Response to referee 1:
Author’s response in Blue

The authors presented measurement results of 17 polycyclic aromatic hydrocarbons (PAHs) in Beijing, China, and Delhi, India in summer. The sampling was conducted with higher time resolutions (~3 hours for daytime samples and ~15 hours for nighttime samples) as compared to traditional 24-h samples. The PAHs were quantified with GC-Q- ToF-MS. Results showed that PAH concentrations were higher in Delhi than those in Beijing, and the summer PAH concentrations were lower than those in winter in Beijing. From the measured PAH profiles, sources of PM-bound PAHs in these two mega-cities in developing countries were inferred. In addition, health risks were calculated from the measured PAH concentrations. The study is well designed and the analysis is rigorous. The manuscript is fairly well written. I recommend Minor Revision before publication, with a few comments as follows.

We thank the reviewer for commenting this paper. Your corrections and recommendations helped us to better present the data and we believe the paper has been improved.

**Major**

1. It was stated in the abstract (and in the conclusion) that “in Delhi 25% of the emissions were attributed to long-range atmospheric transport”. The only evidence the authors used to support this is on L425-427/P9, showing that 25% of data in Delhi had a Bap/(BaP + BeP) ratio of less than 0.5. This evidence is a little bit thin to support such a statement. I suggest the authors to either elaborate this with more evidence, or tone down such an unsupported statement.

The statement of 25 % was removed from the abstract and conclusions, however, the data from BaP/(BaP + BeP) ratio are still useful to support future studies investigating on local and regional emissions in Delhi. Therefore, we prefer to keep this statement in the text, we reported the results as a possible contribution from regional pollution at the sampling site in Delhi. A new discussion was added to the text and detailed in the next question.

Changes to the text:
L.577-580 removed and replaced by: This ratio suggests a larger contribution from local sources in both cities.

2. The issue of oxidation during sampling to the interpretation of results. First, in the paragraph of L192/P5, the authors noted that this effect could be an additional source of uncertainty (10 – 30%) to conventional analytical uncertainties (25 – 30%). The question is, what is the overall uncertainty if both of these two errors are taken into account? Second, after acknowledging this source of potential negative artifact, the authors used it in Section 3.3 to infer particle aging and then to regional transport of PM. Such inference may be conflicting without quantitative assessment on how such “on-filter” oxidation affect the indicator, i.e., the BaP/(BaP + BeP) ratio. Please clarify.

To determine the bias on the results we have used the ‘‘top-down’’ approach where the bias determination can be based on recovery efficiency to correct PAHs concentrations. The analytical uncertainty is due to available information on laboratory test performance. The “on-filter” oxidation is a type of chemical degradation/transformation. Therefore, the values of PAHs concentration has to be considered only as a lower limit due to “on-filter” oxidation. It is, however, different from the analytical uncertainty which estimates the lower and upper limits of the results.

A quantitative assessment of “on-filter” oxidation was not a part of this study, our assessment was based on the concentration of ozone measured at the sampling site and compared to quantitative assessment used in previous studies, as reported in section 2.4 for the error

evaluation. BaP and BeP were among the major compounds quantified in this study, and as shown in Table 1, their mean concentrations are similar in the margin of the analytical uncertainties, this support the statement suggesting local emissions as major contributors of PAHs in both cities.
According to Tsapakis and Stephanou (2003) the relative reactivity of BaP, with respect to degradation on glass fibre filters, was 1.6 times higher than BeP. Taking into account the estimated error on sampling artefact in each city and assuming that "on-filter" oxidation was affecting BaP and BeP, as suggested by Tsapakis and Stephanou (2003), the ratio of BaP/(BaP + BeP) will be affected negatively by an average of 4 % (day) and 1.6 % (night) for Beijing, 7 % (day) and 3 % (night) for Delhi.
This assumption will therefore be affecting Delhi results suggesting more contribution from long range transport.

Changes to the text:
L.427: However, this assumption does not take into account the ‘‘on-filter’’ oxidation errors during sampling. Tsapakis and Stephanou (2003) reported a relative reactivity of BaP of 1.6 times higher than BeP, with respect to degradation on glass fibre filters. Using the reactivity factor of 1.6, the ratio of BaP/(BaP + BeP) will be affected negatively by an average of 4 % (day) and 1.6 % (night) for Beijing, 7 % (day) and 3 % (night) for Delhi. This assumption will therefore be affecting Delhi results suggesting more contribution from long range transport. Therefore, the indicator of particle aging should be used with careful in the summer season unless ozone ambient concentrations are below 30 ppb, and consequently the negative artefacts are considered not significant (Tsapakis and Stephanou 2003).

L.446: Tsapakis and Stephanou (2003) reported a relative reactivity for BaP, Pyrene and Fluorene of 0.86, 0.82, and 0.68 respectively. The relative reactivity of BaP and Pyrene are similar and therefore does not affect the indicator Pyrene/BaP values. Pyrene is by 20 % more reactive than Fluorene, the ‘‘on-filter’’ oxidation has little effect on the indicator Fluorene/Fluorene+Pyrene values, because of the large difference in the defined threshold values which were 6 and 30 for petrol and diesel cars, respectively.

3. Section 3.5. It is not clear why the authors preferred to use only BaP for the cancer risk calculation. Both Table 2 and L524-527/P12 indicated that other PAHs may contribute another half of the risk. Would the reported LECR per million people values be under-estimated if other PAHs are not taken into account?
It is true that other PAHs have high Toxicity Equivalency Factor (TEF) but these TEF are relative to BaP. In Eq. 2 the use of BaP instead of BaPeq was recommended by U.S.EPA, 2002, and Boström et al., 2002, and that's because the unit risk (UR) already include the toxicity values of other PAHs, it is referred to as the surrogate approach.
The use of BaPeq (taken into account other PAHs) instead of BaP will overestimate LECR by 83% for Beijing, and 92 % for Delhi.

**Minor**
1. L146/P4: suggest to change "17-PAHs" to "17 PAHs", and change in a number places (e.g., L223/P5) "24 h mean concentration" to "24-h mean concentration".
"17-PAHs" corrected to "17 PAHs" and 24 h corrected to 24-h in the entire manuscript.

2. L156/P4: please change “PAHs concentrations” to “PAH concentrations”.
“PAHs concentrations” corrected to “PAH concentrations” in the entire manuscript.

3. L187/P4: why higher error could be attributed to samples analysed previously in wintertime? Memory effect? If so, why were the Delhi samples not affected? Were the Delhi samples analysed after Beijing summer samples?
In fact, lower %RSD was attributed to samples analysed in wintertime Beijing. The precision of sample replicates in wintertime Beijing and summer Delhi showed better %RSD (<10%) for few compounds as shown in Table S1. However, the maximum %RSD in summer Beijing was 13.7 % which is acceptable. This is a type of random errors where it is difficult to determine the origin of the error. L185 to L187 were removed from the text as this error is not related to lower PAH concentrations in summer Beijing.
Yes, Delhi samples were analysed after Beijing summer samples.

