

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

Yong Yu, Athanasios Katsoyiannis, Pernilla Bohlin Nizzetto, Eva Brorström-Lundén, Jianmin Ma, Yuan Zhao, Zhiyong Wu, Włodzimierz Tych, David Mindham, Ed Sverko, Enzo Barresi, Helena Dryfhout-Clark, Phil Fellin, and Hayley Hung

Environ. Sci. Technol., **Just Accepted Manuscript** • Publication Date (Web): 12 Feb 2019

Downloaded from <http://pubs.acs.org> on February 12, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

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

Yong Yu^{1,2,*}, Athanasios Katsoyiannis³, Pernilla Bohlin-Nizzetto³, Eva Brorström-Lundén⁴,
Jianmin Ma⁵, Yuan Zhao⁵, Zhiyong Wu¹, Wlodzimierz Tych⁶, David Mindham⁶, Ed Sverko⁷,
Enzo Barresi⁸, Helena Dryfhout-Clark¹, Phil Fellin⁹, Hayley Hung^{1,*}

1. Air Quality Processes Research Section, Environment and Climate Change Canada, Toronto,
M3H 5T4, Canada

2. Key Laboratory of Wetland Ecology and Environment, Northeast Institute of Geography and
Agroecology, Chinese Academy of Sciences, Changchun 130102, China

3. Norwegian Institute for Air Research (NILU), NO-2007 Kjeller, Norway

4. Swedish Environmental Research Institute (IVL), 411 33 Göteborg, Sweden

5. College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

6. Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom

7. State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of
Technology, Harbin 150090, China

8. National Laboratory for Environmental Testing (NLET), Canada Centre for Inland Waters,
Environment and Climate Change Canada, Burlington, L7R 4A6, Canada

9. AirZone One Ltd., Mississauga, L4Z 1X1, Canada

***Corresponding author:**

Dr. Hayley Hung

Tel: 1-416-739-5944; **E-mail:** hayley.hung@canada.ca (H. Hung)

Dr. Yong Yu

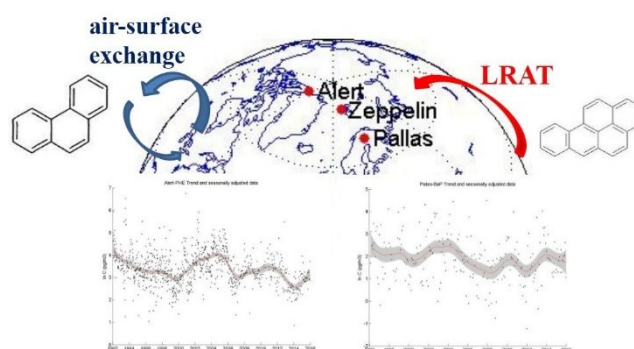
Tel: 86-431-85542296; **E-mail:** yuyong@iga.ac.cn (Y. Yu)

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.

44

45



46

47

48

TOC Art

49 **Introduction**

50 Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic pollutants
51 released into the environment primarily through incomplete combustion of fossil fuels and
52 biomass. They are of great public concern due to their toxicity and potential carcinogenicity.
53 PAHs can undergo long-range atmospheric transport (LRAT) to remote locations and are
54 listed for regulation under the United Nations Economic Commission for Europe (UNECE)
55 Aarhus Protocol on Persistent Organic Pollutants (POPs) in the Convention on Long Range
56 Transboundary Air Pollution (CLRTAP)¹⁻³. Due to their tendency to travel over long
57 distances, PAHs are regularly detected in very remote areas, far away from primary sources.
58 As such, PAHs are ubiquitous in the Arctic environment. Levels of most regulated POPs
59 are declining over time in the Arctic environment, reflecting the effectiveness of national
60 and international emission control initiatives such as CLRTAP and the Stockholm
61 Convention on POPs^{4,5}. However, temporal trends of PAHs measured in various Arctic
62 media did not show consistent declining trends⁶⁻⁸, despite the estimated reduction in global
63 PAH emissions from 592,000 to 499,000 tonnes between 1995 and 2008⁹. Studies have
64 shown that PAHs measured in Arctic marine waters and sediments mainly originate from
65 natural underwater hydrocarbon seeps¹⁰⁻¹², while those measured in air originate from
66 atmospherically-derived sources, making the air the most suitable medium for PAH
67 monitoring to verify the outcome of regulations on PAH emissions. In addition, their
68 occurrence in the Arctic atmosphere is of particular importance because what is detected
69 is the combined result of LRAT, continuous regional emissions (heating, industrial
70 activities), and temporary local emissions due to commercial and other activities (maritime
71 traffic, coal mining etc.). In a warming Arctic, PAH emissions due to increased human
72 activities within the Arctic may also increase.

73

74 PAHs are characterized as "seasonal contaminants" as space heating is one of the most
75 important sources, suggesting that their concentrations in winter are much higher than their
76 respective levels during the warmer months. In addition, some PAHs are subject to
77 photodegradation. With the extended winter darkness in the Arctic, PAHs can behave
78 differently in the Arctic atmosphere than regions that experience a regular diurnal cycle of

79 daylight¹³. For some of the above reasons, PAHs have been identified as emerging
80 contaminants in the Arctic⁶.

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

97 **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 m³ 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 m³ 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 m³ and 30-day integrated (composite of 4 weekly samples)

110 (2009-2015) with a volume of ~16,000 m³ 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™) 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 guideline²¹. 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 breaks²³, 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.

