Atmospheric Research 213 (2018) 302–308

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmosres

Characterization of $PM_{2.5}$-bound nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air of Langfang during periods with and without traffic restriction

Jingbo Zhao[a], Jing Zhang[a,b], Luna Sun[a], Yan Liu[a], Yingchao Lin[a], Yuening Li[a], Ting Wang[a,*], Hongjun Mao[a,*]

[a] *Center for Urban Transport Emission Research, State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China*

[b] *Tianjin Eco-Environmental Mornitoring Center, Tianjin 300191, China*

ARTICLE INFO

Keywords:
nPAHs
oPAHs
$PM_{2.5}$
Diurnal variation
Traffic restriction

ABSTRACT

$PM_{2.5}$-bound nitrated polycyclic aromatic hydrocarbons (nPAHs) and oxygenated polycyclic aromatic hydrocarbons (oPAHs) in ambient air were analysed in Langfang during periods with and without traffic restriction. During traffic restriction periods, 20% of gasoline vehicles and all diesel vehicles were restricted to travel within downtown. The 2-nitrofluoranthene/1-nitropyrene ratios obtained during the sampling periods implied that direct emission, especially from diesel vehicles, is the main source for the nPAHs in Langfang. The primary sources of nPAHs and oPAHs, including diesel vehicle emissions and gasoline vehicle emissions, were reduced in the P2 period. Thus, the concentrations of 1-nitropyrene, 3-nitrobenzanthrone, 9-nitrophenanthrene, 2-nitrofluorene, 7-nitrobenz[*a*]anthracene, 9,10-anthraquinone and benzanthrone were reduced up to 73.3% under this traffic restriction policy. However, the concentrations of 2-nitrofluoranthene and 9-fluorenone formed from gas phase reactions increased slightly. Meanwhile, the chemical profiles of nPAHs and oPAHs changed with traffic fleet variation, and cancer risk levels decreased under the traffic restriction policy. Hence, the traffic restriction policy did effect the ambient concentrations of nPAHs and oPAHs.

1. Introduction

Polycyclic aromatic hydrocarbon (PAH) represent a category of organic pollutants ubiquitous in the atmospheric environment (Baek et al., 1991; Johnh and Joele, 1999; Wei et al., 2012). However, increasing attention has been paid to nitrated polycyclic aromatic hydrocarbons (nPAHs) and oxygenated polycyclic aromatic hydrocarbons (oPAHs). With functional groups attached, nPAHs and oPAHs are sometimes more mutagenic and carcinogenic than their parent PAHs (Arey et al., 1992; Durant Jr et al., 1996; Yang et al., 2010). The parent PAHs are released from incomplete combustion or pyrolysis of materials containing carbon and hydrogen. While nPAHs and oPAHs in ambient air are either from primary emissions or from secondary formation (Li et al., 2015; Reisen and Arey, 2005; Wei et al., 2012), some oPAHs have been reported to be parent compounds of nPAHs formed via atmospheric reactions (Enya et al., 2012; Helmig et al., 1992).

The nPAHs and oPAHs could be emitted during the incomplete combustion of fossil fuel and biomass burning (Albinet et al., 2007; Li et al., 2015; Zhang et al., 2014), produced by gas-phase reactions of PAHs induced by OH or NO_3 radicals (Arey et al., 1986; Atkinson et al., 1990; Bunce et al., 1997) or could result from heterogeneous reactions of particulate PAHs with ozone (Pitts Jr et al., 1978; Perraudin et al., 2007). 1-Nitropyrene (1-NP), 2-nitrofluorene (2-NFl), 3-nitrobenzanthrone (3-NBA), 6-nitrochrysene (6-NCh), 6-nitro-benzo[*a*]pyrene (6-NBaP) and benzo[*a*]antheacene-7,12-dione (BaAQ) are the most abundant nPAHs in diesel exhaust (Albinet et al., 2007; Finlayson-Pitts Jr, 2000; Hayakawa et al., 2000; Phousongphouang and Arey, 2003). 7-Nitrobenz[*a*]anthracene (7-NBaA) and benzanthrone (BZO) are emitted directly from gasoline vehicles (Albinet et al., 2007). 2-Nitrofluoranthene (2-NF) is the most abundant nPAH formed in atmospheric gas-phase reactions and is only produced from the gas-phase reaction between fluoranthene and NO_2 initiated by OH radical during the day and by NO_3 radical during the night (Arey et al., 1986; Finlayson-Pitts Jr, 2000; Kameda et al., 2006). The compound 9-fluorenone (9FO) is mainly produced from the gas-phase reactions (Kojima et al., 2010). 3-Nitrophenanthrene (3-NPh) and 9-nitrophenanthrene (9-NPh) could not only be formed in the atmosphere from gas-phase reactions but also have been identified in exhaust emissions from diesel engines (Heeb

