Characterization of particulate organics accumulated on the ceiling of vehicular tunnels in Hong Kong and Guangzhou, China

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Abstract

Ceiling dusts, the particulate matters accumulated on the ceiling surface of vehicular tunnels, collected from Cross-Harbor Tunnel in Hong Kong and Pear River Tunnel in Guangzhou, were analyzed for their organic compositions. Although the overall results revealed that most of the organic compounds of the ceiling dusts of both tunnels are directly derived from vehicular emission, there are significant differences in the organic content and compositions and distribution of hydrocarbon components in the ceiling dusts from these two tunnels. The ceiling dusts from the tunnel of Hong Kong were characterized by high content of organic carbon and unresolved complex matter compared to the much lower numbers in the ceiling dusts of Guangzhou. The distribution of molecular markers from CHT exhibited a 17α (H)-21β (H)-30-nor hopane ($C_{29}H$) predominance ($C_{29}H > C_{30}H$) and the relative abundance of regular steranes is in an order of $C_{27} > C_{29} > C_{28}$, whereas for the ceiling dusts from PRT, the hopanes displayed a 17α (H)-21β (H)-hopane ($C_{30}H$) dominance ($C_{29}H < C_{30}H$) and the regular steranes are in the order of $C_{29} > C_{27} > C_{28}$. It was also found that there was significant difference in the organic content in the ceiling dusts between the south- and northbound tubes of both CHT and PRT and the reasons for this require further investigation.
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1. Introduction

Fossil fuel not only emits green house gases but also discharge enormous amount of fine particles into the ambient environments due to incomplete combustion (Rogge et al., 1993a). Because the emitted particles and its organic compounds are serious environmental con-taminants and harmful to the health of urban residents (Cohen and Higgins, 1995; Nauss, 1995; Watson and Green, 1995), extensive studies have been carried out on the chemical composition of vehicular particulate organics (Cadle et al., 1999; Miguel et al., 1998; Rogge et al., 1993a,b; Schauer et al., 2002; Yu and Hites, 1981). Vehicular tunnel is a relatively confined traffic passage that is heavily exposed to the exhaust emission and provides a unique environmental setting to study the mixture nature of organic pollutants emitted from the fleet of gasoline and diesel-fueled vehicles and other

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sources. There have been many studies on the freshly emitted airborne particulates and exhaust gases from the inside and at the exit/entrance of the vehicular tunnels (Benner et al., 1989; Fraser et al., 1999; HEI, 2002; Oda et al., 2001; Wingfors et al., 2001). Little attention, however, has been paid to the "ceiling dusts" accumulated on the surface of tunnels' ceiling. Due to the much less interference from geogenic and industrial sourced particulates compared to airborne particulates in open environments, the tunnel ceiling dusts may mainly represent particulate matter derived mostly from vehicular related activities.

Guangzhou and Hong Kong are two major cities in the Pearl River Delta region and has been experiencing a deteriorating air quality in the last decade (Cheng, 1996; Hong Kong EPD, 1997). By 2003, there were more than 2.5million on-use vehicles in the Pearl River Delta region (Cao et al., 2004). The enormous amount of particulate pollutants emitted by the vehicle fleets has a great impact on the atmospheric environment locally and regionally at Pearl River Delta region (Bi et al., 2002 and Mai et al., 2003). Both cities have developed a number of under water/ground tunnels to improve their traffic condition. By studying the organic matter in the ceiling dusts, we are aiming to characterize the organic matter in the ceiling dusts from the vehicular tunnels in both cities and to identify their possible sources, and furthermore we expect that the comparison of organic matter in the tunnel ceiling dusts from both Hong Kong and Guangzhou would provide us some new and useful information that has some significant environmental implications.

2. Samples and experimental procedures

2.1. Samples

Pearl River Tunnel (PRT) of Guangzhou and Cross Harbor Tunnel (CHT) of Hong Kong were selected for sampling ceiling dusts. Both tunnels have twin-tubes in each of which traffic flows in two-lanes in a single direction. PRT opened to traffic in 1994 runs beneath the Pearl River and connects the north bank (major city area) and south bank (newly developed district in Guangzhou) of the river. PRT is 1238.5 m long with a mild slope on both sides. In September of 2003, the traffic count was about 43,500 mixed vehicles in the northbound tube and 53,900 mixed vehicles in the southbound tube in an ordinary day, respectively. CHT served Hong Kong since 1976 runs beneath the Victoria Bay and connects Hong Kong Island and Kowloon Peninsula. The tunnel is 976 m long with inclined segments on both ends. In 2002, the daily traffic load was approximately 61,700 mixed vehicles in the southbound tube and 59,300 mixed vehicles in the north-bound tube. The road surfaces of these vehicular tunnels are cleaned every second day in both Hong Kong and Guangzhou, while the ceilings are never cleaned since the tunnels were built.

The ceiling dusts samples from CHT and PRT were collected from the ceiling surface of these tunnels on 15 April 2002 and 26 April 2003, respectively. For each tunnel, three ceiling dust samples were collected and the locations of these three dust samples were that one at the middle range of the tunnel and the other two were about 200 m apart from the middle of tunnels in each side. The ceiling dusts in CHT are about 1.5–2 cm thick, whereas they are about 0.5 cm thick in PRT. The dust samples were scraped off using a stainless steel scraper into plastic bags and each sample was collected from about 1 m^2 area of the ceiling surfaces and then transported to the laboratory where they were stored in refrigerator below 4 °C for further treatment and analysis. These ceiling dusts appear as dark, dry and very fine powder.

2.2. Experimental procedures

The ceiling dust samples were air-dried in room temperature in a desiccator before solvent extraction. About 10 g of the homogenized ceiling dusts together with an internal standard of n-$C_{24}D_{50}$ (500 ng) was subjected to Soxhlet extraction for 72 h using a solvent mixture of dichloromethane and methanol (9:1). The added n-$C_{24}D_{50}$ was aimed to monitor the experimental performance and for further identification of aliphatic hydrocarbons. Activated copper turnings were used for the removal of elemental sulfur during extraction. The extracts were demoistured with anhydrous Na_2SO_4 prior to filtration to remove insoluble particles and copper turnings. Following the quantification using volumetric method, the solvent extract was then concentrated using a Rotary Evaporator (<35 °C) to a small volume of about 3 ml. Subsequently, the total extracts were dissolved in hexane to precipitate asphaltene. After removing the asphaltene by filtration, the rest of the extract was then subjected to column chromatography and divided into aliphatic fraction, aromatic fraction and polar fraction. The resulting aliphatic and aromatic fractions were quantified by using volumetric method while the asphaltene and polar fraction were air-dried for quantification.

