Environ. Eng. Res. Vol. 11, No. 1, pp. 33~44, 2006
Korean Society of Environmental Engineers

ESTIMATION OF RAIN SCAVENGING RATIO FOR PARTICLE BOUND POLYCYCLIC AROMATIC HYDROCARBONS AND POLYCHLORINATED BIPHENYLS

Hyeon Kook Kim[1], Yongseung Shin[†], Dong Soo Lee[2], Byung-Joo Song[3], and Jong-Guk Kim[3]

[1]Georgia Institute of Technology, Civil and Environmental Engineering, Atlanta, GA 30332, USA
[2]Graduate School of Environmental Studies, Seoul National University, San 56-1 Shilim-Dong, Kwanak-Gu, Seoul 151-742, Korea
[†] Environmental Management Division, Korea Environment Institute, 613-2 Bulkwang-Dong, Eunpyung-Gu, Seoul 122-706, Korea
[3]Department of Environmental Engineering, Chonbuk National University, 664-14 Duckjin-Dong, Duckjin-Gu, Chonju, Chonbuk 561-756, Korea

(received May 2005, accepted February 2006)

Abstract : The objective of this study was to develop and assess a method for estimating the rain scavenging ratios (RSRs) of particle-bound PAHs and PCBs using measured scavenging ratio of particulate matters (PM) and routinely available data of physico-chemical properties of PM. Paired atmospheric and rainwater sampling was conducted for a total of 4 rain events. Assuming equilibrium partitioning in rainwater-gas-PM system, an equation was derived for estimating the RSR of particle-bound chemicals as a function of RSR of PM and three equilibrium partition constants (i.e. dimensionless Henry's law constant, gas-particle partition coefficient, and water-particle partition coefficient). For all PAHs, the model significantly under-predicted the RSR while the model prediction for PCBs agreed with observation mostly within a factor of 5. The RSR model for the chemicals is of limited use as its accuracy critically depends on how close the observed partitioning of the chemicals in the gas-PM-rainwater system is to that estimated under the equilibrium assumption.

Key Words : Rain, Scavenging, Particlulat matter, PAHs, PCBs

INTRODUCTION

Rain scavenging has been identified as a natural cleaning mechanism and an important pathway for chemical exchange between the atmosphere and eco-systems.[1-5] Rain scavenging is by nature highly interactive with a variety of atmospheric chemistry components in a dynamic state.[1] Therefore, empirical approaches adopting the rain scavenging ratios (RSRs) or the layer-average rain scavenging coefficient have been the common practice in quantifying the rain scavenging.[2,3,5-9] RSR is the ratio of the concentration of a compound in rain collected at ground level to concentration of the same compound in the atmosphere at some convenient altitude, and the RSR and the scavenging coefficient are interchangeable. The wet deposition flux of a compound can be obtained by multiplying

---

[†] Corresponding author
E-mail: shiny@kei.re.kr
Tel: 82-02-380-7740, Fax: 82-02-380-7644

the air concentration by the RSR of the compound. The scavenging ratio is often used in atmospheric modeling of semi-volatile organic compounds (SOCs) including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs).[2,10]

The RSR of gaseous pollutants can be estimated by equilibrium partitioning governed by Henry's law. However, the RSR of particles is more complex and controlled by dynamic processes involving particle and rain drop size distributions, vertical distribution of PMconcentration along with meteorological conditions and microphysics.[1-4,11,12] In previous studies, experimental values of the RSRs of particle-bound SOCs have been reported.[5-7,13,14] The RSR of the particle-bound SOCs were often calculated on the basis of average concentrations of unpaired samples (air and rain) collected in the different rain conditions or atmospheric concentrations.[5,9,13] Besides, the values were not directly measured but derived from the measurements of overall RSR. To reduce the uncertainty associated with the RSR, simultaneous measurements of both atmospheric and rain phases in each rain event is important made on an event-base and simultaneously.[2,11] However, since measuring those at every rain event would be extremely difficult,[11,12] it seems very useful to develop models to estimate the RSRs by using variables that are more readily measurable or available.

The present study was undertaken to develop and assess a model to estimate the RSRs of particle-bound SOCs. This study focused on the rain scavenging of particulate phase as it has been identified as dominant mechanism for removal of SOCs during rain events.[4,5,7,13,15] PAHs and PCBs were chosen to investigate the influences of their physicochemical properties and emission characteristics on the scavenging ratio.

MATERIAL AND METHODS

Formulation of the RSRs of Particle-bound Chemicals

The RSR for the particle-bound compound of *i* ($W_p^{(i)}$, dimensionless) is empirically defined as:[6,11]

$$W_p^{(i)} = \frac{C_{rain,p}^{(i)}}{C_{air,p}^{(i)}} \tag{1}$$

wherewhere $C_{rain,p}^{(i)}$ and $C_{air,p}^{(i)}$ are the particle-associated concentrations (ng/m^3) of *i* in rainwater and atmosphere, respectively. In Eq. (1), $C_{rain,p}^{(i)}$ and $C_{air,p}^{(i)}$ can further be described as:

$$C_{rain,p}^{(i)} = TSP_{rain} \times C_{rain,sp}^{(i)} \tag{2}$$

$$C_{air,p}^{(i)} = TSP_{air} \times C_{air,sp}^{(i)} \tag{3}$$

where TSP_{air} and $C_{air,sp}^{(i)}$ are the total suspended particulates (μg/m^3) and the concentration of *i*bound to suspended particulates (ng/μg) in the air, respectively, and TSP_{rain} and $C_{rain,sp}^{(i)}$ are the total suspended particulates (μg/m^3) and the concentration of *i* bound to suspended particulates (ng/μg) in rainwater, respectively.

