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Subway construction activity influence on polycyclic aromatic hydrocarbons in fine particles: Comparison with a background mountainous site

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A B S T R A C T

Intensive construction activities worsened the surrounding atmospheric environment in China. Eighteen polycyclic aromatic hydrocarbons (PAHs) in fine particles ($PM_{2.5}$) were collected at a subway construction site (SC) of Nanjing and compared with a regional background mountainous site (BM) to examine the influence of anthropogenic activities on concentrations, sources and health risks of PAHs. Average PAH concentrations at SC were higher than BM at a factor of about 5.9. All PAH species at SC were higher than BM, with the SC/BM ratios ranging from 1.3 (NaP) to 10.3 (BaP). PAH profiles differed for the two sites. The SC site had higher mass fractions of PAHs from coal combustion and vehicle emission, while the BM site held higher mass percentages of PAHs from long-range transported wood combustion and industrial activities. Lower temperature at BM may lead to the higher mass percentages of low ring PAHs. Coal combustion, traffic emissions and biomass burning were the common sources for PAHs at both SC and BM. Construction workers were exposed to higher BaPeq concentrations, nearly ten times of the background site and their lifetime cancer risk reached to 0.6 per 1,000,000 exposed worker, owing to the influence of coal combustion, vehicle emission and industrial activities at the surroundings of SC.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), formed due to incomplete combustion or pyrolysis of organic material, are a type of organic compounds with high carcinogenicity and mutagenicity. For PAHs in fine particles ($PM_{2.5}$), various source apportionment studies indicated that the major sources are coal combustion, vehicle emission and petroleum in China (Gu et al., 2010; Tan et al., 2011; Li et al., 2014b; Wu et al., 2014a). Meanwhile, PAHs in road dust have also been widely recognized (Yang et al., 1999; Murakami et al., 2005; Han et al., 2009; Zhao et al., 2009). Construction activities including laying foundations, paving road, decorating, and transporting construction materials and wastes emit not only dust, but also particulate and gaseous air pollutants from highly concentrated non-road engines and on-road vehicles. Subramanyam et al. (1994) observed that the presence of construction activities near the sampling site can affect the concentration levels of PAHs. It indicated that the surrounding environment of the construction site is a type of hot-spot sites for PAHs in fine particles and should be paid attention from the view of protecting the health of construction workers or human living near these sites.

Due to the urbanization, construction of urban rail transit system including subway and main roads is now springing out in many megacities of China. According to the National Economic and Social Development of the Twelfth Five Year Plan Outline, the urban rail transit system is in vast development plan (http://www.gov.cn/2011lh/content_1825838_2.htm). Till September 2013, 37 cities have been authorized to construct subways, including most of the megacities, such as Beijing, Tianjin, Shanghai, Guangzhou, Nanjing and Shenzhen (http://finance.chinanews.com/cj/2013/11-25/5542506.shtml). These cities mainly locate at regions with serious haze and $PM_{2.5}$ pollution frequently occurred, such as Beijing–Tianjin–Hebei (Zhao et al., 2013), Yangtze River Delta (YRD) (Ding et al., 2013), Pearl River Delta (Tan et al., 2009, 2011), Sichuan Basin (Tao et al., 2014), Shandong peninsula (Wang et al., 2014), city clusters of central China (Geng et al., 2013), Guanzhong Plain (Wang et al., 2015a), northeast China (Liu et al., 2015) and west-Taiwan Strait (Deng et al., 2014). In addition, the subway construction sites are in close proximity to urban main roads with intense traffic flows. The subway construction sites are surrounded by major sources of PAHs in $PM_{2.5}$, including road dust (Yang et al., 1997, 1999; Zhao et al., 2009) and vehicles of both diesel (Liang et al.,

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2006; Wu et al., 2014b) and gasoline (Elghawi et al., 2010; Wu et al., 2014b). Yang et al. (1997) found that the highest PAH content in road dust from the urban area is located at the aerodynamic particle diameter of 1.8 μm. And dust deposited on the roads can be easily resuspended into the air by traffic turbulence. Contributions of 42% and 36% from diesel and gasoline vehicles were obtained for PAHs in $PM_{2.5}$ at a roadside environment in Beijing (Wu et al., 2014b). Wu et al. (2014b) indicated that the control of construction activities in Beijing is one of the effective measures to improve air quality and also reduced PAH concentrations in $PM_{2.5}$ at a roadside environment were observed during the 2008 Olympic Games period. Therefore, the subway construction activities may deteriorate the surrounding air and raise health risks to workers or people living near the construction sites.