The identification and quantification of aliphatic and aromatic hydrocarbon compounds were conducted using a HP 6890 series II Gas Chromatography interfaced with a HP 5972 mass selective detector using electron impact mode (70 eV). A DB-5 fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used. The injector temperature of GC was 290 °C and the oven temperature was initially held at 60 °C for 5 min, and then programmed in a heating rate of 3 °C/min to 290 °C/min and maintained for

30 min. The mass spectrometer was operated in the electron impact mode with an ion source of 70 eV and at 180 °C. The mass scan range was m/z 50–550 Da. Helium was the carrier gas at 1.2 ml/min flow rate.

The n-alkanes were identified by referring to the internal standard of n-$C_{24}D_{50}$ and retention time, while molecular markers and aromatic compounds were identified by their mass spectra and by comparison with the mass spectrum library supplied with the instrument.

3. Results and discussions

3.1. Hydrocarbon composition of extractable organic matter

The contents of total organic carbon (TOC) and solvent extractable organic matter and their hydrocarbon compositions in ceiling dusts from PRT and CHT were presented in Table 1. The average TOC contents of ceiling dusts from CHT were 20.4% and 28.2% for the north and southbound tubes, respectively, whereas the average TOC in the ceiling dusts from PRT were 13.3% for the northbound tube and 15.2% for southbound tube. Obviously, the TOC contents of the ceiling dust from CHT are much higher than that those of PRT. Consequently, the average contents of soluble organic matter in ceiling dusts from PRT were about 45.6 and 65.0 mg/g in the north- and southbound tubes, respectively. These numbers were significantly lower than

those in the ceiling dusts from CHT (average contents were 77.9 and 94.2 mg/g for the northbound and southbound, respectively).

The comparison of hydrocarbon composition indicated that the contents of aliphatic, aromatic and polar fractions in total extracts of CHT's ceiling dusts were slightly higher than those of PRT's ceiling dusts. The average contents of asphaltene in ceiling dusts of the northbound and southbound tubes were only 11.7 and 27.0 mg/g for PRT, respectively, compared to a 25.5 (northbound) and 52.4 mg/g (southbound) in ceiling dusts from Hong Kong's CHT. The asphaltene fraction contributed the most of hydrocarbon composition differences between the ceiling dusts from Hong Kong and Guangzhou tunnels, as well as between the ceiling dusts of the tubes of both tunnels.

The representative chromatograms of aliphatic hydrocarbons from ceiling dusts of CHT-CD-1 (samples at about 200 m apart from the middle of tunnel), CHT-CD-2 (sampled from the middle range of tunnel), PRT-CD-1 (sampled at about 200 m apart from the middle of tunnel) and PTR-CD-2 (sampled from the middle range of tunnel) are presented in Fig. 1. The appearances of the gas chromatograms of aliphatic hydrocarbons suggest that there are no significant difference in the hydrocarbon composition for these ceiling dust samples from PRT and as well as for these from CHT. Fig. 1 shows that aliphatic hydrocarbons in the ceiling dusts of PRT mainly consisted of n-alkanes and minor amount of unresolved complex matters (UCM) and branched

Table 1
The hydrocarbon composition of extractable organic matter and related diagnostic parameters from GC analysis of aliphatic hydrocarbons in ceiling dusts

Vehicular Tunnel	Pearl River Tunnel		Cross Harbor Tunnel	
Vehicle moving direction	Northbound	Southbound	Northbound	Southbound
TOC (%)	13.3	15.2	20.1	28.0
Total extracts (mg/g)	45.6	65.0	77.7	94.2
Aliphatics (mg/g)	14.7	16.8	23.1	22.0
Aromatics (mg/g)	3.4	4.4	6.0	4.5
Polar (mg/g)	15.0	15.8	21.3	14.9
Asphaltene (mg/g)	11.7	27.0	25.5	52.4
Carbon number range	n-C_{14}–n-C_{35}		n-C_{15}–n-C_{40}	
C_{max}	n-C_{22}		n-C_{21}–n-C_{21}	
CPI	0.99–1.08		1.10–1.16	
Pr/Ph	0.51		0.56	
UCM carbon number range	n-C_{19}–n-C_{31}		n-C_{19}–n-C_{37m}	
UCM Cmax	n-C_{23}		n-C_{26}	
U:R	6.7–7.0		16.5–17.3	
UCM pattern	Unimodal		Unimodal	

Note: The values of TOC (%) and the contents (mg/g) are average number of three samples, while the ratios are the value range for six samples. TOC, Total organic carbon content; CPI, Carbon preference index, calculated as CPI $= \Sigma n$-C_{13}–n-$C_{39}/\Sigma n$-C_{12}–n-C_{40}; Pr/Ph, pristane/phyfane ratio; U:R, unresolved complex matter over the resolved aliphatic hydrocarbon compounds on the total mass chromatogram of aliphatic fraction.
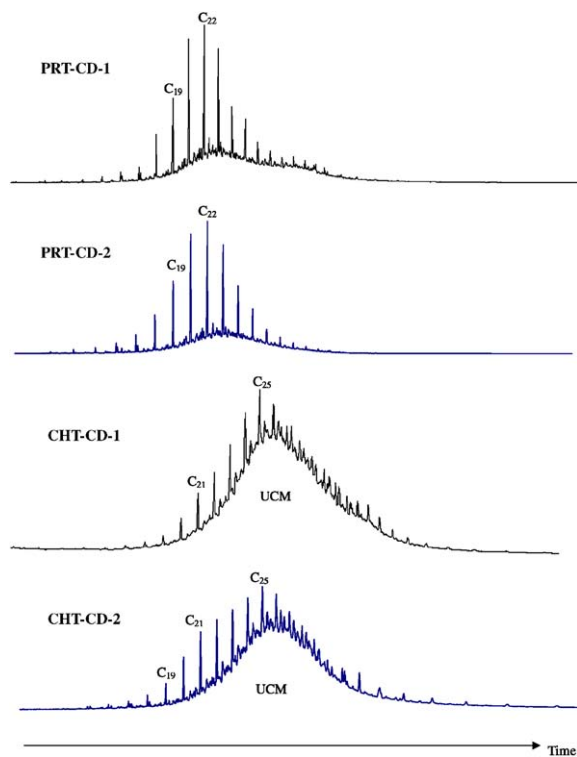
Fig. 1. Ion chromatogram of m/z 85 of aliphatic hydrocarbons in the ceiling dusts of PRT and CHT show the composition and distribution of alkanes and UCM. UCM: unresolved complex mixture.