Substituting Eq. (2) and Eq. (3) with $C_{rain,p}^{(i)}$ and $C_{air,p}^{(i)}$ in Eq. (1) gives:

$$W_p^{(i)} = W_p^{(pm)} \times \frac{C_{rain,sp}^{(i)}}{C_{air,sp}^{(i)}} \tag{4}$$

where $W_p^{(pm)}$ is the RSR of PM (=TSP_{rain}/TSP_{air}, dimensionless). If partitioning equilibrium is assumed for the gas-PM-rainwater system, Eq. (4) can be written as

$$W_p^{(i)} = W_p^{(pm)} \times \frac{K_{pw}^{(i)}}{K_{pg}^{(i)}} \times \frac{1}{H^{(i)'}} \tag{5}$$

where $K_{pw}^{(i)}$ and $K_{pg}^{(i)}$ are the equilibrium partition coefficients ($m^3/\mu g$) for water-PM and gas-PM, respectively, and H' is the dimensionless Henry's law constant.

In summary, we may use the Eq. (4) and Eq. (5) for estimating the RSR of the particle-bound compound *i*. More Aaccurate prediction is obtained by using Eq. (4). However, Eq. (4) requires the measured values for $W_p^{(pm)}$, $C_{air,sp}^{(i)}$ and $C_{rain,sp}^{(i)}$ while Eq. (5) could be used without them. Therefore, Eq. (5) might have more utility than Eq. (4) as a model although Eq. (5) has also a drawback that it requires an equilibrium condition for the system of gas-PM-rainwater.

Study Area and Sampling

Atmospheric and rainwater sampling was conducted for 4 different rain events from September 2002 to March 2003 in Seoul, Korea. Each sample sets consisted of a pair of air and rain samples. Those sample sets were obtained on the roof of a 16 m height building in Seoul National University located in a suburban residential area of south Seoul.

Atmospheric samples were collected for 12 to 24 hours prior to the onset of each rain event and analyzed for TSP, PAHs, and PCBs. Particle-bound and gaseous contaminants were collected by using high-volume air samplers (Model-123V, Kimoto, Japan). Air was drawn through a glass-fiber filter (GFF) (20.3×25.4 cm, EPM 2000, Whatman, USA) and a polyurethane foam (PUF) plug (8×10 cm, Sibata, Japan) at a flow rate of 0.6 m^3/min. Size-segregated PM samples were collected by using an eight stage Micro-Orifice Uniform Deposit Impactor (MOUDI model 100 with rotator, MSP Corp. USA). Rain sampling was conducted on an event basis and analyzed for suspended particulate matters, PAHs and PCBs in particulate and dissolved phases. A sequential precipitation sampler was deployed which is equipped with a 1 m^2 stainless steel collection funnel connected to four serially linked amber glass bottles (4.33 L each). Before sampling, the funnel was cleaned with distilled and de-ionized water, hexane, and acetone. The sampler was opened manually at the onset of rain. The rainwater was collected in the bottles in a sequential manner, i.e., when a bottleis full, the rainwater collects into the next one. Immediately following cessation of the rain, the rainwater samples were returned to the laboratory and vacuum filtered over pre-combusted (at 450°C for 5 hours) GFF (nominal 0.7 μm pore size, Whatman, USA). On site measurements were made for meteorological parameters including ambient temperature, wind speed, and rain intensity by using an automatic weather station (Weather link 5.1, Davis Inst. USA). The data were recorded at every 10 minutes.

Analysis

Prior to sampling, the impactor substrates and GFF were weighed to 0.01 mg with analytical balance (AP-250D, OHAUS, USA) and were re-weighted to determine the mass of PM after sampling. The impactor substrates were dried in a desiccator after sampling to determine liquid-content corrected TSP_{air}. The GFF to filter the rainwater samples was dried for 5 hours at 100°C and placed in a desiccator prior to weighing on the analytical balance.

Four sample sets were analyzed for a total of 14 PAHs and 6 PCBs. The PAHs and PCBs selected in this study included naphthalene (NA), biphenyl (BiP), acenapthylene (ACL), acenapthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthrancene (B[a]A), chrysene (CHR), benzo[a]pyrene (B[a]P), perylene (PER), benzo[ghi]perylene (B[ghi]P), PCB44, PCB70, PCB99, PCB101, PCB138, and PCB153. The sample preparation for instrumental analyses of PAHs and PCBs in air and rainwater was conducted by following Illinois State Water Survey[16] and Integrated Atmospheric Deposition Network.[17] Briefly, a total of eight internal standards (Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, PCB14, PCB65, and PCB166) were added to all the samples before extraction. Air samples (PUFs and GFFs) and PM (GFFs) in rainwater were extracted overnight with acetone and hexane mixture (50:50, v/v) by using accelerated solvent extraction apparatus (ASE - 200, DIONEX, USA). The chemicals in dissolved phase were transferred to PUF by passing the rainwater filtrate at a flow rate of 0.13 L/min through a glass tube (id = 84 mm) loaded with two serially placed PUFs.[18)] The PUFs were Soxhlet extracted for 24 h with acetone and hexane mixture (50:50, v/v). The rainwater extracts were dehydrated by using anhydrous sodium sulfate prior to concentration. All extracts were concentrated and transferred into hexane by using a rotary evaporator to 1 mL and were further evaporated to 0.2 or 0.3 mL under a gentle stream of ultra-pure nitrogen. After the volume reduction, the concentrates were cleaned up on a column loaded with 4 g of 4% hydrated silica gel. The low molecular weight PAHs and PCBs were eluted with 60 mL of hexane. The remaining PAHs on the column were eluted with 25 mL of dichloromethane and hexane mixture (50:50, v/v). The hexane fraction containing low molecular weight PAHs and PCBs was cleaned up with multi-layer silica gel column followed by activated carbon column. The multi-layer column was packed from the bottom with 44% sulfuric acid silica gel 6 g, silica gel 0.5 g, 33% KOH silica gel 1 g, silica gel 0.5 g and 10% silver nitrate silica gel 1 g, and was eluted with 100 mL of n-hexane. Activated carbon (0.5 g) column was eluted with 25 mL of 25% dichloromethane in n-hexane followed by 50 mL toluene.

