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Diurnal concentrations, sources, and cancer risk assessments of $PM_{2.5}$-bound PAHs, NPAHs, and OPAHs in urban, marine and mountain environments

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Abstract

Ambient measurements of $PM_{2.5}$-bounded polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs (NPAHs), and oxy-PAHs (OPAHs) were conducted during the summer in Jinan, China, an urban site, and at Tuoji island and Mt. Tai, two background locations. 3.5 h and 11.5 h sampling intervals in daytime and nighttime were utilized to research the diurnal variations of PAHs, NPAHs, and OPAHs. The concentrations of PAHs, NPAHs, and OPAHs were highest at the urban site and lowest at the marine site. The diurnal patterns of PAHs and NPAHs at the urban and marine sites were dissimilar to those observed at the mountain site partly due to the influence of the boundary layer. Vehicle emissions at the urban site made a large contribution to high molecular weight PAHs. 1N-PYR and 7N-BaA during morning and night sampling periods in JN were relatively high. Fossil fuel combustion and biomass burning were the main sources for all three sites during the sampling periods. The air masses at the marine and mountain sites were strongly impacted by photo-degradation, and the air masses at the marine site were the most aged. Secondary formation of NPAHs was mainly initiated by OH radicals at all the three sites and was strongest at the marine site. Secondary formation was most efficient during the daytime at the urban and mountain sites and during morning periods at the marine site. The average excess cancer risk from inhalation (ECR) for 70 years' life span at the urban site was much higher than those calculated for the background sites.

Keywords

PAHs, NPAHs, OPAHs, marine and mountain sites, diurnal variations

1. Introduction

Increasing levels of ambient particulate matter (PM) pollution from rapid urbanization and economic development in China have drawn worldwide attention and have substantial adverse effect on human health (Wang et al., 2014). The International Agency for Research on Cancer

(IARC) classified PM from outdoor air pollution as carcinogenic to humans in 2013 (Loomis et al., 2013). The toxicity of PM is dependent on the certain chemical components, such as polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives. PAHs are known to be mutagenic, genotoxic, and carcinogenic persistent organic pollutants (Abdel-Shafy and Mansour, 2016; Łuczyński et al., 2005) and are mainly emitted by incomplete combustion of organic materials, such as from coal and biomass burning, vehicle emissions, and industrial processes. NPAHs and OPAHs are nitrated and oxygenated derivatives of PAHs, respectively. Many NPAHs and OPAHs are more toxic than their parent PAHs due to their direct-acting mutagenicity and carcinogenicity (Albinet et al., 2008; Pedersen et al., 2005), and high molecular weight NPAHs and OPAHs generally present a greater hazard to health due to their carcinogenic behavior. NPAHs and OPAHs are not only directly co-emitted with PAHs but also formed through atmospheric photochemical reactions of parent PAHs with OH, NO_x, and O_3 radicals (Reisen and Arey, 2005; Jariyasopit et al., 2014). The relative contributions of primary and secondary sources of NPAHs and OPAHs varies greatly between different sampling sites and periods (Kojima et al., 2010; Li et al., 2015).

To date, surveys of the concentrations, sources, transformation reactions, and long-distance transport of NPAHs and OPAHs have been carried out in 24 h, monthly, and seasonal sampling periods (Albinet et al., 2007, 2008; Zhuo et al., 2017; Zimmermann et al., 2012), which may be influenced by the sampling artifact mainly including oxidative degradation caused by O_3 within the samplers (Balducci et al., 2018; Liu et al., 2014). Possibly due to the limits of current analytical techniques or the low concentration of NPAHs and OPAHs bounded in PM, shorter temporal sampling resolution measurements studies are scarce. As we know, only a few studies

have reported 12 h (Ringuet et al., 2012; Souza et al., 2014), 3 or 4 h (Alam et al., 2015; Tsapakis and Stephanou, 2007), and 3.5 h and 11.5 h time intervals during the daytime and nighttime, respectively (Reisen and Arey, 2005) measurements to analyze the diurnal variation of NPAHs and OPAHs, which were mainly carried out at one or two sampling sites among traffic site, suburban site, rural site, urban site, urban background site and marine background site, and the molecular compositions of NPAHs and OPAHs were different from those in the paper. No research has been found to study the diurnal variation of NPAHs and OPAHs under mountain atmosphere conditions by short time intervals, let alone the detailed comparison among mountain, marine and urban sampling sites. Less resolved measurements are subjected to substantial disadvantages when attempting to understand the physical and chemical processes (e.g., secondary formation) in the atmosphere (Ringuet et al., 2012). Shorter sampling periods are more conducive to exploring the fate and governing factors of NPAHs and OPAHs (Elorduy et al., 2016).

The concentrations and physicochemical properties of chemicals present in the atmospheric environment vary by sampling regions due to many factors, such as differences in population density, life style, or meteorological conditions (Seinfeld et al., 2004; Wang et al., 2012). Therefore, the molecular components and levels of PAHs, NPAHs, and OPAHs in PM may show significant difference between urban and background areas. For example, urban areas in China with greater population, dense traffic, and developed industry emit large amount of pollutants and frequently exhibit haze episodes (Wang et al., 2011b), which leads to high levels of PAHs, NPAHs, and OPAHs. Conversely, background areas are typically characterized by sparse population and less emission sources, and may be significantly impacted by

long-distance transport, where the PAHs, NPAHs and OPAHs may be relatively aged. The majority of previous studies on PAHs, NPAHs, and OPAHs were conducted in urban areas, such as Beijing (Wu et al., 2014), Shenyang (Miller-Schulze et al., 2010), Xi'an (Wei et al., 2015), Guangzhou (Tan et al., 2011), Southern European cities (Alves et al., 2017) and Braga, Portugal (Alves et al., 2016), where PAHs, NPAHs, and OPAHs are present in high concentrations. Limited information has been reported on the sources and properties of PAHs, NPAHs, and OPAHs in background areas in China (Liu et al., 2013) and other developing countries (Lee et al., 2006), which inhibits the characterization and evaluation of regional pollution, transport, and human exposure risk.

