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Atmospheric Polycyclic Aromatic Hydrocarbons in North China: A Winter-Time Study

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The contamination and outflow of atmospheric polycyclic aromatic hydrocarbons (PAHs) in the Chinese Northern Plain, a region with a total area of 300 000 km^2 and a high PAH emission density, were investigated. Polyurethane foam (PUF) and PM_{10} samples were collected at 46 sites located in urban, rural (towns or villages), and control (remote mountain) areas in the winter from November 2005 to February 2006. The observed concentrations of atmospheric PAHs were generally higher than those reported for developed countries and southern Chinese cities. It was found that there was no significant difference in air PAH concentrations between the urban and the rural areas (514 ± 563 ng/m^3 and 610 ± 645 ng/m^3, respectively), while the PAH concentrations at the control sites (57.1 ± 12.6 ng/m^3) were 1 order of magnitude lower than those at the other sites. The primary reason for the similarity in PAH concentrations between urban and rural areas was the fact that the predominant sources of biomass and domestic coal combustion were widely spread over the study area. The partition constants (K_{PM10}) of PAHs were significantly correlated to the corresponding values of subcooled liquid–vapor pressure (p_L^0). However, the regression slopes of log K_{PM10} versus log p_L^0 were much steeper than −1, indicating adsorption dominated over absorption. Three distinct patterns of outflow from the study area were identified by forward trajectory and cluster analysis.

Introduction

Although atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs) in developed countries decreased significantly recently (*1*), emissions from developing countries including China increased (*2*). As a result, global PAH emissions have remained at a relatively sustained rate (*3*). It was estimated that 25 000 tons of PAHs (16 U.S. EPA priority PAHs) were emitted from China in 2003 (*2*). Relatively high levels of PAHs have been detected in the air, water, soil, vegetation, and even food items in China (*4–6*). Health risks of exposure to PAHs were also revealed in several regions in China (*7, 8*). Additionally, the outflow of PAHs from mainland China remains another concern (*9*). Therefore, atmospheric PAH contamination in China has become a major concern for environmental scientists and policy makers.

Recently, the number of papers published on ambient air PAH contamination in China has rapidly increased. The majority of them, however, focused on urban areas (*4, 10, 11*) since it was believed that urban air is more severely contaminated (*12, 13*). Alternatively, it was recognized that the consumption of biofuel and domestic coal, the most important PAH emission activities in China, are the primary energy sources used in rural areas. Therefore, in China, high-density PAH emissions occurred not only in urban districts but also in rural areas, and this is particularly true in the winter (*7, 14*). For this reason, it was suspected that, unlike in developed countries, the difference in atmospheric PAH concentrations between urban and rural areas in China may not be as significant as believed before. It was also suggested that regional atmospheric contamination could be the major reason why the localized remediation efforts often failed to improve the air quality (*15*). As such, a regional survey on atmospheric PAHs is necessary.

The aim of this study was to investigate the distribution of atmospheric PAHs in the Chinese Northern Plain (CNP) during the winter. The primary sources, urban−rural trend, gas−particulate partitioning, and the outflow of PAHs were addressed. The study area located in northern China with a total population of 130 million covers most of the CNP including Beijing, Tianjin, Hebei, and part of Shandong (total size: over 300 000 km^2, similar to the size of Italy). PAH emission density in this region far exceeds the national average (*14*). In fact, this area was also identified as a source region in the Asian continent outflow (*9*).

Methodology

Sampling. Samples were collected from 46 locations (1.5∼18 m heights), which can be classified into three categories of urban, rural, and control sites (Figure S1, Supporting Information). The urban sites are located in commercial or industrial districts, while the rural sites are in suburbs or villages. The two control sites are located in the remote mountain areas at least 50 km away from cities or towns. It should be indicated that the population density in rural areas in this study (∼300/km^2) is significantly greater than those in Europe and North America (*1, 16, 17*).