and cyclic alkanes, while UCM and n-alkanes are major components of aliphatic hydrocarbons for CHT. Table 1 summarized common parameters obtained from the GC analysis of aliphatic hydrocarbons. These chromatograms and parameters suggest that the composition and distribution of aliphatic hydrocarbons in both ceiling dusts were generally comparable but with some clear differences. For the ceiling dusts from PRT, the n-alkanes range from n-C_{14} to n-C_{35} with n-C_{22} as Cmax, while a wider range of n-C_{14}–n-C_{40} with a maximum peak of n-C_{21} is observed for the ceiling dusts from CHT. The major n-alkanes lie between n-C_{17} and n-C_{27} and this alkane range corresponds to the high boiling point components in diesel fuels (Neukom et al., 2002; Rogge et al., 1993b). This implied that these dominated normal alkanes in the ceiling dusts were mainly derived from the emission of diesel fuel driving vehicles due to incomplete combustion. On the other hand, the n-C_{22} as the dominant peak of normal alkanes of aliphatic hydrocarbons in the ceiling dusts of both cities is similar to their corresponding tunnel road dusts (You, 2004) and to the normal alkane distribution found in the gaseous phase of urban ambient air of Guangzhou City but different from that of urban airborne particle (Bi et al., 2003). These may suggest that the aliphatic

hydrocarbons in the ceiling dusts may be partially derived from the vapor-phased alkanes through absorption as the vehicular-emitted particles consist of large portion of black carbon that is capable of adsorption of these gas phase molecules.

The carbon preference index (CPI) was in the range of 0.99~1.01 for ceiling dusts of PRT and comparable to that of petroleum-derived fuels (Azevedo et al., 1999; Bray and Evans, 1961; Simoneit, 1984). However, CPI in ceiling dusts of CHT varies from 1.10 to 1.16, which is slightly higher than that of PRT but it was very close to the CPI value of 1.11 in the urban ambient aerosols of Hong Kong (Cheng, 1996). This may suggest that particulates emitted from vehicles contributed the most of aliphatic hydrocarbon in aerosols of urban area of Hong Kong. Fig. 1 also showed that the ceiling dusts of PRT were relatively rich in n-alkanes below carbon 24 with a [$\Sigma C_{25}+/\Sigma C_{24}-$] ratio of about 0.5 for two samples, whereas the two ceiling dusts from CHT were relatively rich in heavier normal alkanes of carbon number above C_{20} as suggested by the [$\Sigma C_{20}+/\Sigma C_{19}-$] ratio of 16.53.

The unresolved complex matter (UCM) in aliphatic fraction representing these highly branched and cyclic hydrocarbons in aliphatic hydrocarbons occurs as a hump in the chromatogram of total aliphatic fraction (Frysinger et al., 2003). The occurrence of these humps is often indicative of their sources. Natural hydrocarbons derived from vascular plant wax often exhibit no UCM (Azevedo et al., 1999). Similarly gasoline fuels show no UCM hump due to the lack of highly branched and cyclic hydrocarbons. Diesel fuels and lubricating oils, however, often show two clear UCM humps that distribute in the range of n-C_{10}–n-C_{25} and n-C_{14}–n-C_{45}, respectively. Note that these UCM humps often occur as Gaussian-like shape and their peak positions are located at n-C_{19} for diesel fuels and n-C_{27}–n-C_{29} for lubricating oils (Neukom et al., 2002; Rogge et al., 1993a,b). Fig. 1 also showed the envelope of UCM in the ceiling dusts. Table 1 lists the parameters for UCM. As shown in Fig. 1, the envelope of UCM in the ceiling dusts of PRT is much smaller than that in the CHT and suggests that the ceiling dusts from Hong Kong's tunnels are very high in highly branched and cyclic hydrocarbon contents. The UCM in ceiling dusts of PRT appears as a much smaller but broad unimodal hump ranging from n-C_{19} to n-C_{31} and implies a combination of mixture sourced particulate organics input from diesel operated vehicles and lubricate oils. On the other hand, the UCM hump in ceiling dusts of CHT reveals a symmetric shape ranging from n-C_{19} to n-C_{37} and peaks at the position around n-C_{26}. This suggests a strong lubricating (engine) oil contribution (Azevedo et al., 1999; Boyer and Laitinen, 1975; Neukom et al., 2002). The ratio of UCM to resolved components (U:R) could be used to track incomplete combustion of fossil fuels. The U:R

ratios for ceiling dust samples of PRT and CHT were in the ranges of 6.7–7.0 and 16.5–17.3, respectively, representing a typical vehicular emission feature (Simoneit, 1984; Rogge et al., 1993a,b).

The higher TOC in the ceiling dusts of CHT implies a lower content of inorganic particulates, which may in turn result in a higher soluble organic matter. On the other hand, the ceiling dust of PRT was expected to have lower soluble organic matter content compared to the ceiling dusts of CHT. The difference in the relative abundance of hydrocarbon fractions in ceiling dusts of these tunnels may be attributed to a number of reasons including the differences in the duration of tunnel operation. CHT has been in-use since 1976, and thus it has experienced a longer period of exposure to the chronic weathering that would significantly reduce the relative abundance of low carbon number *n*-alkanes while left refractory components (heavier hydrocarbons) remaining intact (Garza and Muth, 1974). Consequently, the ceiling dusts of CHT contained more asphaltene fraction and heavier *n*-alkanes than those in the ceiling dusts of PRT.

