Abstract of Dissertation
（論文の内容の要旨）

Title of Dissertation:
Diurnal and seasonal variations of particle size-fractioned polycyclic aromatic hydrocarbons (PAHs) and their risk assessment in roadside air environment in Bangkok
（バンコクの沿道大気環境における粒径別多環芳香族炭化水素類（PAHs）の日間変動と季節変動及びリスク評価）

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Polycyclic aromatic hydrocarbons (PAHs) have been drawing attention as a major hazardous air pollutant due to their potential carcinogenicity and mutagenicity. At present, however, monitoring data are still insufficient, and information on PAH emission and understanding of atmospheric behavior are subjected to major uncertainties. In the urban environment with heavy traffic, vehicle exhaust is the main source and previous roadside measurements showed much higher levels of PAHs than those at ambient sites. Bangkok was selected as the field of this study, where traffic air pollution and its health effects have long been a serious problem due to the heavy traffic burden and the chronic state of traffic congestion. In developing countries, including Thailand, PAH monitoring data, especially temporal variations on diurnal or seasonal bases are limited. In addition, monitoring data for particle size-fractioned PAH concentrations and profiles are still scarce. Given the background, this study aims at comprehensive and detailed data analysis of atmospheric PAHs at the roadside and their risk assessment for the roadside residents in Bangkok. The objectives of the study are stated as follows.

1) To investigate spatial distribution of PAHs concentrations in Bangkok comparing roadside and general areas,
2) To verify the contribution of vehicle exhaust to roadside atmospheric PAHs in relation to traffic flows,
3) To investigate diurnal variations of particle size-fractioned PAH concentrations and profiles at the roadside,
4) To investigate seasonal variations of particle size-fractioned PAH concentrations and profiles at the roadside, and
5) To assess PAH inhalation risk with the diurnal and seasonal concentration variations

Prior to intensive monitoring at the roadside, spatial distribution of PAH concentrations was investigated in the Bangkok metropolitan area to compare concentrations at the roadside and general areas. The long-term real-time monitoring revealed that the roadside average concentrations were 1.6 to 3.0 times higher than the average concentrations in the general area. Three-day average PAH profiles were similar between the roadside and the general areas, which implies that traffic emission is the common main source for the both areas. Regarding the seasonal variations, average concentrations were lower in the hot season (April, 2004) than in the wet season (September, 2003). This could possibly be attributed to seasonal changes of meteorology, mainly the shift of predominant wind direction, which have accordingly changed the monitoring sites downwind of less vehicle emission sources at the roadside sites and of less polluted areas at the general area sites in the hot season compared to the wet season.

Given the results that higher PAH concentrations were observed at the roadside than the general areas, contribution of vehicle emissions to roadside atmospheric PAHs was verified at R6 site. Relationship between the traffic flow, PAH concentrations and vehicle exhaust at the roadside air environment was analyzed in terms of cyclical patterns of their time-series data. The three time-series data, namely the traffic volume, PAH concentrations monitored as PAS signals, and vehicle exhaust detected as smell sensed by human were all recorded in intervals of 10 seconds. Cross spectral analysis revealed that those time-series data were periodically correlated with each other, possibly dependent on traffic light intervals. It implied that in accordance with the traffic light intervals, congested traffic periodically occurred and concentrated vehicle emissions caused peaks of PAH concentrations and vehicle exhaust smells with certain time lags ranging between 3.0 and 27.6 seconds. In addition, it was revealed that PAH concentrations varied considerably at different locations in the R6 road space. From the results of 30 minutes PAS real-time monitoring simultaneously at five locations, the differences of average PAS signal values between the locations were up to as much as nine times. This spatial variation was considered as one of the major uncertainties in assessing the PAH risk based on single point measurement data in the later chapter.

Intensive PAH measurements were conducted at the two roadside sites, R6 and CC. Diurnal variations of the PAH profiles were investigated into the details in the hot season (April, 2006). 13 total PAHs concentrations in the four time periods of the day, namely morning (m), daytime (d), evening (e) and overnight (o) periods, were 5.5 (m), 7.3 (d), 7.9 (e) and 3.3 ng/m^3

(o) at R6 and 4.1 (m), 4.1 (d), 4.0 (e), and 3.5 ng/m^3 (o). On average PAH concentrations at R6 were higher than those at CC in the hot season. Although the traffic volume was smaller at R6, under the condition that wind was blowing in the direction from the road to the sampling location at both sites for all the four time periods of the day, the higher concentrations at R6 were likely caused by its somewhat closed road space configuration with an elevated highway, which might have restricted air ventilation and solar radiation to cause photochemical degradation of PAHs at R6. Size-fractioned PAH profiles varied between the different time periods of the day. Especially the profiles of the accumulation mode obtained at CC varied the most, suggested by the lower Cronbach α value, possibly due to photochemical reactions promoted in the daytime, which might have been restricted at R6 to the contrary. Moreover, at both sites, the PAH profiles in the different time periods seemed to be directly affected by the diurnal variations of the traffic profiles, suggested by the diurnal variations of the traffic source diagnostic ratios of BghiP/IP.

