APPENDIX 8

HONG KONG GOVERNMENT LABORATORY

Solvent Extractable Organic Compounds

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Appendix:

Report on the Determination of Solvent Extractable Organic Compounds in PM 2.5 Aerosols in Hong Kong for the Ad hoc Project on Suspended Particulate Matters

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Abstract

PM2.5 aerosols were collected in a 6-day cycle using Partisol samplers on 47 mm quartz filters at three air monitoring stations located in a rural, an urban and a roadside site in Hong Kong during the period of November 2000 to October 2001. The sample filters were divided into four seasonal batches according to the observed variations of sea-level pressure and upper-level wind direction over Hong Kong. The composite samples were characterised and quantified for their concentrations of four classes of solvent extractable organic compounds (SEOC) *viz* aliphatic hydrocarbons (AHs), polynuclear aromatic hydrocarbons (PAHs), fatty acids/alkanoic acids (FAs) and alkanols (ROHs) comprising over 100 individual compounds using gas chromatography-mass spectrometry. The total yield of SEOC and yields of total AHs (including the unresolved complex mixture containing branched and cyclic hydrocarbons), PAHs, FAs and ROHs were found to be in the ranges of 125-2060, 54.0-1510, 0.6-17.2, 41.6-520 and < 0.1-12.1 ng m^{-3} respectively. Distinct seasonal variation in concentrations of the total and the four classes of SEOC was observed with higher concentrations in the winter samples and lower concentrations

in the summer samples. Spatial variation was also very obvious with samples collected at the roadside station having the highest concentrations of SEOC in all seasons and the rural samples having the lowest concentrations. Characteristic ratios of petroleum hydrocarbons such as CPI and U:R were worked out for assignment of possible sources of PM2.5. The findings suggest PM2.5 aerosols in Hong Kong originate from both biogenic sources such as microbial activities and vascular plant wax and anthropogenic sources including vehicular exhaust and kitchen emission.

Introduction

Recent concern about the health effects of air pollution has focused on suspended particulate matters or aerosols. Several studies[1-3] review a strong link between the concentrations of suspended particulate concentrations and the mortality and morbidity of the exposed population. It was further confirmed that fine particulate matters have greater impact on human health than the coarser fractions. [4-6] Organic carbon (OC) has been reported by Chow et al[7] to be a major component (*ca.* 40-60 %) of fine suspended particulate (PM2.5) in California. Studies have also been carried out to identify and quantify the individual components of the solvent extractable organic fraction of aerosols. Characterization of solvent extractable organic carbons (SEOC) in total suspended particulate (TSP), [8-11] respirable suspended particulate (RSP),[12-14] and PM2.5[15] were reported.

The Government of the Hong Kong Special Administrative Region has implemented regular TSP and RSP monitoring programmes since mid 1980s. Among other things, high

volume filter samples were collected for speciation of 7 water soluble ions, 16 elements and some species of organic compounds. In 2000, a 12-month ad hoc project was launched, amongst others, to facilitate a better understanding of the mass loading and the composition of PM2.5. To characterize the organic fraction of PM2.5 and to study the seasonal, temporal and spatial variations of SEOC in the aerosols, the study involved sampling of 47 mm filter samples of PM2.5 using Partisol samplers at a frequency of once every 6 days during the period of November 2000 to October 2001 from three strategic locations in Hong Kong. The filter samples at each of the location were grouped into four seasonal batches and the composite samples were characterized and quantified for their concentrations of four classes of SEOC under study, namely aliphatic hydrocarbons (AHs), polycyclic aromatic hydrocarbons (PAHs), fatty acids/alkanoic acids (FAs) and alkanols (ROHs). AHs are emitted into the atmosphere both by biogenic and anthropogenic sources. Anthropognic sources include the combustion of fossil fuels such as petroleum and coal. Biogenic sources include epicuticular waxes shed from vascular plants and suspension of pollen and micro-organisms. PAHs are known to be originated from petroleum products and from fuel combustion. The alkanol homologs greater than C20 are believed to be characteristics of vascular plant waxes and homologs less than C20 are considered to be derived from microbial sources. [16,17] Alkanoic acids are derived from vegetation emission, bacterial activities, hydrolysis and thermal oxidation during the cooking process. Cass and Simoneit reported several series of papers detailing the composition of SEOC of various sources of fine organic aerosols.[18-20]

Experimental

Sampling of PM2.5

Aerosol samples were collected at three sampling stations located at Tsuen Wan (TW), Hok Tsui (HT) and Mong Kok (MK) respectively on quartz filters over periods of 24 hours once every 6 days using Partisol samplers with 2.5 μm inlet at flow rates of 16.7 L/min. An air monitoring station is located on the rooftop of a government building at about 15 – 18 m above ground in TW that is a mixed residential and commercial area. The TW site has also been used as a toxic air pollutants (TAP) station for sampling TAPs. HT is a rural area situated at the southern tip of the Hong Kong Island facing the South China Sea. MK is a mixed commercial and residential area in the Kowloon Peninsular. An air monitoring station is located near the roadside at about 2 m above ground at the MK station. A map illustrating all the sampling locations is shown in Figure 1. Clean and loaded filters were stored and transported to and from the sampling sites in individual containers (Petri-slides, Millipore). Analysis was conducted immediately after measurement of the dust loading, otherwise, samples were stored at 4 °C before analysis.

Analysis of SEOC

The samples collected at each of the three sampling locations were grouped into 4 seasonal batches according to the observed variations of sea-level pressure and upper-level wind direction over Hong Kong. [21] Essentially, SEOC in the composite filter samples were extracted and measured according to the procedures as described previously.[22] Therefore only a brief description is provided herewith.

Standards and Reagents

A standard solution of a mixture of aliphatic hydrocarbons (AHs) from n-octane (nC8) to n-tetracontane (nC40), each at a concentration of approximately 500μg/mL, was purchased from AccStandard Inc. (NH, USA). Standards of polynuclear aromatic hydrocarbons (PAHs) *viz.* naphthalene (Naph), acenaphthylene (Acph), acenaphthene (Acen), fluorene (Fluo), phenanthrene (Phen), anthracene (Anth), 2-methylphenanthrene (2mephen), 1-methylphenanthrene (1mephen), fluoranthene (Flut), pyrene (Pyre), 2-methylfluoranthene (2mflut), 1-methylpyrene (1mepyre), benz(a)anthracene (Bant), chrysene (Chry), benzo(b)fluoranthene (Bbfl), benzo(k)fluoranthene (Bkfl), benzo(e)pyrene (Bep), benzo(a)pyrene (Bap), perylene (Pery), indeno(1,2,3-cd)pyrene (Inpy), dibenz(a,h)anthracene (Daan), benzo(g,h,i)perylene (Bgpe), coroene (Coro)) were purchased from AccuStandard Inc. (NH, USA), and 1,3,5-triphenylbenzene (135tb) from Aldrich Chemical Co. (Gillinghan, UK) as neat chemicals with purity not less than 97%. Standards of methyl esters of saturated fatty acids from octanoic acid methyl ester (C8:0) to hentricontanoic acid methyl ester (C31:0) except nonaconsanoic acid (C29:0), methyl esters of unsaturated fatty acids including myristoleic acid (C14:1), palmitoleic acid (C16:1), linoleic acid (C18:2), oleic acid (C18:1), arachidonic acid (C20:4), cis-11-eicosenoic acid (C20:1), cis-4,7,10,13,16,19-docosahexaenic acid (C22:6), erucic acid (C22:1) and nervonic acid (C24:1) were purchased from Supelco (Bellefonte, PA, USA) as neat chemicals with purity of not less than 98%. Methyl ester of nonaconsanoic acid was purchased from Alltech-Applied Science Labs. (Deerfield, IL, USA) as neat chemical of over 99% purity. Standards of alkanols (ROHs) from 1-decanol (C10) to 1-triacontanol (C30) except 1-pentacosanol (C25) and 1-nonacosanol (C29) were purchased

from Dr. Ehrenstorfer (Augsburg, Germany) as neat chemicals with purity of not less than 98%.

Standards of deuterated aliphatic hydrocarbons including n-hexadecane-D_{34}, n-eicosane-D_{42}, n-tetracosane-D_{50}, n-triacontane-D_{62}, n-dotriacontane-D_{66} and n-hexatriacontane-D_{74} were purchased from Cambridge Isotope Laboratories (Massachusetts, USA) as neat chemical with purity of 98% as internal standards for determination of AHs, FAs and ROHs. A mixed standard solution of acenaphthalene-D_{10}, phenanthrene-D_{10}, chryene-D_{12} and perylene-D_{12}, each at a concentration level of approximately 4000µg/mL, was purchased from Hewlett Packard (Rockville, MD, USA) as internal standards for determination of PAHs.

A methanolic solution containing 14 % Boron trifluoride (BF_3) and a solution of 1% trimethylchlorosilane (TMCS) in bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) (Alltech-Applied Science Labs., Deerfield, IL, USA) were used as derivatization reagents for esterification of fatty acids to the methyl esters of the respective fatty acid (FAMEs) and for derivatization of alkanols to the trimethylsilylethers of the respective alkanols (ROTMSs) respectively.

Standard reference material SRM 1649a (urban dust) was purchased from the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). SRM 1649a is an atmospheric particulate material, 95 % of which is of 100 ± 3 µm particle diameter,

collected in an urban area in Washington DC in 1976 to 1977. Certified values for the concentrations of PAHs were compared with the results obtained in this study.

All solvents (n-hexane, toluene, acetone, dichloromethane) were used as analytical grade (or above) and distilled before used. Diethyl ether (HPLC grade) was used as received. Water was distilled, deionized and washed with dichloromethane before used.

Preparation of standard solutions

Stock standards of AHs (100 μg/mL) and deuterated PAHs (10 μg/mL) were prepared by quantitative dilution of appropriate volumes of the acquired mixed standard solutions using n-hexane and dichloromethane respectively. Mixed stock standards of the PAHs (1 μg/mL), FAs in the forms of their respective methyl esters (2000 μg/mL), ROHs (50 μg/mL), and deuterated aliphatic hydrocarbons (100 μg/mL) were prepared by dissolving appropriate amounts (about 50 mg each) of the concerned chemical standard in 100 mL of dichloromethane, and then by serial dilution of the concentrated mixture solutions with dichloromethane to the designated concentrations. Mixed stock standards of ROTMSs were prepared by derivatization of 1 mL of the stock standard solution of ROHs with 20 μL of 1% TMCS in BSTFA at a reaction temperature of 70°C for about half an hour. All prepared stock standard solutions were stored in capped amber vials and kept under refrigeration at 4°C prior to use.

Working standard solutions of AHs (1 to 20 μg/mL), PAHs (0.01 to 0.5 μg/mL), FAs in the forms of methyl esters of FAs (1 to 50 μg/mL), and ROHs in the forms of

trimethylsilylethers (1 to 10 μg/mL) for calibration were freshly prepared before analysis by quantitative dilution of appropriate volumes of stock mixture with appropriate solvents.

Extraction of SEOC

Filters were grouped together according to the observed variations of sea-level pressure and upper-level wind direction over Hong Kong into seasonal batches. Each of the composite samples was spiked with 100μL of the stock internal standards of AHs and 10 μL of the stock internal standards of PAHs. After spiking with the internal standards, the samples were subjected to ultrasonic extraction procedures that 30mL of n-hexane was used in the first sonication step, and a 20 mL and 10 mL of 2:1 v/v mixture of toluene and iso-propanol was used in the second sonication step and for washing of residues respectively.

Organic extracts and washings were combined, filtered with ashless filter paper (90mm dia., Whatman 42) and concentrated to about 1 mL under a slow stream of nitrogen. 0.5 mL of the BF_3 reagent was added to each of the concentrated extracts. The mixtures were heated to 85°C for half an hour to esterify the fatty acids. The reactions were quenched by addition of organic free distilled and deionized water. Upon completion of the quenching reaction that took about 2 to 5 min, the reaction mixtures were extracted by 3 × 2 mL of dichloromethane. A small amount of anhydrous sodium sulfate was added to each of the combined extracts to remove water, which were then concentrated to near dryness under an inert atmosphere of nitrogen. About 10 mL of n-hexane was added to each of the concentrated extract and the mixtures were re-concentrated to 1 mL under a fine stream of nitrogen.

Column clean-up of SEOC

A column with 1 cm internal diameter and 30 cm length was packed with activated silica gel (100 - 200 Mesh) up to a length of 13 cm. Each of the concentrated organic extracts obtained above were loaded on the top of a packed column and was separated into four classes of organics by elution sequence i) AHs, ii) PAHs iii) FAMEs and iv) ROHs.

All four solvent fractions of each of the sample were collected and concentrated to 1 mL under a fine stream of nitrogen. While the AHs, PAHs and FAMEs fractions were ready for injection into the gas chromatographs for analysis, the ROHs fractions were further treated with 20 μL of the derivatization agent (1%TMCS) and heated to 70°C for about half an hour for conversion of the ROHs to the respective ROTMSs. Upon completion of the reaction, the mixtures were ready for instrumental analysis. To each of the FAMEs and ROTMSs fractions, 10 μL of the stock standard solution of deuterated AHs (100 μg/mL) was added as injection standards.

Instrumental Analysis of SEOC

Identification of SEOC was performed by a GCQ ion trap mass spectrometer (Finnigan, CA, USA) equipped with an operating software (Xcalibur, version 2, ThermoQuest, MI, Italy), 30 m × 0.25 mm id, 0.25 μm film thickness DB-5 MS capillary column (J&W Scientific, CA, USA) and operated in splitless mode. Ultra-pure grade helium of 99.999% purity (Chun Wang Ind. Gases, Hong Kong) was used as the carrier gas at a flow rate of 2

mL min^{-1}. The mass spectrometer (MS) was operated in full scan positive electron ionization (EI) mode at 70 eV. The gas chromatograph (GC) was operated isothermally at 65°C for 5 min, then programmed to 300°C at 10°C min^{-1} and finally held at 300°C for 25 min for the analyses of AHs, FAs and ROHs. For analyses of PAHs, the GC was operated isothermally at 85°C for 2 min, programmed to 280°C at 8°C min^{-1} and held at 280°C for 30 min, then programmed to 300°C at 20°C min^{-1} and kept for 10 min. The transfer line and the ion source were set at 300°C and 200°C respectively. Presence of a SEOC was confirmed by comparison of the retention times and mass fragmentation patterns of the compound in the sample against those of the reference working standard.

