



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

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22
23 **Abstract.**

24 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in air, soil and water and known to
25 have harmful effects on human health and the environment. The diurnal and nocturnal variation of 17-
26 PAHs in ambient particle-bound PAHs were measured in urban Beijing (China) and Delhi (India)
27 during the summer season using GC-Q-TOF-MS. The mean concentration of particles less than 2.5
28 microns (PM_{2.5}) observed in Delhi was 3.6 times higher than in Beijing during the measurement period
29 in both the day-time and night-time. In Beijing, the mean concentration of the sum of the 17 PAHs
30 (Σ 17-PAHs) was 8.2 ± 5.1 ng m⁻³ in daytime, with the highest contribution from Indeno[1,2,3-cd]pyrene
31 (12 %), while at night-time the total PAHs was 7.2 ± 2.0 ng m⁻³, with the largest contribution from
32 Benzo[b]fluoranthene (14 %). In Delhi, the mean Σ 17-PAHs was 13.6 ± 5.9 ng m⁻³ in daytime, and
33 22.7 ± 9.4 ng m⁻³ at night-time, with the largest contribution from Indeno[1,2,3-cd]pyrene in both the
34 day (17 %) and night (20 %). Elevated mean concentrations of total PAHs in Delhi observed at night
35 were attributed to emissions from vehicles and biomass burning and to meteorological conditions
36 leading to their accumulation from a stable and low atmospheric boundary layer. Local emission sources
37 were typically identified as the major contributors to total measured PAHs, however, in Delhi 25 % of
38 the emissions were attributed to long-range atmospheric transport. Major emission sources were
39 characterized based on the contribution from each class of PAHs, with the 4, 5, and 6 ring PAHs
40 accounting ~ 95 % of the total PM_{2.5}-bound PAHs mass in both locations. The high contribution of 5
41 ring PAHs to total PAH concentration in summer Beijing and Delhi suggests a high contribution from
42 petroleum combustion. In Delhi, a high contribution from 6 ring PAHs was observed at night,
43 suggesting a potential emission source from the combustion of fuel and oil in power generators, widely
44 used in Delhi. The lifetime excess lung cancer risk (LECR) was calculated for Beijing and Delhi, with
45 the highest estimated risk attributed to Delhi (LECR = 155 per million people), 2.2 times higher than
46 Beijing risk assessment value (LECR = 70 per million people). Finally, we have assessed the emission
47 control policies in each city and identified those major sectors that could be subject to mitigation
48 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 hours 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
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.

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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. PAHs 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 have calculated the
181 relative standard deviations (%RSD) from replicate analysis ($n = 10$) of two samples. The %RSD
182 average of total PAHs was 8.7 % (range: 3.36 – 13.71 %) for Beijing samples and 4.2 % (range: 2.64 –
183 10.12 %) for Delhi samples. The %RSD average for deuterium labelled compounds spiked over two
184 sample filters was $\sim 3.6 \%$ for both campaigns. The %RSD of each compound is shown in Table S1.
185 The higher precision error ($>10 \%$) attributed to a few compounds in Beijing samples (Table S1) is most
186 probably related to the lower concentration of PAHs in the samples compared to Delhi samples and to
187 samples analysed previously from Beijing in wintertime (Elzein et al., 2019). Moreover, the calibration
188 offset and the influence of the sample matrix on the quantification step are an important source of
189 systematic error and was estimated to be a maximum of 20 %. Therefore, the upper limit estimated
190 error, combining the precision and the systematic effects, is 30 % for Beijing samples and 25 % for
191 Delhi samples.



192 In addition, another type of error has been attributed to sampling artefacts. Previous studies (Schauer et
193 al., 2003, Goriaux et al., 2006, Tsapakis and Stephanou, 2003, Brown and Brown, 2012) have reported
194 a chemical decomposition of PAHs depending on the ambient concentration of ozone and sampling
195 time. Therefore, data from long sampling times and under very high ozone ambient concentrations (>70
196 ppb) may be biased by sampling artefacts of more than 100 % (Schauer et al., 2003, Goriaux et al.,
197 2006). However, at low ozone levels (< 30 ppb), negative artefacts were considered not significant
198 (Tsapakis and Stephanou 2003), whilst, at medium ozone levels (30-50 ppb) PAHs values were
199 underestimated by 30 % (Schauer et al., 2003). Tsapakis and Stephanou 2003, have reported a loss of
200 PAHs by 28 % due to ozone atmospheric concentration about 60 ppb and long sampling times of 24 h.
201 They have also suggested that long sampling time under low ozone concentration (< 30 ppb) do not
202 affect the concentration of collected PAHs in the gas or particle phases, while short sampling time (2
203 h) under ozone concentration about 60 ppb will reduce the concentration of PAHs by 17 %. In this
204 study, ozone concentrations were measured in both campaigns and averaged to the filter sampling time
205 to provide more accurate estimation on the negative sampling artefacts. The ozone concentration in
206 summer Beijing ranged between 3.7 and 140 ppb over the campaign (mean value: 56 ± 31 ppb),
207 approximately 5 times higher than in winter (mean value: 10.4 ± 8.8 ppb, Elzein et al., 2019). Daytime
208 ozone concentration ranged from 12 to 140 ppb (mean value: 63 ± 30 ppb), while over the night-time it
209 ranged from 4 to 74 ppb (mean value: 34 ± 18 ppb). Therefore, based on Tsapakis and Stephanou (2003)
210 study, the negative sampling artefacts due to ozone concentration was estimated to be 20 % for daytime
211 samples (3 h) and 10 % for the night-time samples (15 h) due to lower ozone concentration at night.
212 Using the same approach, daytime ozone concentration in Delhi ranged between 39 and 119 ppb, with
213 a mean value: 75 ± 20 ppb, while the night-time concentration ranged from 14 to 50 ppb (mean value:
214 37 ± 12 ppb). Therefore, the estimation of the negative sampling artefacts on the data from Delhi ranged
215 between 15 and 30 %, with the highest error estimation attributable to daytime-time samples (3 h)
216 because of the higher ozone concentration during the day.

