Polycyclic Aromatic Hydrocarbons not declining in Arctic air despite global emission reduction

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27

28 **Abstract**

29 Two decades of atmospheric measurements of polycyclic aromatic hydrocarbons (PAHs)

30 were conducted at three Arctic sites, i.e., Alert, Canada; Zeppelin, Svalbard; and Pallas,

31 Finland. PAH concentrations decrease with increasing latitude in the order of

32 Pallas>Zeppelin>Alert. Forest fire was identified as an important contributing source.

33 Three representative PAHs, phenanthrene (PHE), pyrene (PYR), and benzo(a)pyrene (BaP)

34 were selected for the assessment of their long-term trends. Significant decline of these

35 PAHs was not observed contradicting the expected decline due to PAH emission reductions.

36 A global 3-D transport model was employed to simulate the concentrations of these three

37 PAHs at the three sites. The model predicted that warming in the Arctic would cause the

38 air concentrations of PHE and PYR to increase in the Arctic atmosphere, while that of BaP,

39 which tends to be particle-bound, is less affected by temperature. The expected decline due

40 to the reduction of global PAH emissions is offset by the increment of volatilization caused

41 by warming. This work shows that this phenomenon may affect the environmental

42 occurrence of other anthropogenic substances, such as, the more volatile flame retardants

43 and pesticides.

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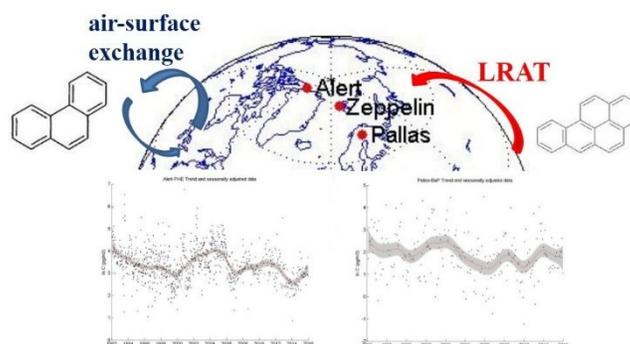
Introduction

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 592,000 to 499,000 tonnes 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

79   daylight[13]. For some of the above reasons, PAHs have been identified as emerging

80   contaminants in the Arctic[6].

81

82   The Arctic Monitoring and Assessment Programme (AMAP) investigated the occurrence

83   of POPs in the Arctic atmosphere for three decades[4,14]. Here, we use long-term

84   measurement datasets (~20 years) of PAHs in Arctic air collected at three AMAP sites, i.e.,

85   Alert, Canada; Zeppelin, Svalbard; and Pallas, Finland, to assess sources, transport

86   pathways and cycling of PAHs in Arctic air; and from their temporal trends try to evaluate

87   the outcome of reduction in PAH global emissions.

88

89   The Arctic is recognized as a key area for studying climate effect on pollutants due to its

90   sensitivity to climate change. Climate change-driven processes, e.g., temperature,

91   precipitations, and winds, may affect the LRAT and temporal trends of POPs in the Arctic

92   atmosphere[15,16]. One approach to test the relationship between climate change and the

93   variation of POPs is by comparing modeling results and long-term monitoring data[17,18].

94   These large datasets may help to provide greater insight on the influence of climate change

95   on temporal trends of PAHs.

96

Methods

98   **Sampling.** The locations of the sampling sites are shown in Figure S1. A super high-

99   volume air sampler (SHV) was employed to collect air samples at the Alert Global

100   Atmosphere Watch Observatory, Nunavut, Canada (82.50°N, 62.33°W, 200 m a.s.l.) from

101   1992 to 2015. One 20-cm glass fiber filter (GFF) and two polyurethane foam (PUF) plugs

102   (20 cm diameter, 4 cm thickness) were used to trap the particle and gas phase compounds

103   separately in approximately 13,500 m^3 of air over a 7-day sampling period. In the

104   Norwegian-operated Zeppelin Observatory, Ny-Ålesund, Svalbard (78.91° N, 11.88° E,

105   478 m a.s.l.), a high-volume air sampler (HV) was employed to sample from 1994 to 2015.

106   Two-day integrated weekly samples with a total sample volume of about 1200 m^3 of air

107   were collected every week with one 11-cm GFF and two PUFs (11 cm in diameter and 5

108   cm in height). In Pallas, Finland (68.0°N, 24.24°E, 340 m a.s.l.), 7-day integrated (1996-

109   2008) with a volume of ~4000 m^3 and 30-day integrated (composite of 4 weekly samples)

110   (2009-2015) with a volume of ~16,000 m^3 air samples were collected with a HV. One 14-

111   cm GFF and three PUFs (11 cm diameter, 4.5 cm thickness) were used to collect the particle

112   and gaseous substances. The sampling frequency and extraction strategy may vary in

113   different years (Table S1), subject to availability of funds. The details about the analytical

114   procedure and breakthrough can be found in the Supporting Information.

115

116   **Data and analysis.** PAH concentrations of Alert are entered into the Research Data

117   Management and Quality Control (RDMQ^{TM}) system which is a software system written

118   in SAS for data management that include an extensive flagging system to highlight

119   anomalies and to perform data quality checks. Data from all three sites were reported to

120   the EBAS database (ebas.nilu.no). To ensure data quality, two large-scale inter-laboratory

121   comparison studies were conducted for the analysis of trace organic chemicals in Arctic air

122   and an air sample was shared among all participating laboratories [19,20].

123

124   Positive Matrix Factorization (PMF, version 5.0) model recommended by the USEPA was

125   used to quantify the contribution of various emission sources to PAHs in the Arctic. For

126   all PAH congeners, the specificity of unknown sources is excluded, and the congeners with

127   weak signal to noise ratio and poor linear relationship were removed based on the PMF

128   guideline[21]. PMF analysis was repeatedly run 20 times with 2 to 6 factors and then the

129   results at the lowest Q value were output for analysis. The details about the PMF model

130   can be found in the Supporting Information.

131

132   Venier et al.[22] compared four time series models, a modified Clausius-Clapeyron equation,

133   a multiple linear regression, digital filtration, and dynamic harmonic regression (DHR). Of

134   these, the DHR model exhibited best performance in fitting the data in the long-term time

135   trends. Moreover, DHR can handle extreme values and time series breaks[23], e.g., the

136   concentrations of PAHs in summer are much lower than those in winter. Therefore, DHR

137   was applied to derive time trends here. A detailed description of the DHR can be found in

138   the Supporting Information.

139

140   **Model Description**. Canadian Model for Environmental Transport of Organochlorine
141   Pesticides (CanMETOP) was used to simulate the transport, deposition and degradation of
142   air pollutants from the surface up to 11 km, which successfully simulated the transport of
143   PAHs[24] and pesticides[25,26]. The model is driven by assimilated Canadian Meteorological
144   Centre (CMC) meteorological data, using a time step length of 30 minutes, spatial
145   resolution of 1° latitude × 1° longitude, and 14 vertical levels to simulate daily mean
146   concentrations of selected PAHs from 1992 to 2015. Estimated global atmospheric
147   emissions of PAHs for 2004 were employed for the simulations.[27] By using an emission
148   inventory (from 2004) in the middle of the time period between 1992 and 2015, we can
149   eliminate the bias which may be introduced by a changing emission which is
150   unknown/uncertain for individual PAH and allow us to focus on the influence of climate
151   change. The details about the CanMETOP, including air-surface flux, sensitivity analysis,
152   can be found in the Supporting Information.

