

Polycyclic Aromatic Hydrocarbons and Related Compounds in Urban and E-waste Recycling Sites of Vietnam and India: Occurrence, Distribution and Toxic Evaluation

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 (MePAHs) 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 and distribution of PAHs and related compounds in soil and sediment from an e-waste recycling area, in coarse particles of road dust (diameter size < 500 μm) and smaller particles (diameter size < 63 μm) 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 an approaches of reporter gene assay (PAH-CALUX, DR-CALUX) and ER-CALUX. 3) Toxicity identification evaluation of dioxin-like compounds (DRCs), PAHs and MePAHs in road dust from Vietnam and India. 4) Cancer risk assessment.

PAHs and related compounds in road dust with diameter size less than 500 μm (RD500) and 63 μm (RD63), ambient air particles (PM_{2.5}, PM₁₀, PM_{>10}), soil and sediment samples

PAHs and MePAHs in RD500 from Hanoi (urban site), Duong Quang (rural site), and in RD63 from Hanoi, Duong Quang, New Delhi (urban site) and Bangalore (rural site), as well as in soil and sediment samples from Bui Dau (e-waste recycling village) were analyzed by using gas chromatography-mass spectrometry.

Total concentrations of 24 major PAHs ($\Sigma_{24}\text{PAHs}$) in urban road dust (mean 1,500 ng/g dw) were 4 times higher than those in rural road dust (mean 430 ng/g dw). Higher concentrations of $\Sigma_{23}\text{PAHs}$ were found in RD63 from Hanoi (mean 1,900 ng/g dw), Bangalore (mean 1,100 ng/g dw), and New Delhi (mean 1,100 ng/g dw) than in RD63 from Duong Quang (mean 620 ng/g dw). 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). 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).

Diagnostic ratios of PAHs indicated vehicular engine combustion as the major PAH emission source in road dust and ambient air particles. 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. The results of calculation of PAHs diagnostic ratios shows that PAHs in sediment were mostly petroleum combustion sources and PAHs in soil were biomass, coal and petroleum combustion emission. MePAHs diagnostic ratios in soil sample indicated that petroleum combustion was main emission sources of MePAHs in Bui Dau.

AhR-mediated and estrogenic toxic activities in road dust and ambient air particles

This is the first study on the exposure risk of AhR agonists, including PAHs and related compounds, in road dust and ambient air particles from a developing country using a combined bio-chemical analytical approach. AhR-mediated activities in road dust and ambient air particle were determined by using DR-CALUX and PAH-CALUX assay (expressed in CALUX-TEQs and CALUX-BaPEQs), estrogenic activities in RD63 were determined by using ER-CALUX (expressed in CALUX-E2EQs)

RD500 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). Significant levels of AhR-mediated activities were also observed in RD63 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).

Large values of CALUX-BaPEQs were found in Hanoi RD63 (mean 35,690 ng/g dw) and Duong Quang RD63 (mean 5,440 ng/g dw) suggested the presence of high levels of AhR agonists in urban and rural road dust. Significantly CALUX-E2EQs found in crude extract for Hanoi RD63 (mean 2.4 ng/g dw) than those for Duong Quang RD63 (mean 1.1 ng/g) 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.

Significantly higher CALUX-BaPEQs in ambient air particles were found for

PM_{2.5} (mean 488 ng/m³) than for PM₁₀ (28 ng/m³), and PM_{>10} (7 ng/m³). 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.

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

Toxic contributions of PAHs in the samples were evaluated by comparison of CALUX-TEQs/CALUX-BaPEQs/CALUX-E2EQs and total theoretical-TEQs/BaPEQs/E2EQs (Theo-TEQs/BaPEQs/E2EQs).

PAHs accounted for 3.5% and 3.2% of the measured CALUX-TEQs in RD500 for urban and rural site, respectively. Benzo[b]-/benzo[k]fluoranthenes (BbF+BkF) were the major TEQ contributors among PAHs followed by indeno[1,2,3-c,d]pyrene (IDP), pyrene (Pyr), chrysene (Chy) and benzo[a]pyrene (BaP). DRCs were also detected in road dust from both Hanoi RD500 and Duong Quang RD500 and their contribution to CALUX-TEQs was counted for < 0.1% only. These results suggest TEQ contribution of other AhR agonists in road dust. Contributions by MePAHs and PAHs to AhR-mediated activity of the RD63 from these areas were also only up to 4.5% (New Delhi), 4.2% (Hanoi) and 3.4% (Bangalore), indicating that major contributors of AhR-mediated activity in the road dust are unknown agonists. Among the compounds analyzed in this study, principal contributors to Theo-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 corresponding unsubstituted compounds.

Contribution of PAHs to the measured CALUX-BaPEQs in road dust was 30% at urban site and 20% at rural site. (BbF+BkF) were also the major BaPEQ contributors among PAHs followed by Chy, IDP, BaP, benzo[j]fluoranthene (BjF) and benz[a]anthracene (BaA). Contribution of PAHs (Theo-BaPEQs) to overall activities in ambient air particles counted for PM_{2.5} at 45%, PM₁₀ at 38% and PM_{>10} at 36%. The results indicated that BbF+BkF are the major agonist contributors to Theo-BaPEQs in fine and 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.

Theo-E2EQs of selected PAHs in road dust accounted for 16% of the CALUX-E2EQs for Hanoi and 6% for Duong Quang only. The principal contributors among target compounds were BbF+BkF at 63% and 65% for urban and rural site, respectively. Significant correlations were also observed between total PAHs and Theo-E2EQs (Pearson's $\rho = 0.91$, $p < 0.001$), suggesting that major contributors of estrogenic activities may share the same sources with PAHs

Cancer risk assessment

Estimated results of incremental life time cancer risk (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 road dust, ambient air particles and soil in the study locations.

Approaches in this study are very useful for the determination of overall toxicities of road dust as well as the other environmental samples. 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.