After the clean up, the concentrates were analyzed by using an HP-6890 GC with an HP-5973 mass selective detector for PAHs and an HP-5890 GC with 63 Ni electron capture detector for PCBs. A DB-5 glass capillary column (with 0.25 mm i.d., 0.25 μm film thickness, and 60 m length, J&W Scientific, USA) was used. The quantification was conducted following the USEPA Method 8270C (USEPA).[19)]

Quality Control

Additional analyses were performed for the mid-point calibration verification standard during a 12-hour analytical shift. Gas chromatograph was recalibrated if the response for any analyte varied from the average initial calibration response by more than 15% in additional determinations. Accuracy and precision were estimated from the analysis of blank, matrix spike, and matrix spike duplicate samples.

The recoveries of PAHs and PCBs ranged from 70% to 115% for PAHs except naphthalene. Naphthalene was not analyzed as its recovery (49.4%) was out of quality control limit. The precisions of PAHs and PCBs were within 10% and 15%, respectively. However, the results of BiP, ACL, and ACT were not presented because significant breakthrough was observed to occur during the gas phase sampling with PUF in an independent study that has been conducted under the conditions of the same sampling procedure, site, and period.[20)]

RESULTS AND DISCUSSION

RSRs of PM, PAHs, and PCBs

As shown in Figure 1, the values of TSP, total particulate PAHs, and total dissolved PAHs in rainwater significantly varied with time during a rain event. This observation indicated that the atmospheric conditions deviate more with time in a rain event from those for a period preceding the rain event. Therefore, the rainwater sampled only in the first bottle was used for all the analyses. The results are summarized in Table 1. The atmospheric and meteorological conditions were typical of the mid-region in Korean peninsular. The values of $W_p^{(pm)}$ ranged from 6.0×10^4 to 3.27×10^6, which was similar to the reported values in previous studies.[7,11)] The RSRs for gaseous and particle-bound chemicals are listed in Table 2. The values of the RSR ranged from 0.5×10^3 to 9.03×10^5 for PAHs and from 0.6×10^3 to 1.61×10^5 for PCBs, which were

Table 1. Meteorological conditions and the measured RSR of PM for the 4 sampling events

Date	Temp. (°C)	Wind Speed (m/sec)	Rain Intensity (mm/hr)	TSP (mg/m^3)	$W_p^{(pm)}$ ($\times 10^5$)	Sampling duration
09/15-16/2002	15.70±0.09	0	0.05	72.71	1.40	13:00-01:00
10/13/2002	16.60±0.99	1.7±0.14	27.6	89.92	0.61	07:00-07:08
10/24/2002	8.93±0.32	0.67±0.55	1.0	40.95	32.69	17:30-20:30
02/21/2003	3.35±0.82	0.65±0.61	0.88	36.42	4.73	15:50-20:00
03/06-07/2003	0.94±0.31	0.47±0.37	1.07	55.38	4.54	07:50-10:56

The error range denotes one standard deviation. TSP: total suspended particulates in air.

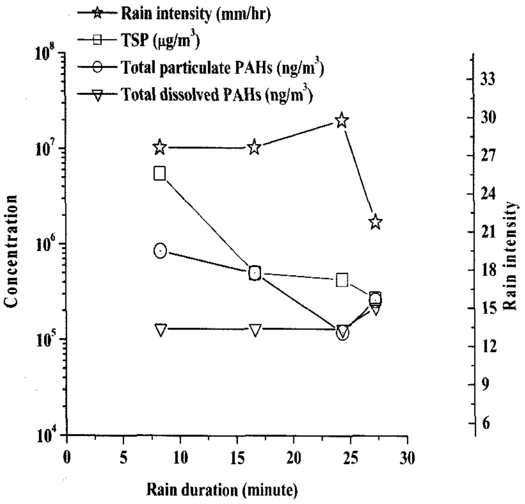

Figure 1. Time changes in total suspended particles (TSPrain), dissolved and particle-bound total-PAHs (Σ-PAHs) in rainwater, and rain intensity during a single rain event, 07:00-07:30, 10/13/2002.

within the range of the previously reported values.[4-7,9,14,20)]

As shown in Figure 2, the particulate phase appeared to play a greater role than gas phase in the cross-media transport (= rain intensity × scavenging ratio × concentration in air) of PAHs and PCBs from air to the ground during the rain events, assuring that scavenging PM was a substantial contributor to the transfer of PAHs and PCBs by the rain scavenging at the present study site. Similar results were reported in a number of studies.[4,5,7,13-15)]

Assessing the Model for Particle-bound PAHs and PCBs

To assess the Eq. (5) by comparing the predicted values of the RSR for the particle-bound PAHs and PCBs with those measured, the equilibrium coefficients were estimated. Values