Alternatively, the difference in the fuels used may have also contributed to these discrepancies. Supporting this, based on Pb isotope composition of urban deposits in Hong Kong, including the ceiling dusts of CHT, Duzgoren-Aydin et al. (2004) showed that the anthropogenic Pb in the surface environment of Hong Kong that originated from Pb ore with a low $^{206}Pb/^{207}Pb$ ratio (such as Australian Pb ore and similar sources in Southeast Asia) were significantly different from those of anthropogenic Pb present in the neighboring Pearl River Delta region. Also, developments in engine technology over the years could also result in compositional discrepancies in the particulate organics emitted from vehicles as different brands of vehicles produce significantly different hydrocarbon content and composition of particulate organics (Rogge et al., 1993a,b).

The apparent association between the number of vehicles and the contents of OC and soluble organic matter in ceiling dusts, and therefore the difference in north- and southbound tubes of the tunnels, may be attributed to the fact that more traffic load often suggests a relatively slow vehicle movement and thus
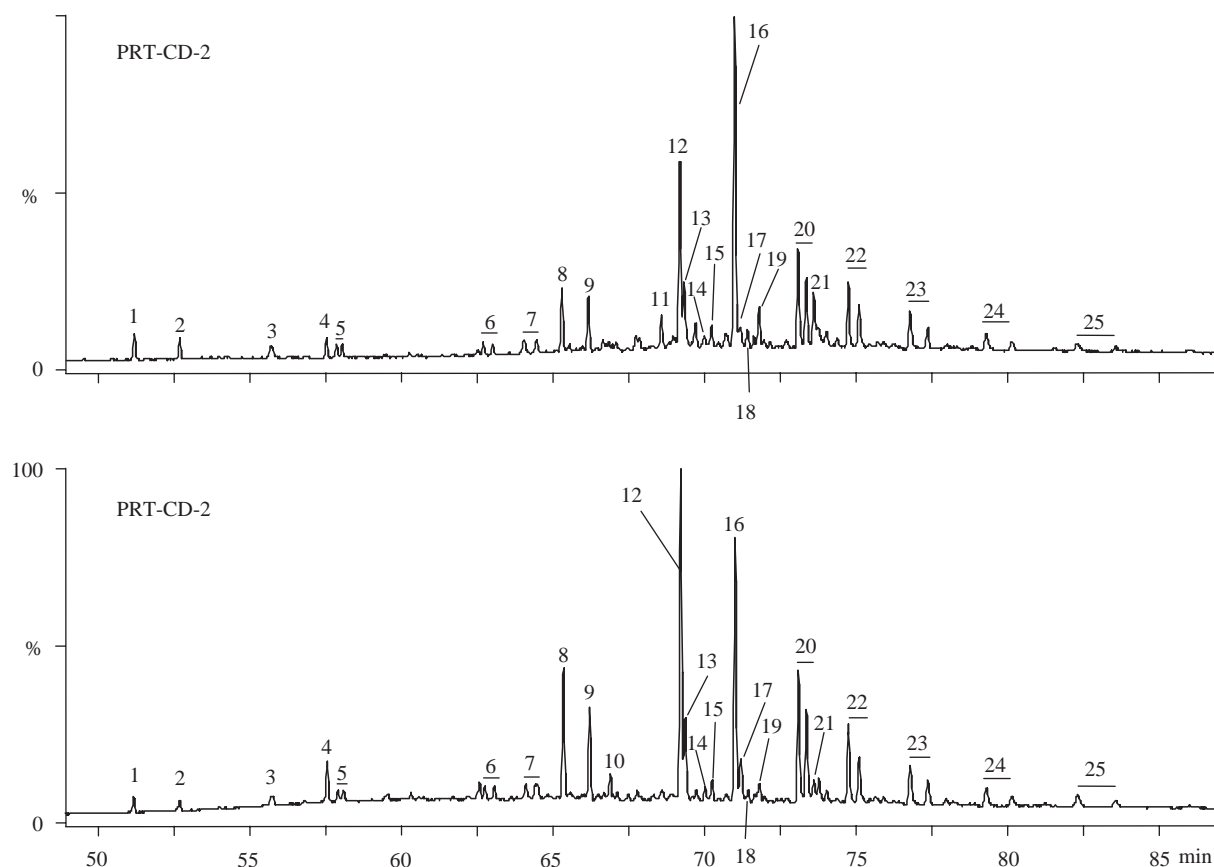

Fig. 2. Representative mass fragmentograms of *m/z* 191 for terpanes in the ceiling dusts of CHT-CD-2 and PRT-CD-2. Peak identifications are listed in Table 2.

high content of organics in the emission gases and particles due incomplete combustion. This and other possible explanations require further investigations.

3.2. Molecular markers

Molecular markers are organic compounds indicative of their original sources and formation pathways. Hopanes and steranes are two series of classical molecular markers that have been extensively studied and applied in petroleum geochemistry (Peters and Moldowan, 1993; and references therein). In terms of environmental research, these molecular markers are also useful in tracing pollution sources and their chemical changes in relevant environment.

Mass fragmentograms of m/z 191 for triterpanes in aliphatic fractions from representative ceiling dust samples of PRT and CHT were presented in Fig. 2. The pentacyclic triterpanes range from C_{27} to C_{35} (lack of C_{28}), whereas the extended hopanes of C_{31}-C_{35} revealed doublets of stereochemical configurations at

C_{22} position. The most abundant hopane compound is 17α (H), 21β (H)-hopane (i.e., C_{30}H) in PRT, while 17α (H), 21β (H)-30-norhopane (i.e., C_{29}H) is the dominant hopane peak for the ceiling dusts from CHT. The ratio of C_{29}H/C_{30}H is 1.19 and 0.60 for the ceiling dusts from CHT and PRT, respectively. The $22S/(22S+22R)$ ratio of 17α (H), 21β (H)-homohopanes is 0.59 for CHT and 0.61 for PRT. These ratios are close to equilibrium ratio of 0.6 in mature oils and indicate an inherited feature of the initial crude oils (Peters and Moldowan, 1993). The low ring number triterpanes mainly consist of tri- and tetra-cyclic triterpanes with C_{24} tetracyclic triterpanes and C_{23} tricyclic triterpanes as the dominant peak in CHT and PRT, respectively.