Quantification of AHs and FAs was performed by a HP 6890 gas chromatograph / flame ionization detector (Hewlett Packard, Rockville, MD, USA) using a 30 m × 0.32 mm id, 0.25 μm film thickness HP-5 capillary column (J&W Scientific, CA, USA). Ultra-pure grade helium of 99.999% purity was used as the carrier and make up gas at flow rates of 2 mL min^{-1} and 25 mL min^{-1}respectively. The detector was fitted with compressed air (Chun Wang Ind. Gases, Hong Kong) at a flow rate of 400 mL min^{-1} and hydrogen, that was generated from a hydrogen generator (Alltech Associate Inc., Deerfield, IL, USA), at a flow rate of 40 mL min^{-1}. The gas chromatograph was operated in the same condition as described earlier for identification of AHs and FAs.

Quantification of PAHs and ROHs was performed by a Trace 2000 gas chromatograph and a Voyager mass spectrometer (ThermoQuest, MI, Italy) fitted with a 30 m × 0.25 mm id, 0.25 μm film thickness DB-5 MS capillary column. The GC/MS system was operated

at selected ion mode (SIM) at 70 eV. Other GC operating conditions were the same as described above for the identification of SEOC. Tables 1 and 2 list the retention time and quantitation ions for PAHs and ROHs.

Five point calibration curves were prepared for the four classes of SEOC by plotting the relative response factors (RRFs) of the calibration standards against the concentration of the standards. The RRF values for AHs, FAs and ROHs were derived from the authentic standards, relative to the deuterated internal standards (or injection internal standards) with the nearest retention time. For PAHs, the RRF values were calculated relative to the deuterated PAHs internal standards. The concentration of an SEOC in a given sample was calculated by an internal standard method with reference to the average RRF obtained from the respective calibration curves. Figures 2 (a-e) show the GC/MS chromatograms of the four classes of SEOC under study.

Quality Control

The retention time (RT) of an SEOC should be within ± 0.2 min. of the mean retention time of the calibration standards, whilst the relative retention time (RRT) of the SEOC to the respective internal standard in the sample injection should be within ± 0.5 % of the mean of those of the reference standards. In addition, the major ions (those with relative abundance > 50 %) in the mass spectrum of the reference standard should be present in that of the sample eluted at the same retention time as the standard. Furthermore a matching of the sample mass spectrum with reference to that of the reference compound

should give a PROB value of ≥ 50. Quantification of an SEOC in a sample would only be proceeded if the RT and RRT of the respective sample peak satisfied all the afore-mentioned requirements.

Besides satisfying the above-mentioned requirements of RT and RRT, the ratios of the primary and secondary quantification ions should agree within ± 30% with the reference values as obtained from the calibration standards if GC/MS was used for quantification. The response for all four classes of SEOC were found to be linear for the calibration range of 1 – 20 for AHs, 0.01 – 0.5 for PAHs, 1 – 50 for FAs (as methyl esters of FAs) and 1 – 10 μg/mL for ROHs (as trimethyl silyl derivatives), with R^2 of 0.995 or better.

Recovery and precision of the analytical procedures were estimated by carrying out replicate analyses of spiked filters (n = 5), each prepared by spiking a 47mm diameter blank quartz filters with 100 μL of 50 μg/mL of mixed AHs standard, with 100 μL of 2.5 μg/mL of mixed PAHs standard, with 100 μL of 100 μg/mL of mixed FAs (as methyl esters) standard and with 100 μL of 25 μg/mL of mixed ROHs (as trimethylsilylethers) standard. The average recoveries of spiked filters were in the range of 85-115% (RSD < 10%).

The most relevant certified reference material identified for evaluation of the developed protocol for the measurement of SEOC is SRM 1649a urban dust that was characterized by NIST and which contains certified values of its PAHs content. Details of the method validation work for examination of SEOC was reported previously[21] and would not be

elaborated in this report. Table 3 summarises the recoveries of PAHs from a certified reference material, SRM1649a Urban Dust.

The total yield of SEOC is defined as the sum of the weight of organic compounds extracted from the four fractions. The unresolved complex mixture (UCM) containing unresolved branched and cyclic hydrocarbons eluted in the AHs fraction was calculated by quantification of the total response (peak area) of the UCM with reference to the average response factors of the calibration standards of AHs. As standards of 1-pentacosanol (C25) and 1-nonacosanol (C29) are not commercially available, the concentrations of C25, C29 were calculated from average RF of C24 and C26, C28 and C30, respectively.

Results and Discussion

Four composite seasonal samples were collected from each of the sampling locations. The total dust loading and total volume of air sampled for the composite samples are summarised in Table 4.

Yields

The total yield of SEOC was found to range from 125 to 2060 ng/m^3. Table 5 illustrates that total yield of identified SEOC accounts for 2.4 to 5.2 % of total carbon (TC) and 3.1 to 10.6 % of organic carbon (OC). The concentrations of various classes of SEOC and compositions of SEOC in the collected PM2.5 samples are summarized in Table 5 and Figure 3. The total yield of SEOC at the rural site, HT and roadside site at MK was found to be lowest and the highest amongst the three selected sites as expected. The

concentrations of total SEOC in PM2.5 aerosols at HT fall in the similar range reported by Fang[15] for a sub-urban seaside site in Hong Kong. The yields of SEOC at three sites show seasonal variation with higher concentration of SEOC detected in winter and lower concentration in summer.

The major components of SEOC at three sites are UCM (unresolved complex mixture contains branched and cyclic hydrocarbons) and FAs accounting for 32-71% and 23-56% of the total SEOC respectively. Resolved AHs, ROHs and PAHs are minor fractions at percentage 5-21%, 0-5% and 1-3%, respectively. The composition of SEOC at MK was found to show little seasonal variation indicating that the sources of SEOC are fairly constant in MK. However, a clear seasonal variation of SEOC is noted for the HT site with higher concentrations of FAs and lower concentrations of AHs and PAHs found in the summer aerosols.

n-Alkanes

The yields of individual AHs are summarized in Table 6 and the total of AHs (Σ AHs) was found to range from 54.0-1510 ng/m^3. The patterns and seasonal variations of AHs at three sites were depicted in Figure 4. The yield of n-alkanes with carbon number 16 to 38 and UCM was found to range 14.6-128 ng/m^3 and 39.4-1380 ng/m^3. Similar to the yields of SEOC, concentrations of AHs are higher in winter and lower in summer and the yields of AHs are highest at MK and lowest at HT.

PAHs

PAHs with three rings to seven rings were identified in all of the filter samples. The concentration of total of PAHs (Σ PAHs) was found to range between 0.6 to 17.2 ng/m^3 and concentrations of individual PAHs are summarized in Table 7. The seasonal pattern of PAHs with highest concentration at MK in winter and lowest concentration at HT in summer is illustrated in Figure 5. The major components of particulate PAHs are phenanthrene, fluoranthene, pyrene, chrysene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene and benzo[ghi]perylene.

Fatty acids and alkanols

The individual concentrations of FAs are tabulated in Table 8 and total of FAs (Σ FAs) was found ranging from 41.6 - 520 ng/m^3. The highest FAs concentration was found in winter at MK and the lowest concentration at HT in summer. The concentrations of alkanols are summarized in Table 9 and Σ ROHs was found at 0 - 12.1 ng/m^3. The compositions of FAs and ROHs are illustrated at Figures 6 and 7. The strong even to odd predominance suggest that higher plant wax is source of ROHs in the atmospheric aerosols of Hong Kong.

Conclusion

Concentrations of SEOC in Hong Kong are in the range of 125 to 2060 ng/m^3. Highest concentration of SEOC were found in winter at the roadside site and the lowest

concentration at the rural site in summer. The UCM and FAs ranging from 32-71% and 23-56% of the total SEOC respectively are the most abundant components of SEOC. Other identified components include resolved AHs (5-21%), ROHs (0-5%) and PAHs (1-3%). It is worth to note that the sampling and analytical protocol adopted in the study is targeted mainly for the particle phase SEOC and would probably resulted in an underestimation of the gaseous and semi-volatile SEOC. This is evidenced by the absence or very low concentrations of low molecular weight SEOC in the collected samples.

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Table 1 Quantification ions for PAHs

Polynuclear aromatic hydrocarbons (PAHs)	Quantification ions	
	1st (Q1)	2nd (Q2)
Naphthlene (Naph)	152	153,151
Acenaphthylene (Acph)	152	153,151
Acenaphthene (Acen)	154	154,152
Fluorene (Fluo)	166	167,165
Phenanthrene (Phen)	178	179,176
Anthracene (Anth)	178	179,176
2-Methylphenanthrene (2Mephen)	192	192,165
1-Methylphenanthrene (1Mephen)	192	192,165
Fluoranthene (Flut)	202	200,101
Pyrene (Pyre)	202	200,101
2-Methylfluoranthene (2Meflut)	216	215,189
2-Methylpyrene (2Mepyre)	216	215,189
Benz[a]anthracene (Bant)	228	226,114
Chrysene (Chry)	228	226,113
Benzo[b]fluoranthene (Bbfl)	252	250,126
Benzo[k]fluoranthene (Bkfl)	252	250,126
Benzo[e]pyrene (Bepy)	252	250,125
Benzo[a]pyrene (Bapy)	252	250,126
Perylene (Pery)	252	250,126
1,3,5-Triphenylbenzene (135Tb)	306	307,289
Indeno[1,2,3-cd]pyrene (Inpy)	276	274,138
Dibenz[a,h]anthracene (Daan)	278	276,139
Benzo[g,h,i]perylene (Bgpe)	276	274,138
Coroene (Coro)	300	298,150
Naphthlene-D_8	136	135,137
Acenaphthalene-D_{10}	164	162,160
Phenanthrene-D_{10}	188	190,186
Chryene-D_{12}	240	236,120
Perylene-D_{12}	264	265,260

Table 2 Quantification ions for ROHs

Alkanol as trimethylsilyl ethers	Quantification ions	
	1st (Q1)	2nd (Q2)
1-Decanol (C10)	215	216, 217
1-Undecanol (C11)	229	230, 231
1-Dodecanol (C12)	243	244, 245
1-Tridecanol (C13)	257	258, 259
1-Tetradecanol (C14)	271	272, 273
1-Pentadecanol (C15)	285	286, 287
1-Hexadecanol (C16)	299	300, 301
1-Heptadecanol (C17)	313	314, 315
1-Octandecanol (C18)	327	328, 329
1-Nonadecanol (C19)	341	342, 343
1-Eicosanol (C20)	355	356, 357
1-Heneicosanol (C21)	369	370, 371
1-Docosanol (C22)	383	384, 385
1-Tricosanol (C23)	397	398, 399
1-Tetracosanol (C24)	411	412, 413
1-Pentacosanol (C25)	425	426, 427
1-Hexacosanol (C26)	439	440, 441
1-Heptacosanol (C27)	453	454, 455
1-Octacosanol (C28)	467	468, 469
1-Nonacontanol (C29)	481	482, 483
1-Triacontanol (C30)	495	496, 497
n-Hexadecane-D_{34}	66	80
n-Eicoane-D_{42}	66	80
n-Tetracosane-D_{50}	66	80
n-Triacontane-D_{62}	66	80
n-Dotriacontane-D_{66}	66	80
n-Hexatriacontane-D_{74}	66	80

Table 3 Summary of the recoveries of PAHs from NIST reference standard SRM 1649a urban dust

PAHs	Certified concentrations[a] mg/kg	Mean recovery (RSD) / % (n = 6)
Phenanthrene (Phen)	4.14 ± 0.37	94 (6.2)
Anthracene (Anth)	0.432 ± 0.082	91 (5.9)
Fluoranthene (Flut)	6.45 ± 0.18	79 (5.7)
Pyrene (Pyre)	5.29 ± 0.25	87 (5.3)
Benz[a]anthracene (Bant)	2.21 ± 0.073	86 (6.3)
Chrysene (Chry)	3.049 ± 0.060	94 (3.3)
Benzo[b]fluoranthene (Bbfl)	6.45 ± 0.64	99 (4.2)
Benzo[k]fluoranthene (Bkfl)	1.913 ± 0.031	85 (9.3)
Benzo[e]pyrene (Bep)	3.09 ± 0.19	94 (7.4)
Benzo[a]pyrene (Bap)	2.509 ± 0.087	95 (2.4)
Perylene (Pery)	0.646 ± 0.075	90 (2.8)
Indeno[1,2,3-cd] pyrene (Inpy)	3.18 ± 0.72	91 (9.2)
Dibenz[a,h]anthracene (Daan)	0.288 ± 0.023	87 (4.2)
Benzo[g,h,i]perylene (Bgpe)	4.01 ± 0.91	87 (7.6)

[a] Certified concentrations were quoted from the certificate provided by the National Institute of Science and Technology, USA.