153

154   **Results and Discussion**

155   **Air concentrations of PAHs**. Details and data availability of PAHs at each site are
156   provided in Table S2. The concentration ranges and detection frequencies of PAHs at the
157   three Arctic sites are summarized in Table S3. In general, concentrations of most PAHs
158   decreased from the most southerly site of Pallas to the most northerly site of Alert in the
159   order of Pallas > Zeppelin > Alert, especially for lighter PAHs, e.g., phenanthrene (PHE),
160   anthracene (ANT), fluoranthene (FLA) and pyrene (PYR). The concentrations of eight of
161   the targeted PAHs which were analyzed at all three sites during the sampling periods, i.e.,
162   PHE, ANT, FLA, PYR, benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), indeno(1,2,3-
163   c,d)pyrene (IcdP), and benzo(g,h,i)perylene (BghiP), are shown in Figure 1. The median
164   concentrations of Σ8PAHs for Alert, Zeppelin and Pallas were 47.8, 76.0 and 404 pg/m^3,
165   respectively. PHE, FLA, and PYR were the most abundant PAHs at all sites, accounting
166   for > 85% of Σ8PAHs at Zeppelin and > 91% of Σ8PAHs at the other two sites. The annual
167   mean concentrations of Σ8PAHs ranged from 49.0 to 363, 91.7 to 523, and 346 to 817
168   pg/m^3 for Alert, Zeppelin, and Pallas, respectively. Higher concentrations of PAHs at
169   Pallas compared to those at Alert and Zeppelin are likely due to Pallas being closer to
170   human settlements than the other two sites.
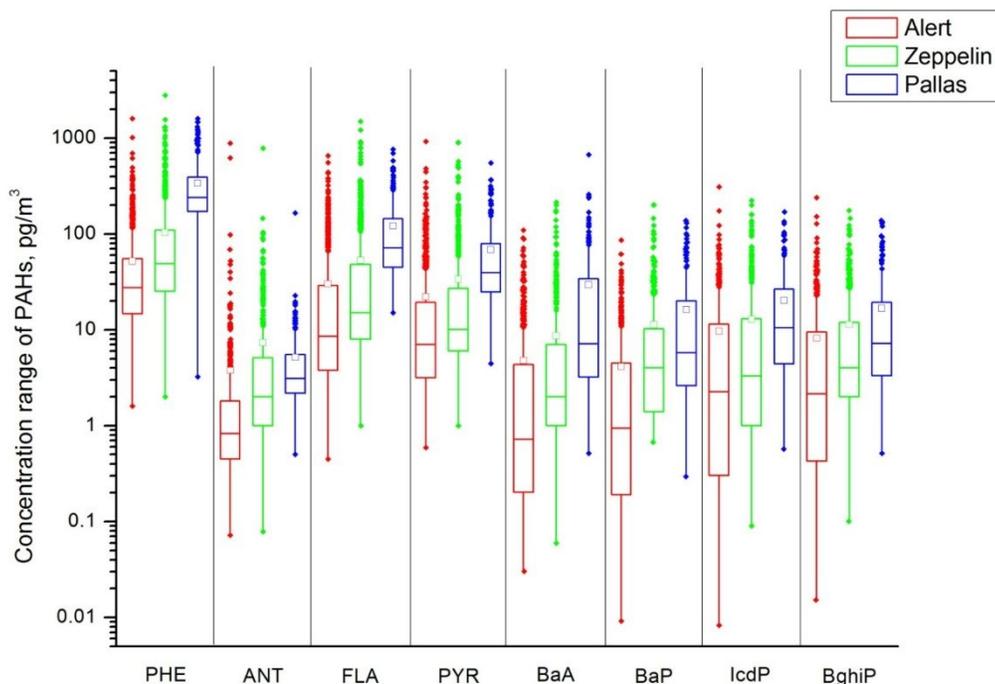
171
172 **Figure 1.** Box-and-whisker plots of 8 PAHs at the three sites during the sampling periods. The
173 boxes represent the 25th and 75th percentiles of the data. The lines in the boxes and square symbols
174 represent the median and the mean, respectively. All the outliers beyond the whiskers are shown
175 individually. Non-detects are not reported in this figure.
176

177 By separating the sampling periods into two parts, i.e. warm seasons (from May to October)

178 and cold seasons (November to April), the seasonality of PAHs was assessed. As shown in

179 Tables S4-S6 and Figure S2, the concentrations and detection frequencies of PAHs in cold,

180 dark seasons are much higher than those in warm, sunny seasons. Specifically, high

181 concentrations of PAHs were always measured in winter months, especially from

182 December to February (Figure S3), which is consistent with previous studies[23,28,29].

183 According to the back trajectory analysis, the air arriving at Alert in these three months

184 includes more air masses originating from Russia than other months (Figure S4). The other

185 two sites are more impacted by air masses coming from Northern Europe and Northwest

186 Russia during December to February compared with the other nine months.

187

188 **Temporal Trends.** Two representative PAHs, namely PHE and PYR, were chosen for

189 temporal trend assessment due to their high concentrations and detection frequencies

190 compared with the other PAHs. BaP was also selected for trend assessment due to its

191 toxicological importance and significantly different physical-chemical properties from

192 PHE and PYR (Table S2) which would render differences in their atmospheric transport

193 pathways. Data of BaP was sufficient only at Pallas for this assessment. Temporal trends

194 of PAHs were assessed with the Dynamic Harmonic Regression (DHR) model using full

195 datasets collected at the three sites, i.e. from 1992 to 2015 for Alert, from 1994 to 2015 for

196 Zeppelin, and 1996 to 2015 for Pallas (Figure 2 and Figure S5). Since PAHs are "seasonal

197 contaminants", the Seasonal Kendall test was performed for the statistical significance of

198 the trends (Z_{SK}) of selected PAHs. Negative Z_{SK} values mean a decline and positive Z_{SK}

199 values mean an increase, and p-values are used to confirm if the trends were statistically

200 significant. Becker et al.[23] previously investigated the occurrence and trends of PAHs in

201 the Canadian Arctic atmosphere from 1992 to 2000, and revealed a significant decrease of

202 PAHs throughout the 1990s, e.g., the Z_{SK} for PHE and PYR were -3.39 and -2.97 ($p<0.01$),

203 respectively. In this study, with 15 more years of data, the temporal trends at Alert showed

204 great variability since 2001. For PHE and PYR, the concentrations at Alert were found to

205 increase significantly between 2001 and 2005 to levels similar to those observed in the

206 early 1990s with Z_{SK} of 2.82 ($p<0.01$) and 2.57 ($p=0.01$), respectively. From 2006 to 2015,

207 they increase and decline again to a lesser extent but generally have no significant trend

208 ($Z_{SK}=-0.94$, $p>0.05$; $Z_{SK}=-1.57$, $p>0.05$). The complex trends since 2001 at Alert are

209 mainly due to the much higher concentrations in summers during 2003 to 2005, which

210 could be associated with the relatively more frequent active forest fire events in Canada,

211 Alaska and Greenland during these years (Figure S6). Similarly, higher PAH

212 concentrations were observed in the summer of 2015 (Figure 2 and Figure S5) which

213 coincide with more frequent forest fires during that year in the same regions (Figure S6).

214 Retene (RET) is an ideal tracer of forest fire activity, high levels of RET were found during

215 2003 to 2005 and 2015 (Figure S5), which confirm the contribution of forest fire events.

