

A comparison of PM_{2.5}-bound polycyclic aromatic hydrocarbons in summer Beijing (China) and Delhi (India)

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Abstract.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in air, soil and water and known to have harmful effects on human health and the environment. The diurnal and nocturnal variation of 17 PAHs in ambient particle-bound PAHs were measured in urban Beijing (China) and Delhi (India) during the summer season using GC-Q-TOF-MS. The mean concentration of particles less than 2.5 microns (PM_{2.5}) observed in Delhi was 3.6 times higher than in Beijing during the measurement period in both the daytime and night-time. In Beijing, the mean concentration of the sum of the 17 PAHs (\sum 17 PAHs) was 8.2 ± 5.1 ng m⁻³ in daytime, with the highest contribution from Indeno[1,2,3-cd]pyrene (12 %), while at night-time the total PAHs was 7.2 ± 2.0 ng m⁻³, with the largest contribution from Benzo[b]fluoranthene (14 %). In Delhi, the mean \sum 17 PAHs was 13.6 ± 5.9 ng m⁻³ in daytime, and 22.7 ± 9.4 ng m⁻³ at night-time, with the largest contribution from Indeno[1,2,3-cd]pyrene in both the day (17 %) and night (20 %). Elevated mean concentrations of total PAHs in Delhi observed at night were attributed to emissions from vehicles and biomass burning and to meteorological conditions leading to their accumulation from a stable and low atmospheric boundary layer. Local emission sources were typically identified as the major contributors to total measured PAHs in both cities. Major emission sources were characterised based on the contribution from each class of PAHs, with the 4, 5, and 6 ring PAHs accounting ~ 95 % of the total PM_{2.5}-bound PAHs mass in both locations. The high contribution of 5 ring PAHs to total PAH concentration in summer Beijing and Delhi suggests a high contribution from petroleum combustion. In Delhi, a high contribution from 6 ring PAHs was observed at night, suggesting a potential emission source from the combustion of fuel and oil in power generators, widely used in Delhi. The lifetime excess lung cancer risk (LECR) was calculated for Beijing and Delhi, with the highest estimated risk attributed to Delhi (LECR = 155 per million people), 2.2 times higher than Beijing risk assessment value (LECR = 70 per million people). Finally, we have assessed the emission control policies in each city and identified those major sectors that could be subject to mitigation measures.

49 **1 Introduction**

50 The significant increase of particulate matter (PM) and gaseous pollutants over the past decades in some
51 rapidly expanding economies, has led to greater emphasis being placed on mitigation of emissions and
52 management air quality health effects. To support such measures requires insight in both the sources of
53 pollution, and the composition of pollution so that most harmful sources may be tackled as a priority.
54 Although there have been recent improvements that have reduced primary particle concentrations in
55 some regions, concentrations of many damaging gases and fine particles continue to exceed WHO
56 guidelines (WHO, 2016), in megacities such as Beijing (Elzein et al., 2019; Lin et al., 2018; Gao and
57 Ji., 2018) and Delhi (Kanawade et al., 2019; Sharma et al., 2007) and in many other cities around the
58 world such as Cairo, Egypt (Cheng et al., 2016) and Islamabad, Pakistan (Mehmood et al., 2020).
59 Growing populations, human activities, energy consumption and natural contributions (volcanic
60 eruptions and forest fires) are an important contributor to particles emissions. PM monitoring and
61 analysis become ever more important because of its adverse effect on human health. The chemical
62 composition of airborne particles influences the health impacts, particularly the abundance of primary
63 and secondary organic matter, metals, and ions (WHO, 2016; Bond et al., 2004; Saikawa et al., 2009).
64 Fine particles become more harmful as particle size decreases (ultrafine), they enter the human body
65 through the lungs and may translocate to other organs causing respiratory diseases and cancer
66 (Schraufnagel., 2020). The greatest adverse effects on human health in epidemiological studies are
67 currently associated with the mass of particles less than 2.5 microns in diameter (PM_{2.5}) (Raaschou-
68 Nielsen et al., 2013, Pun et al., 2017, Hamra et al., 2014). The organic component of PM_{2.5} consists of
69 thousands of compounds, among them polycyclic aromatic hydrocarbons (PAHs), a particular class of
70 species with high toxic potency. They are released into the atmosphere from both natural and
71 anthropogenic sources. PAHs are considered ubiquitous in the environment and can be found in soil
72 and water via dry or wet atmospheric deposition (Menzie et al., 1992, Meador et al., 1995). Their major
73 emissions come from anthropogenic sources and include incomplete combustion of fossil fuels, vehicle
74 exhaust emissions, cigarette emissions, agricultural burning and industrial activities (Saikawa et al.,
75 2009). It has been shown that PAHs can react with atmospheric oxidants leading to the formation of
76 secondary species with direct-acting mutagenicity and carcinogenicity and thus they can be significant
77 contributors to the high toxicity of particles even at low PM levels (Nisbet and LaGoy 1992).
78 Beijing and Delhi often suffer from severe air pollution episodes, reaching high PM_{2.5} concentrations
79 and air quality index levels. The local government in Beijing has declared many different air quality
80 actions since September 2013, resulting in a decrease in the concentration of total PAHs as reported in
81 recent studies for the winter season in Beijing (Chen et al., 2017, Elzein et al., 2019, Feng et al., 2019).
82 This has been attributed to the efforts made by the municipal government of Beijing to improve air
83 quality and control emissions by reducing combustion sources and promoting the use of clean energy
84 sources and electric vehicles.
85 Several anti-pollution measures have been introduced in Delhi in the last two decades such as, Bharat
86 stage (equivalent to Euro standards), switching public transport from running on diesel to compressed
87 natural gas (CNG), and applying "odd-even" vehicle number plate restriction during working days
88 (Guttikunda et al., 2014; Goel and Guttikunda, 2015; Chowdhury et al., 2017). Despite the government
89 effort to tackle air pollution in India and especially in Delhi, recent studies have showed that the air
90 quality continue to be among the poorest in the world causing thousands of premature deaths (Tiwari
91 et al., 2015, Ghude et al., 2016, Chowdhury and Dey., 2016, Pant et al., 2017, Conibear et al., 2018).
92 PAHs emission sources in Delhi have previously been attributed to vehicle emissions, coal combustion,
93 wood and burning leaves (Gadi et al., 2019; Shivani et al., 2019; Gupta et al., 2011; Sharma et al 2007).
94 To the best of our knowledge, data on PM_{2.5}-bound PAHs in Delhi during the summer season (pre-
95 monsoon: March – June) is scarce and limited to other periods of the year with low-time resolution
96 ambient samples (sample averaging time of 24-h). It has been shown that concentrations of ambient

97 particle-bound PAH when collected over long sampling times are subject to higher uncertainties related
98 to sampling artefacts deriving from meteorological effects and oxidant concentrations such as ozone
99 (Goriaux et al., 2006; Tsapakis and Stephanou, 2003, 2007; Ringuet et al., 2012a; Keyte et al., 2013).
100 Using shorter time periods for ambient particle sampling (e.g. 3 and 4 h) has been suggested as offering
101 more accurate diagnosis of emission sources (Tian et al., 2017; Srivastava et al., 2018), shorter time
102 sampling is still scarce and limited to studies outside China and India (Reisen and Arey, 2004;
103 Srivastava et al., 2018). Considering the above and that particles collected during 24-hour sampling
104 time integrate both daytime and night-time chemistry together, we collected high frequency ambient air
105 particle samples (PM_{2.5}) in urban Beijing (China) and Delhi (India) to determine the temporal diurnal
106 and nocturnal variation of PAHs. A great advantage in this study is that all particle samples from both
107 campaigns were collected, extracted and analysed using the same analytical method, which provide a
108 better comparison of the variation in PAHs between cities and on the feasibility and efficiency of
109 implementing emission control policies to improve air quality in both cities.
110

111 **2 Methods**

112 **2.1 Sampling campaigns**

113 Both measurement campaigns were part of the UK NERC / MRC Air Pollution and Human Health
114 (APHH) research programme. The sampling site in Beijing was located at the Institute of Atmospheric
115 Physics, Chinese Academy of Sciences in Beijing (39°58'28" N, 116°22'15" E) and the sampling site
116 in Delhi was located at Indira Gandhi Delhi Technical University for Women (28°39'52.6" N,
117 77°13'54.1" E). In both campaigns, the sampling equipment was installed on the roof of a 2-storey
118 building about 8 m above ground level. Prior to sampling the quartz microfiber filters (Whatman QM-
119 A, 20.3 × 25.4 cm, supplied by VWR U.K.) were baked at 550 °C for 5 h in order to eliminate any
120 organic matter. PM_{2.5} filter samples were collected every 3 hours during daytime and over 15 h at night-
121 time, using a High-Volume Air Sampler (Ecotech HiVol 3000, Victoria, Australia) operating at 1.33
122 m³ min⁻¹. The daytime sampling started at 8:30 in the morning and the filter was changed every 3 h.
123 Night-time sampling began at ~17:30 and ended at 08:30 the following day. Filters were collected for
124 20 days (22 May 2017 to 10 June 2017) totalling 80 filters during Beijing campaign, and for 9 days (28
125 May 2018 to 5 June 2018) totalling 35 filters during Delhi campaign. After sampling, filters were
126 wrapped in aluminium foil, sealed in polyethylene bags and stored at -20 °C until extraction and
127 analysis.
128

