

Variability of polycyclic aromatic hydrocarbons and their oxidative derivatives in wintertime Beijing, China.

Atallah. El zein¹, Rachel E. Dunmore¹, Martyn W. Ward¹, Jacqueline F. Hamilton¹, Alastair C. Lewis²

¹Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, YO10 5DD, United Kingdom

²National Centre for Atmospheric Science, University of York, York, YO10 5DD, United Kingdom

Correspondence to: Atallah. El zein (atallah.elzein@york.ac.uk); Alastair C. Lewis (ally.lewis@ncas.ac.uk)

Abstract. Ambient particulate matter (PM) can contain a mix of different toxic species derived from a wide variety of sources. This study quantifies the diurnal variation and nocturnal abundance of 16 Polycyclic Aromatic Hydrocarbons (PAHs), 10 Oxygenated PAHs (OPAHs) and 9 Nitrated PAHs (NPAHs) in ambient PM in central Beijing during winter. Target compounds were identified and quantified using Gas Chromatography – time of flight mass spectrometry (GC-Q-TOF-MS). The total concentration of PAHs varied between 18 and 297 ng m⁻³ over 3 h daytime filter samples and from 23 to 165 ng m⁻³ in 15 h night-time samples. The total concentrations of PAHs over 24 h varied between 37 and 180 ng m⁻³ (mean: 97 ± 43 ng m⁻³). The total daytime concentrations during high particulate loading conditions for PAHs, OPAHs and NPAHs were 224, 54, and 2.3 ng m⁻³, respectively. [The most abundant PAHs were fluoranthene (33 ng m⁻³), chrysene (27 ng m⁻³), pyrene (27 ng m⁻³), benzo[a]pyrene (27 ng m⁻³), benzo[b]fluoranthene (25 ng m⁻³), benzo[a]anthracene (20 ng m⁻³) and phenanthrene (18 ng m⁻³). The most abundant OPAHs were 9,10-Anthraquinone (18 ng m⁻³), 1,8 Naphthalic anhydride (14 ng m⁻³) and 9-Fluorenone (12 ng m⁻³) and the three most abundant NPAHs were 9-Nitroanthracene (0.84 ng m⁻³), 3-Nitrofluoranthene (0.78 ng m⁻³) and 3-Nitrodibenzofuran (0.45 ng m⁻³).] Σ PAHs and Σ OPAHs showed a strong positive correlation with the gas phase abundance of NO, CO, SO₂, and HONO indicating that PAHs and OPAHs can be associated with both local and regional emissions. Diagnostic ratios suggested emissions from traffic road and coal combustion were the predominant sources for PAHs in Beijing, and also revealed the main source of NPAHs to be secondary photochemical formation rather than primary emissions. PM_{2.5} and NPAHs showed a strong correlation with gas phase HONO. 9-Nitroanthracene appeared to undergo a photo-degradation during the daytime and showed a strong positive correlation with ambient HONO (R=0.90, P<0.001). The lifetime excess lung cancer risk for those species that have available toxicological data (16 PAHs, 1 OPAH and 6 NPAHs) was calculated to be in the range 10⁻⁵ to 10⁻³ (risk per million people range from 26 to 2053).

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1 Introduction

Outdoor air pollution contains a complex set of toxicological hazards and has become the largest detrimental environmental effect on human health (WHO/IARC., 2016). Exposure to outdoor high particulate loading of PM_{2.5} (aerodynamic diameter less than 2.5 μm) is linked to harmful health effects, particularly affecting urban populations (Raaschou et al., 2013; Hamra et al., 2014). The major sources of PM_{2.5} in urban areas are

37 incomplete combustion or gas-to-particle conversion, and they contain a varied mix of chemicals including
38 inorganic ions, organic carbon and elemental carbon (Bond et al., 2004; Saikawa et al., 2009). Polycyclic
39 Aromatic Hydrocarbons (PAHs) and their oxidative derivatives (Nitrated PAHs and Oxygenated PAHs) are one
40 class of species with high toxic potency (Zhang et al., 2009; Jia et al., 2011; Wang et al., 2011a). PAHs released
41 in the atmosphere come from both natural and anthropogenic sources; anthropogenic emissions include
42 incomplete combustion of fossil fuels, agricultural burning, industrial and agricultural activities and are
43 considered predominant (Ravindra et al., 2008; Zhang et al., 2009; Poulain et al., 2011; Kim et al., 2013; Abbas
44 et al., 2018); natural contributions such as volcanic eruptions and forest fires are reported to be a less significant
45 contributor to total emissions (Xu et al., 2006; Abbas et al., 2018).

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46 Vapour phase PAHs can undergo gas phase reactions with oxidants in the atmosphere (including hydroxyl,
47 ozone and nitrate radicals) leading to the generation of a range of nitrated-PAHs and oxygenated-PAHs
48 (Atkinson et al., 1990; Atkinson and Arey., 1994; Sasaki, 1997). Atmospheric reaction with chlorine atoms in
49 the presence of oxygen has also been suggested as a new formation pathway of OPAHs (Riva et al., 2015).
50 OPAHs and NPAHs are often more toxic than the parent PAHs, showing a direct-acting mutagenicity on human
51 cells (Durant et al., 1996; Hannigan et al., 1998; Purohit and Basu, 2000; Wang et al., 2011a; Benbrahim et al.,
52 2012). Beside their formation in the gas phase, OPAHs and NPAHs can also be produced by heterogeneous
53 reactions (Ringuet et al., 2012a; Jariyasopit et al., 2014; Zimmermann et al., 2013; Wenyuan et al., 2014; Keyte
54 et al., 2013). Many of these derivatives can also be linked to primary emissions from motor vehicles and
55 combustion processes (Rogge et al., 1993; Albinet et al., 2007a; Jakober et al., 2007; Shen et al., 2012; Nalin et
56 al., 2016).

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57 Many studies in different countries have focused on studying toxic organic pollutants in PM_{2.5} because they fall
58 within the respirable size range for humans (Sharma et al., 2007; Ringuet et al., 2012b, Farren et al., 2015). In
59 the last decade, a major focus has been given to Chinese cities such as Shanghai, Beijing, Guangzhou, Tianjin,
60 and Shenzhen because of their population growth and geographic peripheral expansion in manufacturing
61 capacity and energy industries which are located throughout each of the city's manufacturing zones.

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62 This has made China the world leader in energy consumption, but also the world's highest emitter of PM_{2.5} and
63 PAHs (Lin et al., 2018; Zhang et al., 2009; Xu et al., 2006). The majority of previous studies have reported PAH
64 concentrations in 24 h averaged samples during short-term and long-term measurements campaigns (Tomaz et
65 al., 2016; Alves et al., 2017; Niu et al., 2017; Benjamin et al., 2014; Wang et al., 2011a). However, a long
66 averaging period creates some limitations such as sampling artefacts, notably where changing atmospheric
67 photolysis conditions (air humidity, temperature, wind direction, ozone or other oxidant concentrations) may
68 have a significant influence on PAHs concentrations and oxidation rates (Albinet et al., 2007b; Albinet et al.,
69 2009, Goriaux et al., 2006, Tsapakis and Stephanou., 2003; Tsapakis and Stephanou., 2007, Ringuet et al.,
70 2012b). More intensive and higher frequency measurements in field campaigns have been suggested as a means
71 to improve the positive matrix factorization model performance (Tian et al., 2017, Srivastava et al., 2018). A
72 few studies have used twice daily (12 h) sampling (Albinet et al., 2008; Zhang et al., 2018; Farren et al., 2015;
73 Ringuet et al., 2012b), obtaining limited information on variability in concentrations during the daytime and
74 night-time (Tsapakis and Stephanou., 2007). Shorter time periods for sampling (3 h and 4 h) are still very
75 limited (Reisen and Arey., 2004; Srivastava et al., 2018). Considering the above, this paper determines the

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76 temporal diurnal and nocturnal variation of the PM_{2.5}-bound concentrations of PAHs, OPAHs and NPAHs from
77 the air of Beijing in China, it shows the role of photochemistry in the formation of OPAHs and NPAHs and
78 associate the fate and evolution of PAHs, OPAHs and NPAHs with the gas phase concentrations of other
79 pollutants (O₃, CO, NO, NO₂, SO₂, HONO), the cancer risk associated with inhalation of PM_{2.5} was calculated.
80 This paper explores the feasibility of higher frequency sampling in Beijing, to support the identification of
81 emissions sources from diagnostic ratios and correlations with atmospheric gas pollutants. These measurements
82 also raise the potential importance of the chemical relationship between NPAHs and HONO which may impact
83 the HONO budget in the atmosphere and, if included, improve related models. This study comes after three
84 years of declaring the anti-pollution action plan and strategy taken by the municipal government of Beijing and
85 published in September 2013 (Ministry of Ecology and Environment The People's Republic of China, Beijing
86 toughens pollution rules for cleaner air, 2013), trying to increase the number of days with good air quality index
87 by prohibiting coal combustion, promoting clean energy vehicles and public transport and helping industrial
88 transformation and upgrading to new technologies.

