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The seasonal changes and spatial trends of particle-associated polycyclic aromatic hydrocarbons in the summer and autumn in Changsha city

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ABSTRACT

16 Polycyclic aromatic hydrocarbons (PAHs) in TSP were identified and quantified in samples collected during May and September of 2008, in Changsha, on three different sites: the city environmental protection agency of Changsha (A), the Middle School Attached to Hunan Normal University (B) and Yuhua district (C). The filters contained the particulate matter were extracted with dichloromethane in ultrasonic bath and then analyzed by gas chromatography/mass spectrometry (GC/MS). The total of 16 PAHs mean concentrations of summer at site A, B, C were 32.503 ng/m^3 , 19.360 ng/m^3 and 26.784 ng/m^3, respectively; while the values for autumn at site A, B, C were 24.982 ng/m^3, 17.088 ng/m^3 and 15.465 ng/m^3, respectively. The mean concentrations of PAHs of all samples in A site were 0.57 times higher than those measured at B site, and 0.38 times higher than at C site. The analysis of their distribution amongst the main emission sources was done through the diagnosis of concentration ratios of PAHs, as well as using statistical methods like principal component analysis. The diagnosis results of concentration ratios of PAHs suggested that the major polluting sources in the Changsha region during the studied period were the combustion of fuels, such as diesel oil, gasoline, wood and coal. The statistical analysis separated the 16 compounds studied into 3 and 4 factors for summer and autumn, separately. Factor 1 in summer represents vehicular emissions. Factor 2 represents emissions from the nature gas. Factor 3 represents emissions from combustion. In autumn, vehicle emissions, combustion sources, natural gas and coke oven were the major emissions.

1. Introduction

Due to the rapid growth of industrial activities, population and traffic density in the past three decades, people are facing serious air pollution problems. One major polluting source that is especially prominent is polycyclic aromatic hydrocarbons (PAHs) (Vera Castellano et al., 2003). PAHs pollution has been proved to be mutagenic and/or carcinogenic, and thus directly posing threats to human population. So the study of PAH pollution is important.

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds composed of two or more fused aromatic rings (Esen et al., 2008), and they are ubiquitous environmental pollutants that are formed in the incomplete combustion of fossil fuels and wood and the volatilization of petroleum. Forest fires and volcano eruption also contribute to the formation of PAH. But by far, anthropogenic sources are responsible for the majority of the PAH input to the atmosphere (Li et al., 2006). Anthropogenic activities such as industry, residential heating, power generation, and motor vehicle use has become major sources of atmospheric PAHs associated with particulates (Kume et al., 2007).

A number of characterization and source identification studies of PAHs have been carried out previously (Qi et al.,

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2002; Guo et al., 2003; Peng et al., 2003; Pan et al., 2003; Guo et al., 2004). Despite their environmental relevance, no intensive research has been conducted in Changsha on PAH levels in the atmosphere. Thus, there is a lack of information about PAH occurrence in the atmosphere of Changsha. But for the limited conditions, the objectives of this paper are confined only to the study of PAHs levels, their distribution patterns, and the seasonal variation characterization and source identification of PAHs bound to TSP in Changsha. Such studies will give scientific support to the management of the city and also provide data for the global database from a unique type of geography and climate of an inland city.

2. Materials and methods

2.1. Description of sampling sites

The climate of Changsha is humid subtropical monsoon climate, characterized by mild temperatures (290.25 K annual mean), with warm summers and cool winters, high humidity (82%), and frequent rainfall (1546 mm/year).

Sampling of ambient air TSP-bound PAHs was performed at several sites (A, B, C) during summer and autumn of 2008 in Changsha, Hunan province, PR China. Three sampling sites were selected based on their different land-use categories, populations and traffic densities. Samples were collected from three sites: the city environmental protection agency of Changsha (A), the Middle School Attached to Hunan Normal University (B) and Yuhua district (C). The locations of the sampling sites in Changsha city are given in Fig. 1.