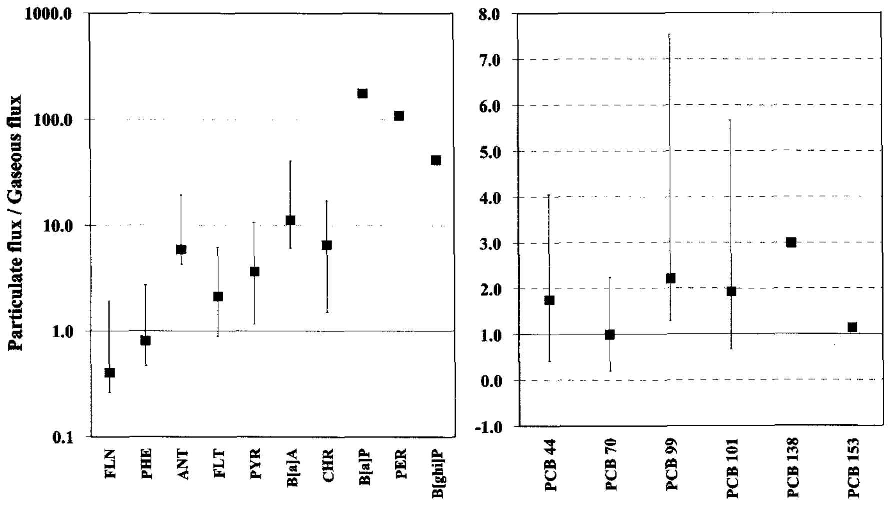

Figure 2. The ratio of the flux by rain scavenging of particulate phase to that of gaseous phasefor (a) PAHs and (b) PCBs. The error bars represent the maximum and the minimum values.

Table 2. Measured RSRs for gaseous and particle-bound PAHs and PCBs (× 10^5)

Date	09/15-16/2002		10/13/2002		10/24/2002		03/06/2003		Geometric Mean	
Scavenging ratio	$W_g^{(i)}$	$W_p^{(pm)}$	$W_g^{(i)}$	$W_p^{(pm)}$	$W_g^{(i)}$	$W_p^{(pm)}$	$W_g^{(i)}$	$W_p^{(pm)}$	$W_g^{(i)}$	$W_p^{(pm)}$
PAHs										
FLN	0.17	3.44	0.09	0.68	0.11	6.37	0.04	0.27	0.09	1.42
PHE	0.13	1.43	0.2	6.94	0.87	5.89	0.14	0.16	0.24	1.75
ANT	NA	2.54	0.02	22.39	0.17	9.84	0.04	0.13	0.05	2.92
FLT	0.17	0.79	0.43	5.85	2.58	7.21	0.62	0.27	0.58	1.72
PYR	0.18	1.9	0.29	5.44	1.87	5.88	0.57	0.26	0.49	1.99
B[a]A	NA	0.26	5.57	4.34	18.21	3.49	4.45	0.24	7.67	0.98
CHR	NA	0.16	1.21	3.89	31.03	4.3	19.62	0.32	9.03	0.96
B[a]P	NA	NA	3.26	3.91	NA	4.12	NA	0.24	3.26	1.57
PER	NA	NA	3.56	11.59	NA	4.29	NA	0.25	3.56	2.32
B[ghi]P	NA	0.19	6.92	2.39	NA	3.7	NA	0.35	6.92	0.88
PCBs										
PCB 44	0.25	2.31	NS	NS	0.15	0.29	0.25	NA	0.21	0.82
PCB 70	0.54	2.7	NS	NS	0.26	0.71	0.61	NA	0.44	1.39
PCB 99	NA	NA	NS	NS	0.03	0.94	0.15	0.58	0.06	0.74
PCB 101	0.38	5.02	NS	NS	0.23	1.17	0.25	0.64	0.28	1.55
PCB 138	2.03	NA	NS	NS	0.38	NA	0.83	1.18	0.86	1.18
PCB 153	0.82	3.13	NS	NS	0.12	NA	NA	0.83	0.31	1.61

NA: not available, NS: not sampled, $W_g^{(i)}$: gas scavenging ratio for chemical species of i and $W_p^{(i)}$: particle scavenging ratio for chemical species of i

of $K_{pw}^{(i)}$ were estimated from the equation ($K_{pw}^{(i)} = 0.41 f_{oc} K_{ow}$) developed by Karickhoff[22] where f_{oc} is organic carbon fraction and K_{ow} is octanol-water partition constant. From Murray and Andren,[15] a value of 0.2 was assumed for f_{oc} in this study. The values of K_{ow} were taken from Yalkowsky and Valvani[23,24] and Yalkowsky *et al.*,[25] respectively, except for those of PCB99 and PCB138.[26] The values of $K_{pg}^{(i)}$ for the PAHs were estimated by using the equation originally developed by Junge[27] and later critically reviewed by Pankow[28] : $\varnothing = c\Theta/(P_L^{S(i)} + c\Theta) = K_{pg}^{(i)}$ (TSP) / [1+$K_{pg}^{(i)}$(TSP)] where $\varnothing$ is the particulate fraction; $P_L^{s(i)}$ is sub-cooled liquid vapor pressure (Pa) of chemical species i estimated by Paasivirta *et al.*[29] that is corrected to ambient temperature; Θ is the total surface area of airborne PM (m^2/m^3) and was calculated as a function of a specific surface area for urban particles taking a constant value of 2.1m^2/g from Sheffield and Pankow,[30] and TSP ($\mu g/m^3$); c is empirical constant set to 0.173 m-Pa as in Junge.[27] The values of $K_{pg}^{(i)}$ for PCBs were estimated by the semi-empirical equation ($\log K_{pg}^{(i)} = -0.715 \log P_L^{s(i)} - 5.141$) proposed by Harner and Biddleman.[31] The values of $H'^{(i)}$ were taken from and temperature corrected according to Paasivirta *et al.*.[29] Additional attempt was made to assess Eq. (5) by using soot-air partition coefficients[32] and other values of $H'^{(i)}$[33] for PAHs. However, the assessment results are not presented as no substantial difference resulted in the prediction bias of Eq. (5).