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90 2 Experimental Steps

91 2.1 Sampling site and method

92 The sampling setup shown in Fig. S1 was located at the Institute of Atmospheric Physics, Chinese Academy of
93 Sciences in Beijing (39°58'28" N, 116°22'15" E) as part of the Air Pollution and Human Health (APHH)
94 research programme. PM_{2.5} filter samples were collected on the roof of a 2-storey building about 8m above
95 ground level using a High-Volume Air Sampler (Ecotech HiVol 3000, Victoria, Australia) operating at 1.33 m³
96 min⁻¹. Daytime particles were collected every three-hours during high PM concentration levels, nine-hours at
97 low PM levels and over 15 h at night-time during 18 continuous days (22 November 2016 to 9 December 2016).
98 Fifty-seven samples in total were collected. The daytime sampling started at 8:30 in the morning and the filter
99 was changed every 3 h. During low particulate loading conditions, the daytime sampling started at 8:30 in the
100 morning for a sampling duration of 9 h. Night-time sampling began at ~17:30 and ended at 08:30 the following
101 day. Prior to sampling, the quartz filters (20.3 × 25.4 cm) (supplied by Whatman (Maidstone, U.K.)) were baked
102 at 550 °C for 5 h in order to eliminate any organic matter. After sampling, filters were wrapped in aluminium
103 foil, sealed in polyethylene bags and stored at -20 °C until extraction and analysis.

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105 2.2 Extraction method and clean up

106 All collected samples were extracted using an Accelerated Solvent Extractor automated system (Dionex, ASE
107 350). Prior to extraction, 1/16th (surface area equivalent to 25.7 cm²) of each filter was cut using a hole puncher
108 (Ø=27 mm) and for each batch of 6 samples, one sample was spiked with a mixture of two deuterated-PAHs
109 (Phenanthrene-D10; Pyrene-D10), two deuterated-OPAHs (9-Fluorenone-D8; 9,10-Anthraquinone-D8), and two
110 deuterated-NPAHs (1-Nitronaphthalene-D7; 3-Nitrofluoranthene-D9), as surrogate standards for PAHs, OPAHs
111 and NPAHs, respectively, with concentration on filters corresponding to 400 ng (40 µl, 10 ng µl⁻¹ in

112 Acetonitrile). All punched samples were cut to small pieces and packed into 5 mL stainless steel extraction cells.
113 Extractions were carried out in acetonitrile as follows: Oven at 120°C, pressure at 1500 psi, rinse volume 60%
114 and 60 s purge time for three consecutive 5 min cycles. Extracts (V=20ml) were evaporated to approximately 6
115 mL under a gentle stream of nitrogen before the clean-up step. All samples and blanks were purified on a SPE
116 silica normal phase cartridge (1g/6ml; Sigma Aldrich) **to reduce the impacts of interfering compounds in the**
117 **matrix and to help maintain a clean** GC injection inlet liner. After the clean-up step, the solution of each sample
118 was evaporated to 1 mL under a gentle stream of nitrogen at room temperature (20°C) and transferred to 1.5 mL
119 autosampler amber vial. Each concentrated sample was stored at 4°C until analysis. **The average recovery**
120 **efficiencies calculated from surrogate standards ranged from 85% to 96% (Phenanthrene-d10: 95 ± 9 %; Pyrene-**
121 **d10: 101 ± 7 %; 9-Fluorenone-d8: 98 ± 13 %; 9,10-Anthraquinone-d8: 102 ± 11 %; 1-Nitronaphthalene-d7: 93**
122 **± 8 %; 3-Nitrofluoranthene-d9: 101 ± 11 %)** and the target compounds concentrations were calculated
123 incorporating measured recovery efficiencies.

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124 2.3 Chemical standards

125 The chemical compounds that have attracted the most attention in previous studies are the 16 priority PAHs and
126 their derivatives, defined by the United States Environment Protection Agency (EPA). The choice of the organic
127 compounds investigated in this study is based on those associated with the particle phase and commercially
128 available standards. All compounds are listed in Table 1 and were purchased from Sigma Aldrich, Alfa Aesar
129 and Santa Cruz Biotechnology in the UK and had a minimum purity of 98%. In parallel to individual standards,
130 a mixed solution of the 16 EPA PAHs (CRM47940, Supelco, Sigma Aldrich) of 10 µg ml⁻¹ in acetonitrile was
131 also used. Standard solutions for calibrations were prepared in acetonitrile (HPLC grade, 99.9% purity, Sigma
132 Aldrich). Deuterated compounds were supplied by C/D/N isotopes and distributed by QMX Laboratories Ltd
133 (Essex, UK).

134 2.4 GC/MS Analysis

135 Target compounds were quantified using a GC - accurate mass Quadrupole Time-of-Flight GC/MS system (GC
136 Agilent 7890B coupled to an Agilent 7200 Q-TOF-MS). Parent PAHs were separated in a 35 min analysis time
137 using a capillary HP-5MS Ultra Inert GC column (Agilent; 5%-Phenyl substituted methylpolysiloxane; length:
138 30 m, diameter: 0.25 mm, film thickness: 0.25 µm). Inlet injections of 1 µL were performed in pulsed splitless
139 mode at 320 °C using an automated liquid injection with the GERSTEL MultiPurpose Sampler (MPS). Helium
140 was used as a carrier gas at 1.4 mL min⁻¹. The GC oven temperature was programmed to 65 °C for 4 min as a
141 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
142 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
143 further 6 min to ensure all analytes eluted from the column. The MS was operated in Electron Ionisation (EI)
144 mode at 70 eV with an emission current of 35 µA. Calibration solutions were injected 3 times in the same
145 sequence for samples and covered the range from 1pg µL⁻¹ to 1000 pg µL⁻¹.

146 **The method development for OPAHs and NPAHs was based on previous studies (Albinet et al., 2006; Albinet**
147 **et al., 2014; Bezabeh et al., 2003; Kawanaka et al., 2007)** using Negative Chemical Ionisation (NCI) performed
148 at 155 eV and 48 µA, with methane (CH₄, research grade 5.5, Air Liquide) as reagent gas. Target compounds

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149 were eluted using the RXi-5ms (Restek GC column) with similar phase and characteristics to HP-5ms. Analysis
150 was performed in 29.2 min and the GC settings were as follows: 1 μL of each sample was injected in pulsed
151 splitless mode at 310 $^{\circ}\text{C}$, Helium flow was set to 1.2 mL min^{-1} , the initial oven temperature of 70 $^{\circ}\text{C}$ was held
152 for 4 min, followed by a heating rate of 60 $^{\circ}\text{C min}^{-1}$ until 190 $^{\circ}\text{C}$ and then raised to 270 $^{\circ}\text{C}$ at rate of 25 $^{\circ}\text{C min}^{-1}$
153 and ended with 5 $^{\circ}\text{C min}^{-1}$ until 320 $^{\circ}\text{C}$, held for 10 min. A 10-point calibration curve within the range 0.5 pg
154 μL^{-1} to 1000 $\text{pg } \mu\text{L}^{-1}$, was obtained with the correlation coefficients from the linear regression from 0.980 to
155 0.999.

156

157 2.5 Data analysis and error evaluation

158 Data acquisition were recorded and processed using the Agilent Qualitative and Quantitative analysis software.
159 Target compounds were isolated using Extracted-Ion Chromatograms (EIC) and identified by the combination
160 of retention time and mass spectral match against the calibration standards measured simultaneously within the
161 samples. The limit of detection (LOD) was defined as the valid lowest measurable peak response to peak noise
162 near the elution time of the target peak ($S/N = 3$) in a mix of standards solutions. As the chemical noise
163 increases during the analysis of real samples the Limit of Quantification (LOQ) was defined $S/N=10$. These
164 recommendations are in accordance with previous analytical studies (Nyiri et al., 2016; Ramírez et al., 2015).
165 LOD values were evaluated from standards solutions and ranged between 1 pg and 20 pg for PAHs, 0.01 pg and
166 0.2 pg (except 1-naphthaldehyde 0.5 pg) for OPAHs and 0.02 pg to 0.25 pg for NPAHs.

167 To determine any sources of contamination during sample preparation and the analytical procedure, the solvent
168 (acetonitrile) and field blanks ($n=2$) were analysed following the same procedure as for the samples (Extraction,
169 SPE, Evaporation). Most target compounds were found to be below LOD ($S/N=3$) or orders of magnitude (up to
170 $10^3 - 10^4$) lower than was found in the samples. A small number of compounds found in field blanks (1,8-
171 Naphthalic anhydride, Benzo[a]fluorenone, 1-Nitronaphthalene, 9-Nitroanthracene) have a higher contribution
172 (4-30 %) to very few filters (2 to 5 samples) collected over a 3 h time period, if this was co-incident with low
173 particulate loading conditions. The contribution to each compound from field blanks has been corrected in the
174 final data.

175 We evaluated the precision of the method by calculating the relative standard deviations (%RSD) from replicate
176 analysis as shown in Table 1. For PAHs, the precision of sample replicates ($n=10$) during inter-day and intra-
177 day varied from 1.8% to 8.9% (mean 5.2%) and 1.2% to 8.7% (mean 3.4%), respectively. The %RSD average
178 for deuterium labelled compounds was about 3.6%. For OPAHs and NPAHs, two different concentrations of
179 standards were analysed (50 pg ; $n=6$ and 400 pg ; $n=6$); inter-day precision of 10 OPAHs gives an average
180 %RSD of 6.8% (range: 5.4 - 8.9%) and intra-day precision of 5.6% (3.2 - 7.8%). Similar to OPAHs,
181 repeatability and reproducibility between days for NPAHs varied from 3.9% to 8.4% (mean 5.5%) and 3.2% to
182 9.7% (mean 5.2%), respectively. Hence, the estimated random error quantified by the standard deviation of the
183 measurements did not exceed 7% on average. The systematic error may be due to the influence of the sample
184 matrix during the analysis sequence on the quantification step and the calibration offset. It was estimated to be a
185 maximum 10% from the measured recovery of the deuterium species (Garrido-Frenich et al., 2006). Therefore,
186 the overall estimated error, combining the precision and the systematic effects, is less than 20%.