217

218 3 Results and discussion

219 3.1 Concentration levels of PM_{2.5} and Benzo[a]pyrene in summer Beijing and Delhi

220 In 2016, the World Health Organisation (WHO, 2016) published an air quality guideline on outdoor air
221 pollution limits to help protect human health and reduce the risk of mortality due to fine particles. The
222 air quality standards for PM_{2.5} were set by the ministry of environment in China and India, and published
223 in the WHO air quality guideline as an annual and 24 h mean concentration. The daily PM_{2.5} (mean 24
224 h) guideline concentration is currently set at 75 and 60 $\mu\text{g m}^{-3}$ for China and India, respectively, while
225 the annual mean guideline concentration is currently set at 35 and 40 $\mu\text{g m}^{-3}$ for China and India,
226 respectively. PM_{2.5} concentrations measured at the two sites were averaged to the filter sampling time
227 and are shown in Fig. 1 and Fig. 2. In Beijing, the average 24 h PM_{2.5} concentration was 39 ± 21 $\mu\text{g m}^{-3}$
228 (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
229 days. The average daytime and night-time PM_{2.5} concentrations in Beijing were 40 ± 24 $\mu\text{g m}^{-3}$ and 38
230 ± 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:
231 110 - 195 $\mu\text{g m}^{-3}$), exceeding the Indian 24 h limit value on all 9 sampling days. The average daytime
232 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.
233 PM_{2.5} concentrations in Delhi have changed little in recent years; between 2008 and 2011 the daily
234 average of PM_{2.5} concentrations was 123 ± 87 $\mu\text{g m}^{-3}$ (Guttikunda and Calori., 2013), while the annual
235 average was reported to be 125.5 ± 77.2 $\mu\text{g m}^{-3}$ between January 2013 and May 2014 (Winter: 196 μg
236 m^{-3} , Summer: 83.6 $\mu\text{g m}^{-3}$, Monsoon: 58.8 $\mu\text{g m}^{-3}$) (Sharma and Mandal., 2017). The limited change
237 seen in recent years may be associated with continued emissions from residential energy use, estimated
238 to contribute about 50 % of PM_{2.5} airborne concentrations (Conibear et al., 2018, Butt et al., 2016). The



239 construction sector is fast growing in India, and the dust emitted from various activities (demolition,
240 excavation, drilling etc.) is also considered an important source of particles (Guttikunda et al., 2014).
241 The WHO has not published a guideline limit value for PAHs, but benzo[a]pyrene (BaP) is often used
242 as a marker of toxicity for all PAHs. The European Union has set an annual mean air quality limit of 1
243 ng m^{-3} for BaP (WHO, 2016). The daily (24 h) concentration of BaP in summer Beijing (this study)
244 ranged from 0.49 to 1.18 ng m^{-3} (average $0.80 \pm 0.17 \text{ ng m}^{-3}$), about 19 times lower than previously
245 observed at this site in winter (Elzein et al., 2019). This is below the 24 h average limit value of 2.5 ng m^{-3} ,
246 set in China by the Ministry of Ecology and Environment in 2012, on all of the 20 days of sampling
247 period. During the short summer measurement period in Delhi, BaP varied between 1.16 and 3.16 ng m^{-3}
248 ($\text{average } 1.78 \pm 0.67 \text{ ng m}^{-3}$), and exceeded the threshold of 2.5 ng m^{-3} on 1 day.

249

250 3.2 Variability of PAHs in summer Beijing and Delhi

251 A time series of the temporal variation of total PAHs in Beijing and Delhi are shown in Fig. 1 and Fig.
252 2, respectively. The box plots in Fig. 3 show a comparison of the measured concentrations of total 17-
253 PAHs between daytime and night-time in both cities.

