

Organic composition in the dry season rainwater of Guangzhou, China

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Abstract This paper reports the results from a study of the organic composition of rainwater collected at Tianhe district of Guangzhou city, P.R. China, during the dry season. Several special setups of a pyrex bottle with a glass funnel were used for the collection of the rainwater. Three fractions (aliphatics, PAHs and fatty acids) were separated from the total extracted organic compounds and identified with GC-MS. The molecular diagnostic ratios were utilized for the source reconciliation. The aliphatic hydrocarbon and the biomarkers (triterpanes and steranes) distribution show a characteristic of the petrochemical source in the rainwater samples. The PAHs diagnostic ratios [e.g. MP/P, MPI, Fl/(Fl + Py)] indicated vehicular emissions. The fatty acids ratios (e.g. $C_{18:1}/C_{18:0}$ and $C_{18:2}/C_{18:0}$) reflect the contribution of cooking emissions, while the higher plant waxes play little part. Moreover, the

values of MP/P, MPI, BaA/(BaA + CT) and BeP/(BeP + BaP) reflected the origin of the long-distance transportation to some extent. On the whole, for the dry season rainwater, all molecular diagnostic ratios indicated the complexity of the organic composition of the rain, which have the characteristics of both a local emission contribution and a long-distance transportation contribution.

Keywords Aliphatics · Fatty acids · Organic composition · PAHs · Rainwater

Introduction

Because of the important role in climate and atmospheric chemistry and harmful effects on human health, atmospheric aerosols have been studied for several decades for their chemical composition and source reconciliation (Simoneit and Mazurek 1982; Sicre et al. 1987; Mazurek et al. 1991; Stephanou 1992; Bayona et al. 1994). Furthermore, the efficient scavenging of the atmospheric aerosols by the precipitation process (rain, snow and fog) has been shown (Chate et al. 2003; Chate and Pranesha 2004; Simcik 2004; Sempere and Kawamura 1994). As rainwater collects air pollutants, in gaseous and liquid phase or through absorption of the particulates, the determination of the pollutant level in rainwater could be of interest as an initial screening of air quality in different areas (Guidotti et al. 2000).

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Up to now, the inorganic ionic composition (such as Cl^- , SO_4^{2-} , NO_3^- , NH_4^+) and organic acids (such as formic and acetic acids) of rainwater have been widely studied for the acidity and the source of the pollutants (Avery et al. 1991; Tanner et al. 2003). Moreover, the organic pollutants [such as polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PEs), pesticides, and polychlorinated biphenyls (PCBs)] in rainwater have also been studied in other areas for the status of the pollution (Laniewski et al. 1999; Satsumabayashi et al. 2001). However, the research of the source reconciliation of the aliphatics, biomarker, PAHs and fatty acids is infrequently mentioned.

Guangzhou city, with an area of 7,434 km² and a population of over 6.4 million, is the economic and culture center of Guangdong province. During the past 20 years, the explosive increases in industrial and agricultural productivity and the growing population have led to serious concerns about environmental pollution and utilization of natural resources. Tianhe district, located in the northeast of Guangzhou city, is a developing new district, and its environmental pollution is more and more attentive. Research into the particulate matters (PM10, PM2.5) in Guangzhou city has been carried out to discover the constitution and source reconciliation (Zhao et al. 2004). For more cognition of the pollutant source, the correlative constitution and source investigation of the rainwater in this area is very necessary.

In this paper, we will report the organic composition, including aliphatic hydrocarbon, polycyclic aromatic hydrocarbon and the fatty acids, in the rainwater samples collected from Tianhe district in Guangzhou city during the dry season, focusing on the whole organic composition and its source reconciliation. The reason for the season chosen for sample collection is that the amount of particulate matter and concentration of pollutants adsorbed should be higher in the dry season and, therefore, the study of rainwater samples can better reflect the origin of the pollutants.

Materials and methods

Sample collection

The sampling site was located in the residential district of the Guangzhou Institute of Geochemistry

(located in the northeast of the Guangzhou city, P.R. China), which is 200 m north of the Guangyuan expressway, 3 km west of the Guangzhou Nitrogenous Fertilizer factory and 4.5 km south of the South China Arboretum.

Thirteen samples were taken on the roof (approximate height 28 m) of the building in the residential district (Table 1). The sampling period of the rainwater was from September 2003 to February 2004, which is the relatively dry season of Guangzhou city.

A setup of a pyrex bottle (500 ml) and a glass funnel (25 cm diam.) was used for the collection of the rainwater, and all the equipment was washed with soap and water, rinsed with distilled water and dried in a kiln at 450°C for 4 h. All sampling was performed in replicate by several setups, placed at 1 m above ground, and the rainwater sample collected from each rain event was analyzed within 48 h after the sampling.

Materials

All solvents were purchased from Guangzhou Reagent Corporation (AR grade) and were redistilled before use. Standard compounds ($\text{C}_{24}\text{D}_{50}$) were acquired initially as a solid of 99% purity (Aldrich Chemical, Gillingham, Dorset, UK). Silica gel (80–100 mesh), alumina (100–200 mesh), cotton wool, paper filters and anhydrous sodium sulphate were extracted with dichloromethane-methanol (93:7) for 72 h. Glass fibre filters were cleaned at 450°C for 4 h. Silica gel and alumina were activated overnight at 180°C and 250°C, respectively, and deactivated with adding 3% water (by weight). After an overnight equilibration, the deactivated silica gel and alumina were stored in hexane for use. Other materials were kept dry (in desiccator) until use. All glassware were washed with soap and water, rinsed with distilled water and dried in a kiln at 450°C for 4 h, and rinsed with the applied organic solvent just before use.

