

EFFECTS OF COARSE PM ON THE NON-EQUILIBRIUM PARTITIONING BETWEEN GAS AND PARTICLE PHASE PAHS

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ABSTRACT

A series of airborne PAHs measurements were performed at central urban and remote sites in Seoul, Korea from September 2001 to April 2002. This paper will present findings of the non-equilibrium behavior of PAHs during the campaign experiments and its implication on the uncertainty of input parameters in modeling such as multimedia environmental fate model. Size segregated concentrations of particulate matters and PAHs in particle-phase as well as in gas-phase were measured. Geometric mean diameter (GMD) of particle-phase PAHs and size segregated gas-particle partition constant (K_p) were calculated in order to address the particle size dependence of K_p and the effect of coarse particles on non-equilibrium partitioning between gas and particle-phase PAHs. At the sampling sites and/or events with more fraction of coarse particles, steeper slope and larger y-intercept of $\log P^0$ -GMD plot were obtained indicating the rapid sorption of lower molecular weight PAHs (LPAHs) whereas slower sorption of higher molecular weight PAHs (HPAHs) onto the coarse particles. Throughout all particle size range, the slopes of $\log P^0$ - $\log K_p$ plot consistently deviated from equilibrium value of -1. Distinctively lowered K_p for HPAHs over the coarse particle range was a major cause of the non-equilibrium behavior. These findings suggest that airborne HPAHs are likely in non-equilibrium with particles whereas LPAHs are rather in equilibrium. Estimation of K_p assuming equilibrium state may not be validated and thus cause significant discrepancy between the measured and estimated ones especially for HPAHs and at the sites and/or events with abundant coarse particles.

INTRODUCTION

The interest in atmospheric behavior of polycyclic aromatic hydrocarbons (PAHs) in the scientific community has recently increased a great deal because of their carcinogenicity and significant amount in environmental media. PAHs are semi-volatile, thus tend to be transported faraway in the atmosphere [1]. Atmospheric fate parameters such including gas-particle partition constant and dry deposition velocity of PAHs play a key role in many

applications such as multimedia fate modeling [2,3]. Gas-particle partition constant is affected by the particle size distribution and their physicochemical properties of compounds as well as environmental conditions. The accurate estimation of partition constant is, therefore, of great importance.

The objective of this study was to quantitatively investigate the atmospheric behavior of airborne PAHs in terms of. size distribution and gas-particle partition constant of PAHs from a series measurements in the ambient air of Seoul metropolitan area.

METHODS

Sampling Sites and Instrumentation

Two sampling sites were set up at Mt. Kwanak (Kwanak site) and Mt. Namsan (Namsan site) in Seoul metropolitan area. It was presumed that Kwanak site located at the southern end of Seoul represented the characteristics of sub-urban area whereas Namsan site located at the central district represented the characteristics of the urban area (fig. 1). Sampling was carried out at the two sites for two or three days per each sampling period.

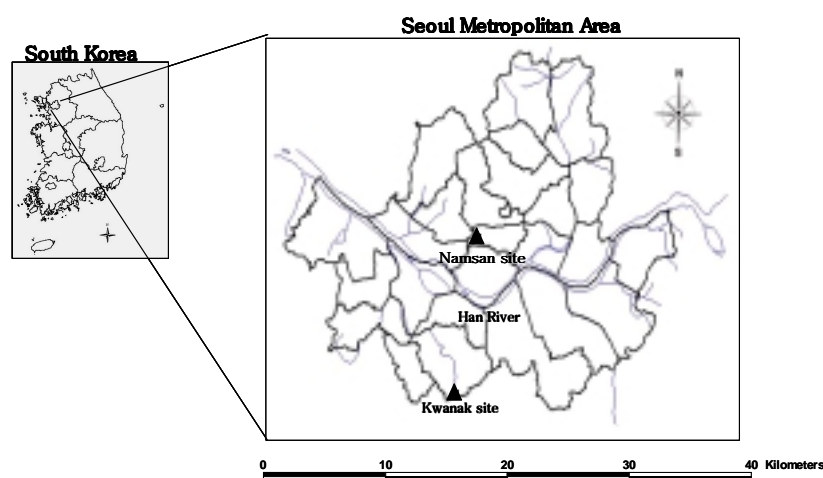


Figure 1. Location of the target area and sampling sites in this study.

