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学位論文要旨 Dissertation Summary

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論文名: **Polycyclic Aromatic Hydrocarbons and Related Compounds in Urban and E-waste Recycling Sites of Vietnam and India: Occurrence, Distribution and Toxic Evaluation**
(Dissertation Title) (ベトナム・インドの都市およびE-wasteリサイクル地域における多環芳香族化合物とその関連物質:汚染の実態、分布および毒性評価に関する研究)

Industrialization and urbanization in recent years are accompanied by degradation of environmental quality in Asian developing countries. Air pollution by vehicles exhaust particles has been known to be associated with polycyclic aromatic hydrocarbons (PAHs) and related compounds. The land use from e-waste recycling area has also been reported or expected to be enriched by PAHs. The toxicities of PAHs and related compounds usually involve a common mechanism such as binding to the aryl hydrocarbon receptor (AhR), induction of AhR-related genes and subsequent transformation to toxic metabolites. PAHs and related compounds have been reported to transactivate AhR and have also been known to act as estrogens by binding estrogen receptor (ER). However, there is much less or substantially no information on detail characterizations and potential sources of various PAH related compounds including methyl PAHs in developing countries. Besides, toxic evaluations of PAHs and its related compounds based on their AhR-mediated and estrogenic activities and mutagenic and carcinogenic potencies seem also very important and urgent issues in the urban areas of developing countries. Based on above the state of knowledge, the main objectives of this dissertation are: 1) Characterization, distribution and toxicity identification evaluation of PAHs and related compounds in coarse particles of road dust (diameter size $< 500 \mu\text{m}$) and smaller particles (diameter size $< 63 \mu\text{m}$) as well as ambient air particles from urban area from Vietnam and India, two of the six countries in Asia reported as having the

highest air pollution in the world. 2) Determination of the AhR-mediated and estrogenic activities in road dust from urban area using new approaches of reporter gene assay (PAH-CALUX) and ER-CALUX. 3) Characterization and distribution of PAHs and Methyl PAHs (MePAHs) in soil and sediment from an e-waste recycling area.

PAHs and AhR-mediated activities in coarse road dust particles (diameter size < 500 μm) from urban areas of Hanoi-Vietnam

This is the first study on the exposure risk of AhR agonists, including PAHs and related compounds, in urban road dust from a developing country using a combined bio-chemical analytical approach. Road dust from Hanoi contained significantly higher DR-CALUX activities (mean 20 ng CALUX-TEQ/g dw) than those from a rural site (mean 5 ng CALUX-TEQ/g dw). Total concentrations of 24 major PAHs ($\Sigma_{24}\text{PAHs}$) in urban road dust (mean 2.5 $\mu\text{g/g dw}$) were also 6 times higher than those in rural road dust (mean 0.4 $\mu\text{g/g dw}$). Diagnostic ratios of PAHs indicated vehicular engine combustion as the major PAH emission source in both sites. PAHs accounted for 10% and 20% of the measured CALUX-TEQs in road dust for urban and rural site, respectively. Benzo[b]-/benzo[k]fluoranthenes (BbF+BkF) were the major TEQ contributors among PAHs. The dioxin-like compounds (DRCs) were also detected in road dust from both rural and urban sites and their contribution to CALUX-TEQs was counted for < 0.1% only. These results suggest TEQ contribution of other AhR agonists in road dust. Estimated results of incremental life time cancer risk (ILCR) indicated that Vietnamese populations, especially those in urban areas such as Hanoi, are potentially exposed to high cancer risk *via* both dust ingestion and dermal contact.

MePAHs, PAHs and their AhR-mediated toxic activities in smaller road dust (diameter size < 63 μm) from Vietnam and India

Methylated polycyclic aromatic hydrocarbons (MePAHs) and PAHs diagnostic ratios in road dust indicated that the main sources of MePAHs in Vietnam were pyrogenic emissions, whereas in India there were mixed sources of pyrogenic and petrogenic emissions. Significant levels of AhR-mediated activities were observed in the road dust from urban sites of Hanoi (mean 40 ng CALUX-TEQ/g dw), New Delhi (mean 20 ng/g dw), and Bangalore (mean 29 ng/g dw). Contributions by MePAHs and PAHs to AhR-mediated activity of the street dust from these areas were only up to 4.5% (New Delhi), 4.2% (Hanoi) and 3.4% (Bangalore), indicating that major contributors of AhR-mediated activity in the street dust are unknown agonists. Among the compounds analyzed in this study, principal contributors to theoretical-TEQs in Vietnam and India were BbF+BkF and methyl benz[a]anthracenes (MeBaAs). Contributions by MeBaAs to Theo-TEQs were found to be at significant and even higher than those of their parent chemicals.