Analytical procedure

A certain volume of rainwater sample was filtrated by glass fibre filters (1 μm) just after collection. Then, the sample was divided into two parts: one was the particle part ($\Phi > 1 \mu\text{m}$) of the rainwater sample (RP) collected by the glass fibre filter; the other was the

Table 1 Sampling condition and general characteristics of the rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China

Sample	Sampling date	Sampling time	Temperature (approx, °C)	Wind direction	pH	Precipitation (mm)	Volume of the samples used for extraction (ml)	Content of the particle(>1 μm) (mg/l)
R-1	2003.09.29	21:27–21:34	29	E	3.92	7.9	500	21
R-2	2003.10.11	15:00–15:30	30	SE	4.66	6.6	500	186.4
R-3	2003.11.08–09	23:10–00:25	22–24	N	6.64	1.3	250	120.8
R-4	2003.11.09–10	23:00–06:00	15–17	N	4.92	11.2	500	15
R-5	2003.11.10	08:00–11:30	17–19	N	5.04	1.8	250	18.4
R-6	2003.11.10	11:30–14:30	18–20	N	4.89	2.9	250	14
R-7	2003.11.17	10:00–16:00	20–21	N	3.80	1.2	200	75.5
R-8	2003.11.20	12:00–12:55	26–27	SE	5.07	7.9	500	71.4
R-9	2003.12.08	09:30–12:00	17–19	N	4.62	1.8	350	44
R-10	2004.02.03	07:00–17:00	7–10	N	5.55	1.8	200	20
R-11	2004.02.04–05	19:00–06:00	5–7	N	5.54	13.2	500	28.8
R-12	2004.02.07	10:00–13:00	12–13	N	5.20	2.6	500	48.2
R-13	2004.02.24–25	16:00–08:00	17–23	E	3.85	–	200	88.5

– Not applicable

soluble part and the particle part ($\Phi < 1 \mu\text{m}$) of the rainwater sample (RS).

RS was extracted three times with dichloromethane using a separating funnel by shaking for 10 min each. The extracts were decanted and combined. The RP was dried by freeze drying for 24 h and put in a desiccator for 24 h before weighing. After weighing, the RP was extracted with dichloromethane-methanol (93:7) for 72 h. All the extracts were dehydrated using anhydrous sodium sulfate. Then, the extract was concentrated with a rotary evaporator (bath temperature $\leq 35^\circ\text{C}$) to approximately 1 ml and 50 ml hexane was added to it, shaken evenly until column chromatography separation.

The organic compounds were separated by 2:1 silica-alumina columns. Three fractions were eluted. Fraction I (F1, 15 ml hexane) contained the aliphatic hydrocarbons; fraction II [F2, 30 ml of DCM-hexane (3:7)] contained the aromatic hydrocarbons; and fraction III [F3, 25 ml of DCM-methanol (1:1)] contained the polar compounds. This was followed by rotary evaporation until approximately 1–2 ml volume and transferred into a vial. Then, under a gentle stream of nitrogen, the samples were reduced almost to dryness and redissolved with a certain volume of hexane.

The fatty acids were extracted from the polar compounds by the following steps: evaporation to

dryness at a temperature below 70°C , alkalification with KOH-methanol (3 ml, 5% KOH to 95% methanol), and extraction with hexane five times for the polar compounds except the fatty acids compounds. Then acidification with 1 ml 25% HCl and extraction with hexane five times for the fatty acids compounds (Fraction IV, F4). The fatty acids fraction was evaporated to dryness under a gentle stream of nitrogen, and trimethylsilylated with Bis(trimethylsilyl)trifluoroacetamide (BSTFA) using the water bath at about 70°C for 1 h.

All samples were analyzed by using gas chromatography with mass selective detection (GC-MS). GC-MS system was performed on a Hewlett-Packard (HP) 6890 series II Gas Chromatography interfaced with a platform II mass selective detector. A $30 \text{ m} \times 0.25 \text{ mm}$ i.d. DB-5 MS capillary column (film thickness $0.25 \mu\text{m}$) was used. The conditions of the gas chromatography were as follows: injector temperature 280°C ; temperature program was an initial oven temperature of 80°C maintained for 5 min(F1, F2)/1 min(F4), increased at 3°C min^{-1} (F1, F2)/ 4°C min^{-1} (F4) to a maximum of 290°C for 30 min. Helium was the carrier gas at a 1.2 ml/min^{-1} flow rate. $1 \mu\text{l}$ sample was injected with splitless model. The temperatures of MS detector are 180°C and the mass scanning ranged from m/z 45 to m/z 580.

The total soluble organic carbon (DOC) contents of the rainwater samples were measured (TOC-V_{CPH/CPN} Analyzer, Shimadzu). The contents of the organic carbon (POC) and the element carbon (PEC) of the filtered particles were also determined (Thermal-optical OCEC Analyzer, Sunset Laboratory).

Quality control

The field blanks were used to determine any background contamination. Method blanks (solvent) and spiked blanks (standards spiked into solvent) were analyzed. The major contaminants observed were primarily residual phthalate esters. These contaminants did not interfere with the recognition of the compounds of interest. In addition, surrogate standards (C₂₄D₅₀) were added to all samples (including quality assurance samples) before extraction to monitor procedural performance and matrix effects. In the chromatograph, the surrogates have about the same height with the samples (Fig. 1a). The mean recoveries (%) for surrogates in field samples were 75–92%.