216 At Zeppelin, significant declining trends were found for PHE and PYR between 1994 and

217 2001 ($Z_{SK}=-2.11$, $p<0.05$; $Z_{SK}=-3.11$, $p<0.01$), which is similar to Alert. Between 2002 and

218 2015, PHE and PYR seem to have reached a steady-state at Zeppelin ($Z_{SK}=-1.79$, $p>0.05$;

219 $Z_{SK}=1.61$, $p>0.05$). At Pallas, PHE and BaP were relatively stable over the two decades

220 ($Z_{SK}=-1.72$, $p>0.05$; $Z_{SK}=-1.38$, $p>0.05$). Significant decline was found for PYR ($Z_{SK}=-$

221   2.37, p<0.05) which is mainly due to high concentrations in the first year of sampling; there

222   is no significant trend for 1997 to 2015 (Z_{SK}=-1.58, p>0.05). According to an estimation,

223   the global emission of PAHs declined significantly from 1992 to 2015, especially in

224   developed countries[9]. However, PAHs found in air at Arctic sites did not seem to reflect

225   this reduction in PAH emissions. In the last decade, human activities in the Arctic, for

226   example resource exploration, research, tourism, fisheries and maritime traffic, have

227   increased substantially due to warming and the corresponding reduction of sea ice, opening

228   up new shipping routes[30]. Such activities are potential new local sources of PAHs in the

229   Arctic.
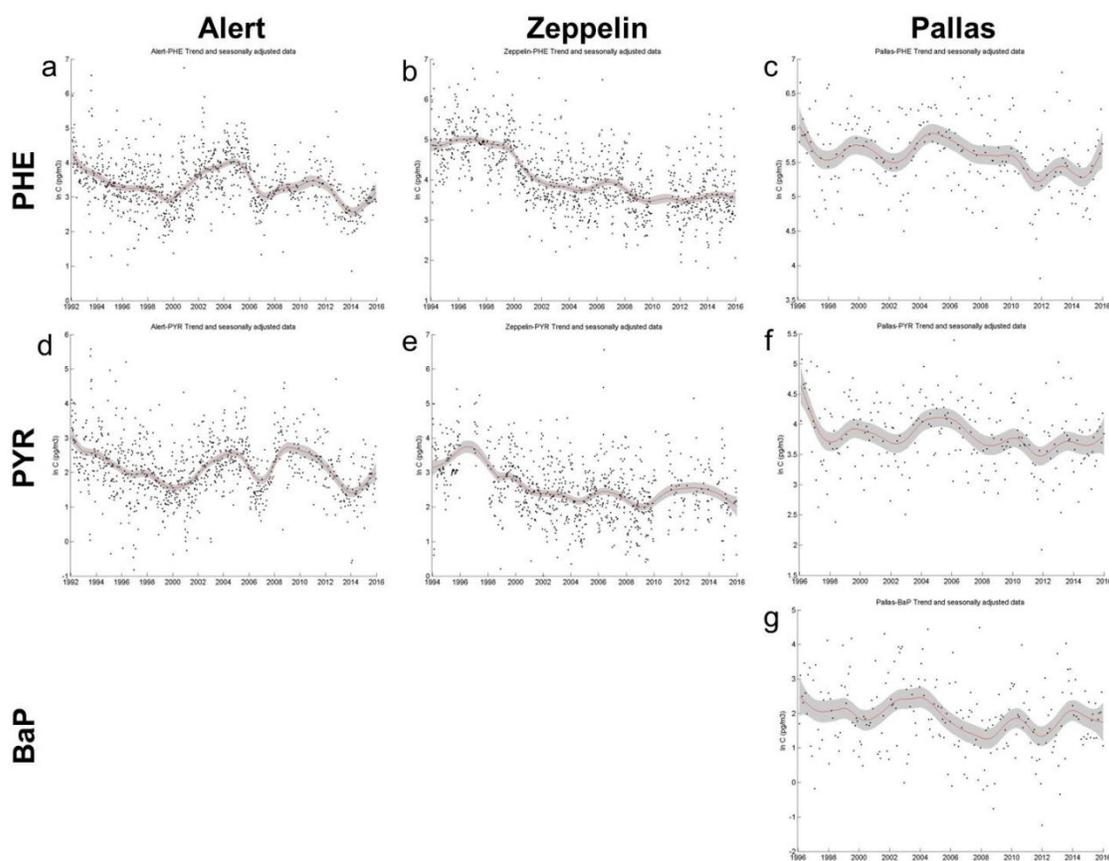
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231   **Figure 2**. Long-term trends of (a, b, c) PHE and (d, e, f) PYR at three sites and (g) BaP at Pallas.
232

233   To better assess this, here we examine whether the sources of PAHs changed during these

234   years using a combination of PAH molecular diagnostic ratios and positive matrix

235   factorization (PMF). Both techniques have been used widely over the years, and even

236   though their limitations are known, when used in combination, it is possible to reduce their

237   inherent weaknesses and strengthen the conclusions on potential sources and trends[3,13,31,32].

238   The PAH ratios, e.g., PHE to the sum of PHE and ANT [PHE/(PHE+ANT)] and FLA to

239   the sum of FLA and PYR [FLA/(FLA+PYR)], are widely used for source identification

240   and, in particular, in order to understand if PAHs are mainly emitted from petroleum

241   sources, or from combustion processes[33,34]. Figure S7 shows the variations of the

242   PHE/(PHE+ANT) and FLA/(FLA+PYR) ratios over the sampling periods for the three

243   sites. The calculated ratios at Pallas and Zeppelin were relatively constant, suggesting the

244   sources of PAHs might not have changed significantly. Variations of PAH ratios were

245   observed at Alert. The ratios of PHE/(PHE+ANT) were increasing and ratios of

246   FLA/(FLA+PYR) were decreasing (especially after 2005), indicating that the sources shift

247   from combustion of coal and wood to petroleum slowly, e.g., vehicle emissions. The ratios

248   of FLA/(FLA+PYR) at Zeppelin and Pallas are significantly higher than those at Alert

249   (t<0.01), which may be reflective of the continued use of coal-fired power plants in Europe.

250   This may also explain the non-declining/slow declining trends for PHE and PYR at these

251   two sites after the early 2000s.

252

253   Figure 3 shows the factor fingerprint obtained from PMF for the three sites. Detailed

254   explanations for the factor source attribution are given in the Supporting Information. PMF

255   was applied to the Alert dataset separately for two time periods; four factors were identified

256   for 1992-2003 but only two factors were found for 2004-2015 confirming a source shift at

257   this site. After 2004, biomass burning, with high loads of 5-6 ring PAHs including IcdP

258   and BghiP[35], become Factor 1 [representing 64.3% of the sum of the measured PAHs

259   (ΣPAHs)] which coincides with the increase in active forest fire events in 2003 to 2005.

260   Factor 2 (35.7% of ΣPAHs) is dominated by more volatile 3-4 ring PAHs with very slight

261   contributions from heavier 5-6 ring PAHs which seems to reflect air-surface exchange.

262   Factor 3 for Zeppelin (10.3% of ΣPAHs) can also be attributed as air-surface exchange.

263   Volatilization of PAHs from surfaces, such as ocean, snow, ice, permafrost and soil, may

264   have become more important in recent years due to retreating sea ice and general warming

265   in the arctic region. Coal combustion was no longer identified as a factor after 2004 at

266   Alert. Coal combustion, which is usually identified by high loadings of PHE, ANT, FLU,

267   FLA[36] and moderate loadings of 5-6 ring PAHs BbF, BkF, BaP, BghiP and IcdP[35] was

268   identified as Factor 1 for both Pallas and Zeppelin, and Factor 3 for Alert before 2004,

269   which accounted for 65.9%, 68.2% and 34.7% of ΣPAHs, respectively. This observation

270   reaffirmed that coal-fire power plants were still major sources of PAHs for the two

271   European sites. Sofowote et al. identified petroleum/petrogenic emissions as a major source

272   of PAHs at a sub-Arctic site, attributed to local oil/gas exploration and LRAT[37]. Alert is

273   located at the highest latitude among the three sites and receives air mass more evenly from

274   North America and Eurasia (Figure S4), and therefore may provide a more general

275   reflection of changes in energy usage pattern.

