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

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Abstract. Ambient particulate matter (PM) can contain a mix of different toxic species derived from a wide variety of sources. This study quantifies the variation in diurnal 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 24h varied between 37 and 180 ng m^{-3} (mean: 97 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}). 9,10-Anthraquinone (18 ng m^{-3}), 1,8 Naphthalic anhydride (14 ng m^{-3}) and 9-Fluorenone (12 ng m^{-3}) were the three major OPAHs species, while 9-Nitroanthracene (0.84 ng m^{-3}), 3-Nitrofluoranthene (0.78 ng m^{-3}) and 3-Nitrodibenzofuran (0.45 ng m^{-3}) were the three most abundant NPAHs. ∑PAHs and ∑OPAHs showed a strong positive correlation with the gas phase abundance of NO, CO, SO_2, 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 dominant source of NPAHs was 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 photodegradation during the daytime and has shown a strong positive correlation with ambient HONO (R=0.90, P<0.001). The lifetime excess lung cancer risk for the species with 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).

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

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

In recent years, many studies in different countries have focused on studying toxic organic pollutants in $PM_{2.5}$ because they lie within the respirable size range for humans (Sharma et al., 2007; Ringuet et al., 2012, Farren et al., 2015). In the last decade, a major focus has been given to Chinese cities because of their population growth and geographic peripheral expansion in manufacturing and energy industries. This has made China the leader in energy consumption, but also the world's highest emitter of $PM_{2.5}$ and PAHs (Lin et al., 2018; Zhang et al., 2009; Xu et al., 2006). The majority of previous studies have reported PAH on 24h $PM_{2.5}$ sampling during short-term and long-term measurements campaigns (Alves et al., 2017; Niu et al., 2017; Benjamin et al., 2014; Wang et al., 2011a). However, a long sampling and averaging period creates some limitations (Tsapakis and Stephanou., 2007), notably where changing atmospheric photolysis conditions (air humidity, temperature, wind direction, ozone or other oxidant concentrations) may have a significant influence on PAHs concentrations and oxidation rates (Tsapakis and Stephanou., 2003; Ringuet et al., 2012). More intensive and higher frequency measurements in field campaigns have been suggested as a means to improve the positive matrix factorization model performance (Tian et al., 2017). A few studies have carried out twice daily (12 h) sampling (Zhang et al., 2018; Farren et al., 2015; Ringuet et al., 2012) obtaining limited information on variability in concentrations during the daytime and night-time (Tsapakis and Stephanou., 2007). Considering the above, this paper determines the temporal diurnal and nocturnal variation of the $PM_{2.5}$-bound concentrations of PAHs, OPAHs and NPAHs from the air of Beijing in China, it shows the role of photochemistry in the formation of OPAHs and NPAHs and associate the fate and evolution of PAHs, OPAHs and NPAHs with the gas phase concentrations of other pollutants (O_3, CO, NO, NO_2, SO_2, HONO), the cancer risk associated with inhalation of $PM_{2.5}$ was calculated.

2 Experimental Steps

2.1 Sampling site and method

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

2.2 Extraction method and clean up

All collected samples were extracted using an Accelerated Solvent Extractor automated system (Dionex, ASE 350). Prior to extraction, 1/16th (surface area equivalent to 25.7 cm^2) of each filter was cut using a hole puncher (Ø=27 mm) and for each batch of 6 samples, one sample was spiked with a mixture of two deuterated-PAHs (Phenanthrene-D10; Pyrene-D10), two deuterated-OPAHs (9-Fluorenone-D8; 9,10-Anthraquinone-D8), and two deuterated-NPAHs (1-Nitronaphthalene-D7; 3-Nitrofluoranthene-D9), as surrogate standards for PAHs, OPAHs and NPAHs, respectively, with concentration on filters corresponding to 400 ng (40 µl, 10 ng μl^{-1} in Acetonitrile). All punched samples were cut to small pieces and packed into 5 mL stainless steel extraction cell. Extractions were carried out in acetonitrile and performed as follows: Oven at 120°C, pressure at 1500 psi, rinse volume 60% and 60 s purge time for three consecutive 5 min cycles. Extracts (V=20ml) were evaporated to approximately 6 mL under a gentle stream of nitrogen before the clean-up step. All samples and blanks were purified on a SPE silica normal phase cartridge (1g/6ml; SIGMA ALDRICH) in order to maintain the GC injection inlet liner. After the clean-up 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 1.5 ml autosampler amber vial. Each concentrated sample was stored at 4°C until analysis by GC-Q-ToF-MS. The average recovery efficiencies ranged from 85% to 96%, and the target compounds concentrations were calculated incorporating measured recovery efficiencies.

2.3 Chemical standards

The chemical compounds that have attracted the most attention in previous studies are the 16 priority PAHs and their derivatives, defined by the United States Environment Protection Agency (EPA). The choice of the organic compounds investigated in this study is based on those associated with the particle phase and commercially available standards. All compounds are listed in Table 1 and were purchased from Sigma Aldrich, Alfa Aesar and Santa Cruz Biotechnology in the UK and had a minimum purity of 98%. 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). Deuterated compounds were supplied by C/D/N isotopes and distributed by QMX Laboratories Ltd (Essex, UK).

2.4 GC/MS Analysis

Target compounds were quantified using a GC - accurate mass Quadrupole Time-of-Flight GC/MS system (GC Agilent 7890B coupled to an Agilent 7200 Q-TOF-MS). Parent PAHs were separated in a 35 min analysis time using a capillary HP-5MS Ultra Inert GC column (Agilent; 5%-Phenyl substituted methylpolysiloxane; length: 30 m, diameter: 0.25 mm, film thickness: 0.25 µm). Inlet injections of 1 µl were performed in pulsed splitless mode at 320 °C using an automated liquid injection with the GERSTEL MultiPurpose Sampler (MPS). Helium 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 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 from the extracted samples eluted from the column. The MS was operated in Electron Ionisation (EI) mode at 70 eV with an emission current of 35 µA. Calibration solutions were injected 3 times in the same sequence for samples and covered the range from 1pg µl^{-1} to 1000 pg µl^{-1}.