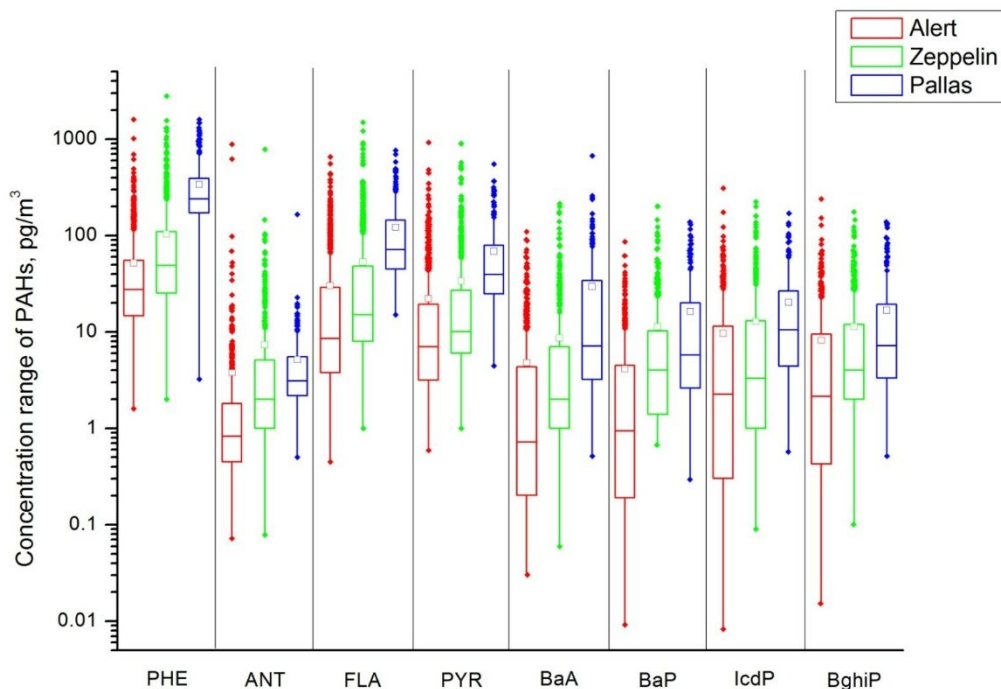
139

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 PAHs²⁴ 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 $\Sigma 8\text{PAHs}$ 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 $\Sigma 8\text{PAHs}$ at Zeppelin and > 91% of $\Sigma 8\text{PAHs}$ at the other two sites. The annual
167 mean concentrations of $\Sigma 8\text{PAHs}$ 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

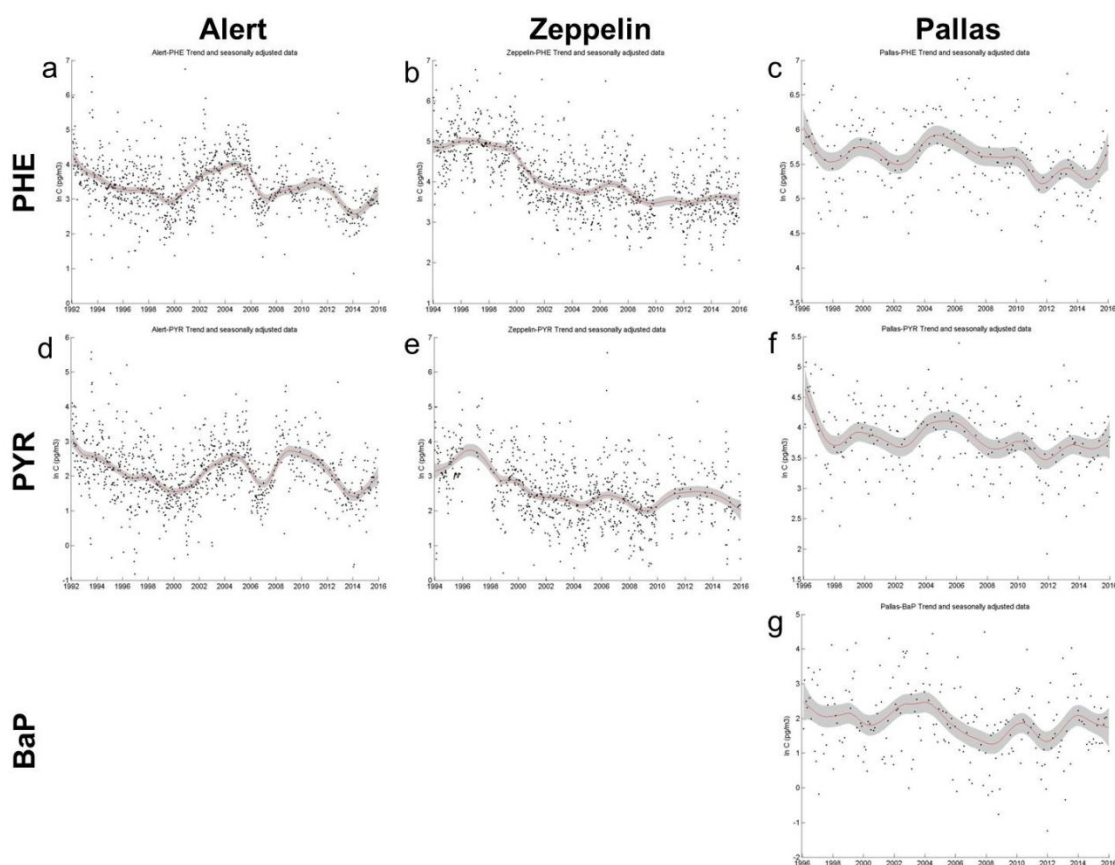
177 By separating the sampling periods into two parts, i.e. warm seasons (from May to October)
 178 and cold seasons (November to April), the seasonality of PAHs was assessed. As shown in
 179 Tables S4-S6 and Figure S2, the concentrations and detection frequencies of PAHs in cold,
 180 dark seasons 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 countries⁹. 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 routes³⁰. Such activities are potential new local sources of PAHs in the
 229 Arctic.