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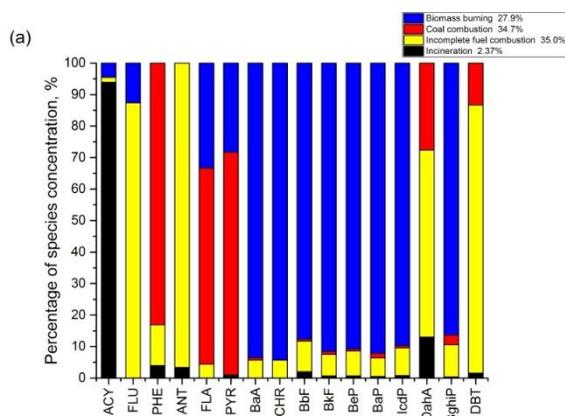
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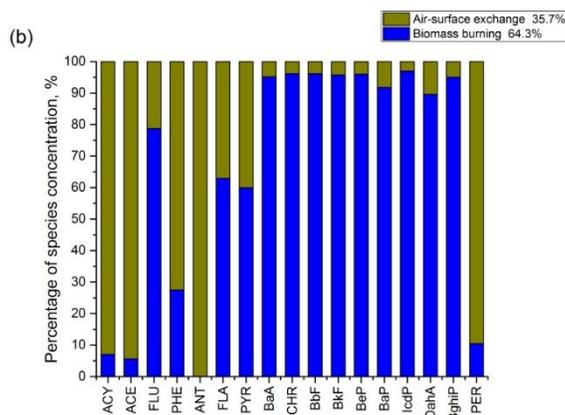
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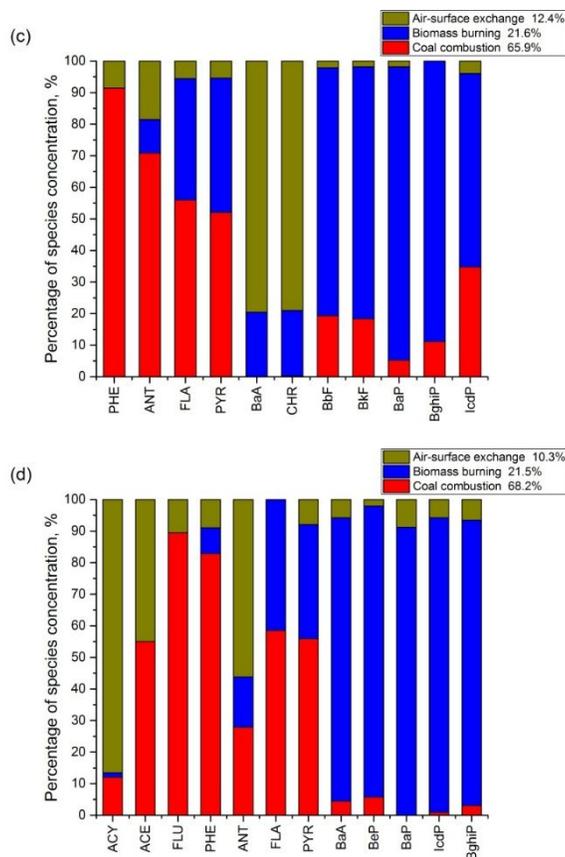
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Figure 3. Factor Fingerprints for (a) Alert (1992-2003), (b) Alert (2004-2015), (c) Pallas (1996-2015), and (d) Zeppelin (1994-2015).

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, i.e. PHE, PYR, and BaP. Figure 4 shows the trends of the monthly mean concentrations of the measured and modelled 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 the1990s by less than one order of magnitude for Alert and Zeppelin, but by 13-17 times for Pallas. A modelling sensitivity analysis (Table S7) indicates that the uncertainty in emission inventory affects modelling results at the Pallas site slightly more than the other two sites. The great discrepancy between the modelled and measured PAHs at Pallas could be associated with the actual emissions in these years being higher than the emissions of 2004[27] which we employed as input for the model. The simulated concentrations of PHE

296   increased significantly over the ~20 years at the three sites, whereas simulated PYR

297   exhibited different trends; increasing concentrations only became apparent since 2008.

298   This difference is probably due to the higher volatility of PHE (Henry's Law constant (H)

299   = 4.78 Pa·m^3·mol^{-1} at 25 °C) compared to PYR (H = 2.13 Pa·m^3·mol^{-1} at 25 °C) (Table

300   S2). Warming within and around the Arctic region would enhance volatilization from

301   surfaces and render higher simulated concentrations of PHE and PYR in the Arctic

302   atmosphere. Figure S8 shows the annual mean of modeled net air-surface flux. The air-

303   surface exchange switched from net deposition to net volatilization around 2005 and the

304   net air-surface flux increased rapidly since then, which accounted for the increment of the

305   simulated concentrations. This observation also corresponds well with the PMF result

306   which identified air-surface exchange as Factor 2 after 2004 at Alert and Factor 3 for

307   Zeppelin. Meanwhile, it explains that the measured concentrations of PHE and PYR did

308   not decrease substantially even though the global emissions declined significantly during

309   the last two decades[9]. The expected decline is offset by the increment caused by greater

310   volatilization due to warming, especially in recent years. Casal et al. measured PAH air-

311   surface exchange from 2013 to 2014 at a coastal Arctic site (Tromso, 69° N) and they found

312   that PAHs were in volatilization zone in warm seasons and in equilibrium zone in cold

313   seasons[38]. The overall simulated concentrations of BaP match the observations well and

314   showed a decreasing trend (Figure 4). Heavier PAHs like BaP are less influenced by

315   temperature due to their relatively low volatility (H=0.20 Pa·m^3·mol^{-1} at 25 °C), but these

316   particle-bound chemicals are subject to LRAT as they can be protected by organic coatings

317   on aerosols[39], and thus the simulation of BaP is more accurate than PHE and PYR. Our

318   conclusions are consistent with Friedman et al.[15] where they evaluated the influence of

319   2000-2050 climate and emission changes on three atmospheric PAHs transport to the