With the rapid economic development, China has the largest emissions of PAHs in the world (annual emission 106 Gg in 2007, accounting for 21% of the global total emission) (Shen et al., 2013), the North of China as one of the most polluted areas have more intensive emission (Xu et al., 2005). In order to investigate the diurnal and spatial variations, sources, secondary formation, long-distance transport, and cancer risk assessments of PAHs, NPAHs, and OPAHs, $PM_{2.5}$ samples were collected in three distinct locations (an urban, a mountain, and a marine site) in the North of China at 3.5 h and 11.5 h intervals during the daytime and nighttime, respectively.

2. Methodology

2.1. Study sites and sampling

$PM_{2.5}$ samples were collected at three sites in the North of China. Jinan (JN), the highly populated capital of Shandong Province, was selected to represent an urban environment. The area is characterized by poor atmospheric diffusion conditions due to the surrounding

mountains on three sides and high pollutant emissions (Yang et al., 2007). The sampling site in JN (36°40'N, 117°03'E; 50 m above sea level; a.s.l.) (Fig. 1) was on the rooftop of a building at the central campus of Shandong University. It is surrounding by school, residential, and commercial areas, with no significant stationary pollution sources. The mountain site was at the summit of Mount Tai (MT, 36°15'N, 117°06'E 1465 m a.s.l.) in the southeast of Shandong Province in the center of Northern China, which represents the mountain background site. It is strongly influenced by the East Asian monsoon circulation and is an ideal location for investigating atmospheric chemistry processing of air pollutants because the measurement site was located above the nighttime planetary boundary layer. The sampling site for MT was located at the Kongjun Hotel, which is far from the frequently visited zones. So the data obtained in the area can be regional representative due to unique geographical location, climatic conditions and negligible anthropogenic emissions. The marine sampling site Tuoji Island (TJ; 38°11'N, 120°44'E; 153 m a.s.l.) was located in the middle of the Bohai Strait at the distance of about 40 km and 70 km from Penglai and Dalian, which is considered as the marine background site. This site had the lowest elevation among the background monitoring stations and is the sole marine atmospheric background station in Northern China. It is an ideal receptor site for investigating continental outflow pollution. Details of the site has been described in greater detail previously (Zhang et al., 2014; Zhang et al., 2016; Zhang et al., 2018).

$PM_{2.5}$ samples were collected in TJ from June 12 to 17, in JN from June 22 to July 04, and in MT from July 09 to 23, 2015 by a mid-volume suspended particle sampler (Model TH-150 A; Wuhan Tianhong Corporation, China). Quartz filters with 1 μm pore size and 88 mm diameter were used to collect samples (Pall Gelman Inc., USA,). Each filter was baked for 6 h at 600°C

before sampling. The flow rate of the samplers was 100 L min^{-1}, and each sampler was calibrated before and after sampling. The sampling time periods per day was 7:00-10:30 (morning), 11:00-14:30 (day), 15:00-18:30 (evening), and 19:00-6:30 the next day (night) local time. The concentration during daytime period means the average concentration during morning, day and evening periods. Frequent rainfall events occurred during the sampling periods at the mountain and urban sites, so 20 samples (5 samples from the four sampling time periods) were selected for each site. Rainy sampling days were excluded from the analysis.

2.2. Sample analysis

Due to short sampling time and low levels of NPAHs and OPAHs at the background sites, the sample filters (three circles with a diameter of 25 mm from every sample filter) obtained in the same time interval at the same sampling site were combined prior to analysis. The combined samples were analyzed by Soxhlet extraction with 150 mL dichloromethane (DCM) for 8 h. The extracted samples were concentrated to about 1 mL by rotary evaporation and then fractionated by silica/alumina gel columns (1 cm internal diameter × 35 cm length). 12 cm alumina (bottom), 12 cm silica (middle), and 1cm anhydrous sodium sulfate (top). The silica and alumina were baked for 6 h at 400 °C by muffle furnace and then activated at 130 °C for 16 h before use. The purification columns were eluted by 20 mL hexane (discarded) and then by 70 mL mixture of hexane and DCM (1:1, v/v) (collected). The elutes were concentrated by a rotary evaporator to about 1 mL at 30±1°C (water bath), added to 10 mL hexane for solvent displacement, and then evaporated again to 1-2 mL by rotary evaporation. The concentrated elutes were further concentrated to 1 mL under high purity nitrogen stream at 30±1 °C. Internal standards

(naphthalene-d_8, anthracene-d_{10}, pyrene-d_{10}, perylene-d_{12}, 1-nitronaphthalene-d_7, 9-nitroanthracene-d_9, 1-nitropyrene-d_9, 6-nitrochrysene-d_{11} and anthraquinone-d_8) were spiked prior to the sample injection into the gas chromatography - mass spectrometer (GC-MS). All used glassware devices were soaked in potassium dichromate lotion, rinsed by purified water and ultrapure water, and then baked at 100 °C until dry.