Table 4 Total dust loading and number of composite filters (Days 1& 3) for determination of SEOC

			Total no. of filters	Total dust loading / mg	Total volume of air sampled / m^3
HT	Winter	12-Nov-2000 to 13-Mar-2001	80	14.45	480.0
	Spring	17-Mar-2001 to 16-May-2001	38	5.44	228.0
	Summer	19-May-2001 to 20-Sep-2001	77	7.31	462.0
	Fall	21-Sep-2001 to 31-Oct-2001	26	4.31	156.0
TW	Winter	12-Nov-2000 to 13-Mar-2001	76	19.94	457.0
	Spring	17-Mar-2001 to 16-May-2001	38	7.57	228.5
	Summer	19-May-2001 to 20-Sep-2001	78	13.32	469.0
	Fall	21-Sep-2001 to 31-Oct-2001	26	5.86	156.3
MK	Winter	12-Nov-2000 to 13-Mar-2001	79	32.49	473.1
	Spring	17-Mar-2001 to 16-May-2001	38	13.19	228.5
	Summer	19-May-2001 to 20-Sep-2001	78	25.46	468.8
	Fall	21-Sep-2001 to 31-Oct-2001	26	9.32	155.9

Table 5 Concentration and composition of various form of carbons in PM2.5 samples

	Total Carbon (TC) / μg m^{-3}	Organic Carbon (OC) / μg m^{-3}	THC yield / μg m^{-3}	SEOC yield / ng m^{-3}			**Total AHs** yield / ng m^{-3}	**Resolved AHs** yield / ng m^{-3}	**UCM** yield / ng m^{-3}	CPI	C_{max}	U:R	**PAHs** yield / ng m^{-3}	**FAs** yield / ng m^{-3}	CPI	C_{max}	**ROHs** yield / ng m^{-3}	CPI	C_{max}
			THC /OC %		***SEOC /TC %***	***SEOC /OC %***	***AHs /SEOC %***	***R-AHs /SEOC %***	***UCM /SEOC %***				***PAHs /SEOC %***	***FAs /SEOC %***			***ROHs /SEOC %***		
HT																			
Winter	7.7	5.8	0.44	184			127	38.3	88.8	1.33	29	2.3	6.3	41.6	5.8	16	8.7	10.2	30
			7.6		***2.4***	***3.1***	***69.3***	***20.9***	***48.4***				***3.4***	***22.6***			***4.7***		
Summer	3.3	2.6	0.23	125			54.0	14.6	39.4	1.50	29	2.7	0.6	70.2	6.6	16	0.0	–	–
			8.8		***3.8***	***4.9***	***43.3***	***11.7***	***31.6***				***0.5***	***56.3***			***0.0***		
TW																			
Winter	17.2	10.7	0.82	640			415	77.3	338	1.26	25	4.4	12.1	201	8.9	16	11.1	10.3	30
			7.7		***3.7***	***6.0***	***65.0***	***12.1***	***52.9***				***1.9***	***31.4***			***1.7***		
Summer	12.3	6.2	0.96	461			304	38.5	265	1.31	25	6.9	4.0	148	10.2	16	4.6	10.0	30
			15.5		***3.7***	***7.4***	***66.0***	***8.4***	***57.6***				***0.9***	***32.1***			***1.0***		
MK																			
Winter	39.3	19.3	3.62	2060			1510	128	1380	1.26	25	10.8	17.2	520	12.6	18:1	12.1	10.4	30
			18.8		***5.2***	***10.6***	***73.3***	***6.2***	***67.1***				***0.8***	***25.3***			***0.6***		
Summer	36.4	14.4	2.50	1510			1140	69.2	1070	1.37	25	15.4	10.0	356	12.6	18:1	2.4	44.7	18
			17.4		***4.1***	***10.4***	***75.5***	***4.6***	***70.9***				***0.7***	***23.6***			***0.2***		

THC = Total weight of extractable organic compounds before column cleanup
SEOC = Sum of yields of four fractions, AHs, PAHs, FAs and ROHs

Table 6 Concentrations (ng m^{-3}) of aliphatic hydrocarbons (AHs) in HT, TW and MK in Hong Kong

AHs	HT				TW				MK			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
n-Tetradecane nC14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
n-Pentadecane nC15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
n-Hexadecane nC16	0.17	0.50	0.51	0.23	0.64	0.66	0.80	0.32	1.01	1.05	1.17	1.10
n-Heptadecane nC17	1.54	1.28	0.95	0.81	1.54	1.54	1.46	0.92	2.19	1.74	1.94	1.89
Pristane	1.68	1.72	1.20	0.63	1.90	1.62	1.24	0.74	1.99	1.61	1.32	0.96
n-Octadecane nC18	1.81	1.94	0.99	0.89	2.16	1.88	1.53	0.96	2.67	2.42	1.87	2.04
Phytane	1.13	1.01	0.61	0.62	1.32	0.99	0.63	0.52	1.64	1.17	0.71	0.86
n-Nonadecane nC19	1.89	2.28	0.75	0.67	2.08	2.19	1.19	0.87	3.38	3.04	1.61	1.92
n-Eicosane nC20	1.90	1.44	0.60	0.51	2.73	2.04	1.19	0.73	5.06	3.44	2.29	1.96
n-Heneicosane nC21	1.53	0.92	0.54	0.32	3.07	1.73	1.22	0.32	7.59	4.22	3.05	1.94
n-Docosane nC22	1.35	0.89	0.46	0.26	4.30	1.95	1.35	0.73	10.3	5.18	3.78	2.78
n-Tricosane nC23	1.43	0.87	0.31	0.45	5.47	2.30	1.49	1.11	11.2	6.12	4.41	3.44
n-Tetracosane nC24	1.71	0.81	0.27	0.51	6.59	2.36	1.80	1.21	11.7	5.68	5.10	4.02
n-Pentacosane nC25	2.29	0.95	0.48	0.48	7.30	3.74	2.74	1.51	13.9	6.90	6.43	5.65
n-Hexacosane nC26	2.35	1.16	0.47	0.65	6.58	3.56	2.76	1.73	10.0	5.34	4.80	6.12
n-Heptacosane nC27	2.79	1.65	0.57	1.12	6.13	3.78	2.86	2.03	8.11	5.27	5.60	7.37
n-Octacosane nC28	1.93	1.81	0.59	1.62	3.56	2.86	2.03	2.00	7.23	4.05	3.60	6.17
n-Nonacosane nC29	3.14	2.26	2.55	2.11	5.78	4.15	3.96	2.70	7.05	4.57	5.08	7.64
n-Triacontane nC30	1.50	1.36	0.49	1.48	2.65	2.02	1.56	1.48	2.44	2.02	2.00	3.93
n-Hentricontane nC31	3.14	1.83	0.82	2.48	5.53	4.85	3.03	4.08	8.55	6.45	6.09	10.4
n-Dotriacontane nC32	1.20	0.72	0.33	0.79	1.68	1.50	1.53	1.31	3.30	2.80	2.64	1.98
n-Tritriacontane nC33	1.75	0.76	0.44	1.39	3.26	2.97	2.19	2.49	6.44	5.31	4.61	6.72
n-Tetratriacontane nC34	0.64	0.54	0.23	0.52	1.19	1.05	0.78	0.50	1.34	0.69	1.05	BDL
n-Pentatriacontane nC35	0.46	0.30	0.19	0.40	0.84	0.72	0.43	0.49	0.81	BDL	BDL	BDL
n-Hexatriacontane nC36	0.32	0.29	0.10	0.29	0.49	0.62	0.31	0.34	BDL	BDL	BDL	BDL
n-Heptatriacontane nC37	0.30	0.18	0.06	0.23	0.25	0.57	0.22	0.31	BDL	BDL	BDL	BDL
n-Octatriacontane nC38	0.34	0.26	0.06	0.24	0.28	0.65	0.18	0.24	BDL	BDL	BDL	BDL
n-Nonatriacontane nC39	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
n-Tetracontane nC40	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
UCM	88.8	48.0	39.4	45.8	338	607	265	165	1379	1150	1068	815

*Trace AHs were identified in field blanks with concentration below detection limit. Method detection limit = 0.02μg/batch sample

Table 7 Concentrations (ng m^{-3}) of polycyclic aromatic hydrocarbons (PAHs) in HT, TW and MK in Hong Kong

PAHs	HT				TW				MK			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Naphthalene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Acenaphthylene	BDL	BDL	BDL	BDL	0.006	0.007	0.004	0.005	0.034	0.032	0.029	0.038
Acenaphthene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Fluorene	0.002	BDL	BDL	BDL	0.002	BDL	BDL	BDL	0.010	0.008	0.014	0.004
Phenanthrene	0.201	0.058	0.014	0.042	0.227	0.133	0.117	0.093	0.515	0.584	0.615	0.597
Anthracene	0.008	0.004	0.001	0.004	0.011	0.009	0.009	0.007	0.034	0.045	0.051	0.044
2-Methylphenanthrene	0.041	0.017	0.008	0.023	0.066	0.051	0.052	0.035	0.220	0.283	0.306	0.239
1-Methylphenanthrene	0.026	0.010	0.002	BDL	0.043	0.035	0.031	0.031	0.141	0.157	0.167	0.139
Fluoranthene	0.428	0.168	0.044	0.228	0.603	0.354	0.346	0.376	1.586	1.592	1.592	1.404
Pyrene	0.353	0.153	0.036	0.218	0.551	0.416	0.405	0.153	2.206	3.321	3.160	1.928
2-Methylfluoranthene	0.021	BDL	BDL	BDL	0.035	0.021	0.022	0.018	0.136	0.123	0.124	0.099
1-Methylpyrene	0.024	BDL	BDL	BDL	0.062	0.047	0.063	0.030	0.349	0.419	0.431	0.287
Benz[a]anthracene	0.095	0.028	0.007	0.045	0.284	0.198	0.201	0.124	0.812	0.568	0.387	0.407
Chrysene	0.215	0.087	0.021	0.123	0.503	0.393	0.319	0.294	1.031	0.810	0.528	0.650
Benzo[e]pyrene	0.651	0.336	0.060	0.415	1.388	0.754	0.445	0.677	1.820	2.062	0.587	1.379
Benzo[b]fluoranthene	0.878	0.322	0.047	0.397	1.965	0.841	0.441	0.683	2.267	1.974	0.493	1.228
Benzo[k]fluoranthene	0.777	0.416	0.076	0.054	1.439	0.804	0.436	0.743	1.594	1.745	0.447	1.315
Benzo[a]pyrene	0.454	0.151	0.031	0.337	0.950	0.450	0.341	0.515	1.280	1.342	0.385	0.989
Perylene	0.038	0.052	0.002	0.072	0.089	0.097	0.059	0.099	0.153	0.168	0.069	0.169
1,3,5-Triphenylbenzene	0.470	0.075	0.012	0.082	0.793	0.128	0.124	0.307	0.714	0.282	0.140	0.404
Dibenz[a,h]anthracene	BDL	BDL	BDL	BDL	0.110	0.053	0.022	0.058	0.073	0.068	BDL	0.064
Benzo[ghi]perylene	0.465	0.290	0.062	0.339	1.114	0.572	0.267	0.646	0.847	0.963	0.214	0.789
Indeno[1,2,3-cd]pyrene	0.979	0.600	0.131	0.661	1.624	0.854	0.400	1.179	1.237	1.303	0.200	0.960
Coroene	0.136	0.140	0.018	0.137	0.254	0.177	0.040	0.241	0.109	0.111	0.018	0.102

*Trace PAHs were identified in field blanks with concentration below detection limit. Method detection limit = 0.002μg/batch sample

Table 8 Concentrations (ng m^{-3}) of fatty acids (FAs) in HT, TW and MK in Hong Kong

FAs	HT				TW				MK			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Octanoic acid (8:0)	0.75	1.00	0.72	BDL	2.19	1.75	1.57	3.19	3.37	2.67	2.78	4.67
Nonanoic acid (9:0)	0.87	0.84	0.82	1.23	3.32	1.56	1.49	3.26	4.45	3.26	2.68	5.80
Decanoic acid (10:0)	0.68	BDL	0.61	BDL	1.21	BDL	0.87	1.28	1.32	0.98	1.08	1.43
Undecanoic acid (11:0)	0.40	BDL	BDL	BDL	0.45	BDL	BDL	3.06	0.53	BDL	1.04	2.22
Dodecanoic acid (12:0)	1.16	1.07	1.27	1.68	2.46	1.63	1.98	2.51	3.31	1.95	2.51	4.10
Tridecanoic acid (13:0)	0.41	BDL	0.51	BDL	0.86	BDL	0.51	BDL	1.09	BDL	0.66	BDL
Myristoleic acid (14:1)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Tetradecanoic acid (14:0)	2.96	5.23	4.03	5.95	8.37	7.59	6.40	8.35	11.76	8.61	7.87	9.53
Pentadecanoic acid (15:0)	2.23	3.11	1.65	4.51	3.64	4.14	4.07	5.09	4.14	4.11	4.15	4.70
Palmitoleic acid (16:1)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	4.66	1.20	3.11	BDL
Hexadecanoic/Palmitic acid (16:0)	20.6	31.3	25.5	34.9	81.0	75.6	65.3	83.2	149	135	110	133
Heptadecanoic acid (17:0)	0.76	1.21	1.08	1.76	2.45	2.39	1.95	2.57	4.13	3.48	2.80	3.30
Linoleic acid (18:2)	BDL	BDL	BDL	BDL	4.90	1.56	6.33	0.23	43.8	14.8	34.1	5.76
cis-9-Octadecanoic/Oleic acid (18:1)	0.26	0.76	0.52	0.31	27.2	7.15	25.0	2.80	180	96.9	128	22.1
Octadecanoic acid (18:0)	5.29	12.5	13.3	11.9	34.4	29.1	21.4	28.1	56.7	52.1	37.7	47.1
Nonadecanoic acid (19:0)	BDL	BDL	0.29	BDL	0.47	BDL	0.24	BDL	0.45	0.53	0.33	BDL
cis-5,8,11,14-Eicosatetraenoic/Arachidonic acid (20:4)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Eicosenoic acid (20:1)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2.77	1.12	1.25	BDL
Arachidic acid (20:0)	0.25	0.69	1.45	1.17	3.47	2.33	1.79	2.75	6.70	5.54	3.87	4.82
Heneicosanoic acid (21:0)	BDL	BDL	0.53	BDL	0.74	BDL	0.25	BDL	1.02	0.51	0.31	BDL
Erucic acid (22:1)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
cis-4,7,10,13,16,19-docosahexaenic acid (22:6)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Docosanoic acid (22:0)	0.49	1.34	2.71	2.24	4.54	2.41	2.04	3.73	19.3	5.52	3.98	6.03
Tricosanoic acid (23:0)	0.23	0.56	1.43	1.12	1.84	0.72	0.47	1.39	1.95	0.98	0.59	1.37
Nervonic acid (24:1)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Tetracosanoic/lignoceric acid (24:0)	0.63	1.36	3.72	2.71	4.99	1.85	1.53	3.53	6.06	3.34	2.29	4.27

Table 8 – cont'd

Pentacosanoic acid (25:0)	0.23	0.44	0.92	0.86	1.08	0.44	0.33	0.96	1.13	0.54	0.31	1.26
Hexacosanoic acid (26:0)	0.61	1.08	2.14	1.87	2.91	1.20	0.97	2.42	2.84	1.64	1.03	2.10
Heptacosanoic acid (27:0)	0.26	0.47	0.61	0.82	0.72	0.48	0.35	0.94	0.81	0.46	0.33	0.79
Octacosanoic acid (28:0)	1.01	1.88	2.45	3.14	3.14	2.03	1.52	3.73	3.20	2.43	1.49	3.60
Nonacosanoic acid (29:0)	0.33	0.56	0.66	1.01	0.79	0.57	0.38	1.12	0.83	0.67	0.39	1.08
Tricontanoic acid (30:0)	0.87	1.24	2.63	2.85	3.08	1.24	1.07	3.26	3.18	1.56	1.09	2.95
Hentricontanoic acid (31:0)	0.33	0.64	0.64	1.12	0.71	0.66	0.39	1.19	0.72	0.73	0.37	1.13