Result and discussion

The characteristic of the carbon abundance

In the rainwater samples of Guangzhou, the contents of total organic carbon (TOC) and dissolved organic carbon (DOC) varied from 1.37 to 12.04 mg/l (mean 5.65 mg/l) and 0.93–8.33 mg/l (mean 3.26 mg/l), respectively. The organic carbon content of the rain-particle samples (POC) was between 0.44 mg/l and 8.84 mg/l (mean 2.48 mg/l), while the elemental carbon content of the rain-particle samples (PEC) varied between 0.02 mg/l and 3.02 mg/l (mean 0.48 mg/l) (Table 2). Likens et al. (1983) reported the carbon abundance of two locations in the northeastern United States (Hubbard Brook Experimental Forest, New Hampshire and Ithaca, New York) in 1983 (New York: annual mean TOC 2.37 mg/l, annual mean DOC 1.88 mg/l, annual mean POC 0.49 mg/l; New Hampshire: annual mean TOC 1.28 mg/l, annual mean DOC 1.09 mg/l, annual mean POC 0.20 mg/l). The concentration of the carbon abundance is higher than those from the northeastern United States, which

Table 2 The carbon abundance in the rain samples collected from Guangzhou city, P.R. China

Sample	TOC (mg/l)	DOC (mg/l)	POC (mg/l)	PEC (mg/l)
1	12.04	8.33	3.71	0.82
2	1.50	1.00	0.50	0.06
3	11.81	2.97	8.84	3.02
4	3.60	2.47	1.13	0.02
5	2.79	2.00	0.79	0.03
6	3.40	2.72	0.68	0.12
7	7.05	3.97	3.08	0.04
8	5.36	2.12	3.24	0.46
9	6.82	3.60	3.22	1.05
10	–	4.36	–	–
11	1.37	0.93	0.44	0.02
12	2.37	1.33	1.04	0.03
13	9.72	6.64	3.08	0.13
Average	5.65	3.26	2.48	0.48

– Not applicable

reflected the obvious contribution of the pollutant emission to the rainwater in Guangzhou.

Aliphatic hydrocarbon

The typical chromatograms of *m/z* 85 for aliphatic fractions in the rainwater samples are presented in Fig. 1b. These chromatograms show that the aliphatic hydrocarbons fraction was dominated by *n*-alkanes. The determination of the homologous *n*-alkanes in the aliphatic fraction of the rainwater samples allowed the determination of their relative distribution, carbon number maximum (C_{max}), carbon preference index (CPI), and wax *n*-alkanes (WNA) content. From Table 3, it can be seen that most of the samples have the *n*-alkane homologs from C₁₄ to C₃₃.

It is possible to assign biogenic signatures to *n*-alkane homologue distribution exhibiting C_{max} ≥ 27, mixed biogenic and petrogenic signatures for C_{max} > 23 and < 26, and petrogenic signatures from *n*-alkanes homologue distribution with maxima < 23. The determination of C_{max} for *n*-alkanes gives the strongest indication of anthropogenic versus natural recent biological input (Azevedo et al. 1999). C_{max} of the rainwater samples are shown in Table 3, from which it could be deduced that the organics of the RS were mainly petrogenic or mixed

Table 3 Molecular diagnostic ratios of the rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China

Compound classes	RP	RS
1. <i>n</i>-Alkanes		
Homologues range; C _{max}	(C _{14–33}); C ₁₆ , C ₁₇ , C ₁₈	(C _{14–33}); C ₁₄ , C ₁₈ , C ₂₄ , C ₂₅
CPI ₁ ^a	0.95–1.38	0.25–1.08
CPI ₂ ^b	0.91–1.20	0.18–1.21
CPI ₃ ^c	0.98–2.51	0.59–1.17
WNA% (%)	11.05–36.51	8.81–29.58
2. <i>n</i>-Alkylcyclohexanes		
Homologues range; C _{max}	(C _{5–19}); C ₁₁ , C ₁₂	(C _{5–19}); C ₉ , C ₁₁ , C ₁₇
CPI ^d	0.69–1.71	1.59–3.54
3. Fatty acids		
Homologues range; C _{max}	(C _{8–24}); C ₁₆	(C _{8–24}); C ₁₆
CPI ^e	6.01–12.96	7.20–13.76
(C ₁₆ + C ₁₈)% (%)	57.77–74.22	63.94–75.14
C _{18:1} /C ₁₈	1.35–3.59	0.80–3.10
C _{18:2} /C ₁₈	0.38–0.96	0.25–1.11
4. PAHs		
MP/P	0.10 ± 0.05	0.30 ± 0.08
MPI ^f	0.07 ± 0.04	0.21 ± 0.04
P/An	14.97 ± 4.56	35.26 ± 9.80
Fl/(Fl + Py)	0.48 ± 0.04	0.61 ± 0.05
(BaA/BaA + CT)	0.08 ± 0.02	0.10 ± 0.02
(BeP/BeP + BaP)	0.68 ± 0.07	0.76 ± 0.07

^a Whole range for *n*-alkanes: $CPI_1 = \sum (C_{13}-C_{35}) / \sum (C_{12}-C_{34})$

^b Petrogenic *n*-alkanes: $CPI_2 = \sum (C_{13}-C_{25}) / \sum (C_{12}-C_{24})$

^c Biogenic *n*-alkanes: $CPI_3 = \sum (C_{25}-C_{35}) / \sum (C_{24}-C_{34})$

^d Whole range for *n*-alkylcyclohexanes: $CPI = \sum (C_{12}-C_{34}) / \sum (C_{13}-C_{35})$

^e Whole range for *n*-alkanoic acids: $CPI = \sum (C_{12}-C_{34}) / \sum (C_{13}-C_{35})$

^f $MPI = [1.5(2-MP + 3-MP)] / [P + 1-MP + 9-MP]$,

where, *n*-MP = corresponding methylphenanthrene isomer concentration, P = phenanthrene concentration

biogenic and petrogenic signatures, while the organics of the RP were mainly petrogenic.