A gas chromatograph coupled (GC, Agilent 7890A) with a triple quadrupole mass spectrometer (MS/MS, Agilent 7000) with a 5% phenyl substituted methylpolysiloxane GC column (HP-5MS, length: 30 m, diameter: 0.25 mm, film thickness: 0.25 μm, Agilent, USA) was used to analyze PAHs. The system was set to use electron impact ionization (EI) in selected ion monitoring (SIM) mode. The oven temperature program was held at 60°C for 1 min, gradually increased to 150 °C at the rate of 40 °C/min where it was held for 5min, and then increased to 300 °C at 4°C/min and held for 15min. 17 different PAHs were detected based on retention time and qualitative and quantitative ions of standard PAHs. The NPAHs and OPAHs was also measured by GC-MS/MS with HP-5MS column using negative chemical ionization (NCI) in SIM mode. The GC oven temperature program for NPAHs and OPAHs was 60 °C for 1 min, ramped at 15 °C /min to 150 °C, to 300 °C at a rate of 5 °C, then held for 15 min.

The targeted analytes included acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHY), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), indeno(1,2,3-cd)pyrene (IcdP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP), coronene (COR), 5-nitroacenaphthene (5N-ACE), 2-nitrofluorene (2N-FLU), 9-nitroanthracene (9N-ANT),

9-nitrophenanthrene (9N-PHE), 3-nitrophenanthrene (3N-PHE), 2-nitroanthracene (2N-ANT), 2+3-nitrofluoranthene (2+3N-FLT), 1-nitropyrene (1N-PYR), 2-nitropyrene (2N-PYR), 7-nitrobenzanthracene (7N-BaA), 6-nitrochrysene (6N-CHR), 6-nitrobenz(a)pyrene (6N-BaP), 9-fluorenone (9FO), anthraquinone (ATQ), phenanthrene-9-aldehyde (PHE-9-ALD), benzanthrone (BZO), benzaanthracene-7,12-dione (BaAQ).

2.3. Quality control and data analysis

The air sampler without a denuder for reactive gaseous species removal may result in sampling artifacts due to the degradation of PAHs and their derivatives (Menichini, 2009; Liu et al., 2014), but the denuder-based sampling system has not yet been used widely in literature. So the sampling artifacts was not considered too much in the paper, which may lead to underestimation of PAHs and their derivatives, especially BaP.

Prior to sample analysis, surrogate standards, including acenaphthene-d_{10}, chrysene-d_{12}, 2-nitrofluorene-d_9 and 3-nitrofluoranthene-d_9, were spiked in 50% randomly loaded filters in order to monitor the complete analysis process. The recoveries were: acenaphthene-d_{10} 84±14%, chrysene-d_{12}: 91±10%, 2-nitrofluorene-d_9: 98±26%, and 3-nitrofluoranthene-d_9: 84±15%. The method recoveries were tested by spiking 50 ng, 100 ng, and 200 ng standards of target PAHs, NPAHs, and OPAHs in the cleaned filters, and the recoveries were 97±15% for PAHs and 90±14% for derivatives. Procedural, lab, and field blanks were analyzed, and the measured values of PAHs, NPAHs, and OPAHs were negligible. The blank values and recoveries were not used to correct the measured values of the samples. Duplicate samples from the same filters, which were extracted and measured by GC-MS/MS using the same protocol above mentioned,

were analyzed, and the average variation was 11.2%.

3. Results and discussion

3.1. Diurnal variation of PAHs, NPAHs, and OPAHs concentrations

The concentrations of the individual PAHs, NPAHs, and OPAHs during the four sampling periods are presented in Fig. 2 and TableS. 1. The concentration of total PAHs at the urban site ranged from 12.17 to 26.65 ng m^{-3}, with a mean of 19.45 ng m^{-3}, which is much higher than those at the marine (between 3.07 and 6.36 ng m^{-3}, with a mean value of 4.44 ng m^{-3}) and mountain sites (ranged from 3.27 to 6.98 ng m^{-3}, with an average of 5.39 ng m^{-3}). A similar diurnal pattern was observed at the marine and urban site with the highest PAHs concentrations during the morning and night sampling periods. This is different from the result that no obviously diurnal pattern for PAHs at Mediterranean marine background site, Finokalia, Island of Crete was found in Tsapakis and Stephanou, (2007). Direct emissions from vehicular traffic during the morning period, and the lower mixing layer height and heavy truck traffic (yellow-labeled vehicles were not banned in the night) during the night period likely contributed to the high PAHs concentrations observed during these times. The concentration is lower during the evening period likely due to the enhanced photochemical activity during the day period. Most individual components showed a similar diurnal pattern at JN and TJ sites, for example FLU, PHE, BaA, CHY, BbF, BkF, BaP, IcdP and BghiP, which all shows a substantial morning and night rush time peak, which is slightly different from the study in PM_{10} in Birmingham UK (Alam et al., 2015) with maximum level during morning period (7:00-11:00), and is similar to that in East of France at three urban sites (Strasbourg, Besancon and Spicheren)

in PM_{10} with highest concentrations during morning (04:00-10:00) and evening (16:00-22:00) times (Delhomme and Millet, 2012). Han et al., (2011) suggested that the peak of PAHs concentration in five US counties (Maricopa, AZ, Anoka, MN, Harris, TX, Pinellas, FL and Jefferson, KY) occurred during morning rush hour times (6:00), and the peak was also observed during nighttime in Sacramento, CA. However, the PAHs measured at the mountain site exhibited higher concentrations during the morning and day periods and the lowest concentrations during the night period. Every individual species showed higher concentration during the daytime (the average concentration during morning, day and evening periods), compared with that during the nighttime at MT. The high elevation of the sampling location (about 1500 m) may have impeded the transport of air masses from ground level to the top of the mountain during the night period, resulting in the lower concentration.

