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ORIGINAL ARTICLE

Levels and distributions of organic source tracers in air and roadside dust particles of Kuala Lumpur, Malaysia

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Abstract The concentrations of *n*-alkanes, unresolved complex mixture (UCM), petroleum molecular markers, other tracers of cooking and burning emissions, and natural background in atmospheric particles and roadside dust particles were measured at eight locations in the city center and the suburbs of Kuala Lumpur, Malaysia. Atmospheric particles were collected using high-volume filtration (PM-10, GFF) over 24 h average periods. Road dusts were swept up, dried and sieved. Both types of samples were extracted with dichloromethane/methanol mixture (3:1 v/v) by ultrasonic agitation. The extracts were then fractionated by column chromatography and the alkanes subjected to gas chromatography–mass spectrometry (GC–MS). Total extracts were also analyzed directly by GC–MS after silylation. The molecular distributions of compounds as well as diagnostic geochemical ratios were determined in order to identify the sources of the organic compounds. Samples collected from a rural area and lubricating oils were also analyzed for comparisons. Anthropogenic and biogenic sources such as vehicular emissions, waxes of higher plants, food cooking operations, and biomass and domestic refuse burning processes contributed to the organic matter content of atmospheric and to lesser extent, roadside dust particles.

Keywords PM-10 aerosol · Molecular markers · Traffic · Refuse burning · Biomass burning · Natural background

Introduction

The emission of pollutants to the atmosphere often involves the direct uncontrolled exposure of large populations to toxic substances. This is especially relevant to urban areas, where the proximity between humans and pollutants is closest.

Fine particles (e.g., PM-10 aerosol particulate matter with an aerodynamic diameter of 10 μm or less) settle very slowly and remain suspended in the atmosphere for considerable time. Medical data suggests that it is the fine fraction of aerosol particulate matter, which becomes deeply imbedded in human lung tissue, causes respiratory problems, and exacerbates other cardiovascular diseases (Miller et al. 1979; Utell and Samet 1996). In addition to the negative health effects, particulate matter reduces visibility, and speeds the deterioration of buildings (Rajkumar and Chang 2000). Organic compounds contribute 10–40% of the PM-2.5 and PM-10 mass in polluted urban areas, while in rural

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areas they represent 30–50% of the PM-10 mass (Chow et al. 1993, 1994).

Street dust is a complex mixture of multiple source contributions: anthropogenic materials such as automobile/truck exhaust particles, lubricating oil residues, tire wear particles, weathered street surface particles, brake lining wear particles, and natural biogenic materials such as leaves and other plant matter that can be pulverized by the passing traffic (Rogge et al. 1993a). All these sources are direct contributors to street dust (Rogge et al. 1993b). Resuspension, dry deposition, street sweeping, rain, and formation of new particles (e.g., vehicle exhaust) drive a dynamic source and sink relationship, which can contribute appreciable amounts of particulate matter and toxic substances to both the atmosphere and hydrosphere (Rogge et al. 1993a, b, c).

n-Alkanes are especially suited for studies directed to the origin and fate of atmospheric aerosols. They are present in all aerosols irrespective whether urban, continental or maritime samples are considered (e.g., Simoneit 1977, 1984). Moreover, they can be derived from both biogenic and anthropogenic sources, which can be differentiated based on their *n*-alkane distribution. Although the mass of *n*-alkanes is undoubtedly a minor fraction of the total organic matter of atmospheric aerosols, their distribution, relatively low reactivity and low volatility make them suitable as monitoring tracers of both atmospheric transport and particle origin (Rogge et al. 1993a; Sicre et al. 1987; Gelencsér et al. 1998; Simoneit 1977). Key parameters associated with *n*-alkanes are the well-established carbon preference index (CPI) and carbon number maximum (C_{max}) (Mazurek and Simoneit 1984).

Molecular markers are either biolipids, synthesized by living organisms and preserved in the environment (e.g., sediments), or geolipids derived from biolipid precursors by alteration but retaining the carbon skeleton (Connan 1981; Simoneit 1984, 1985). Molecular marker analysis can be utilized for organic matter source identification. In this manner, comparisons are possible between known sources and the observed atmospheric organic compound mixtures (e.g., Simoneit 1984, 1985).

The main objectives of this study are to trace the origin of alkanes and other polar lipids associated with atmospheric and roadside dust particles on the basis of key parameters and molecular marker analyses and to compare the organic compound compositions of airborne particles to those of roadside dust particles.

Experimental

Sampling sites

Kuala Lumpur (lat. 3°08′N; long. 101°44′E) is situated in the Klang Valley region, which is a basin located in the southwestern part of the Malaysian Peninsula, surrounded by highlands exceeding 1,500 m altitude in the east and the Straits of Malacca in the west. Thus, the dispersive capability of the atmosphere in the Klang Valley is very restricted. For example, the airflow pattern in the valley at night is from Kuala Lumpur towards the sea. During day, the pattern is reversed to airflow inland from the sea. Such a pattern causes most of the pollutants produced within the valley to remain there over time until complete regional ventilation (Sani 1987).

Urban airborne particles and roadside dust particles were collected from eight sites in the city center and its suburbs (Fig. 1) during the period from November 1998 to January 1999 (three samples for each location). As a control, two samples, each of airborne particles and roadside dust particles were collected in May 2000 at a forest research station (rural site), Bukit Rengit, Pahang, about 110 km from Kuala Lumpur.

The sampling sites were chosen to represent the busiest roads and road-intersections in the city. The average traffic volume for city roads is about 30,000 vehicles per day, whilst for road-intersections it is about 100,000 vehicles per day. The PM-10 air sampler was set up at ground level at a distance of between 5–15 m from the road shoulder at all sites. The data obtained from these sites would represent the ambient roadside concentrations of pollutants to which, human subjects such as pedestrians, street vendors and traffic policemen are exposed. Micallef and Colls (1998) had suggested that, in estimating human exposure to air pollution it is crucial for the measured concentrations to be representative of what people inhale.

Sample acquisition and preparation

Airborne particles were acquired using a PM-10 high-volume air sampler (Ecotech, Australia) fitted with annealed (300°C for 8 h) glass fiber filters (20.3 × 25.4 cm, Whatman EPM 2000, UK), and operated at a flow rate of ~1.12 m^3 min^{-1}. Sampling was carried out over a 24 h period (48 h for rural samples). Before weighing, all fresh and exposed filters were conditioned for 24 h in a dry-box, where the temperature was maintained at 25°C with the relative humidity at 45%. Exposed filters were then folded,

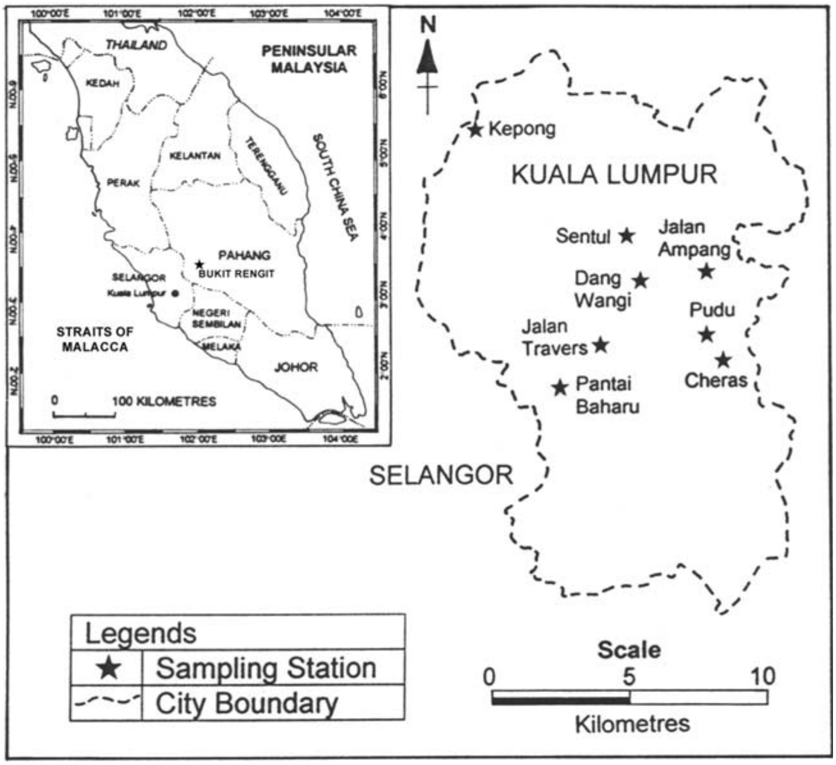


Fig. 1 Location map of the sampling sites in Malaysia

stored in a 500 ml glass jar to which ~5 ml of dichloromethane was added to inhibit microbial activity, and kept refrigerated until the day of analysis.

