Atmospheric bulk deposition of polycyclic aromatic hydrocarbons in Shanghai: Temporal and spatial variation, and global comparison[*]

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ABSTRACT

Atmospheric deposition leads to accumulation of atmospheric polycyclic aromatic hydrocarbons (PAHs) on urban surfaces and topsoils. To capture the inherent variability of atmospheric deposition of PAHs in Shanghai's urban agglomeration, 85 atmospheric bulk deposition samples and 7 surface soil samples were collected from seven sampling locations during 2012–2014. Total fluxes of 17 PAHs were 587-32,300 ng m^{-2} day^{-1}, with a geometric mean of 2600 ng m^{-2} day^{-1}. The deposition fluxes were categorized as moderate to high on a global scale. Phenanthrene, fluoranthene and pyrene were major contributors. The spatial distribution of deposition fluxes revealed the influence of urbanization/industrialization and the relevance of local emissions. Meteorological conditions and more heating demand in cold season lead to a significant increase of deposition rates. Atmospheric deposition is the principal pathway of PAHs input to topsoils and the annual deposition load in Shanghai amounts to ~4.5 tons (0.7 kg km^{-2}) with a range of 2.5–10 tons (0.4–1.6 kg km^{-2}).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous semi-volatile organic compounds originating from anthropogenic and natural sources by incomplete combustion of organic matter and fuels (Liu et al., 2017). PAHs may be present in gas phase and atmospheric particles. They are transported over long distances and meanwhile may occur in many environmental compartments (Jiménez et al., 2015). Given their continuous emission and toxicity to ecosystems and human health even at relatively low levels, PAHs have been considered as environmental hazardous compounds in official air quality standards (EEA, 2016; MEP, 2012).

Human activities environmentally (e.g. coal combustion and vehicle exhaust) emit gaseous and particulate PAHs in the atmosphere (Liu et al., 2015; Wang et al., 2016c). Once to the atmosphere,

PAHs are variably removed through atmospheric deposition and photodegradation processes. Atmospheric deposition has been proved to be a main source of persistent organic pollutants to the open sea and large inland lakes (Jiménez et al., 2015; Jurado et al., 2005). Similarly, the atmospheric input of PAHs may be considered as the principal contributor of overall toxic compound inventory in terrestrial ecosystems. Typically, PAH concentrations in topsoils and atmospheric deposition rates are about 50–1000 times higher than other persistent organic pollutants such as PCBs or dioxins (Degrendele et al., 2016; Park et al., 2002).

Atmospheric deposition includes dry, wet and gas deposition. Atmospheric dry deposition refers mostly to the gravitational settling of atmospheric particles, while wet deposition refers to the pollutants depositing with precipitation or snow (Amodio et al., 2014a). Gas deposition, an air-soil exchange processes, concerns vapor phase diffusion transferring pollutants from the atmosphere to soils where they are sorbed predominantly to soil organic matter (Cetin et al., 2017; Degrendele et al., 2016; Wang et al., 2017). If atmospheric concentrations of pollutants were previously reduced due to the implementation of tighter air pollution laws, the sorbed

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pollutants may be re-volatilized from soils which then become a secondary source for atmospheric pollutants (Bao et al., 2015). Atmospheric bulk deposition is an operational definition, and means accumulation in a continuously open collector that would contain materials that enter during wet and dry periods, consisting of wet and dry deposition, but excluding gas deposition (Jiménez et al., 2015). These atmospheric pathways are important to assess the impact of the long-term input of pollutants into the regional or global environment (Gocht et al., 2007; Jurado et al., 2005).

Shanghai is one of the most comprehensive industrial and commercial cities in China, and the impact of persistent organic pollutants on Shanghai has attracted extensive attention (Wang et al., 2015, 2016b). Previous works revealed that regional variability of PAHs in surface soil originated principally from the influence of urban and industrial areas of Shanghai (Liu et al., 2010), including vehicle exhaust, combustion of coal or biomass, and steel or electric power production (Wang et al., 2013, 2015). Local anthropogenic activities comprise the major sources of atmospheric PAHs in Shanghai (Wang et al., 2016b). To understand the fate of atmospheric PAHs, it is essential to know spatial and temporal variation of their atmospheric deposition. Wang et al. (2016a) investigated seasonal characteristics of atmospheric deposition of PAHs at urban and suburban sites, but no significant difference between them was observed. Liang et al. (2016) examined six sampling sites along a transect from the suburban to the city center of Shanghai and observed a spatial variation of atmospheric deposition. Limited information, however, is available about the influence of atmospheric deposition on PAH contamination in surface soils until now. This promoted us to deploy atmospheric bulk deposition samplers at several locations across Shanghai as well as to collect surface soil samples at the sampling sites.

