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Studies on size distribution and health risk of 37 species of polycyclic aromatic hydrocarbons associated with fine particulate matter collected in the atmosphere of a suburban area of Shanghai city, China☆

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A B S T R A C T

Polycyclic aromatic hydrocarbons (PAHs) in suspended particulate matter (SPM) contribute significantly to health risk. Our objectives were to assess the size distribution and sources of 26 PAHs and 11 polycyclic aromatic compounds (PACs) in SPM in the suburban area, Shanghai city, China. Air sampling was carried out on the rooftop of a five-stories building in the campus of Shanghai University. An Andersen high-volume air sampler was employed to collect ambient size-segregated particles from August to September 2015. The toxic particulate PAHs were determined by the gas chromatography mass spectrometry. The concentrations of total PAHs (TPAHs) in SPM and $PM_{1.1}$ (suspended particulate matter below 1.1 μm) were in the ranges of 4.58–14.5 ng m^{-3} and 1.82–8.56 ng m^{-3}, respectively. 1,8-naphthalic anhydride showed the highest concentrations among 37 species of PAHs and PACs ranging 7.76–47.9 ng m^{-3} and 1.50–17.6 ng m^{-3} in SPM and $PM_{1.1}$, respectively. The concentrations of high molecular weight 5–6 ring PAHs followed a nearly unimodal size distribution with the highest peak in $PM_{1.1}$, while other lower molecular weight PAHs were not dependent on particle sizes. The toxicity analysis indicated that the carcinogenic potency of particulate PAHs primarily existed in $PM_{1.1}$. Regarding meteorological parameters and other pollutants, the positive effect of humidity and NO_2 over PAHs was confirmed. Diagnostic ration indicated that the particulate PAHs in Shanghai were mainly derived from motor-vehicle or petroleum combustion. The highest benzo[*a*]pyrene equivalent (BaPeq) in SPM and $PM_{1.1}$ were 2.15 ng m^{-3} and 1.43 ng m^{-3} calculated by the toxicity equivalency factor, and 69.31 ng m^{-3} and 47.81 ng m^{-3} estimated by the potency equivalency factors, respectively. The highest contributors in the total carcinogenicity of the particulate PAHs were dibenzo[*a,h*]pyrene (46.2% and 45.0%) and benz[*j*]aceanthrylene (80.2% and 83.1%), respectively while benzo[*a*]pyrene is lower contributor than other carcinogenic PAHs.

1. Introduction

Atmospheric fine particulate matter play the major role in air pollution. Fine particles deposit slowly from the atmosphere and may be airborne for days or even weeks, being transported from one region to another region (Harrison et al., 1996). They are the major culprits in visibility degradation (Watson, 2002) and effective loadings of toxic chemicals (NRC, 1998). Very high fine particulates concentrations have been reported in Chinese cities, mainly emitted from coal and biomass combustion and motor-vehicle exhaust (WHO, 2005; Hu et al., 2010).

Various particulate organic compounds constitute around

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20–90% in mass of atmospheric particulate matter (Kanakidou et al., 2005; Turpin et al., 2000), and the most of this mass are non-toxic alkanes. However, the toxic compounds such as polycyclic aromatic compounds (PACs) (including polycyclic aromatic hydrocarbons (PAHs)) forms only tenths percent in atmospheric particulate matter. PAHs are a class of ubiquitous organic compounds (WHO, 2003), and absorbed predominantly on fine particulate matter (Baek et al., 1991; Fan et al., 2009). The sources of PAHs were identified to link with residential biofuel (Zhang et al., 2009), coal combustion (Galarneau, 2008) and vehicular emissions (Sklorz et al., 2007), etc. Being with potential toxic, carcinogenic, genotoxic and mutagenic effects, PAHs and PACs possess a fairly high health risk, and thus raise much attention (Ames et al., 1975; WHO and IARC, 2010; Wei et al., 2015). It was pointed out that benzo[*j*]aceanthrylene, dibenzo[*a,h*]anthracene, benzo[*c*]fluorene and dibenzo[*a,l*]pyrene are more toxic than benzo[*a*]pyrene (WHO and IARC, 2010). Additionally, the carcinogenic 5- and 6-ring particulate PAHs are often associated with the particle sizes below 2.0 μm (Kameda et al., 2005; Ravindra et al., 2008a, b). However, there are few studies reported about atmospheric concentrations of these PAHs. There are many types of PACs such as oxygenated PAHs (OPAHs), methylphenanthrenes (MePhes) and benzothiophenes (BTPhes). Especially, OPAHs are persistent and bioaccumulative with toxic, mutagenic, carcinogenic and estrogenic properties (Kurihara et al., 2005). Some toxic oxy-PAHs are higher than those of their parent-PAHs (Lundstedt et al., 2007). OPAHs are mainly emitted by different combustion sources and are formed during the transportation in the atmosphere by photo-oxidation processes of their parent-PAHs with atmospheric oxidants such as O_3, NOx, and OH radicals (Albinet et al., 2007; Zhang et al., 2011).