*Trace FAs 16:0 and 18:0 were identified in field blanks with concentration below detection limit. Method detection limit = 0.1μg/batch sample

Table 9 Concentrations (ng m^{-3}) of alkanols (ROHs) in HT, TW and MK in Hong Kong

	HT				TW				MK			
ROHs	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
1-Decanol C10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1-Undecanol C11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1-Dodecanol C12	0.21	0.33	BDL	BDL	0.10	0.17	BDL	BDL	0.14	0.14	BDL	BDL
1-Tridecanol C13	0.10	0.13	BDL	BDL	0.09	BDL	0.07	BDL	0.07	BDL	BDL	0.22
1-Tetradecanol C14	0.14	0.21	BDL	BDL	0.18	0.12	0.08	BDL	0.30	0.19	BDL	BDL
1-Pentadecanol C15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.06	BDL	BDL	BDL
1-Hexadecanol C16	0.62	0.51	BDL	BDL	0.74	0.29	0.47	BDL	1.84	0.76	0.54	0.89
1-Heptadecanol C17	BDL	BDL	BDL	BDL	BDL	0.22	BDL	BDL	BDL	0.14	BDL	0.59
1-Octandecanol C18	0.37	0.72	BDL	BDL	0.54	0.36	0.24	0.19	1.59	1.06	0.84	0.96
1-Nonadecanol C19	BDL	BDL	BDL	BDL	BDL	0.26	BDL	0.13	BDL	0.10	BDL	0.50
1-Eicosanol C20	0.22	0.13	BDL	BDL	0.27	0.12	0.16	BDL	0.25	0.22	0.08	0.18
1-Heneicosanol C21	0.08	BDL	BDL	BDL	0.11	BDL	0.05	BDL	0.13	BDL	BDL	BDL
1-Docosanol C22	0.86	0.67	BDL	0.28	0.75	0.23	0.20	0.61	1.05	0.69	BDL	1.40
1-Tricosanol C23	0.18	BDL	BDL	BDL	0.20	BDL	0.06	BDL	0.22	BDL	BDL	BDL
1-Tetracosanol C24	1.19	0.31	BDL	0.17	1.38	0.19	0.34	0.37	1.49	0.37	0.15	0.61
*1-Pentacosanol C25***	0.13	BDL	BDL	BDL	0.16	BDL	0.05	BDL	0.16	BDL	BDL	BDL
1-Hexacosanol C26	1.15	0.30	BDL	0.10	1.09	0.14	0.45	0.23	0.92	0.28	0.18	0.45
1-Heptacosanol C27	0.13	BDL	BDL	BDL	0.17	BDL	0.07	BDL	0.17	BDL	BDL	BDL
1-Octacosanol C28	1.49	0.86	BDL	0.17	1.38	0.19	0.83	0.48	0.98	0.90	BDL	1.96
*1-Nonocosanol C29***	0.16	BDL	BDL	BDL	0.26	BDL	0.12	BDL	0.24	0.10	0.05	0.22
1-Triacontanol C30	1.68	0.64	BDL	0.15	3.70	0.20	1.42	0.55	2.45	1.07	0.52	3.05

*Trace ROHs were identified in field blanks with concentration below detection limit. Method detection limit = 0.04μg/batch sample

**concentration of C25 was calculated using the average RF of C24&C26, concentration of C29 was calculated using the average RF of C28&C30.

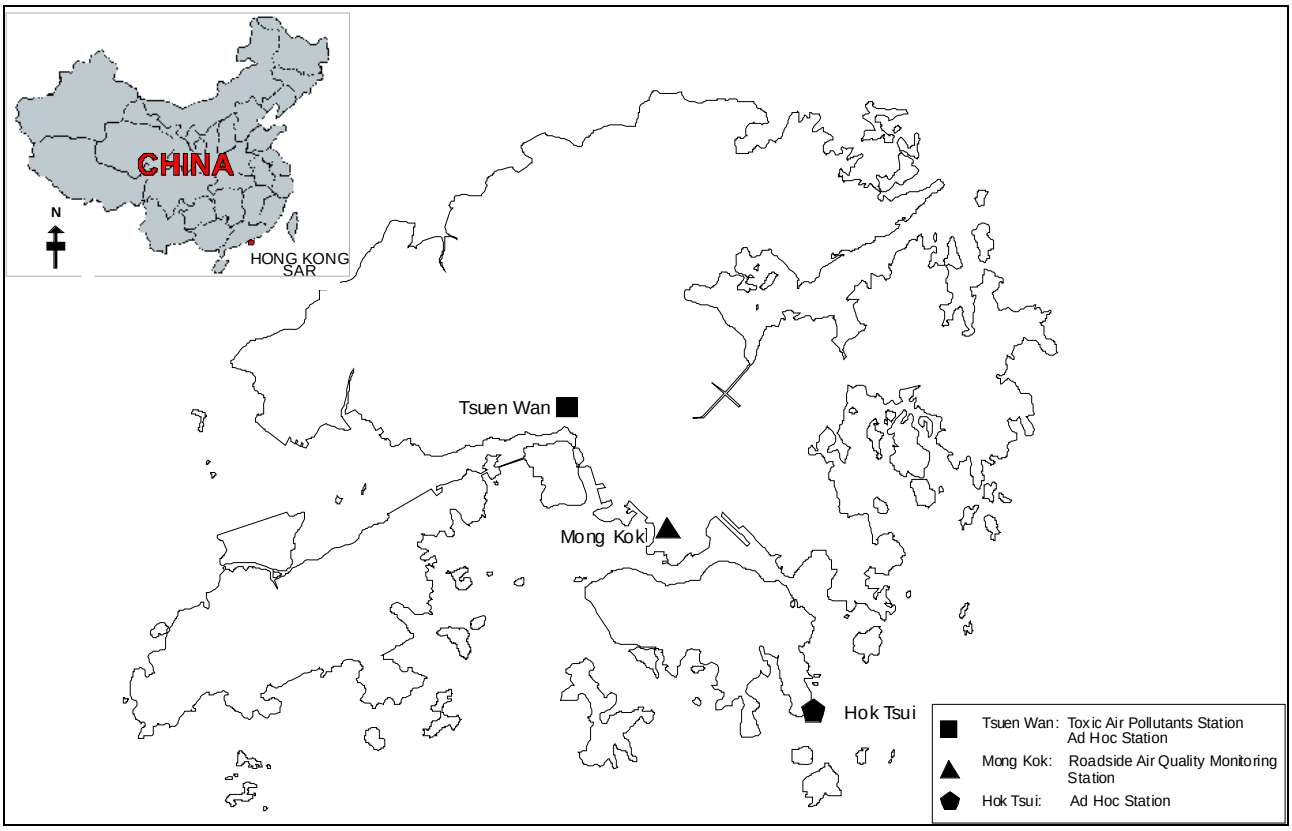
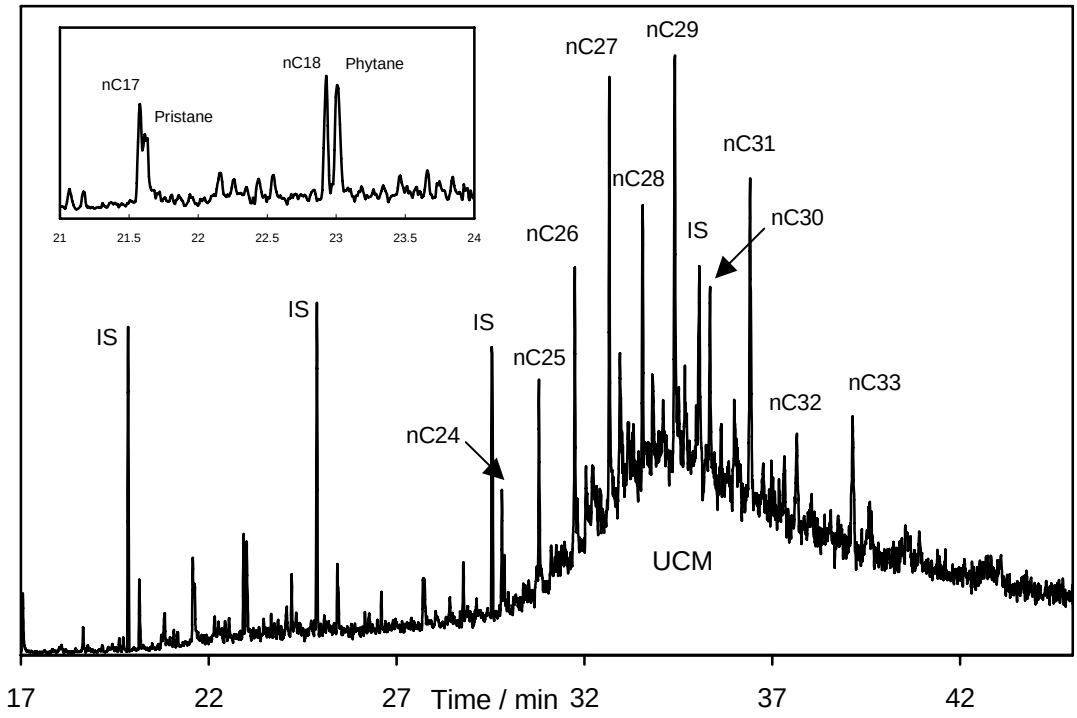
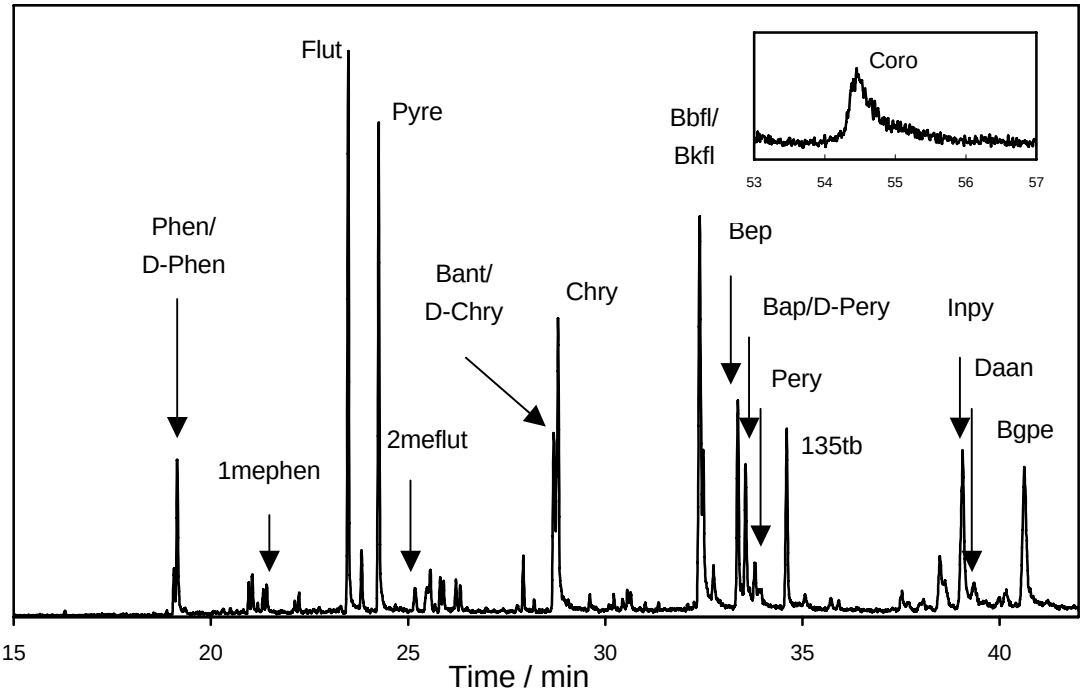

CHINA
N
HONG KONG SAR
Tsuen Wan
Mong Kok
Hok Tsui
Tsuen Wan: Toxic Air Pollutants Station Ad Hoc Station
Mong Kok: Roadside Air Quality Monitoring Station
Hok Tsui: Ad Hoc Station

Figure 2 GC/MS (total ion current TIC) chromatogram of four classes of SEOC, a), AHs, b) PAHs, c) FAs and d) ROHs found in the fine particulate matters collected at Mong Kok, Hong Kong. e) Selected ion chromatogram (m/z = 191) showing the presence of hopanes in the AHs fraction.