254

255 **Beijing:**

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

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



286 may be representative of the urban area of Beijing covering approximately half of the population in
287 Beijing metropolitan.

288 In Figure 1, the concentration of total PAHs in the first 3 h filter (08:30–11:30) of the day appear to be
289 higher than the rest of the day. These elevated concentrations are potentially associated with the early
290 morning rush hour time and vehicle emissions. The average night-time total PAHs concentration (7.2
291 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}
292 respectively. This indicates that the elevated total PAHs concentration in the first 3 h filter (08:30–
293 11:30) of the day is not related to accumulation of air pollutants at night-time but most likely related to
294 direct emissions from traffic in the early morning and particularly petrol combustion emissions (see
295 section 3.3).

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

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

326

327 **Delhi:**

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



334 and Eastern part of India are considered to be the most polluted part of the country (Guttikunda et al.,
335 2014).
336 Similar to Beijing, previous studies in Delhi mainly focused on the 24 h average concentration of total
337 PAHs. They have addressed the problem of air pollution across India, focusing on PM_{2.5} trends, PM_{2.5}
338 health impact, and source apportionment (Chowdhury et al., 2007; Gupta et al., 2011; Chowdhury and
339 Dey., 2016; Pant et al., 2017; Chen et al., 2020), however, PAHs emissions and variation between
340 daytime and night-time have not been measured or discussed previously, and only few studies (Sharma
341 et al., 2007; Singh et al., 2011, Gadi et al., 2019) reported the 24 h mean concentration of \sum_n -PAHs (n
342 > 10) in Delhi itself. In this study, the mean 24 h (combined results from daytime and night-time
343 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
344 a large spatial variation in PAHs concentrations within Delhi; Sharma et al., (2007) reported a mean 24
345 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
346 of Delhi during the summer season of 2003. Singh et al., 2011 reported a mean 24 h value of $45.8 \pm$
347 22.1 ng m^{-3} (~ 2.4 times higher than our mean value) for \sum_{16} -PAHs at the East of Delhi during the
348 summer season of 2008. Gadi et al., (2019) reported an annual average of $277 \pm 126 \text{ ng m}^{-3}$ for the
349 summation of 16-PAHs between December 2016 and December 2017, and $260 \pm 111 \text{ ng m}^{-3}$ for the
350 summer season of 2017 (~ 13.5 times higher than our mean value, and ~ 5.7 times higher than Singh et
351 al., 2011 mean value). In the study of Gadi et al., (2019), the sampling site was in the same campus as
352 this study (Indira Gandhi Delhi Technical University for Women), the low \sum PAHs value in this study
353 is most probably due to the short summer measurement period in Delhi (9 days, 35 samples), coupled
354 with less pollution episodes for PAHs. It appears that the variation of PAHs concentration in Delhi
355 could be affected by multiple factors including the spatial variation, the input from multiple local
356 sources, the surroundings of the sampling site, and the meteorological conditions in the north of Delhi.
357 Therefore, the concentrations of ambient particle-bound PAH over longer averaging period such as the
358 24 h are subject to high uncertainty related to the multiple factors cited above. Higher frequency filter
359 sampling during 24 h can provide a better assessment of PAH concentrations and is more likely to
360 reflect direct source emission signals as modified by meteorology. This perspective also applies to other
361 Indian cities in future studies.
362 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
363 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
364 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
365 daytime, the total PAH concentrations were generally highest during the first filter sample (8:30 to
366 11:30 am) (Fig. 2), following the same trend as for Beijing suggesting vehicle emissions as a dominant
367 source. The mean total PAH concentration at night-time was ~ 1.7 times higher than the mean in
368 daytime. Higher total PAHs concentration at night could be related to emissions from biomass burning,
369 waste burning, solid fuel cooking and heavy duty diesels entering the city at night-time. The higher
370 PAHs concentration at night may also be attributed to the relatively lower temperature at night ($\sim 10^\circ \text{C}$)
371 and lower atmospheric mixing heights (Fig. 4), weaker turbulence leading to lower pollutant dispersion
372 rates and absence of photodecomposition. Moreover, power cuts in India are frequent (Guttikunda et
373 al.,2014), especially when high demand occurs on air conditioners in summer (Harish et al., 2020),
374 which require in situ electricity generation using oil, diesel and petrol (Guttikunda et al.,2014). This
375 may be considered as an additional source of air pollution in a megacity like Delhi. PM_{2.5} concentrations
376 increased on most nights in comparison with the preceding daytime sample. Residential energy use
377 across India has been reported to be an important source of PM_{2.5} emissions, contributing 62 % in
378 summer and 70 % in winter of anthropogenic emissions of PM_{2.5} (Conibear et al., 2018). This was also
379 confirmed in the study of Butt et al., (2016), showing that the impact of residential combustion
380 emissions on atmospheric aerosol across India is very important, accounting for 63 % of anthropogenic
381 black carbon and 78 % of anthropogenic particle organic matter emissions.



