The distribution and source apportionment of aliphatic hydrocarbons in soils from the outskirts of Beijing

Youfeng Zhu ^a, Hui Liu ^a, Hangxing Cheng ^b, Zhiqun Xi ^a,
Xiufeng Liu ^a, Xiaobai Xu ^{a,*}

^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^b Institute of Geochemical and Geophysical Exploration, Beijing 065000, China

Received 16 April 2004; accepted 7 September 2004

(returned to author for revision 15 August 2004)

Available online 9 December 2004

Abstract

We report the first extensive study of the spatial distribution and source apportionment of aliphatic hydrocarbons in soils from the Beijing outskirts. Mixed soil samples (5–30 cm depth) were collected for the quantitative determination of *n*-alkanes, isoprenoids, unresolved complex mixtures and the qualitative determination of hopanes and steranes. The total concentrations, including *n*-alkanes from C₁₃ to C₃₆, pristane and phytane, were in the range of 0.60–39.92 µg/g, with a median value of 1.97 µg/g. No correlation between soil organic matter content or the percentage of clay and the concentrations was found. Carbon preference index (CPI) values for the whole range of *n*-alkanes varied between 0.73 and 4.27, with a median value of 1.64, and a contour map of CPI was drawn. A predominance of odd/even carbon *n*-alkanes and unresolved complex mixtures with different shapes and range were frequently observed. Factor analysis reduced the data set to two principal components explaining 82.82% of the total variation among samples and confirming contributions from low molecular weight species (63.66%) and long-chain *n*-alkanes (19.27%), respectively. Based on the principal component analysis, the concentration profiles and molecular markers, it was concluded that the aliphatic hydrocarbons were from both biogenic and anthropogenic sources.

© 2004 Published by Elsevier Ltd.

1. Introduction

In the past decades, aliphatic hydrocarbons and other lipid compounds in atmospheric aerosols and sediments in coastal oceanic environments have been studied to ascertain their terrestrial, marine or anthropogenic origins (Gagosian et al., 1981; Marty

and Salot, 1982; Prah et al., 1984; Tolosa et al., 1996; Maldonado et al., 1999). Aliphatic hydrocarbons in urban aerosols were also widely studied (Aceves and Grimalt, 1993; Leuenberger et al., 1988) because of increasing consumption of fossil fuel. However, most attention was paid to carcinogenic polycyclic aromatic hydrocarbons. Until now, there are only limited reports on aliphatic hydrocarbons in soils. Nowadays, with petroleum exploration and the manufacturing of petroleum products, oil contamination in the environment is of worldwide concern. When leakage of oil to soil occurs, oil fractions will consequently pollute the air and

* Corresponding author. Tel.: +86 10 82521355; fax: +86 10 62919177.

E-mail address: xuxb@public.bta.net.cn (X. Xu).

groundwater through volatilization, partitioning and leaching. Aliphatic hydrocarbon analysis can be used to fingerprint spilled oils and to provide additional information on the source of hydrocarbon contamination and the extent of degradation of the spilled oil.

The origins of aliphatic hydrocarbons were often identified by diagnostic concentration indices together with molecular markers and multivariate methods (Kavouras et al., 2001; Colombo et al., 1989). Some indices that have been used for many years to identify biogenic and petrogenic sources are: (a) the major hydrocarbons (MHs); (b) low/high molecular weight hydrocarbons (L/H); (c) sum of total *n*-alkanes/*n*-C₁₆; (d) carbon preference index (CPI); (e) *n*-C₁₇/pristane (C₁₇/Pr) and *n*-C₁₈/phytane (C₁₈/Ph); and (f) unresolved complex mixtures (UCMs). Generally speaking, *n*-alkanes from vascular plant origins exhibit a predominance of odd/even carbon markers, higher CPI value and MH usually around C₂₇, C₂₉, C₃₁, compared to those from petroleum related sources (Simoneit et al., 1991). Furthermore, aliphatic fractions extracted from carbon black, diesel soot, urban dust, chimney soot, wood charcoal and vegetation fire residues also show different characteristic diagnostic indices (Fernandes and Brook, 2003).

This paper presents the first extensive study of aliphatic hydrocarbons in soils from Beijing, the capital of China, which has developed at an explosive rate in the past two decades. Detailed information is given on the origins, concentrations and distributions of aliphatic hydrocarbons.