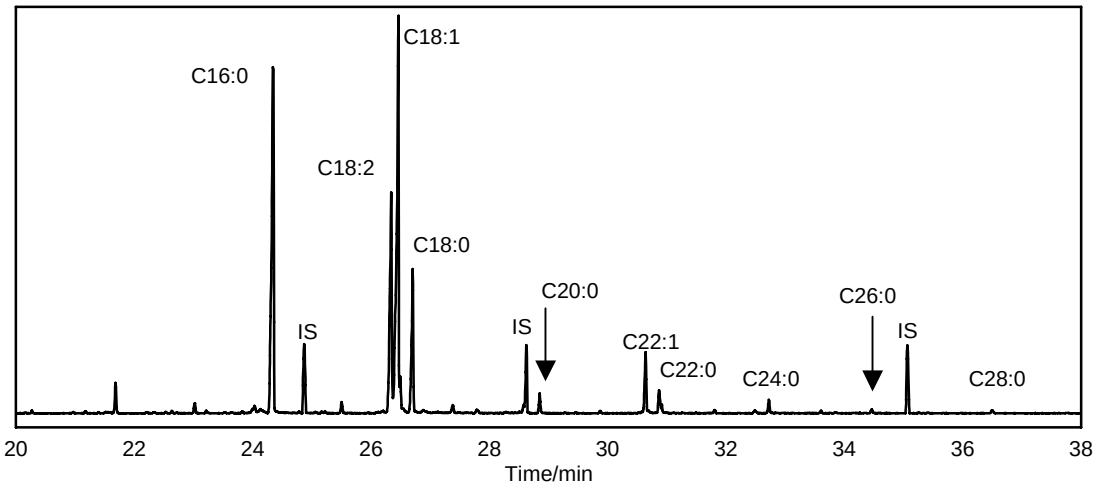
2a)



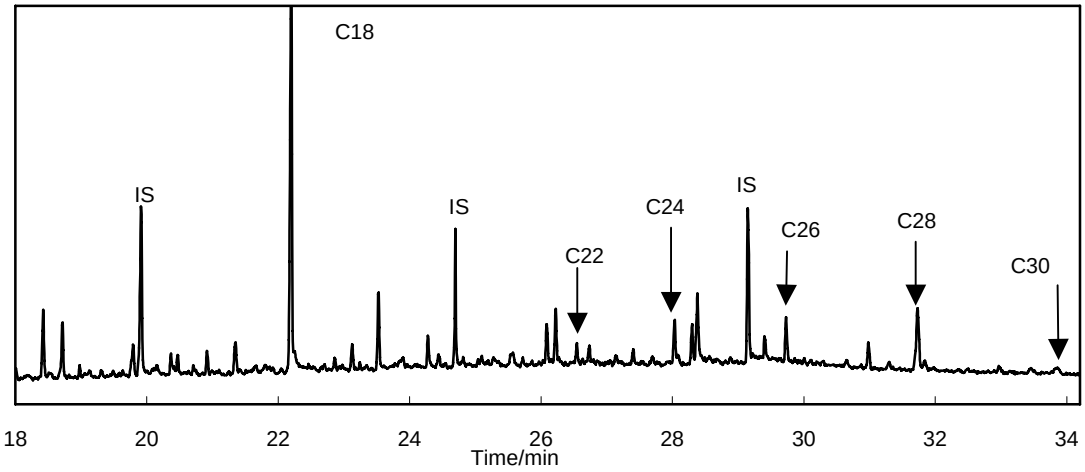
2b)



2c)


C16:0
C18:1
C18:2
C18:0
IS
IS
C20:0
C22:1
C22:0
C24:0
C26:0
IS
C28:0
20
22
24
26
28
30
32
34
36
38
Time/min

2d)


C18
IS
IS
C22
C24
IS
C26
C28
C30
18
20
22
24
26
28
30
32
34
Time/min

2e)

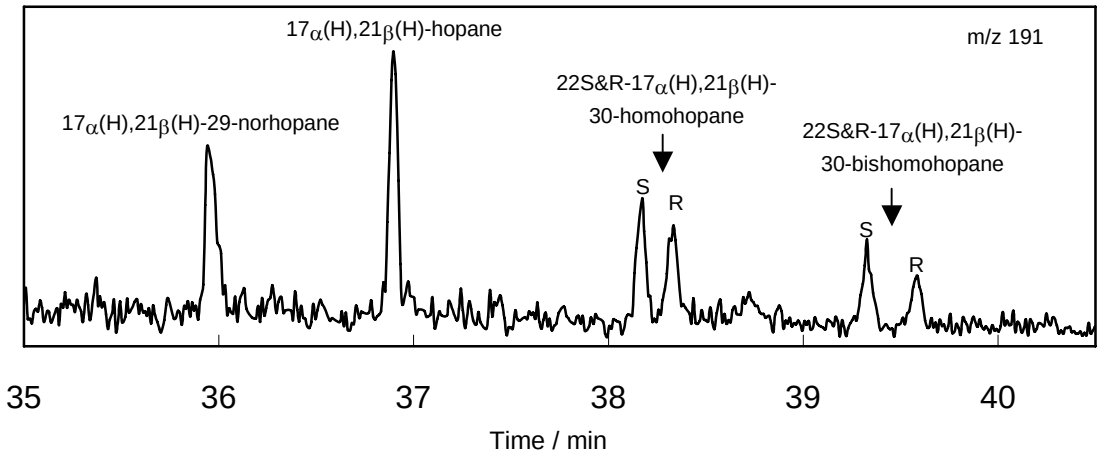
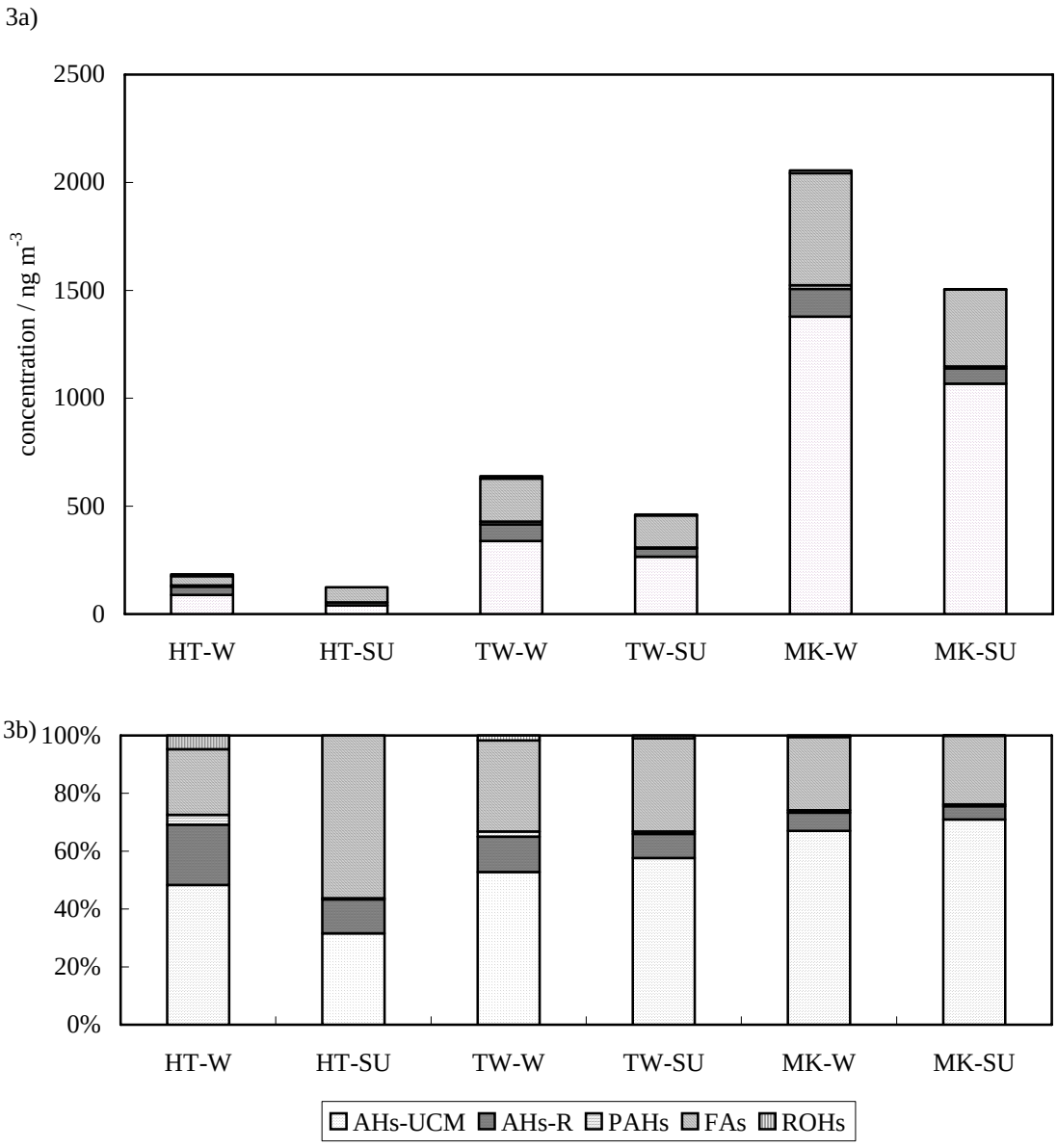

17α(H),21β(H)-hopane
m/z 191
17α(H),21β(H)-29-norhopane
22S&R-17α(H),21β(H)-
30-homohopane
22S&R-17α(H),21β(H)-
30-bishomohopane
S
R
S
R
35
36
37
38
39
40
Time / min

Figure 3 Concentration and relative composition of SEOC in fine at HT, TW and MK in 2000/01



HT = Hok Tsui;
TW = Tusen Wan;
MK = Mong Kok;
W = winter;
SU = summer
AHs-UCM = unresolved complex mixture
AHs-R = resolved aliphatic hydrocarbons
PAHs = polycyclic aromatic hydrocarbons
FAs =fatty acids
ROHs = alkanols

Figure 4 Concentration of AHs in fine particulate samples collected at HT, TW and MK in 2000/01

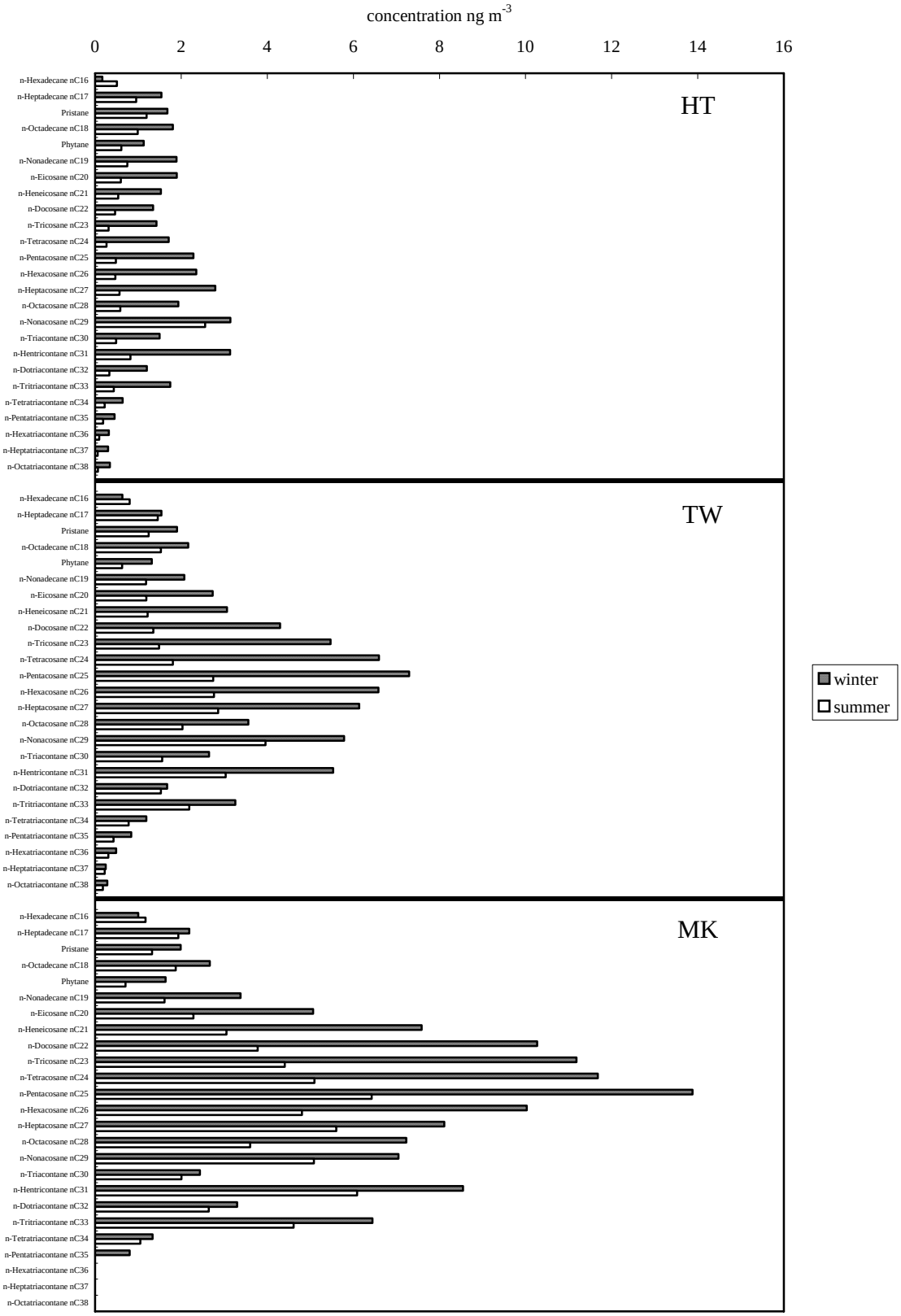


Figure 5 Concentration of PAHs in fine particulate samples collected at HT, TW and MK in 2000/01

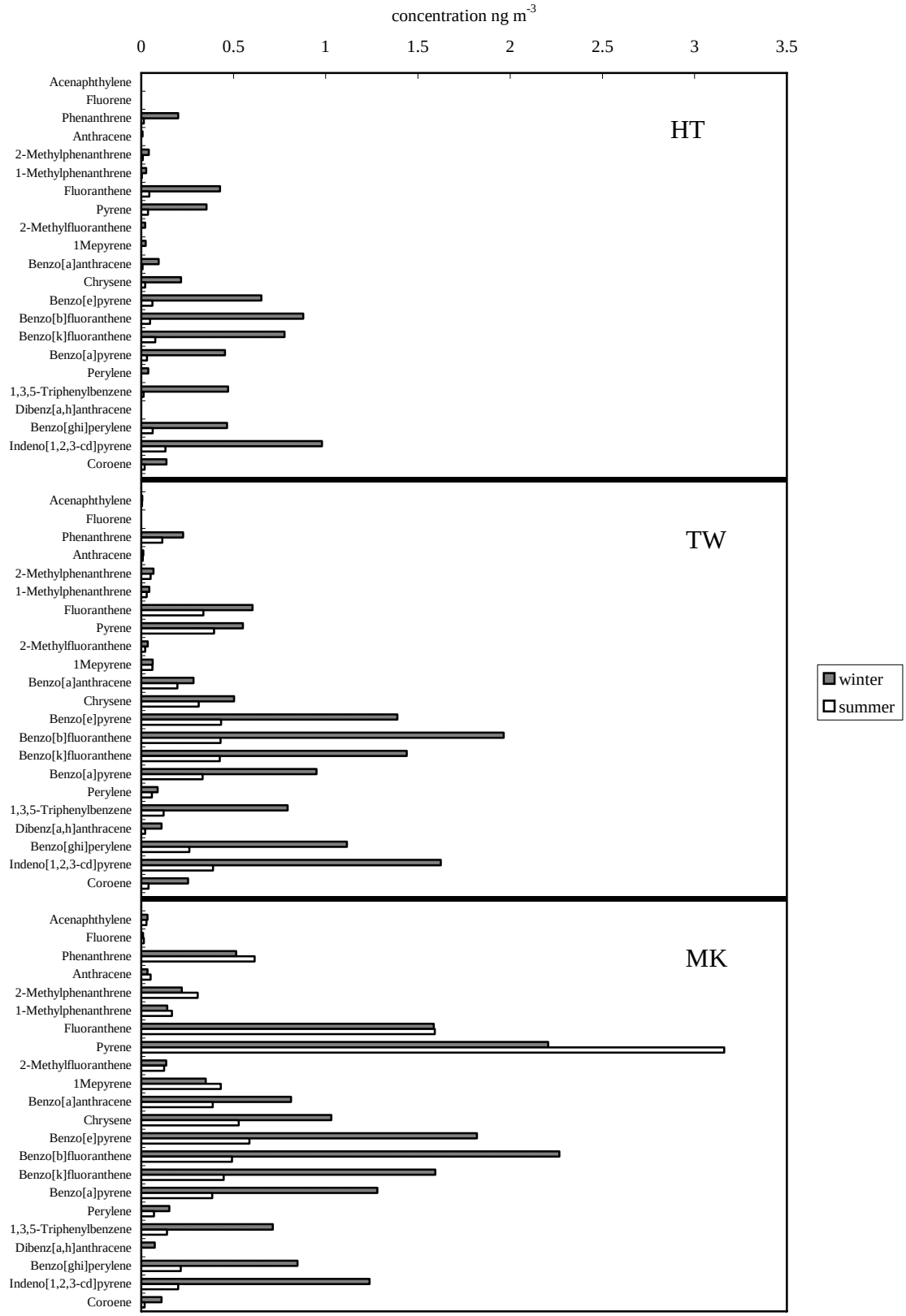


Figure 6 Concentration of FAs in fine particulate samples collected at HT, TW and MK in 2000/01

