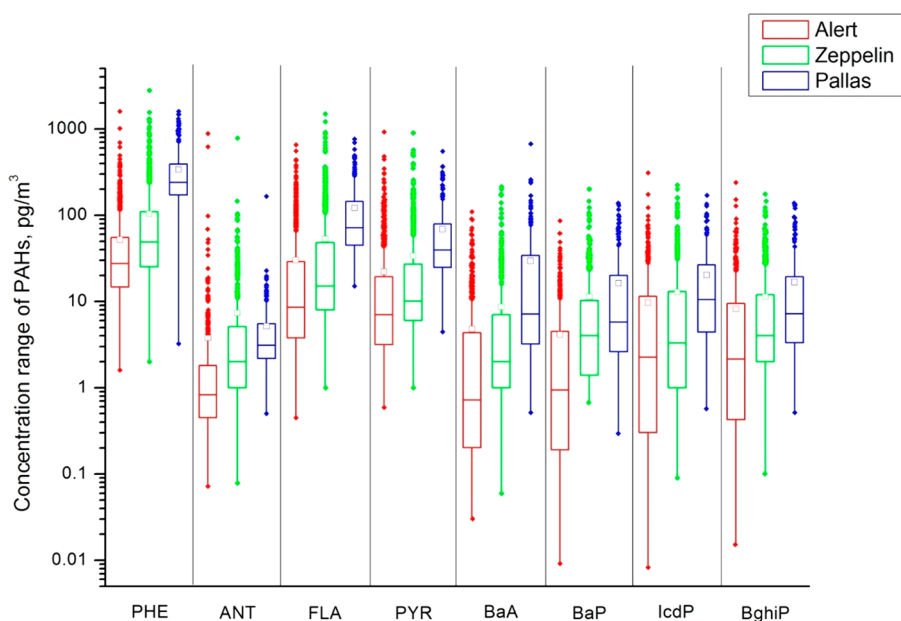


Figure 1. Box-and-whisker plots of 8 PAHs at the three sites during the sampling periods. The boxes represent the 25th and 75th percentiles of the data. The lines in the boxes and square symbols represent the median and the mean, respectively. All the outliers beyond the whiskers are shown individually. Nondetects are not reported in this figure.