4. L199/P5: Tsapakis and Stephanou 2003: please use proper citation.
Corrected as Tsapakis and Stephanou (2003)

5. L207/P5: please add “that” after “than”.
Corrected

6. L414&L425/P9: please use BaP/(BaP + BeP) consistently.
Corrected

7. L418/P9: please change “[ratio = 0.5]” to “(ratio = 0.5)”.
Corrected

8. L431-434/P10: this seems like two sentences. Please revise.
Corrected as follow: We calculated the ratio value for Pyrene/BaP using the data reported in a previous study (Rogge et al., 1993), where the authors quantified more than 100 organic compounds in exhaust emissions fine particulate matter. The ratio value for Pyrene/BaP was ~ 0.7 for noncatalyst-equipped petrol cars, ~1.3 for catalyst-equipped petrol cars and >16 for heavy duty diesel engines.

9. Figure 3: in addition to the non-preferable “17-PAHs” on the graph and in the caption, I do not see the usefulness of putting “17-PAHs” on the graph. Please remove them on the graph and change to “17 PAHs” in the caption.
In Figure 3, ∑17 PAHs was added to the y axis and removed from the x axis. 17 PAHs corrected in the caption and in Figure 1 and 2.

10. Figure 5: please change the title of the y axis to “Bap/(BaP + BeP)”, as well as that in the caption.
Corrected

11. Table 1: please change “PAHs concentrations” to “PAH concentrations”.
Corrected

Response to referee 2:
Author's response in Blue

This paper present a comparison of PM2.5-bound PAHs in Beijing and Delhi. The diurnal and nocturnal variations of 17-PAHs in both cities were discussed, then the major emission sources were identified and the health risk was assessed. The novelty, if it is, as the authors state, is the high-time resolution ambient particle samples (every 3 hours during daytime and over 15 hours at nighttime) during the summer season. A natural question to this study would be what causes the PAHs to exhibit the diurnal and nocturnal variation and what is new findings based on the high-time resolution samples. Unfortunately, this paper does not seem to present new findings. The discussions are also too general. Additionally, the manuscript is generally readable though proofreading and grammar corrections would improve it substantially. Overall, although the data are likely new and can be potentially useful in understanding the variation of PAHs in summer Beijing and Delhi, the paper is not sufficiently rigorous to warrant a publication in ACP. I use the abstract to illustrate my main concerns of the paper. The abstract says: The mean concentration of particles less than 2.5 microns (PM2.5) observed in Delhi was 3.6 times higher than in Beijing during the measurement period. In Beijing, … the highest contribution from Indeno[1,2,3-cd]pyrene, while at night-time… the largest contribution from Benzo[b]fluoranthene (14 %). In Delhi, … the largest contribution from Indeno[1,2,3-cd]pyrene in both the day and night. Local emission sources were typically identified as the major contributors to total measured PAHs, however, in Delhi 25 % of the emissions were attributed to long-range atmospheric transport. 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. The lifetime excess lung cancer risk (LECR) was, 2.2 times higher in Delhi (LECR = 155 per million people) than in Beijing risk assessment value (LECR = 70 per million people). The highlighted results above are not really exciting. In fact, many researches have reported the diurnal and nocturnal variations and source appointment of PAHs in Beijing and Delhi based on the low-time resolution samples. I cannot see new or exciting findings in this paper. So I would suggest they focus on the new findings of the study, which cannot be obtained by the low-time resolution samples.

We thank the reviewer for commenting this paper and we hope our responses below will better clarify the importance of this manuscript, not only to the scientific community but also to policy makers and local governments. We are sorry that the reviewer didn't find the paper exciting, but rigorous analysis of data and factual interpretation can be high value for species where literature observations are relatively sparse.

This manuscript fits well within one of the science focus of ACP (aerosols, field measurements and chemical composition), and also submitted as part of the wider investigation on Beijing air quality (Special Issue: In-depth study of air pollution sources and processes within Beijing and its surrounding region (APHH-Beijing) (ACP/AMT inter-journal SI)). To the best of our knowledge, there is no published work in ACP showing the day/night variation of PAHs in

Delhi. A direct comparison using the same methods and techniques for PAHs in Beijing and Delhi is also absent from the literature. In this work, we have collected, extracted and analysed particle samples using the same analytical method, which provides a sensitive comparison of PAHs and of emission control policies between two megacities, Beijing and Delhi. This study shows that the adverse health effects from inhalation exposure to PAHs in Delhi is 2.2 times higher than in Beijing, assessed using the same LECR method.

Returning to the question of what causes PAHs to exhibit the diurnal and nocturnal variation, and the new findings from high-time resolution samples. As discussed in section 3.2, seasonal variation plays an important role on ambient concentrations of PAHs. However, the variation between day and night depends on many factors including natural impacts and circumference of the sampling location. In both cities, Beijing and Delhi, the concentration of total PAHs in the first 3 h filter (08:30–11:30) of the day appear to be higher than the rest of the day, suggesting a potential relation with the early morning rush hour time and vehicle emissions. Despite the higher boundary layer height during the day in Delhi, PAHs concentration in the first 3 h filter support their direct emissions from local sources especially petrol vehicles.

The difference in PAHs variation between day and night in Beijing is not significant and emission sources were mostly related to petrol combustion emissions and local emission sources rather than contribution from long range transport. However, in Delhi, PAHs variation between day and night was significant. It could be affected by multiple factors including the spatial variation, the input from multiple local sources, the surroundings of the sampling site, and the meteorological conditions in the north of Delhi. The higher total PAHs concentration at night in Delhi could also be related to emissions from biomass burning, waste burning, solid fuel cooking and heavy duty diesels entering the city at night-time. To the best of our knowledge, this is the first time that there has been an attribution of the higher concentration of PAHs at night time to natural influences such as the lower atmospheric mixing heights as shown in Fig. 4. Another important factor that can negatively impact PAHs concentration in daytime is the higher concentration of ozone and on filter oxidation, discussed in section 2.4, 3.2 and 3.3.

So, the new findings are not just about the high-time resolution samples, but also include the important role of natural impacts on PAHs variation such as the boundary layer height at night-time in Delhi. Moreover, the contribution from long range transport in Delhi need more investigation using correlation studies between different types of pollutants. The new findings identified the major sectors that could be subject to mitigation measures and may improve air quality in both cities. The high-time resolution samples clearly provide a better assessment of PAH concentrations and can reflect direct source emission signals as modified by meteorology during the daytime and night-time.  We note that the reviewer did not include any citations to literature reporting equivalent findings and so we contend that whilst of course previous measurement of PAH have been made in both cities, this paper adds new insight into controlling processes and sources.

**Relevant changes made in the manuscript are marked-up in Blue**
**(L.40; 429-437; 443-445; 450-455; 596-597)**
**Text removed from the manuscript marked up in Red**
**(L.40-41; 187-190; 441-442; 596-600)**

# 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 (∑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 ∑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. however, in Delhi 25 % of the emissions were attributed to long-range atmospheric transport. 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.