Steranes are another series of source-specific molecular markers. The distribution of steranes in ceiling dusts from PRT and CHT were illustrated in Fig. 3. The types of molecular markers were generally similar, but their relative abundances are different from each other. The relative abundance of three regular sterane serieses are in an order of $C_{27} > C_{29} > C_{28}$ for ceiling dusts from CHT
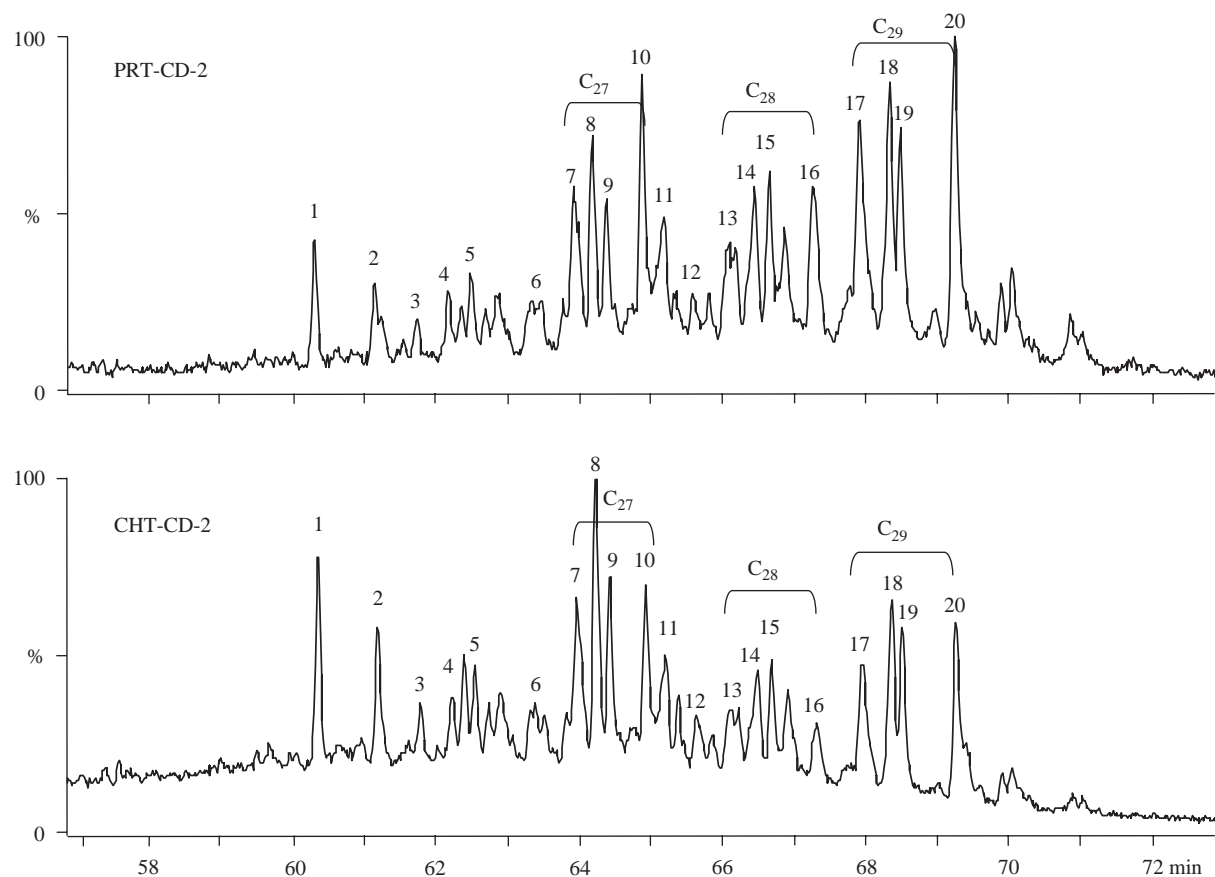

Fig. 3. Representative mass fragmentograms of m/z 217 for steranes in the ceiling dusts of PRT-CD-2 and CHT-CD-2. See Table 3 for peak identification.

Table 2
Identification and relative abundance of terpanes in the ceiling dusts of CHT and PRT

Peak no.	Compound	Carbon number	Relative abundance in CHT (%)	Relative abundance in PRT (%)
1	Tricyclic terpane	C_{23}	5.0	8.2
2	Tricyclic terpane	C_{24}	2.7	5.8
3	Tricyclic terpane	C_{25}	5.4	6.2
4	Tetracyclic terpane	C_{24}	12.3	6.0
5	22R-tricyclic terpane	C_{26}	3.8	4.0
	22S-tricyclic terpane	C_{26}	4.5	4.2
6	22R-tricyclic terpane	C_{28}	3.6	3.8
	22S-tricyclic terpane	C_{28}	4.0	3.6
7	22R-tricyclic terpane	C_{29}	5.7	5.3
	22S-tricyclic terpane	C_{29}	8.2	5.2
8	18α (H)-22,29,30-trinorhopane (Ts)	C_{27}	38.4	18.8
9	17α (H)-22,29,30-trinorhopane (Tm)	C_{27}	28.8	17.2
10	Tricyclic terpane	C_{30}	6.7	0.0
11	Tricyclic terpane	C_{31}	0.0	11.7
12	17α (H)-21β (H)-30-nor hopane (C29 H)	C_{29}	100.0	59.7
13	18α (H)-21β (H)-30-nor neohopane (C29 H)	C_{29}	27.6	22.7
14	Hop-17 (21)-ene	C_{30}	4.0	3.3
15	17β (H)-21α (H)-30-nor hopane (normoretane)	C_{29}	5.3	5.4
16	17α (H)-21β (H)-hopane (C30 H)	C_{30}	83.9	100.0
17	18α (H)-21β (H)-neohopane	C_{30}	14.4	0.0
18	Hop-13 (18)-ene	C_{30}	2.5	5.7
19	17β (H)-21α (H)-30-hopane (moretane)	C_{30}	5.8	10.6
20	22S-17α (H)-21β (H)-30-homohopane	C_{31}	42.4	32.8
	22R-17α (H)-21β (H)-30-homohopane	C_{31}	29.1	21.2
21	Gammacerane	C_{30}	4.7	16.9
22	22S-17α (H)-21β (H)-30-bishomohopane	C_{32}	24.9	23.0
	22R-17α (H)-21β (H)-30-bishomohopane	C_{32}	17.6	15.1
23	22S-17α (H)-21β (H)-30-trishomohopane	C_{33}	16.3	14.9
	22R-17α (H)-21β (H)-30-trishomohopane	C_{33}	10.0	8.5
24	22S-17α (H)-21β (H)-30-tetrakishomohopane	C_{34}	9.6	9.3
	22R-17α (H)-21β (H)-30-tetrakishomohopane	C_{34}	5.2	5.4
25	22S-17α (H)-21β (H)-30-pentakishomohopane	C_{35}	7.8	4.3
	22R-17α (H)-21β (H)-30-pentakishomohopane	C_{35}	5.0	2.6
	Homohopane index: $C_{31}S/(S+R)$		0.59	0.61
	Tm/Ts		0.75	0.92
	$C_{29}H/C_{30}H$		1.19	0.60

and $C_{29} > C_{27} > C_{28}$ for ceiling dusts from PRT. Compared to the ceiling dusts of PRT, the ceiling dusts from CHT contained higher abundance of diasteranes.