Specific goals in this study were 1) to categorize the atmospheric bulk deposition flux of PAHs in Shanghai with respect to global situation, 2) to investigate spatial distribution and seasonal variability of deposition rates of PAHs, 3) to correlate atmospheric deposition to concentrations of PAHs in surface soil, and 4) to provide an estimate of the annual bulk deposition load of atmospheric PAHs in Shanghai.

2. Materials and methods

2.1. Study area and sampling

Shanghai is located in Eastern China, bordered by Jiangsu and Zhejiang provinces in the north and west, and the East China Sea and Hangzhou Bay in the east and south. Atmospheric bulk deposition samplers were deployed during 2012–2014 depending on local urbanization, involving in early- and newly-urbanized areas, suburban areas as well as farmland and more remote sites. As shown in Fig. 1, seven sampling sites were selected, five sites in Shanghai (sites SH1-5, registered population of 24 million), one in Jiaxing city (site JX, population of 4 million) in Zhejiang and one in Haimen city (site HM, population of 1 million) in Jiangsu. Site SH1 is located at the city center of Shanghai (the Bund), site SH2 presents a newly-urbanized area, and site SH3 is situated in a suburban area of Shanghai, but close to industrial areas. Sites SH4 and SH5 are located in more rural areas on the Changxing Island and Chongming Island to reflect background conditions. Details on sampling sites and schedules are provided in the Supporting Information. Atmospheric bulk deposition was determined with a time-integrating passive sampler comprising a borosilicate glass funnel (ID:250 mm) and a large adsorption cartridge packed with 15 g of Amberlite IRA-743 which was fixed on top and at the bottom with glass wool plugs (according to a German standard as described by Gocht et al. (2007)). Particulate and dissolved PAHs from dry and wet deposition were collected by filtration and adsorption, respectively. In the field, the samplers were mounted in a metal box and deployed 1.5–2.0 m above the ground, as shown in Fig. S1. After each sampling campaign, the funnels were cleaned with acetone. 11–13 sampling campaigns of 30–90 day duration each were conducted from July of 2012 to September of 2014. Due to logistical constraints, 5 out of 90 samples total were lost. Surface soils were collected in September of 2014 at the same location to a depth of 5–10 cm; each sample consisted of five subsamples from the surrounding area (within ~4 m^2).

2.2. Sample analysis

PAHs in atmospheric deposition samples were measured as described in detail by Gocht et al. (2007). Briefly, after sampling the funnel was purged in the field with 200 mL acetone for collection of deposited and adsorbed PAHs from the glass surface. The acetone was collected and used to rinse the cartridges in laboratory in a first extraction step. PAHs in the rinsed acetone were liquid-liquid extracted via adding 10 mL cyclohexane and ~2 L Millipore water to separate the phases. Cartridges (and litterfall occasionally collected by the funnel) were further Soxhlet-extracted by a mixture of acetone and hexane. Five deuterated PAHs (500 ng each) were added to the extracts as surrogate standards. The extracts were cleaned up through a silica gel and sodium sulfate column, respectively. Before analysis, a further standard (500 ng of deuterated fluorene) was added for calculation of surrogate standard recoveries. Extracts were analyzed using an Agilent 7890A GC with HP-5 MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) equipped with an Agilent 5975C MSD in EI + selected ion monitoring (SIM) mode. Two alkylated naphthalenes and eighteen parent PAHs (16 US EPA PAHs, benzo[e]pyrene and perylene) were measured and quantified based on surrogate standard recoveries (see Table S2). PAHs in soil were processed according to methods published previously (Liu et al., 2010, 2013b), using Soxhlet extraction followed by silica gel cleanup and quantification by GC-MS. Further experimental details are described in the Supporting Information.

2.3. Quality assurance and quality control

Procedural blanks and field blanks were carried out periodically for quality assurance. A field blank was estimated for each batch, and PAH concentrations of field blanks were less than 10% of measured concentrations of deposition samples, except alkylated and parent naphthalenes (71–79%, see Table S3). The remaining 17 PAHs were evaluated in this study.

Limits of detection (LOD) of PAHs were 0.1–7.0 ng m^{-2} day^{-1} for atmospheric bulk deposition (AD) and 0.01–6.1 ng g^{-1} for soils. Average recoveries of the surrogate standards were 22–94% for the adsorption cartridges and 42–95% for soil. More information on quality assurance and quality control is presented in the Supporting Information (see Tables S2–S3).

2.4. Accumulation time calculation

Atmospheric deposition is important for accumulation of PAHs in topsoils. Assuming that PAHs in soils solely come from atmospheric deposition and no significant leaching or transformation of PAHs in soil occurs, the accumulation time period (AT, in years) needed to achieve the PAH concentrations observed in the topsoils (in ng g^{-1}) was estimated based on the atmospheric deposition fluxes measured (in ng m^{-2} day^{-1}):