129 **2.2 Sample extraction**

130 Collected filters were cut using a cube cutter (1/16 of the filter) measuring a surface area equivalent to
131 24 cm². Each section was then cut into small pieces to fit inside 5 mL stainless steel extraction cells
132 used by a pressurized solvent extractor (Dionex, ASE 350). All samples were extracted in acetonitrile
133 (HPLC-grade) using the following method: Oven at 120°C, pressure at 1500 psi, rinse volume 60 %
134 and 60 s purge time for three consecutive 5 min cycles. The extraction time of each cell was about 25
135 min for a final volume of 20 mL. Prior to purification, extracts (V = 20 mL) were evaporated to
136 approximately 6 mL under a gentle stream of nitrogen. All samples and blanks were purified on solid
137 phase extraction (SPE) silica normal phase cartridge (1g/6mL; Sigma Aldrich) to reduce the impacts of
138 interfering compounds in the matrix and to help maintain a clean GC injection inlet liner. After the
139 purification step, the solution of each sample was evaporated to 1 mL under a gentle stream of nitrogen
140 at room temperature (20 °C) and transferred to a 1.5 mL autosampler amber vial. Each concentrated
141 sample was stored at 4 °C until analysis.
142
143
144

145 **2.3 Analytical procedures**

146 In this study, 17 PAHs were selected based on their presence within the particle phase and commercially
147 available standards. These are listed in Table 1 and standards purchased from Sigma Aldrich, Alfa Aesar
148 and Santa Cruz Biotechnology in the UK with a minimum purity of 97 %. In parallel to individual
149 standards, a mixed solution of the 16 EPA PAHs (CRM47940, Supelco, Sigma Aldrich) of $10 \mu\text{g ml}^{-1}$
150 in acetonitrile was also used. Standard solutions for calibrations were prepared in acetonitrile (HPLC
151 grade, 99.9 % purity, Sigma Aldrich). Phenanthrene-d10 and pyrene-d10 were used as surrogate
152 standards and were spiked over two blank filters and two sample filters from both campaigns, with
153 concentration on filters corresponding to 300 ng ($V = 60 \mu\text{L}$ from $5 \text{ ng } \mu\text{L}^{-1}$ in acetonitrile). Spiked
154 filters solutions were analysed 10 times, and the average recovery efficiencies calculated from surrogate
155 standards was 96 %, ranging from 88 % to 107 % for both compounds, phenanthrene-d10 and pyrene-
156 d10. PAH concentrations were corrected to the average recovery efficiencies. These two deuterated
157 compounds were supplied by C/D/N isotopes and distributed by QMX Laboratories Ltd (Essex, UK).
158 All PAH were quantified using a gas chromatography - time of flight - mass spectrometry system (GC
159 Agilent 7890B coupled to an Agilent 7200 Q-TOF-MS). $1 \mu\text{L}$ of each sample was injected in pulsed
160 splitless mode at $320 \text{ }^\circ\text{C}$ using an automated liquid injection with the GERSTEL MultiPurpose Sampler
161 (MPS). Helium was used as carrier gas at 1.4 mL min^{-1} and target compounds were eluted using the
162 RXi-5ms (Restek GC column, Crossbond diphenyl dimethyl polysiloxane; length: 30 m, diameter: 0.25
163 mm, film thickness: $0.25 \mu\text{m}$). The analysis time of each sample was set to 35 min using the following
164 GC oven temperature programme: $65 \text{ }^\circ\text{C}$ for 4 min as a starting point and then increased to $185 \text{ }^\circ\text{C}$ at a
165 heating rate of $40 \text{ }^\circ\text{C min}^{-1}$ and held for 0.5 min, followed by a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $240 \text{ }^\circ\text{C}$
166 and then ramped at $5 \text{ }^\circ\text{C min}^{-1}$ until $320 \text{ }^\circ\text{C}$ and held isothermally for further 6 min to ensure all analytes
167 eluted from the column. The MS was operated in Electron Ionisation (EI) mode at 70 eV with an
168 emission current of $35 \mu\text{A}$. 10-point calibration solutions were injected 4 times in the same sequence as
169 for samples and covered the range from $1 \text{ pg } \mu\text{L}^{-1}$ to $1000 \text{ pg } \mu\text{L}^{-1}$, with a correlation coefficient from
170 the linear regression between 0.970 and 0.999.

171

172 **2.4 Error evaluation**

173 As part of our method validation and in addition to recovery efficiency corrections, we have evaluated
174 other possible factors that can affect our final true result. In this study, the solvent (acetonitrile) and
175 field blanks ($n = 3$) were analysed following the same procedure as for the samples (Extraction, SPE,
176 Evaporation) to determine any source of contamination during sample preparation and the analytical
177 procedure. Whilst most target compounds were found to be below our limit of detection ($S/N=3$), three
178 PAHs (Fluorene, Phenanthrene, Fluoranthene, and Pyrene) were quantified in field blanks and their
179 contributions to the final data have been corrected.

180 To evaluate the agreement between repeated measurements (precision error), we calculated the relative
181 standard deviations (%RSD) from replicate analysis ($n = 10$) of two samples. The %RSD average of
182 total PAHs was 8.7 % (range: 3.36 – 13.71 %) for Beijing samples and 4.2 % (range: 2.64 – 10.12 %)
183 for Delhi samples. The %RSD average for deuterium labelled compounds spiked over two sample filters
184 was $\sim 3.6 \%$ for both campaigns. The %RSD of each compound is shown in Table S1. Moreover, the
185 calibration offset and the influence of the sample matrix on the quantification step are an important
186 source of systematic error and was estimated to be a maximum of 20 %. Therefore, the upper limit
187 estimated error, combining the precision and the systematic effects, is 30 % for Beijing samples and 25
188 % for Delhi samples.

189 In addition, another type of error has been attributed to sampling artefacts. Previous studies (Schauer et
190 al., 2003, Goriaux et al., 2006, Tsapakis and Stephanou, 2003, Brown and Brown, 2012) have reported
191 a chemical decomposition of PAHs depending on the ambient concentration of ozone and sampling
192 time. Therefore, data from long sampling times and under very high ozone ambient concentrations (>70

193 ppb) may be biased by sampling artefacts of more than 100 % (Schauer et al., 2003, Goriaux et al.,
194 2006). However, at low ozone levels (< 30 ppb), negative artefacts were considered not significant
195 (Tsapakis and Stephanou, 2003), whilst, at medium ozone levels (30-50 ppb) PAHs values were
196 underestimated by 30 % (Schauer et al., 2003). Tsapakis and Stephanou (2003), have reported a loss of
197 PAHs by 28 % due to ozone atmospheric concentration about 60 ppb and long sampling times of 24-h.
198 They have also suggested that long sampling time under low ozone concentration (< 30 ppb) do not
199 affect the concentration of collected PAHs in the gas or particle phases, while short sampling time (2
200 h) under ozone concentration about 60 ppb will reduce the concentration of PAHs by 17 %. In this
201 study, ozone concentrations were measured in both campaigns and averaged to the filter sampling time
202 to provide more accurate estimation on the negative sampling artefacts. The ozone concentration in
203 summer Beijing ranged between 3.7 and 140 ppb over the campaign (mean value: 56 ± 31 ppb),
204 approximately 5 times higher than that in winter (mean value: 10.4 ± 8.8 ppb, Elzein et al., 2019).
205 Daytime ozone concentration ranged from 12 to 140 ppb (mean value: 63 ± 30 ppb), while over the
206 night-time it ranged from 4 to 74 ppb (mean value: 34 ± 18 ppb). Therefore, based on Tsapakis and
207 Stephanou (2003) study, the negative sampling artefacts due to ozone concentration was estimated to
208 be 20 % for daytime samples (3 h) and 10 % for the night-time samples (15 h) due to lower ozone
209 concentration at night. Using the same approach, daytime ozone concentration in Delhi ranged between
210 39 and 119 ppb, with a mean value: 75 ± 20 ppb, while the night-time concentration ranged from 14 to
211 50 ppb (mean value: 37 ± 12 ppb). Therefore, the estimation of the negative sampling artefacts on the
212 data from Delhi ranged between 15 and 30 %, with the highest error estimation attributable to daytime-
213 time samples (3 h) because of the higher ozone concentration during the day.

214

215 **3 Results and discussion**

216 **3.1 Concentration levels of PM_{2.5} and Benzo[a]pyrene in summer Beijing and Delhi**

217 In 2016, the World Health Organisation (WHO, 2016) published an air quality guideline on outdoor air
218 pollution limits to help protect human health and reduce the risk of mortality due to fine particles. The
219 air quality standards for PM_{2.5} were set by the ministry of environment in China and India, and published
220 in the WHO air quality guideline as an annual and 24-h mean concentration. The daily PM_{2.5} (mean 24-
221 h) guideline concentration is currently set at 75 and 60 $\mu\text{g m}^{-3}$ for China and India, respectively, while
222 the annual mean guideline concentration is currently set at 35 and 40 $\mu\text{g m}^{-3}$ for China and India,
223 respectively. PM_{2.5} concentrations measured at the two sites were averaged to the filter sampling time
224 and are shown in Fig.1 and Fig. 2. In Beijing, the average 24-h PM_{2.5} concentration was 39 ± 21 $\mu\text{g m}^{-3}$
225 (range: 16 - 97 $\mu\text{g m}^{-3}$), exceeding the Chinese 24-h limit value ($75 \mu\text{g m}^{-3}$) on 1 day of the 20 sampling
226 days. The average daytime and night-time PM_{2.5} concentrations in Beijing were 40 ± 24 $\mu\text{g m}^{-3}$ and 38
227 ± 24 $\mu\text{g m}^{-3}$, respectively. Delhi showed an average 24-h PM_{2.5} concentration of 143 ± 27 $\mu\text{g m}^{-3}$ (range:
228 110 - 195 $\mu\text{g m}^{-3}$), exceeding the Indian 24-h limit value on all 9 sampling days. The average daytime
229 and night-time PM_{2.5} concentrations in Delhi were 141 ± 51 $\mu\text{g m}^{-3}$ and 140 ± 26 $\mu\text{g m}^{-3}$, respectively.
230 PM_{2.5} concentrations in Delhi have changed little in recent years; between 2008 and 2011 the daily
231 average of PM_{2.5} concentrations was 123 ± 87 $\mu\text{g m}^{-3}$ (Guttikunda and Calori., 2013), while the annual
232 average was reported to be 125.5 ± 77.2 $\mu\text{g m}^{-3}$ between January 2013 and May 2014 (Winter: 196 $\mu\text{g m}^{-3}$,
233 Summer: 83.6 $\mu\text{g m}^{-3}$, Monsoon: 58.8 $\mu\text{g m}^{-3}$) (Sharma and Mandal., 2017). The limited change
234 seen in recent years may be associated with continued emissions from residential energy use, estimated
235 to contribute about 50 % of PM_{2.5} airborne concentrations (Conibear et al., 2018, Butt et al., 2016). The
236 construction sector is fast growing in India, and the dust emitted from various activities (demolition,
237 excavation, drilling etc.) is also considered an important source of particles (Guttikunda et al., 2014).
238 The WHO has not published a guideline limit value for PAHs, but benzo[a]pyrene (BaP) is often used
239 as a marker of toxicity for all PAHs. The European Union has set an annual mean air quality limit of 1
240 ng m^{-3} for BaP (WHO, 2016). The daily (24-h) concentration of BaP in summer Beijing (this study)