CPI is useful in marking an estimate of plant wax contribution versus fossil fuel contamination (Zheng 1997). Few of the samples showed an odd-to-even predominance for the whole range of *n*-alkanes. The CPI₁ values (Table 3; range from 0.95 to 1.38 for the RP and from 0.25 to 1.08 for the RS) were similar to those observed for other urban areas aerosol samples (Kavouras et al. 1998). This indicated the importance of petroleum and diesel residues and gasoline emissions. CPI₂ values varied from 0.91 to 1.20 for the RP and from 0.18 to 1.21 for the RS indicating that the emissions from anthropogenic activities are more

important than terrestrial plants. In addition, CPI₃ values for biogenic *n*-alkanes varied between 0.98 and 2.51 for the RP (between 0.59 and 1.17 for the RS), suggesting that mechanical abrasion of organic lipids from leaf epicuticular waxes is a slight contribution to the *n*-alkanes of the RP for this normal aliphatic homologs range, while little contribution to the normal aliphatic homologs of the RS.

To determine the relative importance of biogenic and petrogenic sources, the contribution of wax terrestrial *n*-alkanes (WNA%) were estimated. The contribution of biogenic wax *n*-alkanes to the total *n*-alkanes concentration in all the samples ranged from 11.05% to 36.51% for the RP and from 8.81% to

29.58% for the RS, indicating a lower input from epicuticular waxes emissions of terrestrial plants.

The *n*-alkylatedcyclohexanes (*n*-CHs), as a homologous series of hydrocarbon compounds, are commonly present in all samples, including the RP and the RS (Fig. 1c), which indicated the sources as crude oil and refinery products, such as diesel fuel (Hostettler et al. 2002). The *n*-CHs homologs are mostly from C₁₁ to C₂₅ in all samples. A slight odd-to-even dominance was displayed for the RS (CPI value varied between 1.59 and 3.54), while indistinct for the RP (CPI value varied between 0.69 and 1.71).

Biomarkers

The biomarkers were also present in the rainwater samples (Table 4), such as terpanes and steranes, which can be used to indicate petroleum residues and the extent of thermal maturation.

The triterpane distribution patterns for the rainwater samples are shown in Fig. 1d. The m/z 191 chromatogram show the 17H(α), 21H(β)-hopane series is present in the samples ranging from C₂₇ to C₃₃ in the RP (from C₂₇ to C₃₁ in the RS, no C₂₈, C_{max} = 30, resolved 22S and 22R stereomers for C₃₁), and minor amounts of C₁₉ to C₂₉ tricyclic triterpanes (not in all samples, no C₂₂ and C₂₇). The C₂₄ tetracyclic triterpane is also present in all samples. The ratios of C₂₉-17H(α), 21H(β)-hopane/C₃₀-17H(α), 21H(β)-hopane, Ts(C₂₇ α , 18 α (H)-22,29,30-trisnorhopane)/Tm(C₂₇ α , 17 α (H)-22,29,30-trisnorhopane) and C₃₁22S/22R are commonly utilized as confirmation indicators. In the rainwater samples, the ratios of C₂₉/C₃₀ (0.40–0.55 for the RP and 0.53–0.82 for the RS), Ts/Tm (0.76–1.47 for the RP and 0.75–2.29 for the RS) and C₃₁22S/22R (1.05–1.56 for the RP and 0.85–2.52 for the RS) indicated that vehicular exhaust sources (Simoneit 1984).

Another group of petroleum biomarkers is comprised of the steranes, which are characterized by the key ions of m/z 217 and 218. The steranes are only obvious in the RP, while indistinct in the RS (Fig. 1e). The dominant steranes are the regular steranes of C₂₇, C₂₈ and C₂₉ and their relative abundances are in the order of C₂₉ > C₂₇ \approx C₂₈. These characteristic sterane hydrocarbons are found only in fossil fuels (Simoneit 1984), thus further confirming the petrochemical component in the rainwater samples.

Table 4 Identification of triterpanes series (m/z 191) and sterane series (m/z 217) in the rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China

No.	Components	m/z
1	C ₁₉ , tricyclic terpane	191
2	C ₂₀ , tricyclic terpane	191
3	C ₂₁ , tricyclic terpane	191
4	C ₂₃ , tricyclic terpane	191
5	C ₂₄ , tricyclic terpane	191
6	C ₂₅ , tricyclic terpane	191
7	C ₂₄ , tetracyclic terpane	191
8	C ₂₆ , tricyclic terpane	191
9	C ₂₈ , tricyclic terpane	191
10	C ₂₉ , tricyclic terpane	191
11	Ts, C ₂₇ α , 18 α (H)-22,29,30-trisnorhopane	191
12	Tm, C ₂₇ α , 17 α (H)-22,29,30-trisnorhopane	191
13	C ₂₉ $\alpha\beta$, 17 α (H), 21 β (H)-30-norhopane	191
14	C ₂₉ $\alpha\beta$, 17 α (H), 21 β (H)-30-norhopane	191
15	C ₂₉ $\beta\alpha$, 17 β (H), 21 α (H)-30-normoretane	191
16	C ₃₀ $\alpha\beta$, 17 α (H), 21 β (H)-30-hopane	191
17	C ₃₀ $\beta\alpha$, 17 β (H), 21 α (H)-30-moretane	191
18	C ₃₁ $\alpha\beta$, 17 α (H), 21 β (H)-30-homohopanes(22S + 22R)	191
19	Gammacerane	191
20	C ₃₁ $\beta\alpha$, 17 β (H), 21 α (H)-homomoretanes (22S + 22R)	191
21	C ₃₂ $\alpha\beta$, 17 α (H), 21 β (H)-bishomohopanes(22S + 22R)	191
22	C ₃₂ $\beta\alpha$, 17 β (H), 21 α (H)-bishomomoretanes(22S + 22R)	191
23	C ₃₃ $\alpha\beta$, 17 α (H), 21 β (H)-trishomohopanes (22S + 22R)	191
24	C ₃₃ $\beta\alpha$, 17 β (H), 21 α (H)-trishomomoretanes(22S + 22R)	191
25	C ₃₄ $\alpha\beta$, 17 α (H), 21 β (H)-tetrashomohopanes(22S + 22R)	191
26	C ₂₇ , 13 β (H),17 α (H)- diacholestane(20S)	217
27	C ₂₇ , 13 β (H),17 α (H)-diacholestane(20R)	217
28	C ₂₇ , 13 α (H),17 β (H)-diacholestane(20S)	217
29	C ₂₇ , 13 α (H),17 β (H)-diacholestane(20R)	217
30	C ₂₈ , 13 β (H),17 α (H)-diaergostane(20S)	217
31	C ₂₈ , 13 β (H),17 α (H)-diaergostane(20R)	217
32	C ₂₇ , 5 α (H),14 α (H),17 α (H)-cholestane(20S)	217
33	C ₂₇ , 5 α (H),14 β (H),17 β (H)-cholestane(20R)	217
34	C ₂₇ , 5 α (H),14 β (H),17 β (H)-cholestane(20S)	217
35	C ₂₇ , 5 α (H),14 α (H),17 α (H)-cholestane(20R)	217
36	C ₂₉ , 13 β (H),17 α (H)-diastigmastane(20R)	217
37	C ₂₉ , 13 α (H),17 β (H)-diastigmastane(20S)	217