In the past decade, the gas/particle distribution (Ma et al., 2011; Wang et al., 2011; Xia et al., 2013; Zhang et al., 2013b), size distribution (Bi et al., 2005; Duan et al., 2005, 2007; Zhou et al., 2005; Wang et al., 2008), seasonal variation (Zhou et al., 2005; Huang et al., 2006; Tan et al., 2006; Hong et al., 2007; Wang et al., 2011, 2015b; Li et al., 2013a; Zhang et al., 2013a; He et al., 2014; Wu et al., 2014b), spatial variation in city scale (Wu et al., 2005, 2014a; Wang et al., 2006, 2008; Gao et al., 2012; Hu et al., 2012; Xia et al., 2013; He et al., 2014) or regional scale (Wang et al., 2011; Zhang et al., 2013b), vertical distribution (Li et al., 2005; Tao et al., 2007) and health risk of PAHs (Xia et al., 2013; Leung et al., 2014) in the atmosphere have been widely investigated in China. These investigations are conducted in both the northern cities—Harbin (Ma et al., 2010), E'erduosi (Wu et al., 2014a), Beijing (Okuda et al., 2002, 2006, 2011; Zhou et al., 2005; Huang et al., 2006; Wang et al., 2008; Ma et al., 2011; Li et al., 2013a; Leung et al., 2014; Wu et al., 2014b), Tianjin (Wu et al., 2005; Shi et al., 2014), Xi'an (Leung et al., 2014), Taiyuan (Xia et al., 2013; Li et al., 2014a) and Zhengzhou (Wang et al., 2015b) and the southern cities—Shanghai (Wang et al., 2014), Nanjing (Wang et al., 2006; He et al., 2014), Hangzhou (Okuda et al., 2002), Fuzhou (Zhang et al., 2013a), Xiamen (Hong et al., 2007; Leung et al., 2014), Chongqing (Okuda et al., 2002), Guiyang (Hu et al., 2012), Guangzhou (Bi et al., 2002, 2005; Duan et al., 2005, 2007; Li et al., 2005; Tan et al., 2006, 2011; Gao et al., 2011, 2012; Leung et al., 2014), Shenzhen (Sun et al., 2015) and Hong Kong (Lee et al., 2001; Leung et al., 2014). To sum up, PAHs in particulate matter exhibited highest concentrations in winter and lowest concentrations in summer (Zhou et al., 2005; Huang et al., 2006; Tan et al., 2006; Wang et al., 2011; Li et al., 2013a; Xia et al., 2013; Zhang et al., 2013a; He et al., 2014; Wu et al., 2014b). For spatial variation, they hold higher concentrations at the roadside environment (Wang et al., 2006; Wu et al., 2014b) or industrial sites (Wu et al., 2014a) or rural sites (Wang et al., 2008, 2011) where obvious sources of them are highly concentrated, such as automobile exhausts, industrial plants and domestic heating/cooking stoves, respectively. For size distribution, most PAHs are mainly associated with fine particles (Bi et al., 2005; Duan et al., 2005; Zhou et al., 2005; Wang et al., 2008; Sun et al., 2015). Recently, Leung et al. (2014) found that the human bronchial epithelial cells exposed to the extracts of PAHs in $PM_{2.5}$ collected in five Chinese megacities demonstrated significant migratory activities, indicating an increase of tumorigenicity. Therefore, the investigation of PAHs in fine particles at sites with obvious emission sources is of great importance, from the view of protecting human health. However, few studies have addressed the concentrations of PAHs in $PM_{2.5}$ at hotspot sites such as the surroundings of subway construction activities till now.