FLT, CHY, BbF, and BghiP were the dominant PAHs at the urban site, accounting for 43.1%-47.3% of total PAHs, in all measurements, which indicates that the major source was likely coal combustion and vehicle emissions. FLU, PHE, FLT, and CHY were dominate in the samples from the marine and mountain sites, accounting for 50.9%-61.5% and 53.3%-61.0%, respectively. The distinctions in the composition profiles at the urban and background sites were likely due to the difference in their emission sources, photochemical degradation rates, and loss due to condensation and deposition during transport (Wang at al., 2009). PAHs with molecular weights between 252-300 (from BbF to COR) accounted for 33.8%-53.4% of the total PAHs with higher percentages found during morning and night periods at the urban site. This was well correlated with the early and late peaks in traffic emissions. Differently, the contribution of high molecular weights (e.g., 5,6,7- ring PAHs) to the total PAHs was significantly lower at the

marine (21.3%-30.7%) and mountain (25.2%-32.7%) sites, which may be attributed to loses during transport and a limited number of motor vehicles at the two sites. Previous studies have also reported that high molecular weight PAHs made a large contribution to the total PAHs in Xi'an, an urban site (Okuda et al., 2010) and in Malaysia, a semi-urban area (Khan et al., 2015).

The concentration of 12 NPAHs at the urban site ranged from 71.41 to 237.6 pg m^{-3}, with a mean value of 153.7 pg m^{-3}. This was 3.61 and 3.27 times higher than in samples from the marine (30.78 - 62.31 pg m^{-3}, average: 42.60 pg m^{-3}) and mountain (32.50 – 68.07 pg m^{-3}, average: 47.00 pg m^{-3}) sites. The total concentration of 12 NPAHs is almost two orders of magnitude lower than the total average concentration of the 17 PAHs measured at the three sites, The three most abundant NPAHs at the urban site were 9N-ANT, 2+3N-FLT, and 2N-PYR, accounting for 78.2%-88.1% of total NPAHs. Similar molecular composition patterns were found at the background sites, accounting for 81.5%-92.9% at the marine site and 81.2%-91.5% at the mountain site. The concentrations of total NPAHs at the marine sites were higher during the morning and night periods compared with those during day and evening periods, which was the same as the observed diurnal variation of PAHs. However, the concentration of NPAH varied considerably at the mountain site, with lowest values observed during the night period and highest during the day period. This was dissimilar to the diurnal cycle of total PAHs.

1N-PYR, which solely originates from direct emissions (mainly from diesel powered engines) (Nielsen, 1984), ranged from 5.09 to 2.22 pg m^{-3} at the urban site, with the greatest concentrations occurring during periods of increased traffic. 7N-BaA exhibited similar diurnal variation as 1N-PYR at the urban site, which is the most abundant compound in diesel fuel particles (Finlayson-Pitts and Pitts, 2000). The concentrations of 7N-BaA were found to be the

highest at the urban sites, followed by the mountain site (from 0.76 to 1.81 pg m^{-3}), and then the marine site (from 1.03 to 1.12 pg m^{-3}). This suggests that local emissions were relatively small contributors at the background sites. The average concentration of 2+3N-FLT in the daytime including morning, day and evening time periods at MT site was much higher than that in the nighttime, but the same level was shown during daytime and nighttime at TJ site, and slightly lower level was found in the daytime at JN than that in nighttime. But 2N-PYR had a peak during morning time and was much higher in the daytime compared with that in the nighttime at the three sites. This is may associated with the daytime formation of 2+3N-FLT and 2N-PYR or 3N-FLT from vehicle emissions possibly had a unexpected role, and the influence of NO_3 is also can't be ignored. Alam et al., (2015) and Tsapakis and Stephanou, (2007) found that the concentrations of 2+3N-FLT and 2N-PYR were higher in daytime than those in nighttime in UK and Mediterranean.

The concentration of the 6 measured OPAHs was higher at the urban site (an average value of 0.85 ng m^{-3}) than at the mountain (0.28 ng m^{-3}) and at the marine site (0.22 ng m^{-3}). This is almost one order of magnitude lower than concurrent concentration of total PAHs. Our measured OPAHs at the urban site were more concentrated than measurements conducted in than Taiyuan (0.71 ng m^{-3}), Dezhou (0.03 ng m^{-3}), and Yantai (0.08 ng m^{-3}) (Li et al., 2015). The concentrations of OPAHs was highest in the morning and day periods at all three sites, which is distinct from the diurnal variations of PAHs and NPAHs. This difference may be partly due to the fact that OPAHs are mainly emitted from solid fuel burning such as coal, firewood, and crop residues in Northern China and vehicle emissions contributed relatively little to OPAHs compared with to PAHs and NPAHs (Li et al., 2015). no obviously diurnal pattern of OPAHs

was found at Finokalia, Island of Crete without local emissions (Tsapakis and Stephanou, 2007). The six OPAHs components all presented higher levels in the daytime than those in the nighttime in marine and mountain background sites. The most abundant OPAH was 9FO, followed by ATQ in the three sites, accounting for 80.9%- 96.1% of total OPAHs.

3.2. Source diagnostics

Diagnostic ratios are frequently used to identify the sources of PAHs because the distributions of the homologues are strongly related with the formation mechanisms of organic species with similar characteristics (Kavouras, 2001). Diagnostic tool should be used with caution because some ratios are variable in the atmosphere due to the different degradation ratios of some PAH species (Ding et al., 2007).