The PM_{10} samples were collected with glass fiber filters (GFFs; 90 mm in diameter, baked at 450 °C for 4 h before sampling) using medium-volume air samplers (TH-105C equipped with PM10-100 inlet, Wuhan Tianhong Intelligent Instrument Corp. Co., Ltd., China) at a flow rate of 100 L/min. The gas-phase PAHs were collected using a polyurethane foam (PUF) plug (Supelco, 22 mm diameter × 7.6 cm) contained in assembled glass cartridges. Particulate matter was trapped with GFFs (22 mm in diameter) in front of the PUF plugs. A TMP 1500 pump (Jiangsu Eltong Electric Corp. Co., Ltd., China) running at a flow rate of 1.5 L/min was employed. Cleaning of the PUF plugs prior to sampling involved Soxhlet extraction with *n*-hexane for 8 h. The PM_{10} and PUF samples were collected simultaneously at each site for 24 h during a period from November 22, 2005, to February 27, 2006. All samples were transported to the laboratory immediately after sampling and stored at −18 °C until the

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analysis was performed. GFFs were weighed prior to and after the sampling. Temperatures during the sampling were retrieved from the National Oceanic Atmospheric Administration (NOAA) database (*18*) and ranged from −17.1 to +8.1 °C.

Sample Analysis. The GFFs were Soxhlet extracted in a 1:1 mixture of dichloromethane and acetone for 20 h. The extracts were concentrated to 1 mL by rotary evaporation at a temperature below 38 °C. A total of 5 mL of *n*-hexane was added and evaporated to 1 mL for solvent exchange. Chromatography columns (10 mm i.d. × 300 mm length) filled with 10 g of silica gel (100–200 mesh, activated at 130 °C for at least 16 h) and covered with a layer of anhydrous sodium sulfate to a depth of 20 mm were used for cleanup. The concentrated extracts were transferred to the silica gel column and sequentially eluted with 25 mL of *n*-hexane and 35 mL of dichloromethane at a flow rate of ∼2 mL/min. The fraction in dichloromethane was solvent-exchanged to *n*-hexane and concentrated to ∼1 mL. The PUF plugs were Soxhlet-extracted in a 1:1 (v/v) mixture of *n*-hexane and cyclohexane for at least 4 h, and then concentrated to ∼1 mL without further cleanup.

The analysis and quantification details were described previously (*19*). Briefly, all samples were analyzed on a gas chromatography−mass spectrometry device (Agilent GC6890/MSD5973), using an HP-5MS capillary column in the selective ion monitoring mode. The PAHs were quantified by the internal standard method using 2-fluoro-1,1′-biphenyl and *p*-terphenyl-*d*14 (J&K Chemical, USA, 2.0 μg/mL). The 16 PAHs detected include naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(*a*)anthracene (BaA), chrysene (CHR), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), dibenz(*a*,*h*)anthracene (DahA), indeno(l,2,3-*cd*)pyrene (IcdP), and benzo(*g*,*h*,*i*)perylene (BghiP).

Quality Control and Quality Assurance. Quality assessment procedures were performed routinely. Laboratory blanks were run for every batch of extraction. Four duplicates of field blanks were collected for both the PUF cartridges and the GFFs. Lower-molecular-weight species (<228) found in the field blanks were generally 1 order of magnitude lower in concentration than those in the samples, except for NAP. As such, NAP was excluded from quantification. Duplicate samples were collected at nine sites. The average coefficient of variation for the total PAHs of these duplicates was 18.7%. The method recoveries of the working standard for the 16 target PAHs spiked in the sample media (100 μL × 10 μg/mL) were 66%∼114% and 59%∼114% for PUF and PM_{10}, respectively. Prior to extraction, samples were spiked with deuterated PAHs as surrogates (250 μL × 4 μg/ml). The average recoveries of NAP-*d*8, ACE-*d*10, ANT-*d*10, CHR-*d*12, and perylene-*d*12 were 65.4%, 76.4%, 84.2%, 78.1%, and 98.5% for the PUF and 64.3%, 78.8%, 94.2%, 83.4%, and 73.4% for PM_{10}, respectively. The detection limits, field blanks, and method recoveries are listed in Table S1, Supporting Information. All measurements were field-blank- and method-recovery-corrected.

All solvents were analytical grade and redistilled. The standard mixture of 16 PAHs was diluted with *n*-hexane (PPH-10JM, Chem Service Inc., U.S.A.). All glassware was cleaned using an ultrasonic cleaner (Kunshan KQ-500B, China) and heated to 400 °C for 6 h.

Trajectory Calculation. Forward trajectories were calculated to address the fate of PAHs and their potential influences on local and remote atmospheric environments. A virtual point source was assumed at the center of the study area (39.14° N, 116.77° E). Five-day forward trajectories starting at a 200 m height were calculated using HYSPLIT 4.8 with NCAR/NCEP reanalysis global meteorological data at 12 h intervals from November 15, 2005, to March 15, 2006 (*18*).