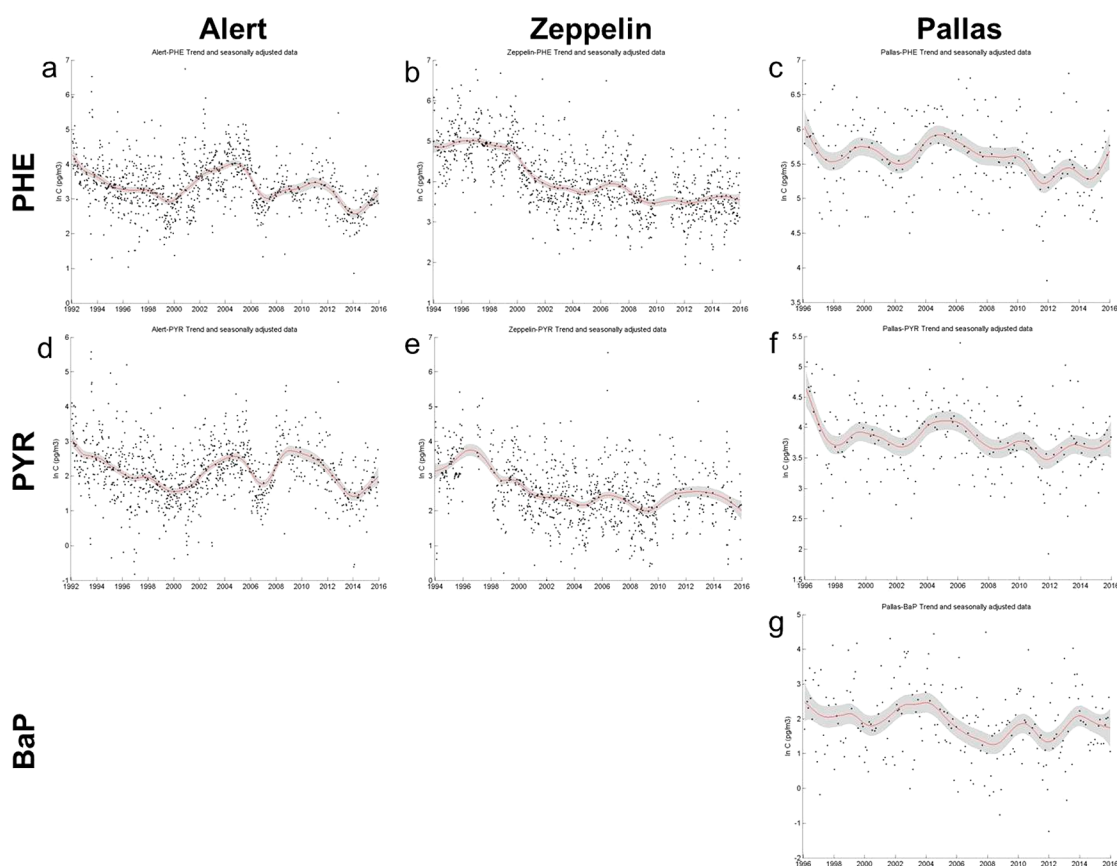


Figure 2. Long-term trends of (a, b, c) PHE and (d, e, f) PYR at three sites and (g) BaP at Pallas.

the order of Pallas > Zeppelin > Alert, especially for lighter PAHs, e.g., phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA) and pyrene (PYR). The concentrations of eight of the targeted PAHs which were analyzed at all three sites during the sampling periods, i.e., PHE, ANT, FLA, PYR, benzo[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), indeno-

[1,2,3-*c,d*]pyrene (IcdP), and benzo[*g,h,i*]perylene (BghiP), are shown in Figure 1. The median concentrations of $\Sigma 8$ PAHs for Alert, Zeppelin and Pallas were 47.8, 76.0, and 404 pg/m^3 , respectively. PHE, FLA, and PYR were the most abundant PAHs at all sites, accounting for >85% of $\Sigma 8$ PAHs at Zeppelin and >91% of $\Sigma 8$ PAHs at the other two sites. The annual mean