320   Arctic.
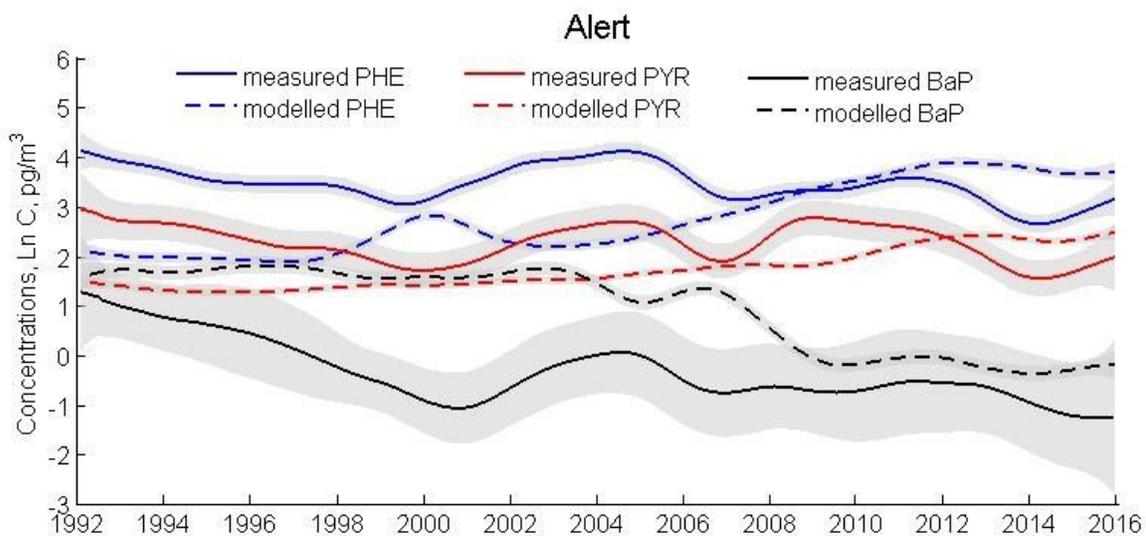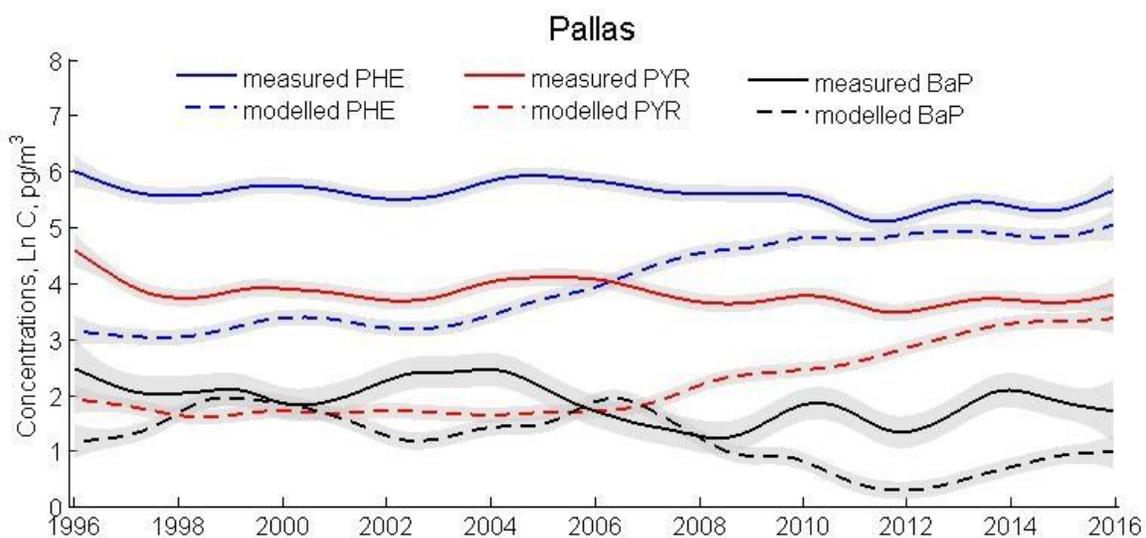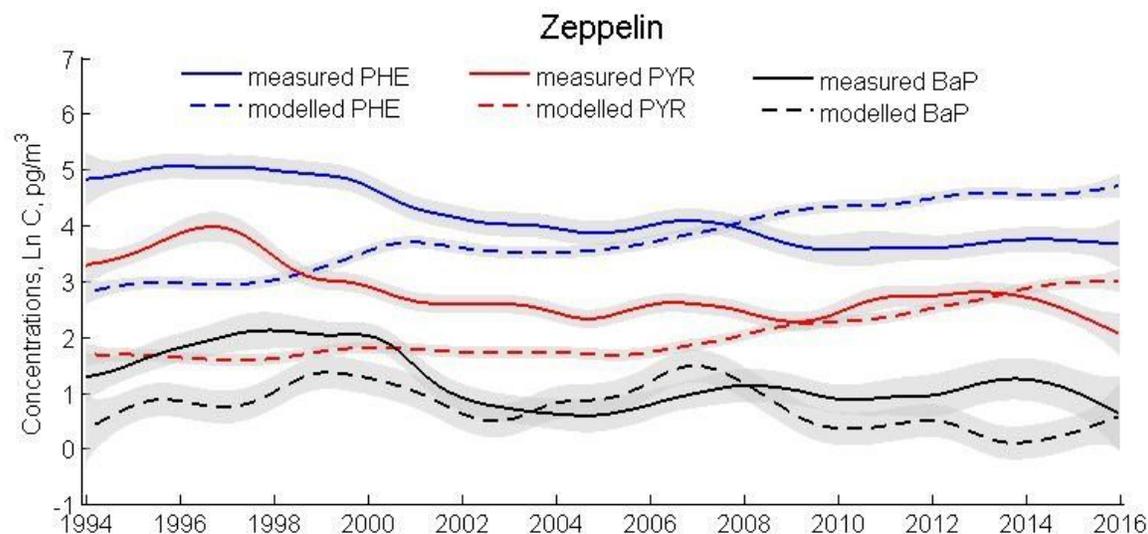
Alert

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Pallas

322

323

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.

326

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 modelling
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 that observed at Alert
and Zeppelin, indicating that there might be some local sources, such as military base at
Alert, science stations at Ny-Ålesund and shipping emissions.

345

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.

359

370

Supporting Information Available

A description of potential in sample breakthrough, DHR, the CanMETOP, air-surface exchange, model evaluation, and PMF results is given in the Supporting Information. Tables and figures summarize concentrations, trends, seasonality, ratios, factor profiles of

375 PAHs at the three sites. This information is available free of charge via the Internet at

376 http://pubs.acs.org

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382 **Notes**

383 The authors declare no competing financial interests.

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References

386 (1) Keyte, I. J.; Harrison, R. M.; Lammel, G., Chemical reactivity and long-range transport
387 potential of polycyclic aromatic hydrocarbons–a review. *Chem. Soc. Rev.* **2013,** *42* (24), 9333-9391.
388 (2) Schuster, J. K.; Harner, T.; Su, K.; Mihele, C.; Eng, A., First Results from the Oil Sands Passive
389 Air Monitoring Network for Polycyclic Aromatic Compounds. *Environ. Sci. Technol.* **2015,** *49* (5),
390 2991-2998.
391 (3) Katsoyiannis, A.; Breivik, K., Model-based evaluation of the use of polycyclic aromatic
392 hydrocarbons molecular diagnostic ratios as a source identification tool. *Environ. Pollut.* **2014,** *184*,
393 488-494.
394 (4) Hung, H.; Katsoyiannis, A. A.; Brorström-Lundén, E.; Olafsdottir, K.; Aas, W.; Breivik, K.;
395 Bohlin-Nizzetto, P.; Sigurdsson, A.; Hakola, H.; Bossi, R., Temporal trends of Persistent Organic
396 Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment
397 Programme (AMAP). *Environ. Pollut.* **2016,** *217*, 52-61.
398 (5) Li, W.-L.; Liu, L.-Y.; Song, W.-W.; Zhang, Z.-F.; Qiao, L.-N.; Ma, W.-L.; Li, Y.-F., Five-year trends
399 of selected halogenated flame retardants in the atmosphere of Northeast China. *Science of the
400 Total Environment* **2016,** *539*, 286-293.
401 (6) De Laender, F.; Hammer, J.; Hendriks, A. J.; Soetaert, K.; Janssen, C., Combining monitoring
402 data and modeling identifies PAHs as emerging contaminants in the Arctic. *Environ. Sci. Technol.*
403 **2011,** *45* (20), 9024-9029.
404 (7) Dahle, S.; Savinov, V.; Petrova, V.; Klungsøyr, J.; Savinova, T.; Batova, G.; Kursheva, A.,
405 Polycyclic aromatic hydrocarbons (PAHs) in Norwegian and Russian Arctic marine sediments:
406 Concentrations, geographical distribution and sources. *Norw. J. Geol.* **2006,** *86* (1), 41-50.
407 (8) Usenko, S.; Simonich, S. L. M.; Hageman, K. J.; Schrlau, J. E.; Geiser, L.; Campbell, D. H.;
408 Appleby, P. G.; Landers, D. H., Sources and Deposition of Polycyclic Aromatic Hydrocarbons to
409 Western U.S. National Parks. *Environ. Sci. Technol.* **2010,** *44* (12), 4512-4518.
410 (9) Shen, H.; Huang, Y.; Wang, R.; Zhu, D.; Li, W.; Shen, G.; Wang, B.; Zhang, Y.; Chen, Y.; Lu, Y.,
411 Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future
412 predictions. *Environ. Sci. Technol.* **2013,** *47* (12), 6415-6424.
413 (10) Harvey, H. R.; Taylor, K. A.; Pie, H. V.; Mitchelmore, C. L., Polycyclic aromatic and aliphatic
414 hydrocarbons in Chukchi Sea biota and sediments and their toxicological response in the Arctic
415 cod, Boreogadus saida. *Deep-Sea Res. Pt. II* **2014,** *102*, 32-55.