---

[*] Corresponding author.
E-mail addresses: wangting@nankai.edu.cn (T. Wang), hongjun_mao@hotmail.com (H. Mao).

https://doi.org/10.1016/j.atmosres.2018.06.015
Received 12 February 2018; Received in revised form 18 June 2018; Accepted 20 June 2018

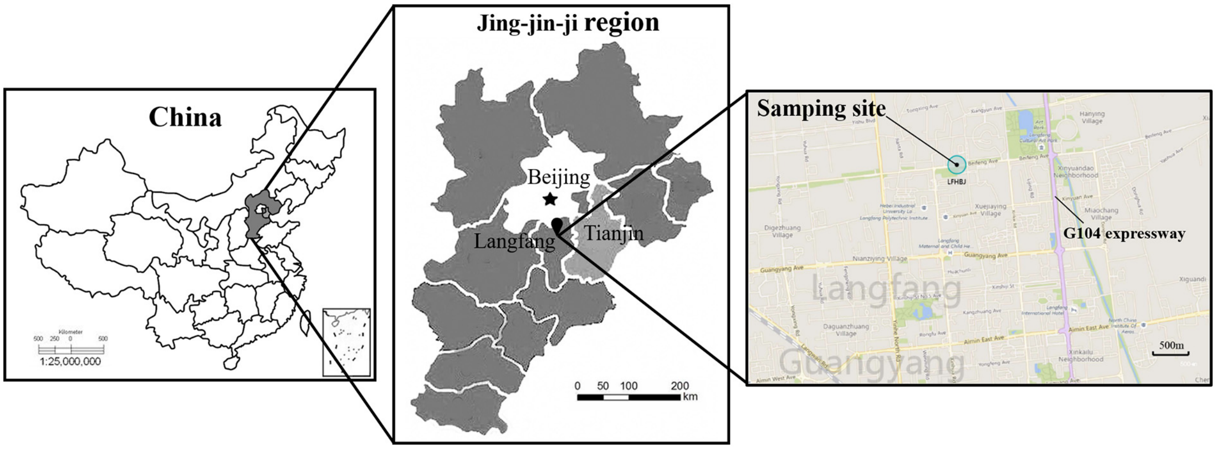

Fig. 1. The location of Jing-jin-ji region and the sampling site in the ambient air automatic monitoring station of Langfang city, Hebei province, China.

et al., 2008; Wei et al., 2012). 9,10-Anthraquinone (ATQ) is emitted from the diesel vehicles and can form from the ozonation of anthracene (Albinet et al., 2007; Perraudin et al., 2007). The ratio of the concentration of 2-NF to that of 1-NP is generally used to assess the relative importance of primary sources versus secondary sources (Anders and Nielsen, 2001; Bamford and Baker, 2003). A value of the 2NF/1NP ratio that is less than five shows the relative extent of primary emission sources, whereas a ratio larger than five highlights the importance of the secondary formation of NPAHs (Ciccioli et al., 1996).

The Jing-jin-ji region refers to Beijing and Tianjin, and includes Langfang as well as the other seven cities of the Hebei province and is the political, cultural and economic centre of China. Beijing is both the capital and the political centre of China (Fig. 1), while Tianjin is the third largest megacity and the fastest growth area in China. Langfang is located approximately midway between Beijing and Tianjin. Particulate matter with an aerodynamic diameter ≤ 2.5 μm ($PM_{2.5}$) is the primary pollutant in many Chinese cities (Zhang and Cao, 2015). Regional transport from surrounding cities is an important source of $PM_{2.5}$ in Beijing and Tianjin (Hu et al., 2015). Based on the data published by the Ministry of Environmental Protection of the People's Republic of China, Langfang was one of the top ten cities with the worst air quality in China in the last decade, and $PM_{2.5}$ has been the primary air pollutant. Langfang contributed 3.2–4.7% to $PM_{2.5}$ concentration in Beijing (Chen et al., 2016). Over 90% of the mass of nPAHs and oPAHs in ambient air are distributed on $PM_{2.5}$ (Albinet et al., 2008; Bandowe et al., 2014; Kawanaka et al., 2004). Much research has been conducted to investigate the concentration of nPAHs and oPAHs in Beijing and Tianjin (Li et al., 2015; Lin et al., 2015a,b). However, there was nearly no research on the concentration of nPAHs and oPAHs in Langfang. Hence, the objectives of this study were (1) to investigate the concentration of $PM_{2.5}$-bound nPAHs and oPAHs in ambient air in Langfang, and (2) to assess the effect of traffic restriction on the concentration and composition of nPAHs and oPAHs. These results would help to understand nPAH and oPAH behavior in ambient air and provide basic information for evaluating the impact of traffic restriction policies on nPAH and oPAH emission.