Roadside dust particles were collected using a small brush and a trowel, air-dried for 4–9 days and sieved to get particles of ≤600 μm. The particles were stored in a 500 ml glass jar, homogenized, and kept in this manner until the day of analysis.

Extraction

The filters were extracted three times using ultrasonic agitation for a fifteen-minute period each with 150 ml of dichloromethane/methanol mixture (3:1 v/v). The extractions were carried out within the filter storage jar. The extracts were then filtered using a filtration unit containing an annealed glass fiber filter for the removal of insoluble particles. The filtrate was first concentrated on a rotary evaporator and then using a stream of dry nitrogen gas, to a volume of approximately 5 ml. The volume was then adjusted to 5.0 ml exactly by addition of dichloromethane. An aliquot of the extracts was quantified by evaporation to dryness and weighing.

About 4 g (8 g for rural samples) of roadside dust particles were extracted by ultrasonic agitation. Three 15 min extractions were carried out in centrifuge tubes with 20 ml of dichloromethane/methanol mixture (3:1 v/v) each time. The extracts were then combined, filtered, concentrated and made up to 10.0 ml with dichloromethane. An aliquot of the extracts was quantified by evaporation to dryness and weighing.

Fractionation

One milliliter of the extract (concentrated to <0.2 ml by using a stream of dry nitrogen gas) was transferred to the top of a glass column (20 × 1.0 cm i.d.) slurry packed with 1.5 g of silica gel (Fluka, St. Louis, MO, 230–400 mesh, activated at 200°C for 4 h) and 2.5 g of neutral alumina (top) (Merck, Hohenbrunm, Germany, 70–230 mesh, activity I, activated at 200°C for 4 h), previously deactivated with 5% of water. The adsorbents were capped with 1.0 g of anhydrous sodium sulfate (activated at 300°C for 4 h), and supported by a small plug of precleaned glass wool inserted at the narrow end of the column. The fraction containing the alkanes was obtained by eluting the column with 8 ml of *n*-hexane. This fraction was then concentrated to 100 μl under reduced pressure at 40°C using a rotary evaporator, and kept frozen in a 2 ml Teflon-lined vial until further analysis.

Quantitative and qualitative analyses were carried out, by using gas chromatography–mass spectrometry (GC–MS). The unresolved complex mixture (UCM) of branched and cyclic hydrocarbons in the GC of the hydrocarbon fraction was quantitated by integration of the total GC signal above baseline minus the sum of the resolved components. Aliquots of the total extracts were analyzed for polar compounds not recovered in the fractionated samples after conversion to the trimethylsilyl (TMS) derivatives prior to GC–MS analyses by reaction with *N*,*O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) and a trace of pyridine for approximately 3 h at 70°C.

Instrumental analysis

The analyses were carried out with a Hewlett-Packard Model 6890 gas chromatograph coupled to a Model 5973 MSD quadrupole mass spectrometer (GC–MS) fitted with a fused silica capillary column coated with 5% phenylmethylsiloxane (Agilent DB-5MS, 30 m long, 0.25 mm i.d., 0.25 μm film thickness). The MS was operated at full-scan mode with an initial flow of 1.2 ml min^{-1}; nominal initial pressure: 10.4 psi; average velocity: 40 cm s^{-1}; injection mode: splitless (1 min); temperature of injector: 290°C. The GC operating conditions were as follows: isothermal at 60°C for 2 min, temperature program 60–300°C at 6°C min^{-1}, held isothermal at 300°C for 20 min and using helium as the carrier gas. Data for qualitative analysis were acquired in the electron impact mode (70 eV) and scanning from 50 to 550 Da at 1.50 s $scan^{-1}$. The total extracts, both underivatized and silylated, were analyzed by GC–MS using the same model instrument and column. The GC was programmed as above and the MS was scanned from 50 to 650 Da at 1.5 s $scan^{-1}$.

Identification and quantification

The identification of *n*-alkanes was based on the GC–MS data (i.e., *m*/*z* 85 fragmentograms and/or mass spectra). GC retention times were compared with those of external standards. The identifications of hopanes and steranes are based primarily on their key ion fragmentograms, mass spectra and GC retention times. Their occurrence is usually at low concentrations, but their overall distribution signatures within samples can be easily determined by GC–MS and utilized for comparison purposes. This is based on the *m*/*z* 191, 217 and 218 key ion intensities in the GC–MS data, which are the base peaks of most 17α(H)-hopanes, *ααα*-steranes and *αββ*-steranes, respectively (Simoneit 1985). Polar compounds were identified as the TMS derivatives by comparison with external standards, key fragment ions, and/or interpretation of mass spectra (Omar et al. 2006). Quantification was performed from the GC–MS total ion current (TIC) profiles using the external standard method. Average response factors were calculated for each compound. All molecular marker quantifications were based on the compound peak area derived from the ion fragmentogram and correlated with the TIC. The limit of detection (LOD) ranges from 0.2 to 3.0 ng g^{-1} for PAH (naphthalene to benzo[ghi]perylene) and 8 ng g^{-1} sample for perdeuterotetracosane.

Recovery and blanks

The glass fiber filters and roadside dust particles were spiked with *n*-tetracosane-d_{50} and the recoveries were found to be 92.76 and 72.85%, respectively. Appropriate corrections were made to the measured concentrations. Procedural blanks for atmospheric particles and roadside dust particles as well as solvent blanks were analyzed and quantified to ensure that there were no significant background interferences. No contaminants were detected in the solvent and roadside particulate blanks except for alkylphthalates. For airborne particulate blanks, the major contaminants detected based on GC–MS analyses were alkylphthalates (*m*/*z* 149) (e.g., butyl-2-methylpropylphthalate and decyldodecylphthalate) and traces of *n*-alkanes ranging from C_{14} to C_{26} with a CPI in the range of 0.61 to 1.10 and C_{max} at 15 or 18.

Results and discussion

PM-10 and road dust extracts

The primary sources of PM-10 organic aerosol include fugitive emissions from motor vehicles, combustion of solid fuels, agricultural dust, marine aerosols, vegetation waxes, and fly ash from refuse and biomass burning. Particles can also be formed in the atmosphere by condensation or transformation of emitted gases such as volatile organic compounds (Rajkumar and Chang 2000).

For atmospheric samples, the urban PM-10 values (Table 1) are below the recommended Malaysian guideline for PM-10 (150 μg m^{-3}, DOE Malaysia, 1998). For urban samples, the percentage ratios of TSEOM to PM-10 (%TSEOM/PM-10) (Table 1) are higher than those measured in Kuala Lumpur during clear weather (7.3%, 12 h, TSP, calculated from Abas and Simoneit 1996). The difference can be explained by particle size considerations. In this study, a PM-10 hi-vol air sampler was used, while Abas and Simoneit (1996) used a TSP hi-vol air sampler. Furthermore,

Table 1 Concentrations of organic source tracers in atmospheric particles and roadside dust particles