Table 4 continued

No.	Components	m/z
38	C ₂₈ , 5 α (H),14 α (H),17 α (H)-ergostane(20S)	217
39	C ₂₈ , 5 α (H),14 β (H),17 β (H)-ergostane(20R)	217
40	C ₂₈ , 5 α (H),14 β (H),17 β (H)-ergostane(20S)	217
41	C ₂₈ , 5 α (H),14 α (H),17 α (H)-ergostane(20R)	217
42	C ₂₉ , 5 α (H),14 α (H),17 α (H)-stigmastane (20S)	217
43	C ₂₉ , 5 α (H),14 β (H),17 β (H)-stigmastane (20R)	217
44	C ₂₉ , 5 α (H),14 β (H),17 β (H)-stigmastane (20S)	217
45	C ₂₉ , 5 α (H),14 α (H),17 α (H)-stigmastane (20R)	217

Polynuclear aromatic hydrocarbon

The polynuclear aromatic hydrocarbons (PAHs) are pyrogenic molecular markers of compounds formed by higher temperature combustive processes (e.g., Simoneit and Mazurek 1982; Simoneit et al. 1991) and due to their toxicity are monitored in major urban areas of the world. More than 30 PAH compounds and several hundred PAH derivatives have been identified since 1976 to have carcinogenic and mutagenic effects, making them the largest single class of chemical carcinogens known (Bjørseth and Ramdahl 1985).

The PAHs relative concentration in the rainwater samples are shown in Fig. 2 and the collective parameters and diagnostic ratios are given in Table 3. The main detected PAHs are shown in Table 5.

The ratio of methyl-phenanthrenes to phenanthrene (MP/P) has been used for source identification of PAHs (Prahl et al. 1984; Takada et al. 1990). MP/P ratios between 1 and 8 represent evidence for enhanced mobile sources or unburned fossil organic material contribution. Ratios below 1 are typical of emissions from stationary combustion sources where fuel is burning at higher temperatures. The Methylphenanthrene Index (MPI) has been used as a hydrocarbon internal maturity parameter (Radke et al. 1982). The influence of combustion temperature on the yields of phenanthrene and its methylated derivatives was evaluated, and the corresponding MPI was calculated. It can be used as a mobile or stationary source diagnostic parameter. Phenanthrene/anthracene (P/An) ratio has been used to distinguish petrogenic from pyrolytic sources (Benlahcen et al. 1997; Baumard

et al. 1998). P/An ratios higher than 10 are seen in petroleum input or diagenetic sources, whereas values lower than 10 are characteristic of combustion processes. In this study, obvious difference was found in the MP/P, P/An and MPI values between the RS and the RP. The values of MP/P (0.10 ± 0.05 for the RP and 0.30 ± 0.08 for the RS) and MPI (0.07 ± 0.04 for the RP and 0.21 ± 0.04 for the RS) are well within the typical range for combustion-derived products (Rogge et al. 1993a, b; Adams et al. 1982; Bayona et al. 1994). It suggests that either unburned fossil PAHs are not well dispersed in the samples or more likely are quantitatively dominated by PAHs of combustion origin during long-range transport (Gogou et al. 1998). The values of P/An greater than 10 (14.97 ± 4.56 for the RP and 35.26 ± 9.80 for the RS) are seen in petroleum input (Benlahcen et al. 1997; Baumard et al. 1998).

In order to further assess the different sources of PAHs present in the examined rainwater samples, other diagnostic ratios, including [benzo(e)pyrene]/[benzo(e)pyrene + benzo(a)pyrene] [BeP/(BeP + BaP)], [benzo(a)anthracene]/[benzo(a)anthracene + chrysene, triphenylene] [BaA/(BaA + CT)] and fluoranthene/(fluoranthene + pyrene) [Fl/(Fl + Py)], can be used. These ratios can suggest a mixed origin of unburned fossil fuel and vehicular emissions (Sicre et al. 1987). Since benzo(a)pyrene decays faster in the atmosphere than benzo(e)pyrene, this ratio has been used as an indicator of the lifetime of the organic aerosol in the atmosphere. Freshly emitted PAHs should have a BeP/(BeP + BaP) ratio equal to 0.50 (Grimmer et al. 1983). In this study, Fl/(Fl + Py) ratio values (Table 3; mean values for the RP 0.48 ± 0.04 and the RS 0.61 ± 0.05) are very similar to vehicular emission and especially to those of catalytic automobiles (≥ 0.4 ; Rogge et al. 1993a). BaA/(BaA + CT) ratio values (0.08 ± 0.02 for the RP and 0.10 ± 0.02 for the RS) and [BeP/(BeP + BaP)] ratio values (0.68 ± 0.07 for the RP and 0.76 ± 0.07 for the RS) are characteristic of a faster decay of benzo(a)pyrene and benzo(a)anthracene and indicated an origin from a distant source (Grimmer et al. 1981, 1983; Pitts et al. 1980). The BaA/(BaA + CT) and BeP/(BeP + BaP) values confirm the information provided by the MP/P and MPI values.