FLT, PYR, IcdP and BghiP have comparable degradation ratios (Behymer and Hites, 1988), so the ratios of FLT/(FLT+PYR) and IcdP/(IcdP+BghiP) can reveal original compositional information during transportation and ensure the accuracy of source evaluation at receptor sites. A FLT/(FLT+PYR) ratio higher than 0.5 indicates coal/biomass burning and between 0.4 and 0.5 indicates petroleum combustion (Pio et al., 2001; Yunker et al., 2002), as shown in Table 1. A ratio of IcdP/(IcdP+BghiP) higher than 0.5 indicates coal/ biomass combustion, and a ratio lower than 0.2 is characteristic of petroleum source. A IcdP/(IcdP+BghiP) ratio between 0.2 and 0.5 (or 0.18-0.40) indicates petroleum combustion (Pio et al., 2001; Yunker et al., 2002). The IcdP/(IcdP+BghiP) ratios ranged from 0.40 to 0.43, with an average value of 0.41 at the urban site (Table 1), implying that petroleum combustion was a strong contributor. Comparable values were also observed in other Chinese cities, such as Shanghai (Feng et al., 2006), Beijing (Okuda et al., 2006), Qingdao (Guo et al., 2003), and Nanjing (Wang et al., 2006). A negligible

difference in the IcdP/(IcdP+BghiP) ratio at the marine (from 0.37 to 0.42, average: 0.39), mountain (from 0.42 to 0.47, average: 0.45), and urban sites was found. The ratio is lower than those obtained in Florence, a urban background site and Athens, a suburban site (all higher than 0.5) in summer (Alves et al., 2017). But the ratios of IcdP/(IcdP+BghiP) at the background sites in this paper were comparable with that previously obtained at the Yellow River Delta National Nature Reserve (YRDNNR) in the summer (0.46) (Zhu et al., 2014). The average values of the FLT/(FLT+PYR) ratio at the urban (0.68), marine (0.68), and mountain (0.66) sites were similar, and all were higher than 0.5 indicating that coal or biomass combustion was a main source. The ratios were slightly higher than those at Florence and Athens (all higher than 0.5, but lower than 0.6) in summer, but much higher than that in Oporto, a urban site (lower than 0.3) (Alves et al., 2017). No obvious diurnal variations of the ratios were observed at the three sites, indicating that the main source did not change during different sampling intervals. In conclusion, the two diagnostic ratios suggest that fossil fuel and biomass combustion were the main sources at the urban and background sites during the summer.

BaA and BaP degrade faster than their corresponding homologues (CHR and BeP), which may significantly influence diagnostic ratios for source and downwind regions (Behymer and Hites, 1988; Zhang et al., 2005). By leveraging these isomer pairs (BaA/CHR and BaP/BeP) the residence time of particulate PAHs in the atmosphere can be evaluated. The ratios of BaP/BeP and BaA/CHR were plotted in Fig. 3A and 3B during the four sampling periods for the urban, marine, and mountain sites. The average ratios were the highest at the urban site (BaA/CHR: 0.46 and BaP/BeP: 0.46), and the lowest ratios were observed at the marine site ((BaA/CHR: 0.34 and BaP/BeP: 0.27), implying that the air masses collected at the urban site were relatively

fresh and most aged at the marine site. The ratios at the marine and mountain sites during the sampling periods were persistently less than 0.4, suggesting that air masses were strongly influenced by photo-degradation and long distance transport likely played an important role (Liu et al., 2013). In the urban area, the ratios of BaA/CHR and BaP/BeP were relatively low in day and evening periods, indicating the influence of photochemical reaction. The diurnal patterns of BaP/BeP in marine area was the same with that in urban area, but was different from that in mountain areas with higher values in day and night periods.

The ratio of 2N-FLT/1N-PYR has been traditionally applied to differentiate primary emission and secondary formation of NPAHs in the atmosphere. 1N-PYR mainly derived from diesel powered engines (Nielsen, 1984), while 2N-FLT is known to be formed by atmospheric photochemical reactions initiated by OH radicals in the daytime and NO_3 radicals in the nighttime, and has never been observed from direct emissions (Arey et al., 1986). A ratio of 2N-FLT/1N-PYR higher than 5 indicates secondary formation of NPAHs, while a ratio lower than 5 indicates the primary emissions (Albinet et al., 2007; Bandowe et al., 2014). In our study, the isomers of 2N-FLT and 3N-FLT were not separated by our GC-column HP-5MS and analytical procedure. However, many previous studies have reported that 2+3N-FLT/1N-PYR can be used in lieu of to replace the original 2N-FLT/1N-PYR ratio due to negligible abundant of 3N-FLT in the air compared with 2N-FLT (Bamford and Baker, 2003). Fig.3C presents the ratios of 2+3N-FLT/1N-PYR from the three sites during the four sampling periods. While the average value at the urban site (17.5) was significant lower than that at the marine (27.3) and mountain (25.8) sites, this diagnostic ratio reveals that atmospheric secondary formation of 2N-FLT dominated at the urban and background sites. The ratio values were comparable to that

obtained in the North China in the hot season (23.6) (Lin et al., 2015), but much lower than that (89.1) observed during the winter in Wanqingsha, the South of China (Huang et al., 2014). The greatest ratio (24.9) at the urban site was found in the day samples during periods of highest photochemical activity, which is similar to that at the mountain site. The ratio at the marine site was the highest in the morning period.