The analysis of OPAHs and NPAHs was conducted using Negative Chemical Ionisation (NCI) performed at 155 eV and 48 µA, with methane (CH_4, research grade 5.5, Air Liquide) as reagent gas. Target compounds were eluted using the Rxi-5ms (Restek GC column) similar phase and characteristics to HP-5ms. Analysis was performed in 29.2 min and the GC settings were selected as follows: 1 µl of each sample was injected in pulsed splitless mode at 310 °C, Helium flow was set to 1.2 ml min^{-1}, the initial oven temperature of 70 °C was held for 4 min, followed by a heating rate of 60 °C min^{-1} until 190 °C and then raised to 270 °C at rate of 25 °C min^{-1} and ended with 5 °C min^{-1} until 320 °C, held for 10 min. A 10 points calibration curve within the concentrations range of 0.5 pg µl^{-1} to 1000 pg µl^{-1}, was performed with the correlation coefficients from the linear regression ranging from 0.980 to 0.999.

2.5 Data analysis and error evaluation

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

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

To determine any sources of contamination during sample preparation and the analytical procedure, the solvent (acetonitrile) and from blank filters were analysed following the same procedure as for the samples (Extraction, SPE, Evaporation). A few target compounds were detected at trace levels but were either below LOD or orders of magnitude lower than in the samples.

3 Results and discussion

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

Studies on $PM_{2.5}$ have rapidly increased over the last few years and various disciplines have contributed to improve understanding about source emissions, chemical composition, and impact on people's behaviour and health. The air quality standards in China are currently 35 µg m^{-3} as a yearly average limit for $PM_{2.5}$ and 75 µg m^{-3} as a 24h average limit (WHO 2016; Ministry of Ecology and Environment The People's Republic of China, 2012). During the sampling period of this study (Nov-Dec 2016), $PM_{2.5}$ was measured every hour and ranged from 3.8 to 438 µg m^{-3}, with an average concentration of 103 µg m^{-3}. The average 24h concentration was 108 µg m^{-3} ranging from 10 to 283 µg m^{-3}, exceeding the 24h limit value on 10 of the 18 sampling days.

Fig. 1 shows the measured concentration of PAHs in the 3 h daytime samples ranging from 18 to 297 ng m^{-3} (average 87.32 ng m^{-3}) and from 23 to 165 ng m^{-3} (average 107.40 ng m^{-3}) in the 15 h night-time samples. The 24h total concentrations (combined results from daytime and night-time samples) of the 16 PAHs varied between 37 and 180 ng m^{-3} (average 97 ng m^{-3}). PAHs derivatives showed the following trends: total OPAHs concentrations varied from 3.3 to 55 ng.m^{-3} (average: 26 ng m^{-3}) in total daytime hours and from 8.9 to 95 ng m^{-3} (average: 41.63 ng m^{-3}) at night-time; OPAHs were approximately 25 and 14 times higher than average NPAHs in the daytime (average: 1.03 ng m^{-3}, range: 0.13-2.3) and night-time (average: 3.06 ng m^{-3}, range: 0.57-6.43), respectively.

PHE (See table 1 for abbreviations), FLT, PYR, BaA, CHR, BbF and BaP were the largest contributors to the total PAHs concentrations, whereas 9-FLON, 9,10-ANQ and 1,8-NANY were the three major O-PAHs species. The most abundant NPAHs were 3-NDBF, 9-NANT and 3-NFLT; contributions of each compound to the total concentration are shown in Fig. 2 and detailed in Table 2. The highest concentrations recorded in this study were in the day of 29 Nov 2016; concentrations of all target compounds in the particulate phase are displayed in Fig. S2. Some nitro-compounds (5-NAC, 1-NPYR, 6-NCHR, 6-NBaP) were below LOQ in few samples while one oxy-compound (1,8-Naphthalic anhydride) was outside the dynamic range and limit of linearity of the calibration curve especially for samples with high mass loading (Table 2). Similar major compounds were found in different urban cities (Xi'an, Jinan, Beijing) of China (Bandowe et al. 2014, Zhang et al. 2018, Wang et al., 2011c). The average of total PAHs concentrations (97 ng m^{-3}) in this study was higher than the average value reported for Guangzhou city in the south of China (average 45.52 ng m^{-3}) (Liu et al., 2015), however, it was lower than average values reported for Xi'an city in winter (range 14-701 ng m^{-3}; average 206 ng m^{-3}) (Wang et al., 2006) and in the suburb of Beijing in winter (average 277 ng m^{-3}) (Feng et al., 2005). The lower average concentration of total PAHs reported in this study can be attributed to the effort from municipal government to improve air quality and control emissions by reducing combustion sources.

Concentrations of PAHs in PM_{10} (range: 3.2 - 222.7 ng m^{-3}) in Beijing were found in previous study to be lower than in $PM_{2.5}$ (Wang et al., 2011c). The concentration of PAHs reported in this study were much lower than reported in certain other megacities, for example, Delhi, India in winter season 2003 (range: 948.96-1345.42 ng m^{-3}; mean: 1157.9 ± 113.74 ng m^{-3}) (Sharma et al., 2007) and Mexico City, Mexico in October 2002 (range: 60-910 ng m^{-3}; mean: 310 ng m^{-3}) (Marr et al., 2004). Average concentration for total PAHs in the first 3 h filter of the day (8:30-11:30 am; Monday to Friday; mean: 112 ng m^{-3}) were higher by 1.5 times than the rest of the day, and 1.6 times higher than the same first 3 h on a Sunday. A potential reason of the elevated concentrations in the morning hours is due to the rush hour traffic during working days, probably coupled to a period of shallow boundary layer.