230
 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

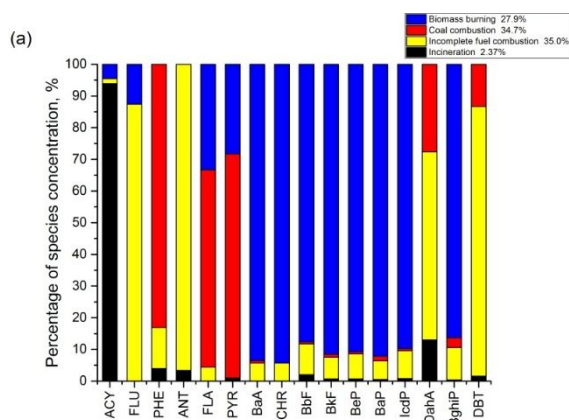
233 To better assess this, here we examine whether the sources of PAHs changed during these
 234 years using a combination of PAH molecular diagnostic ratios and positive matrix
 235 factorization (PMF). Both techniques have been used widely over the years, and even
 236 though their limitations are 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.

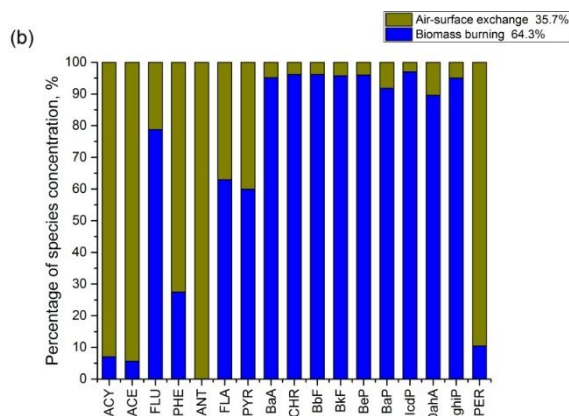
252

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 BghiP³⁵, become Factor 1 [representing 64.3% of the sum of the measured PAHs
259 (Σ PAHs)] which coincides with the increase in active forest fire events in 2003 to 2005.
260 Factor 2 (35.7% of Σ PAHs) 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 Σ PAHs) 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 FLA³⁶ and moderate loadings of 5-6 ring PAHs BbF, BkF, BaP, BghiP and IcdP³⁵ was

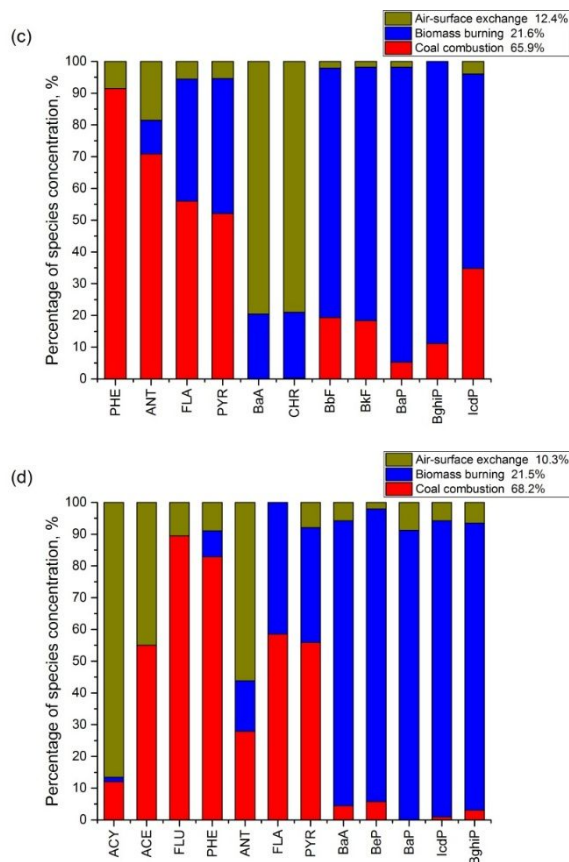
268 identified as Factor 1 for both Pallas and Zeppelin, and Factor 3 for Alert before 2004,
 269 which accounted for 65.9%, 68.2% and 34.7% of ΣPAHs, respectively. This observation
 270 reaffirmed that coal-fire power plants were still major sources of PAHs for the two
 271 European sites. Sofowote 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 LRAT³⁷. 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.
 276