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187 Another source of error can be attributed to sampling artefacts and this has been discussed in previous studies
188 (Schauer, C. et al., 2003, Goriaux, M. et al., 2006, Tsapakis and Stephanou, 2003). The absence of an ozone
189 denuder to trap the gas phase oxidants may lead to an underestimation of the true values of PAHs due to
190 chemical decomposition. Therefore, data from long sampling times and under high ozone ambient
191 concentrations may be biased by sampling artefacts by more than 100 % (Schauer et al., 2003, Goriaux et al.,
192 2006). However, at low ozone levels, negative artefacts were considered not significant (Tsapakis and
193 Stephanou 2003), whilst, at medium ozone levels (30-50 ppb) PAHs values were underestimated by 30 %
194 (Schauer et al., 2003). In addition, heterogeneous reactions during particle sampling may occur only on the
195 monolayer surface coverage with limited diffusion of oxidants to the bulk particles (Keyte et al., 2013 and
196 references therein). Previous studies reported that the formation of NPAHs during high-volume sampling is not
197 significant and calculated to be < 3 % (Arey et al., 1988) and < 0.1 % (Dimashki et al., 2000).
198 Considering the role of ozone (always below 30 ppb in this study, with a mean value: 10.4 ± 8.8 ppb), in
199 addition to sampling time and temperature, the estimation of the negative sampling artefacts on our data range
200 between 10 and 20 %, with the highest error estimation attributable to longest sampling time (15h).

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201 3 Results and discussion

202 3.1 Temporal variations of PAHs, OPAHs and NPAHs in PM_{2.5}

203 The volume of literature on PM_{2.5} has rapidly increased over the last two decades and various disciplines have
204 contributed to improve understanding about source emissions, chemical composition, and impact on people's
205 behaviour and health. In China, the official air quality guidelines for PM_{2.5} expressed as annual mean and 24 h
206 average are $35 \mu\text{g m}^{-3}$ and $75 \mu\text{g m}^{-3}$, respectively (WHO 2016; Ministry of Ecology and Environment The
207 People's Republic of China, 2012). During the sampling period of this study (Nov - Dec 2016), PM_{2.5} was
208 measured every hour and ranged from 3.8 to $438 \mu\text{g m}^{-3}$, with an average concentration of $103 \mu\text{g m}^{-3}$. The
209 average 24 h PM_{2.5} concentration was $108 \pm 82 \mu\text{g m}^{-3}$ (range: 10 - $283 \mu\text{g m}^{-3}$), exceeding the 24 h limit value
210 on 10 of the 18 sampling days. Concurrent PM_{2.5} concentrations were averaged to the filter sampling times (3 h,
211 9 h, 15 h) and are shown in Fig.6 and Fig. S3. The daily (24 h) concentration of Benzo[a]pyrene ranged from
212 4.46 to 29.8 ng m^{-3} (average $15 \pm 8.9 \text{ ng m}^{-3}$), exceeding the 24 h average limit value of 2.5 ng m^{-3} for China
213 (Ministry of Ecology and Environment The People's Republic of China, 2012) on all of the 18 days of sampling
214 period.

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215 Fig. 1 shows the measured concentrations of PAHs in the 3 h daytime samples ranging from 18 to 297 ng m^{-3}
216 (average $87.3 \pm 58 \text{ ng m}^{-3}$) and from 23 to 165 ng m^{-3} (average $107 \pm 51 \text{ ng m}^{-3}$) in the 15 h night-time samples.
217 The 24 h total concentrations (combined results from daytime and night-time samples) of the 16 PAHs varied
218 between 37 and 180 ng m^{-3} (average $97 \pm 43 \text{ ng m}^{-3}$). PAHs derivatives showed the following trends: total
219 OPAHs concentrations varied from 3.3 to 55 ng m^{-3} (average: $26 \pm 16 \text{ ng m}^{-3}$) in daytime and from 8.9 to 95 ng m^{-3}
220 (average: $41.6 \pm 26 \text{ ng m}^{-3}$) at night-time; OPAHs were approximately 25 and 14 times higher than average
221 NPAHs in the daytime (average: $1.03 \pm 0.74 \text{ ng m}^{-3}$, range: 0.13-2.3) and night-time (average: $3.06 \pm 1.8 \text{ ng m}^{-3}$,
222 range: 0.57-6.43), respectively.

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L.171 and L.174

223 PHE (See Table 1 for abbreviations), FLT, PYR, BaA, CHR, BbF and BaP were the largest contributors to the
224 total PAH concentration. 9-FLON, 9,10-ANQ and 1,8-NANY were the three major O-PAHs species. The most
225 abundant NPAHs were 3-NDBF, 9-NANT and 3-NFLT. The temporal profile and contributions of each
226 compound to the total concentration are shown in Fig. 2 and detailed in Table 2. The highest concentrations
227 recorded in this study were in the day of 29 Nov 2016; concentrations of all target compounds in the particulate
228 phase are displayed in Fig. S2. Some nitro-compounds (5-NAC, 1-NPYR, 6-NCHR, 6-NBaP) were below LOQ
229 in a few samples while one oxy-compound (1,8-Naphthalic anhydride) was outside the dynamic range and limit
230 of linearity of the calibration curve for samples with high mass loading (Table 2). Similar dominant compounds
231 were found in different urban cities (Xi'an, Jinan, Beijing) of China (Bandowe et al. 2014, Zhang et al. 2018,
232 Wang et al., 2011c). The average 24 h total PAH concentrations (97 ng m^{-3}) in this study was higher than the
233 average value reported for Guangzhou city in the south of China (average 45.5 ng m^{-3} , from Liu et al., 2015),
234 however, it was lower than average values reported for Xi'an city in winter (range 14-701 ng m^{-3} ; average 206
235 ng m^{-3} from Wang et al., 2006) and in the suburb of Beijing in winter (average 277 ng m^{-3} , from Feng et al.,
236 2005). Our average value (97 ng m^{-3}) was comparable to the reported values in a recent study (Feng et al., 2019)
237 at the campus of Peking University health science centre, a short distance from our sampling site (~1 mile),
238 where the authors reported a total PAHs average concentration in winter Beijing (2014 - 2015) of $88.6 \pm 75 \text{ ng}$
239 m^{-3} . The lower average concentration of total PAHs reported in this study and Feng et al., (2019) can potentially
240 be attributed to the efforts from municipal government to improve air quality and control emissions by reducing
241 combustion sources in the intervening years. The urban location in this study (Fig. S1) was surrounded by busy
242 roads, residential buildings, an underground railway, restaurants and further afield thermal power stations. PAHs
243 concentrations are anticipated to decline closer to the mountains in the North and West of Beijing due to air
244 mass trajectory, aging and distance from emission sources. Results from this study can be considered
245 representative (within the margin of error) of the urban area in Beijing including districts such as Chaoyang,
246 Haidian, Fengtai, Xicheng, Dongcheng, Shijingshan covering an approximate population of 12 million. Future
247 studies in less populated districts and different areas of the metropolitan of Beijing would be helpful for
248 comparison of population exposures.

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249 Concentrations of PAHs in PM_{10} (range: 3.2 - 222.7 ng m^{-3}) in Beijing were found in previous studies to be
250 lower than in $\text{PM}_{2.5}$ (Wang et al., 2011c). The concentration of PAHs in this study were much lower than
251 reported in certain other megacities, for example, Delhi, India in winter season 2003 (range: 948-1345 ng m^{-3} ;
252 mean: $1157 \pm 113 \text{ ng m}^{-3}$ from Sharma et al., 2007) and Mexico City, Mexico in October 2002 (range: 60-910
253 ng m^{-3} ; mean: 310 ng m^{-3} from Marr et al., 2004). Average concentrations for total PAH in the first 3 h filter of
254 the day (8:30-11:30 am; Monday to Friday; mean: 112 ng m^{-3}) were 1.5 times higher than the rest of the day,
255 and 1.6 times higher than the same first 3 h on a Sunday. A potential reason of the elevated concentrations in the
256 morning hours is due to the rush hour traffic during working days, coupled to a period of shallow boundary
257 layer.

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259 The mean total concentrations in Table 2 for the 3 h integration samples of OPAHs and NPAHs were 28.7 ± 21
260 ng m^{-3} (range: 1.8 - 87.9 ng m^{-3}) and $1.17 \pm 1 \text{ ng m}^{-3}$ (range: 0.15 - 3.92 ng m^{-3}). Average night-time was 41.6 ng
261 m^{-3} (OPAHS) and 3.06 ng m^{-3} (NPAHS), concentrations which were 2.6 and 35 times lower than the average
262 total PAH in the night samples. The ratios of mean concentrations of PAH divided by concentration of OPAH

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263 and NPAH for the 3 h samples were 3 and 74. Ratios of combined daytime and night-time samples (24 h) were
264 on average 2.9 (range 1.9 - 4.6) for $\Sigma\text{PAHs}/\Sigma\text{OPAHs}$ and 47.4 (range 25 - 79) for $\Sigma\text{PAHs}/\Sigma\text{NPAHs}$. Lower
265 ratios were reported from a winter study in Xi'an – China, where $\Sigma\text{PAHs}/\Sigma\text{OPAHs}$ ranged from 1.75 to 1.86
266 and $\Sigma\text{PAHs}/\Sigma\text{NPAHs}$ ranged from 34 to 55.2. On the other hand, similar trends to our study were recorded for
267 $\Sigma\text{PAHs}/\Sigma\text{OPAHs}$ in Europe such as Athens in Greece in winter (ratio 28.9/6.9 = 4.2) (Andreou and
268 Rapsomanikis., 2009) and Augsburg in Germany in winter (ratio 11/3.2 = 3.4) (Pietrogrande et al., 2011).
269 Further monitoring studies are needed to confirm trends of NPAHs in China.