The features mentioned above and the differences between ceiling dust of CHT and PRT mainly reflect the source character of original crude oil from which gasoline and diesel fuels and lubricating oils were manufactured. For example, high abundance of Gammacerane is often associated with lacustrine sourced crude oils (Jiang et al., 1988; Fu et al., 1990; Simoneit et al., 1992) and it is not found in gasoline or diesel fuel but they may be derived from lubricating oil (Azevedo et al., 1999; Rogge et al., 1993a,b). The high abundance of Gammacerane in the ceiling dusts of PRT compared to those in CHT (Tables 2 and 3) suggests that fuels used

in Guangzhou were at least partly sourced from the lacustrine sourced petroleum while the fuels in Hong Kong were not and therefore this index could be used to assess the contribution of vehicular emission from Hong Kong and Guangzhou to the air pollution in Pearl River Delta region.

3.3. Composition of aromatic hydrocarbons

The identification of aromatic compounds in the ceiling dusts from CHT and PRT were tabulated in Table 4. The aromatic hydrocarbons of the ceiling dusts were comparable in compound composition, with polycyclic aromatic hydrocarbons dominating the chromatogram. However, the relative abundance of PAHs

Table 3
Identification and relative concentrations of steranes in the ceiling dusts of CHT and PRT

Peak no.	Compound	Carbon number	Relative abundance in CHT (%)	Relative abundance in PRT (%)
1	20S-13 β (H),17 α (H)-diacholestane	C_{27}	68.6	32.3
2	20R-13 β (H),17 α (H)-diacholestane	C_{27}	54.5	30.4
3	20S-13 α (H),17 β (H)-diacholestane	C_{27}	18.6	8.8
4	20S-13 α (H),17 β (H)-diacholestane	C_{27}	19.1	13.7
5	20S-13 β (H),17 α (H)-diacholestane	C_{28}	22.8	15.2
6	20R-13 β (H),17 α (H)-diacholestane	C_{28}	42.8	36.3
7	20S-5 α (H),14 α (H),17 α (H)-cholestane	C_{27}	50.4	44.5
8	20R-5 α (H),14 β (H),17 β (H)-cholestane	C_{27}	100.0	46.0
9	20S-5 α (H),14 β (H),17 β (H)-cholestane	C_{27}	60.1	37.7
10	20R-5 α (H),14 α (H),17 α (H)-cholestane	C_{27}	55.4	77.7
11	20R-13 β (H),17 α (H)-diacholestane	C_{29}	35.7	30.0
12	20S-13 α (H),17 β (H)-diacholestane	C_{29}	23.1	10.3
13	20S-5 α (H),14 α (H),17 α (H)-ergostane	C_{28}	20.7	29.3
14	20R-5 α (H),14 β (H),17 β (H)-ergostane	C_{28}	34.0	45.7
15	20S-5 α (H),14 β (H),17 β (H)-ergotane	C_{28}	36.9	46.7
16	20R-5 α (H),14 α (H),17 α (H)-ergostane	C_{28}	20.1	47.0
17	20S-5 α (H),14 α (H),17 α (H)-stigmastane	C_{29}	42.3	60.1
18	20R-5 α (H),14 β (H),17 β (H)-stigmastane	C_{29}	57.5	69.0
19	20S-5 α (H),14 β (H),17 β (H)-stigmastane	C_{29}	48.2	53.3
20	20R-5 α (H),14 α (H),17 α (H)-stigmastane	C_{29}	65.8	100.0

were different between the ceiling dusts from CHT and PRT. The ceiling dusts from CHT, were dominated by pyrene, chrysene, benzo[ghi]fluoranthene, fluoranthene and benzofluorene, whereas for the ceiling dusts from PRT, pyrene was the dominant peak, followed by chrysene, benzofluorene, benzo[ghi]fluoranthene and fluoranthene. Both ceiling dusts were relatively rich in alkyl-substituted PAH (mainly alkyl-phenanthrenes). Alkylated PAHs are regarded as the products of lower temperature combustion (Jensen and Hites, 1983; Rogge et al., 1993a,b). Therefore, traffic congestion in the tunnel may be responsible for the high abundance of alkyl-PAHs as the vehicles are slowed down or stopped and their engines are running at a lower temperature.

The relative abundances (ratios) of PAH compounds have widely been used as indicator to distinguish their genetic origins between petrogenic sources and pyrolytic sources (as listed in Table 4). Phe/Ant ratio higher than 10 is considered as indication to the petroleum hydrocarbon input and diagenetic sources, whereas ratio lower than 10 is taken as indication to the vehicular related combustion emissions (Tolosa et al., 2004; Wang and Fingas, 2003). In this study, Phe/Ant ratios of 12.09 and 14.32 for the ceiling dusts from CHT and PRT, respectively suggest these PAHs are mainly derived from incomplete combustion of engine fuels. The ratio of Flu/(Flu + Pyr) is 0.34 for PRT and it is slightly higher compared to a value of 0.28 for CHT. More importantly, these values are lower than that of vehicular emission and gasoline engine emission (Azevedo et al.,