In Figure 3, the RSR of particulate PAHs and PCBs predicted by Eq. (5) are compared with the measured values (*i.e.* the result of Eq. (4)). Overall, poor prediction was pronounced for PAHs while for PCBs the predictions showed closer agreement with the measured values. The

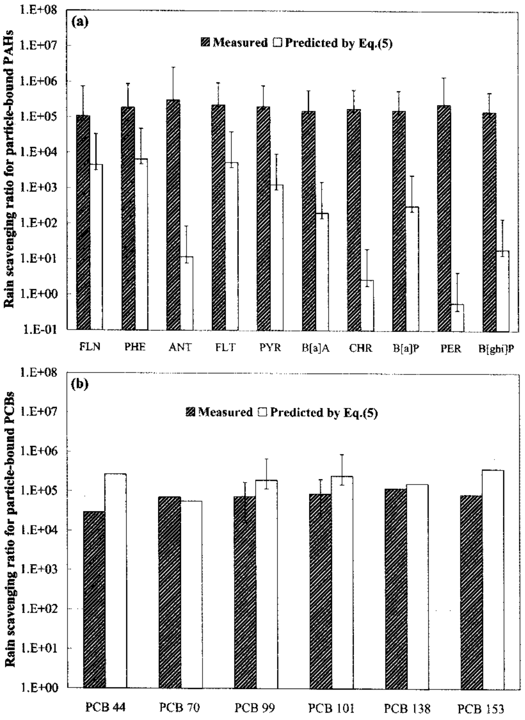

Figure 3. The particulate phase scavenging ratios predicted by Equation (5) as compared to the measured for (a) PAHs and (b) PCBs. The error bars represent the maximum and the minimum values.

largest disparity exceeded six orders of magnitude for perylene.

The present RSR model (*i.e.* Eq. (5)) is intrinsically prone to poorer prediction for PAHs than for PCBs by a few reasons. Most importantly, the use of equilibrium assumption could be in error as equilibrium might not be established between gas and PM or gas and rainwater in the field conditions. Alternatively, even when equilibrium can be assumed, incorrect estimates for the equilibrium coefficients might have been used as they are difficult to determine precisely.[34] For $K_{pw}^{(i)}$, $K_{pg}^{(i)}$, and $H'^{(i)}$, values of large difference were often reported for the same chemicals.[15,21,35,36] Furthermore, the equilibrium values vary with the site-specific conditions. In Figure 4(a) through 4(c), the ratios of the estimated equilibrium partition coefficient to those of the observed are compared for PAHs and PCBs. As shown in Figure 4(a), the observed values and the estimated ones for $K_{pg}^{(i)}$ agreed within a factor of 10 for PCBs while for PAHs, particularly CHR, PER, and B[ghi]P, the disagreement was notably greater. It is not evident whether such disparity indicated that equilibrium state was not achieved at the site, or more accurate or site-specific estimation of the equilibrium coefficients is needed. However, significant deviation of $K_{pg}^{(i)}$ for the PAHs may be attributable to non-equilibrium conditions as often reported in previous studies.[37] Particularly, a fraction of PAHs associated with PM of combustion origin is likely bound within the particle matrix and not exchangeable with the contacting gas phase.[38,39] Non-equilibrium conditions became more complicated by the introduction of fresh coarse particles of soil origin in the studies independently conducted at the present study site.[40,41] Under this circumstance, use of the equilibrium assumption might be inappropriate. Contrarily, PCBs enter into the air as gas and are more likely to be in or near equilibrium with particulate phases,[36] which is consistent with the observation made in this study. As shown in Figure 4(b) and 4(c), the observed $K_{pw}^{(i)}$ and $H'^{(i)}$ were smaller than the equilibrium values except for $K_{pw}^{(i)}$ of PAHs. For the disagreement between the observed and equilibrium values involving aqueous phase, additional reasons should be taken into account. In the present study, filtration of rainwater was conducted with GFF of 0.7μm pore. Consequently, a portion of particle bound PAHs could pass through the GFF and be counted as dissolved, which would lead to underestimation of $K_{pw}^{(i)}$ and $H'^{(i)}$. Such results were previously reported for PAHs and PCBs.[15,36] Besides, the observed values of $K_{pw}^{(i)}$ could further vary with the duration of contact between the scavenged PM and rainwater. The contact time might be insufficient for equilibrium assumption as most of the samples were filtered within 24 hours in the