Seasonal variations of the PAH concentrations were investigated in terms of seasonal average concentrations obtained by the 7-12 days PAS real-time monitoring and of size-fractioned concentrations in the four time periods of the day in each season obtained by the three days MOUDI air sampling. From the PAS real-time monitoring, average 13 total PAHs equivalent concentrations were 3.9, 6.4 and 3.9 ng/m^3 in the hot (April, 2006), cool (December, 2006) and wet (October, 2005) seasons at R6, respectively. Those at CC were 2.7, 5.6 and 4.2 ng/m^3 in the hot (April, 2006), cool (January, 2007) and wet (September, 2005) seasons, respectively. Seasonal trends of the concentrations were in the order of hot ≒ wet ＜ cool at R6, and hot ＜ wet ＜ cool at CC. The concentrations were the highest in the cool season at both sites. The reason might be lower mixing heights due to the cooler climate during the season. From the MOUDI air sampling results, the seasonal trends were the same, except for the lowest concentration in the wet season at R6 when the wind was blowing along the road or from the sampling location to the road at R6. Regarding the seasonal variations of size-fractioned PAH profiles, rainfall events in the wet season seemed to have affected the profiles. The PAH profiles that had undergone rainfall events showed less differences between the particle size modes, suggested by higher Cronbach α values compared to those in other seasons. It implied that PAHs might have experienced less atmospheric aging processes to differentiate their profiles according to particle size modes, because the frequent rainfall events had shortened their atmospheric residence time. When the concentrations at R6 and CC are compared, real-time monitoring results showed higher average concentrations at R6 than at CC in the hot and cool seasons. In the wet season, however, the concentration was higher at CC, because wind was not blowing from the road to the sampling location at R6 as already mentioned in this paragraph,

whereas at CC wind was always blowing from the road to the sampling location. Three-day MOUDI air sampling results showed higher concentrations at R6 in the hot season, as mentioned in the last paragraph, however, not in the wet or cool seasons. The reason for the lower concentrations at R6 in the wet season should be the wind direction, and that in the cool season must be the sampling period that was the end of the year when the business trips were temporarily reduced.

PAH risk was assessed with consideration of the diurnal and seasonal variations of concentrations. Lifetime risk was estimated at 5.6×10^{-5} at R6 and 6.5×10^{-5} at CC based on the three-day MOUDI air sampling data. Lifetime risk in a sole season was already above 1.0×10^{-5} at both sites except for the hot season at CC. Differences of the relative contributions of risk from hourly exposure in the different time periods of the day in the different seasons to the lifetime risk were up to 3.6 times at R6 and 4.1 times at CC. In fact, as the highest exposure level case, 2.5 hours of daily exposure in the overnight period at CC would lead to the lifetime risk of 1.0×10^{-5}. Corresponding to the lifetime risk assessment, loss of life expectancy was estimated as 6.1 hours at R6 and as 7.1 hours at CC. As for the selection of PAHs to be monitored for risk assessment, mainly BbF, IP and DahA should be considered as well as BaP, although it depends on the selection of TEF values in addition. Since contributions of BaP were only 57% at R6 and 64% at CC, contributions of other PAHs are also significant. With regard to the contributions of particle size, more than 80% of the risk could be attributed to the ultrafine and accumulation modes particles (<1.8μm). Considering uncertainties of the risk estimates, lifetime risk estimates based on the three days MOUDI data ranged between $5.6\sim6.7\times10^{-5}$ at R6 and $6.5\sim8.5\times10^{-5}$ at CC with or without the recovery correction or consideration of the detection limits of GC/MS. The risk was estimated higher at CC than at R6. On the other hand, based on PAS real-time monitoring data, the risk was estimated at 6.8×10^{-5} at R6 and 6.5×10^{-5} at CC. The risk was estimated higher at R6 than at CC. Considering the longer monitoring periods by the PAS real-time monitoring, higher risk at R6 than at CC seemed more appropriate since the risk estimate based on the MOUDI data reflected temporary traffic decrease in the cool season. Uncertainty also derived from different TEFs and unit risk values. Their uncertainty was up to 1.5 times due to the different TEFs and two orders ranging between 10^{-7} and 10^{-5} due to the different unit risk values.

In summary, this is the first contribution of such complete data sets of particle size-fractioned PAH profiles at the roadside in different time periods of the day in different seasons throughout a whole year. In the risk assessment, lifetime cancer risk was estimated and the relative contributions of risk from exposure in the different time periods to the lifetime risk

were calculated, which served as more accurate risk estimates than conventional ones. The results pointed out that without continuous exposure to the roadside atmosphere, exposure in certain hours of the day or certain days of the year would reach the significant lifetime risk of 1.0×10^{-5}.

Finally, for the better understanding of PAH atmospheric behavior and more precise risk assessment with less uncertainty, the recommendations are drawn as follows.

1) Considering uncertainties of risk assessment, the exposure location in the road space is one of the major uncertainties. In this study, average PAS signals at the five locations at the R6 site varied up to nine times. In order to make clear the spatial variations of the PAH concentrations, we should conduct a simulation with a dispersion model, which includes PAH specific behavior, such as photochemical reactions and gas/particle partitioning, and road or urban configurations.

2) In line with the PAH modeling mentioned above, further investigation on various vehicle source emissions is recommended, which will better explain temporal variations of atmospheric PAH concentrations and which will be also useful for emission control measures.

3) Because the uncertainties of risk estimates due to different unit risk values or different TEF values were large, ranging both higher and lower than the significant risk level of 10^{-5}, it was still uncertain whether people are really at risk by atmospheric PAH exposure to the extent that risk reduction is immediately needed or not. Therefore, further investigation on the estimates of unit risk and TEFs is desired to reach consensus about PAH risk assessment.