241 ranged from 0.49 to 1.18 ng m⁻³ (average 0.80 ± 0.17 ng m⁻³), about 19 times lower than previously
242 observed at this site in winter (Elzein et al., 2019). This is below the 24-h average limit value of 2.5 ng
243 m⁻³, set in China by the Ministry of Ecology and Environment in 2012, on all of the 20 days of sampling
244 period. During the short summer measurement period in Delhi, BaP varied between 1.16 and 3.16 ng
245 m⁻³ (average 1.78 ± 0.67 ng m⁻³), and exceeded the threshold of 2.5 ng m⁻³ on 1 day.

246

247 **3.2 Variability of PAHs in summer Beijing and Delhi**

248 A time series of the temporal variation of total PAHs in Beijing and Delhi are shown in Fig. 1 and Fig.
249 2, respectively. The box plots in Fig. 3 show a comparison of the measured concentrations of total 17
250 PAHs between daytime and night-time in both cities.

251

252 **Beijing:**

253 The mean 3 h daytime concentration of \sum 17 PAHs in Beijing was 8.2 ± 5.1 ng m⁻³ ranging from 2.6 to
254 31.2 ng m⁻³, while the mean 15 h night-time concentration was 7.2 ± 2.0 ng m⁻³ ranging from 2.8 to 11.4
255 ng m⁻³. The mean 24-h total concentration (combined results from daytime and night-time samples) of
256 the total 17 PAHs was 7.6 ± 1.9 ng m⁻³ (range: 3.9 – 11.3 ng m⁻³). This 24-h average is approximately
257 13 times lower than the average 24-h in winter time Beijing (97 ng m⁻³) reported in our previous study
258 at the same location (Elzein et al., 2019). Similarly, previous studies in urban Beijing (Feng et al., 2005;
259 Wu et al., 2014; Gao and Ji., 2018; Song et al., 2019; Feng et al., 2019) have reported much lower
260 values of PAHs in summer than in winter, showing the important role of seasonal variation in
261 influencing ambient concentrations of PAHs. The dominant reason for this seasonal variation in Beijing
262 is the increase in energy consumption in winter and in particular the emissions from traditional
263 rural/urban heating methods using coal. The effect of dispersion in vertical and horizontal directions
264 and long-range transport due to air mass trajectory can also influence local PAHs concentration.

265 The photochemical effects on particulate PAHs between summer and winter are not clear in the
266 literature and were considered to play a minor role in seasonal variation of PAHs (Wu et al., 2014).
267 However, an important factor that might affect PAH levels is their degradation or transformation due
268 to high ozone ambient concentration level in summer, which were 5 times higher than in winter (Elzein
269 et al., 2019). This factor can negatively bias PAHs levels during filter sampling by more than 100 %
270 (discussed above in section 2.4). The gas phase concentrations of PAHs were not measured in this study,
271 but the distribution of PAHs between the gaseous and particulate phases is an important factor affecting
272 their fate in the environment (Lohmann and Lammel, 2004). The distribution of highly volatile PAHs
273 (e.g. 2-3 ring) are known to be influenced by temperature (Tsapakis and Stephanou., 2005; Gaga and
274 Ari., 2011; Verma et al., 2017), while the low volatile PAHs and PAHs-derivatives (e.g. oxygenated
275 and nitrated-PAHs) are mostly associated to the particle phase (Albinet et al., 2008; Liu et al., 2017,
276 Zhang et al., 2018). The spatial variation within urban Beijing might have little difference on pollutants
277 concentrations (He et al., 2001), the variation will increase when moving to suburban areas because it
278 consists of a large number of factories, airports, and power plant stations. Feng et al. (2005) compared
279 the total PAHs concentration in PM_{2.5} at urban and suburban sites in Beijing at the same period of the
280 year (July and November 2002), and they reported higher values at the suburban site than at the urban
281 site by a factor ~1.5 in summer and ~ 2 in winter. The sampling location in this study is an urban area
282 surrounded by busy roads, residential buildings, an underground railway, and restaurants. Therefore, it
283 may be representative of the urban area of Beijing covering approximately half of the population in
284 Beijing metropolitan.

285 In Figure 1, the concentration of total PAHs in the first 3 h filter (08:30–11:30) of the day appear to be
286 higher than the rest of the day. These elevated concentrations are potentially associated with the early
287 morning rush hour time and vehicle emissions. The average night-time total PAHs concentration (7.2
288 ng m⁻³) was in the range of the second and third "3 h" daytime average values, 7.8 and 6.4 ng m⁻³

289 respectively. This indicates that the elevated total PAHs concentration in the first 3 h filter (08:30–
290 11:30) of the day is not related to accumulation of air pollutants at night-time but most likely related to
291 direct emissions from traffic in the early morning and particularly petrol combustion emissions (see
292 section 3.3).

293 To the best of our knowledge, previous studies in Beijing have not reported higher time resolution data
294 on total PAHs concentration, but mainly focused on the 24-h average concentration. A previous study
295 from Feng et al., (2005) reported a 24-h mean value of $25 \pm 6.8 \text{ ng m}^{-3}$ in summer Beijing (July 2002),
296 approximately 3.3 times higher than our 24-h mean value (7.6 ng m^{-3}). A more recent study from Feng
297 et al., (2019) reported a 24-h mean value of $11 \pm 5.9 \text{ ng m}^{-3}$ in Beijing in warm months (April to June
298 2015), 1.4 times higher than our 24-h mean value. In both studies of Feng et al., (2005 and 2019), the
299 urban sampling site was located at the campus of Peking University health science centre, a short
300 distance from our sampling site (~1 mile). In the same year of 2015 (July to September), Chen et al.,
301 (2017) and Zhang et al., (2020) reported the values of 9.7 ng m^{-3} and 8.9 ng m^{-3} , respectively, for total
302 PAHs concentration in $\text{PM}_{2.5}$. In the study of Chen et al., (2017), the $\text{PM}_{2.5}$ samples were collected at
303 the campus of Beihang university (~2.5 miles from our sampling site). Zhang et al., (2020) sampling
304 site was located at a primary school in the Haidian district (~3.5 miles from our sampling site).
305 Furthermore, Gao and Ji (2018) reported $14.5 \pm 1.3 \text{ ng m}^{-3}$ for total PAHs concentration in $\text{PM}_{2.5}$,
306 collected in summer Beijing (May-July, 2016) in the Haidian district (~4 miles from our sampling site).
307 Accordingly, the majority of previous studies have focused on studying PAHs in the Haidian district
308 (Wu et al., 2014; Chen et al., 2017; Gao and Ji., 2018; Feng et al., 2019; Zhang et al., 2020) because of
309 its high population density. The variation of PAHs concentration from different site locations in the
310 Haidian district may suggest that the spatial variation of PAHs in this area is not significant. Future
311 studies in different districts and rural areas of the metropolitan of Beijing would be helpful for
312 comparison of population exposures and spatial variation.

313 The results from studies of PAHs in summer Beijing in recent years (2015-2020) (Chen et al., 2017,
314 Gao and Ji., 2018, Feng et al., 2019, Zhang et al., 2020) show a continuous decrease in PAH
315 concentrations (range: $7 - 15 \text{ ng m}^{-3}$) in comparison with the previous decade (2000-2010; range: $11 -$
316 31 ng m^{-3}) (Feng et al., 2005, Li et al., 2013, Wu et., 2014). This improvement in air quality (mitigating
317 the emissions of PAHs) could be related to meteorological conditions (e.g. temperature, boundary layer
318 height), but also to the anti-pollution actions adopted by the municipal government of Beijing in 2013
319 to continue tackling air pollution, by reducing combustion sources in the intervening years and
320 promoting the use of clean energy sources such as solar hot water heating systems, banning heavy duty
321 vehicles from circulating in daytime, public transport modernisation, promoting electric vehicles and
322 electric motorbikes.