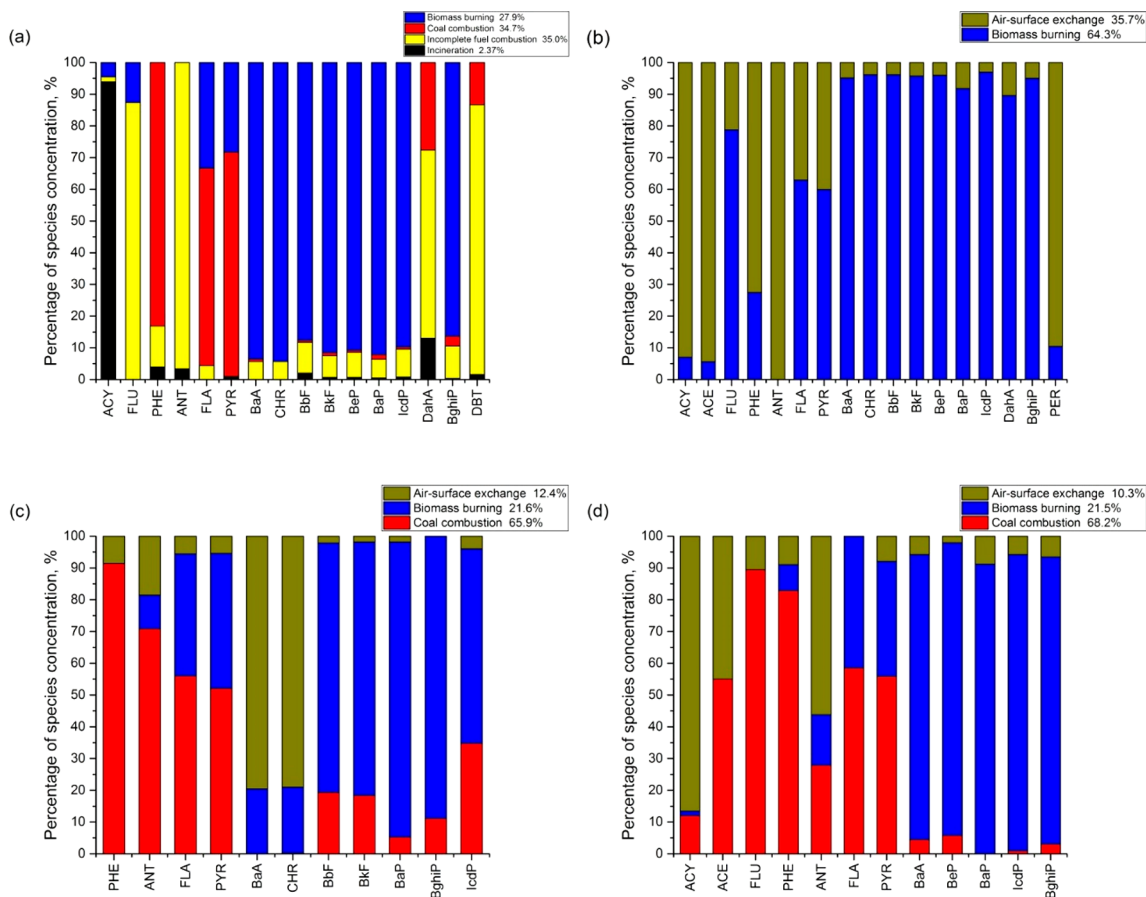


Figure 3. Factor Fingerprints for (a) Alert (1992–2003), (b) Alert (2004–2015), (c) Pallas (1996–2015), and (d) Zeppelin (1994–2015).

concentrations of Σ8PAHs ranged from 49.0 to 363, 91.7 to 523, and 346 to 817 pg/m³ for Alert, Zeppelin, and Pallas, respectively. Higher concentrations of PAHs at Pallas compared to those at Alert and Zeppelin are likely due to Pallas being closer to human settlements than the other two sites.

By separating the sampling periods into two parts, i.e., warm seasons (from May to October) and cold seasons (November to April), the seasonality of PAHs was assessed. As shown in Tables S4–S6 and Figure S2, the concentrations and detection frequencies of PAHs in cold, dark seasons are much higher than those in warm, sunny seasons. Specifically, high concentrations of PAHs were always measured in winter months, especially from December to February (Figure S3), which is consistent with previous studies.^{23,28,29} According to the back trajectory analysis, the air arriving at Alert in these three months includes more air masses originating from Russia than other months (Figure S4). The other two sites are more impacted by air masses coming from Northern Europe and Northwest Russia during December to February compared with the other nine months.

Temporal Trends. Two representative PAHs, namely PHE and PYR, were chosen for temporal trend assessment due to their high concentrations and detection frequencies compared with the other PAHs. BaP was also selected for trend assessment due to its toxicological importance and significantly different physical–chemical properties from PHE and PYR (Table S2) which would render differences in their atmospheric transport pathways. Data of BaP was sufficient only at Pallas for this assessment. Temporal trends of PAHs

were assessed with the Dynamic Harmonic Regression (DHR) model using full data sets collected at the three sites, i.e., from 1992 to 2015 for Alert, from 1994 to 2015 for Zeppelin, and 1996 to 2015 for Pallas (Figure 2 and Figure S5). Since PAHs are “seasonal contaminants”, the Seasonal Kendall test was performed for the statistical significance of the trends (Z_{SK}) of selected PAHs. 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. Becker et al.²³ previously investigated the occurrence and trends of PAHs in the Canadian Arctic atmosphere from 1992 to 2000 and revealed a significant decrease of PAHs throughout the 1990s, e.g., the Z_{SK} for PHE and PYR were -3.39 and -2.97 ($p < 0.01$), respectively. In this study, with 15 more years of data, the temporal trends at Alert showed great variability since 2001. For PHE and PYR, the concentrations at Alert were found to increase significantly between 2001 and 2005 to levels similar to those observed in the early 1990s with Z_{SK} of 2.82 ($p < 0.01$) and 2.57 ($p = 0.01$), respectively. From 2006 to 2015, they increase and decline again to a lesser extent but generally have no significant trend ($Z_{SK} = -0.94$, $p > 0.05$; $Z_{SK} = -1.57$, $p > 0.05$). The complex trends since 2001 at Alert are mainly due to the much higher concentrations in summers during 2003 to 2005, which could be associated with the relatively more frequent active forest fire events in Canada, Alaska, and Greenland during these years (Figure S6). Similarly, higher PAH concentrations were observed in the summer of 2015 (Figure 2 and Figure S5) which coincide with more frequent forest fires during that year in the same regions (Figure S6). Retene (RET) is an ideal tracer of forest fire activity; high