The ratio of 2N-FLT/2N-PYR has been widely used to explore the occurrence and relative importance of OH vs NO_3 radical initiated oxidation pathways for the formation of NPAHs in the atmosphere (Arey et al., 1986). 2N-PYR is formed from PYR reacting with an OH radical in the presence of NO_2, but is not formed from the reaction with NO_3 radical (Arey et al., 1986). A ratio close to 10 indicates the dominance of the OH radical-initiated reaction, while a ratio close to 100 indicates that the NO_3 radical-initiated reactions dominate NPAHs formation (Albinet et al., 2007; Wang et al., 2011a). In our study, the average ratios at the urban (4.0), marine (9.6), and mountain sites (8.8) (Fig.3D) were all less than 10, indicating the domination of day-time OH radical-initiated formation pathways. This is consistent with previously reported values from the summer season in North China (4.5) (Lin et al., 2015) and in Beijing (below 10) (Wang et al., 2011a). The highest ratios were observed during the night period at the urban site, which is similar to trends at the two background sites. The ratios at the background sites were significantly higher than the urban site, which may partly be due to the higher concentration of NO in the urban atmosphere because the reaction of NO_3 with NO leads to low level of NO_3 (Huang et al., 2014).

3.3.Evaluation of excess cancer risk

The lifetime excess cancer risk from inhalation (ECR) of PAH and NPAHs mixtures was applied to assess the carcinogenicity of the samples. This method has been recommended by the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA) and has been widely utilized in many previous studies (Bandowe et al., 2014; Wei et al., 2015; Zhu et al., 2014; Ramirez et al., 2011; Alves et al., 2017). The carcinogenic risk of each PAH or NPAH compound was estimated based on its BaP equivalent concentration (BaP_{eqi}), which is calculated by multiplying individual compound concentration (C_i ng m^{-3}) by the corresponding toxicity equivalency factor (TEF_i) as Eq (1). The TEF values for 15 PAHs and 6 NPAHs were taken from Collins et al., (1998) and Nisbet and Lagoy (1992), who reported the toxic potency of each PAH or NPAH relative to BaP (Petry et al., 1996). The risk of OPAHs was not evaluated due to the lack of available TEF data. Using Eq (1), the toxic equivalency (TEQ) is the sum of target compound BaP_{eq}.

$$BaP_{eqi} = C_i * TEF_i \quad \text{and} \quad TEQ = \sum(C_i * TEF_i) \qquad (1)$$

ECR was assessed by employing Eq (2), where UR_{BaP} is the unit inhalation cancer risk factor of BaP. The UR_{BaP} is defined as the number of people who will develop cancer from the inhalation of 1 ng/m^3 BaP_{eq} within a lifetime of 70 years. The UR_{BaP} was suggested to be 8.7×10^{-5} (ng m^{-3})$^{-1}$ by the World Health Organization (WHO) and 1.1×10^{-6} (ng m^{-3})$^{-1}$ by CalEPA (OEHHA, 1994; WHO, 2000). This means that 8.7 or 0.11 cases per 100,000 people with inhalational exposure to 1 ng/m^3 of BaP over a lifetime of 70 years would have cancer risk.

$$ECR = TEQ * UR_{BaP} \qquad (2)$$

The mean TEQ at the urban site was 2.49 ng m^{-3} for the 21 target compounds, which is substantially higher than for the mountain (0.43 ng m^{-3}) and marine (0.33 ng m^{-3}) sites. The

TEQ at the urban site was much lower than the national standard of 10 ng m^{-3}, but higher than the WHO standard (1 ng m^{-3}) (Ventafridda et al., 1987). The value at the urban location was also much lower than what was previously calculated for Beijing, China (Jia et al., 2011), Xi'an, China (Bandowe et al., 2014) and Zonguldak,Turkey (Akyuz and Cabuk, 2008), but higher than those for western and southern European cities (Martellini et al., 2012; Alves et al., 2017). The values at the marine and mountain locations were comparable with that observed in the YRDNNR in summer (0.45 ng m^{-3}) (Zhu et al., 2014). BbF, BaP, IcdP, and DahA, especially DahA and BaP, contributed significantly to the TEQ value at the three sites. The actual TEQ may be higher in view of the BaP degradation by O_3 during air sampling on the filters (Menichini et al., 2009). The TEQ diurnal patterns at the three sites were consistent with the daily variation of total PAHs concentration, which was highest during morning and night periods at the urban and marine sites and during morning and day periods at mountain site. The contribution of average TEQ of 6 NPAHs to the total TEQ was larger at the background sites (MT, 1.72% and TJ, 1.34%) than that at the urban site (0.41%), which may due to the influence of secondary formation of NPAHs during long-distance transport and high concentration of PAHs at urban site.

The average ECR for 70 years' life span was 2.17×10^{-4} (WHO method) and 2.74×10^{-6} (CalEPA method) at the urban site. Hence, inhalation of the 21 measured compounds could result in 217 or 3 cases of cancer per million adult residents in Jinan, respectively. This was higher than estimates for the marine (29 WHO method and 1 CalEPA method cases per million) and mountain (38 WHO method and 1 CalEPA method cases per million) sites. The lower ECR at background sites is likely attributable to less direct source emissions, lower population, and

favorable diffusion conditions. The acceptable or negligible threshold of ECR using WHO method based on American Environmental Protection Agency is 10^{-6}, so the lifetime excess cancer risk should be paid attention for healthy protection in the future in the Chinese cities.

4. Summary

In this study, PAHs, NPAHs, and OPAHs were investigated during the summer in the Northern China at an urban site and two background sites at 3.5 h and 11.5 h sampling intervals. The average concentrations of PAHs, NPAHs, and OPAHs at the urban site were 19.45 ng m^{-3}, 153.7 pg m^{-3}, and 0.85 ng m^{-3}, respectively, which were 3.61-4.38 and 3.05-3.61 times higher than those at marine and mountain sites, respectively. The concentrations of PAHs and NPAHs were greatest during morning and night periods at the urban and marine sites and during morning and day periods at the mountain site. The concentration of OPAHs was highest during the morning and day periods at all the three sites. The diurnal variations of high molecular weight PAHs (e.g., 1N-PRY and 7N-BaA) at the urban site was closely linked to vehicle emissions.