2. Experimental

2.1. Sampling

The sampling area was 816 km²: 5 km east, 14 km south, 7 km west, and 6 km north from Beijing's fourth-ring road. Soil samples (5–30 cm depth) were collected every 1 km, and 16 cores were pooled to obtain one representative sample for every 16 km² area. Together, 47 samples were analyzed. The soil survey and sampling site map for the Beijing outskirts is shown in Fig. 1. The soil samples are brown and mostly sandy loam and silt loam. Each fully mixed sample was air dried under a hood at room temperature and sieved to pass a 35 mesh sieve. All samples were refrigerated at –4°C until analysis.

2.2. Materials

All solvents, obtained from the Beijing Chemical Factory, were of analytical grade and were redistilled in an all-glass system before use. The *n*-alkane standards were purchased from ChemService Inc.

- A. The third-ring road; E. Beijing airport express;
- B. The fourth-ring road; F. Jingjingtang highway;
- C. The fifth-ring road; G. Jingshi highway.
- D. The Badaling highway;

Fig. 1. Map of soil survey and sampling sites in the Beijing outskirts.

Silica gel (100–200 mesh; Qingdao Haiyang Chemical Co., Shangdong, China) was activated for 16 h at 130°C and kept in a desiccator until use. An aliquot (5 g) of each soil sample was weighed accurately and ground with 5 g anhydrous sodium sulfate. The sample was extracted with petroleum ether/acetone, 1/1 (v/v), using ultrasonication for 3 min and then centrifuged. This procedure was repeated three times. The extracts were combined and concentrated in volume to about 1 mL.

For isolation of the alkane fraction, 10 g of activated silica gel was packed into a glass column using methylene chloride, covered with 2 g of anhydrous Na₂SO₄ at the top and then pre-washed using 40 mL petroleum ether. The sample was loaded on to the column and eluted with 25 mL of petroleum ether to obtain the alkane fraction. The fraction was concentrated to 0.2 mL under a gentle stream of nitrogen.

Quantitative analysis of the alkanes was carried out using an Agilent 6890 gas chromatograph equipped with FID and a DB-5 column (25 m × 0.25 mm i.d., 0.25 μm film thickness) with ultrapure nitrogen as carrier gas and make-up gas. Gas chromatography (GC) conditions were: injector and detector temperature 280 and 300 °C, respectively, initial oven temperature 50°C held for 2 min then ramped to 280°C at 4 °C/min and held for 10 min. A 1 μL sample was injected in the splitless mode and the purge valve was opened at 1 min. Compounds were identified by retention time matched to external integration.

Some samples were also analyzed using a Hewlett–Parkard 6890 gas chromatograph coupled to a 5973

MSD to confirm the identity of each compound. A DB-5 capillary column (25 m × 0.25 mm i.d., 0.25 µm film thickness) was used. The GC oven programme was as described above. The scan range was 50–500 amu and the ionization energy was 70 eV. The injector and transfer line temperature were 280 and 180°C, respectively. Helium was the carrier gas. Data acquisition and processing were controlled using a HP Chem-Station data system.

For quality assurance and quality control, the method blanks (solvent) and spiked matrixes (standards spiked into soil) were analyzed. None of the target compounds was detected. The recovery and relative standard deviation for C₁₃–C₁₈ were in the range of 70.8–86% and 4.2–19.3%, respectively, and those for C₁₉–C₃₆ were in the range of 88.5–97.4% and 2.8–12.4%, respectively. The detection limits of the method range from 3.1 and 12.4 ng/g. All concentrations were expressed on a soil dry weight basis.

Statistical analysis was performed with SPSS 12.0 for Windows Release 12.0.0 (4 Sep. 2003, SPSS Inc., 1989–2003).

3. Results

The concentrations (including *n*-alkanes from C₁₃ to C₃₆, Pr and Ph), diagnostic indices of aliphatic hydrocarbons and soil properties are presented in Table 1. The concentrations of 26 determined compounds were in the range 0.60–39.92 µg/g (median value 1.97 µg/g). No correlations between the concentrations and soil organic matter content or the percentage of clay were found. The spatial distribution of the total concentra-

Table 1
Concentrations and compositional indices of aliphatic hydrocarbons in soil samples