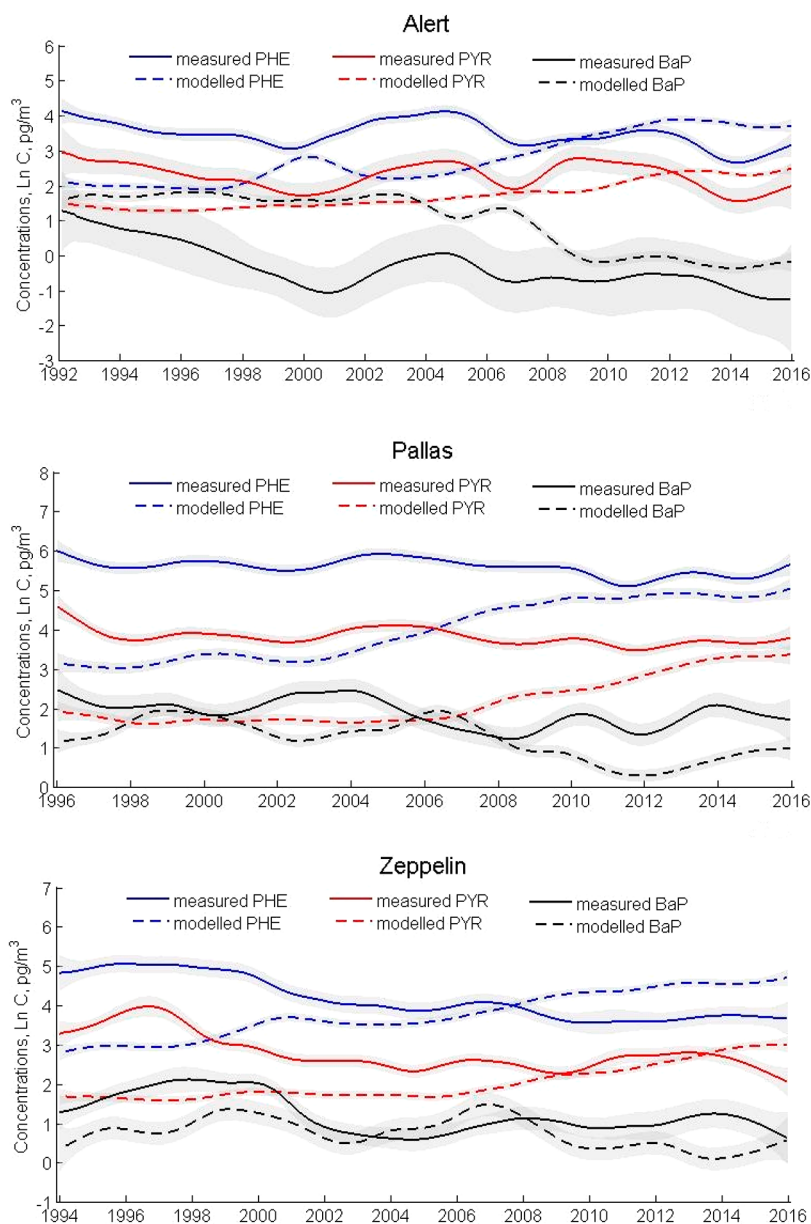


Figure 4. Trends of monthly mean concentrations of three PAHs (measured and simulated) at three sites. The shade represents the standard deviations of the trends.

levels of RET were found during 2003 to 2005 and 2015 (Figure S5), which confirm the contribution of forest fire events. At Zeppelin, significant declining trends were found for PHE and PYR between 1994 and 2001 ($Z_{SK} = -2.11$, $p < 0.05$; $Z_{SK} = -3.11$, $p < 0.01$), which is similar to Alert. Between 2002 and 2015, PHE and PYR seem to have reached a steady-state at Zeppelin ($Z_{SK} = -1.79$, $p > 0.05$; $Z_{SK} = 1.61$, $p > 0.05$). At Pallas, PHE and BaP were relatively stable over the two decades ($Z_{SK} = -1.72$, $p > 0.05$; $Z_{SK} = -1.38$, $p > 0.05$). Significant decline was found for PYR ($Z_{SK} = -2.37$, $p < 0.05$) which is mainly due to high concentrations in the first year of sampling; there is no significant trend for 1997 to 2015 ($Z_{SK} = -1.58$, $p > 0.05$). According to an estimation, the global emission of PAHs declined significantly from 1992 to 2015, especially in developed countries.⁹ However, PAHs found in air at Arctic sites did not seem to reflect this reduction in PAH emissions. In the past decade, human activities in the Arctic, for example, resource exploration, research, tourism, fisheries,

and maritime traffic, have increased substantially due to warming and the corresponding reduction of sea ice, opening up new shipping routes.³⁰ Such activities are potential new local sources of PAHs in the Arctic.