382 The mean 24 h values of Σ PAHs from this study ($19.3 \pm 7.1 \text{ ng m}^{-3}$) and recent previous studies (45.8
383 $\pm 22.1 \text{ ng m}^{-3}$ (Singh et al., 2011) and $260 \pm 111 \text{ ng m}^{-3}$ (Gadi et al., 2019)) are high. This suggests the
384 need for the implementation of a residential emission control strategy through potentially more effective
385 alternative technologies such as the use of non-fossil fuel (biofuel) and clean energy sources (solar,
386 wind, hydro-electric power, natural gas) for domestic use, and the use of in situ power generators by
387 increasing electricity supply and load, and cutting emissions from open waste burning by implementing
388 efficient collection and disposal of waste.

389

390 **3.3 Major PAH, particle aging and traffic emissions**

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

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

428 Since the influence from traffic emissions is very strong in both Beijing and Delhi, related diagnostic
429 ratios were used to distinguish between petrol and diesel, such as, Fluorene/Fluorene+Pyrene (< 0.5 for



430 Petrol engines and > 0.5 for diesel engines) and Pyrene/BaP (Ravindra et al., 2008; Tobiszewski and
431 Namiesnik., 2012; Watson et al., 2016; Zheng et al., 2017). Rogge et al., (1993) have quantified more
432 than 100 organic compounds in exhaust emissions fine particulate matter, we have calculated the ratio
433 value for Pyrene/BaP ~ 0.7 for noncatalyst-equipped petrol cars, ~ 1.3 for catalyst-equipped petrol cars
434 and > 16 for heavy duty diesel engines. A recent study from Perrone et al., (2014) reported PM-phased
435 PAH emission factors for different types of vehicles (Euro 3 standards), the ratio value for Pyrene/BaP
436 was ~ 6 and 30 for petrol and diesel cars, respectively. The results from both ratios
437 (Fluorene/Fluorene+Pyrene and Pyrene/BaP) suggest high contribution from petrol engines to particle
438 composition in Beijing and Delhi (Fig S1).

439

440 3.4 Emission source fingerprints

441 The profiles of specific class of PAHs and their abundance vary largely, depending on the fuel types
442 and combustion conditions (IARC, 2012). Previous studies reported that 2 and 3 aromatic ring PAHs
443 are mostly emitted from wood combustion (Khalili et al., 1995; Larsen and Baker., 2003; Liu et al.,
444 2017); 2, 3 and 4 ring from diesel exhaust emission (Bourotte et al., 2005; Ravindra et al., 2007; De
445 Souza et al., 2016; Zheng et al., 2017); 3 and 4 ring from coal combustion (Harrison, et al., 1996; Liu
446 et al., 2017); 4, 5, and 6 ring from vehicle emissions (Ravindra et al., 2007, Zhao et al., 2020); 5 and 6
447 ring from petrol and oil combustion (Harrison, et al., 1996; Ravindra et al., 2007). In this study, we
448 have classified the 17-PAHs based on their number of aromatic ring; we referred to previous studies
449 and to our knowledge of local sources, sampling site and surroundings, and analytical uncertainties to
450 describe the emission source of each class. The 2 and 3 aromatic ring PAHs were below LOD and LOQ
451 in many samples, however, they are predominantly found in the gas phase and their partitioning to the
452 particle phase is very small because of their high volatility; their percentage in the particle phase was
453 previously reported to be less than 10 % (Ravindra et al., 2007; Liu et al., 2017; Zhao et al., 2020).

454 In this study, the 4, 5, and 6 ring PAHs accounted ~ 95 % of the total $PM_{2.5}$ -bound PAHs concentrations
455 measured in both campaigns (Fig. 6). The mean contribution of the number of ring to the total of PAHs
456 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
457 both, Beijing and Delhi, road traffic is known to be one of the largest emission source of gas and particle
458 phase pollutants (Fang et al., 2016; Zhang et al., 2020; Shivani et al., 2019), which might explain the
459 high contribution from 4, 5 and 6 ring to total PAHs, while diesel and coal combustion may also
460 contribute to the emission of 4 ring PAHs. The 4 ring PAHs concentration in Delhi was higher than in
461 Beijing, the mean concentration of the 4 ring PAHs in daytime and night-time samples was 2.7 and 2.1
462 $ng\ m^{-3}$ in Beijing; 3.1 and $4.1\ ng\ m^{-3}$ in Delhi, respectively (Table 1). In contrast to Beijing ($5 > 4 > 6$
463 ring), the 4 ring PAHs total concentration in Delhi was lower than the 6 ring PAHs (Fig. 6) and a
464 potential emission source could be the common use of fuel and oil in power generators.