270

271 3.2 Diagnostic ratios to identify emission sources

272 The concentration ratios between different PAHs are widely used to assess and identify pollution emission
273 sources (Tobiszewski and Namieśnik., 2012 and references therein). The ratios of FLT/(FLT + PYR) and
274 IcdP/(IcdP + BghiP) isomer pairs are commonly used to distinguish between emission sources such as
275 coal/biomass burning or the incomplete combustion of petroleum. Values of FLT/(FLT + PYR) and IcdP/(IcdP
276 + BghiP) higher than 0.5 indicate dominance of a coal/biomass burning source. Values of FLT/(FLT + PYR)
277 between 0.4 and 0.5 and IcdP/(IcdP + BghiP) between 0.2 and 0.5 suggest a higher influence from fossil fuel
278 combustion. **Values of FLT/(FLT + PYR) less than 0.4 and IcdP/(IcdP + BghiP) less than 0.2,** are mostly related
279 to incomplete combustion (petrogenic origin) (Yunker et al., 2002; Pio et al., 2001). The measured ratios in this
280 study are shown in Fig. 3 and ranged from 0.53 to 0.67 (mean 0.56) during the day (3 h and 9 h samples), while
281 at night (15 h samples) varied between 0.51 and 0.54 (mean 0.52) indicating primary emissions from coal and
282 biomass burning. Lower values were observed for IcdP/(IcdP + BghiP); daytime ratios were between 0.39 and
283 0.5 (3 h and 9 h samples) indicated the dominance of petroleum combustion. At night, the ratio in most samples
284 was slightly higher than 0.5, with some values below, suggesting mixed sources with likely higher contributions
285 coming from residential heating using coal and wood at night.

286 **As shown in Fig. 4,** other ratios can be useful to confirm the contribution from local traffic and to discriminate
287 vehicle emissions such as BaP/BghiP, FLU/FLU+PYR and BaP/BaP+CHR (Tobiszewski and Namieśnik., 2012
288 and references therein). The BaP/BghiP ratios were significantly higher than 0.6 indicating a major influence
289 from road traffic, while FLU/FLU+PYR ratios suggested a predominant petrol contribution (ratio < 0.5) instead
290 of diesel engines (ratio > 0.5). Results shown in Fig. 4 identify traffic emissions and in particular petrol engines
291 as the major emitter of PAHs. In PM_{2.5}, the 5- and 6-rings PAHs species (BaP, IcdP, BghiP) were previously
292 attributed to petrol engines, while lower molecular weight with 3-rings (ACY, AC, FLU, PHE, ANT) and 4-
293 rings (FLT, PYR, BaA, CHR) were closely related to diesel vehicle emissions (Chiang et al., 2012; Wu et al.,
294 2014 and references therein). Previous studies in Beijing and Guangzhou in China suggested similar
295 contributions from coal and petroleum combustion, focusing on vehicular traffic (petrol and diesel) as potential
296 sources for PAHs (Gao and Ji., 2018; Liu et al., 2015; Wu et al., 2014, Niu et al., 2017).

297 NPAHs can be used to track the photochemistry of PAHs with OH and NO₃ radicals, both of which can generate
298 secondary photochemical products of NPAHs and OPAHs from primary PAH emissions (Zhang et al., 2018;
299 Ringuet et al., 2012b; Wang et al., 2011a). 1-NPYR originates mainly from primary emissions and in particular
300 from diesel vehicles (**Keyte et al., 2016, Schulte et al., 2015**), whilst 2-NFLT has been reported to be absent in

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301 direct combustion emissions, instead produced from the gas-phase reactions of FLT with OH radicals in
302 presence of NO_x during the day or NO₃ radicals at night. 2-NPYR comes solely from the reaction of PYR with
303 OH radicals (Ramdahl et al., 1986; Arey et al., 1986; Atkinson et al., 1987; Ciccioli et al., 1996). Accordingly,
304 the ratio 2-NFLT/1-NPYR has been widely used as diagnostic, with a value greater than 5 indicating a major
305 contribution from photochemical processes, whilst a ratio value less than 5 means an important contribution
306 from direct emissions (Albinet et al., 2008; Wang et al., 2011a; Ringuet et al., 2012b; Bandowe et al., 2014;
307 Tomaz et al., 2017; Zhang et al., 2018).

308 In this study, the 2-NFLT was not quantified because the standard compound was not commercially available,
309 subsequently, we have used 3-NFLT isomer as a substitution of 2-NFLT. PAH isomer pairs (Table 1) in
310 standard mixtures showed similar sensitivities for each concentration used, therefore, we assume an equal
311 sensitivity for 2-NFLT and 3-NFLT during analysis. A previous study reported that the concentration of 3-
312 NFLT compared to 2-NFLT is relatively very low in ambient air (Bamford et al., 2003); in addition, the
313 separation of both isomers (2- and 3-NFLT) using the most common GC-MS column for PAHs separation, HP-
314 5ms and DB-5ms, was not possible (Zhang et al., 2018; Bandowe et al., 2014; Ringuet et al., 2012b; Albinet
315 et al., 2008). Hence, we assume that the sum of 2- and 3-NFLT is closely representative of the original ratio 2-
316 NFLT/1-NPYR. Therefore, we adopted the ratio 2+3NFLT/1-NPYR, which varied between 4 and 19 during the
317 daytime (mean: 12) and from 3.6 to 30.4 in the night-time (mean: 8.8) (Fig. S3). Most daytime values exceeded
318 significantly the benchmark ratio of 5, while at night-time the average value was lower. These results indicate
319 the predominance of OH-radicals-initiated reactions controlling the formation of 2-NFLT in presence of NO₂
320 and sunlight.

321 3.3 Correlation with gaseous pollutants

322 O₃, CO, NO, NO₂, SO₂ and HONO were also measured at the same site location as the PM_{2.5} sampling. Inlets
323 were installed outside lab containers at approximately 3-4 m above ground (Fig. S1). Online measurements of
324 the gas phase species have been time-averaged to the filter sampling times. No correlations of significance were
325 seen between PAHs and meteorological parameters (Relative Humidity and Temperature) as shown in Table S1.

326 Σ PAHs and Σ OPAHs had a similar strong positive correlation (R= 0.82 to 0.98) in the 9 h and 15 h samples
327 with CO, NO, NO₂, SO₂ and HONO (Table S1). NO is known as an effective tracer for local traffic emissions, it
328 and behaves as a short-lived intermediate (Bange 2008, Janhäll et al., 2004). CO is mainly produced from
329 incomplete combustion and has a relatively long atmospheric lifetime (3 months on average) and undergoes
330 long-range transport (Peng et al., 2007 and references therein). The high correlations with primary pollutants
331 such as NO and CO during the daytime and night-time indicate that PAHs and OPAHs are primarily emitted
332 from local sources may also be associated with regional scale emissions. Significant correlations were observed
333 with SO₂, a pollutant mostly emitted from power plants outside the city (Lee et al., 2011). This strong
334 relationship with SO₂ could be explained by the contribution of anthropogenic sources such as the Beijing
335 Taiyanggong thermal power station (39°58'42"N 116°26'19"E), and is consistent with the domain air masses
336 arriving at the sites from the North East for much of the time (Fig. S4).

337 In contrast, most of the 3 h day samples showed only moderate correlations (R=0.38 to 0.74) except for HONO
338 where significant correlations (R=0.87 to 0.94) were observed with Σ PAHs, Σ OPAHs and Σ NPAHs (Fig. 5;

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339 Table S1). Furthermore, HONO was significantly correlated with PM_{2.5} during the daytime (Fig. 5) and some
340 significant chemical link between HONO emissions and ambient particles (PM_{2.5}) is implied. A similar
341 conclusion was drawn from recent study in Beijing (Zhang et al., 2019) which suggested a potential chemical
342 relationship between HONO and haze particles (PM_{2.5}) and proposed a high contribution from vehicle emissions
343 to the night-time HONO.

344 For NPAHs, as shown in Table S1, no significant correlation was found in 3 h and 15 h time sampling
345 resolution, except with HONO, where a significant difference between day and night were observed.
346 Surprisingly, the 9 h time resolution showed a strong correlation with CO, NO, NO₂ and SO₂, potentially
347 suggesting a direct emission of NPAHs. More likely these correlations arise because of a formation delay of
348 NPAHs that is smoothed out by the longer daytime sampling period. In a previous study, Zimmermann et al.,
349 (2013) reported the formation of NPAHs from the heterogeneous interaction of ambient particle bound-PAHs
350 with atmospheric oxidant. In line with the observed high values for the ratio 2+3NFLT/1-NPYR (section 3.2)
351 and the trace levels of NPAHs concentrations in the atmosphere; the secondary formation of NPAHs by gas
352 phase reactions followed by adsorption on particles and in parallel the heterogeneous formation on the surface
353 of particles is supported rather than primary emissions.