Results and Discussion

Concentrations of PAHs. The total concentrations of 15 PAHs in vapor (P15 g) and particulate (P15p) phases varied from 5.6 to 914 ng/m^3 and from 16.5 to 1870 ng/m^3, with averages of 204 ng/m^3 and 346 ng/m^3, respectively (Table S2, Supporting Information). The observed PAH concentrations were much higher than those in Birmingham, U.K., measured in 1992 (winter time, P15 g, 122 ng/m^3; P15p, 20.3 ng/m; ref *20*). Similar levels of total PAHs, monitored in February 1988, were reported for an urban site in Chicago (average: 507 ng/m^3) and were considered to be highly contaminated (*13*). Compared with other winter-time particulate PAH concentrations detected in China, our results were comparable with those reported for several northern Chinese cities including Beijing, Tianjin, and Shenyang (∼200–300 ng/m^3 *10, 21, 22*) but much higher than those for a number of cities in southern China, such as Nanjing, Guangzhou, and Hong Kong (<100 ng/m^3 *4, 11, 23*). It should be noted that our measurements were collected at both urban and rural sites, while the literature concentrations were mostly from urbanized sites. This suggests that the atmosphere of this study area was heavily contaminated.

PAH Composition Profile and Source Diagnostics. The predominant PAHs in the gas phase were low-molecular-weight compounds (ACY, FLO, and PHE as the most abundant), while the higher-molecular-weight compounds dominated the particulate phase. Although the patterns of PAH profiles were generally similar to those reported, detailed differences were identified between the following two categories: (1) samples from this study and other northern Chinese cities, particularly those collected in winter, and (2) samples from cities in southern China and developed countries. To be specific, relatively low levels of FLA, PYR, BaA, and CHR in the gas phase and BghiP in the particulate phase were observed in the first category compared to those in the second category (*20, 22, 24*). A reasonable explanation for such a difference is the fact that coal and biofuel are the primary energy sources consumed in northern China, while motor vehicle exhausts were the predominant source of PAHs in the developed countries (*25, 26*).

The above-mentioned explanation can be further elaborated by source diagnostics. The differences in emission sources can be qualitatively identified on the basis of PAH composition profiles represented by diagnostic ratios (*20, 27*). Figure 1 illustrates an example of such diagnostics as a plot of FLA/(FLA + PYR) against IcdP/(IcdP + BghiP) for particulate PAHs. In addition to the data from this study, the results from several other studies are included for a comparison. By rule of thumb, both FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) are greater than 0.5 in the case of coal/biofuel emissions (*27*). In Figure 1, most samples from this study (filled dots) fall in the top-right quadrant, indicating a predominant influence of coal/biofuel combustion. The data from this study that fall out of the quadrant are mostly close to 0.5, which is not necessarily an absolute threshold (*27*). No difference was detected in PAH composition profiles between the urban and rural sites [$p > 0.800$ for both FLA/(FLA + PYR) and IcdP/(IcdP + BghiP), Mann–Whitney test]. Among all the data from the literature (open circles), the only similar to those from this investigation are those from Chicago, where the major PAH source was also coal combustion (*28*). In contrast, the observations from five representative European and Northern American cities appear in the left-bottom quadrant, suggesting typical vehicular emissions (*26*). In addition to the cities discussed above, PAH profiles of other northeastern Asian cities are characterized