277



278



279

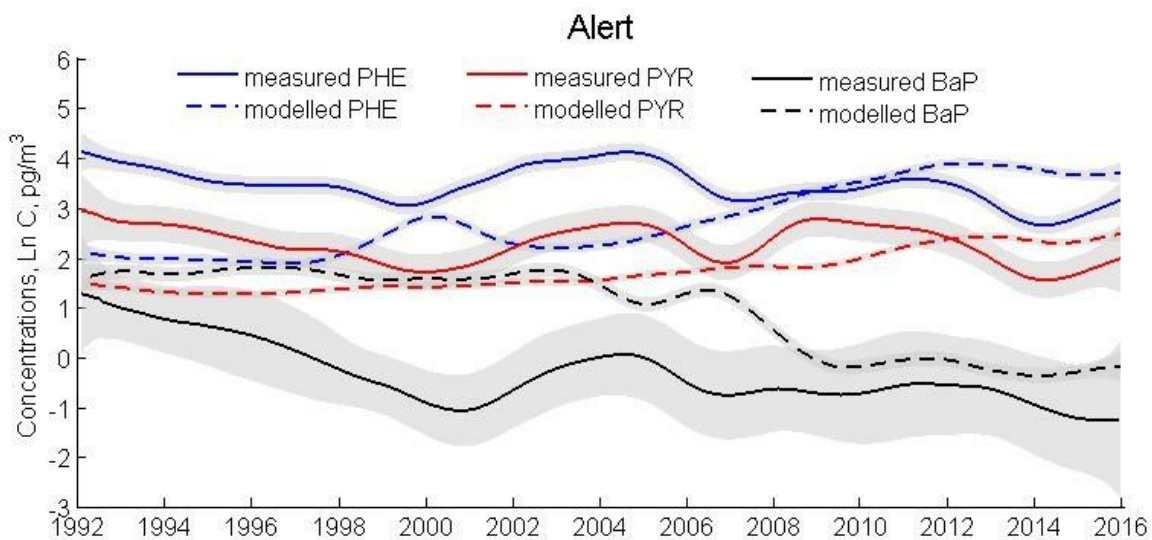
280

281 **Figure 3.** Factor Fingerprints for (a) Alert (1992-2003), (b) Alert (2004-2015), (c) Pallas (1996-
 282 2015), and (d) Zeppelin (1994-2015).

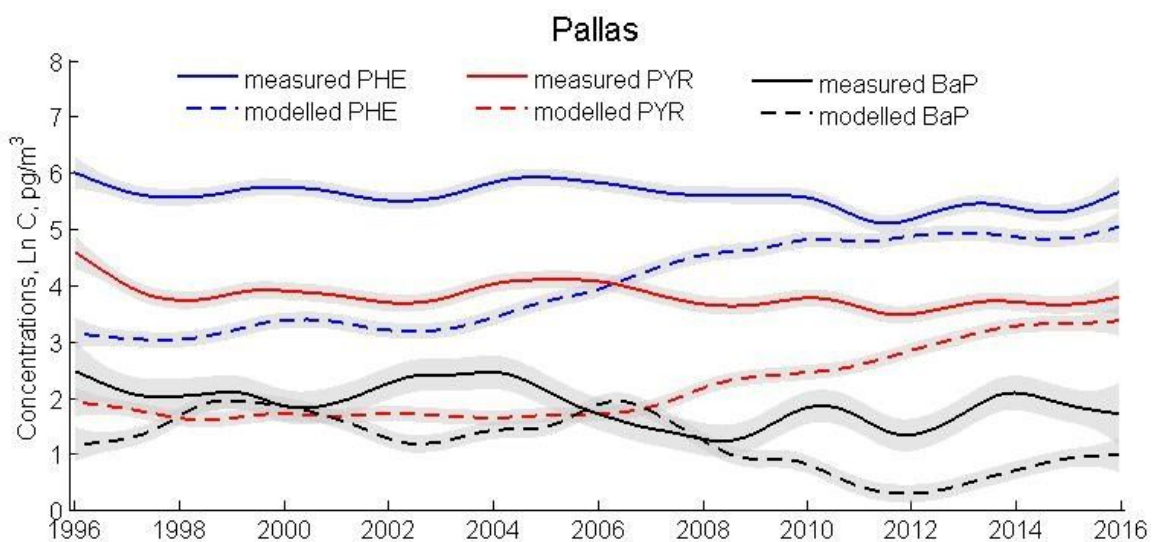
283

284 **Model Simulation.** The changing energy usage pattern is not able to interpret atmospheric
 285 trends of PAHs in the Arctic completely. We used a global numerical model, the
 286 CanMETOP to simulate the transport and occurrences of the three selected PAHs, i.e. PHE,
 287 PYR, and BaP. Figure 4 shows the trends of the monthly mean concentrations of the
 288 measured and modelled PAHs derived by DHR at the three Arctic sites during their
 289 sampling times. As shown in Figure 4, it underestimates the concentrations of PHE and
 290 PYR in the 1990s by less than one order of magnitude for Alert and Zeppelin, but by 13-17
 291 times for Pallas. A modelling sensitivity analysis (Table S7) indicates that the uncertainty
 292 in emission inventory affects modelling results at the Pallas site slightly more than the other
 293 two sites. The great discrepancy between the modelled and measured PAHs at Pallas could
 294 be associated with the actual emissions in these years being higher than the emissions of
 295 2004²⁷ which we employed as input for the model. The simulated concentrations of PHE