Nanjing, as one of the three central cities of YRD, is the host city for the 2014 Youth Olympic Games. Six subway lines were constructed at the same time to meet the transport needs from the year of 2012. It is an ideal site to study the influence of subway construction activities on the chemical compositions of $PM_{2.5}$. Detailed investigations of atmospheric $PM_{2.5}$ are conducted at a subway construction site (SC) during its foundation dredging period. At this period, more vehicles are used for excavation and transportation of construction materials and wastes. For clearly identifying the pollution levels, sources and health risks of PAHs at the subway construction site, a comparative sampling campaign was immediately organized at a remote mountainous (BM) site of YRD—Mt. Huang (1864 m). It is 220 km away from the southeast of Nanjing and is the background reference site of YRD with negligible local anthropogenic sources (Chen et al., 2014).

The main objectives of this study are to: (1) obtain the levels of PAHs in $PM_{2.5}$ at the subway construction site and compare them with the background mountainous site; (2) analyze the influence of sources and meteorological parameters on PAHs in the two sites; and (3) calculate the lifetime health risks by exposure to PAHs in $PM_{2.5}$ for construction workers.

2. Methodology

2.1. $PM_{2.5}$ collection

Daily 24 h $PM_{2.5}$ samples were collected with a sampler (TH-150C, Wuhan Tianhong Ltd., China) at a flow rate of 100 L/min on the rooftop (6 m high) of a guard room of Nanjing University of Information Science & Technology (NUIST). The sampling time lasted from June 14 to July 9, 2013, covering the whole foundation dredging period. The starting time is from about 08:00 am each day. NUIST locates at the suburban of Nanjing, with a steel factory 2 km to the east of the campus and a chemical industry park about 10 km to the northeast. The sampling site faces one road (about 10 m in the east direction) with heavy traffic and the subway is constructed on this road as Fig. 1 shows. Daily 24 h $PM_{2.5}$ samples were collected at Mt. Huang during Oct. 16-Nov. 02, using the same equipment. Mt. Huang is situated in Anhui Province, southeastern China, with an area of 40×30 km^2. The sampling site is set at the summit with an altitude of 1840 m (Fig. 1). The annual average rainfall at the summit is 2369 mm and the average frequency of rainfall is 181 days. With limitation on equipment, the sampling between the two sites was not simultaneous. It should be noted that $PM_{2.5}$ at summer and autumn periods is low in China with less heating activities compared to winter (Li et al., 2014b). And He et al. (2014) found that the PAHs in $PM_{2.1}$ at suburban and urban sites of Nanjing both decreased in winter > spring > autumn > summer. Therefore, the sampling design for the two sites in this study can be accepted. At rainy days, $PM_{2.5}$ was not collected. 17 and 16 samples were obtained for the construction site and Mt. Huang, respectively. Quartz fiber filters (Whatman Company, UK, Ø 90 mm, baked at 800 °C for 2 h) were adopted. After sampling, the filters were sealed in aluminum foil envelopes until weighing. The filters were weighed before and after sampling under a constant temperature (22 °C) and relative humidity (35%) controlled environment by a microbalance (Ohaus Discovery DV214CD) with sensitivity of ± 0.010 mg. Then they were stored at −20 °C until chemical analysis.

2.2. PAH analysis and suitability analysis of the data set

For PAH analysis, filters are extracted ultrasonically with dichloromethane, then concentrated using a rotary evaporator, purified with a silica gel and re-concentrated by rotary evaporation. Finally they were condensed to exactly 1 mL under a gentle nitrogen stream in 60 °C water bath. The extracts were transferred into two ampoule bottles and stored in a refrigerator until analysis. Gas chromatography coupled to mass spectrometry (GC–MS) was used according to the EPA Method TO-13A. For each sample, the procedures of sampling, pretreatment and analysis were completed within one month. PAHs in the final extracts were analyzed with a trace 2000 GC–MS (Thermo Finnigan, USA) apparatus with selected ion monitoring (SIM). Detailed analysis of GC–MS could be found in our former works (Kong et al., 2012; Wu et al., 2014a).

Quantification of PAHs is standardized by the retention times and peak areas of the calibration standards. Internal standard method is adopted. 1000 mg/L reserve liquid including Perylene-d12,

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