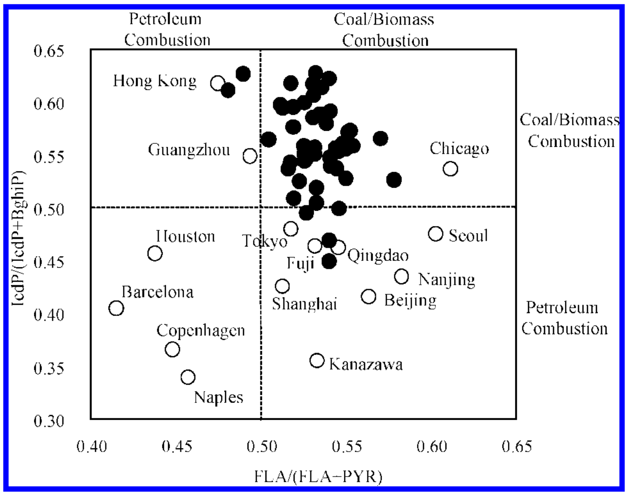

FIGURE 1. Plot of FLA/(FLA + PYR) against IcdP/(IcdP + BghiP) for PAH source diagnostics. Two dash lines represent the thresholds for petroleum combustion and coal/biofuel burning (*27*). In addition to the data in the current study (solid dots), data (winter only) for other cities are included as open circles. These cities include Chicago (*13*), Beijing (*21*), Qingdao (*29*), Naples (*30*), Guangzhou (*23*), Copenhagen (*26*), Hong Kong (*4*), Houston (*31*), Nanjing (*11*), Seoul (*22*), Fuji (*32*), Shanghai (*33*), Tokyo (*34*), Barcelona (*25*), and Kanazawa (*22*).

by mixed sources with high FLA/(FLA + PYR) but low IcdP/(IcdP + BghiP) values.

The relative abundance of BbF + BkF to FLA may help to distinguish between the coal and biofuel combustion sources to a certain extent. Wang et al. summarized the results of atmospheric PAH studies in China and concluded that BbF + BkF levels in aerosols from coal burning are higher than those of the other species (*35*). In this study, BbF + BkF predominated at 22 sites out of 46 in total, while a relatively higher FLA level was detected at other sites, confirming a stronger influence of firewood and straw combustion (*36–38*). This was in agreement with the emission estimates (*14*).

Difference among Sampling Sites. The results of a Mann–Whitney test indicated a significant difference in P15p and P15g between the control and other sites ($p = 0.031$ and 0.024 for P15p and P15g, respectively), but not between the rural and urban sites ($p = 0.826$ and 0.951 for P15p and P15g, respectively).

The two control sites were located at remote areas with low population densities and distances far from the major anthropogenic sources. Consequentially, the measured PAH15 (P15p + P15g, 57.1 ± 12.6 ng/m^3) was 1 order of magnitude lower than the average value of all the samples studied. Still, the level was much higher than those reported for background sites in North America and Europe (<5 ng/m^3 for three European mountain regions and the Great Lakes basin, *1, 39*). Without obvious local sources, it is expected that the PAHs at the two control sites resulted from dispersion in the neighboring areas. Similarity in the sources of PAHs among all sites was confirmed by diagnostics ratios (Figure 1). However, significant differences were found in BaA/(BaA + CHR) ratios between the control sites (0.27 ± 0.00) and other sites (0.44 ± 0.09 for the urban and 0.48 ± 0.08 for the rural sites). Although BaA/(BaA + CHR) is usually greater than 0.35 for combustion sources, it was believed that BaA decays faster than CHR in the atmosphere, leading to a decrease in the BaA/(BaA + CHR) ratio at the sites far away from the combustion sources (*27*).

A series of papers published in recent years reported high levels of PAHs in ambient air in Chinese cities (*21, 29*). According to the emission inventory in China, the dominant emission activities include biofuel burning, domestic coal combustion, and coke production, none of which are limited to urban areas (*2, 14*). Moreover, in rural China, population density is relatively high and the efficiency of energy utilization is particularly low (*40, 41*). Not limited to cities, emission density mapping revealed PAH emission sources spread all over eastern China (*14*). Such a distribution pattern of emission was consistent with the observed ambient concentrations in this study: no significant difference in PAH15 was found between the urban (514 ± 563 ng/m^3, $n = 17$) and rural sites (610 ± 645 ng/m^3, $n = 27$). This distribution pattern leads to widespread exposure of both urban and rural populations to high levels of PAHs. In fact, high levels of indoor exposure to Chinese rural residents of pollutants from coal/biofuel combustion have been reported (*42*). Another consequence of such distribution patterns is that the localized abatement measures often failed to generate expected outcomes: the BaP levels in Beijing remained relatively constant (10~20 ng/m^3) in recent winters, despite a series of remediation measures (*15, 21, 43*). For the reason that major PAH emission sources are not limited to petroleum consumption, even in urbanized areas in northern China, cutting traffic emissions in this region would not be as efficient as in several U.K. cities (*44*).

