LEVEL AND PATTERN OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN ASIAN DUST SAMPLES AT GOSAN, KOREA

Choi S-D[1], Lee J Y[2], Kim J Y[3], Ghim Y S[4], Kim Y P[5]

[1]School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), 100, Banyeon-ri, Eonyang-eup, Ulsan, 689-805, Republic of Korea; [2]Science and Technology Branch, Environment Canada, 4905 Dufferin St., Toronto, ON, Canada, M3H 5T4; [3]Center for Environmental Technology Research, Korea Institute of Science and Technology (KIST), 39-1 Hawolgok-dong, Seongbuk-gu, Seoul, 136-791, Republic of Korea; [4]Department of Environmental Science, Hankuk University of Foreign Studies, San 89, Wangsan-ri, Mohyeon-myeon, Yongin, 449-791, Republic of Korea; [5]Department of Environmental Science and Engineering, Ewha Womans University, 11-1 Daehyun-dong, Seodaemun-gu, Seoul, 120-750, Republic of Korea

Abstract

Polycyclic aromatic hydrocarbons (PAHs) in both gaseous and particulate phases were measured at Gosan, Korea, a remote background site, for 15 days from March 29 to April 12, 2002. During the sampling period, a severe Asian dust (AD) event (April 8–10) originating from Mongolia and northern China was observed throughout the Korean peninsula and Jeju Island where the sampling site is located. The levels of particulate PAHs doubled from 1.3 to 2.7 ng/m^3 during the AD event and apparent changes in gas/particle partitioning were also observed. These results imply that Asian dust can be an important carrier of PAHs from industrial areas of China to remote sites in Northeast Asia.

Introduction

Long-range transport of air pollutants is one of the major environmental issues in Northeast Asia. Particularly, China is the greatest emission source of polycyclic aromatic hydrocarbons (PAHs) in the world, and unlike other developed countries, emissions from China have increased[1]. PAHs emitted from China are expected to be carried by prevailing northwesterly winds across the Korean Peninsula and Japan.

Another critical environmental issue in Northeast Asia is "Asian dust (AD)", also called yellow sand. The source regions of AD are deserts and loess areas in northern China and Mongolia; Southern China, Korea, and Japan are major receptor regions of AD. Although AD mainly consists of mineral particles and source regions are generally remote background areas, anthropogenic sulfate and nitrate were reported to be scavenged by AD particles during long-range transport[2]. Therefore, we can expect that the level and pattern of PAHs and other persistent toxic substances (PTS) in receptor regions can be altered by AD particles passing over industrial regions of China.

Appreciably higher concentrations of particle associated PAHs were measured in central Taiwan during AD events in March and April 2002[3]. Similarly, increases of most individual PAHs in Qingdao, eastern China were also observed during two AD events (March 20 and April 7–8, 2002), but a difference in PAH compositions between these AD events and non-AD periods was not found[4]. In addition, elevated PAH concentrations were observed at Kanazawa in the western margin of central Japan when AD particles were transported by near surface winds sweeping up PAH-polluted soils[5]. Considering these previous studies, the influence of AD events on the fate of PAHs seems to greatly depend on different source regions of AD and transport pathways.

To investigate long-range transport of air pollutants over Northeast Asia, several intensive field sampling campaigns were conducted at Gosan, Jeju Island, Korea between November 2001 and August 2003[6]. The present study focuses on the campaign performed in spring 2002 when a strong AD event was observed. Unlike the former studies measuring particulate PAHs during AD events[3-5], both gaseous and particulate PAHs were measured in this study. As a result, not only levels and patterns of PAHs, but also gas/particle (G/P) partitioning were examined to evaluate the influence of AD on the behavior of PAHs.

Materials and Methods

Sampling site and sampling procedures

The sampling site of this study, Gosan (33°17´N, 126°10´E, 72 m above sea level), is located at the western edge of Jeju Island located about 100 km south of the Korean Peninsula (Figure 1). The Gosan station is one of national background monitoring sites; the Korean Ministry of Environment continuously measures concentrations of criteria pollutants, such as CO, O_3, NO_2, SO_2, and particulate matter of less than 10 microns aerodynamic diameter (PM_{10}). The data collected during the PAH sampling period were obtained for correlation analysis with the PAH data. $PM_{2.5}$ data measured in our previous study[6] were also used for the correlation analysis.