	Atmospheric particles[a]		Roadside dust particles[b]	
	Urban ($n = 24$)	Rural ($n = 2$)	Urban ($n = 24$)	Rural ($n = 2$)
TSEOM	18.11 ± 11.34	4.96 ± 2.64	7.64 ± 3.90	11.45 ± 0.54
PM-10	65.96 ± 18.88	27.88 ± 8.73	–	–
TSEOM/PM-10 (%)	27.68 ± 15.83	17.15 ± 4.12	–	–
n-Alkanes (C_{19}–C_{34})	102.87 ± 50.60	20.33 ± 21.33	7.36 ± 4.77	2.75 ± 2.00
CPI[c]	1.09 ± 0.07	1.67 ± 0.16	1.82 ± 0.69	1.40 ± 0.26
C_{max}	25	31	31	31
Plant wax *n*-alkanes (W)[c]	4.43 ± 2.42	5.24 ± 6.01	1.86 ± 1.17	0.28 ± 0.07
Plant wax *n*-alkanes (%)[c]	4.65 ± 2.03	22.84 ± 5.61	29.29 ± 17.38	12.58 ± 6.58
UCM	4889.17 ± 2584.24	125.00 ± 49.50	450.42 ± 281.29	35.00 ± 7.07
U:W	1299.26 ± 844.83	53.88 ± 52.36	355.64 ± 372.24	132.41 ± 58.69
PAHs[d]				
Phenanthrene	0.35	0.040	0.045	0.032
Anthracene	0.08	0.002	0.004	ND
Fluoranthene	0.12	0.013	0.028	0.003
Pyrene	0.32	0.022	0.038	0.004
Benzanthracene	0.15	0.010	0.004	ND
Chrysene	0.18	0.015	0.020	0.003
Benzo[*b*/*k*]fluoranthenes	0.57	0.007	0.008	ND
Benzo[*e*]pyrene	0.55	0.014	0.012	0.002
Benzo[*a*]pyrene	0.42	0.006	0.005	ND
Perylene	0.15	0.005	0.003	ND
Indenopyrene	0.64	0.02	0.005	0.002
Benzo[*ghi*]perylene	1.35	0.061	0.200	0.004
Anthanthrene	0.15	0.006	0.002	ND
Coronene	1.13	0.052	0.020	0.004
Total	6.16	0.273	0.214	0.054
Petroleum molecular markers				
Pristane	0.204 ± 0.098	0.058 ± 0.015	0.074 ± 0.081	0.046 ± 0.028
Phytane	0.233 ± 0.086	0.046 ± 0.006	0.075 ± 0.057	0.029 ± 0.005
Hopanes (C_{27}–C_{35})	1.188 ± 0.890	tr.	0.389 ± 0.150	0.053 ± 0.041
Steranes (C_{27}–C_{29})	0.161 ± 0.104	ND	0.050 ± 0.025	ND
Vegetation lipids	$n = 4$	$n = 2$	$n = 4$	$n = 2$
n-Alkanols (C_{22}–C_{32})				
Docosanol	0.26 ± 0.1	2.7 ± 2.0	0.09 ± 0.06	0.005
Tetracosanol	0.21 ± 0.03	6.3 ± 4.0	0.06 ± 0.04	0.006 ± 0.002
Hexacosanol	0.40 ± 0.1	10.5 ± 6.2	0.44 ± 0.15	0.019 ± 0.005
Octacosanol	0.39 ± 0.15	10.9 ± 5.7	0.67 ± 0.30	0.020 ± 0.008
Triacontanol	0.33 ± 0.12	3.6 ± 0.9	0.63 ± 0.22	0.022 ± 0.004
Dotriacontanol	0.21 ± 0.15	2.0 ± 1.1	0.25 ± 0.11	0.011 ± 0.003
Tetracontanol	ND	0.8 ± 0.8	0.09 ± 0.06	ND
C_{max}	26	28	28	30
Triterpenols	$n = 4$	$n = 2$	$n = 4$	$n = 2$
α-Amyrin	5.4 ± 1.6	0.7 ± 0.05	0.55 ± 0.41	0.045 ± 0.022
β-Amyrin	9.0 ± 2.4	1.2 ± 0.71	1.2 ± 1.0	0.11 ± 0.05
α-Amyrone	3.05 ± 1.1	0.7 ± 0.32	0.37 ± 0.31	0.08 ± 0.05
β-Amyrone	3.2 ± 1.9	0.6 ± 0.25	0.55 ± 0.36	0.03 ± 0.01
α-Amyryl acetate	1.6 ± 0.7	0.4 ± 0.27	0.3 ± 0.14	ND
β-Amyrone	1.0 ± 0.4	0.3 ± 0.14	0.4 ± 0.11	ND
n-Alkanoic acids	$n = 4$	$n = 2$	$n = 4$	$n = 2$
Docosanoic acid	0.2 ± 0.2	25.2 ± 11.5	0.06 ± 0.10	0.3 ± 0.24
Tetracosanoic acid	0.4 ± 0.3	9.0 ± 6.2	0.01 ± 0.01	0.4 ± 0.31
Hexacosanoic acid	0.35 ± 0.3	10.1 ± 6.8	0.03 ± 0.02	0.3 ± 0.05
Octacosanoic acid	0.1 ± 0.06	7.1 ± 4.9	0.03 ± 0.03	0.2 ± 0.11
Triacontanoic acid	ND	2.5 ± 2.0	0.04 ± 0.03	ND
Dotriacontanoic acid	ND	1.3 ± 0.9	ND	ND
Tetracontanoic acid	ND	0.4 ± 0.4	ND	ND
Soil resuspension	$n = 4$	$n = 2$	$n = 4$	$n = 2$
α-Glucose	1.0 ± 0.9	8 ± 1.1	0.02 ± 0.004	0.009 ± 0.008
β-Glucose	1.1 ± 0.8	5 ± 2.3	0.03 ± 0.009	0.008 ± 0.007
Sucrose	ND	2 ± 0.2	0.07 ± 0.04	0.010 ± 0.006

Table 1 continued

	Atmospheric particles[a]		Roadside dust particles[b]	
	Urban (n = 24)	Rural (n = 2)	Urban (n = 24)	Rural (n = 2)
Mycose	ND	5 ± 0.8	0.10 ± 0.07	0.11 ± 0.009
Arabitol	ND	12 ± 6	ND	ND
Mannitol	ND	11 ± 7	ND	ND
Burning emissions	n = 4	n = 2	n = 4	n = 2
1. Biomass burning				
Saccharides				
Levoglucosan	60 ± 31	32 ± 21	tr.	ND
Mannosan	0.9 ± 0.8	0.9 ± 0.4	ND	ND
Galactosan	1.4 ± 0.6	2.3 ± 1.1	ND	ND
1, 5-Anhydro-β-glucofuranose	2.3 ± 1.8	2.7 ± 2.0	ND	ND
Sterols				
Campesterol	1.6 ± 0.39	ND	0.1 ± 0.02	0.06 ± 0.04
Stigmasterol	2.8 ± 1.47	ND	0.25 ± 0.06	0.11 ± 0.08
Sitosterol	4.9 ± 3.1	ND	1.4 ± 0.09	0.24 ± 0.19
Diterpenoid				
Dehydroabietic acid	3.6 ± 1.2	0.2 ± 0.01	0.83 ± 0.3	0.03 ± 0.01
2. Refuse (plastics) burning				
Diethylhexylphthalate	83 ± 21	16 ± 5	12 ± 7.4	4.3 ± 2.1
1, 3, 5-Triphenylbenzene	2.1 ± 1.3	tr.	ND	ND
Tris (2, 4-di-*tert*-butylphenyl) phosphate	1.9 ± 1.1	tr.	0.16 ± 0.09	0.05 ± 0.05
3. Food cooking operations				
n-Alkanoic acids				
Lauric acid	3 ± 2.1	5 ± 1.6	0.42 ± 0.31	0.54 ± 0.22
Myristic acid	7 ± 1.7	8 ± 0.9	0.51 ± 0.46	0.74 ± 0.6
Palmitic acid	44 ± 10.6	14.7 ± 3.3	6.58 ± 2.87	2.20 ± 1.7
Stearic acid	4.4 ± 2.2	6 ± 1.08	2.54 ± 1.05	0.52 ± 0.33
Total $C_{18:1}$ and $C_{18:2}$ acids	1.1 ± 0.9	0.8 ± 0.6	0.32 ± 0.21	0.03 ± 0.09
Sterols				
Cholesterol	3.7 ± 2.9	ND	0.69 ± 0.42	0.35 ± 0.16
Monoacylglycerols				
2-monopalmitin	13.3 ± 6.2	4.3 ± 1.3	ND	ND
1-monopalmitin	4.3 ± 3.7	1.4 ± 0.9	ND	ND
Diacylglycerols				
Palmitopalmitins	2.4 ± 1.9	2.1 ± 0.8	ND	ND
Total all compounds	5276 ± 2743	386 ± 189	491 ± 304	49 ± 16

– Not applicable, *ND* not detected, *tr* trace

[a] Concentrations of TSEOM and PM-10 are in µg m^{-3}, while those for lipid compounds are in ng m^{-3}

[b] Concentration of TSEOM is in mg g^{-1}, while for lipid compounds concentrations are in µg g^{-1}

[c] Wax $C_n = C_n – 0.5\ [C_{n+1} + C_{n-1}]$, where n = 25, 27, 29, 31, 33. Negative values were taken as zero (Simoneit et al. 1991b). CPI = 0.5 $(\Sigma C_{25}–C_{33}/\Sigma C_{26}–C_{34} + \Sigma C_{25}–C_{33}/\Sigma C_{24}–C_{32})$ (Bray and Evans 1961). % Plant wax n-alkanes = Σ wax C_n/total n-alkanes × 100

[d] Data from report by Omar et al. (2002)

because anthropogenic (petrogenic) materials are preferentially attached to smaller particles (Sicre et al. 1987), they will be more concentrated on PM-10 particles rather than TSP. For rural samples, %TSEOM/PM-10 (Table 1) is in the same range as those measured in rural Finocalia, Island of Crete, Greece (3.80–23.30%, 20–24 h, TSP, Gogou et al. 1996). The similarity can be explained in the same way as discussed above. Since natural (biogenic) materials preferentially accumulate in larger particles (Sicre et al. 1987), so PM-10 particles and TSP will have almost the same amount of these materials.