354 HONO plays a key role in tropospheric photochemistry, however its sources and their relative contributions to
355 ambient HONO are still unclear, especially in the daytime. To help understand the mechanism of HONO
356 formation in the atmosphere, each NPAHs compound has been correlated with HONO concentrations. The
357 available data in Table S2 shows diurnal and nocturnal differences for individual correlation of NPAHs with
358 HONO with the exception for 1-NPYR, which originates mainly from primary emissions and shows a strong
359 correlation during the day and night. 9-Nitroanthracene had distinctive behaviour, accumulating during the night
360 and appearing to undergo a photo-degradation during the daytime (Fig. 6). As shown in Table S2, 9-
361 Nitroanthracene showed a strong positive correlation with HONO (R=0.90, P<0.001) in the daytime while no
362 significant relationship was found at night-time (R=0.15, P>0.05). This suggests 9-nitroanthracene as a possible
363 source of HONO during the daytime via the OH radical-initiated reaction leading to OH (ortho) addition and
364 followed by intramolecular hydrogen transfer from the phenolic hydroxyl group to the nitro group.

365 There was a significant positive correlation between ANT and 9-NANT (R= 0.90, 3 h; R=0.94, 9 h; R=0.90, 15
366 h; P<0.001), which may be an indication that 9-NANT is closely related to ANT. In this respect, additional
367 simulation chamber measurements of the gas phase reaction of ANT with NO₃ radicals and for 9-
368 Nitroanthracene with OH radicals in presence of light and under different atmospheric parameters are required
369 for more precise assessment.

370

371 3.4 Exposure assessment

372 The toxicity equivalency factor (TEF) represents an estimate of the relative toxicity of a chemical compared to a
373 reference chemical. For PAHs, Benzo[a]pyrene was chosen as the reference chemical because it is known as the
374 most carcinogenic PAH (OEHHA., 1994, 2002) and is commonly used (Albinet et al., 2008; Tomaz et al., 2016;
375 Alves et al., 2017; Bandowe et al., 2014; Ramirez et al., 2011) as an indicator of carcinogenicity of total PAHs.

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376 The toxicity of the total PAHs expressed as BaP equivalents (BaP_{eq}) is calculated from the TEFs of each target
377 compound (Table S3) multiplied by its corresponding concentration Eq. (1):

$$378 \quad \sum [BaP]_{eq} = \sum_i^{n=1} (C_i \times TEF_i) \quad (1)$$

379 where C_i correspond to the concentration of individual target compound (PAHs, OPAHs and NPAHs) in ng m⁻³.

380

381 A widely applied procedure from the Office of Environmental Health Hazards Assessment (OEHHA) of the
382 California Environmental Protection Agency (CalEPA) and also the World Health Organisation (WHO) was
383 used here to evaluate and calculate the potential of contracting cancer from inhalation and exposure to PM_{2.5}-
384 bound PAHs; commonly known as the lifetime excess cancer risk (ECR) Eq. (2).

$$385 \quad ECR = \sum [BaP]_{eq} \times UR_{BaP} \quad (2)$$

386

387 where two values are mostly used for UR_[BaP] (1.1x10⁻⁶ (ng m⁻³)⁻¹ (OEHHA., 2002, 2005) and 8.7x10⁻⁵ (ng m⁻³)⁻¹
388 (WHO., 2000)); Eq. (2) describes the inhalation unit risk associated with high probability of contracting cancer
389 when exposed continuously to 1 ng m⁻³ of BaP_{eq} concentration over a lifetime of 70 years.

390 As shown in Table 3, the BaP_{eq} concentration includes the sum of 16 PAHs, 1 OPAH and 6 NPAHs, with the
391 cancer risk evaluated using different sampling times according to CalEPA and WHO guidelines. The risk values
392 may be underestimated due to lack of toxicity data for OPAHs and because our assessment excludes the gas
393 phase contributions i.e. are only based on the health risk evaluation of the particulate phase. The average 24 h
394 BaP_{eq} for the whole sampling period was 23.6 ± 12.4 ng m⁻³ (Table 3). As shown in Table 2, 6-NCHR has not
395 been quantified in all samples, its contribution to the total BaP_{eq} is relatively high (mean: 8%, range: 1 - 24%) in
396 comparison with the three major contributor from the PAH group: BaP (mean: 47.5%, range: 24 - 64%), DahA
397 (mean: 17.8%, range: 10 - 32%) and BbF (mean: 10.1%, range: 7 - 21%). In this study, the ECR attributable to
398 all polycyclic aromatic compounds (PACs) in urban air of Beijing ranged from 10⁻⁵ to 10⁻³ > 10⁻⁶ (Table 3)
399 suggesting an elevated potential cancer risk for adults (Chen and Liao., 2006; Bai et al., 2009).

400 It is worth noting that inhalation exposure is not the only risk related to PAHs and cancer in humans. Other
401 sources of exposure include dermal contact and ingestion of the re-suspended dusts in matrices such as road
402 dusts and soils all of which increase the risk value for urban residents (Wang, et al., 2011b; Wei et al., 2015). In
403 this study, the 24 h average estimated cancer risk (Table 3) from inhalation exposure to ambient PM_{2.5} based on
404 CalEPA and WHO guidelines were 2.6 x 10⁻⁵ and 2.05 x 10⁻³, respectively. Using the highest calculated ECR
405 (2.05 x 10⁻³) gives an estimate of 2027 additional cancer cases per million people exposed (29 cases/year) in
406 comparison to the estimate based on CalEPA of 26 persons (0.37 cases/year).

407 ECR trends were reported in previous studies from Beijing and other populated area (Bandowe et al., 2014;
408 Alves et al., 2017; Ramírez et al., 2011; Jia et al., 2011, Liu et al., 2015, Song et al., 2018, Feng et al., 2019). In
409 this study we considered the combination of all samples (n=54) to estimate the average 24 h cancer risk

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410 ($\sum[\text{BaP}]_{\text{eq}}=23.6 \pm 12 \text{ ng m}^{-3}$; range 8 – 44 ng m^{-3}) and compare it with previous studies. An average value of 17
411 ng m^{-3} (range 2-64 ng m^{-3}) was reported for Xi'an for the whole year between July 2008 and August 2009
412 (Bandowe et al., 2014). After considering the same winter period (November and December) as in our study, the
413 average values reported for Xi'an city (31-33 ng m^{-3}) were higher than our results. In contrast, our average value
414 was comparable to those reported in a recent study in Beijing, ranging from 21 to 38 ng m^{-3} in cold months
415 (Feng et al., 2019), whilst in the previous study of Chen et al. 2017, they reported an average of 31.4 ng m^{-3} for
416 outdoor air in Beijing in winter. Lower and more varied values have been also reported in Beijing in winter. Liu
417 et al. (2007) reported an average BaP_{eq} concentration of 13.0 ng m^{-3} and 27.3 ng m^{-3} at two sampling sites on
418 Peking University campus and 82.1 ng m^{-3} for samples collected from busy road street. It is clear that direct
419 comparison with Beijing air from other studies is limited due to the variable number of compounds considered
420 in each study and the differences in sampling sites and sampling periods. Other areas of uncertainty include TEF
421 reference values and the range of BaP UR which were extrapolated from animal bioassays with limited evidence
422 regarding the carcinogenicity to humans.

423 Seasonal variability is also crucial in estimating BaP_{eq} concentrations; it has been shown that BaP_{eq} values in
424 cold months are always higher than warm months due to the increase in coal combustion, central and residential
425 heating, lower photochemical transformation and lower volatilisation of gases favouring particle formation in
426 winter. Previous observations in Beijing recorded $\sum[\text{BaP}_{\text{eq}}]$ of 11.1 ng m^{-3} in autumn (Jia et al., 2011) and 11.0
427 ng m^{-3} in warm months (April to June) (Feng et al., 2019). In comparison with Guangzhou city (south of China),
428 BaP_{eq} was 9.24 ng m^{-3} in winter and reported to be 1.6 and 6.2 times greater than autumn and summer,
429 respectively (Liu et al., 2015). Our results were considerably higher than those estimated for western European
430 cities during the winter, such as **Grenoble: 1.4 ng m^{-3} (Tomaz et al., 2016), Oporto: 3.56 ng m^{-3} , Florence: 1.39**
431 **ng m^{-3} and Athens: 0.43 ng m^{-3} (Alves et al., 2017). ECR values estimated for each city were 31 (Grenoble), 6.6**
432 **(Oporto), 17 (Florence) and 54 (Athens)** times lower than our ECR estimation. Lower ECR levels in western
433 European cities were attributed to cleaner energy sources, less densely populated cities, waste exporting and
434 recycling and more effective environmental regulations.

435

436 4 Conclusions

437 Temporal variations and chemical composition of $\text{PM}_{2.5}$ were measured in Beijing-China from 22 November
438 2016 to 9 December 2016, focusing in particular on the diurnal and nocturnal chemical formation of PAHs,
439 OPAHs and NPAHs. The 24 h average concentration of $\text{PM}_{2.5}$ was 108 $\mu\text{g m}^{-3}$ ranging from 10 to 283 $\mu\text{g m}^{-3}$,
440 exceeding the 24 h limit value for China on 10 out of 18 sampling days. The 24 h concentrations of $\sum\text{PAH}_{16}$
441 varied between 37 and 180 ng m^{-3} (average 97 \pm 43 ng m^{-3}), while $\sum\text{OPAH}_{10}$ ranged from 13 to 70 ng m^{-3}
442 (average 35.6 \pm 19 ng m^{-3}) and $\sum\text{NPAH}_9$ from 0.87 to 4.4 ng m^{-3} (average 2.29 \pm 1.2 ng m^{-3}). Daytime
443 concentrations during pollution episodes for PAHs, OPAHs and NPAHs were 224, 54, and 2.3 ng m^{-3} ,
444 respectively. The daily concentration of **Benzo[a]pyrene** exceeded the 24 h average limit value of 2.5 ng m^{-3} for
445 China on all sampling days in this study, indicating elevated risk of disease among inhabitants.