## 1 Introduction

The significant increase of particulate matter (PM) and gaseous pollutants over the past decades in some rapidly expanding economies, has led to greater emphasis being placed on mitigation of emissions and management air quality health effects. To support such measures requires insight in both the sources of pollution, and the composition of pollution so that most harmful sources may be tackled as a priority. Although there have been recent improvements that have reduced primary particle concentrations in some regions, concentrations of many damaging gases and fine particles continue to exceed WHO guidelines (WHO, 2016), in megacities such as Beijing (Elzein et al., 2019; Lin et al., 2018; Gao and Ji., 2018) and Delhi (Kanawade et al., 2019; Sharma et al., 2007) and in many other cities around the world such as Cairo, Egypt (Cheng et al., 2016) and Islamabad, Pakistan (Mehmood et al., 2020). Growing populations, human activities, energy consumption and natural contributions (volcanic eruptions and forest fires) are an important contributor to particles emissions. PM monitoring and analysis become ever more important because of its adverse effect on human health. The chemical composition of airborne particles influences the health impacts, particularly the abundance of primary and secondary organic matter, metals, and ions (WHO, 2016; Bond et al., 2004; Saikawa et al., 2009). Fine particles become more harmful as particle size decreases (ultrafine), they enter the human body through the lungs and may translocate to other organs causing respiratory diseases and cancer (Schraufnagel., 2020). The greatest adverse effects on human health in epidemiological studies are currently associated with the mass of particles less than 2.5 microns in diameter ($PM_{2.5}$) (Raaschou-Nielsen et al., 2013, Pun et al., 2017, Hamra et al., 2014). The organic component of $PM_{2.5}$ consists of thousands of compounds, among them polycyclic aromatic hydrocarbons (PAHs), a particular class of species with high toxic potency. They are released into the atmosphere from both natural and anthropogenic sources. PAHs are considered ubiquitous in the environment and can be found in soil and water via dry or wet atmospheric deposition (Menzie et al., 1992, Meador et al., 1995). Their major emissions come from anthropogenic sources and include incomplete combustion of fossil fuels, vehicle exhaust emissions, cigarette emissions, agricultural burning and industrial activities (Saikawa et al., 2009). It has been shown that PAHs can react with atmospheric oxidants leading to the formation of secondary species with direct-acting mutagenicity and carcinogenicity and thus they can be significant contributors to the high toxicity of particles even at low PM levels (Nisbet and LaGoy 1992).

Beijing and Delhi often suffer from severe air pollution episodes, reaching high $PM_{2.5}$ concentrations and air quality index levels. The local government in Beijing has declared many different air quality actions since September 2013, resulting in a decrease in the concentration of total PAHs as reported in recent studies for the winter season in Beijing (Chen et al., 2017, Elzein et al., 2019, Feng et al., 2019). This has been attributed to the efforts made by the municipal government of Beijing to improve air quality and control emissions by reducing combustion sources and promoting the use of clean energy sources and electric vehicles.

Several anti-pollution measures have been introduced in Delhi in the last two decades such as, Bharat stage (equivalent to Euro standards), switching public transport from running on diesel to compressed natural gas (CNG), and applying "odd-even" vehicle number plate restriction during working days (Guttikunda et al., 2014; Goel and Guttikunda, 2015; Chowdhury et al., 2017). Despite the government effort to tackle air pollution in India and especially in Delhi, recent studies have showed that the air quality continue to be among the poorest in the world causing thousands of premature deaths (Tiwari et al., 2015, Ghude et al., 2016, Chowdhury and Dey., 2016, Pant et al., 2017, Conibear et al., 2018). PAHs emission sources in Delhi have previously been attributed to vehicle emissions, coal combustion, wood and burning leaves (Gadi et al., 2019; Shivani et al., 2019; Gupta et al., 2011; Sharma et al 2007).

To the best of our knowledge, data on $PM_{2.5}$-bound PAHs in Delhi during the summer season (pre-monsoon: March – June) is scarce and limited to other periods of the year with low-time resolution ambient samples (sample averaging time of 24-h). It has been shown that concentrations of ambient particle-bound PAH when collected over long sampling times are subject to higher uncertainties related to sampling artefacts deriving from meteorological effects and oxidant concentrations such as ozone (Goriaux et al., 2006; Tsapakis and Stephanou, 2003, 2007; Ringuet et al., 2012a; Keyte et al., 2013). Using shorter time periods for ambient particle sampling (e.g. 3 and 4 h) has been suggested as offering more accurate diagnosis of emission sources (Tian et al., 2017; Srivastava et al., 2018), shorter time sampling is still scarce and limited to studies outside China and India (Reisen and Arey, 2004; Srivastava et al., 2018). Considering the above and that particles collected during 24-hour sampling time integrate both daytime and night-time chemistry together, we collected high frequency ambient air particle samples ($PM_{2.5}$) in urban Beijing (China) and Delhi (India) to determine the temporal diurnal and nocturnal variation of PAHs. A great advantage in this study is that all particle samples from both campaigns were collected, extracted and analysed using the same analytical method, which provide a better comparison of the variation in PAHs between cities and on the feasibility and efficiency of implementing emission control policies to improve air quality in both cities.

## 2 Methods

### 2.1 Sampling campaigns

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

### 2.2 Sample extraction

Collected filters were cut using a cube cutter (1/16 of the filter) measuring a surface area equivalent to 24 $cm^2$. Each section was then cut into small pieces to fit inside 5 mL stainless steel extraction cells used by a pressurized solvent extractor (Dionex, ASE 350). All samples were extracted in acetonitrile (HPLC-grade) using the following method: Oven at 120°C, pressure at 1500 psi, rinse volume 60 % and 60 s purge time for three consecutive 5 min cycles. The extraction time of each cell was about 25 min for a final volume of 20 mL. Prior to purification, extracts (V = 20 mL) were evaporated to approximately 6 mL under a gentle stream of nitrogen. All samples and blanks were purified on solid phase extraction (SPE) silica normal phase cartridge (1g/6mL; Sigma Aldrich) to reduce the impacts of interfering compounds in the matrix and to help maintain a clean GC injection inlet liner. After the purification step, the solution of each sample was evaporated to 1 mL under a gentle stream of nitrogen at room temperature (20 °C) and transferred to a 1.5 mL autosampler amber vial. Each concentrated sample was stored at 4 °C until analysis.