The mean total concentrations in Table 2 for the 3 h integration samples of OPAHs and NPAHs were 28.74 ng m^{-3} (range: 1.8 - 87.9 ng m^{-3}) and 1.17 ng m^{-3} (range: 0.15 - 3.92 ng m^{-3}), respectively. Average night-time was 41.63 ng m^{-3} (OPAHs) and 3.06 ng m^{-3} (NPAHs), concentrations which were 2.6 and 35 times lower than the average total PAHs in the night samples, respectively. The ratios of mean concentration of PAHs divided by concentration of OPAHs and NPAHs for the 3 h samples were 3.03 and 74, respectively. Ratios of combined daytime and night-time samples (24h) were on average 2.93 (range 1.9 - 4.6) for PAHs/OPAHs and 47.36 (range 25 - 79) for PAHs/NPAHs. Lower ratios were reported from winter study in Xi'an – China, where PAHs/OPAHs ranged from 1.75 to 1.86 and PAHs/NPAHs ranged from 34 to 55.2. On the other hand, similar trends to our study were recorded for ∑PAHs/∑OPAHs in Europe such as Athens in Greece in winter (ratio 28.91/6.91 = 4.18) (Andreou and Rapsomanikis., 2009) and Augsburg in Germany in winter (ratio 11/3.2 = 3.43) (Pietrogrande et al., 2011). Further monitoring studies are needed to confirm trends of NPAHs in China.

The daily concentration of BaP ranged from 4.46 to 29.8 ng m^{-3} (average 15 ng m^{-3}), exceeding the 24h average limit value of 2.5 ng m^{-3} for China on all of the 18 days of sampling period (Ministry of Ecology and Environment The People's Republic of China, 2012).

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3.2 Diagnostic ratios to identify emission sources

The concentration ratios between different PAHs are widely used to assess and identify pollution emission sources (Tobiszewski and Namieśnik., 2012 and references therein). The ratios of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) isomer pairs are commonly used to distinguish emission sources such as coal/biomass burning or the incomplete combustion of petroleum. Values of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) higher than 0.5 indicate dominance of a coal/biomass burning source. Values of FLT/(FLT + PYR) between 0.4 and 0.5 and IcdP/(IcdP + BghiP) between 0.2 and 0.5 suggest a higher influence from fossil fuel combustion; values less than 0.4 and 0.2, are mostly related to incomplete combustion (petrogenic origin) (Yunker et al., 2002; Pio et al., 2001). The measured ratios in this 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 at night (15 h samples) varied between 0.51 and 0.54 (mean 0.52) indicating primary emissions from coal and biomass burning. Lower values were observed for IcdP/(IcdP + BghiP) where daytime ratios were between 0.39 and 0.5 (3 h and 9 h samples) indicating the dominance of petroleum combustion. At night, the ratio in most samples was slightly higher than 0.5, with some values below, suggesting mixed sources with likley higher contributions coming from residential heating using coal and wood at night.

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

On the other hand, some NPAHs can be used to track the photochemistry of PAHs with OH and NO_3 radicals, both of which can generate secondary photochemical products of NPAHs and OPAHs from primary PAH emissions (Zhang et al., 2018; Ringuet et al., 2012; Wang et al., 2011a). As 1-NPYR originates mainly from primary emissions and in particular from diesel vehicles (Ringuet et al., 2012 and references therein), formation of 2-NFLT has been reported to be absent in direct combustion emissions and to be produced from the gas-phase reactions of FLT with OH radicals in presence of NOx during the day or NO_3 radicals at night; while 2-NPYR comes solely from the reaction of PYR with OH radicals (Ramdahl et al., 1986; Arey et al., 1986; Atkinson et al., 1987; Ciccioli et al., 1996). Accordingly, the ratio 2-NFLT/1-NPYR has been widely used, with a value greater than 5 indicating a major contribution from photochemical processes, whilst a ratio value less than 5 means an important contribution from direct emissions (Zhang et al., 2018; Bandowe et al., 2014; Ringuet et al., 2012; Wang et al., 2011a; Albinet et al., 2008).

In this study, the 2-NFLT was not quantified because the standard compound was not commercially available, subsequently, we have used 3-NFLT isomer as a substitution of 2-NFLT. A previous study reported that the concentration of 3-NFLT compared to 2-NFLT is relatively very low (Bamford et al., 2003); in addition, the separation of both isomers (2- and 3-NFLT) using the most common GC-MS column for PAHs separation, HP-5ms and DB-5ms, was not possible (Zhang et al., 2018; Bandowe et al., 2014; Ringuet et al., 2012; Albinet et al., 2008). Hence, in this study we assume that the sum of 2- and 3-NFLT is closely representative of the original ratio 2-NFLT/1-NPYR. Therefore, we adopted the ratio 2+3NFLT/1-NPYR which was varied between 4 and 19 during the daytime (mean: 12) and from 3.6 to 30.4 in the night-time (mean: 8.8) (Fig. S3). Most daytime values have exceeded significantly the benchmark ratio of 5, while at night-time the average value was lower than average daytime value. These results could illustrate the predominance of OH-radicals-initiated reaction during the day and the dominating atmospheric formation route for 2-NFLT in presence of NO_2 and sunlight.

3.3 Correlation with atmospheric gas pollutants

The O_3, CO, NO, NO_2, SO_2 and HONO concentrations were also measured at the same site location (Institute of Atmospheric Physics in Beijing) as the $PM_{2.5}$ sampling. Sampling inlets were installed outside the containers at approximately 3-4 m above ground (Fig. S1). Online measurements of the gas phase species have been time-averaged to the filter sampling times. No correlations of significance were seen between PAHs and meteorological parameters (Relative Humidity and Temperature).