For roadside soil particles, the TSEOM values (Table 1) are lower than that measured in urban Pasadena, CA, USA (29.83 mg g^{-1}, dp ≤ 2 µm, calculated from Rogge et al. 1993a). This might be due to the larger particle size analyzed in the current study (i.e., ≤600 µm compared to ≤2 µm), because organic compounds (e.g., n-alkanes and PAHs) are more enriched on smaller particles (few µm) than larger particles (Sicre et al. 1987; Aceves and Grimalt 1993; Tang et al. 1994; Venkataraman and Friedlander 1994; Venkataraman et al. 1994; Menichini and Monfredini 1995).

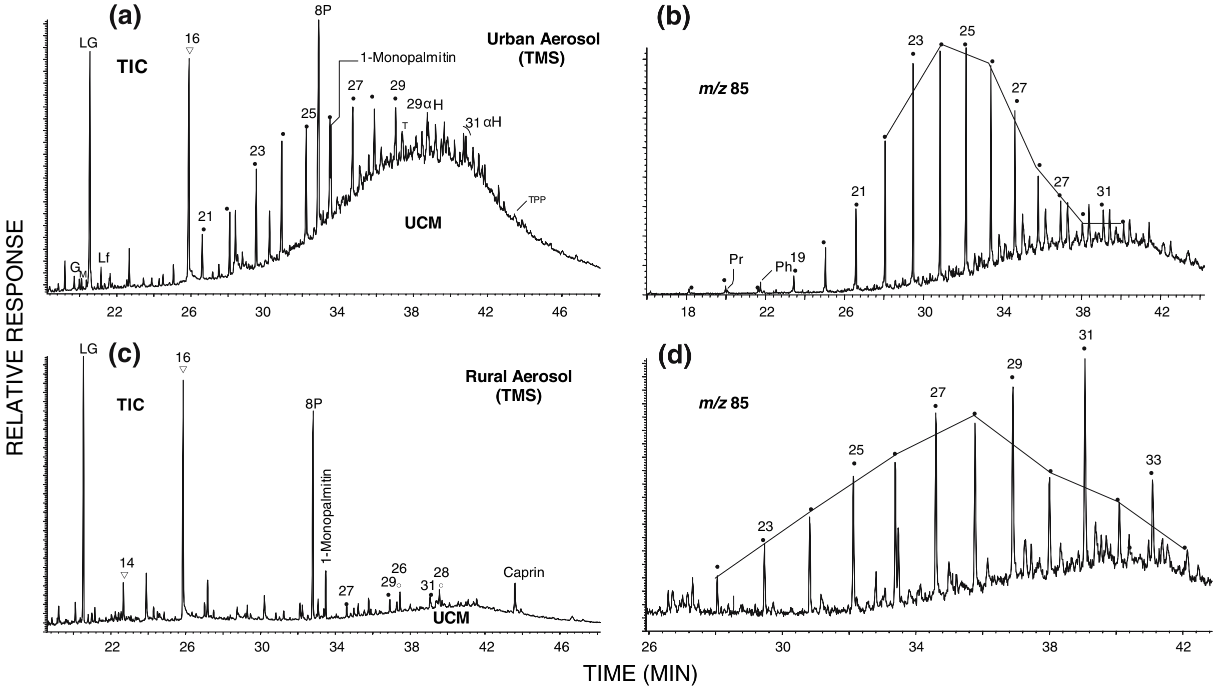


Fig. 2 Salient features of the GC-MS data for total extracts of typical aerosol samples: **a** Urban silylated (TMS) total ion current (TIC) trace, **b** *m/z* 85 key ion for *n*-alkanes, **c** rural silylated TIC, and **d** *m/z* 85 for *n*-alkanes. *Numbers* refer to carbon chain length of homologous compounds, ● *n*-alkanes, ○ *n*-alkanols, ▽ *n*-alkanoic acids, *UCM* unresolved complex mixture, *G* galactosan, *M* mannosan, *LG* levoglucosan, *Lf* 1,5-anhydro-*β*-glucofuranose, *8P* diethylhexylphthalate, *T* 1,3,5-triphenylbenzene, *αH* hopanes, *TPP* tris(2,4-di-tert-butylphenyl) phosphate, *Pr* pristane, *Ph* phytane

The major compound classes in the total extractable organic matter of both atmospheric particle and road dust samples in the urban and rural locales are aliphatic hydrocarbons. Secondary components consist of molecular markers from burning of biomass and urban refuse, with a minor input of lipids from food cooking operations and natural products from regional vegetation (Table 1).

n-Alkanes and unresolved complex mixture (UCM)

Incomplete combustion of fuel and engine lubricating oil emits *n*-alkanes with no carbon number preference in the range of C_5–C_{34} (Simoneit 1984, 1985). Plant waxes, on the other hand, contain *n*-alkanes ranging from about C_{21} to C_{37} (Tulloch 1976) with odd carbon number predominances and a $\mathrm{C}_{\max}$ in the range of C_{25}–C_{33}, depending on the plant species as well as the season and locality (e.g., Eglinton and Hamilton 1967; Simoneit 1977; Simoneit and Mazurek 1982; Mazurek et al. 1991; Rogge et al. 1993a; Stephanou and Stratigakis 1993; Abas and Simoneit 1998).

The CPI, a measure of the carbon number predominance, is useful to determine the degree of biogenic versus petrogenic input. The carbon number maximum of the most abundant *n*-alkanes ($C_{\max}$) can also be used as an indicator of relative source input (Mazurek and Simoneit 1984).

The concentrations of *n*-alkanes in atmospheric rural samples are lower than those observed for urban samples (Fig. 2c vs. a; Table 1). Urban samples have major *n*-alkanes from C_{19} to C_{34} with a $C_{\max}$ at 25 (Figs. 2b, 3a), which is not characteristic of biogenic sources (i.e., higher plant waxes). The CPI value of these samples (Table 1) indicates a major contribution from petroleum residues derived from vehicular emissions. Rural samples show a $C_{\max}$ at 31 (Figs. 2d, 3a). This high molecular weight $C_{\max}$ fits with the interpretation that plant waxes of tropical vegetation are composed of higher molecular weight epicuticular wax components which are preferentially biosynthesized due to the higher ambient temperatures (Abas and Simoneit 1996, 1998). The CPI values measured for those samples (Table 1) have a slight odd carbon number predominance indicating a higher contribution of *n*-alkanes from higher plants in rural samples compared to urban samples, with some petrogenic input. This is also illustrated by the line drawn on the *m/z* 85 plots, where the excess *n*-alkanes above the envelope represent plant wax (Figs. 2b, d, also 5b, calculated as W in Table 1, Simoneit et al. 1991b). To conclude, *n*-alkanes in urban samples are derived mainly from

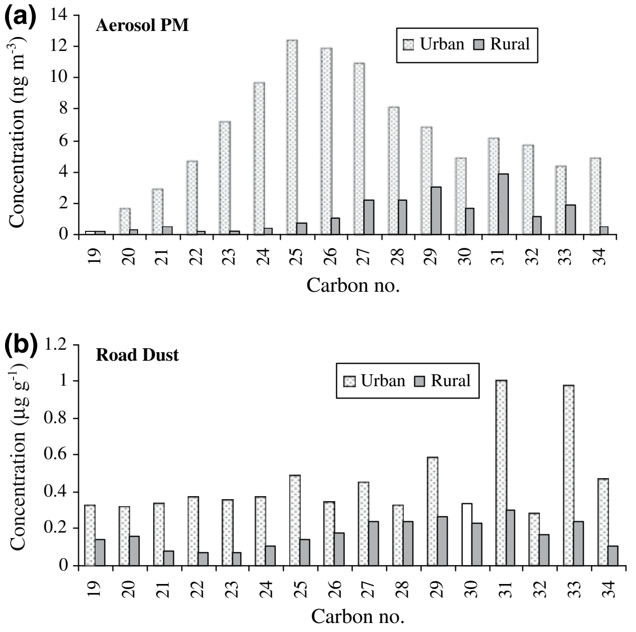


Fig. 3 Molecular distribution of *n*-alkanes in **a** atmospheric particles and **b** roadside dust particles

petroleum residues of vehicular emissions with minor contribution from higher plant waxes. This is supported by the lower CPI values and the shift of C_{max} to lower molecular weight (i.e., C_{25}). The contribution from higher plant waxes is more apparent in rural samples. This is supported by the increase in CPI values and the shift of C_{max} to 31, which is indicative of higher plant waxes of tropical vegetation.

