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POLYCYCLIC AROMATIC HYDROCARBONS IN ASIAN ATMOSPHERE

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Introduction

Asia is one of the most prosperous areas of the world. However, rapid industrialization and urbanization in this region have resulted in a mass of environmental concerns. Several studies have focused on persistent organic chemicals, such as polychlorinated biphenyls (PCBs)[1], polybrominated diphenyl ethers (PBDEs)[1], organochlorine pesticides (OCPs)[1], short-chain chlorinated paraffins (SCCPs)[2], as well as polycyclic aromatic hydrocarbons (PAHs)[3,4]. PAHs are among the most toxic organic pollutants of concern in Asia, especially in China, where PAH concentrations are significantly higher than those in other countries[4].

In 2012-2013, the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) carried out a Soil and Air Monitoring Program (Asia-SAMP) in 5 Asian countries, including China, Japan, India, South Korea, and Vietnam, to study the occurrence of persistent toxic substances in these countries. In this study, we measured 47 PAHs in air samples at 176 sampling sites collected from these 5 countries from September 2012 to August 2013. The main objectives of this work are to investigate the levels of PAHs in the atmosphere for different seasons across the study area.

Materials and methods

Sampling

Passive air samplers (PASs) coupled with polyurethane foam (PUF) disks were deployed at 176 sites (11 background, 83 rural and 82 urban) across China, Japan, South Korea, Vietnam and India. PUF disks were developed for four periods: period 1 (September-November 2012); period 2 (December 2012-February 2013); period 3 (March-May 2013); period 4 (June-August, 2013). After sampling, the sampled PUF disks were sent to the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) laboratories, where they were stored cold (-20 ^{o}C) and in the dark until extraction. It should be note that the PUF disk PAS analysis considers only the gas-phase transfer of contaminants.

Sample extraction and analysis

Samples were extracted and analyzed according to the methods established at the National Laboratory for Environmental Testing (NLET), Environment Canada. Detailed information on sample collection, treatment, analysis and air concentration calculation can be found in our previous studies[5]. In the present study, 47 PAH compounds (including 21 parent- and 26 alkylated-PAHs) were determined.

Toxic equivalency factor: BaP equivalency

We ranked the carcinogenic PAHs according to their relative potency factor (RPF) to benzo(a)pyrene (BaP)[6]. The BaP equivalent (BaP_{eq}) concentration were calculated by multiplying each individual PAH concentration with its RPF and determined the concentration of total PAH expressed as BaP_{eq}.

Quality assurance/quality control

All analytical procedures were monitored using strict quality assurance and control measures. One field blank and one laboratory blank were added for every 10 samples, all PAH compounds but naphthalene, 1-methylnaphthalene and 2-methylnaphthalene were under detection limit in field blanks. Surrogate standard recoveries in samples ranged from 68% to 115% (mean 87±19%). The final results were corrected using the corresponding period of the field blanks but not the surrogate recoveries. The method detection limits (MDLs) for PAHs ranged from 0.0241 to 3.12 ng/sample. Observations below the MDLs were assigned a value of 2/3 the MDLs.

Results and discussion

General distribution

The spatial distribution of annual mean air concentrations of PAHs from 176 sampling sites are shown in Figure 1. In all 5 Asian countries, the annual mean concentrations of Σ_{47}PAHs (sum of 21 parent and 26 alkylated PAHs) were in the range of 6.29-688 (128±132, mean±SD) ng/m^3 (Figure 1 (a)), among

which 4.10-409 (76.9±74.6) ng/m^3 for 16 EPA priority PAHs (Σ16EPA-PAHs) (Figure 1 (b)), 1.56-381 (46.2±57.8) ng/m^3 for 26 alkylated PAHs (Σ_{26}alkyl-PAHs) (Figure 1 (c)), and 0.0928-34.8 (5.64±6.86) ng/m^3 for BaP_{eq} (Figure 1 (d)). Higher concentrations were generally observed in urban areas, and lower concentrations were in rural/background areas. It was not unexpected that strong urban-rural-background transect was presented in the study area. Concentrations of Σ_{47}PAHs in air samples were in the order of urban (143±117 ng/m^3) > rural (126±147 ng/m^3) > background (22.4±11.4 ng/m^3), showing the typical "urban-rural transect pattern"[5] or "primary distribution pattern"[7].