Estrogenic and AhR-mediated activities in road dust

The PAH-CALUX, a very new approach, could be very powerful method for determination of AhR-mediated activities due to its specific response to AhR ligands and deal with rapid metabolites of PAHs and related compound. Large values of AhR-mediated activities (expressed in CALUX-BaPEQs) and estrogenic activities (expressed in CALUX-E2EQs) were found in road dust suggested the presence of high levels of AhR agonists and ER agonists in urban and rural road dust. Significantly CALUX-E2EQs found in crude extract of road dust suggesting that both high levels of PAHs and OHPAHs could be presented in road dust, therefore monitoring OHPAHs in Hanoi road dust should also be considered in future studies. Toxic contributions of PAHs in the samples were evaluated by comparison of CALUX-BaPEQs measured with PAH-CALUX/CALUX-E2EQs measured with ER-CALUX and total theoretical BaPEQs/17 β -Estradiol equivalents (E2EQs). Contribution of PAHs to the measured CALUX-BaPEQs in road dust was 30% at urban site and 20% at rural site. The principal contributors among target compounds were BbF+BkF at 63% and 65% for urban and rural site, respectively. E2EQs of selected PAHs in road dust accounted for 5.7% of the CALUX-E2EQs for urban site and 2.3% for rural only. The principal contributors as potent AhR agonists were also BbF+BkF (78.4% and 85% for urban and rural site, respectively). Much higher contribution of PAHs to overall toxic activities in road dust measured by PAH-CALUX compared to those in the same size particles as well as larger particles obtained by using DR-CALUX, suggesting that the approach of PAH-CALUX is suitable method and should be selected instead of DR-CALUX for further studies on toxic evaluation of PAHs and related compounds in environmental samples.

Toxicity identification and evaluation of PAHs and MePAHs in ambient air particles

Significantly higher AhR-mediated activities (expressed in CALUX-BaPEQs) in ambient air particles were found for PM_{2.5} than for PM₁₀, and PM_{>10}. AhR-mediated activities from all fractions in different extractable ambient air particles indicated a large amount of AhR agonists bound to smaller particles rather than large particles. Total PAHs were found at higher levels in PM_{2.5} (mean 737 ng/m³) than PM₁₀ (mean 19 ng/m³) and PM_{>10} (mean 9 ng/m³). MePAHs were also found in ambient air particle at higher levels in PM_{2.5} (mean 93 ng/m³) than in PM₁₀ (mean 4.5 ng/m³) and PM_{>10} (mean 2.7 ng/m³). Contribution of PAHs (Theo-BaPEQs) to overall activities in ambient air particles counted for PM_{2.5} at 98%, PM₁₀ at 66% and PM_{>10} at 66%. The results indicated that BbF+BkF are the major agonist contributors to Theo-BaPEQs in fine particles while dibenz[a,h]anthracene (DBA) are major agonist contributor to Theo-BaPEQs in coarse particles. Strong correlation between AhR-mediated activities and mutagenic as well as carcinogenic potencies (Pearson's $\rho = 0.97$ and 0.99 , $p < 0.001$), indicated that the higher AhR-mediated activities in

ambient air particles suggesting in higher mutagenic and carcinogenic potencies. Estimated results of ILCR showed greater than the acceptable level of 10^{-6} via ingestion, dermal contact pathways indicating that local residents face to high potential risks of cancer when they frequently exposed to ambient air particles in this region.

Characterization and distribution of PAHs and MePAHs in soil and sediment

Total PAHs in sediment was 970 ng/g dw, and in soil 3,770 ng/g dw. These results indicated larger amount of PAHs deposited to soil in Bui Dau e-waste recycling village. The diagnostic ratios of the IDP/(IDP + BgP) and BaA/(BaA + Chry) shows that PAHs in sediment were mostly petroleum combustion sources, and PAHs in soil were biomass, coal and petroleum combustion emission. Total MePAH concentrations in soil (mean 510 ng/g dw) were higher than those in sediment (mean 370 ng/g dw). MePAHs diagnostic ratios in soil sample indicated that petroleum combustion was main emission sources of MePAHs in Bui Dau. Significant levels of PAHs and MePAHs have been identified in the soil and sediment of Bui Dau e-waste recycling village, suggesting that the agricultural land use in Bui Dau can potentially pose carcinogenic risks. The potential health hazards of the PAHs in this area can be confirmed not only very high levels of PAHs, mutagenic and carcinogenic equivalents but also by the values more than the acceptable level for cancer risk obtained by incremental life time cancer risk.

The results of this study indicate the necessity to use effect-based bioassays in addition to chemical analysis to avoid missing non-target toxic contributors in risk assessment of human exposure to toxic chemicals in the environment.