Site A is located at the center of several large-scale computer markets, and is located among the streets and avenues with intense automobile and bus traffic. The emission sources of anthropogenic pollution are concluded to mainly be vehicle emissions by automobile and bus traffic, and some busy thoroughfares were around A.

Site B, the Middle School Attached to Hunan Normal University, which is located between the urban and the country region of Changsha City and is surrounded by Changsha Higher Education Mega Center, is a site close to areas of heavy traffic and large population of campus residents.

Site C, which is located at Xiangzhang Road, is a residential district mixed with some institutions.

2.2. Sample collection

During summers and autumns, the month of May and September are the months of the heaviest pollution. And Vasilakos et al. (2007) and Hong et al. (2007) think that the random sampling could meet the experiment demand, so this research apply random sampling mode. Twenty-seven samples were intermittently collected between May and September 2008 with an average sampling period of 8 h during 7 am to 5 pm, using a standard medium-volume total suspended particle (TSP) sampler at a flow rate of 100 L/min (TH-105C,Tianhong Intelligent Instrument, China). All samples were taken during the daytime.

Glass fiber filters (GFFs, ϕ90 mm) used to determine the concentration of total suspend particulate (TSP) were baked out at 450 °C for 12 h and stored in sealed bag prior to sampling. They were labeled and let sit for 24 h in a desiccator, under controlled temperature and relative humidity conditions before and after the sampling, to prevent hydration of the filters' surface. They were then weighted, using an analytical scale with a precision of 0.010 mg, and stored in a refrigerator at −18 °C packed in sealed bag till extraction and analysis.

To avoid any contamination, great cautions was taken during the sampling. All sample materials were transported to the sampling site in sealed bags in order to prevent exposure to ambient air. Control groups including filters were placed in the field to determine background contamination level during sample handling and preparation for the analysis. At each site, the samples were collected for 4 or 5 days in a season.

2.3. Analytical procedure

Particulate matter containing PAHs samples collected on the GFFs were cut into small pieces, and then extracted for 30 min twice in an ultrasonic bath (SB, model 3200) with 20 mL dichloromethane (DCM) solvent at certain time. All the extracts were transferred and concentrated to a volume of 1 mL using a stream of nitrogen. The concentrated extracts were fractionated by column chromatography to separate PAHs from other polar organic interfering materials.

The column was packed by adding 15 cm silica gel 100–200 (Merck, Qingdao; activated at 105 °C for 24 h), 1 cm of anhydrous sodium sulfate (baked at 600 °C for 6 h) in DCM-slurry in the given order. A further 40 mL of hexane was used to rinse the column. The extract (1 ml DCM) was applied to the top of the column and eluted with 25 ml hexane and 25 ml hexane-dichloromethane (V:V = 1:1) successively. The second fraction was enriched in PAHs.

The fraction containing PAHs was concentrated to 0.1 mL using a rotary evaporator, transferred to a 2 mL vial and preserved in a refrigerator at −18 °C till gas chromatography–mass spectrometry (GC/MS) analysis.

The PAHs were identified by means of a gas chromatography coupled with a mass spectrometry detector (GC/MS, Thermo-Finnigan, Trace GC, Polaris Q). The detection mode used for the identification was selective ion monitoring (SIM).

The GC was equipped with a DB-5 MS capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm), with helium as the carrier gas. The oven temperature program was as follows: hold at 60 °C for 3 min, increased to 300 °C at a rate of 3 °C/min and a final hold at 300 °C for 20 min. The injector and detector temperatures were 250 °C and 280 °C, respectively. 1 μl sample was injected in a splitless mode.

2.4. Quality assurance/quality control (QA/QC)

Field control samples, which accompanied samples to the sampling sites, and the laboratory control samples, were analyzed by the same procedure as the samples to determine any background contamination. Field blanks and laboratory blanks showed no detectable PAHs. Instrument solvent blanks were run to check the status of the analytical system.

PAHs recoveries were determined from the surrogate standards added prior to extraction. The average and the range of the recoveries were 73% ± 19% and 88% ± 21% for anthracene-d10 and perylene-d12, respectively.