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446 Diagnostic ratios of different species were used to distinguish between possible emission sources of PAHs. Coal
447 combustion and road traffic emissions (petrol engines) were found overall to be the two dominant sources. In
448 addition, high ratios of 2+3Nitrofluoranthene/1-Nitropyrene indicated significant secondary formation of
449 NPAHs, especially in daytime via the OH radical-initiated reaction pathway.

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450 PAHs and OPAHs concentrations were correlated with CO, NO, NO₂, SO₂ and HONO, indicating that both are
451 associated with local and regional primary emissions and in particular to traffic sources. Correlations seen
452 previously between PM_{2.5} and HONO suggested a possible links and a potential source of HONO that would
453 affect the budget of HONO and OH radicals. The strong positive correlation between individual NPAHs and
454 HONO during daytime was also suggestive of a potential link between these two classes of chemicals in air.
455 One of the dominant NPAHs, the 9-Nitroanthracene had distinctive behaviour, accumulating at night and
456 photodegrading in daytime.

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457 The lifetime excess cancer risk attributable to the summation of polycyclic aromatic compounds measured here
458 and associated with PM_{2.5} inhalations in Beijing was in the range of 10⁻³ according to WHO guidelines,
459 confirming that there is statistically elevated risk of contracting cancer from this class of pollutants in this
460 location.

461

462

463 *Author contributions:* AE led the analysis and prepared the manuscript with contributions from all authors. ACL
464 and JFH contributed to the analysis, interpretation and writing of the paper. RED provided the data on the gas
465 phase measurements and collected the filter samples in the field. MWW supported laboratory chemical analysis
466 on the GC-Q/ToF-MS. All authors contributed to the corrections of the paper.

467

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

469

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476

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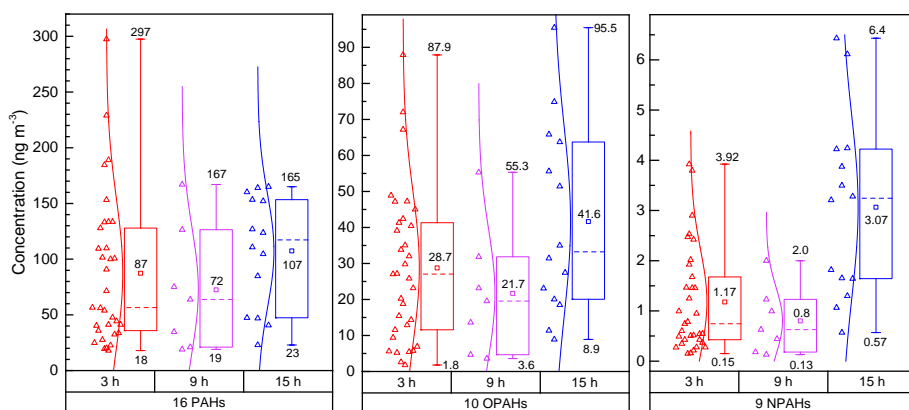
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809 **Figure 1.** Concentrations of ΣPAHs, ΣOPAHs and ΣNPAHs in PM_{2.5} samples during the daytime (3 h; 9
 810 h) and night-time (15 h). Box plot represents the 25th and 75th percentiles range of the observed
 811 concentrations and the bottom and top lines indicate minimum and maximum concentrations. Square
 812 symbols represent the mean concentration, and the short dash line within the boxes represent the median.
 813 Empty Triangles correspond to the data measured over 3 h, 9 h and 15 h samples. The lines between data
 814 points and boxes reflect a normal distribution curve.
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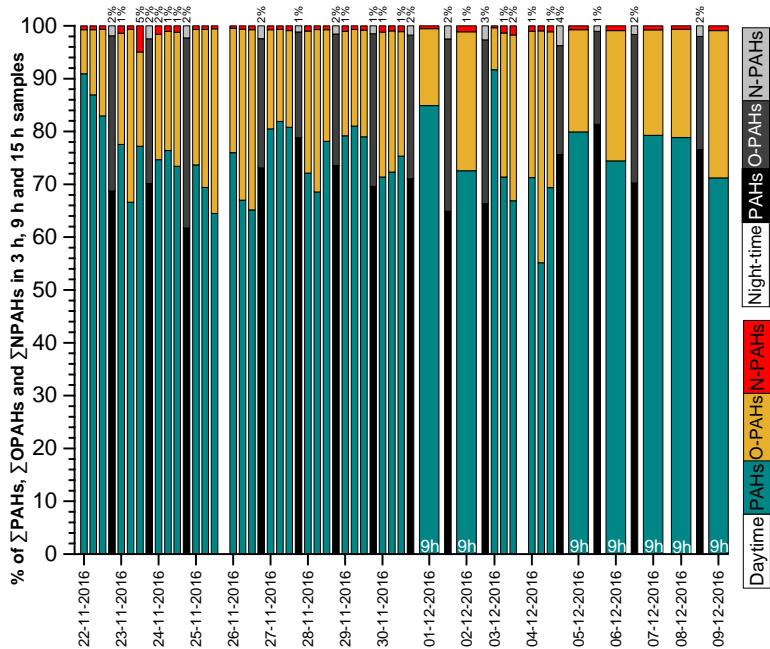
818 **Table 1.** List of measured PAHs, OPAHs and NPAHs and their Abbreviations. Compounds are listed in order of
 819 elution.

Compound/Formula	Abbreviation	Accurate Mass (<i>m/z</i>)	%RSD	
16 PAHs			Monitored ions in EI mode	Inter-day Intra-day
Naphthalene/C ₁₀ H ₈	NAP	128.0628-127.0543-102.0464	4.6	3.2
Acenaphthylene/C ₁₂ H ₈	ACY	152.0629-151.0546-126.0463	4.1	2.1
Acenaphthene/ C ₁₂ H ₁₀	AC	153.0705-154.0779-152.0634	5.5	6.1

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Fluorene/C ₁₃ H ₁₀	FLU	166.0782-165.0708-164.0621	4.0	2.9
Phenanthrene/C ₁₄ H ₁₀	PHE	178.0789-176.0626-152.0622	4.6	3.0
Anthracene/C ₁₄ H ₁₀	ANT	178.0787-176.0627-152.0620	4.7	4.2
Fluoranthene/C ₁₆ H ₁₀	FLT	202.0788-200.0626-101.0388	1.8	4.5
Pyrene/C ₁₆ H ₁₀	PYR	202.0788-200.0626-101.0389	3.2	1.9
Benzo[a]anthracene/C ₁₈ H ₁₂	BaA	228.0927-226.0783-101.0388	6.2	1.2
Chrysene/C ₁₈ H ₁₂	CHR	228.0943-226.0784-101.0387	6.0	2.6
Benzo[b]fluoranthene/C ₂₀ H ₁₂	BbF	252.0941-250.0784-126.0467	4.7	2.0
Benzo[k]fluoranthene/C ₂₀ H ₁₂	BkF	252.0940-250.0783-126.0468	8.9	8.7
Benzo[a]pyrene/C ₂₀ H ₁₂	BaP	252.0940-250.0783-126.0466	5.2	2.3
Indeno[1,2,3-cd]pyrene/C ₂₂ H ₁₂	IcdP	276.0939-274.0783-138.0467	7.2	2.6
Dibenz[a,h]anthracene/C ₂₂ H ₁₄	DahA	278.1097-276.0941-139.0545	7.7	4.3
Benzo[ghi]perylene/C ₂₂ H ₁₂	BghiP	276.0942-274.0783-138.0467	5.4	2.6
10 OPAHs		Monitored ions in NCI mode		
1,4-Naphtoquinone/C ₁₀ H ₆ O ₂	1,4-NAQ	158.0420	6.3	5.1
1-Naphthaldehyde/C ₁₁ H ₈ O	1-NALD	156.0557	8.9	7.8
9-Fluorenone/C ₁₃ H ₈ O	9-FLON	180.0639	5.7	6.2
9,10-Anthraquinone/C ₁₄ H ₈ O ₂	9,10-ANQ	208.0572	5.6	3.2
1,8-Naphthalic anhydride/ C ₁₂ H ₆ O ₃	1,8-NANY	198.0436	6.4	5.6
Phenanthrene-9- carboxaldehyde/C ₁₅ H ₁₀ O	PHCA	206.0777	5.4	4.9
Benzo[a]fluorenone/ C ₁₇ H ₁₀ O	BaFLU	230.0791	6.4	3.2
7H-Benz[de]anthracene-7-one/ C ₁₇ H ₁₀ O	BANTone	230.0781	7.2	5.8
1-Pyrenecarboxaldehyde/ C ₁₇ H ₁₀ O	1-PYRCA	230.0786	7.5	7.2
1,2-Benzanthraquinone/ C ₁₈ H ₁₀ O ₂	1,2-BANQ	258.0743	8.5	7.4
9 NPAHs		Monitored ions in NCI mode		
1-Nitronaphthalene/C ₁₀ H ₇ NO ₂	1-NNAP	173.0551	4.7	4.4
3-Nitrodibenzofuran/ C ₁₂ H ₇ NO ₃	3-NDBF	213.0475	4.4	5.1
5-Nitroacenaphthene/ C ₁₂ H ₉ NO ₂	5-NAC	199.0682	5.6	5.3
2-Nitrofluorene/C ₁₃ H ₉ NO ₂	2-NFLU	211.0689	5.0	5.4
9-Nitroanthracene/C ₁₄ H ₉ NO ₂	9-NANT	223.0697	5.9	3.9
3-Nitrofluoranthene/C ₁₆ H ₉ NO ₂	3-NFLT	247.0688	6.4	4.1
1-Nitropyrene/C ₁₆ H ₉ NO ₂	1-NPYR	247.0691	3.9	3.2
6-Nitrochrysene/C ₁₈ H ₁₁ NO ₂	6-NCHR	273.0847	4.7	5.4