∑PAHs and ∑OPAHs had a similar strong positive correlation (R= 0.82 to 0.98) in the 9 h and 15 h samples with CO, NO, NO_2, SO_2 and HONO (Table S1). NO is known as an effective tracer for local traffic emissions, it is a short-lived intermediate in a variety of chemical reactions in both the troposphere and the stratosphere with an approximate residence time of 1 day (Bange 2008, Janhäll et al., 2004). CO is mainly produced from incomplete combustion and has a relatively long atmospheric lifetime (3 months on average) and has been reported to undergo long-range transport (Peng et al., 2007 and references therein). This suggests that the observed high correlations with primary pollutants NO and CO during the daytime and night-time indicate that PAHs and OPAHs are primarily emitted from traffic and can be associated with both local and regional scale emissions. In addition, similar significant correlations were observed with SO_2, this gas is mostly emitted from power plants emissions outside the city with approximately 50 h (Lee et al., 2011) atmospheric residence time. This relationship could be explained by the contribution of anthropogenic sources such as the Beijing Taiyanggong thermal power station (39°58′42″N 116°26′19″E). This suggestion is in accordance with our measured air masses showing that winds arriving at the site blow from the North East for much of the time (Fig. S4).

In contrast, most of the 3 h day samples showed only moderate correlations (R=0.38 to 0.74) except for HONO where significant correlations (R=0.87 to 0.94) were observed with ∑PAHs, ∑OPAHs and ∑NPAHs (Fig. 5; Table S1). Furthermore, HONO was significantly correlated with $PM_{2.5}$ during the daytime (Fig. 5). In light with these findings, a strong chemical link between HONO emissions and ambient particles ($PM_{2.5}$) can be concluded. A similar conclusion was drawn from recent study in Beijing (Zhang et al., 2019) which suggested a potential chemical relationship between HONO and haze particles ($PM_{2.5}$) and proposed a high contribution from vehicle emissions to the night-time HONO.

For NPAHs, no significant correlation was found in 3 h and 15 h time sampling resolution, except with HONO, where a significant difference between day and night were observed. Surprisingly, the 9 h time resolution showed a strong correlation with CO, NO, NO_2 and SO_2, potentially suggesting a direct emission of NPAHs. More likely these correlations arise because of a formation delay of NPAHs that is smoothed out by the longer daytime sampling period. In a previous study, Zimmermann et al., (2013) reported the formation of NPAHs from the heterogeneous interaction of ambient particle bound-PAHs with atmospheric oxidant. In line with the observed high values for the ratio 2+3NFLT/1-NPYR (section 3.2) and the trace levels of NPAHs concentrations in the atmosphere; the secondary formation of NPAHs by gas phase reactions followed by adsorption on particles and in parallel the heterogeneous formation on the surface of particles is supported rather than primary emissions.

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

In addition, there was a significant positive correlation between ANT and 9-NANT (R= 0.90, 1/3 h; R=0.94, 1/9 h; R=0.90, 1/15 h; P≤0.001), which may be an indication that 9-NANT is closely related to ANT. In this respect, additional simulation chamber measurements of the gas phase reaction of ANT with NO_3 radicals and for 9-Nitroanthracene with OH radicals in presence of light and under different atmospheric parameters are required for more precise assessment.

3.4 Exposure assessment

The toxicity equivalency factor (TEF) represent an estimate of the relative toxicity of a chemical compared to a reference chemical. For PAHs, Benzo(a)pyrene was chosen as the reference chemical because it is known as the most carcinogenic PAH (OEHHA., 1994, 2002) and is commonly used as an indicator of carcinogenicity of total PAHs (Alves et al., 2017; Bandowe et al., 2014; Ramírez et al., 2011). The toxicity of the total PAHs expressed as BaP equivalents (BaP_{eq}) is calculated from the TEFs of each target compound (Table S3) multiplied by its corresponding concentration Eq. (1):

$$\sum [BaP]_{eq} = \sum_{i}^{n=1} (C_i \, x \, TEF_i) \qquad (1)$$

where C_i correspond to the concentration of individual target compound (PAHs, OPAHs and NPAHs) in ng m^{-3}.

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

$$ECR = \sum [BaP]_{eq} \times UR_{BaP} \tag{2}$$

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

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

It is worth noting that inhalation exposure is not the only risk with the potential to contract cancer to humans, other sources of exposure such as dermal contact and ingestion of the re-suspended dusts in real environmental matrices such as road dusts and soils could increase the risk value for urban residents (Wang, et al., 2011b; Wei et al., 2015). In our study, the 24h average estimated cancer risk from inhalation exposure to ambient $PM_{2.5}$ based on CalEPA and WHO guidelines were 2.6 x 10^{-5} and 2.05 x 10^{-3}, respectively. Hence, the highest calculated ECR (2.05 x 10^{-3}) estimates 2027 additional cases per million people exposed (29 cases/year) in comparison to the estimate based on CalEPA in which 26 persons (0.37 cases/year) may have a chance of cancer development.

ECR trends were reported in previous studies from Beijing and other populated area (Bandowe et al., 2014; Alves et al., 2017; Ramírez et al., 2011; Jia et al., 2011, Liu et al., 2015, Feng et al., 2018, Song et al., 2018). In this study we considered the combination of all samples (n=54) to estimate the average 24h cancer risk ($\sum[BaP]_{eq}$=23.6 ± 12 ng m^{-3}; range 8 – 44 ng m^{-3}) and compare it with previous studies. An average value of 17 ng m^{-3} (range 2-64 ng m^{-3}) was reported for Xi'an for the whole year between July 2008 and August 2009 (Bandowe et al., 2014). After considering the same winter period (November and December) as in our study, the average values reported for Xi'an city (31-33 ng m^{-3}) were higher than our results. In contrast, our average value was comparable to those reported in a recent study in Beijing, ranging from 21 to 38 ng m^{-3} in cold months (Feng et al., 2018), whilst in the previous study of Chen et al. 2017, they reported an average of 31.4 ng m^{-3} for outdoor air in Beijing in winter. Lower and more varied values have been also reported to Beijing city in winter. Liu 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 Peking University campus and 82.1 ng m^{-3} for samples collected from busy road street. It is clear that direct comparison with Beijing air from other studies can be limited due to the number of PACs considered in each study and the differences in sampling sites and sampling periods. Other areas of uncertainty include TEF reference values and the range of BaP UR which were extrapolated from animal bioassays with limited evidence regarding the carcinogenicity to humans.