465 The distribution of ring PAHs in Figure 6 shows a comparison between the results from this study and
466 our previous study in winter Beijing (Elzein et al., 2019). The contributions from 2, 3 and 4 rings were
467 higher in winter than in summer, and the ring PAHs are distributed as $4 > 5 > 6 > 2-3$ ring (Fig. 6).
468 Ambient temperature highly affects the gas/particle partitioning of 2-3 ring PAH (Tsapakis and
469 Stephanou., 2005; Gaga and Ari., 2011; Verma et al., 2017). Therefore, higher contributions from 2, 3
470 and 4 rings in winter Beijing are likely due to lower temperature and to the use of coal and wood
471 combustion for residential heating. The 2-3 and 6 ring PAHs contributions in winter Beijing are
472 relatively similar, while in summer Beijing the contribution from 6 ring PAHs is ~ 20 % higher than 2-
473 3 ring, most probably due to the effect of ambient temperature on 2-3 ring PAH. The 5 ring PAHs
474 (representative of vehicle emissions) contribute the most to the total PAH concentration in summer
475 Beijing and Delhi, suggesting a high contribution from petroleum combustion.

476 Finally, identifying PAH markers emitted from specific emission sources (types of fuel, types of coal,
477 types of waste, etc.) in ambient air is still complex due to the similarity of PAH profiles from different



478 source types, which may quickly blend in the air with interferences from both nearby and remote
479 emission sources. A more complete assessment of emission source types at specific locations would
480 require the use of individual PAHs as source markers combined with other chemical constituents of
481 PM_{2.5} (elements and ions) and with gas phase air pollutants known to be released from the same source
482 such as VOCs markers.

483

484 3.5 Health risk assessment

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

$$494 \quad [\text{BaP}]_{\text{eq}} = \sum_{i=1}^N \text{PAH}_i \times \text{TEF}_i \quad (1)$$

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

$$503 \quad \text{LECR} = \text{BaP} \times \text{UR} \quad (2)$$

504

505 **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

506 *SD : Standard deviation

507 As shown in Table 2, the LECR attributable to the 15 PAHs in urban air of Beijing and Delhi was 7 x
508 10⁻⁵ and 15.5 x 10⁻⁵ (> 10⁻⁶), respectively, suggesting an elevated lifetime cancer risk for adults (Chen
509 and Liao., 2006; Bai et al., 2009), especially when considering the population size associated with each
510 city. The LECR value for Delhi gives an estimate of 85 additional cancer cases per million people
511 exposed, in comparison to Beijing. The LECR for Beijing in winter (Elzein et al., 2019) was much
512 higher than in summer (this study) and showed 1235 additional cases, and this was mostly attributed to
513 the increase in use of fossil fuels for central and residential heating, in addition to meteorological
514 conditions such as lower volatilisation at low temperatures and lower photochemical transformation. It
515 is however the annual mean which is directly related to cancer risk.

516 Although BaP is widely used as indicator of all PAHs carcinogenicity, this approach is still under debate
517 and may not give a very good representation of the whole mixture potency (U.S.EPA, 2002, Boström



518 et al., 2002). Delgado-Saborit et al., (2011) have used the TEFs to calculate the percentage contribution
519 of each PAH to total carcinogenicity following Eq. (3):

520

$$521 \quad (\% \text{Carc. Potential})_i = \frac{(\text{RC} \times \text{TEF})_i}{\sum_{i=1}^N (\text{RC} \times \text{TEF})_i} \times 100 \quad (3)$$

522 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
523 the PAH mixture in Beijing (B) and Delhi (D) are: Benzo[a]pyrene (B: 46 %; D: 48 %),
524 Dibenzo[a,h]anthracene (B: 23 %; D: 19 %), Benzo[b]fluoranthene (B: 15 %; D: 13 %),
525 Benzo[k]fluoranthene (B: 5 %; D: 5 %), and Indeno[1,2,3-cd]pyrene (B: 6 %; D: 10 %). The sum of all
526 other PAHs used in this study was about 5 %.

527
528 Since the majority of people (~ 90%) spend most of their time indoor, the total PAH burden from
529 inhalation has been related to indoor air, and BaP is used as a marker for the carcinogenic potential of
530 all PAHs irrespective of the environment (indoor or outdoor) (Delgado-Saborit et al., 2011). In this
531 study, the health risk evaluation was only based on inhalation exposure to PAHs in the particulate phase.
532 The risk values can increase due to the presence of PAHs derivatives in the particulate phase such as
533 the nitrated-PAHs (Elzein et al., 2019), and in particular from 6-Nitrochrysene and 1,6-dinitropyrene
534 who have been attributed a high TEF value equal to 10 (OEHHA., 1994; WHO., 2003; Lundstedt et al.,
535 2007). Dermal exposure to PAHs is also an important risk factor for skin cancer but toxicity values for
536 dermal exposures are still not available (U.S.EPA, 2002), in addition ingestion exposure to PAHs from
537 soil, sediments and water is high (Li et al., 2010), and both exposures (dermal+ingestion) can highly
538 exceed the risk from inhalation (U.S.EPA, 2002).