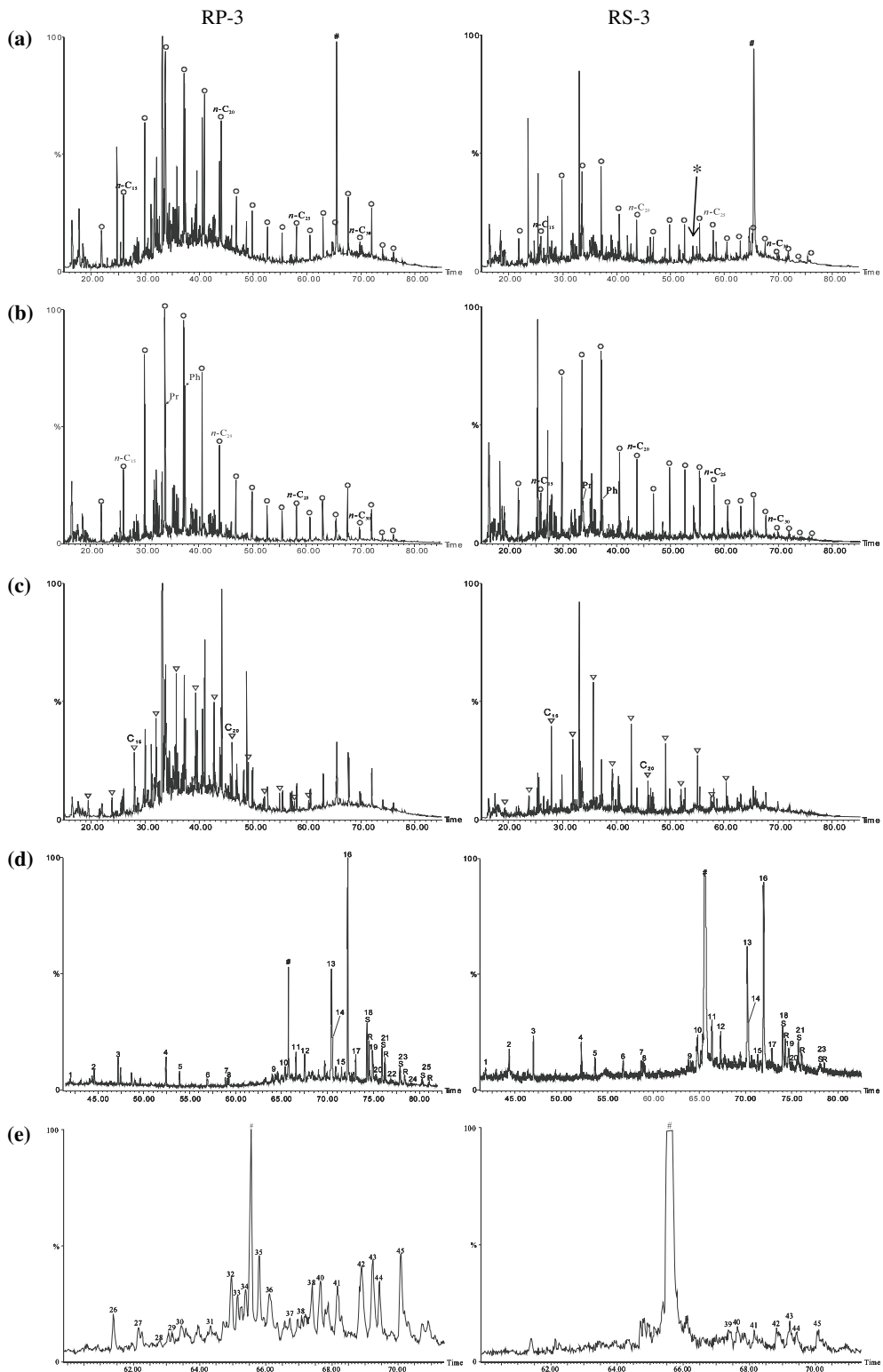


Fig. 1 The typical chromatograms for aliphatic fractions in the rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China. **(a)** Total ion current, **(b)** m/z 85 fragmentogram characteristic of *n*-alkanes, **(c)** m/z 83 fragmentogram for CHs, **(d)** m/z 191 fragmentogram for triterpanes, peaks 1 to 25 are referred to Table 3, **(e)** m/z 217 fragmentogram for steranes, peaks 26 to 45 are referred to Table 3. #: contaminant, ○: *n*-alkanes, ▽: *n*-alkylatedcyclohexanes, *: Std-D-C₂₄

Fatty acids

As *n*-alkanoic acids are emitted from an important variety of sources in the environment (Simoneit and Mazurek 1982; Simoneit 1984a, 1989; Rogge et al. 1991, 1993a, b, c, 1993d; Hildemann et al. 1994), their presence should be taken into consideration with caution. The distribution pattern of fatty acids (RP and RS) is shown in Fig. 3. All the samples have the homologs from C₈ to C₂₄, and show a strong even/odd predominance (CPI values varied from 5.87 to 12.96 for the RP and from 7.20 to 13.76 for the RS). Among the detectable fatty acids, the two most abundant acids, C₁₆ (palmitic acid) and C₁₈ (stearic acid) accounted for approximately 57.7–74.2% of the total fatty acids in the RP (63.9–75.1% in the RS).