Seasonal variability is also crucial in estimating BaP_{eq} concentrations; it has been shown that BaP_{eq} values in cold months are always higher than warm months due to the increase in coal combustion, central and residential heating, lower photochemical transformation and lower volatilisation of gases favorising particle formation in winter. Previous observations in Beijing recorded $\sum[BaP_{eq}]$ of 11.1 ng m^{-3} in autumn (Jia et al., 2011) and 11.0 ng m^{-3} in warm months (April to June) (Feng et al., 2018). In comparison with Guangzhou city (south of China), 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, respectively (Liu et al., 2015). Our results were considerably higher than those estimated for western European cities during the winter, such as Oporto: 3.56 ng m^{-3}, Florence: 1.39 ng m^{-3} and Athens: 0.43 ng m^{-3} (Alves et al., 2017). ECR values estimated for each city were 6.6, 17 and 55 times lower than our ECR estimation. Lower ECR levels in western European cities were attributed to cleaner and renewable energy sources, less populated cities, waste exports and recycling and more efficient environmental regulations.

4 Conclusions

Temporal variations and chemical composition of $PM_{2.5}$ were measured in Beijing-China from 22 November 2016 to 9 December 2016, focusing in particularly on the diurnal and nocturnal chemical formation of PAHs, OPAH and NPAHs. The 24h average concentration of $PM_{2.5}$ was 108 µg m^{-3} ranging from 10 to 283 µg m^{-3}, exceeding the 24h limit for China on 10 days of the 18 sampling days. The 24h concentrations of $\sum PAH_{16}$ varied between 37 and 180 ng m^{-3} (average 97 ng m^{-3}), while $\sum OPAH_{10}$ ranged from 13 to 70 ng m^{-3} (average 35.62 ng m^{-3}) and $\sum NPAH_9$ from 0.87 to 4.4 ng m^{-3} (average 2.29 ng m^{-3}). Daytime concentrations during pollution episodes for PAHs, OPAHs and NPAHs were 224, 54, and 2.3 ng m^{-3}, respectively. The daily concentration of BaP exceeded the 24h average limit of 2.5 ng m^{-3} for China on all sampling days in this study, indicating elevated risk of disease among inhabitants.

Diagnostic ratios of different species were used to distinguish between possible emission sources of PAHs. Coal combustion and road traffic emissions (petrol engines) were found overall to be the two dominant sources. In addition, the high ratios of 2+3NFLT/1-NPYR observed reveal the significance of secondary formation of NPAHs, especially in daytime, and the dominance of the OH radical-initiated reaction pathway.

PAHs and OPAHs concentrations were correlated with CO, NO, NO_2, SO_2 and HONO, indicating that these compounds can be associated with both local and regional primary emissions and mostly related to traffic contribution. Correlation between $PM_{2.5}$ and HONO suggested a possible link with $PM_{2.5}$ as a potential source of HONO, affecting the tropospheric budget of HONO and OH radicals. The strong positive correlation between individual NPAHs and HONO during daytime was also suggestive of a potential link between these two classes of chemicals in air. One of the dominant NPAHs, the 9-NANT had a distinctive behaviour, accumulating at night and photodegrading in daytime.

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

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

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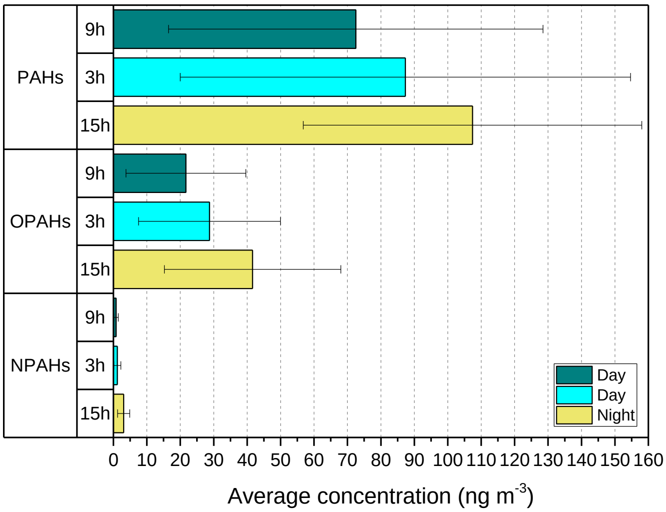

Figure 1. Average distribution diagram of ∑PAHs, ∑OPAHs and ∑NPAHs in $PM_{2.5}$ samples during the daytime (1/3 h; 1/9 h) and night-time (1/15 h). Error bars reflect standard deviations.

Table 1. List of measured PAHs, OPAHs and NPAHs and their Abbreviations. Compounds are listed in order of elution.

Compound/Formula	Abbreviation	Accurate Mass (*m/z*)	%RSD	
16 PAHs		Monitored ions in EI mode	Interday	Intraday
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
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/$C_{10}H_6O_2$	1,4-NAQ	158.0420	6.3	5.1
1-Naphthaldehyde/$C_{11}H_8O$	1-NALD	156.0557	8.9	7.8
9-Fluorenone/$C_{13}H_8O$	9-FLON	180.0639	5.7	6.2
9,10-Anthraquinone/$C_{14}H_8O_2$	9,10-ANQ	208.0572	5.6	3.2
1,8-Naphthalic anhydride/ $C_{12}H_6O_3$	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-Pyrenecaboxaldehyde/ $C_{17}H_{10}O$	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/$C_{10}H_7NO_2$	1-NNAP	173.0551	4.7	4.4
3-Nitrodibenzofuran/ $C_{12}H_7NO_3$	3-NDBF	213.0475	4.4	5.1
5-Nitroacenaphthene/ $C_{12}H_9NO_2$	5-NAC	199.0682	5.6	5.3
2-Nitrofluorene/$C_{13}H_9NO_2$	2-NFLU	211.0689	5.0	5.4
9-Nitroanthracene/$C_{14}H_9NO_2$	9-NANT	223.0697	5.9	3.9
3-Nitrofluoranthene/$C_{16}H_9NO_2$	3-NFLT	247.0688	6.4	4.1
1-Nitropyrene/$C_{16}H_9NO_2$	1-NPYR	247.0691	3.9	3.2
6-Nitrochrysene/$C_{18}H_{11}NO_2$	6-NCHR	273.0847	4.7	5.4
6-Nitrobenzo[a]pyerene/ $C_{20}H_{11}NO_2$	6-NBaP	297.0845	8.4	9.7