Depending on countries, the concentrations of Σ_{47}PAHs, Σ_{16}EPA-PAHs, Σ_{26}alkyl-PAHs and BaP_{eq} were respectively 34.8-688 (194±149), 15.7-409 (115±81.2), 7.44-381 (72.1±68.8), and 0.492-34.8 (7.89±8.28) ng/m^3 in China, 6.29-14.0 (9.56±2.04), 4.10-8.27 (5.76±1.20), 1.56-5.09 (3.24±0.988), and 0.0928-0.714 (0.288±0.161) ng/m^3 in Japan, 13.8-75.2 (28.7±15.3), 8.63-51.8 (19.9±11.2), 2.81-12.5 (5.98±2.49), and 0.610-2.66 (1.21±0.572) ng/m^3 in South Korea, 24.3-170 (71.3±32.8), 15.2-87.0 (42.8±17.9), 8.03-79.9 (26.5±15.2), and 1.26-10.6 (4.34±2.50) ng/m^3 in Vietnam, and 14.6-236 (96.1±62.5), 9.91-164 (62.3±46.5), 4.41-69.8 (30.8±19.5), and 0.951-19.0 (5.79±4.23) ng/m^3 in India. The levels of PAHs were significantly higher in China than the other countries, followed by India ($p<0.01$).

Comparison with other studies

Air PAHs pollution in the five countries has been attracted more attention in the past two decades[8-12]. In China, the published data on air contamination of PAHs have increased rapidly during the past two decades. Generally, concentrations of PAHs in the previous measurements were in line with previous measurement. In Japan and South Korea, the monitoring data were started from 1990s and 2000s, respectively. PAHs concentrations in the present study were much lower than those measurements collected in the past 20 years, indicating the declining trend of air pollution of PAHs during the past several years. In Vietnam and India, up to now, the published data mostly focus on the largest cities (e.g. Hanoi and Ho Chi Minh City in Vietnam, Delhi, Agra, Tiruchirappalli, and Mumbai in India). These results were comparable with those from our study. More importantly, our results displayed a comprehensive survey for air concentrations of PAHs on a national scale in these two countries.

In addition to the above five countries, our results were also compared with those from other region. e.g.; Kuwait (5.2~13 ng/m^3)[13], Germany (0.8~5 ng/m^3)[14], Turkey (1.6~838 ng/m^3)[15], Spain (3.5~84 ng/m^3)[16], Mexico (6.1~180 ng/m^3)[17], USA (5.7~56 ng/m^3)[18] and so on. Generally, the air concentration of PAHs were at a moderate to high levels in China, India and Vietnam, but close to the lower end in Japan and South Korea.

Seasonal distribution

The air concentrations of PAHs displayed seasonal changes in the present study. The study area was separated into three parts (Northern Region, Central Region and Southern Region), in order to better known the seasonal changes of atmospheric PAHs levels. The Northern Region is defined as the area including the Japan, South Korea northern part of China. The Southern Region is defined as the area including Vietnam, India and 4 provinces in the southernmost point of China. The Central Region, which included the rest of the other regions in the southern part of China.

In the Northern Region, statistical analysis results ($p<0.01$) showed that the concentrations of Σ_{47}PAHs followed the sequence of period 2 (132±178 ng/m^3) > period 1 (91.0±100 ng/m^3) > period 4 (64.1±91.6 ng/m^3) > period 3 (33.7±46.1 ng/m^3). Reduced photochemical degradation and increased source emissions would contribute to the higher PAHs concentrations in period 2 (winter), especially in high latitude areas. In North China (>120 °N), there are 4-6 months (November to next February or October to next March) domestic heating period per year. Ma et al.[5] reported that the ratios of the air PAHs concentrations between heating and non-heating periods were 2.5 for urban samples, 2.7 for rural samples and 3.1 for background samples in Harbin, North China.