To better assess this, here, we examine whether the sources of PAHs changed during these years using a combination of PAH molecular diagnostic ratios and positive matrix factorization (PMF). Both techniques have been used widely over the years, and even though their limitations are known, when used in combination, it is possible to reduce their inherent weaknesses and strengthen the conclusions on potential sources and trends.^{3,13,31,32} The PAH ratios, e.g., PHE to the sum of PHE and ANT [$\text{PHE}/(\text{PHE}+\text{ANT})$] and FLA to the sum of FLA and PYR [$\text{FLA}/(\text{FLA}+\text{PYR})$], are widely used for source identification and, in particular, to understand if PAHs are mainly emitted from petroleum sources, or from combustion processes.^{33,34} Figure S7 shows the variations of the $\text{PHE}/(\text{PHE}+\text{ANT})$ and $\text{FLA}/(\text{FLA}+\text{PYR})$

+PYR) ratios over the sampling periods for the three sites. The calculated ratios at Pallas and Zeppelin were relatively constant, suggesting the sources of PAHs might not have changed significantly. Variations of PAH ratios were observed at Alert. The ratios of PHE/(PHE+ANT) were increasing and ratios of FLA/(FLA+PYR) were decreasing (especially after 2005), indicating that the sources shift from combustion of coal and wood to petroleum slowly, e.g., vehicle emissions. The ratios of FLA/(FLA+PYR) at Zeppelin and Pallas are significantly higher than those at Alert ($t < 0.01$), which may be reflective of the continued use of coal-fired power plants in Europe. This may also explain the nondeclining/slow declining trends for PHE and PYR at these two sites after the early 2000s.

Figure 3 shows the factor fingerprint obtained from PMF for the three sites. Detailed explanations for the factor source attribution are given in the Supporting Information. PMF was applied to the Alert data set separately for two time periods; four factors were identified for 1992–2003, but only two factors were found for 2004–2015 confirming a source shift at this site. After 2004, biomass burning, with high loads of 5–6 ring PAHs including IcdP and BghiP,³⁵ become Factor 1 [representing 64.3% of the sum of the measured PAHs (Σ PAHs)] which coincides with the increase in active forest fire events in 2003 to 2005. Factor 2 (35.7% of Σ PAHs) is dominated by more volatile 3–4 ring PAHs with very slight contributions from heavier 5–6 ring PAHs which seems to reflect air–surface exchange. Factor 3 for Zeppelin (10.3% of Σ PAHs) can also be attributed as air–surface exchange. Volatilization of PAHs from surfaces, such as ocean, snow, ice, permafrost and soil, may have become more important in recent years due to retreating sea ice and general warming in the arctic region. Coal combustion was no longer identified as a factor after 2004 at Alert. Coal combustion, which is usually identified by high loadings of PHE, ANT, FLU, FLA³⁶ and moderate loadings of 5–6 ring PAHs BbF, BkF, BaP, BghiP, and IcdP³⁵ was identified as Factor 1 for both Pallas and Zeppelin and Factor 3 for Alert before 2004, which accounted for 65.9%, 68.2%, and 34.7% of Σ PAHs, respectively. This observation reaffirmed that coal-fire power plants were still major sources of PAHs for the two European sites. Sofowote et al. identified petroleum/petrogenic emissions as a major source of PAHs at a sub-Arctic site, attributed to local oil/gas exploration and LRAT.³⁷ Alert is located at the highest latitude among the three sites and receives air mass more evenly from North America and Eurasia (Figure S4) and therefore may provide a more general reflection of changes in energy usage pattern.

Model Simulation. The changing energy usage pattern is not able to interpret atmospheric trends of PAHs in the Arctic completely. We used a global numerical model, the CanMETOP, to simulate the transport and occurrences of the three selected PAHs, PHE, PYR, and BaP. Figure 4 shows the trends of the monthly mean concentrations of the measured and modeled PAHs derived by DHR at the three Arctic sites during their sampling times. As shown in Figure 4, it underestimates the concentrations of PHE and PYR in the 1990s by less than 1 order of magnitude for Alert and Zeppelin but by 13–17 times for Pallas. A modeling sensitivity analysis (Table S7) indicates that the uncertainty in emission inventory affects modeling results at the Pallas site slightly more than the other two sites. The great discrepancy between the modeled and measured PAHs at Pallas could be associated