323

324 **Delhi:**

325 The population in Delhi is projected to continue growing and to become the most populous city in the
326 world with 39 million people in 2030 (United Nations, 2019), living within a geographic area of 1483
327 km^2 , of which 783 km^2 is designated as rural and 700 km^2 as urban (Nagar et al., 2014). The summer or
328 pre-monsoon season (March-June) has very high temperatures and low precipitation. The city is
329 surrounded by different climatic zones; the Thar desert in the west, the central hot plains to the south,
330 the Himalayas to the north, and the Indo Gangetic plain in the east (Nagar et al., 2014). The northern
331 and Eastern part of India are considered to be the most polluted part of the country (Guttikunda et al.,
332 2014).

333 Similar to Beijing, previous studies in Delhi mainly focused on the 24-h average concentration of total
334 PAHs. They have addressed the problem of air pollution across India, focusing on $\text{PM}_{2.5}$ trends, $\text{PM}_{2.5}$
335 health impact, and source apportionment (Chowdhury et al., 2007; Gupta et al., 2011; Chowdhury and
336 Dey., 2016; Pant et al., 2017; Chen et al., 2020), however, PAHs emissions and variation between

337 daytime and night-time have not been measured or discussed previously, and only few studies (Sharma
338 et al., 2007; Singh et al., 2011, Gadi et al., 2019) reported the 24-h mean concentration of $\sum n$ -PAHs (n
339 > 10) in Delhi itself. In this study, the mean 24-h (combined results from daytime and night-time
340 samples) of the 17 PAHs was $19.3 \pm 7.1 \text{ ng m}^{-3}$ ranging from 13.3 to 35 ng m^{-3} . Previous studies showed
341 a large spatial variation in PAH concentrations within Delhi; Sharma et al., (2007) reported a mean 24-
342 h value of $624.04 \pm 376.48 \text{ ng m}^{-3}$ (~ 32 times higher than our mean value) for $\sum 12$ -PAHs at the South
343 of Delhi during the summer season of 2003. Singh et al., 2011 reported a mean 24-h value of $45.8 \pm$
344 22.1 ng m^{-3} (~ 2.4 times higher than our mean value) for $\sum 16$ -PAHs at the East of Delhi during the
345 summer season of 2008. Gadi et al., (2019) reported an annual average of $277 \pm 126 \text{ ng m}^{-3}$ for the
346 summation of 16-PAHs between December 2016 and December 2017, and $260 \pm 111 \text{ ng m}^{-3}$ for the
347 summer season of 2017 (~ 13.5 times higher than our mean value, and ~ 5.7 times higher than Singh et
348 al., 2011 mean value). In the study of Gadi et al., (2019), the sampling site was in the same campus as
349 this study (Indira Gandhi Delhi Technical University for Women), the low \sum PAHs value in this study
350 is most probably due to the short summer measurement period in Delhi (9 days, 35 samples), coupled
351 with less pollution episodes for PAHs. It appears that the variation of PAHs concentration in Delhi
352 could be affected by multiple factors including the spatial variation, the input from multiple local
353 sources, the surroundings of the sampling site, and the meteorological conditions in the north of Delhi.
354 Therefore, the concentrations of ambient particle-bound PAH over longer averaging period such as the
355 24-h are subject to high uncertainty related to the multiple factors cited above. Higher frequency filter
356 sampling during 24-h can provide a better assessment of PAH concentrations and is more likely to
357 reflect direct source emission signals as modified by meteorology. This perspective also applies to other
358 Indian cities in future studies.

359 The mean 3 h \sum PAHs concentration in daytime samples in Delhi was $13.6 \pm 5.9 \text{ ng m}^{-3}$ (~ 1.7 higher
360 than in Beijing) ranging from 8.4 to 36.6 ng m^{-3} , and the mean 15 h night-time samples was 22.7 ± 9.4
361 ng m^{-3} (~ 3.2 higher than in Beijing) ranging from 13.8 to 42.9 ng m^{-3} as shown in Figure 3. During the
362 daytime, the total PAH concentrations were generally highest during the first filter sample (8:30 to
363 11:30 am) (Fig. 2), following the same trend as for Beijing suggesting vehicle emissions as a dominant
364 source. The mean total PAH concentration at night-time was ~ 1.7 times higher than the mean in
365 daytime. Higher total PAHs concentration at night could be related to emissions from biomass burning,
366 waste burning, solid fuel cooking and heavy duty diesels entering the city at night-time. The higher
367 PAHs concentration at night may also be attributed to the relatively lower temperature at night ($\sim 10 \text{ }^\circ\text{C}$)
368 and lower atmospheric mixing heights (Fig. 4), weaker turbulence leading to lower pollutant dispersion
369 rates and absence of photodecomposition. Moreover, power cuts in India are frequent (Guttikunda et
370 al.,2014), especially when high demand occurs on air conditioners in summer (Harish et al., 2020),
371 which require in situ electricity generation using oil, diesel and petrol (Guttikunda et al.,2014). This
372 may be considered as an additional source of air pollution in a megacity like Delhi. $\text{PM}_{2.5}$ concentrations
373 increased on most nights in comparison with the preceding daytime sample. Residential energy use
374 across India has been reported to be an important source of $\text{PM}_{2.5}$ emissions, contributing 62 % in
375 summer and 70 % in winter of anthropogenic emissions of $\text{PM}_{2.5}$ (Conibear et al., 2018). This was also
376 confirmed in the study of Butt et al., (2016), showing that the impact of residential combustion
377 emissions on atmospheric aerosol across India is very important, accounting for 63 % of anthropogenic
378 black carbon and 78 % of anthropogenic particle organic matter emissions.

379 The mean 24-h values of \sum PAHs from this study ($19.3 \pm 7.1 \text{ ng m}^{-3}$) and recent previous studies (45.8
380 $\pm 22.1 \text{ ng m}^{-3}$ (Singh et al., 2011) and $260 \pm 111 \text{ ng m}^{-3}$ (Gadi et al., 2019)) are high. This suggests the
381 need for the implementation of a residential emission control strategy through potentially more effective
382 alternative technologies such as the use of non-fossil fuel (biofuel) and clean energy sources (solar,
383 wind, hydro-electric power, natural gas) for domestic use, end the use of in situ power generators by

384 increasing electricity supply and load, and cutting emissions from open waste burning by implementing
385 efficient collection and disposal of waste.

386

387 **3.3 Major PAH, particle aging and traffic emissions**

388 In both campaigns, a high proportion of 5 and 6-ring PAHs were found in the particle phase (Table 1).
389 In Beijing, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene and Indeno[1,2,3-cd]pyrene
390 were the four most abundant particle-bound PAHs in daytime samples, while Benzo[b]fluoranthene,
391 Indeno[1,2,3-cd]pyrene, and Benzo[ghi]perylene were the three dominant particle-bound PAHs in
392 night-time samples. Six major compounds were found in Delhi day and night samples,
393 Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene (BaP), Benzo[e]pyrene (BeP),
394 Indeno[1,2,3-cd]pyrene, and Benzo[ghi]perylene; the mean concentration of these compounds were
395 higher at night. Generally, the 2 and 3-ring PAHs are predominantly found in the gas phase and the 4-
396 ring PAHs partition between the gas and particle phase (Liu et al., 2013, Zhang et al., 2018). The study
397 from Liu et al., (2013) suggested that ambient temperature largely controls the gas-particle partitioning
398 of 2, 3, and 4-ring PAHs concentration in the gas and particle phases.

399 A number of molecular diagnostic ratios for source apportionment have been proposed in literature and
400 are still under debate (Larsen and Baker., 2003; Katsoyiannis et al., 2011; Keyte et al., 2013; Zheng et
401 al., 2017). They were considered uncertain in some studies because the results were not consistent and
402 reproducible and did not reflect known differences in sources in space and time unless the source is
403 very strong and the sampling measurements are made close to the known source. In addition, they may
404 be biased by atmospheric reactions and selective loss processes (Katsoyiannis et al., 2011; Zheng et al.,
405 2017). Among the PAHs, BaP is known to be a particularly carcinogenic compound inducing a
406 mutagenic effect in experimental animals and is used as key PAH marker of total exposure (WHO,
407 2016, IARC, 2012). BaP is mostly emitted from coal and biomass burning, and vehicle exhaust
408 emissions (Harrison et al., 1996; WHO, 2016). The sampling site in both Beijing and Delhi was at a
409 short distance from busy roads with significant vehicle exhaust emissions. BaP lifetime is affected by
410 light and oxidants in the atmosphere, BaP is far more reactive than its isomer BeP (Butler and Crossley,
411 1981, Ringuet et al., 2012b), thus the decline of the ratio $BaP/(BaP + BeP)$ can be regarded as an
412 indicator of particle aging (Liu et al., 2013; Watson et al., 2016). Considering the above, $BaP/(BaP +$
413 $BeP)$ has been used in this study to assess the contribution of local sources on particle composition.
414 Generally, there is no defined threshold value for $BaP/(BaP + BeP)$ which can distinguish aged particles
415 from freshly emitted. However, Watson et al., (2016) suggested that similar amounts of BaP and BeP
416 (ratio = 0.5) indicates that particles are freshly emitted and mostly affected by local emissions rather
417 than long range atmospheric transport. Moreover, Liu et al., (2013) compared BaP and BeP ratios at
418 remote sites and emission source regions and reported BaP/BeP lower than 0.4 means aged aerosol type,
419 while a value higher than 0.4 indicates local emission source. In this study, a ratio of $BaP/(BaP + BeP)$
420 higher than 0.5 has been considered to characterize local emission sources. The ratio of $BaP/(BaP +$
421 $BeP)$ has been calculated for both campaigns and results are shown in Figure 5. This ratio mainly varied
422 between 0.5 and 0.6 in Beijing, indicating a dominant contribution from local sources. In Delhi, 25 %
423 of the data were below 0.5 indicating that aged particles might contribute to the air masses collected at
424 the sampling site but local emissions of PAH are still a significant source. However, this assumption
425 does not take into account the “on-filter” oxidation errors during sampling. Tsapakis and Stephanou
426 (2003) reported a relative reactivity of BaP of 1.6 times higher than BeP, with respect to degradation
427 on glass fibre filters. Using the reactivity factor of 1.6, the ratio of $BaP/(BaP + BeP)$ will be affected
428 negatively by an average of 4 % (day) and 1.6 % (night) for Beijing, 7 % (day) and 3 % (night) for
429 Delhi. This assumption will therefore be affecting Delhi results suggesting more contribution from long
430 range transport. Therefore, the indicator of particle aging should be used with careful in the summer