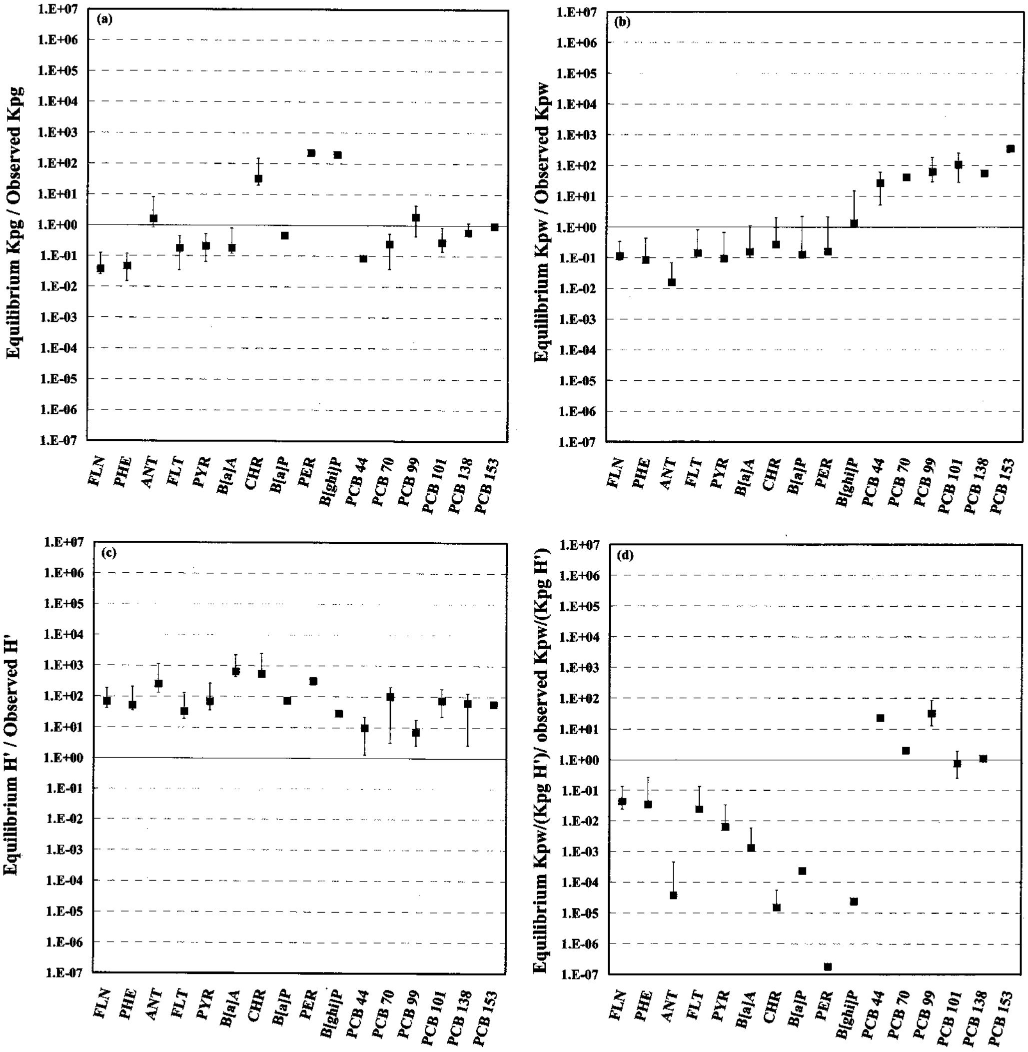

Figure 4. The ratios of the estimated equilibrium values to the observed for (a) K_{pg}, (b) K_{pw}, (c) H' and (d) (K_{pw}/K_{pg} H') of PAHs and PCBs. The error bars represent the maximum and the minimum values.

present study.

Because the individual disparities of the three partition equilibrium constants may be combined into $\frac{K_{pw}^{(i)}}{K_{pg}^{(i)}} \times \frac{1}{H^{(i)'}}$ to determine the overall prediction bias of Eq. (5), not only the magnitude but the direction of the disparity (*i.e.*, underestimation or overestimation) are important. Therefore, use of Eq. (5) is subject to large variability in prediction bias (up to a few orders of magnitude) that is significantly greater than individual error of the equilibrium coefficient. The marked difference between PAHs and PCBs shown in Figure 4(d) is obviously a result of the fact that for PCBs both $K_{pw}^{(i)}$ and $H'^{(i)}$ were over-predicted by about two orders of magnitude to eventually cancel out in the relationship of $K_{pw}^{(i)}$ / $H'^{(i)}$ while for PAHs, $K_{pw}^{(i)}$ was under-predicted and $H'^{(i)}$ was over-predicted to magnify the bias.

Uncertainty of a model depends on that of the model parameters used in the model equation and the value of model parameters can vary in orders of magnitude depending on each value selected from literatures for estimating those parameters. Thus, in order to assess the uncertainty range of the RSR of particle-bound PAHs and PCBs calculated by using Eq. (5), the model parameters with ranges(*i.e.*, $K_{pw}^{(i)}$, $K_{pg}^{(i)}$ and $H^{'(i)}$) were examined with respect to each probable minimum, maximum and mean value **at 25 °C**. The model parameters were calculated by adopting the literature values of K_{ow}, $P_L^{s(i)}$ and $H^{'(i)}$[35] Figure 5 shows the uncertainty range of RSRs for the selected PAHs and PCBs calculated from Eq. (5) when using the model parameters with ranges. The predicted RSRs **at 25 °C** in this study (black-filled square points in Figure 5) were comparable with the mean predictions **at 25 °C** based on the literatures (empty- circled points in Figure 5). This result presents that the predicted scavenging ratios in the current study are in an acceptable range.

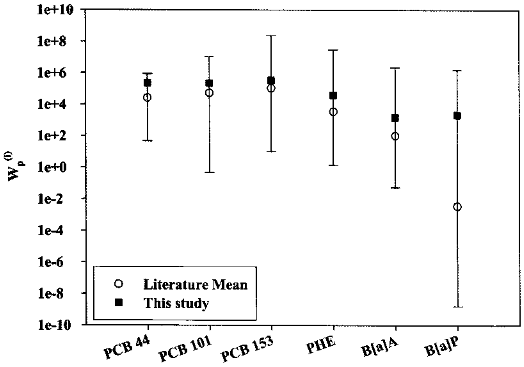

Figure 5. Uncertainty ranges of calculated scavenging ratio ($W_p^{(i)}$) at 25 °C of selected PCBs and PAHs. The error bars represent the maximum and the minimum values of calculated $W_p^{(i)}$ at 25 °C using model parameters cited from literatures.