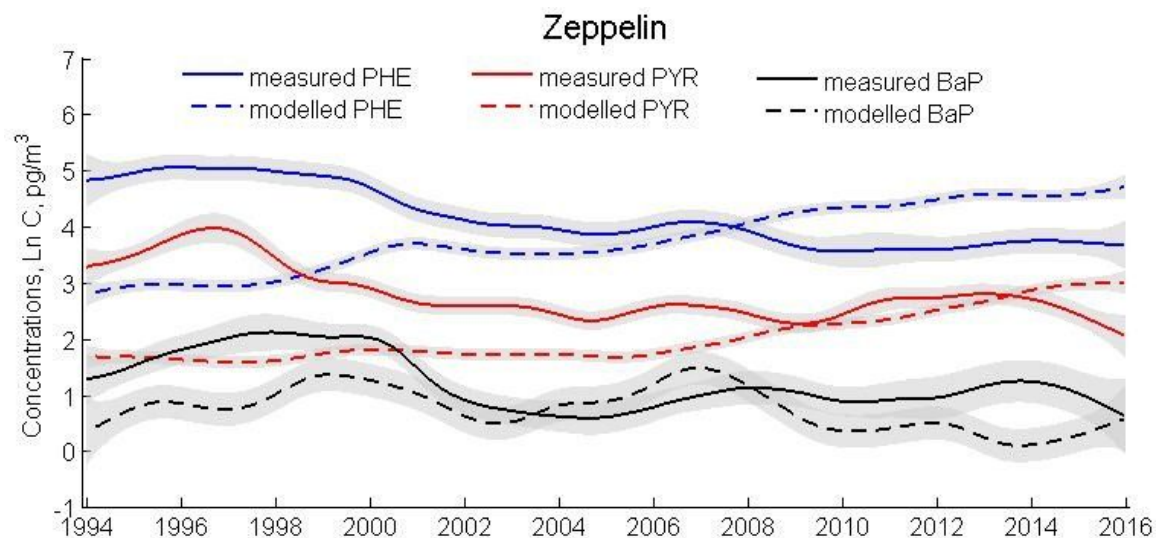
296 increased significantly over the ~20 years at the three sites, whereas simulated PYR
297 exhibited different trends; increasing concentrations only became apparent since 2008.
298 This difference is probably due to the higher volatility of PHE (Henry's Law constant (H)
299 = $4.78 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at $25 \text{ }^\circ\text{C}$) compared to PYR ($H = 2.13 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at $25 \text{ }^\circ\text{C}$) (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 decades⁹. 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 seasons³⁸. 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 ($H=0.20 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at $25 \text{ }^\circ\text{C}$), but these
316 particle-bound chemicals are subject to LRAT as they can be protected by organic coatings
317 on aerosols³⁹, 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.



321



322



323

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

326

327 Simulated concentrations of PHE at two high-latitude sites, Alert and Zeppelin, increased
 328 from 1998 to 2000, likely due to the warming phase during those years and the modelling
 329 sensitivity to temperature (Figure S9, Table S7), whereas a slight increase was found at
 330 Pallas (Table S8), which is consistent with the conclusion by Ding et al.⁴⁰ that the most
 331 prominent warming in the Arctic occurred in northeastern Canada and Greenland. This
 332 observation shows that Arctic sites are useful in investigating the influence of climate
 333 change on the occurrence of PAHs and other contaminants. The highest annual mean
 334 temperatures over the ~20 years at Alert were observed in 1998 and 2001 (Figure S9),
 335 when the model predicted a period of rising concentrations of PHE in air at Alert. Moreover,
 336 simulated concentrations of PYR slightly increased but no such increase was found for BaP
 337 (Table S8) due to its lower H (Table S2) resulting in a lower tendency to volatilize from
 338 oceans and ice-covered surfaces. The second rising period, for both PHE and PYR, were
 339 found after 2008. The Arctic sea ice was drastically reduced in this century, specifically,
 340 it reached a minimum record in 2007 and 2012⁴¹⁻⁴³. The more volatile PAHs, PHE and PYR,
 341 can be released from the melting Arctic ice and the recently opened ocean (Table S7).
 342 Simulated concentration ranges of PHE and PYR are smaller than that observed at Alert
 343 and Zeppelin, indicating that there might be some local sources, such as military base at
 344 Alert, science stations at Ny-Ålesund and shipping emissions.

345

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

359

360 **Acknowledgments**

361 The authors thank all site and laboratory operators and students at the three stations.
362 Financial support for the monitoring programs was provided by the Northern Contaminants
363 Program (NCP), Crown-Indigenous Relations and Northern Affairs Canada (Alert); the
364 Swedish Environmental Protection Agency and Finnish Meteorological Institute (FMI)
365 (Pallas); and the Norwegian Environment Agency (Zeppelin). We thank the Canadian
366 Forces Station Alert for supporting data collection at Alert. We appreciate Dr. Marta
367 Venier's assistance on DHR, Dr. Philip Cheung's assistance on assimilation of Canadian
368 Meteorological Center (CMC) meteorological data, Prof. Tao Huang's assistance on
369 sensitivity analysis and Prof. Xingming Zheng's assistance on ArcGIS.

370

371 **Supporting Information Available**

372 A description of potential in sample breakthrough, DHR, the CanMETOP, air-surface
373 exchange, model evaluation, and PMF results is given in the Supporting Information.
374 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>

377

378 **Author Information**

379 **Corresponding author:**

380 Dr. **Hayley Hung** E-mail: hayley.hung@canada.ca

381 Dr. **Yong Yu** E-mail: yuyong@iga.ac.cn

382 **Notes**

383 The authors declare no competing financial interests.

384

385 **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.; Klungsoyr, 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.

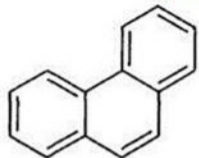
413 (10) Harvey, H. R.; Taylor, K. A.; Pie, H. V.; Mitchelmore, C. L., Polycyclic aromatic and aliphatic
414 hydrocarbons in Chukchi Sea biota and sediments and their toxicological response in the Arctic
415 cod, *Boreogadus saida*. *Deep-Sea Res. Pt. II* **2014**, *102*, 32-55.

- 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.