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

555

556 4 Conclusions

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



564 In Beijing and Delhi, 17-PAHs were quantified using a GC-Q-TOF-MS and the measured
565 concentrations compared between daytime and night-time, showing a high relative proportion (~ 95 %)
566 of 4, 5 and 6-ring PAHs in the particle phase. In Beijing, $\sum 17$ -PAHs concentrations varied between 2.6
567 and 31.2 ng m⁻³ (average 8.2 ± 5.1 ng m⁻³) in daytime, and from 2.8 to 11.4 ng m⁻³ (average 7.2 ± 2.0
568 ng m⁻³) at night-time. In Delhi, $\sum 17$ -PAHs concentrations varied between 8.4 and 36.6 ng m⁻³ (average
569 13.6 ± 5.9 ng m⁻³) in daytime, and from 13.8 to 42.9 ng m⁻³ (average 22.7 ± 9.4 ng m⁻³) at night-time.
570 In Beijing, Indeno[1,2,3-cd]pyrene was the highest contributor to the mean total PAHs during daytime
571 (12 %) and Benzo[b]fluoranthene at night (14 %) at night-time. In Delhi, Indeno[1,2,3-cd]pyrene was
572 the largest contributor to the total PAHs in both the day (17 %) and night-time (20 %).
573 The elevated mean concentration of total PAHs in Delhi at night was attributed to emissions from
574 biomass burning, waste burning, open fire cooking along with meteorological conditions facilitating the
575 accumulation of air pollutants as a result of low atmospheric boundary layer heights.
576 The ratio of BaP/BaP+BeP has been used to evaluate the contribution from local sources against long
577 range atmospheric transport of particle-bound PAHs. This ratio varied between 0.5 and 0.6 in Beijing,
578 indicating a larger contribution from local sources, while in Delhi, 25 % of the data were below 0.5,
579 indicating a possible contribution from regional pollution at the sampling site, but local emissions were
580 still the dominant source of PAHs found in the particle phase. Flu/Flu+Pyr and Pyr/BaP were used as
581 diagnostic ratios to distinguish between petrol and diesel, and results suggest petrol combustion
582 emissions as a major source in Both Beijing and Delhi.
583 PAHs were classified according to their number of aromatic rings to characterize major emission
584 sources. The 4, 5, and 6 ring PAHs accounted ~ 95 % of the total PM_{2.5}-bound PAHs concentrations in
585 both campaigns. The 5 ring PAHs contribute the most to the total PAH concentration in summer Beijing
586 and Delhi, suggesting a high contribution from petroleum combustion. In Beijing, the 4 ring PAHs total
587 concentration was higher than the 6 ring by 8 % during the day and 5 % at night, while in Delhi, the 6
588 ring PAHs total concentration was higher than the 4 ring PAHs by 7 % during the day and 18 % at
589 night; a potential emission source of 6 ring PAHs in Delhi could be the common use of fuel and oil in
590 power generators. Due to the similarity of PAH profiles from different source types, it would be
591 beneficial to use other source markers such as elements and ions in PM_{2.5} and VOCs markers from the
592 gas phase to better identify the differences in emission sources.
593 The lifetime excess lung cancer risk was calculated for Beijing and Delhi, with the highest estimated
594 risk attributed to Delhi (LECR = 155 per million people), 2.2 times higher than Beijing risk assessment
595 value (LECR = 70 per million people). The results from this study suggest focusing attention on
596 mitigating the emission of major contributors to the total carcinogenic potential, being the 5 and 6 ring
597 PAHs (mostly emitted from petrol and oil combustion), in order to reduce adverse health effects from
598 inhalation exposure to PAHs in the particulate phase.

599 Finally, in Beijing, the anti-pollution actions since 2013 appear to have had a positive effect on the air
600 quality, while in Delhi, despite the government effort to mitigate air pollutants emission, a strict
601 implementation of emission control policies is still needed with particular focus on mitigating
602 residential emissions and burning, increasing the electricity supply to cover peak demand in summer
603 and limiting the use of local power generators as well as, promoting cleaner vehicles. Future studies in
604 different districts of Beijing (other than Haidian) and Delhi (other than old Delhi) and rural areas would
605 be helpful for comparison of population exposures and spatial variation. Higher frequency filter
606 sampling (every 3 h) can provide a better assessment of PAH concentrations and photochemistry and
607 can lead to better conclusions on direct source emission signals as modified by meteorology during the
608 daytime and night-time.
609



