



Measurement and source identification of polycyclic aromatic hydrocarbons (PAHs) in the aerosol in Xi'an, China, by using automated column chromatography and applying positive matrix factorization (PMF)

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ABSTRACT

In this study, we measured polycyclic aromatic hydrocarbons (PAHs) in aerosols in Xi'an, China from 2005 to 2007, by using a modified Soxhlet extraction followed by a clean-up procedure using automated column chromatography followed by HPLC/fluorescence detection. The sources of PAHs were apportioned by using the positive matrix factorization (PMF) method. The PM₁₀ concentration in winter ($161.1 \pm 66.4 \mu\text{g m}^{-3}$, $n = 242$) was 1.5 times higher than that in summer ($110.9 \pm 34.7 \mu\text{g m}^{-3}$, $n = 248$). Σ PAH concentrations, which are the sum of the concentrations of all detected PAHs, in winter ($344.2 \pm 149.7 \text{ ng m}^{-3}$, $n = 45$) was 2.5 times higher than that in summer ($136.7 \pm 56.7 \text{ ng m}^{-3}$, $n = 24$) in this study. These strong seasonal variations in atmospheric PAH concentration are possibly due to coal combustion for residential heating. According to the source apportionment with PMF method in this study, the major sources of PAHs in Xi'an are categorized as (1) mobile sources such as vehicle exhaust that constantly contribute to PAH pollution, and (2) stationary sources such as coal combustion that have a large contribution to PAH pollution in winter.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that consist of two or more fused aromatic rings. Atmospheric PAHs mostly originate from the incomplete combustion of organic matter (e.g., fossil-fuel combustion). Researchers have paid much attention to PAHs because of (1) their toxicity, mutagenicity, carcinogenicity, and endocrine-disrupting potential, and (2) their characteristic composition which allows us to identify different sources of aerosols (Okuda et al., 2006).

Sample extraction procedures are often considered to be the most time- and solvent-consuming processes in the analytical methods used for detecting PAHs in aerosol samples. Recently, various attempts have been made to solve this problem by testing many extraction techniques, such as automated Soxhlet extraction, microwave-assisted extraction, sonication, supercritical fluid extraction (SFE), and pressurized solvent extraction (PSE) (Letellier et al., 1999; Park et al., 2002; Szolar et al., 2002; Bi et al., 2005; Okuda et al., 2006). In this study, we used a modified Soxhlet extraction method called Soxhlet-Warm. Heated solvent accelerates the extraction from the samples in this method. The Soxhlet-Warm method gave similar results in terms of the extraction efficiency as compared to other

methods such as SFE or PSE (Kočič et al., 2007). After the extraction, many researchers have applied the column chromatography to separate PAHs from co-extracts that often have negative effects to the precision and accuracy in the instrumental analysis. In many cases, however, the clean-up procedure has been done manually, therefore researchers have been forced to spend too much time doing it (Kumata et al., 2006; Liu et al., 2007; Okuda et al., 2006; Sofowote et al., 2008). Okuda et al. (2009) developed an automated column chromatography system, which allows the researchers to achieve the clean-up procedure for the determination of PAHs more effectively. We applied this novel technique to the determination of PAHs in aerosol collected in Xi'an, China.

Chinese inland cities, such as Xi'an, have been behind in the economical development compared with the coastal cities, such as Beijing or Shanghai. These inland cities are going to develop rapidly while many environmental protection laws are enforced in order to improve the air quality. Therefore we should pay much attention to the air quality of inland cities because it would be uncertain that the air quality would become better or worse in the near future. It is also important to investigate the current situation of the air quality especially when the city is going to change during a very short period of time. We considered Xi'an as a representative of the Chinese inland cities. Xi'an (area of 1066 km², population 5.1 million), located on the Guanzhong Plain at the south edge of the Loess Plateau, is the largest city in northwestern China. The climate of Xi'an is dominated by large variations in the East Asian monsoons. During winter, the northerly

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Asian winter monsoon winds prevail, and they are associated with the transporting of Asian dust from Chinese deserts and nearby loess areas (Zhang et al., 2002). In summer, the monsoon winds bring moisture to the region from the south. Along with the rapid increase in the number of vehicles and energy consumption in the past decades, Xi'an is facing long-term air quality problems with aerosol as a major pollutant (Zhang et al., 2002; Cao et al., 2005; Shen et al., 2008). Although the air quality has been improved during the past decade (Zhang et al., 2002; Shen et al., 2008), the aerosol is still the major problem in the atmospheric environment in Xi'an. It is very important to identify the pollutant sources in order to reduce them. The source identification is often achieved by using receptor models, such as a chemical mass balance model (Samara et al., 2003; Shu et al., 2001; Zheng et al., 2002; Okuda et al., 2004) and factor analysis (Chen et al., 2002; Henry et al., 1994; Kim et al., 2004; Poirot et al., 2001). A previous study reported that the predicted results obtained by the two types of receptor models (CMB model and factor analysis) would give similar results when compared to each other (Maykut et al., 2003). We applied the positive matrix factorization (PMF) method, which has been a recently developed factor analysis and considered a reliable receptor modeling (Paatero and Tapper, 1994; Moon et al., 2008), to apportion the sources of PAHs.

In this study, we measured PAHs by using the Soxhlet-Warm method followed by a clean-up procedure using automated column chromatography followed by HPLC/fluorescence detection. The sources of PAHs were apportioned by using the PMF method.

