# CHAPTER 4

# CONCLUSION

# 4

# Conclusion

The solvent-extractable hydrocarbons present in $PM_{10}$ airborne particles and roadside soil particles of Kuala Lumpur, Malaysia have been characterized using GCMS techniques. Scaled-down alumina-silica column has been used in the fractionation step prior to analysis by GCMS. In addition to being fast and economical, this step results in a satisfactory recovery for most alkanes and PAHs. However, the use of this fractionation step prior to analysis by GC-FID would not be ideal due to the interference from the alkanes that mask the trace amount of PAHs in the samples. Depending on the extracted ion fragmentogram, analysis by GCMS could solve the problem. The recoveries for the multi-step procedure give satisfactory results and the compounds of interest could be identified and quantified.

$TPM_{10}P$ values range from 43.59 ± 12.41 to 90.97 ± 13.09 $\mu g/m^3$, which are comparable to those measured in Kuala Lumpur over a one-year period (50 to 90 $\mu g/m^3$, DOE Malaysia, 1998). These values are still below the recommended primary standard (health-based) (150 $\mu g/m^3$ (24 h), US national ambient air quality standards (NAAQS), (Radojević and Bashkin, 1999)). However, most of these values exceeded the recommended secondary standard (welfare-based) (50 $\mu g/m^3$ (24 h), US national ambient air quality standards (NAAQS), (Radojević and Bashkin, 1999)).

The major hydrocarbons identified are n-alkanes in the range of $C_{11}$ to $C_{34}$, n-alkylcyclohexanes ranging from $C_{16}$ to $C_{28}$, isoprenoid hydrocarbons including pristane and phytane, $C_{27}$ to $C_{35}$ 17α(H)-hopanes including the 22R and 22S isomers for homologs ≥ $C_{31}$, $C_{27}$ to $C_{29}$ 5α(H),14α(H),17α(H)- and 5α(H),14β(H),17β(H)-steranes with the 20S and 20R isomers, and PAHs ranging from phenanthrene (3 rings) to coronene (7 rings).

The atmospheric concentrations of n-alkanes in urban Kuala Lumpur vary from 56.34 ± 9.84 to 178.90 ± 41.05 ng/m$^3$, which fall in between the two previously measured values for Malaysia (26 ng/m$^3$, 24 h, TSP, Abas and Simoneit, 1996, and 290 ng/m$^3$, 24 h, TSP, Fang *et al.*, 1999). The concentrations of n-alkanes in urban roadside particulate samples range from 6.10 ± 4.97 to 13.88 ± 10.07 μg/g. These values are lower than those measured by Zakaria *et al.*, (2000) in Kuala Lumpur (50, 65, and 460 μg/g).

n-Alkanes in urban atmospheric samples are derived mainly from petroleum residues of vehicular emissions with minor contribution from higher plant waxes. This is supported by the lower CPI values (CPI ~ 1) and the shift of $C_{max}$ to lower molecular weight (e.g., $C_{25}$). The contribution from higher plant waxes is more apparent in forest samples. This is supported by the increase in CPI values and the shift of $C_{max}$ to $C_{31}$, which is indicative of higher plant waxes of tropical vegetation. In most of the roadside soil particulate samples studied, the biogenic input is more apparent than the petrogenic input compared to airborne particulate samples. This can be illustrated by the higher CPI values and the high molecular weight $C_{max}$. The close CPI values observed for lubricating oils to those observed for most of airborne particulate and some roadside soil particulate samples confirms that n-alkanes in those samples are of petrogenic origins.

For all the samples studied, the unresolved complex mixture (UCM) maximizes in the range of $C_{29}$ to $C_{31}$ resembling that of used oil (car and motorcycle) and fresh lubricating oil. Moreover, high U:R values are observed for these samples. This indicates that both urban and forest samples are contaminated by unburned lubricating oil residues with the former being more affected.

The positive correlation between CPI and the percentage of n-alkanes from higher plant waxes, which is consistent with the negative correlation found between CPI and U:R reveals the effectiveness of both CPI and U:R ratios as indicators of biogenic versus petrogenic input.

For atmospheric and roadside soil particulate samples, the presence of n-alkylcyclohexanes, pristane, phytane, hopanes, and steranes together with the UCM reflects the contamination by petroleum residues. The molecular distribution of hopanes and steranes closely matches that of lubricating oils indicating that these compounds are chiefly derived from the engine lubricants. Based on the interpretations of the geochemical diagnostic ratios, all the samples studied are contaminated by thermally mature petroleum residues, which may be derived from marine carbonate source rocks deposited under anoxic (reducing) conditions. This is consistent with the finding of Zakaria *et al.* (2000) that the petroleum used in formulating the Malaysian lubricating oil is of Middle Eastern origin (i.e. marine carbonate). Furthermore, no contribution from biomass burning to these samples is observed. This is supported by the low abundances of βα-moretanes relative to αβ-hopanes and 22R $C_{31}$-homohopane relative to the 22S epimer.

Urban atmospheric samples have total PAHs concentrations in the range of 1.84 ± 1.01 to 11.29 ± 4.99 ng/m$^3$. These values are on the lower side compared to the data obtained from other places but are close to those measured in Malaysia (7 ng/m$^3$ and 9 ng/m$^3$, 24 h, TSP, Fang *et al.*, 1999). It should be mentioned that the US EPA has not established a Reference Dose (RfD; an estimate of a daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime) or a Reference Concentration (RfC; an estimate of a continuous inhalation exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime) for PAHs [1]. However, another organization [2] has recommended levels of PAHs in air of homes be no higher than 0.004 ppm. In this study, PAHs concentrations are in the range of $1.85 \times 10^{-7}$ to $1.07 \times 10^{-6}$ ppm [3], which are much lower than the recommended value. The total PAHs concentrations in urban roadside soil particles ranges from 0.19 ± 0.10 to 0.26 ± 0.17 μg/g. It is difficult to compare the values obtained in the current study with those reported in the literature since the particles are of different sizes. However, these values are on the lower side compared to the values measured in other urban places. The lower molecular weight PAHs are shown to be more enriched in roadside soil particles, whereas high molecular weight ones are more abundant in airborne particulate samples.

The distribution patterns of PAHs, the positive correlations between BgP and total PAHs, and the diagnostic ratios indicate that PAHs in urban and forest airborne particulate samples and roadside soil particles are of mixed petrogenic pyrolytic sources (i.e. gasoline and diesel vehicles emissions). Furthermore, the absence of retene (m/z 234), which is a molecular marker of forest fires and wood combustion indicates that there is no contribution from biomass burning to these samples. The presence of dibenzothiophene, which is common in crude petroleums and lubricating oils, may indicate such an origin in these samples.

The results of solvent-extractable hydrocarbons in $PM_{10}$ airborne particles and roadside soil particles indicate that both petrogenic and biogenic sources are the major sources of hydrocarbons in the City of Kuala Lumpur and its immediate surrounding.

---

[1] http://www.epa.gov/ttn/uatw/hlthef/polycycl.html.
[2] Wisconsin Department of Health and Family Services (http://www.dhfs.state.wi.us/index.htm).
[3] ppm = $pg/m^3 \times 10^{-9} \times 24.45$ / molecular weight of the compound.