Generally, the *n*-alkanoic acids homologs less than C₂₀ are commonly thought to be derived in part from microbial sources while homologs greater than C₂₂ are thought to come from vascular plant wax (Simoneit and Mazurek 1982). The ratios of >C₂₂/_<C₂₀ *n*-alkanoic acids are very low in all samples (from 0.003 to 0.012 in RS and from 0.003 to 0.02 in RP), which indicate little contribution of plant wax. Although homologues <C₂₀ are primarily associated with microbial sources (Simoneit and Mazurek 1982), other sources of fine organic aerosols also release *n*-alkanoic acids, including meat cooking processes (Rogge et al. 1991; Schauer et al. 1999a), gasoline and diesel vehicles (Rogge et al. 1993a; Schauer et al. 1999b, 2002), fuel oil combustion (Rogge et al. 1997) and cigarette smoke (Rogge et al. 1994). In urban regions, a major source of alkanolic acids <C₂₀ is from cooking and biomass combustion (Rogge et al. 1991, 1993a,b, 1994; Zheng et al. 1997). In Chinese type cooking, stir-frying is one of the main contributors to fatty acid emissions because a large portion of the oils used in cooking the food is vaporized (Zheng et al. 1997).

The presence of unsaturated fatty acid such as palmitoleic (C_{16:1}), oleic (C_{18:1}) and linoleic (C_{18:2})

Table 5 Identification of polycyclic aromatic compounds in the rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China

No.	Components	Molecule formula	Base ion
1	Naphthalene	C ₁₀ H ₈	128
2	Methyl-naphthalene	C ₁₁ H ₁₀	142
3	Dimethyl-naphthalene	C ₁₂ H ₁₂	156
4	Trimethyl-naphthalene	C ₁₃ H ₁₄	170
5	Tetramethyl-naphthalene	C ₁₄ H ₁₆	184
6	1,1'-Biphenyl	C ₁₂ H ₁₀	154
7	Methyl-biphenyl	C ₁₃ H ₁₂	168
8	Dimethyl-biphenyl	C ₁₄ H ₁₄	182
9	Trimethyl-biphenyl	C ₁₅ H ₁₆	196
10	Dibenzofuran	C ₁₂ H ₈ O	168
11	Methyl-dibenzofuran	C ₁₃ H ₁₀ O	182
12	Dimethyl-dibenzofuran	C ₁₄ H ₁₂ O	196
13	Fluorene	C ₁₃ H ₁₀	166
14	Methyl-fluorene	C ₁₄ H ₁₂	180
15	Dimethyl-fluorene	C ₁₅ H ₁₄	194
16	Dibenzothiophene	C ₁₂ H ₈ S	184
17	Methyl-dibenzothiophene	C ₁₃ H ₁₀ S	198
18	Dimethyl-dibenzothiophene	C ₁₄ H ₁₂ S	212
19	Trimethyl-dibenzothiophene	C ₁₅ H ₁₄ S	226
20	Phenanthrene	C ₁₄ H ₁₀	178
21	Anthracene	C ₁₄ H ₁₀	178
22	Methyl-phenanthrene	C ₁₅ H ₁₂	192
23	Dimethyl-phenanthrene	C ₁₆ H ₁₄	206
24	Trimethyl-phenanthrene	C ₁₇ H ₁₆	220
25	Retene	C ₁₈ H ₁₈	219
26	Fluoranthene	C ₁₆ H ₁₀	202
27	Pyrene	C ₁₆ H ₁₀	202
28	Benzo[ghi]fluoranthene,	C ₁₈ H ₁₀	226
29	Benzo[e]pyrene,	C ₂₀ H ₁₂	252
30	Benzo[a]pyrene	C ₂₀ H ₁₂	252
31	Terphenyl	C ₁₈ H ₁₄	230
32	Acenaphthene	C ₁₂ H ₁₀	154
33	Acenaphylene	C ₁₂ H ₈	152

acids, suggests recent biogenesis. Since unsaturated fatty acids are known to be very unstable and are easily oxidized and degraded in the environment (Kawamura and Gagosian 1987; Simoneit and Mazurek 1982), the abundance of these compounds in the samples may also be used to estimate whether the material is aged. Moreover, because of the C_{18:1} acids

