STUDY ON ATMOSPHERIC BEHAVIOR OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AREA, JEONJU

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(Received, accepted)

Abstract: Between June and November 2002, the atmospheric concentrations and dry deposition fluxes of polycyclic aromatic hydrocarbons (PAHs) in Chonju were measured four times each over five days. The total concentration of PAHs in ambient air was 84 ng/m$^3$, with about 90% existing in the vapor phase. Plots of log ($K_p$) vs. log ($P_{Lo}$) indicated that PAHs partitioning was not in equilibrium and the particulate characteristics did not change with seasonal variations. The PAHs fluxes to a water surface sampler (WSS) and a dry deposition plate (DDP) were about 14.15 and 1.92 $\mu$g/m$^2$/d, respectively. The flux of the gaseous phase, acquired by subtracting the DDP from the WSS results, was about 12.23 $\mu$g/m$^2$/d. A considerable correlation was shown between the atmospheric concentrations and deposition fluxes in the gaseous phase, but not in the particulate phase, as the fluxes of the particulate phase were dependent on the physical velocity differences of the particulates based on the particle diameter.

Key Words: Deposition flux, Gas/Particle partitioning, PAHs, Size-distribution

INTRODUCTION

The atmosphere is a major pathway for the transport and deposition of polycyclic aromatic hydrocarbons (PAHs), which are emitted by automobiles and other combustion sources. After being emitted into the atmosphere, PAHs become partitioned between the gaseous phase and atmospheric aerosols. The partitioning of gaseous-particulate phase is controlled by the vapor pressure of PAHs and the total suspended particulate concentration. Particulate PAHs are also distributed into different aerosol size fractions. Gas/particle partitioning and the particle size distribution affect the removal rate of PAHs from the atmosphere due to dry and wet deposition.\textsuperscript{1) Many studies have been conducted to understand their fate of PAHs in the atmosphere by focusing on the gas/particle partitioning, size-distribution and photochemical loss, etc. Due to their significant contribution to the pollution budget of many natural waters, interest in the atmospheric deposition of PAHs has increased over the past decade.\textsuperscript{2,3) However, unlike wet deposition, no acceptable sampling method for dry deposition
currently exists. Dry deposition is normally estimated either by multiplying the measured atmospheric concentrations and theoretically calculated deposition velocities, or the direct determination of deposition fluxes using surrogate. However, the accuracy of extrapolating these types of measurements to real water bodies remains an area of debate. Deposition to a natural water surface differs in several ways from that to a flat surface: (1) the water-body creates a region of high humidity over the surface, which leads to the growth of hygroscopic particles, (2) the spray generated by breaking waves may lead to particle scavenging or the release of particles into the atmosphere, and (3) the surface has an increased roughness due to ripples. Considering the differences between surrogate and water surfaces, the use of water as the surrogate surface would satisfactorily reflect the natural water characteristics, and would also be good for application to natural water.

The objective of this study was to understand the behavior of PAHs in ambient air and their dry deposition characteristics.

**EXPERIMENTAL METHODS**

**Sample Collection**

Ambient and deposition samples were collected a total of four times between June and November 2002. In addition, to study the size distribution of PAHs, a 5-stage cascade impactor was employed. The sampling was conducted on the roof of a five-story building (Engineering College 6th building) on the campus of Chobuk National University, Jeonju city, for five consecutive days. The detail sampling method is refer our previous report. A water surface sampler (WSS) and dry deposition plate (DDP) were used to measure the dry deposition fluxes (see Fig. 1), with a design similar to that used in previous studies. The WSS plate had a diameter and water depth of 39.4 and 0.5 cm, respectively. Water entered into the WSS plate from the center, which overflowed from a triangular weir located on the outside. Overflowed water passed through a XAD-2 resin column, with analytes trapped in the resin before complete cycling. A knife-edge deposition plate, made from acryl, was used to collect the dry deposition fluxes of particulate PAHs, with a design similar to those used in wind-tunnel studies. Glass strips placed on top of the plate were coated with approximately 3-4 mg of Ape-
Analytical Method
The procedures used in this study were a combination of the methods developed at the University of Indiana\textsuperscript{11}, the US EPA 8270\textsuperscript{12} and US EPA TO-13A.\textsuperscript{13} Each sample was extracted using a Soxhlet and ASE (accelerated solvent extractor; Dionex, ASE-200) with an acetone-hexane mixture. The extraction of wetted samples from the WSS was performed with DCM in a separating funnel, followed by Soxhlet extraction. Extracts were cleaned using a column chromatography cleanup procedure, with 5 g of 4% deactivated silica as the stationary phase. The column was pre-washed with 20 mL hexane. PAHs eluted with 20 mL of 50% DCM in hexane. The final elutes were concentrated to 200 μL and exchanged into hexane by nitrogen purging prior to the GC analysis. The final elutes of the DDP samples were contaminated with a small amount of grease, which required removal prior to injection onto the column, as this could cause interference as well as damage the GC column. Therefore, the samples were placed into a freezer, where the grease would coagulate. The only separated upper layer from the vial was acquired for the GC analysis. Twenty-four PAHs, including five alkyl compounds and a biphenyl, were analyzed by gas chromatography/mass spectrometry (HP5890/HP5973), employing a DB-5 column (30 m × 0.25 mm × 0.25 μm).