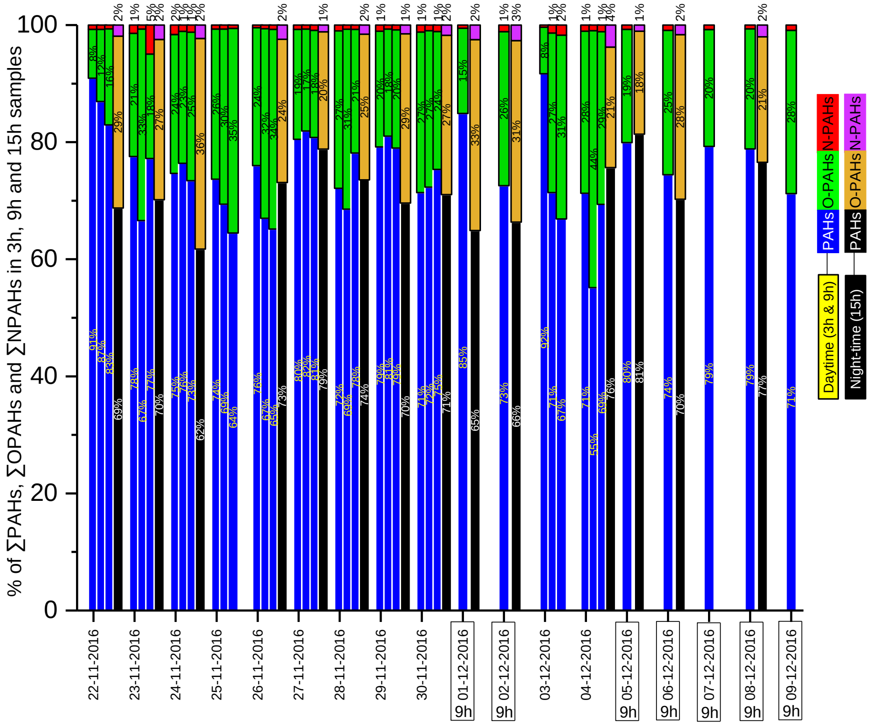

Figure 2. Temporal profile of ∑PAHs, ∑OPAHs and ∑NPAHs in $PM_{2.5}$ samples during the daytime and night-time. Percentage below 1% for NPAHs are omitted for clarity.

Table 2. Minimum, maximum and average atmospheric concentrations of PAHs, OPAHs and NPAHs in $PM_{2.5}$. Compounds in bold represent the highest mean contribution to the sum of all compounds.

Compound	Concentrations (ng m^{-3}) Minimum-maximum	Average	Average contribution to total (%)
16 PAHs	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)
NAP	(0.05-0.8)/(0.1-0.4)/(0.06-0.6)	(0.31)/(0.24)/(0.27)	(0.48)/(0.39)/(0.25)
ACY	(0.01-1.2)/(0.1-0.8)/(0.1-1.2)	(0.31)/(0.31)/(0.58)	(0.35)/(0.46)/(0.50)
AC	(0.03-0.13)/(0.02-0.09)/(0.01-0.2)	(0.07)/(0.04)/(0.07)	(0.15)/(0.08)/(0.06)
FLU	(0.05-1.3)/(0.1-1.0)/(0.1-1.5)	(0.43)/(0.41)/(0.63)	(0.53)/(0.65)/(0.56)
PHE	**(1.2-23.1)/(1.9-16.3)/(1.5-13.7)**	**(7.38)/(6.30)/(8.40)**	**(8.83)/(9.04)/(7.84)**
ANT	(0.5-3.4)/(0.3-1.9)/(0.3-2.9)	(1.07)/(0.79)/(1.43)	(1.48)/(1.23)/(1.32)
FLT	**(1.4-41.8)/(3.0-17.6)/(3.2-11.7)**	**(12.86)/(9.10)/(8.97)**	**(13.93)/(13.96)/(9.67)**
PYR	**(0.7-34.6)/(2.1-15.7)/(2.9-10.7)**	**(9.85)/(7.48)/(8.09)**	**(10.36)/(11.04)/(8.69)**
BaA	**(1.3-27.7)/(1.3-17.5)/(2.1-18.8)**	**(6.69)/(6.52)/(12.03)**	**(7.17)/(8.23)/(11.04)**
CHR	**(1.4-37.5)/(2.1-20.8)/(2.7-15.9)**	**(10.49)/(9.17)/(11.27)**	**(11.23)/(12.38)/(10.78)**
BbF	**(1.5-35.3)/(2.1-21.3)/(2.3-20.4)**	**(10.34)/(8.93)/(10.79)**	**(11.19)/(11.76)/(10.42)**
BkF	(1.6-15.4)/(1.2-7.4)/(1.3-6.6)	(5.51)/(3.94)/(4.30)	(6.76)/(5.80)/(4.43)
BaP	**(1.4-37.3)/(1.5-20.7)/(3.2-35.2)**	**(8.81)/(8.40)/(18.91)**	**(9.12)/(10.28)/(16.15)**
IcdP	(1.7-16.1)/(0.9-11.6)/(1.0-18.3)	(4.79)/(4.65)/(9.75)	(6.06)/(5.70)/(8.03)
DahA	(1.9-5.2)/(0.7-2.9)/(0.5-6.9)	(2.54)/(1.46)/(3.02)	(4.43)/(2.46)/(2.56)
BghiP	(2.53-17.0)/(1.2-10.7)/(1.4-15.4)	(5.80)/(4.70)/(8.80)	(7.86)/(6.47)/(7.62)
Total	(18-297)/(19-167)/(23-165)	(87.32)/(72.5)/(107.40)	
10 OPAHs	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)
1,4-NAQ	(0.02-8.1)/(0.16-3.1)/(0.1-4.2)	(2.25)/(1.27)/(1.66)	(6.22)/(5.39)/(3.70)
1-NALD	(0.2-0.8)/(0.07-0.5)/(0.08-0.9)	(0.43)/(0.20)/(0.49)	(2.71)/(1.19)/(1.25)
9-FLON	**(0.49-14.9)/(0.7-6.0)/(0.8-11.4)**	**(6.76)/(2.56)/(4.26)**	**(25.84)/(14.30)/(10.25)**
9,10-ANQ	**(0.3-36.4)/(1.2-46.1)/(2.8-36.04)**	**(8.31)/(13.33)/(14.28)**	**(24.31)/(35.83)/(32.74)**
1,8-NANY[a]	**(0.3-16.3)/(1.0-6.9)/(3.7-9.3)**	**(7.09)/(3.69)/(6.81)**	**(37.86)/(33.25)/(45.64)**
PHCA	(0.1-0.9)/(0.05-0.6)/(0.06-1.9)	(0.26)/(0.20)/(0.71)	(1.42)/(0.99)/(1.50)
BaFLU	(0.06-10.8)/(0.1-8.1)/(0.4-15.1)	(2.77)/(2.72)/(5.99)	(7.47)/(9.73)/(12.07)
BANTone	(0.08-15.1)/(0.04-8.3)/(0.5-19.8)	(2.46)/(2.63)/(9.27)	(6.10)/(9.05)/(19.12)
1-PYRCA	(0.007-1.8)/(0.008-1.5)/(0.05-4.2)	(0.31)/(0.39)/(1.31)	(0.74)/(1.24)/(1.96)