Gas-Particulate Partitioning. Gas-particulate partitioning plays an important role in the atmospheric transport of semivolatile PAHs. The partitioning is usually described by the partitioning coefficient K_p (*45*):

$$K_p = (F/\mathrm{TSP})/A \tag{1}$$

where F and A are the concentrations in the particulate and gas phases, respectively (ng/m^3), and TSP is the concentration of total particulate matter (μg/m^3). A linear relationship between log K_p and log p_L^0 (p_L^0 is the compound's subcooled liquid–vapor pressure, Pa) for the nonpolar organic compounds has been established (*46*):

$$\log K_p = m_r \log p_L^0 + b_m \tag{2}$$

where m_r and b_m are empirical constants. In this study, K_{PM10} was calculated instead of K_p. Since most of the particulate-phase PAHs occur in fine particles (*10, 25*), and proportional relationships were often observed between PM$_{10}$ and TSP in this region (*47*), when K_p in eq 2 is replaced with K_{PM10}, only the intercept, rather than the slope, was changed. A similar substitution was conducted for PM$_{2.5}$ (*48*). In this study, the log K_{PM10} of PHE, ANT, FLA, and PYR are plotted against log p_L^0, as in Figure 2. Since the gas-phase concentrations of higher-molecular-weight compounds from BaA to BghiP were frequently below the detection limits and there were possible breakthrough effects for ACY, ACE, and FLO (*49*), these compounds are not included. The data were not adjusted for filter adsorption or PUF breakthrough effects (*39*).

The slopes (m_r, −1.30 or −1.48 for different log p_L^0 values) were much steeper than those reported in the literature (usually between −0.5 and −1.0, *39, 52*). It was suggested that a m_r steeper than −1 indicated adsorption dominating over absorption (*52*). Dachs and Eisenreich reported a case of dominating adsorption onto soot carbon in gas-particulate partitioning, from which the m_r value derived was close to −1 (*53*). Even without an elaborate modeling illustration of adsorption versus absorption, the dominating adsorption could still be inferred in this study. The adsorption of PAHs is primarily associated with elemental carbon (EC), while absorption is mainly related to organic carbon (OC) (*53*). However, there is no evidence that the atmospheric OC/EC level in the study area in winter was lower than those in the other areas (*54*). Although, it was suggested that a stronger adsorption of PAHs to airborne particles may result in longer half-lives (*55*). Future investigation is necessary for looking into the phenomenon.

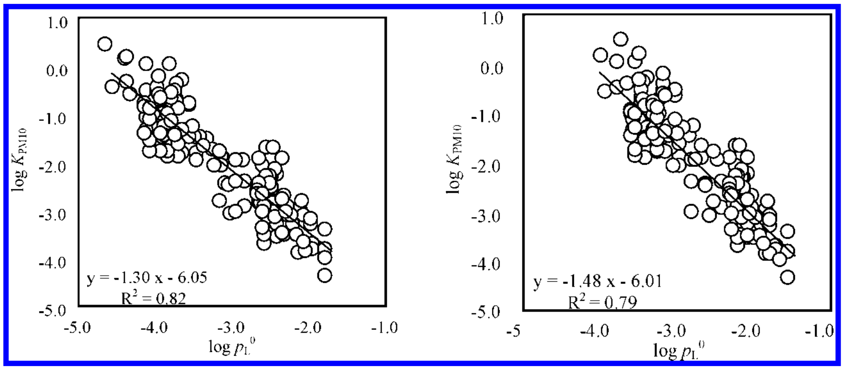

FIGURE 2. Linear relationship between log K_{PM10} and log p_L^0 for all samples collected in this study based on two sets of log p_L^0 from the literature (*50, 51*), respectively.