CONCLUSION

A model for RSR of particle-bound PAHs and PCBs was derived from the RSR of PM and the equilibrium assumption describing the partitioning of the chemicals among gas, PM, and rainwater. The model's predicting power critically depends on how close the observed partitioning of the chemicals in the gas-PM-rainwater system is to that estimated under the equilibrium assumption. Therefore, the use of the RSR model (Eq. (5)) may be limited for occasions where the chemicals are in or near equilibrium partitioning equilibrium conditions and accurate estimates of equilibrium partition constants are available. Nevertheless, the RSR model may be useful in offering a first approximation when no measured data are available.

ACKNOWLEDGEMENT

The authors are grateful to the financial support from NIER under the grant of the EDC project on environmental fate and transport.

NOMENCLATURE

PM : particulate matter
RSR : rain scavenging ratio
c : empirical constant set to 0.173 m-Pa
$C_{air,p}^{(i)}$: particle-associated concentrations of *i* in atmosphere (ng/m^3)
$C_{rain,p}^{(i)}$: particle-associated concentrations of *i* in rainwater and atmosphere (ng/m^3)
$C_{air,sp}^{(i)}$: concentration of *i* bound to suspended particulates in the air (ng/μg)
$C_{rain,sp}^{(i)}$: concentration of *i* bound to suspended particulates in rainwater (ng/μg)
f_{oc} : organic carbon fraction
$H^{'}$: dimensionless Henry's law constant
K_{ow} : octanol-water partition constant
$K_{pg}^{(i)}$: equilibrium partition coefficients for gas-PM (m^3/μg)
$K_{pw}^{(i)}$: equilibrium partition coefficients for water-PM (m^3/μg)
$P_L^{s(i)}$: sub-cooled liquid vapor pressure (Pa)

of chemical species i

TSP_{air} : total suspended particulates in the air (μg/m^3)

TSP_{rain} : total suspended particulates in rainwater (μg/m^3)

$W_p^{(pm)}$: RSR of PM (dimensionless)

$W_p^{(i)}$: RSR for the particle-bound compound of i (dimensionless)

Θ : total surface area of airborne PM (m^2/m^3)

$\varnothing$: fraction of the compound associated with PM

REFERENCES

1. Hales, J. M., "The mathematical characterization of precipitation scavenging and precipitation chemistry," In: Hutzinger, O., Editor, The Handbook of Environmental Chemistry, Vol. 4, Part A, Springer, Berin, Heidelberg, New York, Tokyo, pp. 150-217 (1986).
2. Tsai, W., Cohen, Y., Sakugawa, H., and Kaplan, I. R., "Dynamic partitioning of semivolatile organics in gas/particle/rain phases during rain scavenging," *Environ. Sci. Technol.*, **25**, 2012-2023 (1991).
3. Mircea, M., Stefan, S., and Fuzzi, S., "Precipitation scavenging coefficient: influence of measured aerosol and raindrop size distributions," *Atmos. Environ.*, **34**, 5169-5174 (2000).
4. Offenberg, J. H., and Baker, B. E., "Precipitation scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbons along an urban to over-water transect," *Environ. Sci. Technol.*, **36**, 3763-3771 (2002).
5. Van Ry, D. A., Gigliotti, C. L., Glenn, T. R., Nelson, E. D., Totten, L. A., and Eisenreich, S. J., "Wet deposition of polychlorinated biphenyls in urban and background areas of the mid-Atlantic states," *Environ. Sci. Technol.*, **36**, 3201-3209 (2002).
6. Ligocki, M. P., Leuenberger, C., and Pankow, J. F., "Trace organic compounds in rain-III. Particle scavenging of neutral organic compounds," *Atmos. Environ.*, **19**, 1619-1626 (1985b).
7. Franz, T. P., and Eisenreich, S. J., "Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota," *Environ. Sci. Technol.*, **32**, 1771-1778 (1998).
8. Andronache, C., "Estimates of sulfate aerosol wet scavenging coefficient for locations in the Eastern United States," *Atmos. Environ.*, **38**, 795-804 (2004).
9. Sahu, S. K., Pandit, G. G., and Sadasivan, S., "Precipitation scavenging of polycyclic aromatic hydrocarbons in Mumbai, India," *Sci. Total Environ.*, **318**, 245-249 (2004).
10. Van Jaarsveld, J. A., Van Pul, W. A. J., and De Leeuw, F. A. A. M., Modeling Transport and Deposition of Persistent Organic Pollutants in the European Region, *Atmos. Environ.*, **31**, 1011-1024 (1997).
11. Slinn, W. G. N., Hasse, L., Hicks, B., Hohan, A. W., Lai, D., Liss, P. S., Munnich, K. O., Sehmel, G. A., and Vittori, O., "Some aspects of the transfer of atmospheric trace constituents past the air-sea interface," *Atmos., Environ.*, **12**, 2055-2087 (1978).
12. Seinfeld, J. H., and Pandis, S. N., *Atmospheric chemistry and physics*, Wiley & Sons, Inc., New York, pp. 100-1026 (1998).
13. Dickhut, R. M., and Gustafson, K. E., "Atmospheric washout of polycyclic aromatic hydrocarbons in the southern chesapeake bay region," *Environ. Sci. Technol.*, **29**, 1518-1525 (1995).
14. Poster, D. L., and Baker, J. E., "Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. Scavenging of polycyclic aromatic hydrocarbons by rain," *Environ. Sci. Technol.*, **30**, 349-354 (1996b).
15. Murray, M. W., and Andren, A. W., "Precipitation scavenging of PCB conginers in the Great Lakes region," *Atmos. Environ.*,

26A, 883-897 (1992).