QA/QC
The QA/QC plan was performed according to the modified “quality control” section of the US EPA test method SW-846. All glassware was meticulously cleaned with hot water and then rinsed with either MeOH or DCM prior to use. All reagents were of pesticide residue quality or their equivalents. PUF (Sibata) and XAD-2 resin (Supelco) were precleaned by Soxhlet extraction. The GFF (Whitman) were also baked in a muffle furnace at 450°C. Before operating the GC-MSD, a system performance and calibration was conducted for all samples. PAHs species were identified and quantified by their relative retention times and response factors to internal standards, respectively. All samples were spiked with a mixture of deuterated PAHs (d10-Flu, d10-Pyr), as a surrogate standard, prior to extraction to monitor the analytical recovery. Surrogate recovery for achieving acceptable accuracy was regarded as 60–120% in US EPA Method. Recoveries of d10-Flu and d10-Pyr fell within the acceptant limits for all samples, with ranges of 61–84 and 88–95%, respectively. The MDL for the ambient air and deposition samples ranged from 0.6 to 3.4 pg/m$^3$ and 1.4 to 16 ng/m$^2$.d, respectively.

RESULTS AND DISCUSSION
Atmospheric Concentration and Dry Deposition Fluxes
The PAH compounds measured in this study, and their abbreviations, are summarized in Table 1. The atmospheric concentrations of total PAHs (Σ24-PAHs) ranged from 70 to 102 ng/m$^3$, with an average of 84 ng/m$^3$. This result was similar and/or lower than previous studies which reported the average concentrations of 16-PAHs in ambient air were 89.29, 520.47, and 46.83 ng/m$^3$ in Seoul, Kyungsan, and Chongju, respectively.\textsuperscript{14-16} The individual PAH concentrations ranged from 0.02 to 33.4 ng/m$^3$ (see the Fig. 2). The most abundant PAH species was NaP, which accounted for about 30% of the total PAHs concentration. In addition, Flu, PhA, FluA and Pyr were also predominant. These results were similar to those found in previous studies.\textsuperscript{9,17} The average concentrations in the gaseous and particulate phases were 80 and 4.9 ng/m$^3$, respectively. The gaseous phase accounted for about 90% of the total PAHs concentration.

The dry deposition flux (F, μg/m$^2$.d) was measured by multiplying the deposition velocity (Vd, cm/sec) and atmospheric contaminant concentration (C, ng/m$^3$). The deposition fluxes for PAHs were determined by direct measurement using deposition plates, and compared to the calculated fluxes using the modeled deposition velocity and measured atmospheric concentration. The calculated
Table 1. PAHs measured in the present work, and their abbreviations