Air sampling was conducted using a high volume air sampler (Hi-Vol). Air was filtered through a glass fiber filter (20.3×25.4cm, EPM 2000, Whatman) at a rate of 600 L/min. The vapor phase compounds were trapped on a PUF plug contained in an aluminum cylinder. The analysis of PUF and filters were carried out separately to give each gas phase and particle phase concentration. For size-segregated sampling of atmospheric particles a cascade impactor, Anderson 1 ACFM non-viable Ambient Particle Sizing Sampler (APSS) was

deployed at Kwanak site in the very vicinity to the Hi-Vol sampler. At Namsan site, a Hi-Vol type cascade impactor (HVIC; Anderson, USA) was used.

Table 1. Cut-off sizes (μm) of each stage for the particle sizing samplers.

Stage	1	2	3	4	5	6	7	8	Backup
APSS	9.0	5.8	4.7	3.3	2.1	1.1	0.65	0.43	<0.43
HVIC	7.2	3.0	1.5	0.95	0.49	-	-	-	<0.49

Chemical Analysis of PAHs

In total, 24 polycyclic aromatic hydrocarbons (PAHs) including alkylated PAHs were the target compounds of this study. NOAA method was referred and modified for PAH analysis in this study. Detailed analytical methods are described elsewhere [4]. Dried samples of PUF from HiVol, glass fiber filters from cascade impactor, and Mylar strips from deposition plate were spiked with surrogate standards (Naphthalene- d_8 , Acenaphthene- d_8 , Phenanthrene- d_8 , Chrysene- d_8 , and Phelylene- d_8), and extracted with dichloromethane (DCM) for 16 hours in Soxhlet apparatus. The extracts were concentrated and cleaned up with silica/alumina chromatography column. The extracts were transferred into a chromatography column packed with glass fiber, alumina (10g), silicagel (20g), and sodium sulfate dehydrates (10g) and then eluted with DCM (100ml). The eluted extracts were concentrated and followed by high pressure liquid chromatography (HPLC) clean-up. Solvent was exchanged by n-hexane and the extracts were concentrated to a final volume of 0.5ml. Internal standards (Terphenyl- d_{14}) were added to the final extracts and analyzed for PAHs using GC/MS.

RESULTS AND DISCUSSION

Geometric mean diameter (GMD) of particle-phase PAHs usually decreases as molecular weight and/or vapor pressure, P_L^0 decreases [5]. In this study, GMDs of different PAHs were positively correlated with their vapor pressure. The slope, m_g in fig.2 quantifies the physicochemical dependence of geometric mean diameters of the compounds at each site or an event, representing the difference of size distributions of individual PAHs with different volatility. The y-intercepts, b_g are considered as GMDs of a reference chemical with vapor pressure of 1 torr at each site or an event. Steeper slopes and larger y-intercepts were consistently observed at Kwanak site during the entire period. Rapid partitioning of the low molecular weight PAHs (LPAHs) and slower sorption of the high molecular weight PAHs (HPAHs) from gas-phase onto aerosols may account for the higher and at Kwanak site [6].