1,2-BANQ	(0.02-3.6)/(0.03-2.6)/(0.2-10.3)	(0.87)/(0.90)/(2.77)	(2.3)/(3.24)/(4.33)
Total	(1.8-87.9)/(3.6-55.3)(8.9-95.5)	(28.74)/(21.68)/(41.63)	
9 NPAHs	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)
1-NNAP	(0.01-0.1)/(0.008-0.04)/(0.005-0.03)	(0.03)/(0.01)/(0.01)	(4.38)/(3.08)/(0.57)
3-NDBF	**(0.08-1.5)/(0.02-0.06)/(0.03-2.4)**	**(0.33)/(0.03)/(0.89)**	**(33.39)/(7.92)/(22.39)**
5-NAC[b]	(0.04-0.1)/(<LOQ)/(0.03-0.35)	(0.08)/(<LOQ)/(0.18)	(5.64)/(<LOQ)/(4.67)
2-NFLU	(0.03-0.3)/(0.01-0.3)/(0.01-0.5)	(0.08)/(0.09)/(0.26)	(10.15)/(10.00)/(7.28)
9-NANT	**(0.01-1.2)/(0.06-0.1)/(0.4-2.4)**	**(0.36)/(0.41)/(1.18)**	**(27.13)/(53.45)/(47.5)**
3-NFLT	**(0.05-1.2)/(0.02-0.5)/(0.04-1.2)**	**(0.34)/(0.21)/(0.54)**	**(24.56)/(23.45)/(17.67)**
1-NPYR[c]	(0.01-0.1)/(0.01-0.06)/(0.008-0.2)	(0.05)/(0.06)/(0.02)	(2.92)/(2.48)/(2.01)
6-NCHR[d]	(0.05-0.2)/(<LOQ)/(0.009-0.02)	(0.09)/(<LOQ)/(0.01)	(5.6)/(<LOQ)/(0.5)
6-NBaP[e]	(<LOQ)/(<LOQ)/(0.02-0.08)	(<LOQ)/(<LOQ)/(0.05)	(<LOQ)/(<LOQ)/(1.26)
Total	(0.15-3.92)/(0.13-2.0)/(0.57-6.43)	(1.17)/(0.80)/(3.06)	

[a] Quantified in 28/54 samples
[b] Quantified in 7/54 samples
[c] Quantified in 35/54 samples
[d] Quantified in 5/54 samples
[e] Quantified in 11/54 samples
[NA] Not available due to lack of data for 3 h samples.

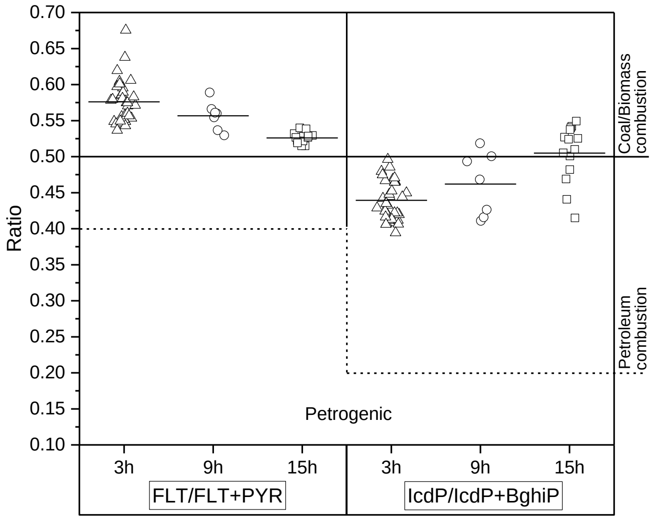

Figure 3. Column scatter of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) in the particulate phase at three different time sampling, open triangles and circles represent the daytime data for 3 h and 9 h samples, respectively, open squares represent the night-time data of 15 h. The dash line separates the petroleum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

Table 3. Average Concentration of $\sum BaP_{eq}$ in ng m^{-3} and cancer risk assessment for the sum of 16PAHs, 1OPAH and 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)	28.28	3.17 x 10^{-5}	2.46 x 10^{-3}	31[b] – 2460[c]
24h (n=54)	**23.6**	**2.6 x 10^{-5}**	**2.05 x 10^{-3}**	**26[b] – 2053[c]**