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Abbreviation</th>
<th>Formular</th>
<th>M.W.</th>
<th>Ring No.</th>
</tr>
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<tr>
<td>Naphthalene</td>
<td>Nap</td>
<td>C_{10}H_{8}</td>
<td>128.16</td>
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<tr>
<td>2-methylnaphthalene</td>
<td>2-M-Nap</td>
<td>C_{11}H_{10}</td>
<td>142.20</td>
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<td>1-methylnaphthalene</td>
<td>1-M-Nap</td>
<td>C_{11}H_{10}</td>
<td>142.20</td>
<td>2</td>
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<td>Biphenyl</td>
<td>Bp</td>
<td>C_{12}H_{10}</td>
<td>154.21</td>
<td>2</td>
</tr>
<tr>
<td>2,6-dimethyl-naphthalene</td>
<td>2,6-dM-Nap</td>
<td>C_{12}H_{12}</td>
<td>156.22</td>
<td>2</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>AcPy</td>
<td>C_{12}H_{8}</td>
<td>152.20</td>
<td>3</td>
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<tr>
<td>Acenaphthene</td>
<td>AcP</td>
<td>C_{12}H_{10}</td>
<td>154.21</td>
<td>3</td>
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<td>2,3,5-trimethylnaphthalene</td>
<td>235-trM-Nap</td>
<td>C_{13}H_{14}</td>
<td>170.25</td>
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<tr>
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<td>Flu</td>
<td>C_{13}H_{10}</td>
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<tr>
<td>Phenanthrene</td>
<td>PhA</td>
<td>C_{14}H_{10}</td>
<td>178.22</td>
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</tr>
<tr>
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<td>AnT</td>
<td>C_{14}H_{10}</td>
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<tr>
<td>1-methylphenanthrene</td>
<td>1-M-PhA</td>
<td>C_{15}H_{12}</td>
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<tr>
<td>Fluoranthene</td>
<td>FluA</td>
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<td>Pyr</td>
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<td>B[a]A</td>
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<tr>
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<tr>
<td>Benzo[b]fluoranthene</td>
<td>B[b]F</td>
<td>C_{20}H_{12}</td>
<td>252.32</td>
<td>4</td>
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<tr>
<td>Benzo[k]fluoranthene</td>
<td>B[k]F</td>
<td>C_{20}H_{12}</td>
<td>252.32</td>
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<tr>
<td>Benzo[e]pyrene</td>
<td>B[e]P</td>
<td>C_{20}H_{12}</td>
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<tr>
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<td>B[a]P</td>
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<td>Perylene</td>
<td>Pery</td>
<td>C_{20}H_{12}</td>
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<td>Indeno[1, 2, 3-c,d]pyrene</td>
<td>InP</td>
<td>C_{22}H_{12}</td>
<td>276.34</td>
<td>6</td>
</tr>
<tr>
<td>Benzo[g,h,i]pyrene</td>
<td>B[g,h,i]P</td>
<td>C_{22}H_{12}</td>
<td>276.34</td>
<td>6</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>D[a,h]A</td>
<td>C_{22}H_{14}</td>
<td>278.35</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 2. Atmospheric concentrations and dry deposition fluxes of the PAHs.

Fluxes for each particle size interval and gaseous phase were then totaled in order to calculate the total flux.3

\[ F_i = F_g + \sum F_{p,j} = C_g \cdot V_g + \sum C_{p,j} \cdot V_{p,j} \]  

(1)

Where \( F_g \) and \( F_{p,j} \) are the contributions of the gaseous-phase and each particulate size to the dry deposition flux, respectively, and \( C_g \) is the gaseous phase concentration in the PUF plug. \( V_g \) is dry deposition velocity calculated using the two-film model,18 \( C_{p,j} \) the particulate concentration in each impactor stage, and \( V_{p,j} \) the calculated dry deposition velocity of the midpoint cut-off diameter of each impactor stage, as determined by the Noll and Fang model.19

The meteorological conditions, atmospheric concentration and dry deposition flux are given in Table 2. With the WSS, which represent the total fluxes (gas + particle), the dry deposition fluxes of PAHs were found to range from 10.2 to 18.7 \( \mu g/m^2/d \), with an average of 14.1 \( \mu g/m^2/d \). Lee et al., (2003) reported that the deposition fluxes of particulate PAHs ranged from 7.85 to 29.30 \( \mu g/m^2/d \).20 The NaP-family, Bp, Flu and PhA were the predominant compounds. With the DDP, which describes the particulates, the ranges of dry deposition fluxes of PAHs were between 0.4 ~ 5.9 \( \mu g/m^2/d \), with an average 1.9 \( \mu g/m^2/d \), with middle-weight molecular compounds predominating. The dry deposition fluxes of the gaseous phase were calculated by subtracting the particulate phase fluxes measured with the DDP from the total fluxes measured with the WSS.
Although this method can give rise to an error in the determination of gaseous fluxes, due to difference in aerodynamic shape and surface characteristics between the WSS and DDP, it has been used in other studies on dry deposition employing the WSS and DDP.\(^7\)\(^9\) In the calculation of gaseous phase fluxes, high molecular weight (>252) compounds were excluded, as they almost exclusively exist in the particulate phase within the atmosphere. The calculated gaseous phase deposition fluxes were found to range between 9.8 ~ 18 \(\mu g/m^2.d\), with an average 12.2 \(\mu g/m^2.d\), with the NaP-family, Bp, Flu and PhA being the predominant compounds.