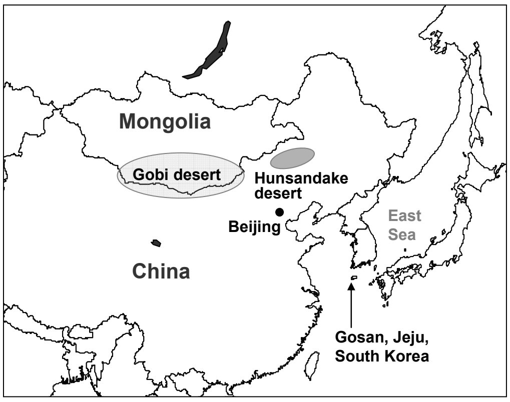

Figure 1. Location of the sampling site, Gosan on Jeju Island in Korea. Two major deserts, where severe AD events originated in March–April 2002, are also shown.

Ambient air sampling was conducted for 15 days between March 29 and April 11, 2002. A high-volume air sampler (DHV-1000s, Sibata, Japan) was operated. The gaseous and particulate PAHs were collected on polyurethane foam (PUF) disks and quartz fiber filters (QFF), respectively. PUF and QFF field blanks were also prepared and analyzed for each set of field samples with the same procedure.

Instrumental analysis

PAHs collected on the PUFs and QFFs were extracted by duplicate sonication for 30 min with 350 mL of dichloromethane (DCM). Before extraction, 50 μL of 10 ppm triphenyl phosphate (Aldrich) were spiked to each sample as an internal standard. The 16 US-EPA priority PAHs were identified and quantified using an Agilent 6890 gas chromatograph (GC) equipped with a 5973N mass selective detector (MSD). A more detailed description on the instrumental analysis can be found elsewhere[7].

Results and Discussion

Asian dust events in April 2002

Temporal variations of the mass concentrations of PM_{10} and $PM_{2.5}$ during the sampling period are shown in Figure 2. A strong AD event, originating from the Hunsandake desert in Inner Mongolia, was observed for three days (April 8–10). High levels of PM_{10} with a daily average of 445 μg/m^3 were measured for this AD event. The variations of $PM_{2.5}$ are broadly correlated with those of PM_{10} (r = 0.55, $p < 0.05$), but the levels of $PM_{2.5}$ in late March/early April were relatively high due to a weak AD event originating from the Gobi desert[6]. However, this was not officially recorded as an AD event in South Korea because this Asian dust passed over Korea at high elevation and the major receptor region was Japan. Therefore, the strong AD event between April 8 and 10 will be henceforth referred to as the AD event in this study.

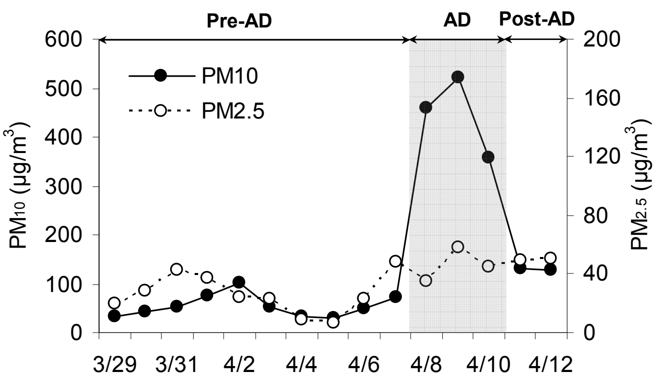

Figure 2. Temporal variations of concentrations of particulate matter (PM_{10} and $PM_{2.5}$) during the sampling period (AD = Asian dust event).

According to the backward trajectory analysis (data not shown), air masses passed over various regions including southeastern China, the East China Sea, and the Korean peninsula during the pre-AD period, whereas the majority of air masses arriving at Gosan came from Mongolia and northern China during the AD and post-AD periods. Considering both the spatial distribution of PAH emissions from northern China[8] and the air trajectories passing over loess regions around Beijing during the AD event[5], PAHs and particles are expected to have been transported together to Gosan.

Temporal variations of PAH levels and profiles

The daily concentrations of total PAHs and gas/particle fractions were considered to investigate the influence of Asian dust on the atmospheric behavior of PAHs (Figure 3). Large fluctuations of PAH concentrations are observed during the pre-AD period (2.3±1.4 ng/m^3) compared with PAH levels during the AD (2.9±0.4 ng/m^3) and post-AD periods (4.0±0.5 ng/m^3). This result can be explained by relatively complex air trajectories (i.e. various source regions) during the pre-AD period. Considering the daily air trajectories (data not shown) and PAH concentrations together, the higher levels of PAHs are generally observed when air masses passed over northern China (e.g. Beijing and Tianjin) and the Shandong peninsula, which were identified as major PAH sources of the Asian continental outflow[9].