16. Basu, I., "*Analysis of PCBs, Pesticides, and PAHs in air and precipitation samples: IADN project sample preparation procedure,*" School of public and environmental affairs, Indiana University, Bloomington, IN (1995).
17. Harlin, K., and Surratt, K., "*Analysis of PCBs, Pesticides, and PAHs in air and precipitation samples: sample preparation procedures,*" Illinois State Water Survey, Champaign, IL (1995).
18. Naes, K., Axelman, J., Näf, C. and Broman, D., "Role of soot carbon and other carbon matrices in the distribution of PAHs among particles, DOC, and the dissolved phase in the effluent and recipient waters of an aluminum reduction plant," *Environ. Sci. Technol.*, **32**, 1786-1792 (1988).
19. USEPA, Method 8270 C., "*Semivolatile organic compounds by gas chromatography/ mass spectrometry (GC/MS),*" United States Environmental Protection Agency, EPA report. SW-846 (1996).
20. Shin, Y. S., *Atmospheric fate process of PAHs and their effects on the uncertainties of multimedia fate modeling*, Ph.D Dissertation, Seoul National University, Seoul, Korea (2003).
21. Ligocki, M. P., Leuenberger, C., and Pankow, J. F., "Trace organic compounds in rain-II. Gas scavenging of neutral organic compounds," *Atmos. Environ.*, **19**, 1609-1617 (1985A).
22. Karickhoff, S. W., "Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils," *Chemosphere*, **10**, 833-849 (1981).
23. Yalkowsky, S. H., and Valvani, S. C., "Solubilities and partitioning. 2. Relationships between aqueous solubilities, partition coefficients, and molecular surface areas of rigid aromatic hydrocarbons," *J. Chem. Eng. Data*, **24**, 127-129 (1979).
24. Yalkowsky, S. H., and Valvani, S. C., "Solubility and Partitioning. I: Solubility of nonelectrolytes in water," *J. Pharm. Sci.*, **69**, 912-922 (1980).
25. Yalkowsky, S. H., Valvani, S. C., and Mackay, D., "Estimation of the aqueous solubility of some aromatic compounds," *Residue Rev.*, **85**, 43-55 (1983).
26. Rapaport, R. A., and Eisenreich, S. J., "Chromatographic determination of octanol-water partition coefficients (KOW's) for 58 polychlorinated biphenyl congeners," *Environ. Sci. Technol.*, **18**, 163-170 (1984).
27. Junge, C. E., "Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants," In: Suffet, I.H., ed. Fate of pollutants in the air and water environments, New York: Wiley and Sons, pp. 7-26 (1977).
28. Pankow, J. F., "Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere," *Atmos. Environ.*, **21**, 2275 - 2283 (1987).
29. Paasivirta, J., Sinkkonen, S., Mikkelson, P., Rantio, T., and Wania, F., "Estimation of vapor pressures, solubilities and henry's law constants of selected persistent organic pollutants as functions of temperature," *Chemosphere*, **39**, 811-832 (1999).
30. Sheffield, A. E., and Pankow, J. F., "Specific surface area of urban atmospheric particulate matter in Portland, Oregon," *Environ. Sci. Technol.*, **28**, 1759-1766 (1994).
31. Harner, T., and Bidleman, T. F., "Octanol-air partition coefficient for describing particle/ gas partitioning of aromatic compounds in urban air," *Environ. Sci. Technol.*, **32**, 1494-1502 (1998).
32. Dachs, J., and Eisenreich, S. J., "Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons," *Environ. Sci. Technol.*, **34**, 3690-3697 (2000).
33. Bamford, H. A., Poster, D. L., and Baker, J. E, "Temperature dependence of henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4°C and 31°C" *Environ. Toxicol. Chem.*, **18**, 1905-1912 (1999).

34. Volckens, J., and Leith, D., "Effects of sampling bias on gas-particle partitioning of semi-volatile compounds," *Atmos. Environ.*, **37**, 3385-3393 (2003).
35. Mackay, D., Shiu, W. Y., and Ma, K. C., *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals*, Vol. II Lewis Publisher, Chelsea, Michigan (1992).
36. Poster, D. L., and Baker, J. E., "Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Concentrations and distributions of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in rainwater," *Environ. Sci. Technol.*, **30**, 341-348 (1996a).
37. Ngabé, B., and Poissant, L., "Polycyclic aromatic hydrocarbons in the air in the st. lawrence basin (Que'bec)," *Environ. Sci. Technol.*, **37**, 2094-2099 (2003).
38. Pankow, J. F., and Biddleman, T. F., "Effects of temperature, TSP and per cent non-exchangeable material in determining the gas-particle partitioning of organic compounds," *Atmos. Environ.*, **25A**, 2241-2249 (1991).
39. Sitaras, I. E., Bakeas, E. B., and Siskos, P. A., "Gas-particle partitioning of seven volatile polycyclic aromatic hydrocarbons in a heavy traffic urban area," *Sci. Total Environ.*, **327**, 249-264 (2004).
40. Shin, Y. S., Lee, D. S., Park, J. S., Kim, J. G., and Kim, S. H., *Effect of coarse PM on the non-equilibrium partitioning between gas and particle phase PAHs*, IUAPPA 13th World Clean Air and Environmental Protection Congress, London. UK, (2004).
41. Kim, S. K., *Integrated assessment of multimedia fates of PAHs and PCBs in Seoul metropolitan area, Korea*, Ph.D Dissertation, Seoul National University, Seoul, Korea (2004).