431 season unless ozone ambient concentrations are below 30 ppb, and consequently the negative artefacts
432 are considered not significant (Tsapakis and Stephanou 2003).
433 Since the influence from traffic emissions is very strong in both Beijing and Delhi, related diagnostic
434 ratios were used to distinguish between petrol and diesel, such as, Fluorene/Fluorene+Pyrene (< 0.5 for
435 Petrol engines and > 0.5 for diesel engines) and Pyrene/BaP (Ravindra et al., 2008; Tobiszewski and
436 Namiesnik., 2012; Watson et al., 2016; Zheng et al., 2017). We calculated the ratio value for Pyrene/BaP
437 using the data reported in a previous study (Rogge et al., 1993), where the authors have quantified more
438 than 100 organic compounds in exhaust emissions fine particulate matter. The ratio value for
439 Pyrene/BaP was ~ 0.7 for noncatalyst-equipped petrol cars, ~ 1.3 for catalyst-equipped petrol cars and
440 > 16 for heavy duty diesel engines. A recent study from Perrone et al., (2014) reported PM-phased PAH
441 emission factors for different types of vehicles (Euro 3 standards), the ratio value for Pyrene/BaP was
442 ~ 6 and 30 for petrol and diesel cars, respectively. The results from both ratios
443 (Fluorene/Fluorene+Pyrene and Pyrene/BaP) suggest high contribution from petrol engines to particle
444 composition in Beijing and Delhi (Fig S1). Tsapakis and Stephanou (2003) reported a relative reactivity
445 for BaP, Pyrene and Fluorene of 0.86, 0.82, and 0.68 respectively. The relative reactivity of BaP and
446 Pyrene are similar and therefore does not affect the indicator Pyrene/BaP values. Pyrene is by 20 %
447 more reactive than Fluorene, the “on-filter” oxidation has little effect on the indicator
448 Fluorene/Fluorene+Pyrene values, because of the large difference in the defined threshold values which
449 were 6 and 30 for petrol and diesel cars, respectively.

450

451 **3.4 Emission source fingerprints**

452 The profiles of specific class of PAHs and their abundance vary largely, depending on the fuel types
453 and combustion conditions (IARC, 2012). Previous studies reported that 2 and 3 aromatic ring PAHs
454 are mostly emitted from wood combustion (Khalili et al., 1995; Larsen and Baker., 2003; Liu et al.,
455 2017); 2, 3 and 4 ring from diesel exhaust emission (Bourotte et al., 2005; Ravindra et al., 2007; De
456 Souza et al., 2016; Zheng et al., 2017); 3 and 4 ring from coal combustion (Harrison, et al., 1996; Liu
457 et al., 2017); 4, 5, and 6 ring from vehicle emissions (Ravindra et al., 2007, Zhao et al., 2020); 5 and 6
458 ring from petrol and oil combustion (Harrison, et al., 1996; Ravindra et al., 2007). In this study, we
459 have classified the 17 PAHs based on their number of aromatic ring; we referred to previous studies
460 and to our knowledge of local sources, sampling site and surroundings, and analytical uncertainties to
461 describe the emission source of each class. The 2 and 3 aromatic ring PAHs were below LOD and LOQ
462 in many samples, however, they are predominantly found in the gas phase and their partitioning to the
463 particle phase is very small because of their high volatility; their percentage in the particle phase was
464 previously reported to be less than 10 % (Ravindra et al., 2007; Liu et al., 2017; Zhao et al., 2020).

465 In this study, the 4, 5, and 6 ring PAHs accounted ~ 95 % of the total $PM_{2.5}$ -bound PAH concentrations
466 measured in both campaigns (Fig. 6). The mean contribution of the number of ring to the total of PAHs
467 in Beijing $PM_{2.5}$ was distributed in the order $5 > 4 > 6$ ring, and in Delhi as $5 > 6 > 4$ ring (Fig. 6). In
468 both, Beijing and Delhi, road traffic is known to be one of the largest emission source of gas and particle
469 phase pollutants (Fang et al., 2016; Zhang et al., 2020; Shivani et al., 2019), which might explain the
470 high contribution from 4, 5 and 6 ring to total PAHs, while diesel and coal combustion may also
471 contribute to the emission of 4 ring PAHs. The 4 ring PAHs concentration in Delhi was higher than in
472 Beijing, the mean concentration of the 4 ring PAHs in daytime and night-time samples was 2.7 and 2.1
473 $ng\ m^{-3}$ in Beijing; 3.1 and 4.1 $ng\ m^{-3}$ in Delhi, respectively (Table 1). In contrast to Beijing ($5 > 4 > 6$
474 ring), the 4 ring PAHs total concentration in Delhi was lower than the 6 ring PAHs (Fig. 6) and a
475 potential emission source could be the common use of fuel and oil in power generators.

476 The distribution of ring PAHs in Figure 6 shows a comparison between the results from this study and
477 our previous study in winter Beijing (Elzein et al., 2019). The contributions from 2, 3 and 4 rings were
478 higher in winter than in summer, and the ring PAHs are distributed as $4 > 5 > 6 > 2-3$ ring (Fig. 6).

479 Ambient temperature highly affects the gas/particle partitioning of 2-3 ring PAH (Tsapakis and
 480 Stephanou., 2005; Gaga and Ari., 2011; Verma et al., 2017). Therefore, higher contributions from 2, 3
 481 and 4 rings in winter Beijing are likely due to lower temperature and to the use of coal and wood
 482 combustion for residential heating. The 2-3 and 6 ring PAHs contributions in winter Beijing are
 483 relatively similar, while in summer Beijing the contribution from 6 ring PAHs is ~ 20 % higher than 2-
 484 3 ring, most probably due to the effect of ambient temperature on 2-3 ring PAH. The 5 ring PAHs
 485 (representative of vehicle emissions) contribute the most to the total PAH concentration in summer
 486 Beijing and Delhi, suggesting a high contribution from petroleum combustion.
 487 Finally, identifying PAH markers emitted from specific emission sources (types of fuel, types of coal,
 488 types of waste, etc.) in ambient air is still complex due to the similarity of PAH profiles from different
 489 source types, which may quickly blend in the air with interferences from both nearby and remote
 490 emission sources. A more complete assessment of emission source types at specific locations would
 491 require the use of individual PAHs as source markers combined with other chemical constituents of
 492 PM_{2.5} (elements and ions) and with gas phase air pollutants known to be released from the same source
 493 such as VOCs markers.

494

495 **3.5 Health risk assessment**

496 Although PAHs have long been recognized as carcinogenic environmental pollutants, BaP is still the
 497 only PAH allowing a quantitative risk assessment (WHO, 2000, Boström et al., 2002). BaP is used as
 498 the most common reference chemical as being representative for PAH mixtures from emissions of coke
 499 ovens and similar combustion processes in urban air (WHO, 2000). Relative potencies of individual
 500 PAHs (relative to BaP) have also been published as toxicity equivalency factors (TEF) (Nisbet and
 501 LaGoy, 1992; Larsen et al, 1998; Durant et al, 1996, OEHHA., 1994). Thus, the carcinogenic risk of
 502 the mixture of PAHs can be expressed as BaP equivalents (BaP_{eq}). The equivalent exposure to the index
 503 compound (i.e. BaP) can be calculated from the TEF of each target compound (Table S2) multiplied by
 504 its corresponding concentration in ng m⁻³.

$$505 \quad [\text{BaP}]_{\text{eq}} = \sum_{i=1}^N \text{PAH}_i \times \text{TEF}_i \quad (1)$$

506 To estimate the statistical potential of contracting cancer from inhalation and lifetime exposure to PM_{2.5}-
 507 bound PAHs, commonly known as the lifetime excess cancer risk (LECR) shown in Eq. (2), we have
 508 used the WHO unit risk (UR) estimate of 8.7 x 10⁻⁵ (ng m⁻³)⁻¹ (WHO, 2000), meaning that 8.7 people
 509 per 100 000 people may contract lung cancer when exposed continuously to 1 ng m⁻³ of BaP
 510 concentration over a lifetime of 70 years. This risk refers to the total PAH mixture and not only to the
 511 BaP content (U.S.EPA, 2002, Boström et al., 2002) and is referred to as the surrogate approach. The
 512 use of BaP_{eq} instead of BaP in Eq.2, overestimates the LECR, and therefore the use of the actual
 513 measured BaP concentration better assesses the lifetime cancer risk following Eq. (2)

$$514 \quad \text{LECR} = \text{BaP} \times \text{UR} \quad (2)$$

515

516 **Table 2.** Mean concentration of BaP_{eq}, BaP and LECR assessment for Beijing and Delhi.