1999; Kavouras et al., 2001). Furthermore, BaA and BaP are two most photoactive compounds among these PAHs and can be preferentially degraded by light and oxidants (Matsuzawa et al., 2001). BaA/(BaA + Chr + Try) ratio was 0.14 and 0.25 for the ceiling dusts from CHT and PRT, respectively. These ratios were higher than that of crude oil and lower than that of particulates emitted from diesel and gasoline vehicles (Azevedo et al., 1999). Note that BaP was only detected in trace level in the ceiling dusts of CHT. However, in the ceiling dusts of PRT, the ratio of BaP/BeP was 0.26 and close to that of fresh particulate matter at Lincoln/Holland tunnel, but it was lower than that of the vehicular emission and gasoline engine emission (Benner et al., 1989; Khalili et al., 1995). The relative low concentration of BaA and BaP suggests that the photoxidation may play some role in the alteration and distribution of aromatic hydrocarbons in the ceiling dusts of CHT. Furthermore, a number of sulfur- and oxy-PAHs were also identified in aromatic hydrocarbon fraction in both ceiling dusts. These compounds include C_2-dibenzothiophene, benzonaphthothiophene benzo-naphthofuran, dibenzofuran, fluorene-9-one and its alkyl-substituted derivatives. These were considered as typical combustion compounds found in the particulate matter emitted from vehicular emission (Dennis et al., 1981; Oda et al., 2001; Schulze et al., 1984; Tong et al., 1984). Therefore, these compounds are addition indicators to the source of organic matter in the ceiling dusts.

Table 4
Identification and relative concentrations of individual PAH compounds and related diagnostic ratios in the ceiling dusts of PRT and CHT

Peak No.	Compound	Quantification ion	Relative abundance in CHT (%)	Relative abundance in PRT (%)
1	Phenanthrene	178	13.3	17.6
2	Anthracene	178	1.1	1.2
3	C1-Phenanthrene	192	22.5	35.7
4	Dimethyldibenzothiophene	212	16.0	15.4
5	C2-Phenanthrene	206	38.0	69.4
6	Fluoranthene	202	39.2	51.5
7	Pyrene	202	100.0	100.0
8	C3-Phenanthrene	220	41.8	47.6
9	Retene	219/234	1.0	4.3
10	C1-Pyrene	216	38.5	55.4
11	Benzofluorene	216	33.1	61.7
12	C4-Phenanthrene	234	8.0	21.3
13	Benzonaphthothiophene	234	16.4	20.0
14	Benzo[ghi]fluoranthene	226	44.5	54.4
15	C2-pyrene	230	27.5	42.1
16	Benzo[a]anthracene	228	5.4	8.1
17	Chrysene/triphenylene	228	8.8	23.3
18	C1-chrysene	242	19.1	36.8
19	Benzo[b + k]fluoranthene	252	27.8	27.7
20	Benzo[e]pyrene	252	19.0	19.4
21	Benzo[a]pyrene	252	0.2	5.1
22	Indeno[cd]pyrene	276	1.9	2.8
23	Benzo[ghi]perylene	276	5.4	8.7
Diagnostic ratios				
Phe/Ant			12.09	14.32
BaA/(BaA + Chr + Try)			0.14	0.25
BaP/BeP			0.01	0.26
Flu/(Flu + Pyr)			0.28	0.34
IcdP/(IcdP + BghiP)			0.26	0.24
BghiP/BeP			0.28	0.45
BaP/BghiP			0.04	0.59
MPh/Phe			1.69	2.03

Abbreviation: Phe, phenanthrene; Ant, anthracene; BaA benzo[a]anthracene; Chr, chrysene; Try, triphenylene; BaP, benzo[a]pyrene; Bep, benzo[e]pyrene; Flu, fluranthene; Pyr, pyrene; IcdP, indeno[1,2,3-cd]pyrene; BghiP, benzo[ghi]perylene; MPh, methyl phenanthrene.

4. Conclusions

(1) The ceiling dusts from CHT and PRT were different in their organic contents and the composition and distribution of hydrocarbon compounds including molecular markers and aromatic compounds. The ceiling dusts of CHT shown a much higher contents of organic carbon, soluble organic matter and UCM than those in the ceiling dusts of PRT.

(2) The composition and distribution of aliphatic and aromatic hydrocarbon compounds suggests that the organic matter in the ceiling dusts were mainly derived from vehicular emission. The presence of high molecular weight *n*-alkanes suggested that a small portion of particulate organics might originate from the tire wear or lubricating oil in CHT.

(3) It was found that the ceiling dusts from the southbound tubes of both tunnels are much higher in organic contents than those from the northbound tubes and this appear to be related to the higher traffic loads in the southbound tubes, but the exact reasons need further investigation.

(4) Molecular markers exhibited $C_{29}H > C_{30}H$ in hopane series and the relative abundance of the regular sterane is in an order of $C_{27} > C_{29} > C_{28}$ for ceiling dusts of CHT, whereas the order was $C_{29}H < C_{30}H$ in hopane series and $C_{29} > C_{27} > C_{28}$ in sterane series

for ceiling dusts of PRT. These characteristics are mainly inherited from the crude oils from which fuels and lubricating oil were manufactured, suggesting different sources of fuels and lubricating oil used in these two cities.

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References

Azevedo, D.A., Moreira, L.S., de Siqueira, D.S., 1999. Composition of extractable organic matter in aerosols from urban areas of Rio de Janeiro city, Brazil. Atmospheric Environment 33, 4987–5001.

Benner, B.A., Gordon, G.E., Wlse, S.A., 1989. Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study. Environmental Science and Technology 23, 1269–1278.

Bi, X., Sheng, G., Peng, P., Zhang, Z., Fu, J., 2002. Extractable organic matter in PM10 from LiWan district of Guangzhou City, PR China. The Science of the Total Environment 300, 213–228.

Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J., 2003. Distribution of particulate- and vapor-phase *n*-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. Atmospheric Environment 37, 289–298.

Boyer, K.W., Laitinen, H.A., 1975. Automobile exhaust particulates properties of environmental significance. Environmental Science and Technology 279, 457–1086.

Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. Geochimica Et Cosmochimica Acta 22, 2–15.

Cadle, S.H., Mulawa, P.A., Hunsanger, E.C., Nelson, K., Ragazzi, R.A., Barrett, R., Gallagher, G.L., Lawson, D.R., Knapp, K.T., Snow, R., 1999. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado Area. Environmental Science and Technology 33, 2328–2339.

Cao, J.J., Lee, S.C., Ho, K.F., Zou, S.C., Fung, K., Li, Y., Watson, J.G., Chow, Judith, C., 2004. Spatial and Seasonal variation of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China. Atmospheric Environment 38, 4447–4456.