Recent years, with the rapid economic development in China, it has brought serious urban air pollution. About 5.8% of the pollution contribution was estimated in China's land area, where 30% of the population lives. Since the air pollution level was found that exceeded the national ambient benzo[*a*]pyrene (BaP) standard of 10 ng/m^3 (Xu et al., 2013) especially in the urban atmosphere, as the results, it was reported that 1.6% of the lung cancer morbidity in China may be caused by inhalation exposure to urban atmospheric PAHs (Zhang and Tao, 2009).

The economic expansion over the past decades in China has been one of the strongest in the world history. Therefore, the growing energy consumption and rapid urbanization, an increase in ambient air pollution seemed inevitable (Kan et al., 2009). Conventionally, predominant air pollution with suspended particulate matter used to be caused from coal combustion in China. However, in many Chinese cities, because of the rapid increase recently in the number of motor vehicles (e.g. motorization), urban air pollution has gradually changed from the conventional coal combustion type to the mixed coal combustion and traffic emission type which lead automobile exhaust gases (Watts, 2005). In the near future, it is considered a similar global problem occurs in the other developing Asian or Africa countries or other areas. Since Shanghai is the most developed city in China, the results in this study can prove the basic data and become a good model case study or as a basis for taking out the future countermeasures in the urban atmosphere.

Shanghai is located on the eastern coast of China. It is the largest developing city in China, with a population of approximately 20 million and an area of 7037.5 km^2. It is also a strong commercial and industrial base, with the largest petrochemical complex and the largest steel output in China. The rapid economic development and urbanization in this region during the last two decades have resulted in severe air pollution (Liu et al., 2007, 2008). Air pollution was found to be associated with lung cancer and cardiorespiratory diseases in Shanghai. An increase of 10 μg/m^3 of PM_{10} corresponded to increases in all-cause mortality of 0.25% [95% confidence interval (CI): 0.14%, 0.37%] (Kan et al., 2008).

Four major objectives of this study focused on the ambient particles collected in a suburban area of Shanghai city are: (1) to investigate suspended particulate matter (SPM) and fine particulates such as $PM_{1.1}$ (suspended particulate matter below 1.1 μm in aerodynamic diameter) in terms of PAHs levels, compositional pattern and their size distribution; (2) to elucidate potential relationships between meteorological parameters, PAHs, PACs concentrations, and other air pollutants; (3) to identify the sources of PAHs by using the diagnostic ratios; and (4) to assess the human health risk of PAHs in SPM of the suburban area of Shanghai city, China.

2. Materials and methods

2.1. The description of the sampling site of the suburban area of Shanghai city, China

Because the objective of this study is to investigate the general atmospheric environment of Shanghai suburban area, ambient particle samples were collected at the rooftop (approximately 30 m above the ground level) of D building on the suburban campus of Shanghai University in Shanghai China (latitude 31°19′ N, longitude 121°39′ E) (Fig. 1) where is situated very close to residential zone and roadside. The sampling site is 1.5 km from the nearest highway with heavy traffic and is surrounded by residential areas. There are several small chemical industrial plants located northwestern of the campus (1.5 km). Therefore, the particulate samples were not only reflected in the ambient particle samples transported to residential zone, but also significantly influenced by local vehicular emissions due to its proximity to traffic. The concentrations of PM_{10} and $PM_{2.5}$, and meteorological data of Shanghai during the sampling period were obtained from the national official website (http://www.tianqihoubao.com/aqi/shanghai.html) which provided weather data of major cities in China. During the sampling periods, the relative humidity in the Shanghai covered a range of 40%–100%, and the temperatures varied from 17 to 32 °C.

2.2. Air sample collection for suspended particulate matter

The sampling campaign was conducted intermittently for three weeks of the summer season from August 25 to September 14, 2015. Size-segregated samples of suspended particulate matter were collected on the quartz fibre filters (8 × 10 inch^2, Pallflex Product, 2500QATUP) using a new model Andersen high-volume air sampler (HV-1000R, Shibata Co., Tokyo, Japan) equipped with five stages of an Andersen impactor (Shibata Co., Tokyo, Japan). Five stage size-segregated suburban suspended particulate samples (particle sizes ranging from ≦1.1, 1.1–2.0, 2.0–3.3, 3.3–7.0 and ≧7.0 μm in aerodynamic diameter) were collected on the quartz fibre filters with a flow rate of 0.566 m^3 min^{-1}. The quartz fibre filters were used for collecting suspended particulate samples because they are thermally resistant and can be heat-treated to remove any PAHs present in the blank filter before sampling. Each sampling time was 47 h. After collection, all filter samples were dried at room temperature, the filters were wrapped in cleaned aluminium foil, sealed in plastic bags, and then stored at −30 °C until being submitted for analysis.

2.3. Preparation of standard chemicals of 37 species of PAHs and PACs

The standard chemicals of 37 species of PACs including methyl-PAHs, benzothiophenes and oxy-PAHs for analysis of urban