Sampling location	Mean [BaP] _{eq} ± SD* (ng m ⁻³)	Mean BaP ± SD* (ng m ⁻³)	LECR	LECR per million people
Beijing / 24-h	1.47 ± 0.35	0.8 ± 0.17	7 x 10 ⁻⁵	70
Delhi / 24-h	3.42 ± 1.35	1.78 ± 0.67	15.5 x 10 ⁻⁵	155

517 *SD : Standard deviation

518 As shown in Table 2, the LECR attributable to the 15 PAHs in urban air of Beijing and Delhi was 7 x
 519 10⁻⁵ and 15.5 x 10⁻⁵ (> 10⁻⁶), respectively, suggesting an elevated lifetime cancer risk for adults (Chen

520 and Liao., 2006; Bai et al., 2009), especially when considering the population size associated with each
521 city. The LECR value for Delhi gives an estimate of 85 additional cancer cases per million people
522 exposed, in comparison to Beijing. The LECR for Beijing in winter (Elzein et al., 2019) was much
523 higher than in summer (this study) and showed 1235 additional cases, and this was mostly attributed to
524 the increase in use of fossil fuels for central and residential heating, in addition to meteorological
525 conditions such as lower volatilisation at low temperatures and lower photochemical transformation. It
526 is however the annual mean which is directly related to cancer risk.

527 Although BaP is widely used as indicator of all PAHs carcinogenicity, this approach is still under debate
528 and may not give a very good representation of the whole mixture potency (U.S.EPA, 2002, Boström
529 et al., 2002). Delgado-Saborit et al., (2011) have used the TEFs to calculate the percentage contribution
530 of each PAH to total carcinogenicity following Eq. (3):
531

$$532 \quad (\% \text{Carc. Potential})_i = \frac{(\text{RC} \times \text{TEF})_i}{\sum_{i=1}^N (\text{RC} \times \text{TEF})_i} \times 100 \quad (3)$$

533 where RC is the relative abundance marker of an individual PAH to the carcinogenic marker BaP ($\text{RC} = (\text{PAH})_i / (\text{BaP})$). Using Eq.3, the compounds that contribute most to the total carcinogenic potential of
534 the PAH mixture in Beijing (B) and Delhi (D) are: Benzo[a]pyrene (B: 46 %; D: 48 %),
535 Dibenzo[a,h]anthracene (B: 23 %; D: 19 %), Benzo[b]fluoranthene (B: 15 %; D: 13 %),
536 Benzo[k]fluoranthene (B: 5 %; D: 5 %), and Indeno[1,2,3-cd]pyrene (B: 6 %; D: 10 %). The sum of all
537 other PAHs used in this study was about 5 %.
538

539 Since the majority of people (~ 90%) spend most of their time indoor, the total PAH burden from
540 inhalation has been related to indoor air, and BaP is used as a marker for the carcinogenic potential of
541 all PAHs irrespective of the environment (indoor or outdoor) (Delgado-Saborit et al., 2011). In this
542 study, the health risk evaluation was only based on inhalation exposure to PAHs in the particulate phase.
543 The risk values can increase due to the presence of PAHs derivatives in the particulate phase such as
544 the nitrated-PAHs (Elzein et al., 2019), and in particular from 6-Nitrochrysene and 1,6-dinitropyrene
545 who have been attributed a high TEF value equal to 10 (OEHHA., 1994; WHO., 2003; Lundstedt et al.,
546 2007). Dermal exposure to PAHs is also an important risk factor for skin cancer but toxicity values for
547 dermal exposures are still not available (U.S.EPA, 2002), in addition ingestion exposure to PAHs from
548 soil, sediments and water is high (Li et al., 2010), and both exposures (dermal+ingestion) can highly
549 exceed the risk from inhalation (U.S.EPA, 2002).

550 PAHs in the gas phase are mostly low molecular weight (2-3 ring PAHs) and their partitioning to the
551 particle phase is small (Ravindra et al., 2007; Liu et al., 2017; Zhao et al., 2020) with lower TEF values
552 (Table S2), therefore, their contribution to total carcinogenic potential is low (< 5 % in this study).
553 Previous studies may consider a variable number of PAHs and other aromatics with known TEF such
554 as the nitrated-PAHs, including different references for TEF values which make a direct comparison of
555 the carcinogenic risk between studies not ideal. However, as particulate-PAH concentrations are lower
556 in warm months, related BaP_{eq} values were also lower in warm months. Feng et al., 2019 reported an
557 average BaP_{eq} total concentration of 20 PAHs equal to 1.9 and 21.9 ng m^{-3} in summer and winter
558 Beijing, respectively. In this study, the summer BaP_{eq} total concentration of 15 quantified PAHs in
559 Beijing was 1.47 ng m^{-3} , while in our previous study for winter Beijing (Elzein et al., 2019), the BaP_{eq}
560 total concentration of 16 quantified PAHs and 7 derivatives was 23.6 ng m^{-3} . The results from this study
561 suggest to focus attention on mitigating the emission of major contributors to the total carcinogenic
562 potential (Benzo[a]pyrene, Dibenzo[a,h]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, and
563 Indeno[1,2,3-cd]pyrene) in order to reduce adverse health effects from exposure to this class of air
564 pollution. These compounds are 5 and 6 ring PAHs, and were mostly related to emission from petrol
565 and oil combustion (Harrison, et al., 1996; Ravindra et al., 2007).

566

567 **4 Conclusions**

568 Diurnally-resolved samples of ambient PM_{2.5} were collected in Beijing-China from 22 May 2017 to 10
569 June 2017 (20 days), and in Delhi from 28 May 2018 to 5 June 2018 (9 days). The 24-h average
570 concentration of PM_{2.5} was $39 \pm 21 \mu\text{g m}^{-3}$ (range: 16 - 97 $\mu\text{g m}^{-3}$) in Beijing, exceeding the Chinese
571 24-h guideline value (75 $\mu\text{g.m}^{-3}$) on 1 day of the 20 sampling days, while in Delhi the 24-h average
572 concentration of PM_{2.5} was $143 \pm 27 \mu\text{g m}^{-3}$ (range: 110 - 195 $\mu\text{g m}^{-3}$) exceeding the Indian 24-h
573 guideline value (60 $\mu\text{g.m}^{-3}$), on all 9 sampling days. High contribution to PM_{2.5} emissions was attributed
574 to residential energy use emissions and to the construction sector.

575 In Beijing and Delhi, 17 PAHs were quantified using a GC-Q-TOF-MS and the measured
576 concentrations compared between daytime and night-time, showing a high relative proportion (~ 95 %) of 4, 5 and 6-ring PAHs in the particle phase. In Beijing, Σ 17 PAH concentrations varied between 2.6
577 and 31.2 ng m^{-3} (average $8.2 \pm 5.1 \text{ng m}^{-3}$) in daytime, and from 2.8 to 11.4 ng m^{-3} (average 7.2 ± 2.0
578 ng m^{-3}) at night-time. In Delhi, Σ 17 PAH concentrations varied between 8.4 and 36.6 ng m^{-3} (average
579 $13.6 \pm 5.9 \text{ng m}^{-3}$) in daytime, and from 13.8 to 42.9 ng m^{-3} (average $22.7 \pm 9.4 \text{ng m}^{-3}$) at night-time.

581 In Beijing, Indeno[1,2,3-cd]pyrene was the highest contributor to the mean total PAHs during daytime
582 (12 %) and Benzo[b]fluoranthene at night (14 %) at night-time. In Delhi, Indeno[1,2,3-cd]pyrene was
583 the largest contributor to the total PAHs in both the day (17 %) and night-time (20 %).

584 The elevated mean concentration of total PAHs in Delhi at night was attributed to emissions from
585 biomass burning, waste burning, open fire cooking along with meteorological conditions facilitating the
586 accumulation of air pollutants as a result of low atmospheric boundary layer heights.

587 The ratio of BaP/(BaP + BeP) has been used to evaluate the contribution from local sources against
588 long range atmospheric transport of particle-bound PAHs. This ratio suggests a larger contribution from
589 local sources in both cities. Flu/Flu+Pyr and Pyr/BaP were used as diagnostic ratios to distinguish
590 between petrol and diesel, and results suggest petrol combustion emissions as a major source in Both
591 Beijing and Delhi.

592 PAHs were classified according to their number of aromatic rings to characterize major emission
593 sources. The 4, 5, and 6 ring PAHs accounted ~ 95 % of the total PM_{2.5}-bound PAH concentrations in
594 both campaigns. The 5 ring PAHs contribute the most to the total PAH concentration in summer Beijing
595 and Delhi, suggesting a high contribution from petroleum combustion. In Beijing, the 4 ring PAHs total
596 concentration was higher than the 6 ring by 8 % during the day and 5 % at night, while in Delhi, the 6
597 ring PAHs total concentration was higher than the 4 ring PAHs by 7 % during the day and 18 % at
598 night; a potential emission source of 6 ring PAHs in Delhi could be the common use of fuel and oil in
599 power generators. Due to the similarity of PAH profiles from different source types, it would be
600 beneficial to use other source markers such as elements and ions in PM_{2.5} and VOCs markers from the
601 gas phase to better identify the differences in emission sources.

602 The lifetime excess lung cancer risk was calculated for Beijing and Delhi, with the highest estimated
603 risk attributed to Delhi (LECR = 155 per million people), 2.2 times higher than Beijing risk assessment
604 value (LECR = 70 per million people). The results from this study suggest focusing attention on
605 mitigating the emission of major contributors to the total carcinogenic potential, being the 5 and 6 ring
606 PAHs (mostly emitted from petrol and oil combustion), in order to reduce adverse health effects from
607 inhalation exposure to PAHs in the particulate phase.