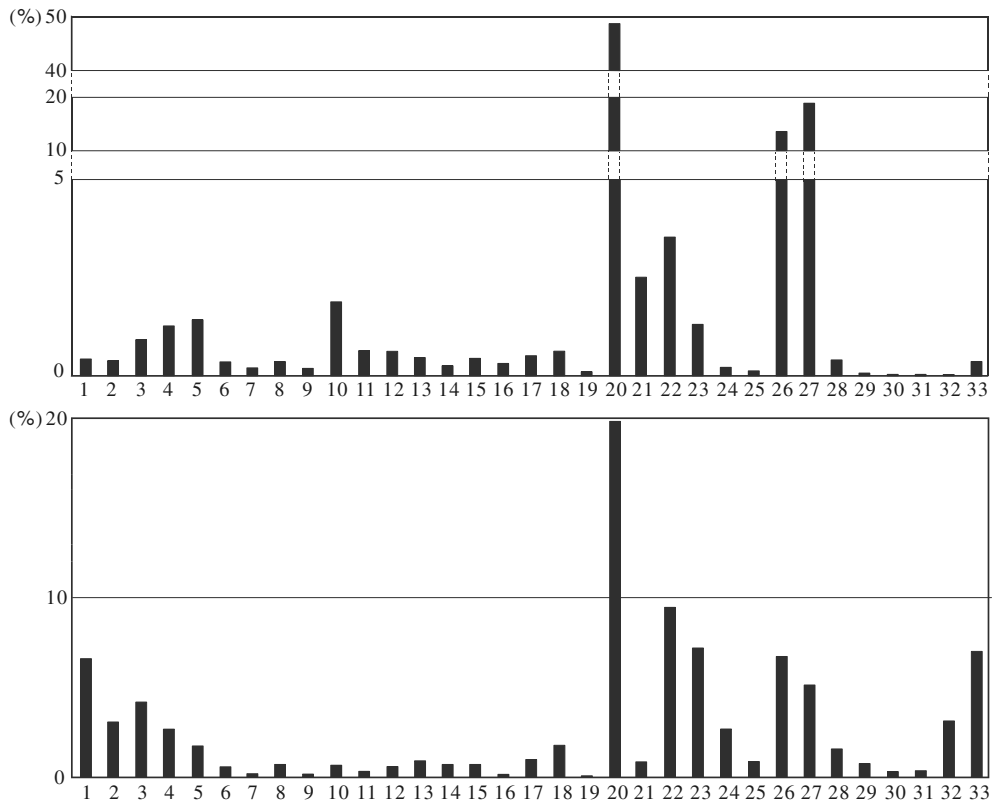


Fig. 2 Relative abundance of PAHs in rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China. (a) RP-3, (b) RS-3. The corresponding components 1 to 33 are referred to Table 4

can be produced during the cooking process, the presence of $C_{18:1}$ acids is often been treated as the sign of the cooking emission (Zheng et al. 1997, 2000). The ratios of $C_{18:1}/C_{18}$ and $C_{18:2}/C_{18}$ can be used. High ratios would indicate a strong source while low ratios could be due to the long-distance transport of the compounds. It can be seen in Table 3 that the ratios of $C_{18:1}/C_{18}$ range from 1.35 to 3.59 and the ratios of $C_{18:2}/C_{18}$ range from 0.83 to 2.64 in the RP, while from 0.80 to 3.10 for $C_{18:1}/C_{18}$ and from 0.52 to 2.32 for $C_{18:2}/C_{18}$ in the RS. This suggests the local cooking emission is the main contributor of the fatty acids in rainwater.

Conclusion

In this paper, the organic compositions and source reconciliation of rainwater samples collected from

TianHe district of Guangzhou city during dry season have been studied. All samples were divided into two parts: the RP [the particle part ($\Phi > 1 \mu\text{m}$)] and the RS [the soluble part and the particle part ($\Phi < 1 \mu\text{m}$)]. It is noticed that certain difference existed between the RP and the RS, but the type of the origin have no distinct disparity.

The aliphatic hydrocarbon distribution display the petrogenic or mixed biogenic and petrogenic signatures. The CPI values (CPI_1 , CPI_2 and CPI_3), WNA% and the existence of the n -CHs indicated the petroleum emissions are more dominant than the plant wax inputs. The triterpanes and steranes show a characteristic of the vehicular exhaust and petrochemical source. The PAHs diagnostic ratios of P/An, Fl/(Fl + Py) reflect the petroleum input and vehicular emission, while the ratios of MP/P, MPI indicated the combustion emission. Moreover, the values of MP/P, MPI, BaA/(BaA + CT) and BeP/(BeP + BaP) indicated the possible origin during long-range transport.

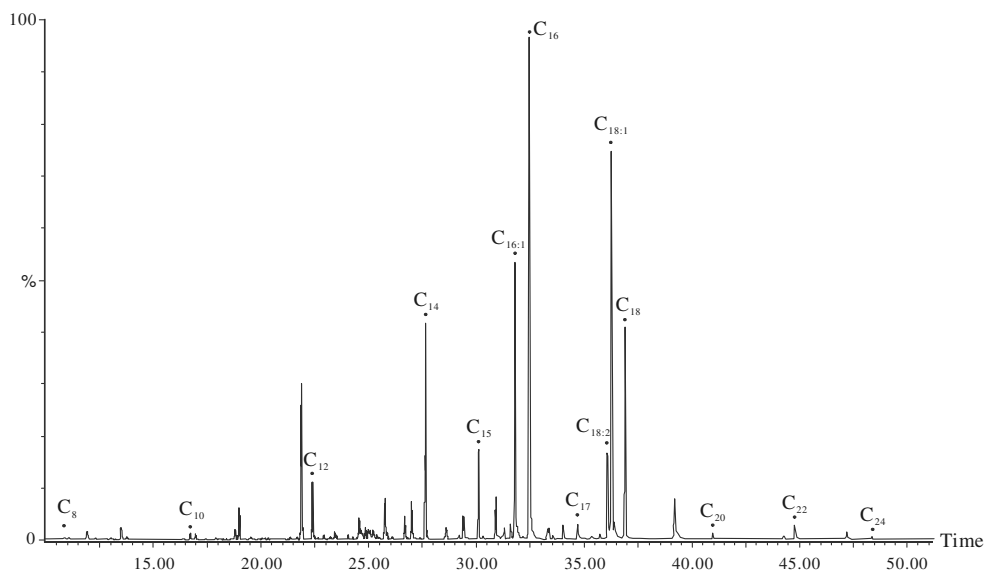


Fig. 3 The fatty acids distribution pattern of the rainwater samples collected from the Tianhe district of Guangzhou city, P.R. China

The fatty acids distribution show the small contribution of the plant wax, and the ratios of $C_{18:1}/C_{18}$ and $C_{18:2}/C_{18}$ indicated that local cooking oil emission is the main contributor of the fatty acids in rainwater.

In this study, the collected rainwater samples can be characterized by anthropogenic origin. The petrogenic origin should be the most important source of the samples. And the cooking emission may be the origin of the fatty acids. The higher plant waxes play little role to the origin. On the whole, because the rain is formed at high altitudes, per se, the origin of the organic composition in the rain has a higher blended characteristic more complex than in the air. As a result, the origin of the organic composition of the rain has to some extent both local emission contribution and long-distance transportation contribution.

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