2. Experiments

2.1. Aerosol sample collection

The sampling site is located in the southeastern part of downtown Xi'an city. The detail of the site was described elsewhere (Shen et al., 2008, 2009), but in brief, the north and east of the sampling site are residential areas and the campus of Xi'an Jiaotong University, while the south and west are the South Second Ring and Xingqin Roads, where the traffic is heavy. The TSP (total suspended particles) samples were collected on 47-mm diameter cellulose nitrate membranes (0.8 μm pore size, AAWP04700, Millipore Corp.) at the rooftop of a 15-m high building. Twenty-four hour TSP (10:00 am to 10:00 am, local time) samples were collected every third day from October 3rd, 2005 to October 10th, 2007 using a low-volume air sampler (Tokyo Dylec Corp., Japan) operating at a flow rate of 5 L min^{-1} . We also collected blank samples, which were exposed to the air whereas no air had passed through the filter, in order to consider the background contamination that was provided by gravitational deposition of the aerosols.

2.2. PAH extraction using modified Soxhlet method (Soxhlet-Warm)

Filter samples were extracted by the modified Soxhlet apparatus (Büchi B-811) with the following procedure. The solvent used was dichloromethane (80 mL), the upper heater (on the sample vessel) was set at 120 °C (heater level 6), and the lower heater (on the solvent beaker) was set at 180 °C (heater level 9). Extraction time was 30 min for the hot extraction mode, which means both of the heaters were active, followed by 50 min for the rinse mode, which means only the lower heater was active whereas the upper heater was turned off. After the extraction, the solvent volume was reduced by rotary evaporation under a reduced pressure (60 kPa) at 35 °C in a water bath. The solvent of the concentrated dichloromethane solution was exchanged with *n*-hexane by adding 1 mL of *n*-hexane. Then the *n*-hexane solution was reduced to 0.1 mL under a gentle air stream at room temperature.

2.3. PAH purification by automated column chromatography

The clean-up process for the PAHs was achieved successfully by the use of the aminopropylsilane chemically-bonded stationary-phase column chromatography (Wise et al., 1977; Okuda et al., 2000, 2006). Sep-pak Vac NH_2 (NH_2 -column, 500 mg/3 cc, 2 cm \times 1 cm i.d., Waters Co.) in the conditioning process we add 5 mL of *n*-hexane to the NH_2 -column. Then, 0.1 mL of the concentrated sample solution in *n*-hexane was applied on the NH_2 -column and eluted with 1.5 mL of *n*-hexane (Fraction 1) followed by 4 mL of *n*-hexane/dichloromethane (3:1 v/v) (Fraction 2). Fraction 2 contained PAHs. Then, 3 mL of dichloromethane were added (Fraction 3). Every procedure except for transferring the concentrated sample solution on the column top was done by the automated column chromatography system (Okuda et al., 2009).

2.4. PAH determination by HPLC/fluorescence detection

In order to avoid the evaporated loss of PAHs, 50 μL of dimethylsulfoxide (DMSO) were added to the sample solution (Fraction 2) in the sample vial. The sample solution was evaporated under a gentle air stream, and then 450 μL of acetonitrile were added to the sample vial for the HPLC/FLD analysis. The HPLC equipment (Shimadzu Co.) consisted of a SCL-10A_{VP} system controller, a DGU-12A degasser, two LC-10AT_{VP} pumps, a SIL-10AD_{VP} auto-injector, a CTO-10As_{VP} column oven, and a RF-10A_{XL} fluorescence detector. The separation column was a SPELCOSIL LC-PAHs (ODS, 3.0 mm i. d. \times 250 mm length, particle size: 5 μm , Spelco, Co.). The mobile phase was an Acetonitrile (AceCN)/water gradient program (65% AceCN at the beginning, 5 min hold, 14 min linear gradient to 86% AceCN, 12 min linear gradient to 90% AceCN, 4 min linear gradient to 100% AceCN and 5 min hold). The flow rate was 0.6 mL min^{-1} . The column oven temperature of 35 °C was maintained. The injection volume was 20 μL . The excitation and emission wavelengths were changed according to a time program (Ex: 254 nm and Em: 375 nm at 0 min, 260/420 nm at 10.0 min, 254/390 nm at 13.4 min, 260/420 nm at 21.8 min, 293/498 nm at 34.3 min, and 300/420 nm at 41.0 min). We determined 15 PAHs that were shown along with their abbreviations in Table 1. The detection limits for all PAHs were less than 5 pg (Okuda et al., 2006).

We analyzed PAHs in the aerosol samples collected in Xi'an by using the Soxhlet-Warm extraction method, followed by the automated column chromatography system, and HPLC/FLD. The procedure we used in this study was exactly the same as that reported in a previous paper (Okuda et al., 2009), which was quite precise (RSD was less than 10%, $n = 4$) and had the PAHs recoveries of 63–136% when SRM1649a (Urban Dust Standard Reference Material provided by NIST) was analyzed.

2.5. Data analysis by the positive matrix factorization (PMF) method

Detailed concept of the source identification by PMF has been described elsewhere (Paatero and Tapper, 1994; Eberly, 2005; Moon et al., 2008). We used the EPA PMF ver. 1.1 (Eberly, 2005). We used 15 species of PAHs and 94 days result as the input data. We selected the random seed mode with 100 of the number of random starting point. We examined the number of factors from 3 to 10. We compared each plot that showed the estimated PAHs, which is the sum of the concentrations of all PAHs obtained by the PMF estimation, versus the observed PAHs concentrations obtained by our field measurement. We selected 6 factors that gave the best correlation ($r^2 = 0.9861$) for further discussion in this study. We didn't adopt any results obtained by trying the rotation since it was unknown at this time as to how strongly a rotation should be pulled to estimate the uncertainty due to rotational ambiguity (Eberly, 2005).

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