Yi et al.\(^7\) highlighted the uncertainties relating to the interaction between the grease used to collect particles and the vapor phase of the contaminant. The flux measured using the DDP was overestimated compared to the calculated flux. Especially, those for low-middle weight compounds, including AcP, showed wide differences, up to 2-orders. The possible explanations for PAHs existing in the plate samples could be: (1) some gaseous phase PAHs may be captured by grease, and (2) there are probably certain deficiencies in the modeling.

In this study, the gaseous phase fluxes of PAHs were larger than those in the particulate phase. This is reasonable, as the PAHs in air are mostly in the gaseous phase, and the deposition flux is proportional to the concentration. The vapor to particulate ratio of the PAHs atmospheric concentration was found to be about 30; however, that of the PAHs deposition flux was only about 6. This difference in the ratios between the atmospheric concentration and dry deposition flux can be explained by differences in the deposition phenomenon affecting the particulate and gaseous phases. As seen in Figure 3, a correlation exists between the gaseous phase deposition and gaseous phase concentration. However, in the case of the particulate phase, the dry deposition fluxes were not correlated with the atmospheric concentration. Different particulate deposition velocities, base on the diameter, could be the reason for the low particulate phase correlation.

**Gas/particle Partitioning**

The partitioning of SOCs between the gaseous and particulate phases is described as either surface adsorption onto or absorption into organic matter. In any given situation, both adsorptive and absorptive partitioning will occur.\(^2\)\(^1\) The absorption and adsorption processes lead to a...
linear relationship between $\log K_p$ and $\log P_L^{0}$, as shown in the following equation.

$$\log K_p = b_r - m_r \log(P_L^{0}) = \log\left(\frac{N_s \cdot A_{SP} \cdot T \cdot e^{(O, -Q, /)_RT}}{1600} + \frac{760 f_{om} \cdot R \cdot T}{10^6 MW_{om} \cdot \xi}ight) - \log(P_L^{0})$$

(2)

Where $b_r$ and $m_r$ are the slope and y-intercept of the regression line from the plot of $\log K_p$ vs. $\log P_L^{0}$, respectively. At equilibrium, the slope for either adsorption or absorption should be almost -1.22-24)

In eq.(2), an estimate of the y-intercept can be obtained, which can be specified for both adsorptive and absorptive partitioning. For a general urban area, Whitby25 and Bidleman1) reported that the average total surface area ($\Theta$, cm$^2$/cm$^3$) and total volume ($V_s$, cm$^3$/cm$^3$ air) are $1.1\times10^{-5}$ and $7.0\times10^{-11}$, respectively. If a particle density ($\rho$, g/cm$^3$) of 1.4 is assumed, the specific surface area of the average urban TSP load will be 98 $\mu g$/m$^3$, with reasonable ranges of $f_{om}$, MW$_{om}$, and $\xi$ is 0.1 ~ 0.3, 100 ~ 300 and 1 ~ 5.21,26) As a range for the y-intercept, $b_r$ can range from -8.9 ~ -7.3, and when partitioning is assumed at equilibrium ($m_r = -1$), the regression line of $\log K_p$ vs $\log P_L^{0}$, as shown in Figure 4, is illustrated with a dotted line. This can be regarded as the thermodynamic equilibrium line for an average urban area.

The y-intercept and slope were also determined from directly measured data. In this study, the determined ranges for the y-intercept and slope were -4.1 ~ -4.5 and -0.48 ~ -0.63, respectively. Even though the slopes obtained in this study were not equal to -1, their intercept values were very similar. This suggests that the particle characteristics did not change. Possible reasons for these close intercepts could be: (1) the long duration of the sampling, which would mask changes in the wind direction; the particulate characteristics, including the surface area, of the atmosphere will fluctuate with different sources according to the wind direction. However, in this study, sampling was conducted over a long period in order to obtain a sufficient sample volume, with a restricted flow rate, to overcome the detection limit and sample loss problems. (2) It is also possible that fluctuations in the particulate characteristics were less than other areas, as the wind direction at our study site was comparatively constant; about 30 km east of the Yellow Sea shoreline, which is indirectly affected by both land and sea breezes.