416   (11) Yunker, M. B.; Macdonald, R. W.; Snowdon, L. R.; Fowler, B. R., Alkane and PAH biomarkers
417   as tracers of terrigenous organic carbon in Arctic Ocean sediments. *Org. Geochem.* **2011,** *42* (9),
418   1109-1146.
419   (12) Foster, K. L.; Stern, G. A.; Carrie, J.; Bailey, J. N. L.; Outridge, P. M.; Sanei, H.; Macdonald, R.
420   W., Spatial, temporal, and source variations of hydrocarbons in marine sediments from Baffin Bay,
421   Eastern Canadian Arctic. *Sci. Total Environ.* **2015,** *506–507*, 430-443.
422   (13) Katsoyiannis, A.; Sweetman, A. J.; Jones, K. C., PAH Molecular Diagnostic Ratios Applied to
423   Atmospheric Sources: A Critical Evaluation Using Two Decades of Source Inventory and Air
424   Concentration Data from the UK. *Environ. Sci. Technol.* **2011,** *45* (20), 8897-8906.
425   (14) Hung, H.; Kallenborn, R.; Breivik, K.; Su, Y.; Brorström-Lundén, E.; Olafsdottir, K.; Thorlacius,
426   J. M.; Leppänen, S.; Bossi, R.; Skov, H., Atmospheric monitoring of organic pollutants in the Arctic
427   under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Sci. Total Environ.*
428   **2010,** *408* (15), 2854-2873.
429   (15) Friedman, C. L.; Zhang, Y.; Selin, N. E., Climate Change and Emissions Impacts on Atmospheric
430   PAH Transport to the Arctic. *Environ. Sci. Technol.* **2014,** *48* (1), 429-437.
431   (16) Ma, J.; Hung, H.; Tian, C.; Kallenborn, R., Revolatilization of persistent organic pollutants in
432   the Arctic induced by climate change. *Nature Clim. Change* **2011,** *1* (5), 255-260.
433   (17) Kong, D.; MacLeod, M.; Hung, H.; Cousins, I. T., Statistical Analysis of Long-Term Monitoring
434   Data for Persistent Organic Pollutants in the Atmosphere at 20 Monitoring Stations Broadly
435   Indicates Declining Concentrations. *Environ. Sci. Technol.* **2014,** *48* (21), 12492-12499.
436   (18) Macleod, M.; Riley, W. J.; Mckone, T. E., Assessing the influence of climate variability on
437   atmospheric concentrations of polychlorinated biphenyls using a global-scale mass balance model
438   (BETR-global). *Environ. Sci. Technol.* **2005,** *39* (17), 6749-56.
439   (19) Schlabach, M.; Farag-Clement, R.; Hung, H.; Kallenborn, R.; Su, Y.; Aas, W., AMAP/EMEP/NCP
440   inter-laboratory study for POP analysis 2010. EMEP/CCC-Report 7/2011. Norwegian Institute for
441   Air Research, Kjeller, Norway.   133 p. **2012**.
442   (20) Su, Y.; Hung, H., Inter-laboratory comparison study on measuring semi-volatile organic
443   chemicals in standards and air samples. *Environ. Pollut.* **2010,** *158* (11), 3365-3371.
444   (21) Paatero, P.; Hopke, P. K.; Begum, B. A.; Biswas, S. K., A graphical diagnostic method for
445   assessing the rotation in factor analytical models of atmospheric pollution. *Atmos. Environ.* **2005,**
446   *39* (1), 193-201.
447   (22) Venier, M.; Hung, H.; Tych, W.; Hites, R. A., Temporal Trends of Persistent Organic Pollutants:
448   A Comparison of Different Time Series Models. *Environ. Sci. Technol.* **2012,** *46* (7), 3928-3934.
449   (23) Becker, S.; Halsall, C. J.; Tych, W.; Hung, H.; Attewell, S.; Blanchard, P.; Li, H.; Fellin, P.; Stern,
450   G.; Billeck, B., Resolving the long-term trends of polycyclic aromatic hydrocarbons in the Canadian
451   Arctic atmosphere. *Environ. Sci. Technol.* **2006,** *40* (10), 3217-3222.
452   (24) Zhang, Y.; Shen, H.; Tao, S.; Ma, J., Modeling the atmospheric transport and outflow of
453   polycyclic aromatic hydrocarbons emitted from China. *Atmos. Environ.* **2011,** *45* (17), 2820-2827.
454   (25) Zhang, L.; Ma, J.; Venkatesh, S.; Li, Y.-F.; Cheung, P., Modeling Evidence of Episodic
455   Intercontinental Long-Range Transport of Lindane. *Environ. Sci. Technol.* **2008,** *42* (23), 8791-8797.
456   (26) Zhang, L.; Ma, J.; Tian, C.; Li, Y.; Hung, H., Atmospheric transport of persistent semi-volatile
457   organic chemicals to the Arctic and cold condensation in the mid-troposphere – Part 2: 3-D
458   modeling of episodic atmospheric transport. *Atmos. Chem. Phys.* **2010,** *10* (15), 7315-7324.
459   (27) Zhang, Y.; Tao, S., Global atmospheric emission inventory of polycyclic aromatic
460   hydrocarbons (PAHs) for 2004. *Atmos. Environ.* **2009,** *43* (4), 812-819.
461   (28) Anttila, P.; Brorström-Lundén, E.; Hansson, K.; Hakola, H.; Vestenius, M., Assessment of the
462   spatial and temporal distribution of persistent organic pollutants (POPs) in the Nordic atmosphere.
463   *Atmos. Environ.* **2016,** *140*, 22-33.