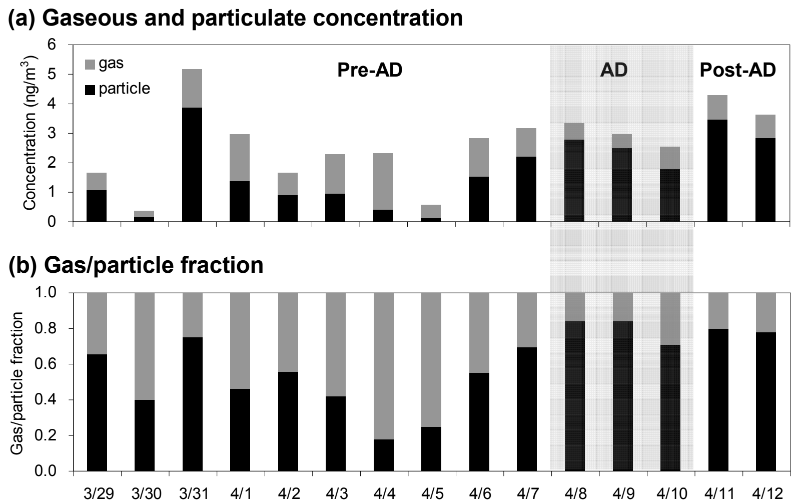

Figure 3. Temporal variations of concentrations of PAHs and gas/particle fractions during the sampling period.

The average concentrations of particulate PAHs during the AD and post-AD periods (2.7 ng/m^3) are statistically higher ($p < 0.01$) than those of the pre-AD period (1.3 ng/m^3). In addition, the daily concentrations of total PAHs are highly correlated with the particle bound fraction ($r = 0.66$, $p < 0.01$), i.e. when the total PAH concentrations were high, the ratios of particulate to gaseous PAH concentrations were also high. In particular, the highest concentration of PAHs was observed on March 31, when the weak Asian dust event occurred[6].

Although the influence of AD was not so direct on March 31, the level of $PM_{2.5}$ increased by the influence of AD passing over at high altitude. This result straightforwardly suggests that fine particles might be an important carrier of PAHs. A similar phenomenon (i.e. higher levels of particulate PAHs and $PM_{2.5}$) was observed during the post-AD period (April 11–12).

Gas/particle partitioning

The partitioning behavior of PAHs was investigated by fitting the measured data to the following G/P partitioning model (equation 1).

Two parameter model: $\Phi = 1 / (1 + 10^{-m \cdot \log(P_L/\mathrm{Pa}) - b'})$ (1)

where, Φ is the fraction of each PAH in the particle phase calculated from the measured data, A, m, and b' are fitting parameters, and P_L is the vapor pressure of the sub-cooled liquid in Pa[10].

The values of m during the AD and post-AD periods, which have an average of -0.7, are more close to -1 than those of the pre-AD period (m = -0.3). This is well observed in Figure 4 illustrating averaged fitting curves for the three sampling periods. The curves for the AD and post-AD periods are shifted to the upper right when log P_L is smaller than -2, indicating an increased contribution of particulate PAHs. Accordingly, it can be concluded that relatively high levels of fine particles during the AD and post-AD periods resulted in the change of G/P partitioning behavior.

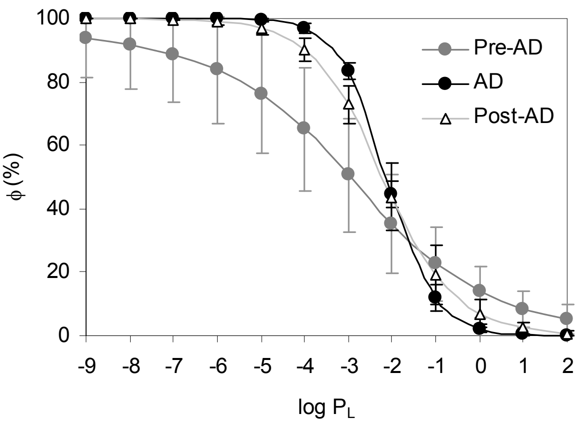

Figure 4. Averaged fitting curves for the nonlinear two-parameter model during the three sampling periods (pre-AD, AD, and post-AD). Error bars represent standard deviations.

Acknowledgements

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