608 Finally, in Beijing, the anti-pollution actions since 2013 appear to have had a positive effect on the air
609 quality, while in Delhi, despite the government effort to mitigate air pollutants emission, a strict
610 implementation of emission control policies is still needed with particular focus on mitigating
611 residential emissions and burning, increasing the electricity supply to cover peak demand in summer
612 and limiting the use of local power generators as well as, promoting cleaner vehicles. Future studies in

613 different districts of Beijing (other than Haidian) and Delhi (other than old Delhi) and rural areas would
614 be helpful for comparison of population exposures and spatial variation. Higher frequency filter
615 sampling (every 3 h) can provide a better assessment of PAH concentrations and photochemistry and
616 can lead to better conclusions on direct source emission signals as modified by meteorology during the
617 daytime and night-time.

618

619 *Author contributions:* AE conducted the chemical analysis, analysed the data and prepared the
620 manuscript. ACL, JFH and RMH contributed to the interpretation, writing and corrections of the paper.
621 ERV calculated and provided the data on Delhi planetary boundary layer height. RG supported on site
622 filter collection and helped to set up the laboratory at the field site. AE and SJS conditioned and
623 collected the filter samples in Beijing. GJS and BSN conditioned and collected the filter samples in
624 Delhi. LRC and MSA measured and provided the data on PM_{2.5} in Delhi. All authors reviewed and
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626

627 *Competing interests.* The authors declare that they have no competing interests.

628

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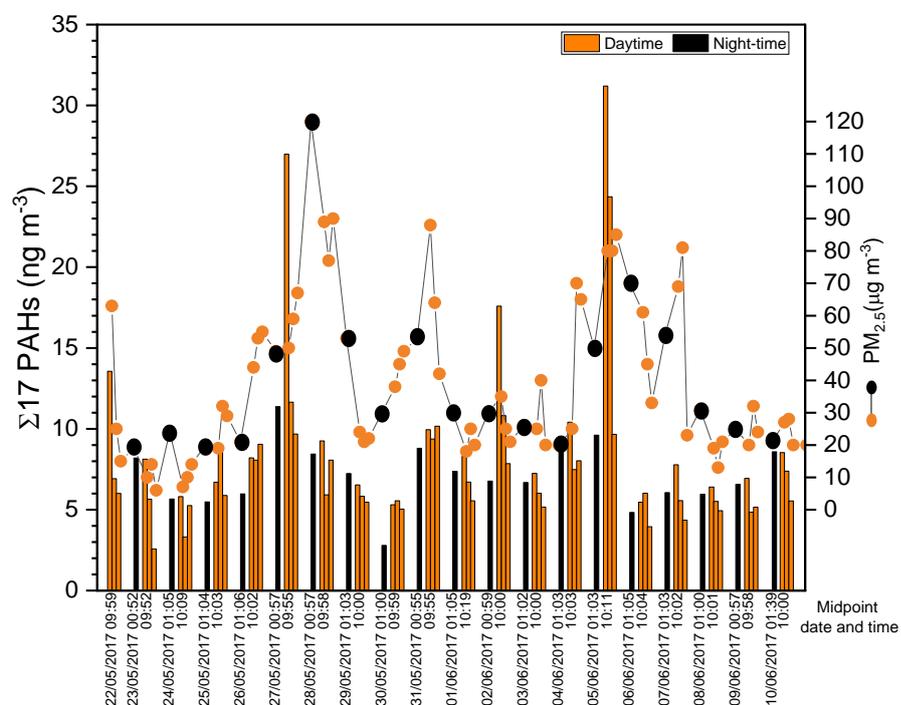
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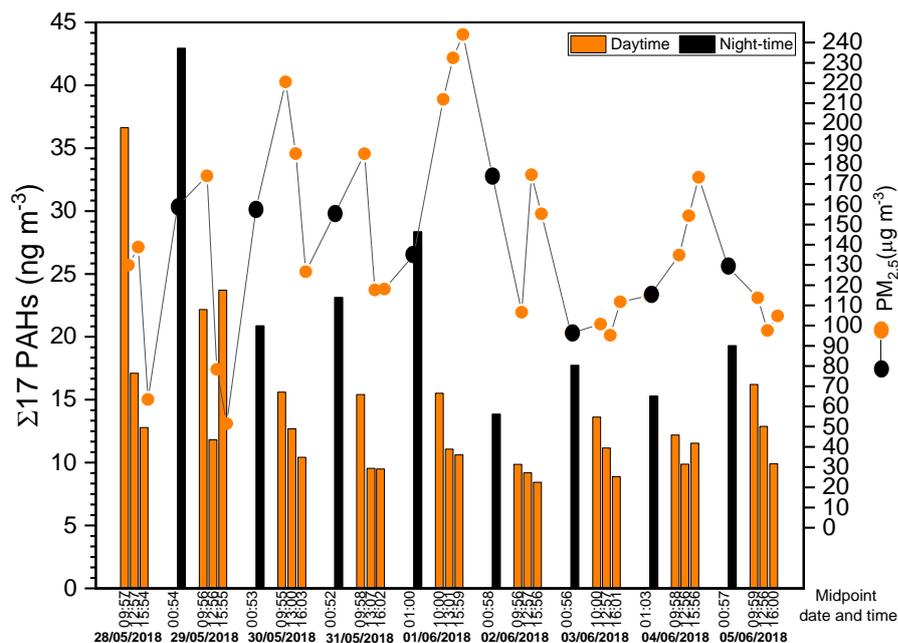
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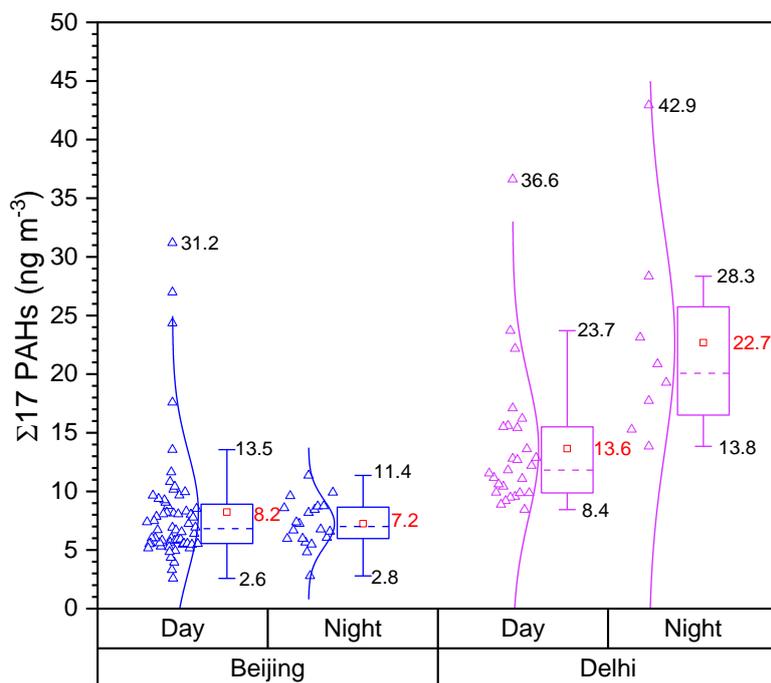
1005 **Figure 1** Temporal variation of total PAHs and PM_{2.5} concentrations in summer Beijing. PM_{2.5}
1006 concentrations were averaged to the filter sampling time, approximately 3 h in daytime and 15 h at
1007 night. The 3 h midpoint time tick labels at noon (~13:00) and in the afternoon (~16:00) have been
1008 omitted for clarity.

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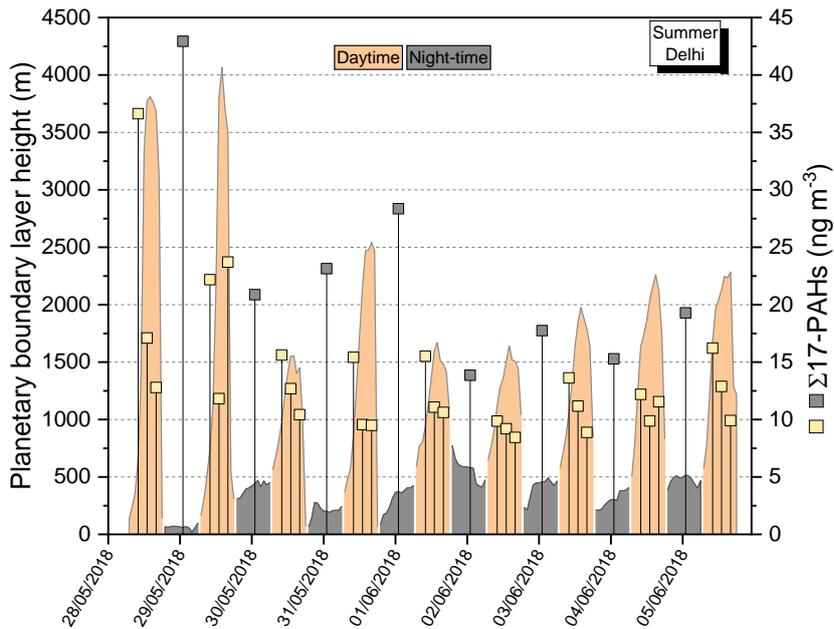
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Figure 2 Temporal variation of total PAHs and PM_{2.5} concentrations in summer Delhi. PM_{2.5} concentrations were averaged to the filter sampling time, approximately 3 h in daytime and 15 h at night.