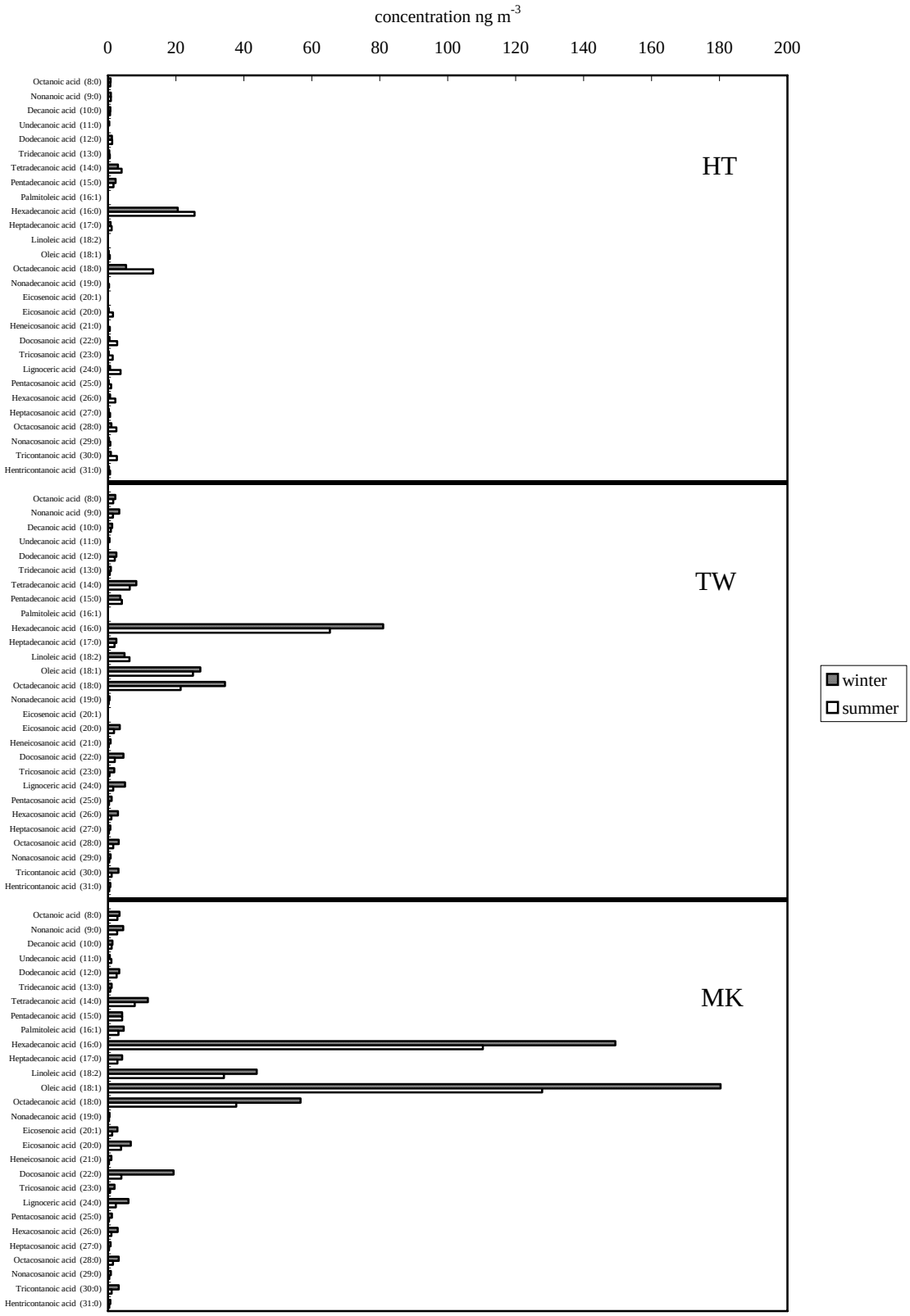
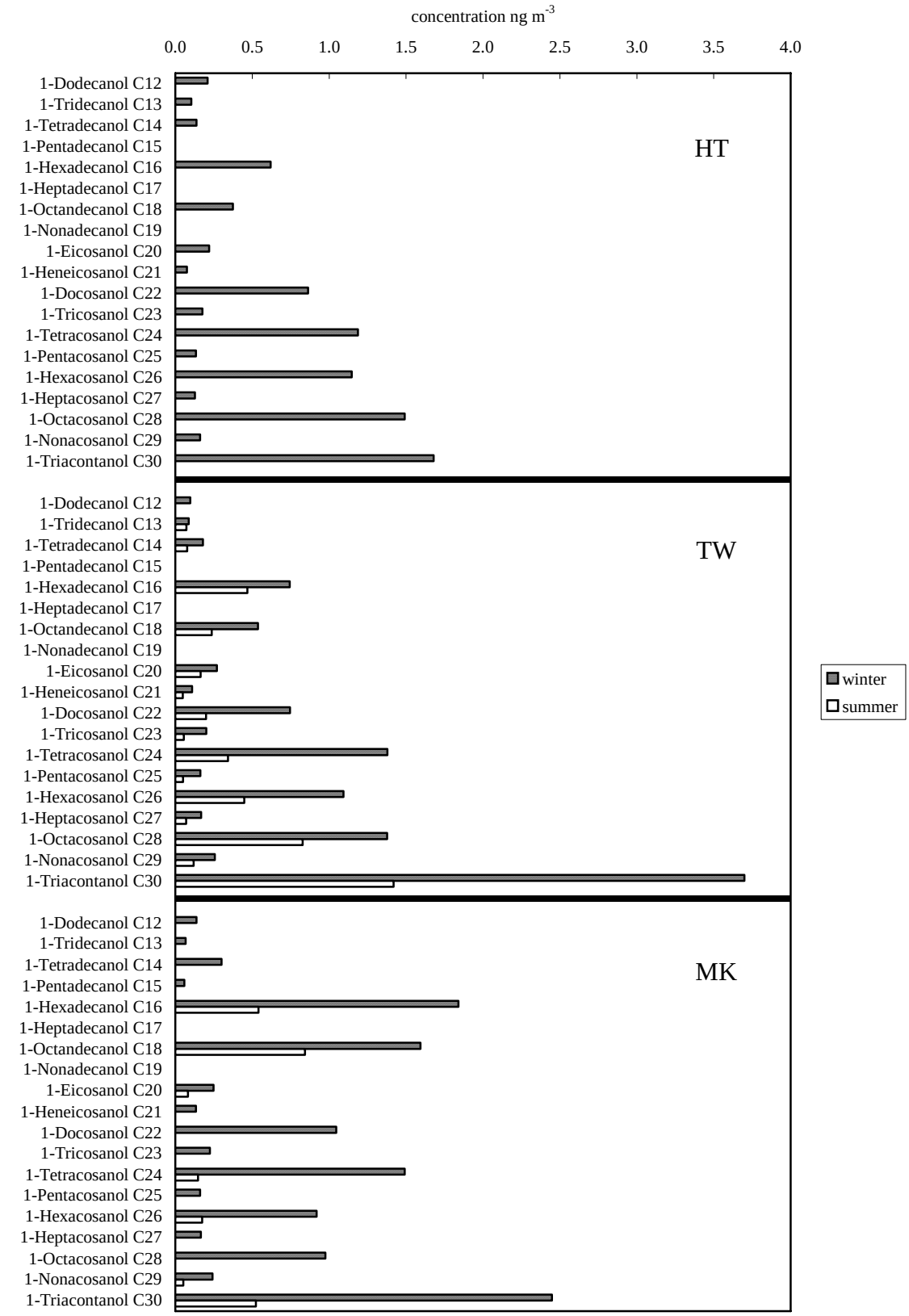


Figure 7 Concentration of ROHs in fine particulate samples collected at HT, TW and MK in 2000/01



Analytical Procedures for Determination of Total Extractable Hydrocarbons (THC) in Air Particulate (PM 2.5)

(* This procedure could not be reproduced without the prior written consent of the Government Chemist.)

Safety Precaution : This procedure involves volatile chemicals. Apply precautions as described in the Government Laboratory Safety Manual when handling such chemicals. For example, use eye and hand protection and where necessary carry out the work in a fume hood to avoid inhalation of vapours.

Introduction

Airborne particulates are collected on quartz filters by high-volume samplers or similar devices.

Loaded filters are extracted with distilled n-hexane, followed by toluene/iso-propanol 2:1 v/v by ultrasonic agitation..

The extracts are evaporated to dryness and the weights of the dried extracts are recorded as total extractable hydrocarbons (THC) extracted per weight of the sample filters analysed.

Reagents

All reagents and organic solvents used should be of analytical reagent grade or equivalent unless otherwise specified. All standards should be stored below 10°C or less and protect from light.

Spike Standard: standard liquid paraffin solution in n-hexane.

Weigh about 400 mg of liquid paraffin to the nearest 0.1 mg in a 100 mL volumetric flask and make up to the volume with n-hexane.

Solvents – Solvents used in the method include n-hexane, toluene and iso-propanol must be analytical reagent grade (or above) and distilled.

Apparatus

Ultrasonic agitator.

Filter papers, 90mm Dia., Whatman 42 or equivalent.

Glass boiling tubes and stoppers of appropriate sizes.

Stemless glass filter funnels of appropriate sizes.

Beakers of appropriate sizes.

Joint clips of appropriate sizes

Aluminium dishes, 100mL.

Procedures.

Prior to sample extraction, aluminium dishes, which have been pre-rinsed with cyclohexane, are conditioned in a climatic cabinet until constant weight ie. the difference between two measurements taken in consecutive days should not be greater than 0.07 mg.

Follow the Work Instruction for the operation procedures of the robotic weighing system for weight measurement of the aluminium dishes.

The mean weight of each clean dish is recorded and taken as the unloaded dish weight.

Cut the samples into small pieces and placed in a stoppered glass tube.

Add 30mL n-hexane to the glass tube. Stop the glass tube with stopper and clip.

Sonicate the filter samples for 30 minutes.

Filter the extract into another glass boiling tube.

Repeat the extraction procedures with 20mL of toluene/isopropanol (2:1 v/v).

Wash the residue with 10mL of toluene/isopropanol (2:1 v/v) and combine the extract.

The combined extract is transferred to an pre-weighed aluminium dish and evaporated to dryness on an aluminium foiled platform over a water bath.

The dried aluminium dish, loaded with THC, is conditioned inside the climatic cabinet until constant weight. The mean weight of the loaded dish is recorded and taken as the loaded dish weight.

The weight of the THC in each sampled filter is taken as the weight difference between the corresponding loaded and unloaded aluminium dish.

Repeat the above steps for the analysis of filter blank and reagent blank.

For blank spike determination, add 1 mL of standard liquid paraffin solution to blank filter and repeat steps 4.7 to 4.12.

Calculation/Result interpretation

Calculate the concentration of THC (*C*) in the sample in ng/m^3 as follows :

$$C = (Ws\text{-}Wsb) \times 1000000/F$$

where :

Ws = weight of THC in the sample filter in mg

Wsb = weight of THC in the blank filter paper (sb) in mg

F = total volume of air sampled in m^3

Quality control parameters

Detection limit : 0. 01 mg.

Precision (RSD) : less than 20 %.

Average recoveries for spiked blank filters : 94 % (RSD 14%), based on eleven replicate analysis.

Quality control plan:

6.4.1 Blank spike for every 20 samples, or every batch, whichever is the less.
6.4.2. Acceptance Limit for recovery of blank spike: ± 25 %.

Reference

***NIOSH Manual of Analytical Methods,* 2 nd Edition,** 5**, Method No. P&CAM 217.**

***Guidelines for PM-10 Sampling and Analysis Applicable to Receptor Modelling*, USEPA, EPA-452/R-94-009.**

Operating Procedures of the Robotic Weighing System, AC/MSWIs/5.

Characterization of Solvent Extractable Organic Compounds (SEOC) in Air Particulate (PM 2.5)

Safety Precautions: This method involves carcinogenic and toxic materials such as dichloromethane, BF_3/MeOH, BSTFA+1%TMCS. Apply precautions as described in the Code of Safe Practice of this Laboratory when handling such materials. Use eye goggles and hand gloves and where necessary carry out the work in a fume hood to avoid inhalation of vapor.

1. Introduction

1.1. A solvent extraction – gas chromatographic method has been developed for the measurement for four classes of solvent extractable organic compounds (SEOC) *viz* aliphatic hydrocarbons (AHs), polynuclear aromatic hydrocarbons (PAHs), fatty acids (FAs) and alkanols (ROHs), in ambient carbonaceous aerosols.

1.2. The developed method was validated by the analysis of reference urban dust SRM 1649a from the National Institute of Standards and Technology. The concentrations for selected polynuclear aromatic hydrocarbons in the reference dust were found to fall within the certified and reference concentrations.

1.3. This method includes the qualitative and quantitative analysis of the four classes of solvent extractable organic compounds collected on quartz filters by air samplers or similar devices followed by solvent extraction, column chromatographic cleanup and gas chromatography / mass spectrometry GC/MS and/or flame ionisation GC/FID analysis.