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821 **Figure 2.** Time-series of ΣPAHs, ΣOPAHs and ΣNPAHs in PM_{2.5} samples during the daytime (3 h and 9
 822 h) and night-time (15h). Percentage below 1% for NPAHs are omitted for clarity. Night-time data on
 823 25/11/2016, 03/12/2016 and 07/12/2016 are not available due to lack of samples.
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829 **Table 2. Minimum, maximum and average atmospheric concentrations of PAHs, OPAHs and NPAHs in PM_{2.5}.**830 **Compounds in bold represent the highest mean contribution to the sum of all compounds.**

Compound	Concentrations (ng m ⁻³)		Average contribution to total (%)
	Minimum-maximum	Average	
16 PAHs	(3 h)/(9 h)/(15 h)	(3 h ± SD*)/(9 h ± SD)/(15 h ± SD)	(3 h)/(9 h)/(15 h)
NAP	(0.05-0.8)/(0.1-0.4)/(0.06-0.6)	(0.31 ± 0.2)/(0.24 ± 0.1)/(0.27 ± 0.2)	(0.48)/(0.39)/(0.25)
ACY	(0.01-1.2)/(0.1-0.8)/(0.1-1.2)	(0.31 ± 0.3)/(0.31 ± 0.2)/(0.58 ± 0.4)	(0.35)/(0.46)/(0.50)
AC	(0.03-0.13)/(0.02-0.09)/(0.01-0.2)	(0.07 ± 0.02)/(0.04 ± 0.03)/(0.07 ± 0.07)	(0.15)/(0.08)/(0.06)
FLU	(0.05-1.3)/(0.1-1.0)/(0.1-1.5)	(0.43 ± 0.3)/(0.41 ± 0.3)/(0.63 ± 0.4)	(0.53)/(0.65)/(0.56)
PHE	(1.2-23.1)/(1.9-16.3)/(1.5-13.7)	(7.38 ± 5.5)/(6.30 ± 5.3)/(8.4 ± 4.0)	(8.83)/(9.04)/(7.84)
ANT	(0.5-3.4)/(0.3-1.9)/(0.3-2.9)	(1.07 ± 0.7)/(0.79 ± 0.6)/(1.43 ± 0.8)	(1.48)/(1.23)/(1.32)
FLT	(1.4-41.8)/(3.0-17.6)/(3.2-11.7)	(12.9 ± 10.0)/(9.10 ± 5.7)/(8.97 ± 2.7)	(13.9)/(13.9)/(9.67)
PYR	(0.7-34.6)/(2.1-15.7)/(2.9-10.7)	(9.85 ± 8.2)/(7.48 ± 5.0)/(8.1 ± 2.5)	(10.4)/(11)/(8.69)
BaA	(1.3-27.7)/(1.3-17.5)/(2.1-18.8)	(6.69 ± 6.4)/(6.52 ± 5.9)/(12 ± 5.9)	(7.17)/(8.23)/(11)
CHR	(1.4-37.5)/(2.1-20.8)/(2.7-15.9)	(10.5 ± 8.7)/(9.17 ± 7.17)/(11.3 ± 4.8)	(11.2)/(12.4)/(10.8)
BbF	(1.5-35.3)/(2.1-21.3)/(2.3-20.4)	(10.3 ± 8.5)/(8.93 ± 7.3)/(10.8 ± 5.0)	(11.2)/(11.8)/(10.4)
BkF	(1.6-15.4)/(1.2-7.4)/(1.3-6.6)	(5.51 ± 3.8)/(3.94 ± 2.7)/(4.3 ± 1.5)	(6.76)/(5.80)/(4.43)
BaP	(1.4-37.3)/(1.5-20.7)/(3.2-35.2)	(8.81 ± 8.6)/(8.40 ± 7.5)/(18.9 ± 12.4)	(9.12)/(10.3)/(16.1)
IcdP	(1.7-16.1)/(0.9-11.6)/(1.0-18.3)	(4.79 ± 3.5)/(4.65 ± 4.3)/(9.75 ± 6.4)	(6.06)/(5.70)/(8.03)
DahA	(1.9-5.2)/(0.7-2.9)/(0.5-6.9)	(2.54 ± 0.7)/(1.46 ± 0.8)/(3.0 ± 2.1)	(4.43)/(2.46)/(2.56)
BghiP	(2.53-17.0)/(1.2-10.7)/(1.4-15.4)	(5.80 ± 3.5)/(4.70 ± 3.7)/(8.8 ± 5.1)	(7.86)/(6.47)/(7.62)
Total	(18-297)/(19-167)/(23-165)	(87.3 ± 58)/(72.5 ± 56)/(107 ± 51)	
10 OPAHs	(3 h)/(9 h)/(15 h)	(3 h ± SD)/(9 h ± SD)/(15 h ± SD)	(3 h)/(9 h)/(15 h)
1,4-NAQ	(0.02-8.1)/(0.16-3.1)/(0.1-4.2)	(2.25 ± 2.4)/(1.27 ± 1.2)/(1.66 ± 1.3)	(6.22)/(5.39)/(3.70)
1-NALD	(0.2-0.8)/(0.07-0.5)/(0.08-0.9)	(0.43 ± 0.1)/(0.20 ± 0.1)/(0.49 ± 0.3)	(2.71)/(1.19)/(1.25)
9-FLON	(0.49-14.9)/(0.7-6.0)/(0.8-11.4)	(6.76 ± 4.4)/(2.56 ± 1.9)/(4.26 ± 2.8)	(25.8)/(14.3)/(10.2)
9,10-ANQ	(0.3-36.4)/(1.2-24.8)/(2.8-36)	(8.31 ± 8.8)/(8.65 ± 8.5)/(14.3 ± 9.9)	(24.3)/(35.8)/(32.7)
1,8-NANY^a	(0.3-16.3)/(1.0-6.9)/(3.7-9.3)	(7.09 ± 5.4)/(3.69 ± 2.9)/(6.81 ± 2.8)	(37.9)/(33.2)/(45.6)
PHCA	(0.1-0.9)/(0.05-0.6)/(0.06-1.9)	(0.26 ± 0.17)/(0.20 ± 0.19)/(0.71 ± 0.57)	(1.42)/(0.99)/(1.50)
BaFLU	(0.06-10.8)/(0.1-8.1)/(0.4-15.1)	(2.77 ± 3.0)/(2.72 ± 2.9)/(5.99 ± 4.8)	(7.47)/(9.73)/(12.1)
BANTone	(0.08-15.1)/(0.04-8.3)/(0.5-19.8)	(2.46 ± 3.3)/(2.63 ± 2.9)/(9.27 ± 7.3)	(6.10)/(9.05)/(19.1)
1-PYRCA	(0.007-1.8)/(0.008-1.5)/(0.05-2.4)	(0.31 ± 0.4)/(0.39 ± 0.5)/(1.0 ± 0.9)	(0.74)/(1.24)/(1.96)
1,2-BANQ	(0.02-3.6)/(0.03-2.6)/(0.2-3.9)	(0.87 ± 0.96)/(0.90 ± 0.96)/(1.99 ± 1.4)	(2.3)/(3.24)/(4.33)