In the Southern Region, the concentrations of Σ_{47}PAHs in period 1 (135±99.7 ng/m^3) and period 2 (104±71.7 ng/m^3) were significant higher ($p<0.01$) than that in period 3 (33.4±21.1 ng/m^3) and period 4 (53.1±28.9 ng/m^3). Surface temperature, rainfall, sunshine hours, relative humidity, wind speed and airmass origin were the main influence factors for the distribution of atmosphere PAHs in the Southern Region[19].

In the Central Region, the concentrations of Σ_{47}PAHs observed in period 2 (103±175 ng/m^3), period 1 (86.5±71.8 ng/m^3) and period 4 (82.1±136 ng/m^3) were not significant different, but were all significant higher ($p<0.01$) than that in period 3 (45.8±28.8 ng/m^3). Compare to the other two regions, the seasonal distribution of the concentrations of Σ_{47}PAHs seemed more uniform in the Central Region, which showed that relatively stable emission of PAHs in this area.

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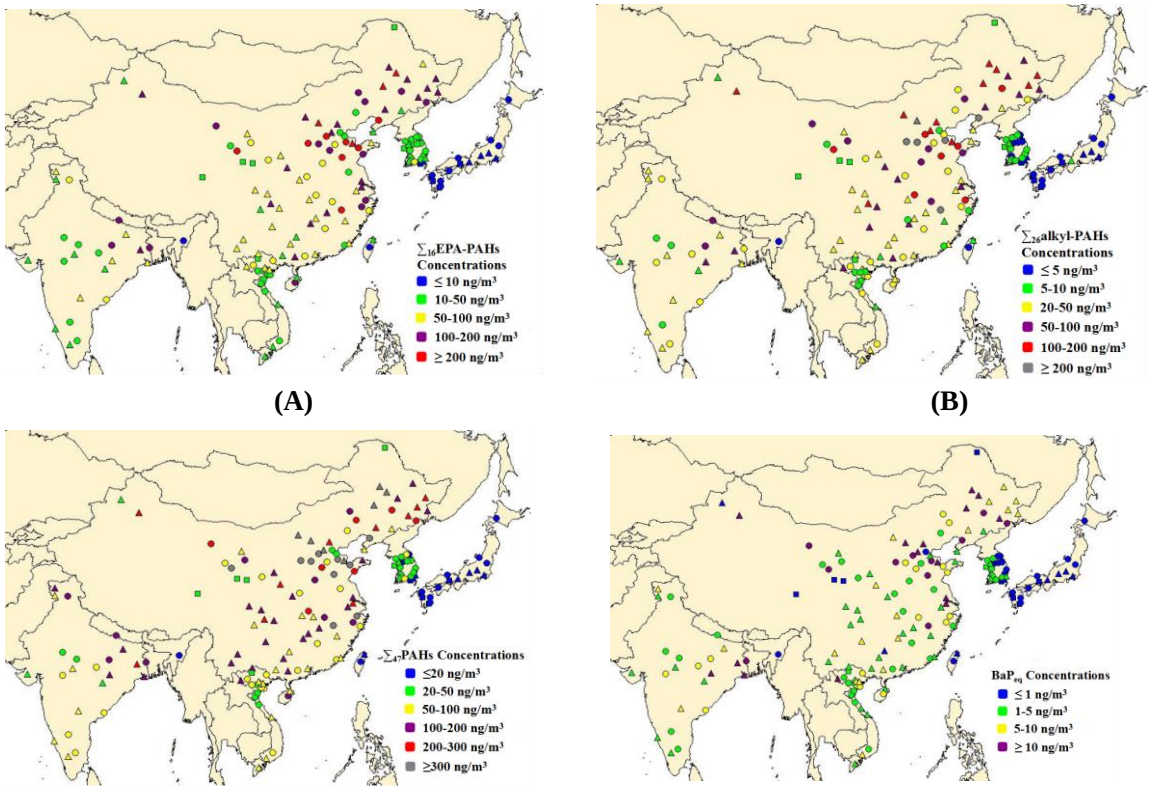

Figure 1. Distribution of annual mean (a) 16 EPA priority PAHs, (b) total 26 alkylated PAHs, (c) total 47 PAHs, and (d) BaP_{eq} concentrations (ng/m^3) in atmosphere from 176 sites, among which 11 are background sites (foursquare), 83 are rural sites (roundness), and 82 are urban sites (triangle).