610 *Author contributions:* AE conducted the chemical analysis, analysed the data and prepared the
611 manuscript. ACL, JFH and RMH contributed to the interpretation, writing and corrections of the paper.
612 ERV calculated and provided the data on Delhi planetary boundary layer height. RG supported on site
613 filter collection and helped to set up the laboratory at the field site. AE and SJS conditioned and
614 collected the filter samples in Beijing. GJS and BSN conditioned and collected the filter samples in
615 Delhi. LRC and MSA measured and provided the data on PM_{2.5} in Delhi. All authors reviewed and
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617

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

619

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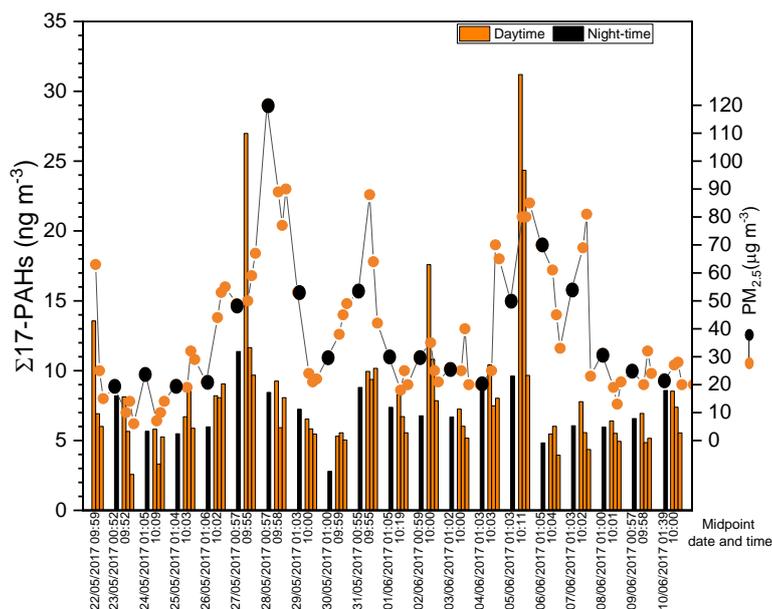
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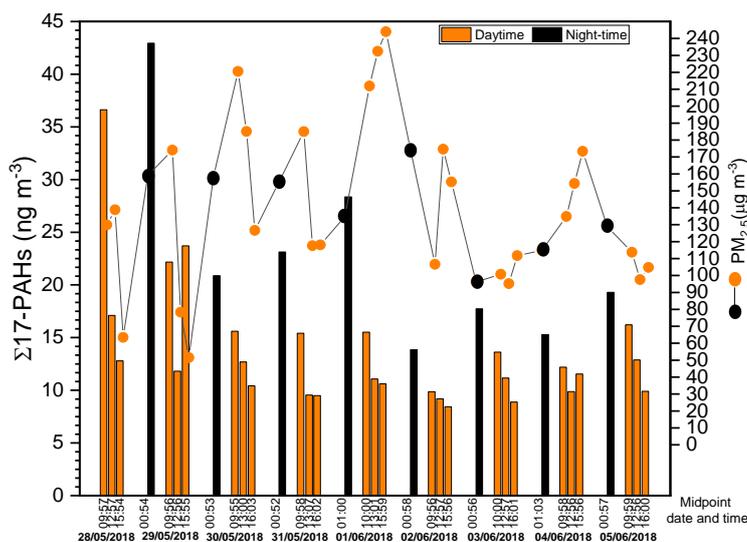
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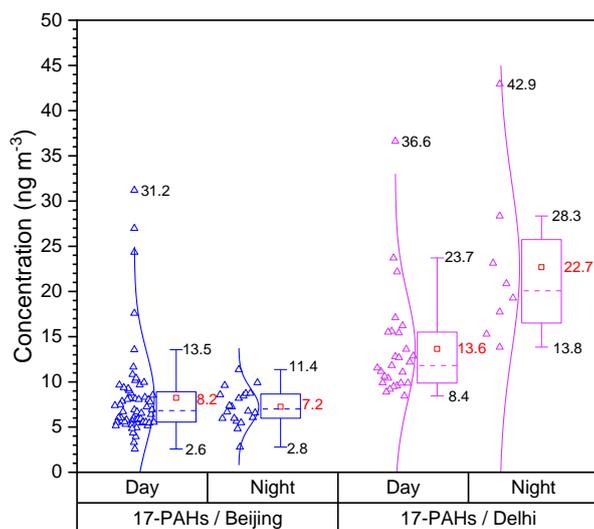