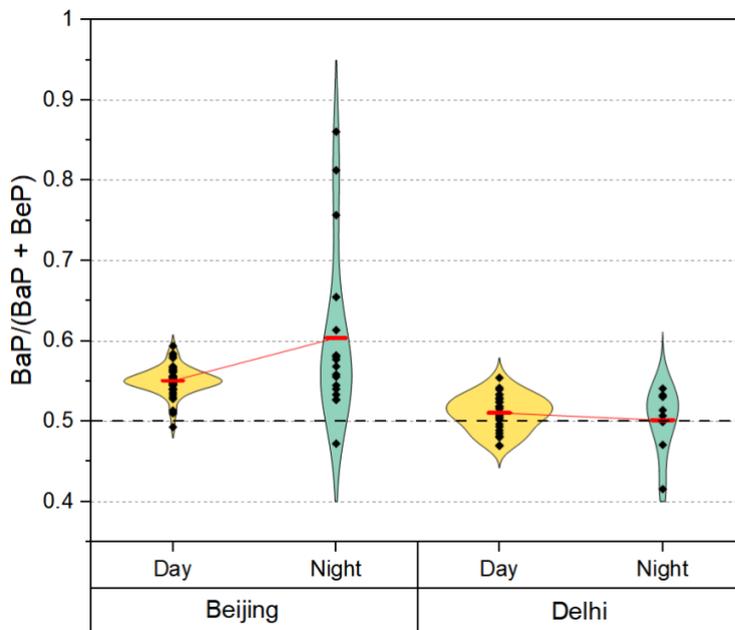
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Figure 3. Concentrations of 17 PAHs in PM_{2.5} samples during the daytime (3 h) and night-time (15 h). Box plots represents the 25th and 75th percentiles range of the observed concentrations and the whisker numbers reflect the data within 1.5 times the interquartile range (IQR). Red square symbols represent the mean concentration, and the short dash line within the boxes represent the median. Empty Triangles correspond to the data measured over 3 h and 15 h in Beijing (Blue) and in Delhi (Purple). The lines between data points and boxes reflect a normal distribution curve.



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1023 **Figure 4** Planetary boundary layer height in summer Delhi 2018 (Lat 28.625, Lon 77.25; source:
 1024 ECMWF ERA5 in 0.25°, 1-hour time resolution). Square symbols represent the temporal variation of
 1025 total PAHs in daytime and night-time.



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1027 **Figure 5.** Ratio of BaP/(BaP + BeP) in PM_{2.5} samples during the daytime (every 3 h) and night-time
 1028 (15 h). Violin plots represent the data distribution between day and night and the wider sections
 1029 represent the higher density of data smoothed by a kernel density estimator. Red rectangle symbols
 1030 represent the mean concentration, and the red line connect the mean values between day and night.
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1035 **Table 1.** Minimum, maximum and mean concentrations of individual PAHs in PM_{2.5}. Compounds in
 1036 bold represent the highest mean contribution to the sum of all compounds.

Compound/ring	Summer Beijing: PAH concentrations (ng m ⁻³)		Summer Delhi: PAH concentrations (ng m ⁻³)	
	Variation	Mean ± SD*	Variation	Mean ± SD*
	Daytime / Night-time	Daytime / Night-time	Daytime / Night-time	Daytime / Night-time
17 PAHs	3 h / 15 h	3 h / 15 h	3 h / 15 h	3 h / 15 h
Naphthalene/2	0.07-0.29 / 0.02-0.15	0.14 ± 0.06 / 0.06 ± 0.04	0.07-0.62 / 0.35-0.58	0.29 ± 0.14 / 0.45 ± 0.09
Acenaphthylene/3	0.08-0.12 / 0.02-0.08	0.10 ± 0.03 / 0.04 ± 0.02	0.05-0.15 / 0.15-0.29	0.09 ± 0.02 / 0.19 ± 0.06
Acenaphthene/3	< LOD	< LOD	< LOD	< LOD
Fluorene/3	0.09-0.15 / 0.02-0.07	0.13 ± 0.03 / 0.05 ± 0.01	0.04-0.09 / 0.03-0.09	0.07 ± 0.02 / 0.05 ± 0.02
Phenanthrene/3	0.16-1.28 / 0.07-0.42	0.37 ± 0.25 / 0.28 ± 0.09	0.14-0.58 / 0.56-0.86	0.26 ± 0.12 / 0.70 ± 0.10
Anthracene/3	< LOD	< LOD	< LOD	< LOD
Total 2-3 ring PAHs	0.04-1.30 / 0.06-0.62	0.38 ± 0.29 / 0.41 ± 0.13	0.15-1.24 / 0.98-1.87	0.62 ± 0.28 / 1.36 ± 0.29
Fluoranthene/4	0.15-5.78 / 0.25-1.58	0.74 ± 0.99 / 0.66 ± 0.31	0.36-1.76 / 0.8-1.28	0.67 ± 0.29 / 1.04 ± 0.16
Pyrene/4	0.12-2.84 / 0.19-1.12	0.56 ± 0.58 / 0.56 ± 0.21	0.37-2.10 / 0.82-1.36	0.69 ± 0.36 / 1.07 ± 0.18
Benzo[a]anthracene/4	0.43-1.22 / 0.12-0.53	0.56 ± 0.16 / 0.30 ± 0.10	0.59-1.59 / 0.49-1.32	0.75 ± 0.20 / 0.72 ± 0.27
Chrysene/4	0.42-3.27 / 0.28-1.12	0.81 ± 0.51 / 0.62 ± 0.20	0.64-2.35 / 0.88-1.95	0.94 ± 0.34 / 1.20 ± 0.35
Total 4 ring PAHs	1.14-13.4 / 0.84-4.24	2.67 ± 2.19 / 2.14 ± 0.77	2.04-7.83 / 3.05-6.17	3.10 ± 1.19 / 4.10 ± 1.02
Benzo[b]fluoranthene/5	0.44-3.76 / 0.41-1.78	0.97 ± 0.65 / 1.02 ± 0.33	0.87-3.73 / 1.34-4.86	1.40 ± 0.59 / 2.41 ± 1.12
Benzo[k]fluoranthene/5	0.56-2.67 / 0.31-1.06	0.93 ± 0.43 / 0.68 ± 0.19	0.96-3.38 / 1.05-3.44	1.39 ± 0.48 / 1.80 ± 0.75
Benzo[a]pyrene/5	0.63-2.56 / 0.34-1.15	0.95 ± 0.38 / 0.71 ± 0.19	0.95-3.41 / 1.10-3.92	1.40 ± 0.51 / 2.01 ± 0.90
Benzo[e]pyrene/5	0.55-2.08 / 0.12-0.92	0.80 ± 0.32 / 0.47 ± 0.22	0.88-3.67 / 1.04-5.70	1.37 ± 0.61 / 2.14 ± 1.49
Dibenzo[a,h]anthracene/5	0.69-0.78 / 0.14-0.26	0.74 ± 0.05 / 0.19 ± 0.03	0.64-0.91 / 0.12-1.08	0.76 ± 0.11 / 0.39 ± 0.27
Total 5 ring PAHs	0.65-12 / 1.21-4.24	3.57 ± 1.97 / 2.98 ± 0.80	3.68-15.11 / 4.81-19.0	5.69 ± 2.36 / 8.88 ± 4.49
Indeno[1,2,3-cd]pyrene/6	0.65-3.27 / 0.39-1.57	1.03 ± 0.47 / 0.93 ± 0.31	1.32-6.36 / 2.12-8.62	2.29 ± 1.11 / 4.45 ± 2.03
Benzo[ghi]perylene/6	0.44-2.45 / 0.14-1.37	0.77 ± 0.37 / 0.80 ± 0.3	1.08-6.08 / 2.01-7.53	1.97 ± 1.13 / 3.90 ± 1.76
Total 6 ring PAHs	0.43-5.71 / 0.66-2.72	1.76 ± 0.86 / 1.72 ± 0.54	2.47-12.44 / 4.12-15.7	4.26 ± 2.24 / 8.34 ± 3.64
Total 17 PAHs	2.6-31.2 / 2.8-11.4	8.2 ± 5.1 / 7.2 ± 2.0	8.4-36.6 / 13.8-42.9	13.6 ± 5.9 / 22.7 ± 9.4
Total 16-PAHs Winter Beijing (Elzein et al., 2019)	18-297 / 23-165	87.3 ± 58 / 107 ± 51		

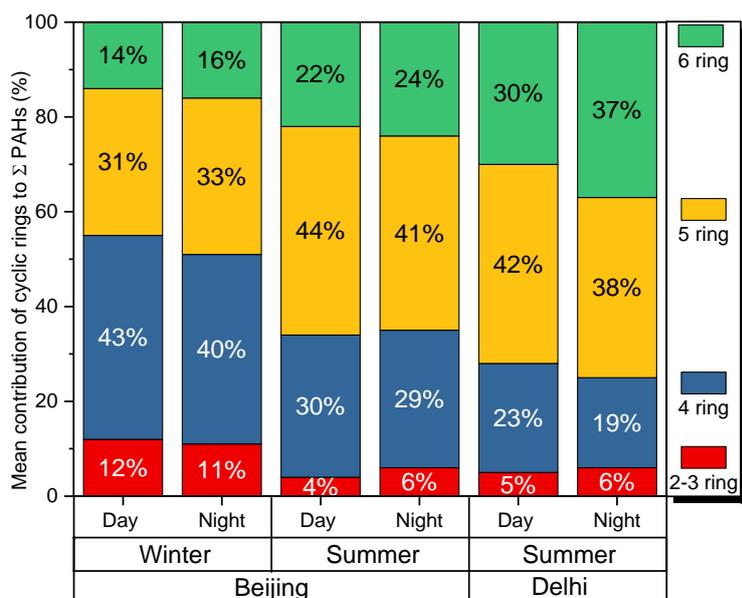
1037 * SD: Standard Deviation

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1043 **Figure 6.** Distribution of PAHs compounds by number of cyclic rings in $PM_{2.5}$ samples collected during
 1044 the daytime (every 3 h) and night-time (15 h) for summer Beijing 2017 and Delhi 2018 (this study) and
 1045 winter Beijing 2016 (Elzein et al., 2019).

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