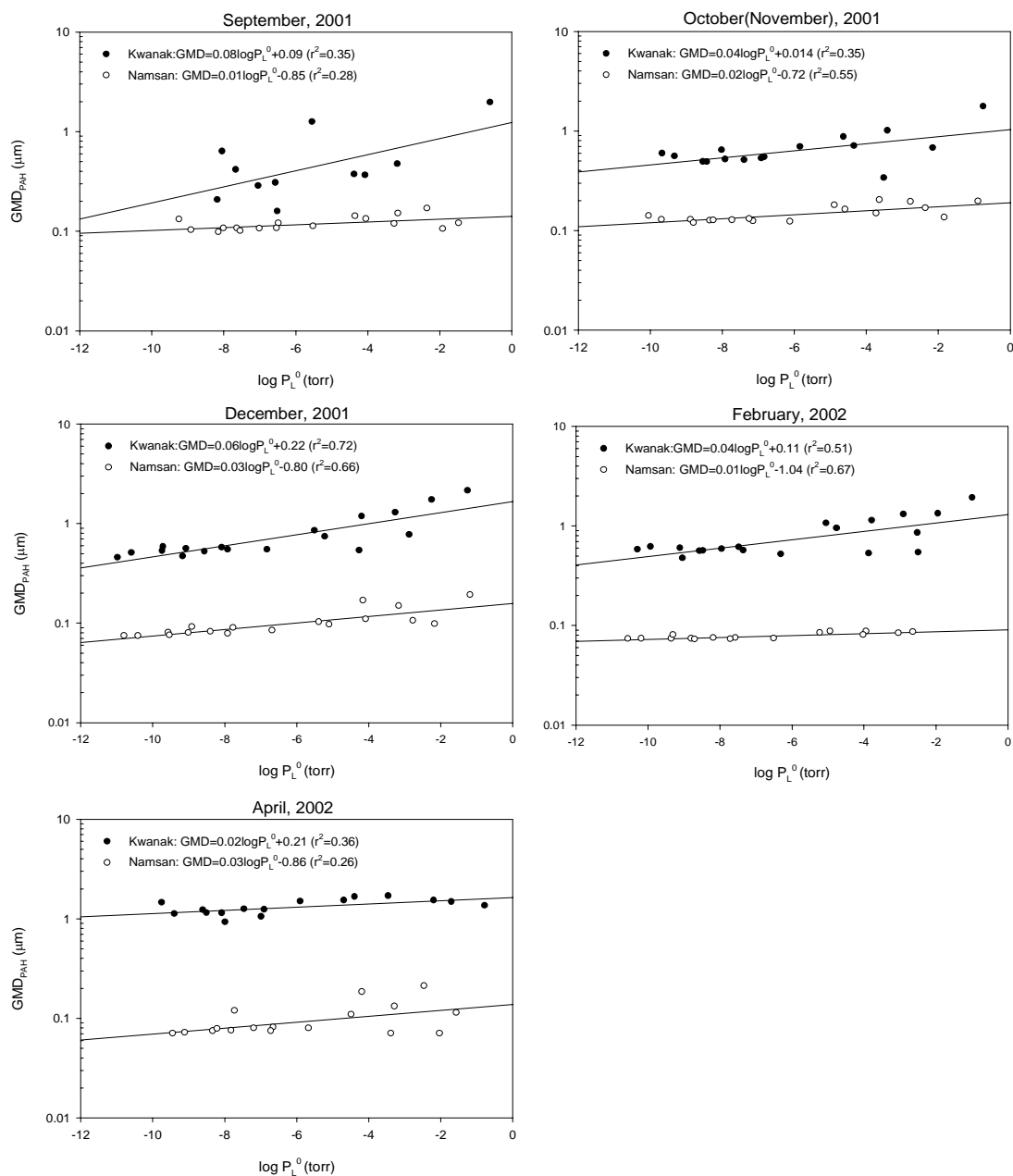


Figure 2. Dependence of GMDs on the vapor pressure of PAHs at two sites.

Since a large portion of PAHs are emitted in gas-phase at the very moment of combustion from the sources, the m_g of log P_L⁰ versus GMD_{PAH} plot approaches zero at the source area indicating little difference in GMD among the PAHs. While being transported to a remote area, air mass with still abundant gaseous PAHs can encounter coarser particles and redistribution to the coarser particles would result in increase of the GMDs. The larger GMDs of particle-phase PAHs were also observed at remote Kwanak site in this study.

The extent of redistribution should vary with vapor pressure of compounds. A linear fit between K_p and the sub-cooled liquid vapor pressure of compounds, P_L^0 has often been observed [7]. In order to examine the size dependency of K_p , K_p was calculated as grouped into four size ranges and plotted against P_L^0 in logarithmic scale. Deviations from -1 value at equilibrium were often reported and often attributed to non-equilibrium conditions or sampling artifacts [8].