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Total	(1.8-87.9)/(3.6-55.3)(8.9-95.5)	(28.7 ± 21)/(21.7 ± 18)/(41.6 ± 26)	
9 NPAHs	(3 h)/(9 h)/(15 h)	(3 h ± SD)/(9 h ± SD)/(15 h ± SD)	(3 h)/(9 h)/(15 h)
1-NNAP	(0.01-0.1)/(0.008-0.04)/(0.005-0.03)	(0.03 ± 0.02)/(0.01 ± 0.01)/(0.01 ± 0.008)	(4.38)/(3.08)/(0.57)
3-NDBF	(0.08-1.5)/(0.02-0.06)/(0.03-2.4)	(0.33 ± 0.31)/(0.03 ± 0.01)/(0.89 ± 0.84)	(33.4)/(7.92)/(22.4)
5-NAC ^b	(0.04-0.1)/(<LOQ)/(0.03-0.35)	(0.08 ± 0.05)/(<LOQ)/(0.18 ± 0.13)	(5.64)/(<LOQ)/(4.67)
2-NFLU	(0.03-0.3)/(0.01-0.3)/(0.01-0.5)	(0.08 ± 0.06)/(0.09 ± 0.11)/(0.26 ± 0.21)	(10.15)/(10.00)/(7.28)
9-NANT	(0.01-1.2)/(0.06-0.1)/(0.4-2.4)	(0.36 ± 0.37)/(0.41 ± 0.31)/(1.18 ± 0.6)	(27.1)/(53.4)/(47.5)
3-NFLT	(0.05-1.2)/(0.02-0.5)/(0.04-1.2)	(0.34 ± 0.3)/(0.21 ± 0.2)/(0.54 ± 0.4)	(24.6)/(23.4)/(17.7)
1-NPYR ^c	(0.01-0.1)/(0.01-0.06)/(0.008-0.2)	(0.05 ± 0.03)/(0.06 ± 0.05)/(0.02 ± 0.02)	(2.92)/(2.48)/(2.01)
6-NCHR ^d	(0.05-0.2)/(<LOQ)/(0.009-0.02)	(0.09 ± 0.06)/(<LOQ)/(0.01 ± 0.007)	(5.6)/(<LOQ)/(0.5)
6-NBaP ^e	(<LOQ)/(<LOQ)/(0.02-0.08)	(<LOQ)/(<LOQ)/(0.05 ± 0.01)	(<LOQ)/(<LOQ)/(1.26)
Total	(0.15-3.92)/(0.13-2.0)/(0.57-6.43)	(1.17 ± 1.0)/(0.80 ± 0.66)/(3.06 ± 1.8)	

831 ^a Quantified in 28/54 samples

832 ^b Quantified in 7/54 samples

833 ^c Quantified in 35/54 samples

834 ^d Quantified in 5/54 samples

835 ^e Quantified in 11/54 samples

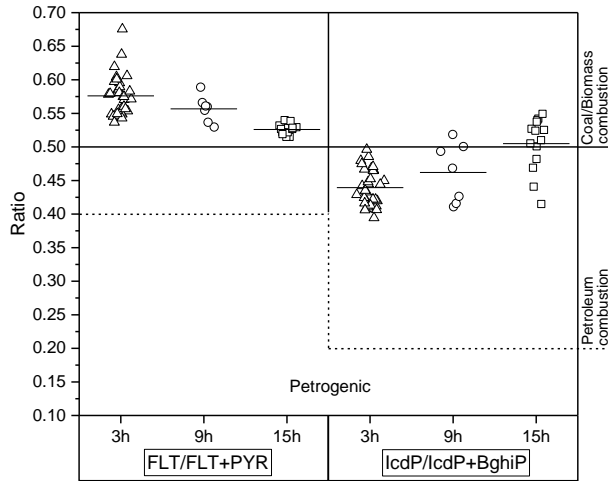
836 * SD: Standard Deviation

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842 **Figure 3. Column scatter of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) in the particulate phase at three different**
 843 **time sampling averages, open triangles and circles represent the daytime data for 3 h and 9 h samples, open squares**
 844 **represent the night-time data of 15 h. The dashed line separates the petroleum combustion source from petrogenic**
 845 **source for both ratios. The solid short line on each data set represent the mean value of ratios.**

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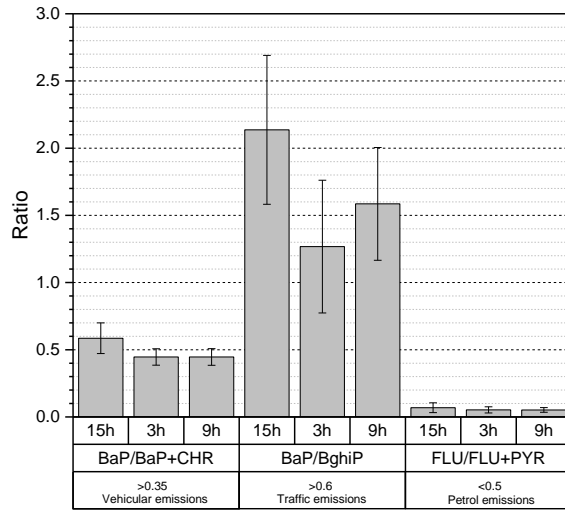
848 **Table 3. Average concentration of \sum BaP_{eq} in ng m⁻³ and cancer risk assessment for the sum of 16PAHs, 10PAH and**
 849 **6NPAHs.**

Sampling hours	\sum [BaP] _{eq} ng m ⁻³	UR _{BaP} = 1.1x10 ⁻⁶ (CalEPA)	UR _{BaP} = 8.7x10 ⁻⁵ (WHO)	Risk per million people
9 h (daytime, n=40) ^a	15.9 ^a	1.75 x 10 ⁻⁵	1.38 x 10 ⁻³	17 ^b – 1383 ^c
15 h (night-time, n=14)	28.3	3.17 x 10 ⁻⁵	2.46 x 10 ⁻³	31 ^b – 2460 ^c
24 h (n=54)	23.6	2.6 x 10⁻⁵	2.05 x 10⁻³	26^b – 2053^c

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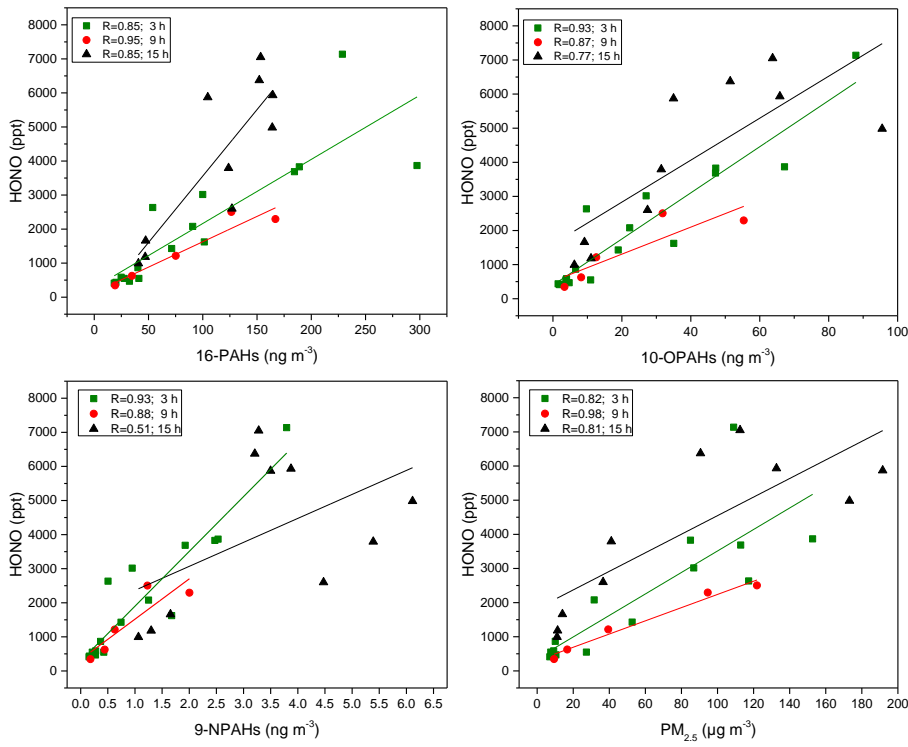
^a Average includes combined 3 h samples in each day (n=33) and 9 h samples (n=7)
^b Calculated Value according to CalEPA
^c Calculated Value according to WHO
 n: number of samples

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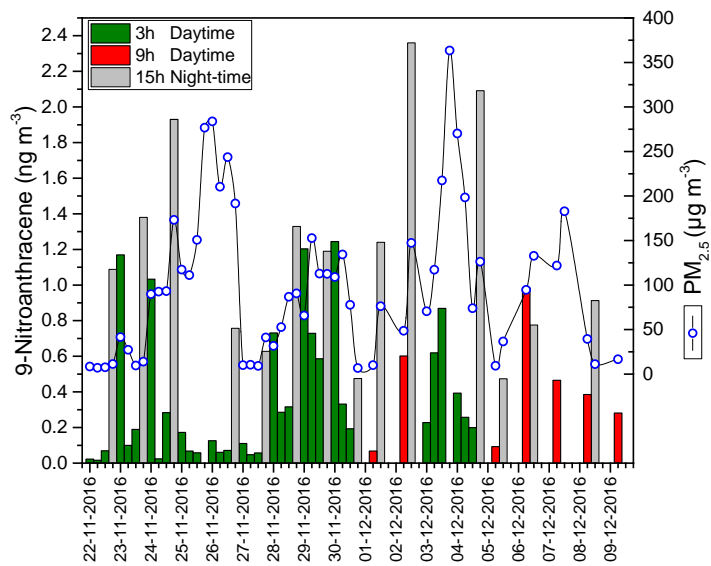


856 **Figure 4. Column distribution of BaP/BaP+CHR, BaP/BghiP and FLU/FLU+PYR in the particulate phase for three**
 857 **different sampling periods. 3 h and 9 h represent samples collected during the day and 15 h for samples at night.**
 858 **Error bars reflect standard deviations.**

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877 **Figure 5. Correlation coefficients of Σ PAHs, Σ OPAHs, Σ NPAHs and PM_{2.5} with HONO. Time sampling resolution of**
 878 **3 h and 9 h refer to daytime concentrations and 15 h to nocturnal concentrations. Significance levels were between**
 879 **0.001 and 0.05 except for HONO and NPAHs at night, P level > 0.05 and Pearson coefficient 0.52.**



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883 **Figure 6.** Temporal variation of 9-Nitroanthracene and PM_{2.5} over the entire winter campaign.

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