On the basis of diagnostic ratios, the main sources of PAHs were found to be fossil fuel and biomass combustion. The air masses at the background sites, especially at the marine site, were more aged compared with those at the urban site. The atmospheric reactions were most efficient at the marine site, followed by the mountain site. The main reaction pathway was OH-initiated radical reactions at the urban and background sites. The contribution of secondary formation to the total PAHs was largest during the day period at the urban and mountain sites and during morning period at the marine site.

The mean toxicity equivalency factor at the urban site was higher than those at marine and mountain sites and greater than the guidelines suggested by the World Health Organization. The average excess cancer risk from inhalation (ECR) for 70 years' life span was highest at the urban site.

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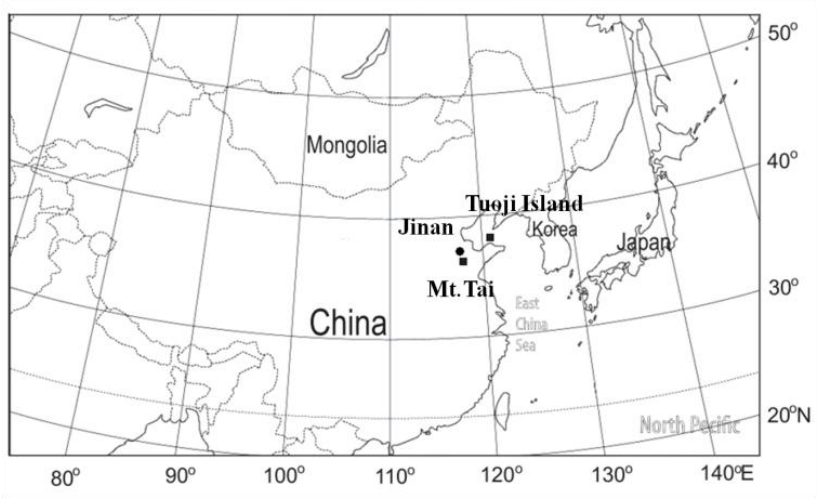

Fig. 1. The three sampling locations (Wang et al., 2009). The squares indicate background sampling sites.

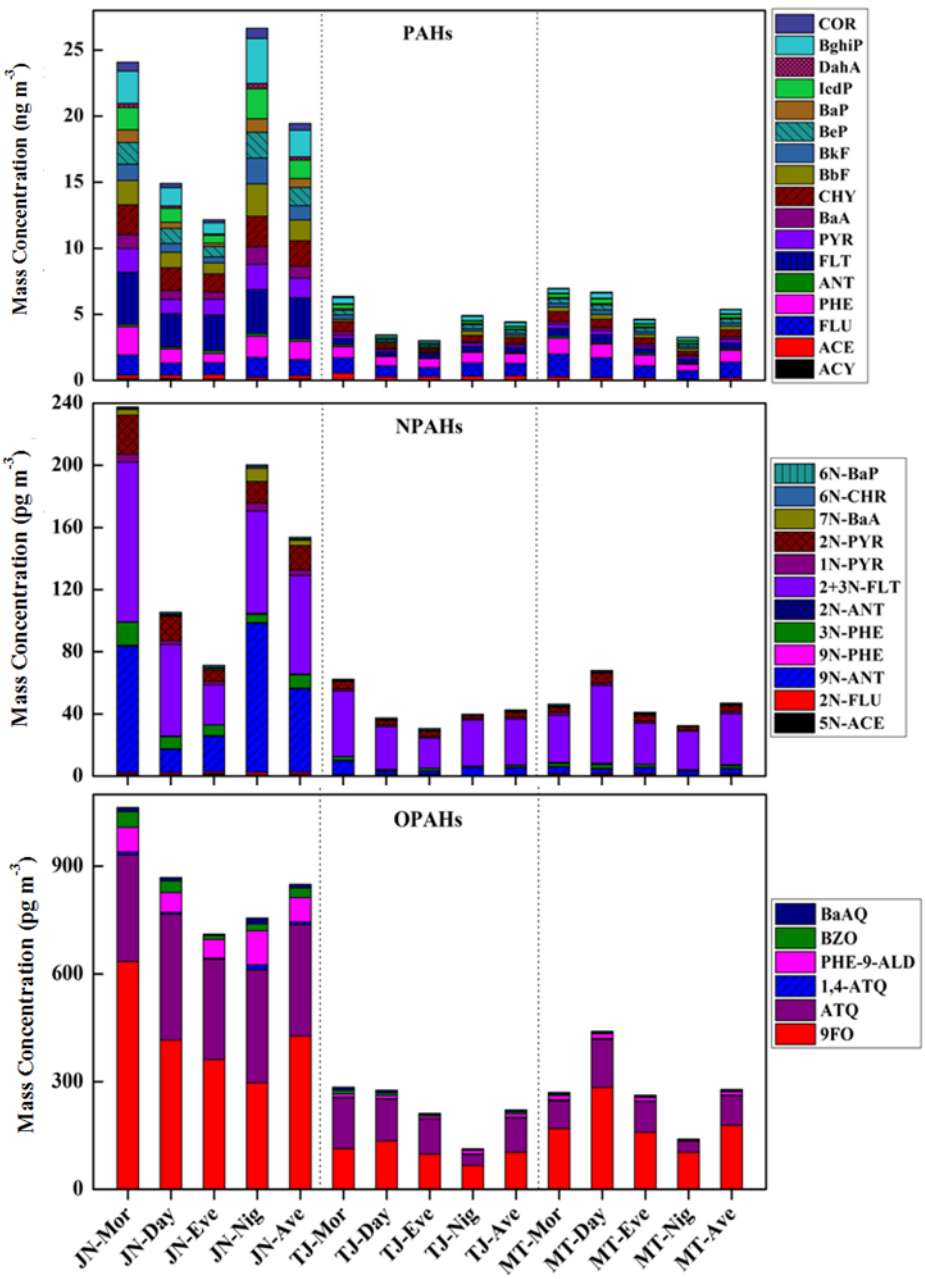

Fig. 2. Diurnal variation (Mor: morning, Eve: evening, Nig: night) and average (Ave) concentration of PAHs, NPAHs, and OPAHs at the urban (JN), marine (TJ) and mountain (MT) locations.