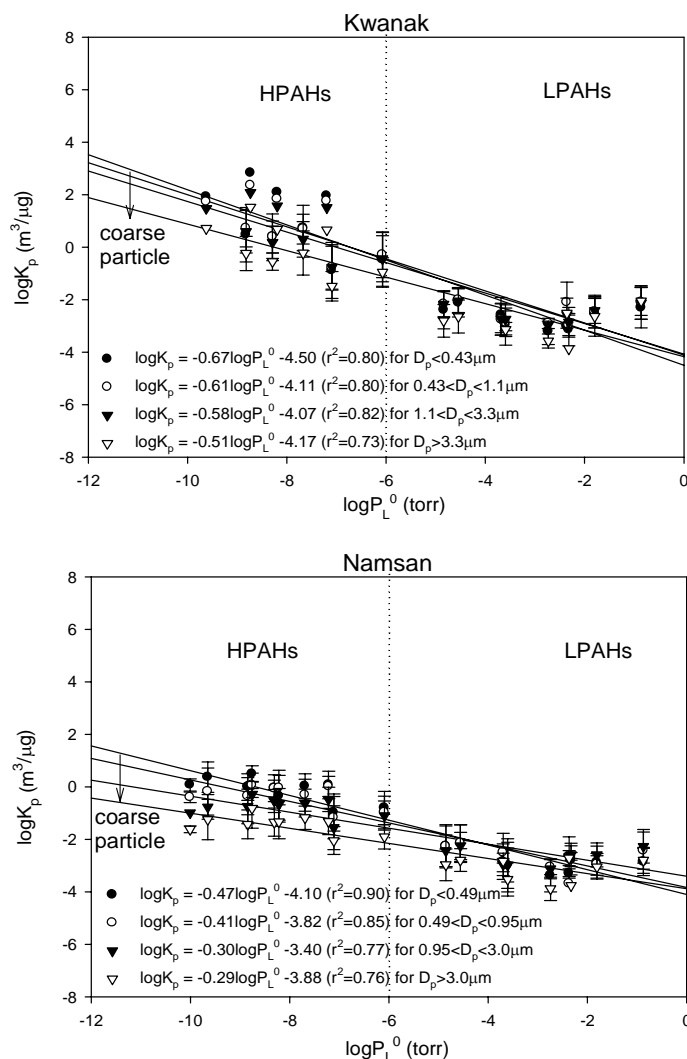


Figure 3. Particle size segregated dependency of $\log P_L^0$ vs $\log K_p$.

As shown in fig.3, the observed slopes in this study significantly deviated from -1 for all particle size ranges, more pronounced for larger size ranges. It is noticeable that size range dependency of K_p was more distinguishable for HPAHs (with more than four rings) i.e., wider ranges of K_p values were observed over the different particles sizes. Slower sorption of the HPAHs onto the particles newly introduced into the contaminated air might have mainly

attributed to the low K_p values. Fine particles would give PAHs relatively sufficient time required for the equilibrium between gas and particle phases, leading to K_p close to that of equilibrium. On the other hand, LPAHs showed narrower range of K_p values over the particle size ranges owing to quick equilibrium. At Kwanak remote from the source area, gas-particle partitioning approached closer to equilibrium value.

SUMMARY

The airborne PAHs concentrations both in the gas and particulate phases were measured at the two distinct, central urban and remote sites in Seoul metropolitan area. Site-specific size distributions of particle-phase PAHs at the two sites were observed, probably associated with the proximity to urban emission sources. Geometric mean diameters of both particulate matter and PAHs were consistently larger at Kwanak located remote from the emission sources. Geometric mean diameter of PAHs varied depending on their vapor pressure, P_L^0 i.e., heavy molecular weight PAHs tend to be sorbed onto the fine particles whereas light molecular weight PAHs were redistributed onto the coarse particles. Such a dependency of GMD was pronounced at a remote site even under the non-equilibrium conditions.

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