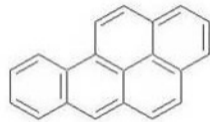
- 464 (29) Halsall, C. J.; Barrie, L. A.; Fellin, P.; Muir, D.; Billeck, B.; Lockhart, L.; Rovinsky, F. Y.; Kononov,
465 E. Y.; Pastukhov, B., Spatial and temporal variation of polycyclic aromatic hydrocarbons in the
466 Arctic atmosphere. *Environ. Sci. Technol.* **1997**, *31* (12), 3593-3599.
- 467 (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.; Tripathi, 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

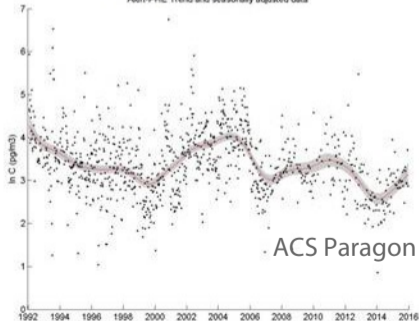
air-surface exchange



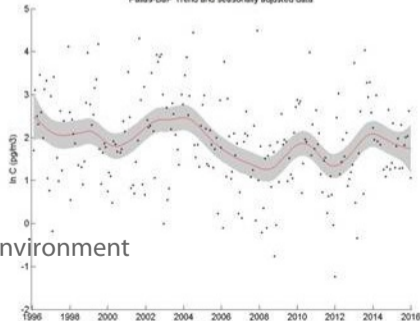
LRAT



Alert-PHE Trend and seasonally adjusted data



Pallas-BaP Trend and seasonally adjusted data



ACS Paragon Plus Environment

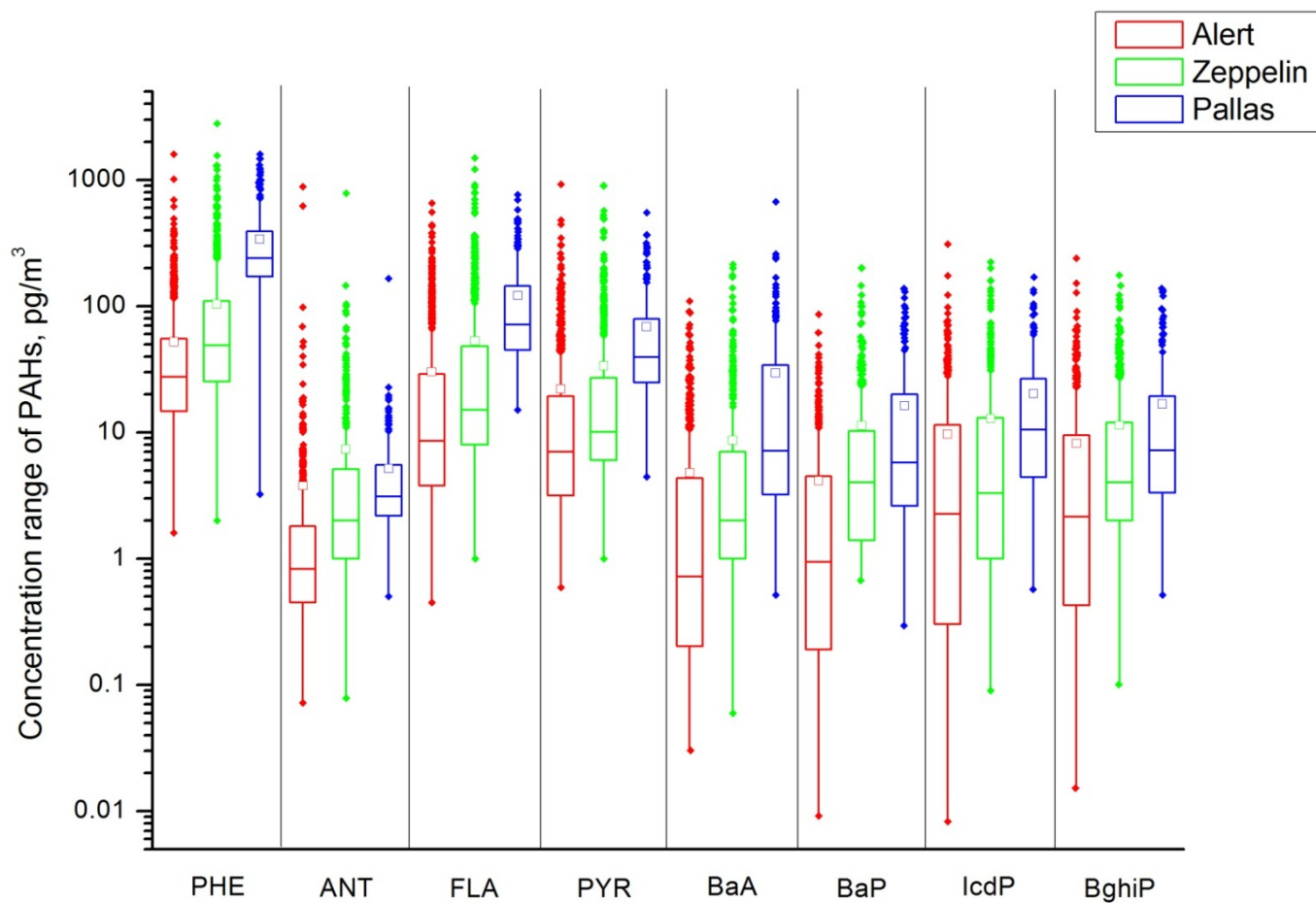


Figure 1. Box-and-whisker plots of 8 PAHs at the three sites during the sampling periods. The boxes represent the 25th and 75th percentiles of the data. The lines in the boxes and square symbols represent the median and the mean, respectively. All the outliers beyond the whiskers are shown individually.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