## 2.3 Analytical procedures

In this study, 17 PAHs were selected based on their presence within the particle phase and commercially available standards. These are listed in Table 1 and standards purchased from Sigma Aldrich, Alfa Aesar and Santa Cruz Biotechnology in the UK with a minimum purity of 97 %. In parallel to individual standards, a mixed solution of the 16 EPA PAHs (CRM47940, Supelco, Sigma Aldrich) of 10 µg ml$^{-1}$ in acetonitrile was also used. Standard solutions for calibrations were prepared in acetonitrile (HPLC grade, 99.9 % purity, Sigma Aldrich). Phenanthrene-d10 and pyrene-d10 were used as surrogate standards and were spiked over two blank filters and two sample filters from both campaigns, with concentration on filters corresponding to 300 ng (V = 60 µL from 5 ng µL$^{-1}$ in acetonitrile). Spiked filters solutions were analysed 10 times, and the average recovery efficiencies calculated from surrogate standards was 96 %, ranging from 88 % to 107 % for both compounds, phenanthrene-d10 and pyrene-d10. PAH concentrations were corrected to the average recovery efficiencies. These two deuterated compounds were supplied by C/D/N isotopes and distributed by QMX Laboratories Ltd (Essex, UK).

All PAH were quantified using a gas chromatography - time of flight - mass spectrometry system (GC Agilent 7890B coupled to an Agilent 7200 Q-TOF-MS). 1 µL of each sample was injected in pulsed splitless mode at 320 °C using an automated liquid injection with the GERSTEL MultiPurpose Sampler (MPS). Helium was used as carrier gas at 1.4 mL min$^{-1}$ and target compounds were eluted using the RXi-5ms (Restek GC column, Crossbond diphenyl dimethyl polysiloxane; length: 30 m, diameter: 0.25 mm, film thickness: 0.25 µm). The analysis time of each sample was set to 35 min using the following GC oven temperature programme: 65 °C for 4 min as a starting point and then increased to 185 °C at a heating rate of 40 °C min$^{-1}$ and held for 0.5 min, followed by a heating rate of 10 °C min$^{-1}$ to 240 °C and then ramped at 5 °C min$^{-1}$ until 320 °C and held isothermally for further 6 min to ensure all analytes eluted from the column. The MS was operated in Electron Ionisation (EI) mode at 70 eV with an emission current of 35 µA. 10-point calibration solutions were injected 4 times in the same sequence as for samples and covered the range from 1 pg µL$^{-1}$ to 1000 pg µL$^{-1}$, with a correlation coefficient from the linear regression between 0.970 and 0.999.

## 2.4 Error evaluation

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

To evaluate the agreement between repeated measurements (precision error), we calculated the relative standard deviations (%RSD) from replicate analysis (n = 10) of two samples. The %RSD average of total PAHs was 8.7 % (range: 3.36 – 13.71 %) for Beijing samples and 4.2 % (range: 2.64 – 10.12 %) for Delhi samples. The %RSD average for deuterium labelled compounds spiked over two sample filters was ~ 3.6 % for both campaigns. The %RSD of each compound is shown in Table S1. The higher precision error (>10 %) attributed to a few compounds in Beijing samples (Table S1) is most probably related to the lower concentration of PAHs in the samples compared to Delhi samples and to samples analysed previously from Beijing in wintertime (Elzein et al., 2019). Moreover, the calibration offset and the influence of the sample matrix on the quantification step are an important source of systematic

error and was estimated to be a maximum of 20 %. Therefore, the upper limit estimated error, combining the precision and the systematic effects, is 30 % for Beijing samples and 25 % for Delhi samples.
In addition, another type of error has been attributed to sampling artefacts. Previous studies (Schauer et al., 2003, Goriaux et al., 2006, Tsapakis and Stephanou, 2003, Brown and Brown, 2012) have reported a chemical decomposition of PAHs depending on the ambient concentration of ozone and sampling time. Therefore, data from long sampling times and under very high ozone ambient concentrations (>70 ppb) may be biased by sampling artefacts of more than 100 % (Schauer et al., 2003, Goriaux et al., 2006). However, at low ozone levels (< 30 ppb), negative artefacts were considered not significant (Tsapakis and Stephanou, 2003), whilst, at medium ozone levels (30-50 ppb) PAHs values were underestimated by 30 % (Schauer et al., 2003). Tsapakis and Stephanou (2003), have reported a loss of PAHs by 28 % due to ozone atmospheric concentration about 60 ppb and long sampling times of 24-h. They have also suggested that long sampling time under low ozone concentration (< 30 ppb) do not affect the concentration of collected PAHs in the gas or particle phases, while short sampling time (2 h) under ozone concentration about 60 ppb will reduce the concentration of PAHs by 17 %. In this study, ozone concentrations were measured in both campaigns and averaged to the filter sampling time to provide more accurate estimation on the negative sampling artefacts. The ozone concentration in summer Beijing ranged between 3.7 and 140 ppb over the campaign (mean value: 56 ± 31 ppb), approximately 5 times higher than that in winter (mean value: 10.4 ± 8.8 ppb, Elzein et al., 2019). Daytime ozone concentration ranged from 12 to 140 ppb (mean value: 63 ± 30 ppb), while over the night-time it ranged from 4 to 74 ppb (mean value: 34 ± 18 ppb). Therefore, based on Tsapakis and Stephanou (2003) study, the negative sampling artefacts due to ozone concentration was estimated to be 20 % for daytime samples (3 h) and 10 % for the night-time samples (15 h) due to lower ozone concentration at night. Using the same approach, daytime ozone concentration in Delhi ranged between 39 and 119 ppb, with a mean value: 75 ± 20 ppb, while the night-time concentration ranged from 14 to 50 ppb (mean value: 37 ± 12 ppb). Therefore, the estimation of the negative sampling artefacts on the data from Delhi ranged between 15 and 30 %, with the highest error estimation attributable to daytime-time samples (3 h) because of the higher ozone concentration during the day.