1.4. Solvents, reagents, glassware, and other sample processing hardware may yield artefacts and/or interference to sample analysis. All these materials must be demonstrated to be free from interference under the conditions of the analysis by analysing reagent blank.

2. Reagents

All reagents and organic solvents used should be of analytical reagent grade or equivalent unless otherwise specified. All standards should be stored below 10°C or less and protect from light.

2.1. Stock standards were prepared by quantitative dilution of appropriate volumes of the acquired mixed standard solutions using appropriate solvent or by dissolving appropriate amounts (about 50 mg each) of the concerned chemical standard in appropriate solvent, and then by serial dilution of the concentrated mixture solutions with appropriate solvent to the designated concentrations. Mixed stock standards of ROTMSs were prepared by derivatization of 1 mL of the stock standard solution of ROHs with 20 μL of 1% TMCS in BSTFA at a reaction temperature of 70°C for about half an hour.

2.2. Calibration standard solutions – At least five calibration standards should be prepared by dilution of stock standard solutions. One of the calibration standards

should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS and GC/FID systems.

2.3. Working standard solutions – working standard solutions were freshly prepared before analysis by quantitative dilution of appropriate volumes of stock mixture with appropriate solvents.

2.4. Internal standard solutions – Pre-deuteriated aliphatic and polynuclear aromatic hydrocarbons are suggested as internal standards for GC/MS analyses of AH and PAH fractions. For FAs and ROHs analyses, no suitable pre-deuteriated compound is commercially available. Pre-deuteriated aliphatic hydrocarbons were added to FAs and ROHs fractions prior to GC/MS and GC/FID analyses as injection standards. The standards are listed at follow:

Pre-deuteriated aliphatic hydrocarbons (D-AHs)
n-Hexadecane-D_{34}
n-Eicocane-D_{42}
n-Tetracosane-D_{50}
n-Triacontane-D_{62}
n-Dotriacontane-D_{66}
n-Hexatriacontane-D_{74}
Pre-deuteriated polynuclear aromatic hydrocarbons (D-PAHs)
Naphthalene-D_8
Acenaphthalene-D_{10}
Phenanthrene-D_{10}
Chryene-D_{12}
Perylene-D_{12}

2.5. Solvents – Solvents used in the method include dichloromethane, n-hexane, toluene, isopropanol and acetone must be analytical reagent grade (or above) and distilled. HPLC grade diethyl ether is used as received and water is deionized, distilled and washed with dichloromethane before used.

2.6. Derivatization reagents – Prior to the GC/MS and GC/FID analysis, fatty acids are esterified as methyl esters by boron trifluoride (BF_3) reagent in methanol and alkanols are derivatized as trimethylsilyl ethers by 1% trimethylchlorosilane in bis-(trimethylsilyl)-trifluoroacetamide (BSTFA+1%TMCS). The derivatization reagents are used as received.

2.7. Activated silica gel (Si), 100-200 mesh by baking at 400-500°C for at least 2 hrs.

2.8. Sodium sulfate (Na_2SO_4), anhydrous, analytical reagent grade or equivalent.

3. Apparatus

3.1. Ultrasonic agitator.

3.2. Filter papers, 90mm Dia., Whatman 42 or equivalent.

3.3. Glass boiling tubes and stoppers of appropriate sizes.

3.4. Stemless glass filter funnels of appropriate sizes.

3.5. Beakers of appropriate sizes.

3.6. Joint clips of appropriate sizes

3.7. Reaction vials of appropriate sizes.

3.8. Chromatographic column :
Pyrex, 1cm ID and 30cm length.

3.9. Gas chromatograph (GC) – An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

3.10. Mass spectrometer (MS) – Capable of scanning from 35 to 650 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

3.11. Frame ionisation detector (FID).

3.12. Column – 30 m x 0.25 mm ID, 0.25 μm film thickness silicone-coated fused-silica capillary column DB-5MS or equivalent. 30 m x 0.32 mm ID, 0.25 μm film thickness silicone-coated fused-silica capillary column HP-5 or equivalent.

3.13. Syringes of appropriate sizes.

3.14. Amber vials with glass inserts of appropriate sizes.

4. Procedures.

A) Solvent extraction of filters

4.1. Cut the filter samples into small pieces in a glass boiling tube.

4.2. Add 10μL of a 100ppm of pre-deuterated aliphatic hydrocarbon internal standard mixture and 10μL of a 10ppm pre-deuterated polynuclear aromatic hydrocarbons internal standard mixture to the filter samples.

4.3. Add 30mL n-hexane to the glass tube. Stop the glass tube with stopper and clip.

4.4. Sonicate the filter samples for 30 minutes.

4.5. Filter the extract into another glass boiling tube.

4.6. Repeat the extraction procedures with 20mL of toluene/isopropanol (2:1 v/v).

4.7. Wash the residue with 10mL of toluene/isopropanol (2:1 v/v) and combine the extract.

B) Esterification of fatty acids as methyl esters in SEOC

4.8. Reduce volume of the extract by a slow stream of N_2 to about 1mL and transfer to a reaction vial.

4.9. Add about 0.5mL BF_3/MeOH to the reaction vial with the SEOC extract. Tightly cap the vial and heat the mixture to about 85°C for half an hour.

4.10. Cool down the vial and decap carefully. Add 2mL dichloromethane-washed distilled water to quench the reaction for 2-5 mins.

4.11. Extract the mixture with 3 × 2mL dichloromethane and add small amount of anhydrous sodium sulphate to organic extract.

4.12. Transfer and combine the organic extract to another test tube. Concentrate the dichloromethane extracts to nearly dryness under an inert atmosphere of nitrogen.

4.13. Add 10mL n-hexane and re-concentrate the extract to about 1mL under a slow stream of nitrogen.

C) Fractionalization of solvent extractable organic compound (SEOC) by column chromatography

4.14. Pack a column with activated silica gel and n-hexane.

4.15. Pre-elute the column with 20mL n-hexane and discard the eluate.

4.16. Load the extract on the top of the column.

4.17. Elute the column with 20mL of n-hexane to collect AHs fraction.

4.18. Elute the column with 30mL of n-hexane/toluene (1:1, v/v) to collect PAHs fraction.

4.19. Elute the column with 30mL of n-hexane/diethyl ether (9:1, v/v) to collect FAs fraction.

4.20. Elute the column with 30mL of acetone to collect ROHs fraction.

D) Derivatization of alkanols as trimethylsilylethers

4.21. Evaporate the ROHs fraction to about 1mL by a fine stream of N_2 and transfer to reaction vial. Further evaporate it to nearly dryness.

4.22. Add about 0.2 mL 1% trimethylchlorosilane in bis-(trimethylsilyl-trifluoroacetamide (BSTFA+1%TMCS) to the reaction vial, cap it tightly and heat to about 70°C for half an hours.

4.23. Cool down the vial and evaporate the reaction mixture under N_2 to nearly dryness.

E) GC/MS or GC/FID analyses of the sample

4.24. Add 10μL of a 100ppm of pre-deuterated aliphatic hydrocarbon to FAs and ROH fractions as injection standard.

4.25. Concentrate the four fractions of organic compounds under a stream of nitrogen to less than 1mL. Transfer them to 1mL vials, further evaporate the organics to less than 0.2ml.

4.26. Make up AHs fraction to 0.2 mL with n-hexane, other three fractions to 0.2 mL with dichloromethane. Make appropriate modification of final volume if necessary.

4.27. Analyse the AHs, PAHs, FAs and ROHs fractions with full-scan mode of GC/MS accordingly for the identification of compounds.

4.28. Analyse the AHs, PAHs, FAs and ROHs fractions with selected ion mode (SIM) of GC/MS or GC/FID accordingly for the quantification of identified compounds.

4.29. Set up the instrument for analysis according to instruction manuals. Analyst may modify the suggested conditions to optimise resolution and signal response to meet analysis requirements. Suggested operation conditions for the GC/MS system are as follows:

4.29.1. Aliphatic hydrocarbons **(AHs).**

Column :	30 m x 0.25 mm ID, 0.25 film thickness silicone-coated fused-silica capillary column DB5-MS or equivalent.
Carrier gas :	Helium
Carrier flow :	2 mL min^{-1} (~ 10 psig column head pressure)
Oven temperature :	65°C (5 min.), 10°C/min., 300°C (25min.)
Injector temperature :	250 °C
Injector :	Splitless
Sample volume :	1-3 μL
Ionization energy :	70 eV
Ionization mode :	EI
Transfer line temperature :	300 °C
Full scan conditions :-	
Mass range :	50-650 amu
Scan time :	1 sec/scan
SIM conditions :-	
SIM ions :	
AHs	primary ion = m/z 85, secondary ion = m/z 99
D-AHs	primary ion = m/z 66, secondary ion = m/z 80

4.29.2. Polynuclear aromatic hydrocarbons **(PAHs).**

Column :	30 m x 0.25 mm ID, 0.25 film thickness silicone-coated fused-silica capillary column DB5-MS or equivalent.
Carrier gas :	Helium
Carrier flow :	2 mL min^{-1} (~ 10 psig column head pressure)
Oven temperature :	85°C (2 min.), 8°C/min., 280°C (30 min.), 20°C/min., 300°C (15min.)
Injector temperature :	250 °C
Injector :	splitless
Sample volume :	1 - 3 μL
Ionization energy :	70 eV
Ionization mode :	EI
Transfer line temperature :	300 °C
Full scan conditions :-	
Mass range :	50-650 amu
Scan time :	1 sec/scan
SIM conditions :-	
SIM ions :	Listed at 4.29.3

4.29.3. Quantification ions for PAHs

Polynuclear aromatic hydrocarbons (PAHs)	Quantification ions	
	1st (Q1)	2nd (Q2)
Naphthlene (Naph)	152	153,151
Acenaphthylene (Acph)	152	153,151
Acenaphthene (Acen)	154	154,152
Fluorene (Fluo)	166	167,165
Phenanthrene (Phen)	178	179,176
Anthracene (Anth)	178	179,176
2-Methylphenanthrene (2Mephen)	192	192,165
1-Methylphenanthrene (1Mephen)	192	192,165
Fluoranthene (Flut)	202	200,101
Pyrene (Pyre)	202	200,101
2-Methylfluoranthene (2Meflut)	216	215,189
2-Methylpyrene (2Mepyre)	216	215,189
Benz[a]anthracene (Bant)	228	226,114
Chrysene (Chry)	228	226,113
Benzo[b]fluoranthene (Bbfl)	252	250,126
Benzo[k]fluoranthene (Bkfl)	252	250,126
Benzo[e]pyrene (Bepy)	252	250,125
Benzo[a]pyrene (Bapy)	252	250,126
Perylene (Pery)	252	250,126
1,3,5-Triphenylbenzene (135Tb)	306	307,289
Indeno[1,2,3-cd]pyrene (Inpy)	276	274,138
Dibenz[a,h]anthracene (Daan)	278	276,139
Benzo[g,h,i]perylene (Bgpe)	276	274,138
Coroene (Coro)	300	298,150
Naphthlene-D_8	136	135,137
Acenaphthalene-D_{10}	164	162,160
Phenanthrene-D_{10}	188	94,80
Chryene-D_{12}	240	236,120
Perylene-D_{12}	264	265,260

4.29.4. Fatty acids as methyl esters **(FAs).**

Column :	30 m x 0.25 mm ID, 0.25 film thickness silicone-coated fused-silica capillary column DB5-MS or equivalent.
Carrier gas :	Helium
Carrier flow :	2 mL min^{-1} (~ 10 psig column head pressure)
Oven temperature :	65°C (5 min.), 10°C/min., 300°C (25min.)
Injector temperature :	250 °C
Injector :	splitless
Sample volume :	1 - 3 μL
Ionization energy :	70 eV
Ionization mode :	EI
Transfer line temperature :	300 °C
Full scan conditions :-	
Mass range :	50-650 amu
Scan time :	1 sec/scan
SIM conditions :-	
SIM ions :	
Sat' FAMEs	primary ion = m/z 74, secondary ion = m/z 87
Unsat' FAMEs	primary ion = m/z 67, secondary ion = m/z 79, 81
D-AHs	primary ion = m/z 98, secondary ion = m/z 114

4.29.5. Alkanols as trimethylsilylethers **(ROHs).**

Column :	30 m x 0.25 mm ID, 0.25 film thickness silicone-coated fused-silica capillary column DB5-MS or equivalent.
Carrier gas :	Helium
Carrier flow :	2 mL min^{-1} (~ 10 psig column head pressure)
Oven temperature :	65°C (1 min.), 10°C/min., 300°C (15min.)
Injector temperature :	250 °C
Injector :	splitless
Sample volume :	1 - 3 μL
Ionization energy :	70 eV
Ionization mode :	EI
Transfer line temperature :	300 °C
Full scan conditions :-	
Mass range :	50-650 amu
Scan time :	1 sec/scan
SIM conditions :-	
SIM ions :	
ROTMSs	Listed at 4.29.6
D-AHs	primary ion = m/z 66, secondary ion = m/z 80

4.29.6. Quantification ions for ROHs

Alkanol as trimethylsilyl ethers	Quantification ions	
	1st (Q1)	2nd (Q2)
1-Decanol (C10)	215	216, 217
1-Undecanol (C11)	229	230, 231
1-Dodecanol (C12)	243	244, 245
1-Tridecanol (C13)	257	258, 259
1-Tetradecanol (C14)	271	272, 273
1-Pentadecanol (C15)	285	286, 287
1-Hexadecanol (C16)	299	300, 301
1-Heptadecanol (C17)	313	314, 315
1-Octandecanol (C18)	327	328, 329
1-Nonadecanol (C19)	341	342, 343
1-Eicosanol (C20)	355	356, 357
1-Heneicosanol (C21)	369	370, 371
1-Docosanol (C22)	383	384, 385
1-Tricosanol (C23)	397	398, 399
1-Tetracosanol (C24)	411	412, 413
1-Pentacosanol (C25)	425	426, 427
1-Hexacosanol (C26)	439	440, 441
1-Heptacosanol (C27)	453	454, 455
1-Octacosanol (C28)	467	468, 469
1-Nonacontanol (C29)	481	482, 483
1-Triacontanol (C30)	495	496, 497
n-Hexadecane-D_{34}	66	80
n-Eicoane-D_{42}	66	80
n-Tetracosane-D_{50}	66	80
n-Triacontane-D_{62}	66	80
n-Dotriacontane-D_{66}	66	80
n-Hexatriacontane-D_{74}	66	80

4.30. Set up the instrument for analysis according to instruction manuals. Analyst may modify the suggested conditions to optimise resolution and signal response to meet analysis requirements. Suggested operation conditions for the GC/FID system are as follows:

4.30.1. Aliphatic hydrocarbons **(AHs) and** Fatty acids as methyl esters **(FAs).**

Column :	30 m x 0.32 mm ID, 0.25 film thickness silicone-coated fused-silica capillary column HP5 or equivalent.
Carrier gas :	Helium
Carrier flow :	2 mL min^{-1}
Support gases	Hydrogen and Compressed air
Hydrogen flow :	40 mL min^{-1}
Air flow :	400 mL min^{-1}
Helium make up flow :	25 mL min^{-1}
Oven temperature :	65°C (5 min.), 10°C/min., 300°C (25min.)
Injector temperature :	250 °C
Injector :	Splitless
Sample volume :	1-3 μL

4.31. For the compounds of interest positively identified, record the area (response) of the characteristic ion.

4.32. Determine the concentration of individual compounds of interest from the corresponding values of relative response factor (RRF).