As in the case of the aerosols, the urban road dust contains dominant *n*-alkanes, but the difference between urban and rural is less pronounced. The *n*-alkanes are in the range of C_{19}–C_{34} (Table 1). Both urban and rural samples exhibit a C_{max} at 31 (Fig. 4b) that is indicative of a dominant higher plant wax input. For urban samples, the high CPI value (Table 1) reflects an appreciable input from biogenic sources. For rural samples, the measured CPI value (Table 1) indicates an incorporation of biogenic materials with a concomitant petrogenic input.

GC or GC–MS TIC traces of hydrocarbons or total extracts obtained from urban samples usually contain a large UCM consisting of branched and cyclic (naphthenic) compounds (e.g., Figs. 2a, 5a, d). These hydrocarbons are derived mainly from fossil fuel utilization (i.e., the major components of both diesel and auto engine exhaust, the lubricant oil) (Simoneit 1984, 1985; Rogge et al. 1993c). Biogenic hydrocarbons derived from higher plants exhibit no UCM (Simoneit and Mazurek 1982). Since the UCM is derived solely from fossil fuel utilization, the $U{:}W$ ratio (i.e., the ratio of UCM to plant wax *n*-alkanes) can be used to assess the level of contamination by petroleum product emissions from vehicular traffic.

In urban atmospheric and roadside dust particles, the concentrations of UCM and $U{:}W$ values are higher than rural samples (Table 1). Both urban and rural samples (atmospheric samples and roadside dust particles) are contaminated by biodegraded petroleum residues (Peters and Moldowan 1993) with the former being more affected. In addition, urban atmospheric samples are more enriched in petroleum residues than urban roadside dust particles. In contrast, rural atmospheric samples have less petrogenic input than rural roadside dust particles. The differences are explained further below. The positive correlation between total UCM and total *n*-alkanes is more significant in atmospheric samples than roadside dust particles (Fig. 6a vs. b). Since the UCM is derived only from petrogenic sources, this indicates that the input of hydrocarbons from such emissions is more evident in atmospheric samples compared to roadside dust particles.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are not detectable in these total extract analyses and have been determined on separated fractions by monitoring the molecular ion ($M^{\bullet+}$) intensities by GC–MS (Omar et al. 2002). PAH are reported here for comparison with the novel aromatic hydrocarbon from burning of rubbish (Simoneit et al. 2005). The PAHs found in all aerosols and road dust ranged from phenanthrene to coronene with concentrations highest for the high molecular weight compounds (Omar et al. 2002). The highest concentration observed in urban aerosols was for benzo[ghi]perylene. The total PAHs in rural aerosols was lower than that of urban and all road dusts had even lower concentrations (Table 1). Burning of refuse in open fires contributes significant amounts of PAHs to the smoke, including the specific tracer 1, 3, 5-triphenylbenzene (Simoneit et al. 2005). The triphenylbenzene concentration in these urban aerosols was high relative to the total PAHs (Table 1). Thus input from refuse burning, as discussed further below, is a significant regional source of aerosol particulate matter.

Molecular markers

Traffic emissions (petroleum)

The isoprenoid hydrocarbons pristane and phytane (e.g., Figs. 2b, 5b) are present in diesel fuel, lubricating

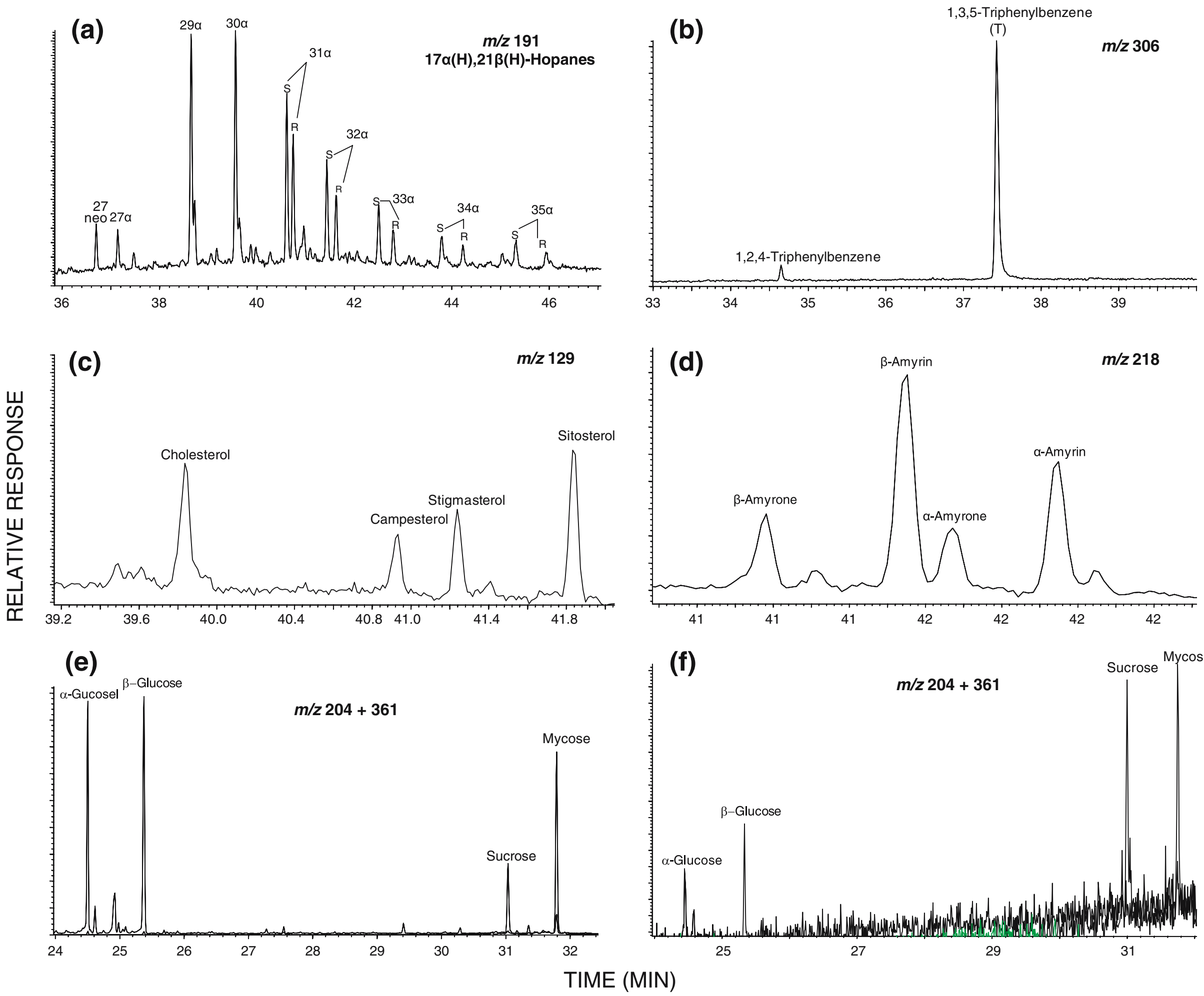


Fig. 4 Representative mass fragmentograms illustrating key tracers in the aerosols: **a** *m/z* 191 key ion for the petroleum derived 17α(H),21β(H)-hopanes, **b** *m/z* 306 key ion for triphenylbenzenes derived from burning of plastics, **c** *m/z* 129 key ion for the sterols as TMS, and **d** *m/z* 218 key ion for the triterpenoids as TMS, **e** and **f** *m/z* 204 and 361 key ions for saccharides

oil, and in both auto and diesel engine exhaust (Simoneit 1984, 1985). The concentrations of these compounds in both atmospheric and roadside dust particles are presented in Table 1. The presence of pristane and phytane coupled with the UCM confirm the contamination by petroleum residues.