## 3 Results and discussion

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

In 2016, the World Health Organisation (WHO, 2016) published an air quality guideline on outdoor air pollution limits to help protect human health and reduce the risk of mortality due to fine particles. The air quality standards for $PM_{2.5}$ were set by the ministry of environment in China and India, and published in the WHO air quality guideline as an annual and 24-h mean concentration. The daily $PM_{2.5}$ (mean 24-h) guideline concentration is currently set at 75 and 60 µg $m^{-3}$ for China and India, respectively, while the annual mean guideline concentration is currently set at 35 and 40 µg $m^{-3}$ for China and India, respectively. $PM_{2.5}$ concentrations measured at the two sites were averaged to the filter sampling time and are shown in Fig.1 and Fig. 2. In Beijing, the average 24-h $PM_{2.5}$ concentration was 39 ± 21 µg $m^{-3}$ (range: 16 - 97 µg $m^{-3}$), exceeding the Chinese 24-h limit value (75 µg $m^{-3}$) on 1 day of the 20 sampling days. The average daytime and night-time $PM_{2.5}$ concentrations in Beijing were 40 ± 24 µg $m^{-3}$ and 38 ± 24 µg $m^{-3}$, respectively. Delhi showed an average 24-h $PM_{2.5}$ concentration of 143 ± 27 µg $m^{-3}$ (range: 110 - 195 µg $m^{-3}$), exceeding the Indian 24-h limit value on all 9 sampling days. The average daytime and night-time $PM_{2.5}$ concentrations in Delhi were 141 ± 51 µg $m^{-3}$ and 140 ± 26 µg $m^{-3}$, respectively. $PM_{2.5}$ concentrations in Delhi have changed little in recent years; between 2008 and 2011 the daily average of $PM_{2.5}$ concentrations was 123 ± 87 µg $m^{-3}$ (Guttikunda and Calori., 2013), while the annual average was reported to be 125.5 ± 77.2 µg $m^{-3}$ between January 2013 and May 2014 (Winter: 196 µg $m^{-3}$, Summer: 83.6 µg $m^{-3}$, Monsoon: 58.8 µg $m^{-3}$) (Sharma and Mandal., 2017). The limited change seen in recent years may be associated with continued emissions from residential energy use, estimated to contribute about 50 % of $PM_{2.5}$ airborne concentrations (Conibear et al., 2018, Butt et al., 2016). The construction sector is fast growing in India, and the dust emitted from various activities (demolition, excavation, drilling etc.) is also considered an important source of particles (Guttikunda et al., 2014). The WHO has not published a guideline limit value for PAHs, but benzo[a]pyrene (BaP) is often used as a marker of toxicity for all PAHs. The European Union has set an annual mean air quality limit of 1 ng $m^{-3}$ for BaP (WHO, 2016). The daily (24-h) concentration of BaP in summer Beijing (this study) ranged from 0.49 to 1.18 ng $m^{-3}$ (average 0.80 ± 0.17 ng $m^{-3}$), about 19 times lower than previously observed at this site in winter (Elzein et al., 2019). This is below the 24-h average limit value of 2.5 ng $m^{-3}$, set in China by the Ministry of Ecology and Environment in 2012, on all of the 20 days of sampling period. During the short summer measurement period in Delhi, BaP varied between 1.16 and 3.16 ng $m^{-3}$ (average 1.78 ± 0.67 ng $m^{-3}$), and exceeded the threshold of 2.5 ng $m^{-3}$ on 1 day.

### 3.2 Variability of PAHs in summer Beijing and Delhi

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

**Beijing:**

The mean 3 h daytime concentration of ∑17 PAHs in Beijing was 8.2 ± 5.1 ng $m^{-3}$ ranging from 2.6 to 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 ng $m^{-3}$. The mean 24-h total concentration (combined results from daytime and night-time samples) of 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 13 times lower than the average 24-h in winter time Beijing (97 ng $m^{-3}$) reported in our previous study at the same location (Elzein et al., 2019). Similarly, previous studies in urban Beijing (Feng et al., 2005; Wu et al., 2014; Gao and Ji., 2018; Song et al., 2019; Feng et al., 2019) have reported much lower values of PAHs in summer than in winter, showing the important role of seasonal variation in influencing ambient concentrations of PAHs. The dominant reason for this seasonal variation in Beijing is the increase in energy consumption in winter and in particular the emissions from traditional rural/urban heating methods using coal. The effect of dispersion in vertical and horizontal directions and long-range transport due to air mass trajectory can also influence local PAHs concentration.
The photochemical effects on particulate PAHs between summer and winter are not clear in the literature and were considered to play a minor role in seasonal variation of PAHs (Wu et al., 2014). However, an important factor that might affect PAH levels is their degradation or transformation due to high ozone ambient concentration level in summer, which were 5 times higher than in winter (Elzein et al., 2019). This factor can negatively bias PAHs levels during filter sampling by more than 100 % (discussed above in section 2.4). The gas phase concentrations of PAHs were not measured in this study, but the distribution of PAHs between the gaseous and particulate phases is an important factor affecting their fate in the environment (Lohmann and Lammel, 2004). The distribution of highly volatile PAHs (e.g. 2-3 ring) are known to be influenced by temperature (Tsapakis and Stephanou., 2005; Gaga and Ari., 2011; Verma et al., 2017), while the low volatile PAHs and PAHs-derivatives (e.g. oxygenated and nitrated-PAHs) are mostly associated to the particle phase (Albinet et al., 2008; Liu et al., 2017, Zhang et al., 2018). The spatial variation within urban Beijing might have little difference on pollutants concentrations (He et al., 2001), the variation will increase when moving to suburban areas because it consists of a large number of factories, airports, and power plant stations. Feng et al. (2005) compared the total PAHs concentration in $PM_{2.5}$ at urban and suburban sites in Beijing at the same period of the year (July and November 2002), and they reported higher values at the suburban site than at the urban site by a factor ~1.5 in summer and ~ 2 in winter. The sampling location in this study is an urban area surrounded by busy roads, residential buildings, an underground railway, and restaurants. Therefore, it

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

In Figure 1, the concentration of total PAHs in the first 3 h filter (08:30–11:30) of the day appear to be higher than the rest of the day. These elevated concentrations are potentially associated with the early morning rush hour time and vehicle emissions. The average night-time total PAHs concentration (7.2 ng $m^{-3}$) was in the range of the second and third "3 h" daytime average values, 7.8 and 6.4 ng $m^{-3}$ respectively. This indicates that the elevated total PAHs concentration in the first 3 h filter (08:30–11:30) of the day is not related to accumulation of air pollutants at night-time but most likely related to direct emissions from traffic in the early morning and particularly petrol combustion emissions (see section 3.3).

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

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

**Delhi:**

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

Similar to Beijing, previous studies in Delhi mainly focused on the 24-h average concentration of total PAHs. They have addressed the problem of air pollution across India, focusing on $PM_{2.5}$ trends, $PM_{2.5}$ health impact, and source apportionment (Chowdhury et al., 2007; Gupta et al., 2011; Chowdhury and Dey., 2016; Pant et al., 2017; Chen et al., 2020), however, PAHs emissions and variation between daytime and night-time have not been measured or discussed previously, and only few studies (Sharma et al., 2007; Singh et al., 2011, Gadi et al., 2019) reported the 24-h mean concentration of ∑n-PAHs ($n > 10$) in Delhi itself. In this study, the mean 24-h (combined results from daytime and night-time samples) of the 17 PAHs was 19.3 ± 7.1 ng $m^{-3}$ ranging from 13.3 to 35 ng $m^{-3}$. Previous studies showed a large spatial variation in PAH concentrations within Delhi; Sharma et al., (2007) reported a mean 24-h value of 624.04 ± 376.48 ng $m^{-3}$ (~ 32 times higher than our mean value) for ∑12-PAHs at the South of Delhi during the summer season of 2003. Singh et al., 2011 reported a mean 24-h value of 45.8 ± 22.1 ng $m^{-3}$ (~ 2.4 times higher than our mean value) for ∑16-PAHs at the East of Delhi during the summer season of 2008. Gadi et al., (2019) reported an annual average of 277 ± 126 ng $m^{-3}$ for the summation of 16-PAHs between December 2016 and December 2017, and 260 ± 111 ng $m^{-3}$ for the summer season of 2017 (~ 13.5 times higher than our mean value, and ~ 5.7 times higher than Singh et al., 2011 mean value). In the study of Gadi et al., (2019), the sampling site was in the same campus as this study (Indira Gandhi Delhi Technical University for Women), the low ∑PAHs value in this study is most probably due to the short summer measurement period in Delhi (9 days, 35 samples), coupled with less pollution episodes for PAHs. It appears that the variation of PAHs concentration in Delhi could be affected by multiple factors including the spatial variation, the input from multiple local sources, the surroundings of the sampling site, and the meteorological conditions in the north of Delhi. Therefore, the concentrations of ambient particle-bound PAH over longer averaging period such as the 24-h are subject to high uncertainty related to the multiple factors cited above. Higher frequency filter sampling during 24-h can provide a better assessment of PAH concentrations and is more likely to reflect direct source emission signals as modified by meteorology. This perspective also applies to other Indian cities in future studies.