4.33. Analyse calibration check standards and record the response in peak area for each compound.

4.34. Carry out a blank determination and make appropriate blank corrections.

5. Calculation/Result interpretation

5.1. All analytes of interest shall be quantified with reference to the internal standard/injection standard. The internal standard used shall be the one nearest the retention time of the given analyte. Use the primary ions for quantitation. If interferences are noted, the next most intense ion, secondary ion(s) will be used.

5.2. Calculate the response factors (RF) for each compound relative to one of the internal standards / injection standards as follows:

$$RF = \frac{A \times Cis}{Ais \times C}$$

where :

A = peak area of the GC/MS or GC/FID signal for the compound of interest

Ais = peak area of the GC/MS or GC/FID signal for the specific internal/injection standard

Cis = Concentration of the specific internal/injection standard in ng/μL

C = Concentration of the compound of interest in ng/μL

5.3. Calculate the concentration of the compound of interest in sample in μg/m^3 as follows:

$$C = \left(\frac{A \times Qis}{Ais \times RF} - Mrb - Mfb \right) \times DF \times \frac{1}{Va}$$

where :

C = concentration of the compound of interest in sample in ng/μL

A = peak area of the GC/MS or GC/FID signal for the compound of interest

Ais = peak area of the GC/MS or GC/FID signal for the corresponding internal standard

Qis = amount of internal standard injected in ng

RF = relative response factor of the compound in calibration standard

Mrb = amount of the compound of interest in the reagent blank

Mfb = amount of the compound of interest in the filter blank
DF = dilution factor
Va = total volume of air sampled in m^3

5.4. Report the results to 3 significant figures.

6. Quality control parameters

6.1. Recoveries of standard spike: 85-115% (RSD < 10%)

6.2. For every batch analysis one filter blank.

6.3. The response for all four classes of EOC should be linear for the corresponding working range with coefficient of correlation > 0.995.

6.4. Compounds are reported as positively identified if the PROB value of library search results ≥ 50 with mass fragmentation patterns of reference compounds or mass spectra in National Institution of Standards and Technology (NIST) standard library.

6.5. All ions used in the SIM should be present in the sample spectrum and the primary and secondary quantitation ion chromatograms should have similar peak shapes. The relative intensities of the major ions should agree within ± 30%.

6.6. Recovery and precision: Recoveries of replicate analyses (n = 5) of blank filter spiked with four classes of standard are listed in following tables:

Table 1 Recovery and precision of replicate analyses (n = 5) of 5ppm AHs spiked standards

Aliphatic Hydrocarbons (AHs)	Retention Time (min.)	Recovery (%)	RSD (n =5) (%)
n-Tetradecane (nC14)	19.2	85	11.0
n-Pentadecane (nC15)	16.1	85	9.9
n-Hexadecane (nC16)	17.9	90	10.1
n-Heptadecane (nC17)	19.2	95	10.5
Pristane (Pris)	19.3	95	11.0
n-Octadecane (nC18)	20.4	89	3.2
Phytane (Phy)	20.5	89	4.8
n-Nonadecane (nC19)	21.5	86	5.1
n-Eicoane (nC20)	22.5	85	13.1
n-Heneicoane (nC21)	23.6	87	7.9
n-Docosane (nC22)	24.5	90	6.5
n-Triacosane (nC23)	25.5	90	7.3
n-Tetracosane (nC24)	26.4	102	6.1
n-Pentacosane (nC25)	27.2	99	3.4
n-Hexacosane (nC26)	28.1	102	5.1
n-Heptacosane(nC27)	28.9	97	7.5
n-Octacosane (nC28)	29.8	95	17.7
n-Nonacosane (nC29)	30.7	104	9.8
n-Triacontane (nC30)	31.8	103	8.2
n-Hentriacontane (nC31)	32.9	101	5.7
n-Dotriacontane (nC32)	34.4	103	9.1
n-Tritriacontane (nC33)	36.0	91	2.9
n-Tetratriacontane (nC34)	38.0	89	3.4
n-Pentatriacontane (nC35)	40.4	85	7.1
n-Hexatriacontane (nC36)	43.3	85	4.6
n-Heptatriacontane (nC37)	46.8	85	9.3
n-Octatriacontane (nC38)	51.0	86	3.6
n-Nonatriacontane (nC39)	56.2	85	9.0
n-Tetracontane (nC40)	62.5	87	10.0
n-Hexadecane-D_{34}	17.6	–	–
n-Eicoane-D_{42}	22.2	–	–
n-Tetracosane-D_{50}	26.0	–	–
n-Triacontane-D_{62}	31.2	–	–
n-Dotriacontane-D_{66}	33.5	–	–
n-Hexatriacontane-D_{74}	41.2	–	–

Method detection limit = 0.02µg/batch sample

Table 2 Recovery and precision of replicate analyses (n = 5) of 250ppb PAHs spiked standards

Polynuclear aromatic hydrocarbons (PAHs)	Retention Time (min.)	Recovery (%)	RSD (%)
Naphthlene (Naph)	11.0	93	3.9
Acenaphthylene (Acph)	15.6	93	3.9
Acenaphthene (Acen)	16.2	99	5.1
Fluorene (Fluo)	17.7	97	5.9
Phenanthrene (Phen)	20.6	101	1.3
Anthracene (Anth)	20.7	99	1.9
2-Methylphenanthrene (2Mephen)	22.2	99	2.4
1-Methylphenanthrene (1Mephen)	22.5	91	3.3
Fluoranthene (Flut)	24.2	95	2.8
Pyrene (Pyre)	24.8	91	1.4
2-Methylfluoranthene (2Meflut)	25.6	90	2.6
2-Methylpyrene (2Mepyre)	26.6	92	3.6
Benzo[a]anthracene (Bant)	28.7	99	3.5
Chrysene (Chry)	28.9	96	2.0
Benzo[b]fluoranthene (Bbfl)	34.0	94	2.4
Benzo[k]fluoranthene (Bkfl)	34.2	103	6.9
Benzo[e]pyrene (Bepy)	35.7	95	6.3
Benzo[a]pyrene (Bapy)	36.1	102	6.6
Perylene (Pery)	36.7	103	0.5
1,3,5-Triphenylbenzene (135Tb)	37.2	98	1.6
Indeno[1,2,3-cd]pyrene (Inpy)	46.3	98	3.1
Dibenz[a,h]anthracene (Daan)	46.7	94	1.7
Benzo[g,h,i]perylene (Bgpe)	49.2	86	2.0
Coroene (Coro)	67.3	85	2.8
Naphthlene-D_8	11.0	–	–
Acenaphthalene-D_{10}	16.1	–	–
Phenanthrene-D_{10}	20.5	–	–
Chryene-D_{12}	28.9	–	–
Perylene-D_{12}	36.6	–	–

Table 3 Summary of the recoveries for the PAH with 6 replicated analysis of SRM 1649a urban dust

PAHs	Certified concentrations[a] mg/kg	Mean recovery (RSD) / % (n = 6)
Phenanthrene (Phen)	4.14 ± 0.37	94 (6.2)
Anthracene (Anth)	0.432 ± 0.082	91 (5.9)
Fluoranthene (Flut)	6.45 ± 0.18	79 (5.7)
Pyrene (Pyre)	5.29 ± 0.25	87 (5.3)
Benz[a]anthracene (Bant)	2.21 ± 0.073	86 (6.3)
Chrysene (Chry)	3.049 ± 0.060	94 (3.3)
Benzo[b]fluoranthene (Bbfl)	6.45 ± 0.64	99 (4.2)
Benzo[k]fluoranthene (Bkfl)	1.913 ± 0.031	85 (9.3)
Benzo[e]pyrene (Bep)	3.09 ± 0.19	94 (7.4)
Benzo[a]pyrene (Bap)	2.509 ± 0.087	95 (2.4)
Perylene (Pery)	0.646 ± 0.075	90 (2.8)
Indeno[1,2,3-cd] pyrene (Inpy)	3.18 ± 0.72	91 (9.2)
Dibenz[a,h]anthracene (Daan)	0.288 ± 0.023	87 (4.2)
Benzo[g,h,i]perylene (Bgpe)	4.01 ± 0.91	87 (7.6)

[a] Certified concentrations were quoted from the certificate provided by the National Institute of Science and Technology, USA.

Table 4 Recovery and precision of replicate analyses (n = 5) of 10ppm FAMEs spiked standards

Fatty acid methyl esters (FAMEs)	Retention Time (min.)	Recovery (%)	RSD (n = 5) (%)
Octanoic/Caprylic acid methyl ester (C8:0)	10.5	92	8.5
Nonanoic/Pelargonate acid methyl ester (C9:0)	12.4	94	8.8
Decanoic/Capric acid methyl ester (C10:0)	14.0	97	8.2
Undecanoic acid methyl ester (C11:0)	15.5	93	8.7
Dodecanoic/Lauric acid methyl ester (C12:0)	16.9	95	8.3
Tridecanoic acid methyl ester (C13:0)	18.2	99	8.8
Myristoleic acid methyl ester (C14:1)	19.4	98	9.5
Tetradecanoic/Myristic acid methyl ester (C14:0)	19.5	99	6.1
Pentadecanoic acid methyl ester (C15:0)	20.6	102	4.8
Palmitoleic acid methyl ester (C16:1)	21.5	100	6.0
Hexadecanoic/Palmitic acid methyl ester (C16:0)	21.8	106	5.8
Heptadecanoic acid methyl ester (C17:0)	22.8	102	8.0
9,12-Octadecadienoic/Linoleic acid methyl ester (C18:2)	23.6	98	5.3
cis-9-Octadecanoic/Oleic acid methyl ester (C18:1)	23.7	104	8.6
Octadecanoic/Stearic acid methyl ester (C18:0)	23.9	95	8.2
Nonadecanoic acid methyl ester (C19:0)	24.9	100	1.6
cis-5,8,11,14-Eicosatetraenoic/Arachidonic acid methyl ester (C20:4)	25.2	98	3.9
cis-11-Eicosenoic acid methyl ester (C20:1)	25.5	106	4.2
Eicosanoic/Arachidic acid methyl ester (C20:0)	25.7	100	4.3
Heneicosanoic acid methyl ester (C21:0)	26.6	102	1.9
cis-4,7,10,13,16,19-Docosahexaenic acid methyl ester (C22:6)	27.0	97	3.2
Erucic acid methyl ester (C22:1)	27.5	102	3.2
Docosanoic/Behenic acid methyl ester (C22:0)	27.8	99	1.8
Tricosanoic acid methyl ester (C23:0)	28.3	99	1.8
Nervonic acid methyl ester (C24:1)	29.0	99	4.8
Tetracosanoic/Lignoceric acid methyl ester (C24:0)	29.2	94	4.0
Pentacosanoic acid methyl ester (C25:0)	30.0	98	3.6
Hexacosanoic acid methyl ester (C26:0)	31.0	97	2.8
Heptacosanoic acid methyl ester (C27:0)	32.1	101	2.4
Octacosanoic acid methyl ester (C28:0)	33.4	98	6.0
Nonacosanoic acid (C29:0)	34.9	97	3.8
Tricontanoic/Melissic acid methyl ester (C30:0)	36.7	101	2.8
Hentricontanoic acid methyl ester (C31:0)	38.8	100	4.6
n-Hexadecane-D_{34}	17.6	–	–
n-Eicoane-D_{42}	22.2	–	–
n-Tetracosane-D_{50}	26.0	–	–
n-Triacontane-D_{62}	31.2	–	–
n-Dotriacontane-D_{66}	33.5	–	–
n-Hexatriacontane-D_{74}	41.2		

Table 5 Recovery and precision of replicate analyses (n = 5) of 2.5ppm ROHs spiked standards

Alkanols as trimethylsilyl ethers	Retention Time (min.)	Recovery (%)	RSD (%)
1-Decanol (C10)	16.4	86	8.1
1-Undecanol (C11)	18.0	85	4.8
1-Dodecanol (C12)	19.6	87	5.4
1-Tridecanol (C13)	21.1	85	2.5
1-Tetradecanol (C14)	22.6	89	1.4
1-Pentadecanol (C15)	23.9	85	7.9
1-Hexadecanol (C16)	25.2	85	4.8
1-Heptadecanol (C17)	26.3	87	4.5
1-Octandecanol (C18)	27.6	94	8.5
1-Nonadecanol (C19)	28.7	88	1.9
1-Eicosanol (C20)	29.9	85	4.8
1-Heneicosanol (C21)	30.9	87	5.6
1-Docosanol (C22)	32.0	88	5.2
1-Tricosanol (C23)	32.9	88	8.1
1-Tetracosanol (C24)	33.9	85	5.1
1-Pentacosanol (C25)	34.8	–	–
1-Hexacosanol (C26)	35.8	88	5.6
1-Heptacosanol (C27)	36.9	86	9.9
1-Octacosanol (C28)	38.2	88	9.5
1-Nonacontanol (C29)	39.6	–	–
1-Triacontanol (C30)	41.3	103	10.0
n-Hexadecane-D_{34}	19.7	–	–
n-Eicoane-D_{42}	25.3	–	–
n-Tetracosane-D_{50}	29.9	–	–
n-Triacontane-D_{62}	35.8	–	–
n-Dotriacontane-D_{66}	38.2	–	–
n-Hexatriacontane-D_{74}	46.0	–	–

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