[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

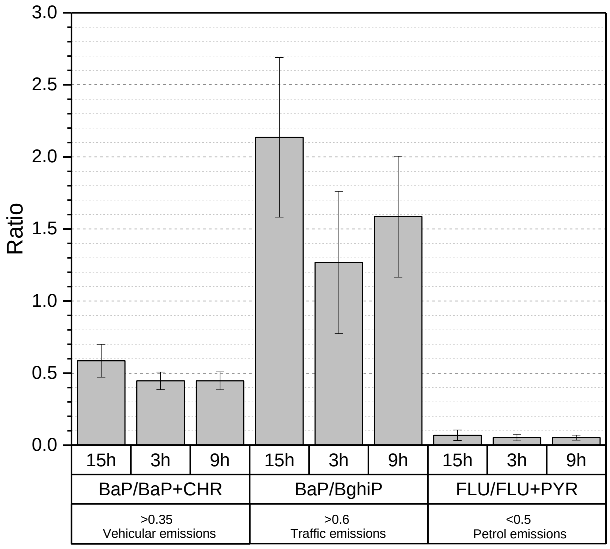

Figure 4. Column distribution of BaP/BaP+CHR, BaP/BghiP and FLU/FLU+PYR in the particulate phase at three different time sampling. 3 h and 9 h represent samples collected during the day and 15 h for samples at night. Error bars reflect standard deviations.

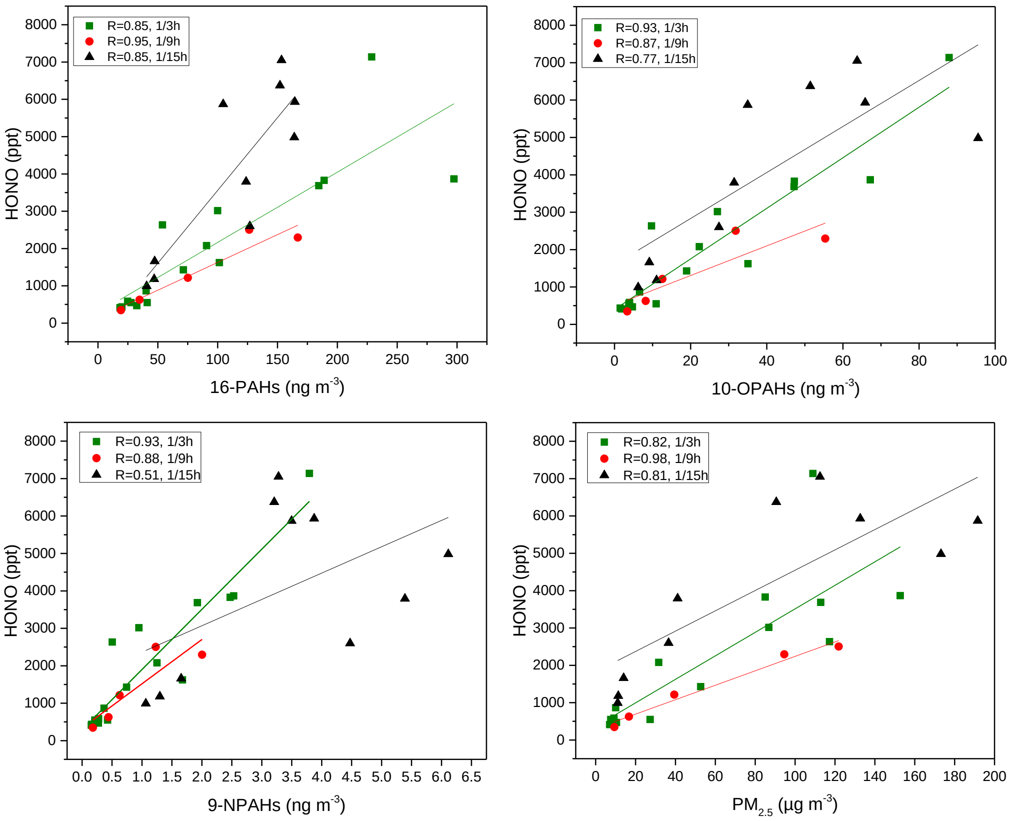

Figure 5. Correlation coefficient of ∑PAHs, ∑OPAHs, ∑NPAHs and PM$_{2.5}$ with HONO. Time sampling resolution 1/3 h and 1/9 h refer to diurnal concentrations and 1/15 h to nocturnal concentrations. Significance levels were between 0.001 and 0.05 except for HONO and NPAHs at night, P level > 0.05 and Pearson coefficient 0.52.

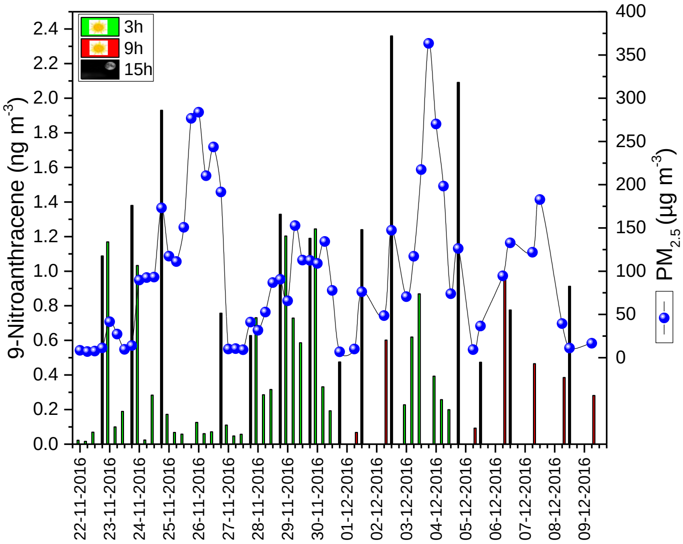

Figure 6. Temporal variation of 9-Nitroanthrance and $PM_{2.5}$ during the entire winter campaign.