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

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

### 3.3 Major PAH, particle aging and traffic emissions

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

A number of molecular diagnostic ratios for source apportionment have been proposed in literature and are still under debate (Larsen and Baker., 2003; Katsoyiannis et al., 2011; Keyte et al., 2013; Zheng et al., 2017). They were considered uncertain in some studies because the results were not consistent and reproducible and did not reflect known differences in sources in space and time unless the source is very strong and the sampling measurements are made close to the known source. In addition, they may be biased by atmospheric reactions and selective loss processes (Katsoyiannis et al., 2011; Zheng et al., 2017). Among the PAHs, BaP is known to be a particularly carcinogenic compound inducing a mutagenic effect in experimental animals and is used as key PAH marker of total exposure (WHO, 2016, IARC, 2012). BaP is mostly emitted from coal and biomass burning, and vehicle exhaust emissions (Harrison et al., 1996; WHO, 2016). The sampling site in both Beijing and Delhi was at a short distance from busy roads with significant vehicle exhaust emissions. BaP lifetime is affected by light and oxidants in the atmosphere, BaP is far more reactive than its isomer BeP (Butler and Crossley, 1981, Ringuet et al., 2012b), thus the decline of the ratio BaP/(BaP + BeP) can be regarded as an indicator of particle aging (Liu et al., 2013; Watson et al., 2016). Considering the above, BaP/(BaP + BeP) has been used in this study to assess the contribution of local sources on particle composition. Generally, there is no defined threshold value for BaP/(BaP + BeP) which can distinguish aged particles from freshly emitted. However, Watson et al., (2016) suggested that similar amounts of BaP and BeP (ratio = 0.5) indicates that particles are freshly emitted and mostly affected by local emissions rather than long range atmospheric transport. Moreover, Liu et al., (2013) compared BaP and BeP ratios at remote sites and emission source regions and reported BaP/BeP lower than 0.4 means aged aerosol type, while a value higher than 0.4 indicates local emission source. In this study, a ratio of BaP/(BaP + BeP) higher than 0.5 has been considered to characterize local emission sources. The ratio of BaP/(BaP + BeP) has been calculated for both campaigns and results are shown in Figure 5. This ratio mainly varied between 0.5 and 0.6 in Beijing, indicating a dominant contribution from local sources. In Delhi, 25 % of the data were below 0.5 indicating that aged particles might contribute to the air masses collected at the sampling site but local emissions of PAH are still a significant source. However, this assumption does not take into account the ‘‘on-filter’’ oxidation errors during sampling. Tsapakis and Stephanou (2003) reported a relative reactivity of BaP of 1.6 times higher than BeP, with respect to degradation on glass fibre filters. Using the reactivity factor of 1.6, the ratio of BaP/(BaP + BeP) will be affected negatively by an average of 4 % (day) and 1.6 % (night) for Beijing, 7 % (day) and 3 % (night) for Delhi. This assumption will therefore be affecting Delhi results suggesting more contribution from long range transport. Therefore, the indicator of particle aging should be used with careful in the summer season unless ozone ambient concentrations are below 30 ppb, and consequently the negative artefacts are considered not significant (Tsapakis and Stephanou 2003).

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

### 3.4 Emission source fingerprints

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

In this study, the 4, 5, and 6 ring PAHs accounted ~ 95 % of the total $PM_{2.5}$-bound PAH concentrations measured in both campaigns (Fig. 6). The mean contribution of the number of ring to the total of PAHs 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 both, Beijing and Delhi, road traffic is known to be one of the largest emission source of gas and particle phase pollutants (Fang et al., 2016; Zhang et al., 2020; Shivani et al., 2019), which might explain the high contribution from 4, 5 and 6 ring to total PAHs, while diesel and coal combustion may also contribute to the emission of 4 ring PAHs. The 4 ring PAHs concentration in Delhi was higher than in Beijing, the mean concentration of the 4 ring PAHs in daytime and night-time samples was 2.7 and 2.1 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 ring), the 4 ring PAHs total concentration in Delhi was lower than the 6 ring PAHs (Fig. 6) and a potential emission source could be the common use of fuel and oil in power generators.

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

Finally, identifying PAH markers emitted from specific emission sources (types of fuel, types of coal, types of waste, etc.) in ambient air is still complex due to the similarity of PAH profiles from different source types, which may quickly blend in the air with interferences from both nearby and remote emission sources. A more complete assessment of emission source types at specific locations would require the use of individual PAHs as source markers combined with other chemical constituents of $PM_{2.5}$ (elements and ions) and with gas phase air pollutants known to be released from the same source such as VOCs markers.

### 3.5 Health risk assessment

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

$$[\mathrm{BaP}]_{\mathrm{eq}} = \sum_{\mathrm{i}=1}^{\mathrm{N}} \mathrm{PAH_i} \times \mathrm{TEF_i} \qquad (1)$$

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

$$\mathrm{LECR} = \mathrm{BaP} \times \mathrm{UR} \qquad (2)$$

**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 |

* SD : Standard deviation

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

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

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

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

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

PAHs in the gas phase are mostly low molecular weight (2-3 ring PAHs) and their partitioning to the particle phase is small (Ravindra et al., 2007; Liu et al., 2017; Zhao et al., 2020) with lower TEF values (Table S2), therefore, their contribution to total carcinogenic potential is low (< 5 % in this study). Previous studies may consider a variable number of PAHs and other aromatics with known TEF such as the nitrated-PAHs, including different references for TEF values which make a direct comparison of the carcinogenic risk between studies not ideal. However, as particulate-PAH concentrations are lower in warm months, related $BaP_{eq}$ values were also lower in warm months. Feng et al., 2019 reported an average $BaP_{eq}$ total concentration of 20 PAHs equal to 1.9 and 21.9 ng $m^{-3}$ in summer and winter

Beijing, respectively. In this study, the summer $BaP_{eq}$ total concentration of 15 quantified PAHs in Beijing was 1.47 ng $m^{-3}$, while in our previous study for winter Beijing (Elzein et al., 2019), the $BaP_{eq}$ total concentration of 16 quantified PAHs and 7 derivatives was 23.6 ng $m^{-3}$. The results from this study suggest to focus attention on mitigating the emission of major contributors to the total carcinogenic potential (Benzo[a]pyrene, Dibenzo[a,h]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, and Indeno[1,2,3-cd]pyrene) in order to reduce adverse health effects from exposure to this class of air pollution. These compounds are 5 and 6 ring PAHs, and were mostly related to emission from petrol and oil combustion (Harrison, et al., 1996; Ravindra et al., 2007).