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996 **Figure 1** Temporal variation of total PAHs and PM_{2.5} concentrations in summer Beijing. PM_{2.5}
997 concentrations were averaged to the filter sampling time, approximately 3 h in daytime and 15 h at
998 night. The 3 h midpoint time tick labels at noon (~13:00) and in the afternoon (~16:00) have been
999 omitted for clarity.
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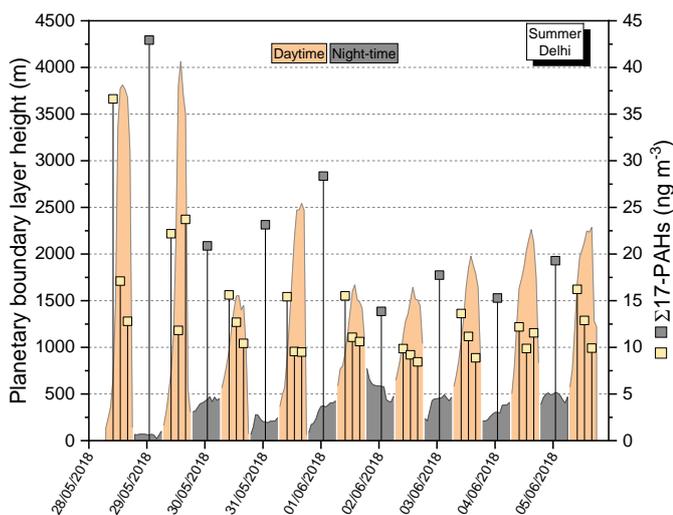
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Figure 2 Temporal variation of total PAHs and PM_{2.5} concentrations in summer Delhi. PM_{2.5} concentrations were averaged to the filter sampling time, approximately 3 h in daytime and 15 h at night.



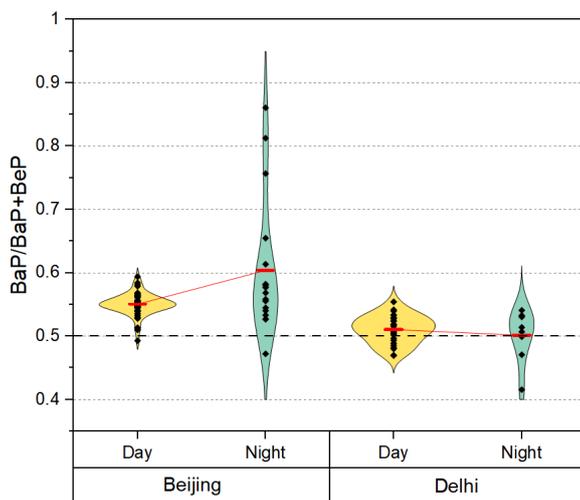
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Figure 3. Concentrations of 17-PAHs in PM_{2.5} samples during the daytime (3 h) and night-time (15 h). Box plots represents the 25th and 75th percentiles range of the observed concentrations and the whisker numbers reflect the data within 1.5 times 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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1014 **Figure 4** Planetary boundary layer height in summer Delhi 2018 (Lat 28.625, Lon 77.25; source:
 1015 ECMWF ERA5 in 0.25°, 1-hour time resolution). Square symbols represent the temporal variation of
 1016 total PAHs in daytime and night-time.



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1018 **Figure 5.** Ratio of BaP/BaP+BeP in PM_{2.5} samples during the daytime (every 3 h) and night-time (15
 1019 h). Violin plots represent the data distribution between day and night and the wider sections represent
 1020 the higher density of data smoothed by a kernel density estimator. Red rectangle symbols represent the
 1021 mean concentration, and the red line connect the mean values between day and night.
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1026 **Table 1.** Minimum, maximum and mean concentrations of individual PAHs in PM_{2.5}. Compounds in
 1027 bold represent the highest mean contribution to the sum of all compounds.

Compound/ring	Summer Beijing: PAHs Concentrations (ng m ⁻³)		Summer Delhi: PAHs 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		

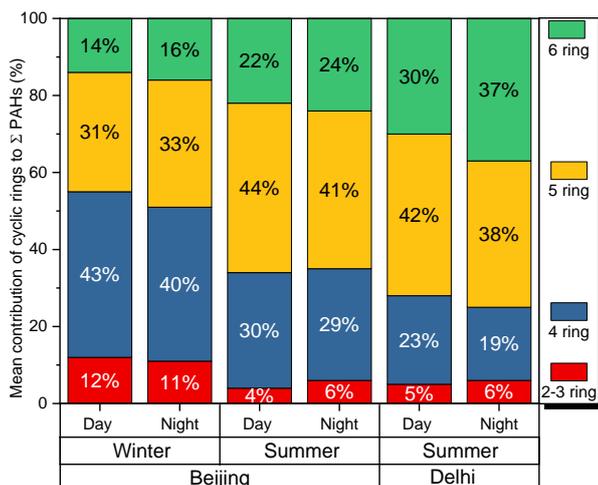
1028 * SD: Standard Deviation

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1034 **Figure 6.** Distribution of PAHs compounds by number of cyclic rings in PM_{2.5} samples collected during
 1035 the daytime (every 3 h) and night-time (15 h) for summer Beijing 2017 and Delhi 2018 (this study) and
 1036 winter Beijing 2016 (Elzein et al., 2019).

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