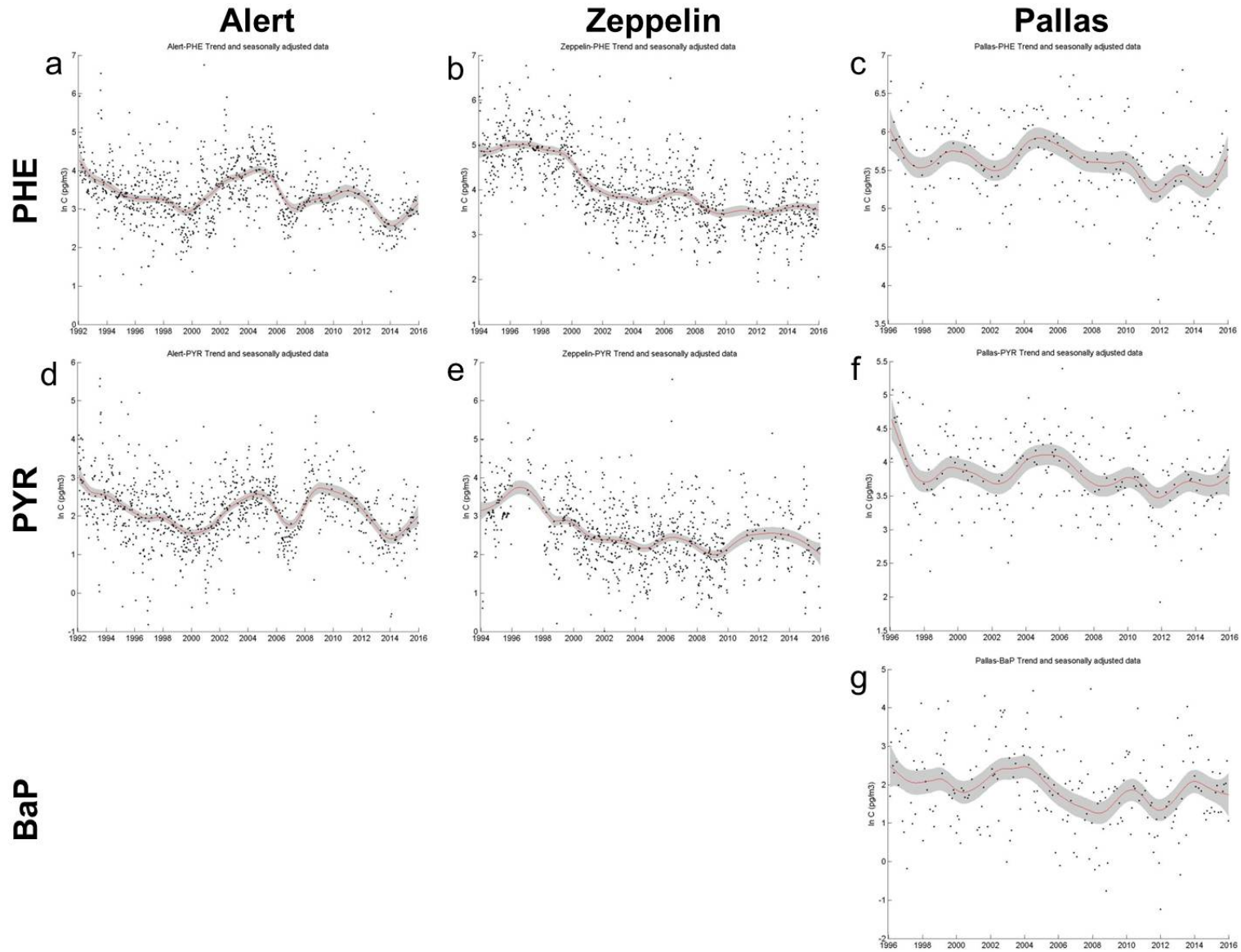


Figure 2. Long-term trends of (a, b, c) PHE and (d, e, f) PYR at three sites and (g) BaP at Pallas.