with the actual emissions in these years being higher than the emissions of 2004²⁷ which we employed as input for the model. The simulated concentrations of PHE increased significantly over the ~20 years at the three sites, whereas simulated PYR exhibited different trends; increasing concentrations only became apparent since 2008. This difference is probably due to the higher volatility of PHE (Henry's Law constant, $H = 4.78 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at 25 °C) compared to PYR ($H = 2.13 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at 25 °C) (Table S2). Warming within and around the Arctic region would enhance volatilization from surfaces and render higher simulated concentrations of PHE and PYR in the Arctic atmosphere. Figure S8 shows the annual mean of modeled net air–surface flux. The air–surface exchange switched from net deposition to net volatilization around 2005, and the net air–surface flux increased rapidly since then, which accounted for the increment of the simulated concentrations. This observation also corresponds well with the PMF result which identified air–surface exchange as Factor 2 after 2004 at Alert and Factor 3 for Zeppelin. Meanwhile, it explains that the measured concentrations of PHE and PYR did not decrease substantially even though the global emissions declined significantly during the last two decades.⁹ The expected decline is offset by the increment caused by greater volatilization due to warming, especially in recent years. Casal et al. measured PAH air–surface exchange from 2013 to 2014 at a coastal Arctic site (Tromsø, 69° N) and they found that PAHs were in a volatilization zone in warm seasons and in an equilibrium zone in cold seasons.³⁸ The overall simulated concentrations of BaP match the observations well and showed a decreasing trend (Figure 4). Heavier PAHs like BaP are less influenced by temperature due to their relatively low volatility ($H = 0.20 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at 25 °C), but these particle-bound chemicals are subject to LRAT as they can be protected by organic coatings on aerosols,³⁹ and thus the simulation of BaP is more accurate than PHE and PYR. Our conclusions are consistent with Friedman et al.¹⁵ where they evaluated the influence of 2000–2050 climate and emission changes on three atmospheric PAHs transport to the Arctic.

Simulated concentrations of PHE at two high-latitude sites, Alert and Zeppelin, increased from 1998 to 2000, likely due to the warming phase during those years and the modeling sensitivity to temperature (Figure S9, Table S7), whereas a slight increase was found at Pallas (Table S8), which is consistent with the conclusion by Ding et al.⁴⁰ that the most prominent warming in the Arctic occurred in northeastern Canada and Greenland. This observation shows that Arctic sites are useful in investigating the influence of climate change on the occurrence of PAHs and other contaminants. The highest annual mean temperatures over the ~20 years at Alert were observed in 1998 and 2001 (Figure S9), when the model predicted a period of rising concentrations of PHE in air at Alert. Moreover, simulated concentrations of PYR slightly increased but no such increase was found for BaP (Table S8) due to its lower H (Table S2) resulting in a lower tendency to volatilize from oceans and ice-covered surfaces. The second rising period, for both PHE and PYR, were found after 2008. The Arctic sea ice was drastically reduced in this century; specifically, it reached a minimum record in 2007 and 2012.^{41–43} The more volatile PAHs, PHE, and PYR, can be released from the melting Arctic ice and the recently opened ocean (Table S7). Simulated concentration ranges of PHE and PYR are smaller than those observed at Alert and Zeppelin, indicating that there might be some local sources, such as the

military base at Alert, science stations at Ny-Ålesund, and shipping emissions.

In summary, two decades of measurements of PAHs in air at Arctic sites did not show a significant decreasing trend that one would have expected to occur relating to a global reduction of PAH emissions. Model simulation indicates that climate change may enhance the volatilization of lighter PAHs and thus alter the expected decline. In view of increasing PAH emissions due to human activities in the North as a result of warming, e.g. increased shipping, tourism, and resource development activities, both direct and indirect climate change impacts of contaminant cycling in the Arctic environment must be considered in assessing environmental and health risks. While efforts should continue to reduce PAH emissions, monitoring of PAHs and other chemicals of emerging arctic concern is essential to better understand climate change influence on the occurrence and transport of these contaminants to and within the Arctic. To simulate the concentrations of PAHs more accurately, scientists should continue to update the emission inventory bearing in mind the effect of climate change, in particular, with forest fire as an increasingly important source.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.8b05353](https://doi.org/10.1021/acs.est.8b05353).

Potential in sample breakthrough, DHR, the CanMETOP, air–surface exchange, model evaluation, and PMF results. Tables and figures summarize concentrations, trends, seasonality, ratios, and factor profiles of PAHs at the three sites. (PDF)

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Notes

The authors declare no competing financial interest.

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