## 4 Conclusions

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

In Beijing and Delhi, 17 PAHs were quantified using a GC-Q-TOF-MS and the measured 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, ∑17 PAH concentrations varied between 2.6 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 ng $m^{-3}$) at night-time. In Delhi, ∑17 PAH concentrations varied between 8.4 and 36.6 ng $m^{-3}$ (average 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.

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

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

The ratio of BaP/(BaP + BeP) has been used to evaluate the contribution from local sources against long range atmospheric transport of particle-bound PAHs. This ratio suggests a larger contribution from local sources in both cities. varied between 0.5 and 0.6 in Beijing, indicating a larger contribution from local sources, while in Delhi, 25 % of the data were below 0.5, indicating a possible contribution from regional pollution at the sampling site, but local emissions were still the dominant source of PAHs found in the particle phase. Flu/Flu+Pyr and Pyr/BaP were used as diagnostic ratios to distinguish between petrol and diesel, and results suggest petrol combustion emissions as a major source in Both Beijing and Delhi.

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

The lifetime excess lung cancer risk 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). The results from this study suggest focusing attention on mitigating the emission of major contributors to the total carcinogenic potential, being the 5 and 6 ring PAHs (mostly emitted from petrol and oil combustion), in order to reduce adverse health effects from inhalation exposure to PAHs in the particulate phase.

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

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

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

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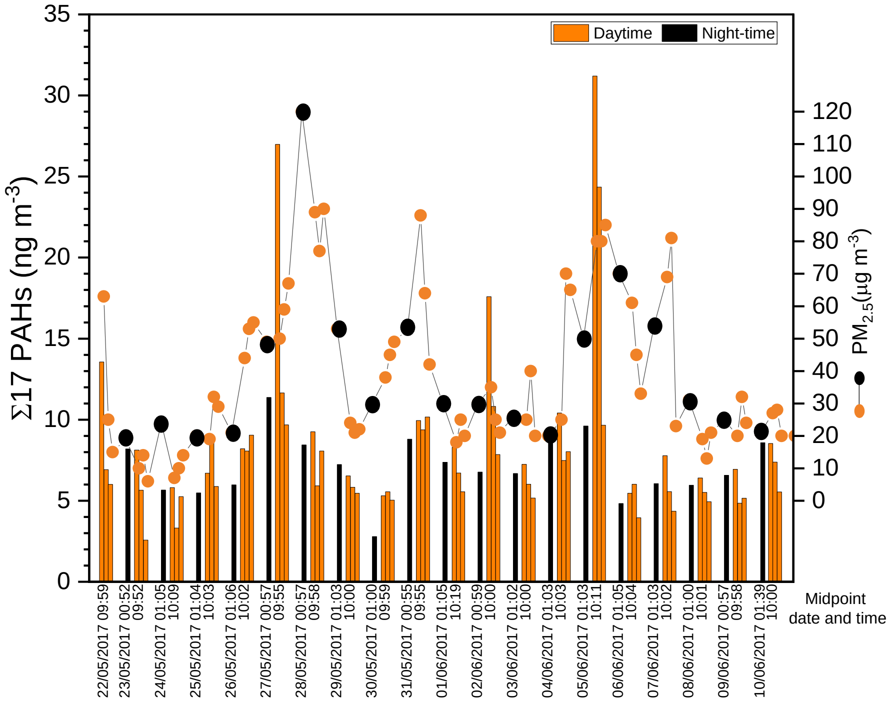

**Figure 1** Temporal variation of total PAHs and PM$_{2.5}$ concentrations in summer Beijing. PM$_{2.5}$ concentrations were averaged to the filter sampling time, approximately 3 h in daytime and 15 h at night. The 3 h midpoint time tick labels at noon (~13:00) and in the afternoon (~16:00) have been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

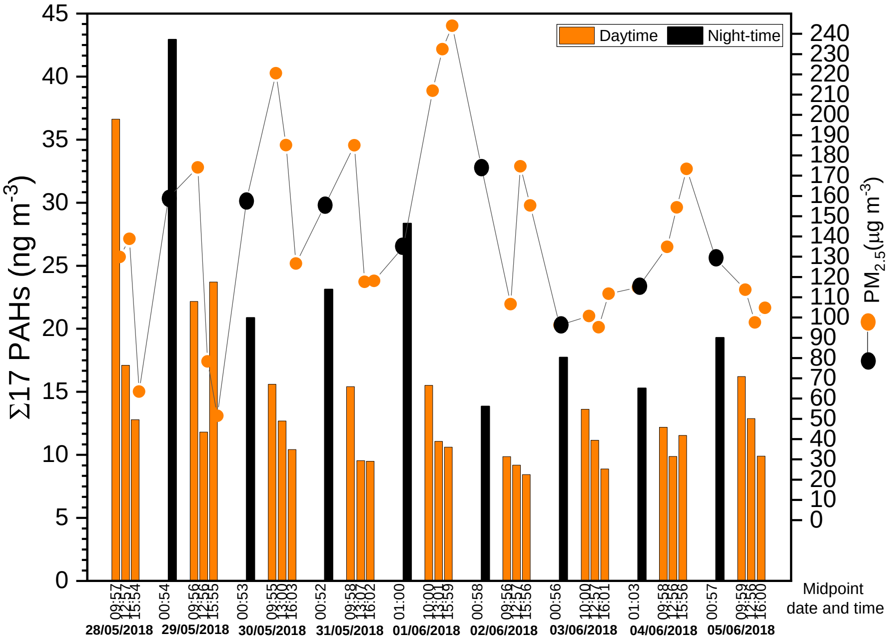

**Figure 2** Temporal variation of total PAHs and PM$_{2.5}$ concentrations in summer Delhi. PM$_{2.5}$ concentrations were averaged to the filter sampling time, approximately 3 h in daytime and 15 h at night.