464   (29) Halsall, C. J.; Barrie, L. A.; Fellin, P.; Muir, D.; Billeck, B.; Lockhart, L.; Rovinsky, F. Y.; Kononov,
465   E. Y.; Pastukhov, B., Spatial and temporal variation of polycyclic aromatic hydrocarbons in the
466   Arctic atmosphere. *Environ. Sci. Technol.* **1997,** *31* (12), 3593-3599.
467   (30) Jorundsdottir, H. O.; Jensen, S.; Hylland, K.; Holth, T. F.; Gunnlaugsdottir, H.; Svavarsson, J.;
468   Olafsdottir, A.; El-Taliawy, H.; Riget, F.; Strand, J.; Nyberg, E.; Bignert, A.; Hoydal, K. S.; Halldorsson,
469   H. P., Pristine Arctic: Background mapping of PAHs, PAH metabolites and inorganic trace elements
470   in the North-Atlantic Arctic and sub-Arctic coastal environment. *Sci. Total Environ.* **2014,** *493*, 719-
471   728.
472   (31) Wang, C.; Wu, S.; Zhou, S.; Sill, Y.; Song, J., Characteristics and Source Identification of
473   Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Soils: A Review. *Pedosphere* **2017,** *27* (1), 17-
474   26.
475   (32) Khairy, M. A.; Lohmann, R., Source apportionment and risk assessment of polycyclic aromatic
476   hydrocarbons in the atmospheric environment of Alexandria, Egypt. *Chemosphere* **2013,** *91* (7),
477   895-903.
478   (33) Yunker, M. B.; Macdonald, R. W.; Vingarzan, R.; Mitchell, R. H.; Goyette, D.; Sylvestre, S., PAHs
479   in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and
480   composition. *Org. Geochem.* **2002,** *33* (4), 489-515.
481   (34) Galarneau, E., Source specificity and atmospheric processing of airborne PAHs: Implications
482   for source apportionment. *Atmos. Environ.* **2008,** *42* (35), 8139-8149.
483   (35) Chen, P.; Li, C.; Kang, S.; Yan, F.; Zhang, Q.; Ji, Z.; Tripathee, L.; Rupakheti, D.; Rupakheti, M.;
484   Qu, B.; Sillanpaa, M., Source apportionment of particle-bound polycyclic aromatic hydrocarbons
485   in Lumbini, Nepal by using the positive matrix factorization receptor model. *Atmos. Res.* **2016,**
486   *182*, 46-53.
487   (36) Wang, K.; Shen, Y.; Zhang, S.; Ye, Y.; Shen, Q.; Hu, J.; Wang, X., Application of spatial analysis
488   and multivariate analysis techniques in distribution and source study of polycyclic aromatic
489   hydrocarbons in the topsoil of Beijing, China. *Environ. Geol.* **2009,** *56* (6), 1041-1050.
490   (37) Sofowote, U. M.; Hung, H.; Rastogi, A. K.; Westgate, J. N.; Deluca, P. F.; Su, Y.; McCarry, B. E.,
491   Assessing the long-range transport of PAH to a sub-Arctic site using positive matrix factorization
492   and potential source contribution function. *Atmos. Environ.* **2011,** *45* (4), 967-976.
493   (38) Casal, P.; Castro-Jimenez, J.; Pizarro, M.; Katsoyiannis, A.; Dachs, J., Seasonal soil/snow-air
494   exchange of semivolatile organic pollutants at a coastal arctic site (Tromso, 69 degrees N). *Sci.*
495   *Total Environ.* **2018,** *636*, 1109-1116.
496   (39) Zhou, S.; Lee, A. K. Y.; McWhinney, R. D.; Abbatt, J. P. D., Burial Effects of Organic Coatings
497   on the Heterogeneous Reactivity of Particle-Borne Benzo a pyrene (BaP) toward Ozone. *J. Phys.*
498   *Chem. A* **2012,** *116* (26), 7050-7056.
499   (40) Ding, Q.; Wallace, J. M.; Battisti, D. S.; Steig, E. J.; Gallant, A. J. E.; Kim, H.-J.; Geng, L., Tropical
500   forcing of the recent rapid Arctic warming in northeastern Canada and Greenland. *Nature* **2014,**
501   *509*, 209-212.
502   (41) Comiso, J. C.; Parkinson, C. L.; Gersten, R.; Stock, L., Accelerated decline in the Arctic Sea ice
503   cover. *Geophys. Res. Lett.* **2008,** *35* (1), 179-210.
504   (42) Comiso, J. C., Large Decadal Decline of the Arctic Multiyear Ice Cover. *J. Climate* **2012,** *25* (4),
505   1176-1193.
506   (43) Liu, Y.; Key, J. R., Less winter cloud aids summer 2013 Arctic sea ice return from 2012
507   minimum. *Environ. Res. Lett.* **2014,** *9* (4), 044002.