Hopanes and steranes are not present in gasoline and diesel fuel because they are in the higher boiling fraction of petroleum, but are found in lubricating oils. Thus, hopanes and steranes occur in both auto and diesel engine exhausts from the lubricants (Simoneit 1984, 1985). Because these hydrocarbons are unique molecular markers for petroleum, they are generally specific for vehicular exhaust in the environment (i.e., atmospheric and roadside dust particles). Rogge et al. (1993c) showed that roughly 85% of all particle-associated hopanes and steranes emitted to the atmosphere in Los Angeles are derived from internal combustion engines. It was concluded that these compounds could be used as markers for the contribution of vehicle derived aerosols because they are sufficiently stable in the atmosphere (e.g., Simoneit 1984, 1985; Simoneit et al. 1988).

In this study, the 17α(H), 21β(H)-hopanes range from C_{27} to C_{35} including the 22S and 22R epimers for C_{31} to C_{35} (no C_{28}, e.g., Figs. 4a, 5c) and the ααα- and αββ-steranes range from C_{27} to C_{29} as the 20S and 20R isomers in both urban atmospheric particles and roadside dust particles. Hopanes were detected at trace levels in the rural atmospheric samples, significant in the rural roadside dust particles, whereas steranes were not detected in both types of rural samples (Table 1). For urban atmospheric and roadside dust particles, the distribution patterns of hopanes and steranes match each other and with fresh lubricating oil (ESSO, Cambridge, MA) (Fig. 7), indicating that particle

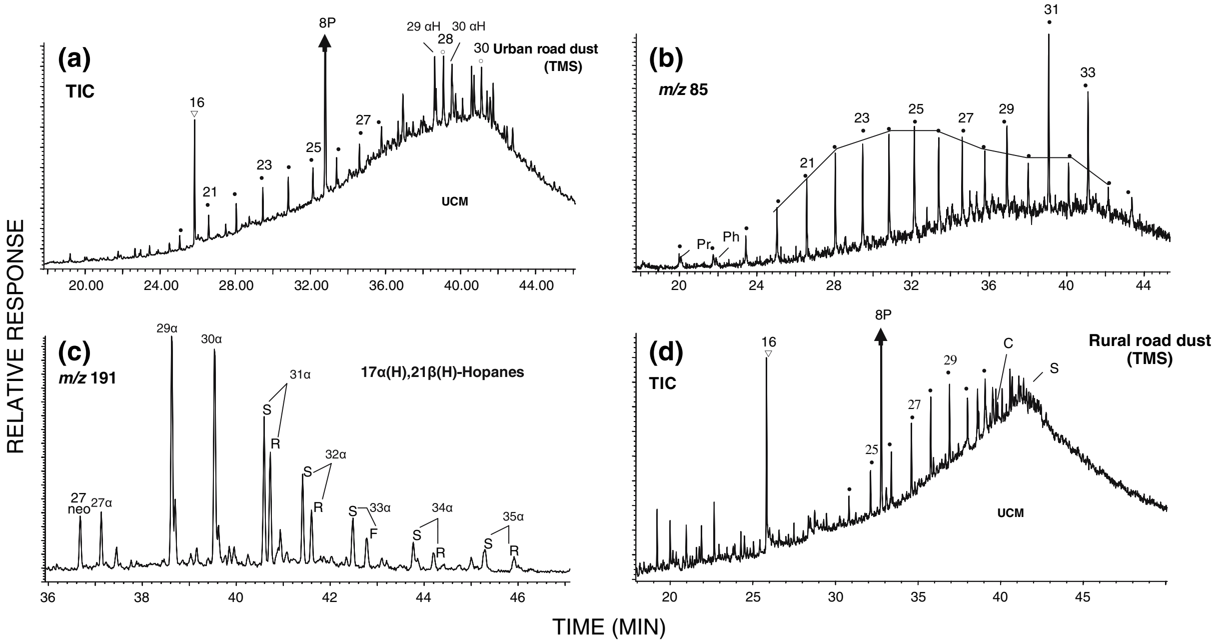


Fig. 5 Salient features of the GC-MS data for total extracts of typical roadside dust samples: **a** Urban silylated, TIC trace, **b** *m/z* 85 key ion for *n*-alkanes, **c** *m/z* 191 key ion for the 17α(H),21β(H)-hopanes, and **d** rural silylated, TIC trace. *Numbers* and *symbols* as in Fig. 2, *C* cholesterol, *S* sitosterol

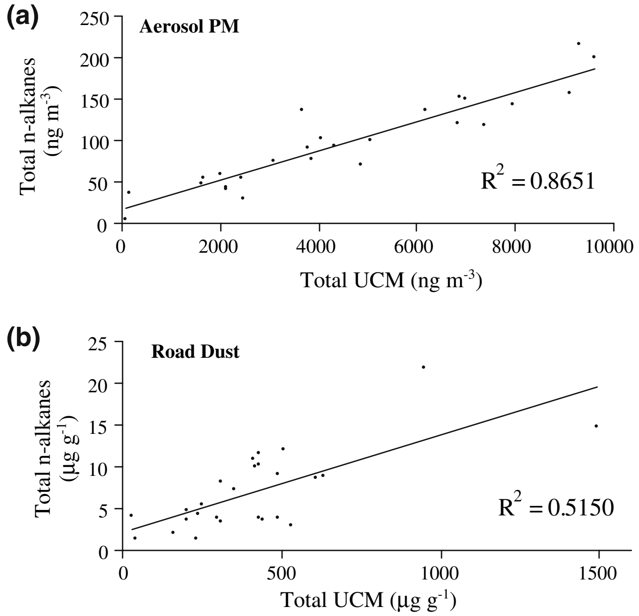


Fig. 6 Correlation between total UCM and total *n*-alkanes for **a** airborne particles [urban and rural] and **b** roadside dust particles [urban and rural]

fallout and entrainment from traffic emissions, as well as from the atmosphere to road dust is an efficient and important process in urban areas. Thus, the presence of hopanes and steranes in atmospheric particles and roadside dust particles, coupled with the presence of pristane, phytane, and UCM, confirm the input of petroleum residues to these environments.

Natural background (vegetation)

In order to better evaluate the relative input from various hydrocarbon sources, the concentrations of plant wax *n*-alkanes and their percentage of the total *n*-alkanes were calculated (Simoneit et al. 1991a, b; Table 1). The relative contributions of plant wax *n*-alkanes to the overall alkane distributions are illustrated schematically in their *m/z* 85 key ion plots (Figs. 2b, d, 5b). The excess *n*-alkanes above the envelope drawn to represent the fossil fuel-derived homologs are from plant wax. In the urban atmospheric samples, the percentage of plant wax *n*-alkanes is lower than in rural samples, which indicates greater plant wax input to rural samples. In the urban roadside dust particles, the percentage is higher, than in rural samples. This is because rural samples were collected from a car park rather than the forest floor. Generally, urban roadside dust particles are more enriched in higher plant wax *n*-alkanes than urban atmospheric samples. For atmospheric samples, the CPI shows a very good positive correlation with the percentage of *n*-alkanes from higher plant waxes, while a moderate positive correlation is observed for roadside dust particles (Fig. 8a vs. b). This reveals the effectiveness of CPI as an

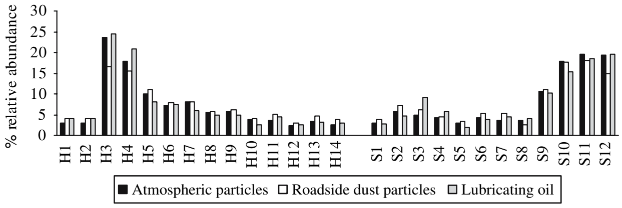


Fig. 7 Molecular distributions of 17α(H),21β(H)-hopanes (H1=Ts, H2=Tm, H3=$C_{29}\alpha\beta$, H4=$C_{30}\alpha\beta$, H5=C_{31}S, H6=C_{31}R, H7=C_{32}S, H8=C_{32}R, H9=C_{33}S, H10=C_{33}R, H11=C_{34}S, H12=C_{34}R, H13=C_{35}S, H14=C_{35}R) and steranes (S1=$C_{27}\alpha\alpha\alpha$S, S2=$C_{27}\alpha\beta\beta$R, S3=$C_{27}\alpha\beta\beta$S, S4=$C_{27}\alpha\alpha\alpha$R, S5=$C_{28}\alpha\alpha\alpha$S, S6=$C_{28}\alpha\beta\beta$R, S7=$C_{28}\alpha\beta\beta$S, S8=$C_{28}\alpha\alpha\alpha$R, S9=$C_{29}\alpha\alpha\alpha$S, S10=$C_{29}\alpha\beta\beta$R, S11=$C_{29}\alpha\beta\beta$S, S12=$C_{29}\alpha\alpha\alpha$R)

indicator of biogenic versus petrogenic input. Moreover, for atmospheric samples, the equation derived from the correlation [% plant wax *n*-alkanes = 30.699 (CPI)—28.785] may be applied to calculate the percentage of plant wax *n*-alkanes by using CPI only.