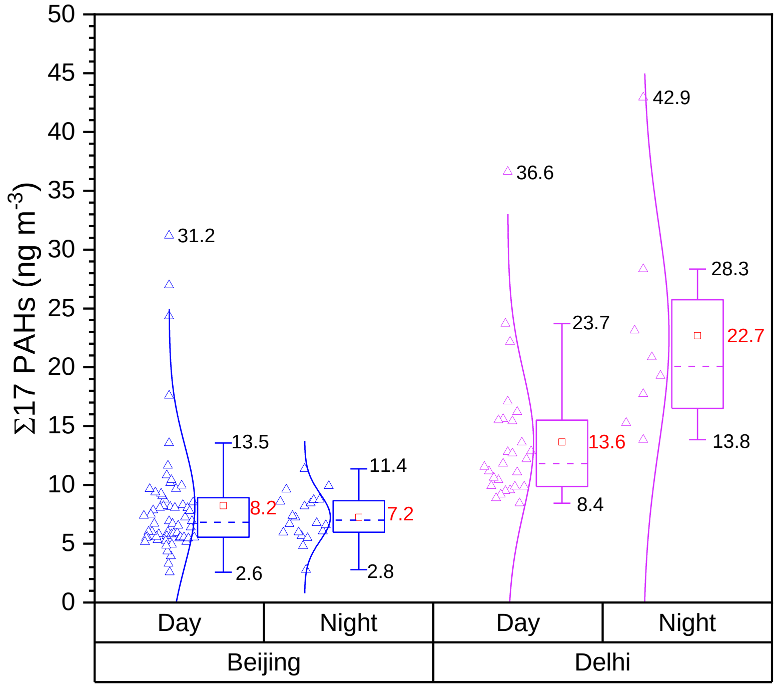

**Figure 3.** Concentrations of 17 PAHs in $PM_{2.5}$ samples during the daytime (3 h) and night-time (15 h). Box plots represents the 25th and 75th percentiles range of the observed concentrations and the whisker numbers reflect the data within 1.5 times the interquartile range (IQR). Red square symbols 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.

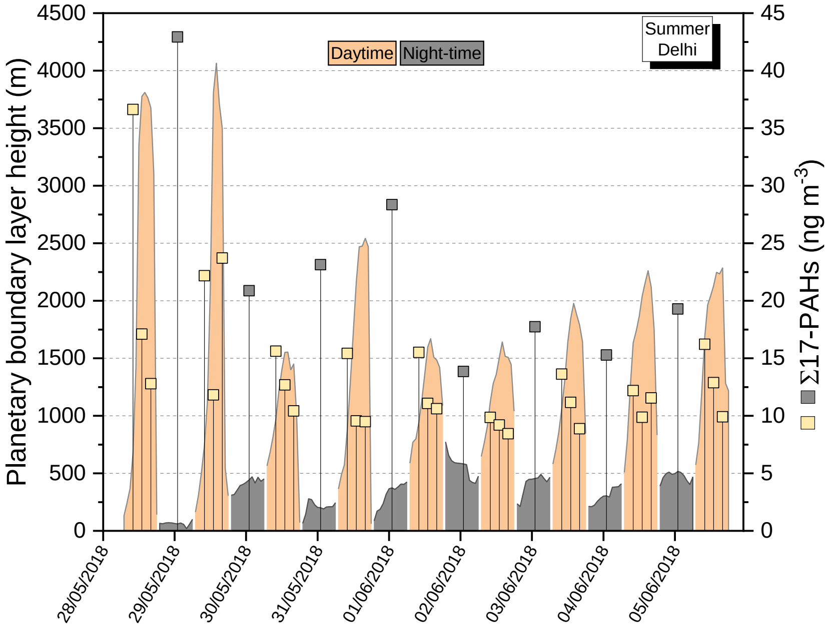

**Figure 4** Planetary boundary layer height in summer Delhi 2018 (Lat 28.625, Lon 77.25; source: ECMWF ERA5 in 0.25°, 1-hour time resolution). Square symbols represent the temporal variation of total PAHs in daytime and night-time.

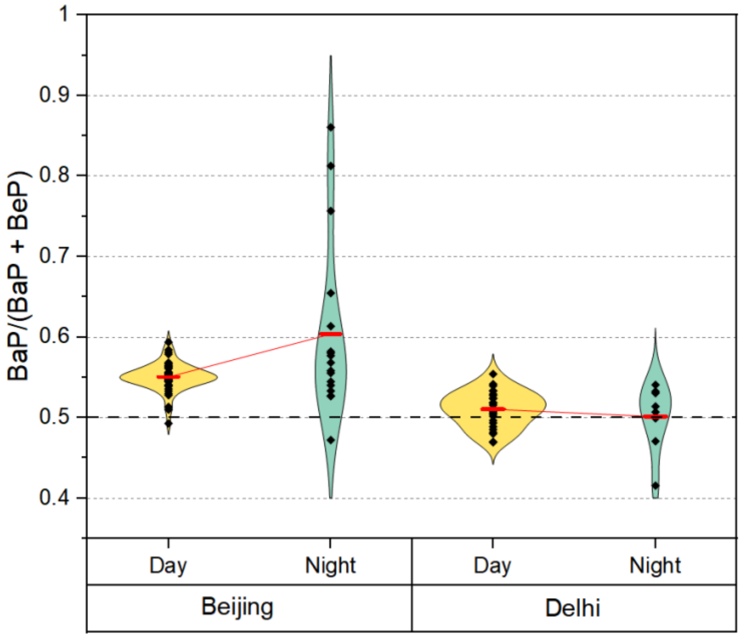

**Figure 5.** Ratio of BaP/(BaP + BeP) in $PM_{2.5}$ samples during the daytime (every 3 h) and night-time (15 h). Violin plots represent the data distribution between day and night and the wider sections represent the higher density of data smoothed by a kernel density estimator. Red rectangle symbols represent the mean concentration, and the red line connect the mean values between day and night.

**Table 1.** Minimum, maximum and mean concentrations of individual PAHs in $PM_{2.5}$. Compounds in 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 Daytime / Night-time | Mean ± SD* Daytime / Night-time | Variation Daytime / Night-time | Mean ± SD* 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 | | |

* SD: Standard Deviation

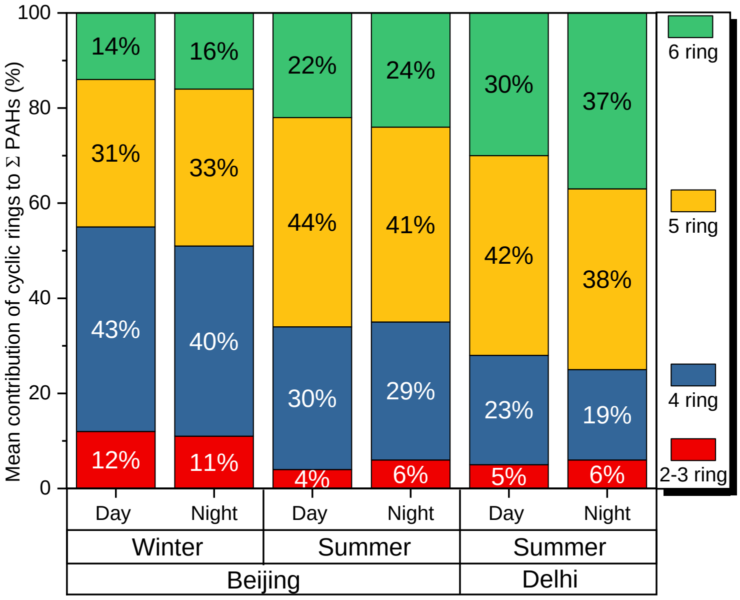

**Figure 6.** Distribution of PAHs compounds by number of cyclic rings in $PM_{2.5}$ samples collected during the daytime (every 3 h) and night-time (15 h) for summer Beijing 2017 and Delhi 2018 (this study) and winter Beijing 2016 (Elzein et al., 2019).