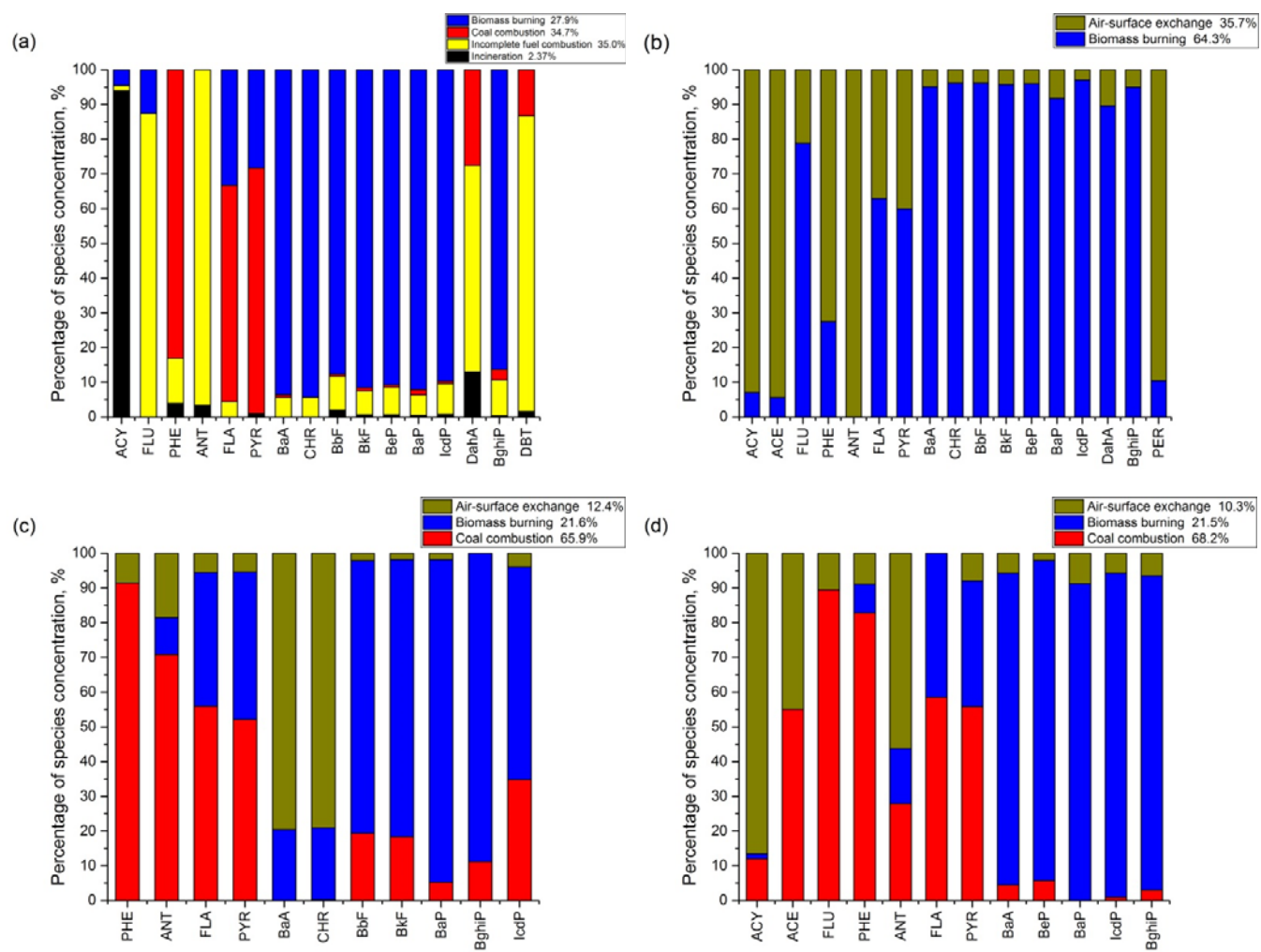


Figure 3. Factor Fingerprints for (a) Alert (1992-2003), (b) Alert (2004-2015), (c) Pallas (1996-2015), and (d) Zeppelin (1994-2015).

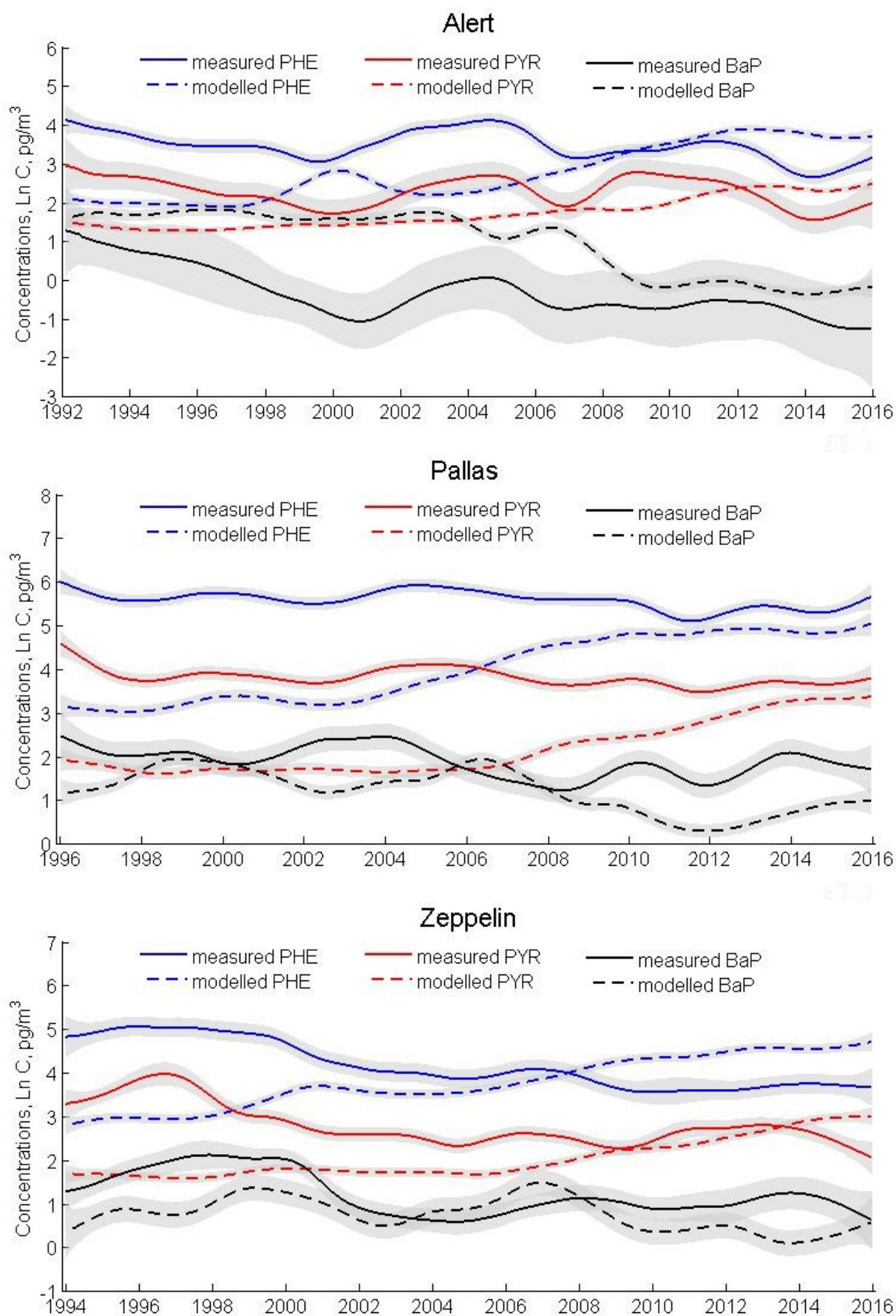


Figure 4. Trends of monthly mean concentrations of three PAHs (measured and simulated) at three sites. The shade represents the standard deviations of the trends.