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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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HIGHLIGHTS

- Diurnal variations of NPAHs and OPAHs were analyzed at urban and background sites.
- The air masses collected at the marine site was the most aged.
- Fossil fuel combustion and biomass burning were the main sources.
- The secondary formation of NPAHs at urban site was strongest during the daytime.
- The excess cancer risk in Jinan was higher than those in the background sites.

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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.

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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 (Reisen and Arey, 2005) time intervals measurements to analyze the diurnal variation of NPAHs and OPAHs, which were mainly carried out at one or two different types of sampling sites, and the tested 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. The studies using long sampling time intervals 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 has 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

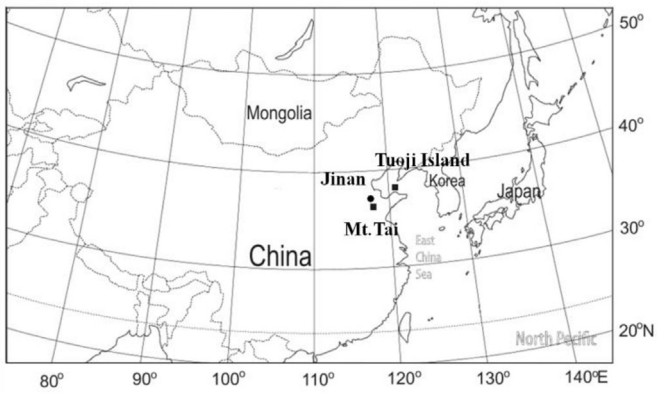

Fig. 1. The three sampling locations (Wang et al., 2009). The squares indicate background sampling sites.