Experimentally determined $m_r$ values reported in the literature, in fact, often exclude -1, as was the case in this study.17,24,27) In this study, the determined $m_r$ values were shallower and the $b_r$ value greater than would be expected at equilibrium, as shown in Figure 4. This was caused by both the low $K_p$ for low $P_L^{0}$, which would result from adsorption kinetics, and the high $K_p$ for
high P\textsubscript{L}, which would occur due to sampling artifacts and non-exchangeability. When relatively clean particles enter a contaminated atmosphere or contaminated vapor enters a relatively clean atmosphere; conversely, gas-to-particle adsorption will begin. High volatile compounds will attain gas-particle equilibrium more quickly than low volatile compounds; thus, the logK\textsubscript{p} values of high volatile compounds will be close to equilibrium, but those with low volatility will be lower than the equilibrium line shown in Figure 4. Non-exchangeability can occur for PAHs as they are formed during combustion processes. Since high volatile species may become trapped inside particles during their formation, and low volatile compounds will tend to be strongly sorbed onto the particulate phase, the high volatile compounds for the fraction of bound particles will elevate the K\textsubscript{p} values. Sampling artifacts, including the adsorption of gaseous phase PAHs onto particles on the filter and onto the filter itself, and blow-off of gaseous PAHs from particles collected on the filter, will complicate gas-particle partitioning measurements. Despite these shortcomings, high volume samplers have been widely used. Lohmann and Lammel reviewed the temperature, relative humidity and gas-phase adsorption to filter correction, as well as the effects of organic matter and black carbon on G/P partitioning. Mader and Pankow reported the corrected gas-particle partitioning results for adsorption artifacts using front and backup filters in the case of a high volume sampler, and also suggest that small amounts of organic carbon can have significant effects on the gas-particle partitioning of SOCs from a controlled field experiment. Ligocki and Pankow corrected their PAH measurements for backup adsorption using various correction factors, from 11 to 50\% for PAH compounds. However, despite these various efforts, the mechanism of G/P partitioning is still not clear.

### Size-distribution

Figure 5 shows the normalized distributions of PAHs and the particle masses with particle size. Particle matter predominated in both the fine and coarse ranges (1~7 \(\mu\text{m}\)), while PAHs were mainly distributed in the fine particle range (<2 \(\mu\text{m}\)). PAHs were also distributed among the particulate size fractions based on molecular weight: the size-distribution of PAHs with 2-rings was similar to that of the particle matter, those with 3-rings had a shape correlated with 2-ring and 4-6-ring mixtures, and those with 4-6 rings, which have a high molecular weight, predominated in the fine particles, ranging from 60 to 80\%. Specifically, PAHs with low and middle molecular weights were evenly distributed between the fine and coarse particulates. However, PAHs with high molecular weights were primarily associated with the fine particulates, which agree with the other literature findings.

### Dry Deposition Velocity of PAHs

The dry deposition velocities of PAHs were calculated by dividing the atmospheric concentration into the dry deposition flux values (\(V_d=\text{Flux/Conc.}\)) (Fig. 6). The average deposition velocity of gaseous phase PAHs was calculated to be 0.18 cm/sec, but those of individual compounds did not vary (0.48~0.03 cm/sec). The possible explanations for the similarity in the deposition velocities among the compounds may be: (1) that gaseous phase deposition is controlled by the gas/liquid equilibrium; and (2) chemical characteristics, such as solubility and vapor pressure, which were similar for all the compounds. The average deposition velocity of the particulates was higher than that of the gaseous phase, at 4 cm/sec; however, those of individual compounds varied. The deposition velocities of low-middle weight compounds, such as NaP, AcPy, Flu, PhA and FluA, ranged from 0.6 to 8.0 cm/sec, while those of high weight compounds were very low, ranging from 0.05 to 0.16 cm/sec. The difference in the deposition velocities between the gaseous and particulate phases could be due to both the size-distribution and difference in the velocity resulting from the particle diameter. From these results, it could be concluded that the dry deposition of high weight molecular PAHs influenced...
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CONCLUSION

In this study, the concentration and deposition flux of PAHs were studied using a surrogate surface (knife-edge plate and water surface), and high volume air and cascade impactor samplers in an urban area. The Junge-Pankow model was used to estimate the gas-particle partitioning of PAHs in ambient air. Partitioning between the velocity of micron sized particulates, while the deposition velocity of low-middle weight molecular PAHs is due to coarse particles.
gaseous and particulate phases did not reach equilibrium, but the particle characteristics did not change with sampling time. The deposition flux of gas phase PAHs was also estimated using the margin of flux between the WSS and DDP samplers. The velocities of the dry deposited particulate PAHs varied for individual compounds, while that of gaseous PAHs did not.

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