Cheng, Y., 1996. Characteristics and origin of toxic organic pollutants in aerosols from the major cities in Pearl River Delta. Unpublished dissertation. Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, pp. 55–56 (in Chinese).

Cohen, A.J., Higgins, M.W.P., 1995. Health effects of diesel exhaust: epidemiology. In: Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects (A Special Report of the Institute's Diesel Working Group). Health Effects Institute, Cambridge, MA, pp. 251–292.

Dennis, S., Frank, S.C.L., Thomas, J.P., 1981. The identification of polynuclear aromatic hydrocarbon (PAH) derivatives in mutagenic fractions of diesel particulate extracts. International Journal of Environmental Analytical Chemistry 9, 93–144.

Duzgoren-Aydin, N.S., Li, X.D., Wong, S.C., 2004. Lead contamination and isotope signatures in the urban environment of Hong Kong. Environment International 30, 209–217.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 1999. Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere. Atmospheric Environment 33, 2715–2724.

Frysinger, G., Gaines, R.B., Xu, L., Reddy, C.M., 2003. Resolving the complex mixture in etroleum-contaminated sediments 37, 1653–1662.

Fu, J.M., Sheng, G.Y., Xu, J.Y., Eglinton, G., Gowar, A.P., Jia, R.F., Fan, S.F., Peng, P.A., 1990. Application of biological markers in the assessment of paleoenvironments of Chinese non-marine sediments. Organic Geochemistry 16, 769–779.

Garza, M.E., Muth, J., 1974. Characterization of crude, semirefined and refined oils by gas-liquid chromatography. Environmental Science and Technology 8, 249–255.

HEI, 2002. Emissions from Diesel and Gasoline Engines Measured in Highway Tunnels. Health Effects Institute, Cambridge, MA.

Hong Kong EPD, 1997. Air quality in Hong Kong 1996. Report number EPD/TR6/97, Air service group, Hong Kong government.

Jensen, T.E., Hites, R.A., 1983. Aromatic diesel emissions as a function of engine conditions. Analytical Chemistry 55, 594–599.

Jiang, Z.S., Philp, R.P., Lewis, C.A., 1988. Fractionation of biological markers in crude oils during migration and the effects on correlation and maturation parameters. Organic Geochemistry 13, 561–571.

Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Baer, D.V., Oyola, P., 2001. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. Environmental Science and Technology 35, 2288–2294.

Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atmospheric Environment 29, 533–542.

Mai, B., Qi, S., Zeng, E.Y., Yang, Q., Zhang, G., Fu, J., Sheng, G., Peng., P., Wang, Z., 2003. Distribution of polycyclic aromatic hydrocarbons in the coastal region off macao, China: assessment of input sources and transport pathways using compositional analysis. Environmental Science and Technology 37, 4855–4863.

Matsuzawa, S., Nasser-Ali, L., Garrigues, P., 2001. Photolytic behavior of polycyclic aromatic hydrocarbons in diesel particulate matter deposited on the ground. Environmental Science and Technology 35, 3139–3143.

Miguel, A.H., Kirchstetter, T.W., Harley, R.A., Hering, S.V., 1998. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environmental Science and Technology 32, 450–455.

Nauss, K.M., 1995. Critical Issues in Assessing the Carbinogenicity of Diesel Exhaust: A Synthesis of Current Knowledge in Diesel Exhaust: A Critical Analysis of Emissions Exposure and Health Effects. Health Effects Institute, Cambridge, MA.

Neukom, H.-P., Grob, K., Biedermann, M., Noti, A., 2002. Food contamination by C_{20}–C_{50} mineral paraffins from the atmosphere. Atmospheric Environment 36, 4839–4847.

Oda, J., Nomura, S., Yasuhara, A., Shibamoto, T., 2001. Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel. Atmospheric Environment 35, 4819–4829.

Peters, K.E., Moldowan, J.M., 1993. The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice-Hall Inc., Englewood cliffs, NJ.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol. 2. noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science and Technology 27, 636–651.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1993b. Source of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. Environmental Science and Technology 27, 1892–1904.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C1–C32 organic compounds from gasoline-powered motor vehicles. Environmental Science and Technology 36, 1169–1180.

Schulze, J., Hartung, A., Kieb, H., 1984. Identification of oxygenated polycyclic aromatic hydrocarbons in diesel particulate matter by capillary gas chromatography and capillary gas chromatography/mass spectrometry. Chromatographia 19, 391–397.

Simoneit, B.R.T., 1984. Organic matter of the troposphere-β Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. Atmospheric Environment 18, 51–67.

Simoneit, B.R.T., Sheng, G., Chen, X., Fu, J., Zhang, J., Xu, Y., 1992. Molecular marker study of extractable organic mater in aerosols from urban areas of China. Atmospheric Environment 25A (10), 2111–2129.

Tolosa, I., de Mora, S., Sheikholeslami, M.R., Villeneuve, J.-P., Bartocci, J., Cattini, C., 2004. Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments. Marine Pollution Bulletin 148, 44–60.

Tong, H., Sweetman, J., Karasck, F., 1984. Quantitative analysis of polycyclic compounds in diesel exhaust particulate extracts by combined chromatographic techniques. Journal of Chromatography 312, 183–204.

Wang, Z.D., Fingas, M.F., 2003. Development of oil hydrocarbon fingerprinting and identification techniques. Marine Pollution Bulletin 47, 423–452.

Watson, A.Y., Green, G.M., 1995. Noncancer effects of diesel emissions: animal study. In: Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects, A Special Report of the Institute's Diesel Working Group. Health Effects Institute, Cambridge, MA, pp. 139–164.

Wingfors, H., Sjödin, Å., Haglund, P., Brorstrőm-Lundén, E., 2001. Characterization and determination of profiles of polycyclic aromatic hydrocarbons in a traffic tunnel in Gothenburg, Sweden. Atmospheric Environment 35, 6361–6369.

You, M., 2004. Comparison of organic pollutants and elemental composition between the roads and roadside sediments from Hong Kong and Guangzhou metropolis areas. Ph.D. Dissertation, Guangzhou Institute of Geochemistry, CAS.

Yu, M.L., Hites, R.A., 1981. Identification of organic compounds on diesel engine soot. Analytical Chemistry 53, 951–954.