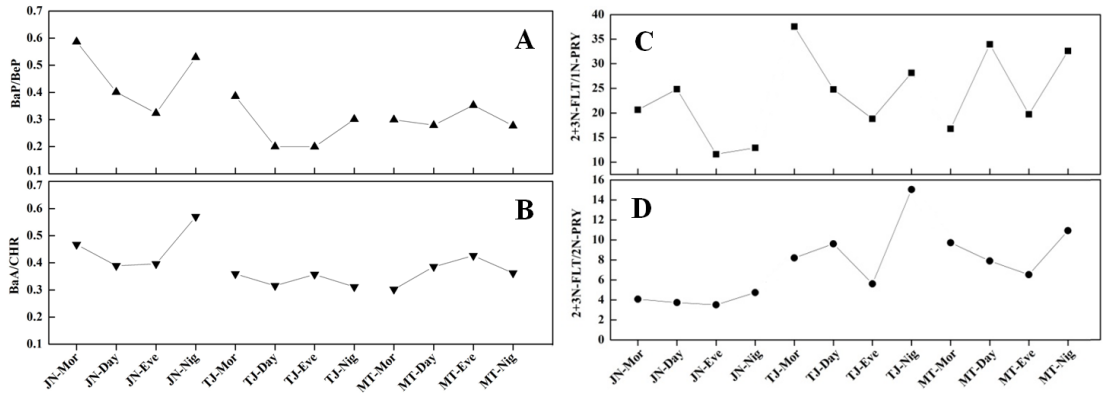

Fig. 3. Ratios of BaP/BeP (A), BaA/CHR (B), 2+3N-FLT/1N-PYR (C) and 2+3N-FLT/2N-PYR (D) at the three different sites during four sampling periods (Mor: morning, Eve: evening, Nig: night).

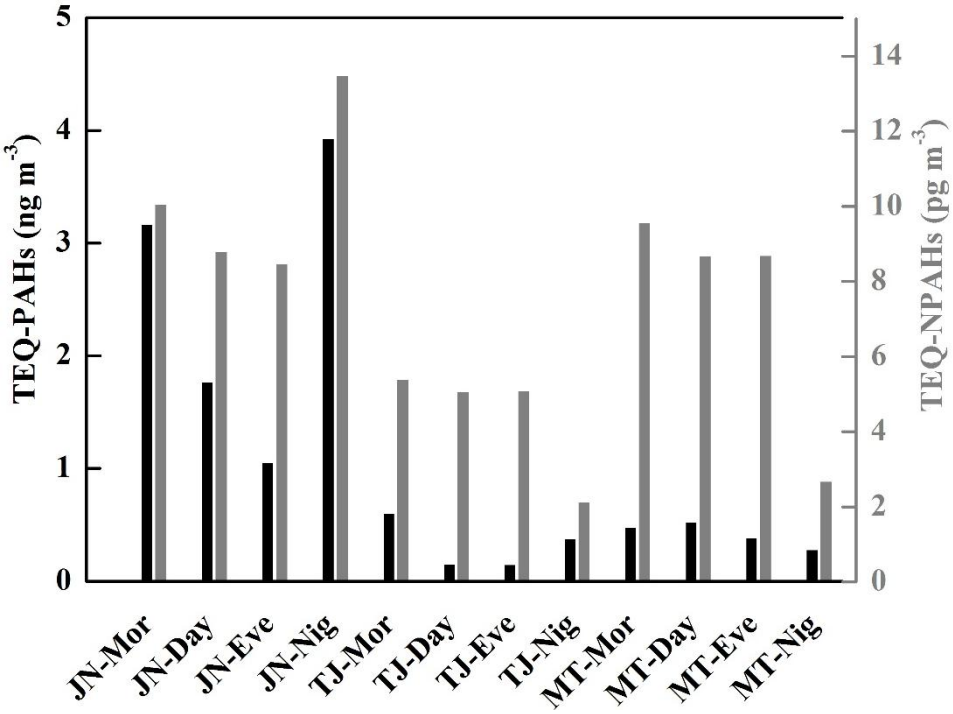

Fig. 4. TEQ of particulate PAHs and NPAHs during the four different sampling periods at the three locations.

Table 1

Diagnostic ratios of particulate PAHs at the three locations during the four sampling periods.

	FLT/(FLT+PYR)	IcdP/(IcdP+BghiP)
JN		
Morning	0.68	0.41
Day	0.70	0.43
Evening	0.70	0.41
Night	0.63	0.40
TJ		
Morning	0.66	0.39
Day	0.67	0.42
Evening	0.73	0.39
Night	0.66	0.37
MT		
Morning	0.65	0.47
Day	0.67	0.46
Evening	0.69	0.42
Night	0.63	0.45
Reference source emissions		
	>0.5 coal/ biomass combustion	>0.5 coal/ biomass combustion
	<0.5 and >0.4 petroleum combustion	<0.5 and >0.2 petroleum combustion
	<0.2 petroleum source	<0.2 petroleum source