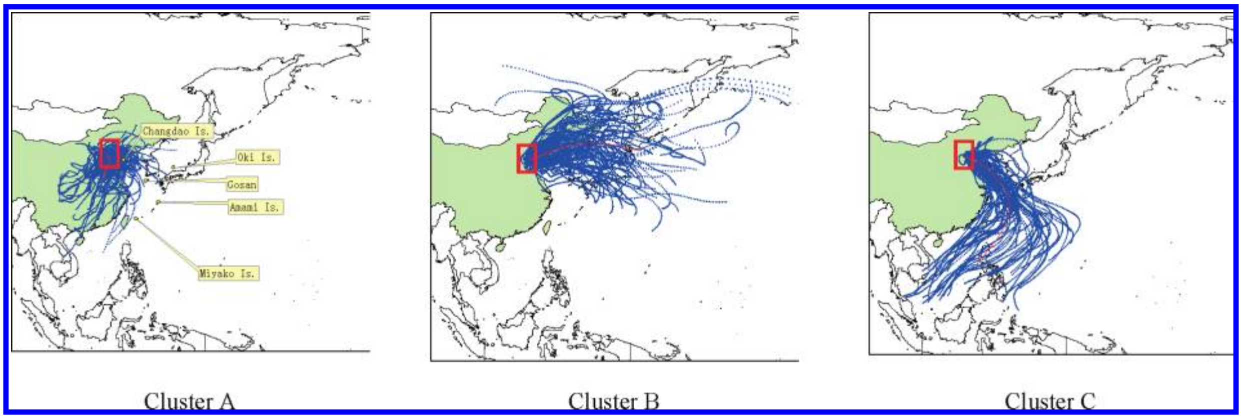

FIGURE 3. The 5-day forward trajectories from the study areas. Both original calculated trajectories (blue lines) and the mean trajectory for each cluster (red lines) are presented. The study area is marked as a red square. Changdao, Gosan, Oki Island, Amami Island, and Miyako Island are marked (*9, 60–62*).

Since adsorption was the predominant mechanism of the partitioning, the enthalpy of desorption from the surface ($H_{\text{desorption}}$, J/mol) can be calculated for individual compounds (ref *56* and the Supporting Information). The calculated $H_{\text{desorption}}$ values for PHE and FLA (77.5 kJ and 119 kJ, respectively) were substantially higher than those reported for the St. Lawrence Basin in Canada (60–70 kJ for both PHE and FLA), suggesting a strong adsorption of PAHs (*57*). Besides the low temperature and high PM_{10} concentrations, strong adsorption was another reason for the relatively lower vapor concentrations of FLA, PYR, BaA, and CHR in this study.

Long-Range Air Transport. Recently, many studies have been conducted on the outflow of Asian continent air pollutants which could even reach the western U.S. coast (*9, 58*). It will be interesting to determine where PAHs would be transported from this study area. Since PAH concentrations in the study area change dramatically in the vertical profile (*59*), the measured ground-level concentrations could not represent the air mass concentration over the boundary layer. Therefore, it should be indicated that the calculated trajectories in this study revealed only the directions and pathways of PAH outflow and cannot be directly related to the measured concentrations. The calculated 5-day forward trajectories were clustered into three categories using HYSPLIT, according to the fact that the total spatial variance varied 30% and 2%, when the number of categories increased from two to three and from three to four, respectively. The trajectories of each group together with mean trajectories are illustrated in Figure 3.

Of the total 240 trajectories, 92 of them (38.3%) fell into the first category (cluster A). Cluster A is characterized by stagnant air parcels and stable atmospheric conditions mainly under the influence of a continental high between strong cold surges. For this category, PAHs and other air pollutants tend to accumulate in the local environment, causing severe air contamination. Seven out of eight of the most contaminated days with an air pollution index (API, an index of air pollution integrating the concentrations of SO_2, NO_x, and PM_{10}.) greater than 200 occurred on these days (*63*). Under these conditions, the outflow of PAHs from the study area was limited to adjacent regions and rarely traveled beyond Changdao. Clusters B (85 trajectories, 35.4%) and C (63 trajectories, 26.3%) were in good agreement with the zonal and meridional modes described by Wu et al. (*64*). These clusters are distinguished in the direction and intensity of convection air flow. The zonal mode (cluster B) was substantially different from the traditional East Asian winter monsoon (EAWM) and is not related to the Siberian high/East Asian trough (*64*). Instead, strong zonal wind obstructed the southward cold surge in the middle-high latitudes of Asia, and this was related to the occurrence of tropical circulation anomalies (e.g., the Philippine Sea anticyclone) (*64*). On the other hand, the meridional mode (cluster C) represented the ordinary EAWM and was closely associated with the winter-time southward cold surges in the low troposphere in East Asia (*64*). In both clusters B and C, strong wind facilitated the dispersion of atmospheric pollutants in the study area. Better air quality with an API < 50 in Beijing occurred mostly on these days (*63*). During this time, continental outflow of the PAHs occurred. In the case of cluster B, PAHs traveled east, sometimes northeast to the Pacific, while the outflow of cluster C was southerly directed. Different vertical diffusion features were also revealed for the three categories in terms of the mean trajectory endpoint height (240, 1043, and 102 m for clusters A, B, and C, respectively).

Acknowledgments

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Supporting Information Available

Sampling information; detection limits, field blanks, and method recoveries; measured concentrations of target PAHs; and $H_{\text{desorption}}$ calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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