Additional compounds attributed to plant wax are *n*-alkanols and triterpenoids. The *n*-alkanols (e.g., Figs. 2c, 5a) range from C_{22} to C_{32} with $C_{\max}$ at 28 for both aerosol and road dust samples and are typical of tropical vegetation (Simoneit 1977). Their concentrations are given in Table 1. The triterpenoids consist mainly of β-amyrin (I, chemical structures cited are shown in Appendix 1), α-amyrin (II), with varying amounts of their oxidation products β-amyrone (I) and α-amyrone (II), respectively (e.g., Fig. 4d, Table 1).

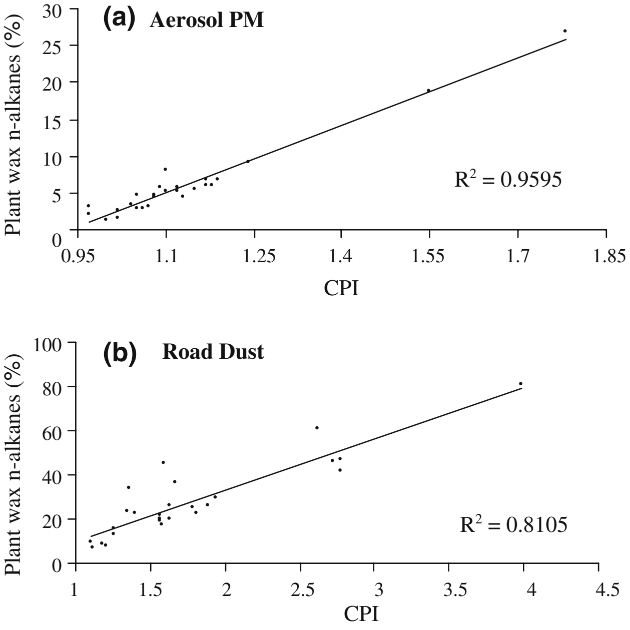


Fig. 8 Correlation between CPI and % plant wax *n*-alkanes for *a* airborne particles [urban and rural] and *b* roadside dust particles [urban and rural]

Burning emissions

Molecular markers for three types of fugitive burning processes are found in these aerosol samples but not in the road dust samples. These emissions are from open burning of biomass and refuse, and from food cooking operations.

Biomass burning Emissions from burning of biomass (e.g., wood, paper) are significant and consist of the saccharide tracers from the thermal decomposition of cellulose (Simoneit et al. 1999). These are levoglucosan (III, the major compound), mannosan (IV), galactosan (V), and 1, 5-anhydro-β-glucofuranose (VI) (e.g., Fig. 2a, c; Table 1). They are detectable only in the urban and rural aerosol samples and not in road dust. A minor amount of dehydroabietic acid (VII) is found in the aerosols. It is a specific tracer for conifer wood smoke (Oros and Simoneit 2001; Simoneit 2002), indicating that some of the biomass burned in this air shed consists of conifer wood. The phytosterols (e.g., Fig. 4c) are also introduced into atmospheric particles by burning biomass (Rogge et al. 1998). Sterols are found in eukaryotes such as higher plants and algae (Huang and Meinschein 1976; Boon et al. 1979; Lee et al. 1979). The phytosterols in smoke from burning processes of biomass consist mainly of sitosterol (VIII, $R = \beta C_2H_5$), campesterol (VIII, $R = \alpha CH_3$) and stigmasterol (IX) (Table 1; Simoneit 2002). The hopanes and moretanes described for tropical biomass burning (Fang et al. 1999; Abas et al. 2004) were not present in these samples.

Refuse burning Open burning of domestic refuse in both urban and rural areas is a global problem. Domestic garbage consists primarily of plastics, papers and plant detritus. A series of source specific molecular markers for burning such material has been defined (Simoneit et al. 2005). Burning paper emits the same saccharide molecular markers as wood described above, so the apportionment between burning of biomass and refuse is not absolute. The key molecular markers specific for burning of plastics (mainly polyethylene, PE, and minor polyethylene terephthalate, PETP) are diethylhexylphthalate (DEHP, X, e.g., Figs. 2a, 5a) and 1,3,5-triphenylbenzene (XI, e.g., Fig. 4b), with traces of 1, 2, 4-triphenylbenzene, the oxidized derivative of the antioxidant tris (2, 4-di-*tert*-butylphenyl) phosphite (XII) and benzene 1, 4-dicarboxylic acid (terephthalic acid, XIII). These compounds are significant in the aerosol particles from both the urban and rural areas, but the corresponding road dust samples lack 1, 3, 5-triphenylbenzene and terephthalic acid (e.g., Figs. 2a, c, 4b, 5a, d). The concentrations of these molecular markers are given in Table 1 and the levels of 1, 3, 5-triphenylbenzene are higher than any other PAH. Open burning of refuse is expected to be a continuous anthropogenic activity throughout the year in a tropical region and thus contributes to the total atmospheric particulate matter. However, the molecular markers of plastics in the road dusts, i.e., DEHP and tris (2, 4-di-*tert*-butylphenyl) phosphate, indicate detrital plastic particles from litter and not fallout from burning rubbish.

Food preparation operations Grilling and deep-frying of foods in both restaurants and domestic settings emit high concentrations of particulate matter as smoke (fat droplets and char) to the urban atmosphere (Rogge et al. 1991; Schauer et al. 1996). The common molecular markers utilized to assess these processes in urban regions are cholesterol (VIII, $R = H$, e.g., Figs. 2a, c, 4c), monoacylglycerols (e.g., 1-monopalmitin, XIV) and diacylglycerols (e.g., 2-palmito-1-palmitin, XV and 3-palmito-1-palmitin, XVI) (Rogge et al. 1991, Schauer et al. 1996; Nolte et al. 1999). The concentrations of cholesterol and the dominant mono- and diacylglycerols are given in Table 1. The highest emissions from cooking operations are point sources such as restaurants and cafeterias. It should be pointed out that these same molecular markers can also be emitted from rendering and crematorium operations, and possibly from burning of oil palm litter or palm oil refining (these sources have not been characterized). These molecular markers are not detectable in the road dust samples.

Soil resuspension

Resuspension of soil particulate matter in the atmosphere occurs during agricultural activities and by natural wind erosion of denuded land. Transport of soil particulate matter is regional and global (e.g., Simoneit et al. 2004a). The molecular markers developed for soil resuspension are mono- and disaccharides (Simoneit et al. 2004b) and they are detectable as significant compounds of the aerosols, but only in traces in the road dusts (Table 1). The key molecular markers for soil are the ubiquitous monosaccharides α- and β-glucose (XVII) and the disaccharides sucrose (XVII) and mycose (XIX) (e.g., mass fragmentograms *m/z* 204 and 361 in Fig. 4e, f). Mycose is characteristic of fungal detritus in soil and the other saccharides are primary sugars of biota, mainly from soil (Simoneit et al. 2004b). Mannitol (XX) and arabitol are also found in some aerosol samples and are additional molecular markers for fungal detritus in soil. Thus, soil particulate matter is a component of these aerosols and the source may be regional or longer-range transport from Asia.

Source apportionment

The dominant sources of compounds in all aerosol samples are emissions from traffic as hydrocarbons, especially in the urban area of Kuala Lumpur (Fig. 9). The levels of PM-10 and TSEOM for Kuala Lumpur (Table 1) are lower than those reported there during the southeastern Asia regional haze of September 1997 (~400 μg m^{-3} TSP and 95 μg m^{-3} TSEOM, Abas et al. 2004). The other sources are minor. The natural background from vegetation wax is essentially equivalent to traffic emissions in the rural aerosols and the various source types for burning with soil resuspension are also significant (Fig. 9). The road dust samples from both urban and rural areas reflect organic source compositions from particle fallout of traffic with minor inputs of detritus from the other sources (Fig. 9).