2. Methods and materials

2.1. Sample collection

Langfang (116°38′07″ - 116°44′06″E, 39°28′42″- 39°32′54″N) is located midway between Beijing and Tianjin and is the geographic centre of the Jing-jin-ji region. $PM_{2.5}$ samples were collected at the roof of Langfang Bureau of Environment Protection (Fig. 1), which is approximately 20 m above the ground level and 50 m north of Beifeng Road (a main road of Langfang city), Guangyang district, and approximately 1300 m east of the G104 expressway. There are no other pollution sources around the sampling site. Traffic emission is the main air pollutant source in the sampling area.

In order to cope with pollution causing a heavy haze in downtown Langfang, a traffic restriction policy was conducted from September 16 to 18 in 2015 (07:00 to 20:00 on Sep. 16 and 17; 07:00 to 12:00 on Sep. 18). During the traffic restriction period, 20% of gasoline vehicles and all diesel vehicles were restricted to travel in downtown. Thus, sampling was conducted between Sep. 14 and 20 to investigate the concentrations of nPAHs and oPAHs with and without traffic restriction. The diurnal $PM_{2.5}$ samples were collected in daytime (P2, 07:00 to 17:00) and nighttime (P1, 00:00 to 07:00; P3, 17:00 to 00:00 the next day). The results from the P2 period reflect the effect of human activities on the nPAHs and oPAHs concentrations, especially including gasoline vehicle emissions. The P1 period had with relatively less human activity, and there were more heavy-duty diesel vehicles emissions in the P3 period. Air samples were drawn at a rate of approximately 100 L/min through quartz fiber filters (90 mm diameter, PALL) using a medium-volume sampler (TH-150AII, Tianhong, CHN) equipped with a $PM_{2.5}$ size-selective inlet. The filters were baked at 600 °C in a muffle furnace for 2 h before sampling. Then, before and after sampling, the filters were equilibrated under constant temperature (22 ± 1 °C) and relative humidity (35 ± 1%) for 48 h. The sampled filters were wrapped with annealed aluminum foil and stored in a refrigerator at −18 °C until analysis.

2.2. Sample extraction, clean-up, and analysis

The filters were spiked with 6-nitrochrysene-d_{11} and 9-nitroanthracene-d_9 as recovery surrogate standards and then ultrasonically extracted with 60 mL dichloromethane. Each extract was concentrated to 1 mL and then purified through a silica gel and alumina column that was eluted with 20 mL (discarded). Then the column was eluted with 50 mL hexane/dichloromethane (1:1 *v*/v), and the extract contained the nPAHs and oPAHs was collected. The extract volume was then reduced almost to dryness then dissolved in hexane/dichloromethane (1:1 v/v) for the detection of nPAHs and oPAHs (Li et al., 2015; Wei et al., 2012).

The nPAHs and oPAHs were analysed using a gas chromatograph (Agilent 7890A GC) coupled with a mass spectrometry (Agilent 5975C MS) and an HP-5MS capillary column in negative chemical ionization mode. The gas chromatograph oven temperature was programmed to increase from 40 °C to 150 °C at a rate of 15 °C/min, then to 300 °C at a rate of 5 °C/min, and then was held at 300 °C for 15 min (Li et al., 2015; Wei et al., 2012). The carrier gas was high purity helium. Details can be found in the Supporting Information (SI). The mass spectrometer was operated in selected ion monitoring mode (Table S1 in SI). Nine nPAHs and four oPAHs were quantified, which were the most abundant and