508
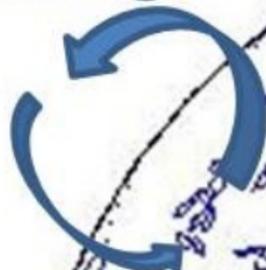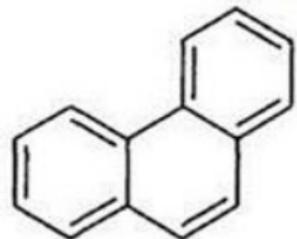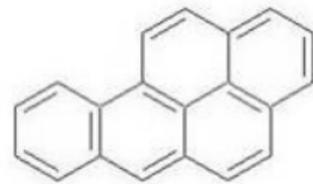
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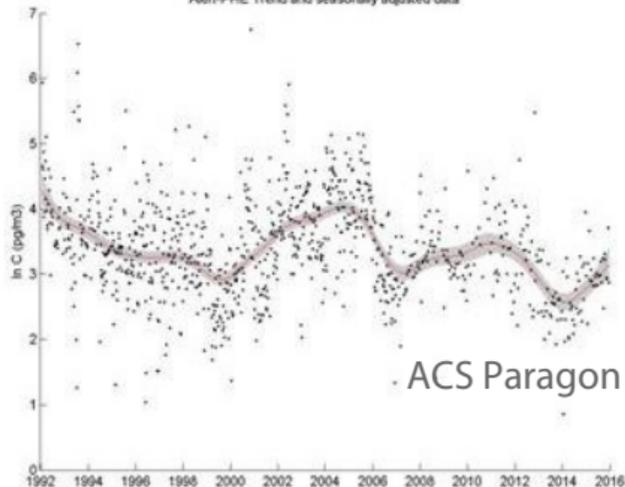
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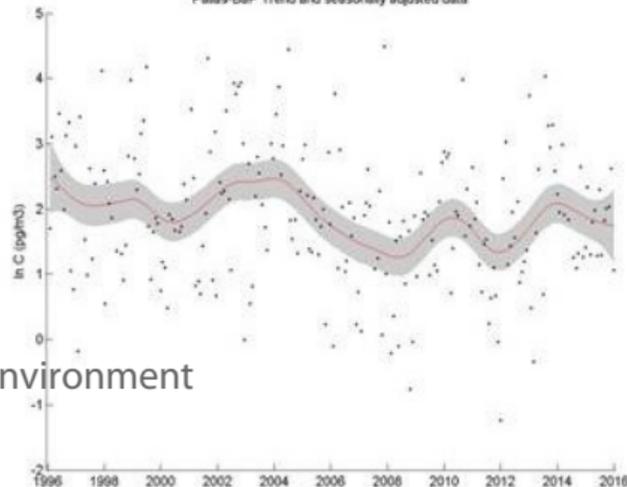
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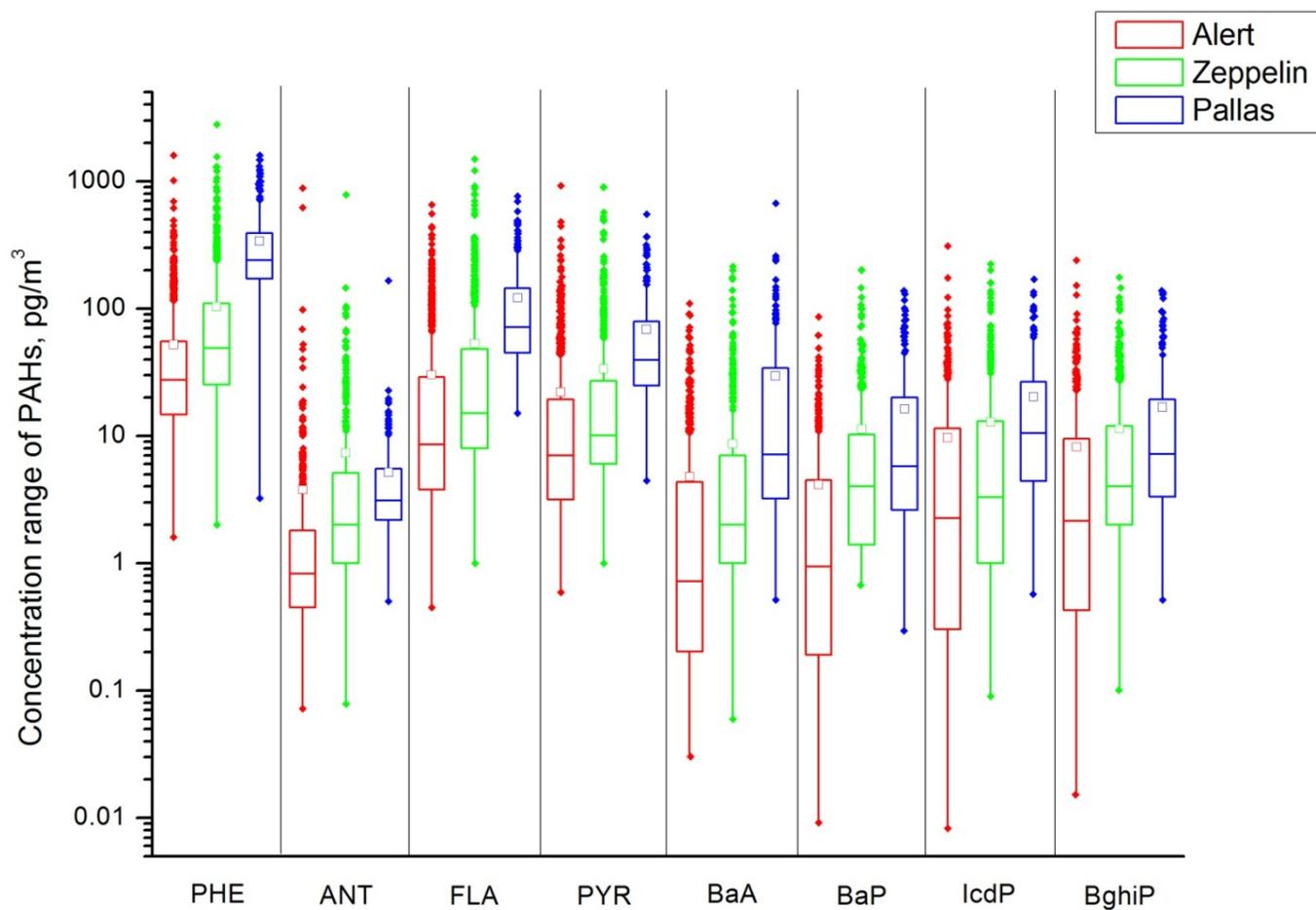
Figure 1. Box-and-whisker plots of 8 PAHs at the three sites during the sampling periods. The boxes represent the 25th and 75th percentiles of the data. The lines in the boxes and square symbols represent the median and the mean, respectively. All the outliers beyond the whiskers are shown individually. Non-detects are not reported in this figure.
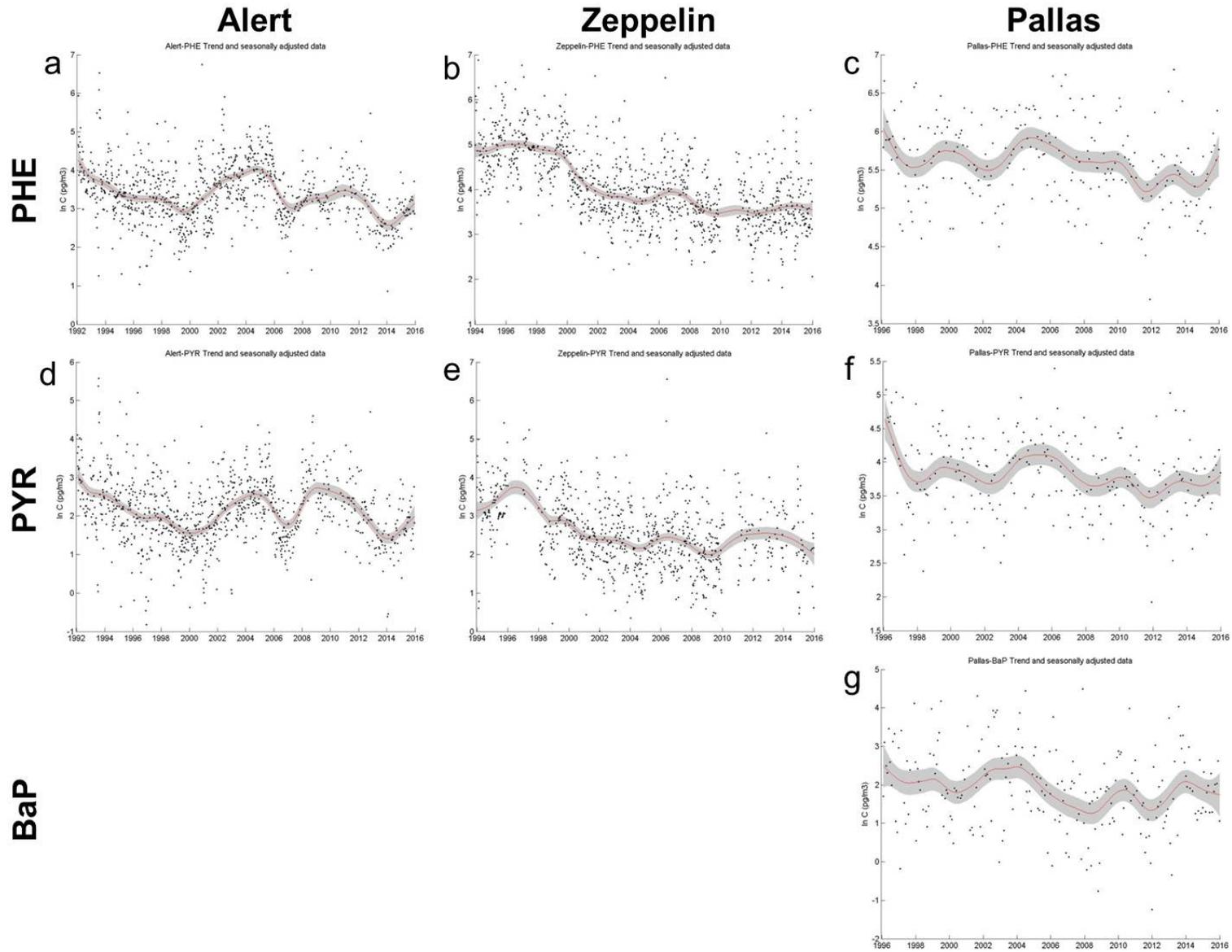
Figure 2. Long-term trends of (a, b, c) PHE and (d, e, f) PYR at three sites and (g) BaP at Pallas.

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

Alert


Pallas

Zeppelin

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.