Comparison between airborne particles and roadside dust

From the previous discussion, it was obvious that urban airborne particles are more enriched in *n*-alkanes derived from petrogenic sources, whereas in urban roadside dust particles the biogenic input of *n*-alkanes is more apparent. This can be explained by particle size considerations that are important to particle deposition

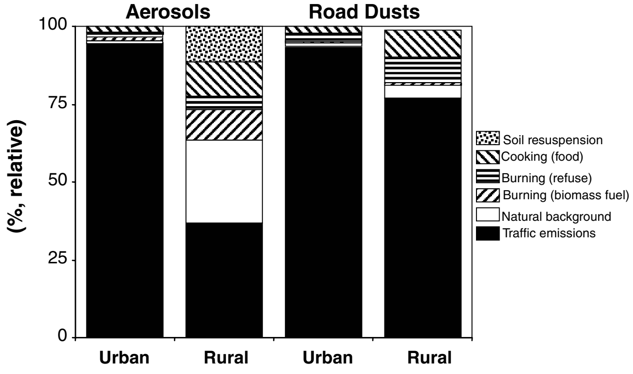


Fig. 9 Summary bar graphs of the major sources for the organic compounds identified in the urban and rural aerosol and road dust samples. (Derived from the sums of compound masses for each source type in Table 1, expressed as relative percent excluding the uncharacterized TSEOM remainder)

from the atmosphere. Petrogenic residues preferentially occur in the submicron particles (Sicre et al. 1987) that deposit slowly from the atmosphere (Clarke 1992). Biogenic materials (e.g., mechanically generated leaf and soil dusts), in contrast, preferentially accumulate in the larger particles, which deposit more readily by gravitational sedimentation or impaction (Sicre et al. 1987; Rogge et al. 1993b). Thus, roadside dust particles are enriched in biogenic materials (natural background), whereas airborne particles are more enriched in petrogenic residues. For rural airborne particles, the higher biogenic input compared to forest dust particles is because the latter were collected from a car park, while the former were sampled away from direct petrogenic sources (i.e., major roads).

Biomass burning molecular markers such as levoglucosan, are only detected in atmospheric particles. Also, the key molecular markers for burning of plastics and cooking operations, such as 1, 3, 5-triphenylbenzene (Simoneit et al. 2005), cholesterol and mono- and diacylglycerides (Schauer et al. 1996; Nolte et al. 1999) are present at significant levels only in atmospheric and not roadside dust particles. The presence of plant wax, sitosterol and the plasticizer DEHP with the tris (2, 4-di-*tert*-butylphenyl) phosphate indicate an input of plant and plastic litter to the road dust samples based on the absence of saccharides characteristic of that source (Simoneit et al. 2004b). However, soil particles are part of the urban and rural aerosols.

Conclusions

The solvent-extractable alkanes and polar lipids present in PM-10 atmospheric particles and roadside dust particles of Kuala Lumpur, Malaysia have been characterized using GC–MS techniques. The urban PM-10 concentration is 66 ± 19 μg m^{-3}: a value still below the recommended primary standard (health-based) [150 μg m^{-3} (24 h), US national ambient air quality standards (NAAQS)], but exceeding the recommended secondary standard (welfare-based) [50 μg m^{-3} (24 h), US NAAQS].

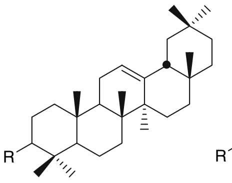
n-Alkanes in urban atmospheric samples are derived mainly from petroleum residues of vehicular emissions with minor contribution from higher plant waxes. This is supported by the lower CPI values (CPI ~ 1) and the shift of $C_{\max}$ to lower molecular weight (C_{25}). The contribution from higher plant waxes is more apparent in rural samples. This is supported by the increase in CPI values and the shift of $C_{\max}$ –C_{31}, which is indicative of higher plant waxes of tropical vegetation. In roadside dust particles, the biogenic input is more apparent than the petrogenic input compared to atmospheric samples. This can be illustrated by the higher CPI values and the high molecular weight $C_{\max}$.

For atmospheric and roadside dust particulate samples, the presence of 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.

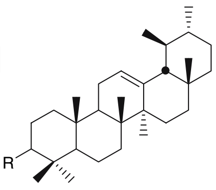
In atmospheric particles, the significant concentrations of anhydrosaccharides, especially levoglucosan, indicate an input from wood/paper burning. Open burning of domestic refuse such as plastics also contributes to atmospheric particles, which is apparent by the presence of 1, 3, 5-triphenylbenzene coupled with diethylhexyl phthalate. Emissions from food preparation operations are evident in the atmospheric particles (mono- and diacylglycerides and cholesterol), but not in roadside dust. Litter particulate matter from vegetation, based on the presence of sitosterol and plant wax, and from plastics, based on the input DEHP with minor tris-(2,4-di-*tert*-butylphenyl) phosphate, are significant in the road dusts.

Acknowledgments This project was supported by the Government of Malaysia through MPKSN Grant No: 08-02-03-0010. The cooperation of the Chief of Police of Kuala Lumpur City is greatly appreciated.

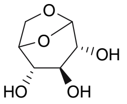
Appendix 1. Chemical structures cited



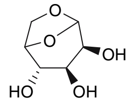
I. β-Amyrin, R=β(OH)
β-Amyrone, R=O



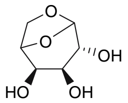
II. α-Amyrin, R=β(OH)
α-Amyrone, R=O



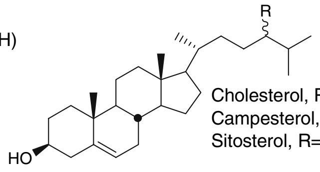
III. Levoglucosan



IV. Mannosan

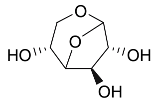


V. Galactosan

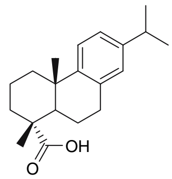


Cholesterol, R=H
Campesterol, R=αCH$_3$
Sitosterol, R=βC$_2$H$_5$

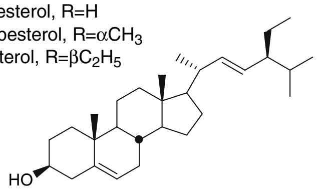
VIII. Sterols



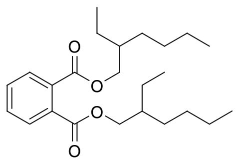
VI. 1,6-Anhydro-β-glucofuranose



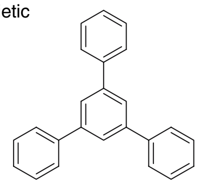
VII. Dehydroabietic acid



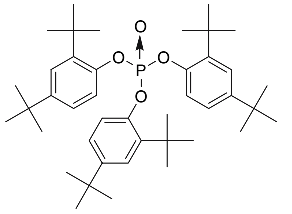
IX. Stigmasterol



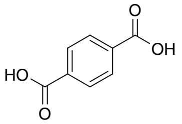
X. Di-2-ethylhexyl phthalate



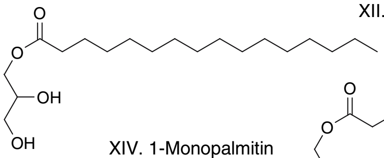
XI. 1,3,5-Triphenylbenzene



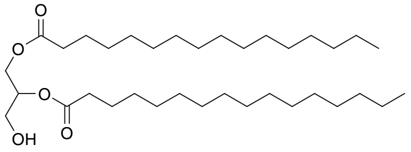
XII. Tris(2,4-di-*tert*-butylphenyl)phosphate



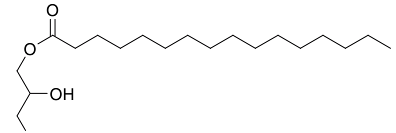
XIII. Terephthalic acid



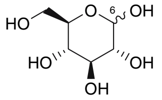
XIV. 1-Monopalmitin



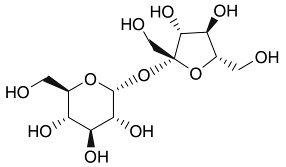
XV. 2-Palmito-1-palmitin



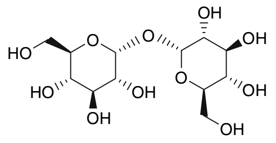
XVI. 3-Palmito-1-palmitin



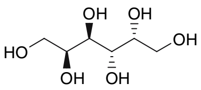
XVII. Glucose
(α=6αOH, β=6βOH)



XVIII. Sucrose



XIX. Mycose (trehalose)



XX. Mannitol

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