	Minimum	Maximum	Median
SOM (g/kg)	6.60	32.51	16.50
Clay (%)	6.80	22.33	11.02
SUM (µg/g) ^a	0.60	39.92	1.97
C _n /C ₁₆	10.3	147.6	27.7
U/R	0.29	10.44	2.08
C ₁₇ /Pr	0.19	2.04	1.62
C ₁₈ /Ph	0.60	1.98	1.47
Pr/Ph	0.68	7.63	0.97
CPI ₁	0.73	4.27	1.64
CPI ₂	0.38	1.39	1.05
CPI ₃	0.59	21.8	2.69
WaxC _n (%)	10.52	59.02	26.58
L/H ₁ ^b	0.05	1.66	0.49
L/H ₂ ^c	0.08	6.42	0.84

^a Total amount of determined aliphatic hydrocarbons.

^b L/H₁: the ratios of low (C₁₀–C₂₄) to high (C₂₀–C₃₆).

^c L/H₂: low (C₁₃–C₂₄) to high (C₂₅–C₃₆) MW *n*-alkanes, respectively.

tions of aliphatic hydrocarbons (Fig. 2) showed that relatively higher levels were clustered in the northeast and north sites of the city.

A data set containing 47 samples and 26 compounds (Table 2) was used for the principal component analysis.

Fig. 2. The spatial distribution of aliphatic hydrocarbons in soils from the Beijing outskirts.

Table 2
Compounds analyzed (µg/g)

Compounds	Minimum	Maximum	Mean	SD (n = 47)
<i>n</i> -C ₁₃	nd	0.11	0.03	0.03
<i>n</i> -C ₁₄	nd	0.19	0.05	0.05
<i>n</i> -C ₁₅	nd	0.38	0.11	0.09
<i>n</i> -C ₁₆	nd	0.87	0.15	0.16
<i>n</i> -C ₁₇	0.03	1.58	0.22	0.28
Pr	0.02	0.87	0.15	0.17
<i>n</i> -C ₁₈	0.03	1.17	0.21	0.24
Ph	0.02	0.86	0.15	0.18
<i>n</i> -C ₁₉	0.01	0.87	0.16	0.17
<i>n</i> -C ₂₀	0.02	0.63	0.14	0.14
<i>n</i> -C ₂₁	0.02	0.68	0.12	0.14
<i>n</i> -C ₂₂	0.01	0.47	0.10	0.11
<i>n</i> -C ₂₃	0.02	0.58	0.10	0.12
<i>n</i> -C ₂₄	0.01	0.49	0.09	0.10
<i>n</i> -C ₂₅	0.02	2.04	0.26	0.45
<i>n</i> -C ₂₆	0.01	2.05	0.18	0.36
<i>n</i> -C ₂₇	0.01	3.36	0.42	0.64
<i>n</i> -C ₂₈	nd	3.70	0.27	0.61
<i>n</i> -C ₂₉	0.01	6.23	0.70	1.20
<i>n</i> -C ₃₀	nd	4.23	0.31	0.76
<i>n</i> -C ₃₁	nd	5.46	0.50	1.10
<i>n</i> -C ₃₂	nd	3.36	0.23	0.65
<i>n</i> -C ₃₃	nd	3.26	0.24	0.64
<i>n</i> -C ₃₄	nd	1.44	0.10	0.29
<i>n</i> -C ₃₅	nd	1.04	0.08	0.22
<i>n</i> -C ₃₆	nd	0.78	0.06	0.15

nd, not detected. In data processing, “0.0002 µg/g” was used to replace “nd”.

The first two principal components (PCs) account for 82.82% of the total variance, with eigenvalues >1. The combination of variables and their loadings is shown in Fig. 3(a). PC1 and PC2 were associated with low ($C_n < 24$) and high ($C_n > 25$) molecular weight n -alkanes and contained 63.55% and 19.27% of the total variance, respectively. By plotting the scores of the first two PCs, the sampling sites can be grouped in three clusters (Fig. 3(b)): (1) a first cluster with a single sample located in northeast of the city and which contained the highest amount of PC2, (2) a second cluster formed by the sample located in the north sites and characterized by the highest values of PC1, and (3) a dense third cluster containing the remaining samples that have the lowest values for both PCs.

4. Discussion

4.1. Diagnostic indices

UCMs are mainly composed of branched alkanes, cycloalkanes and aromatics and are one of the indicators of petrogenic inputs (Frysinger et al., 2003). One or two raised baseline humps can be observed in the gas chromatograms. The peaks usually appear near the n -C₁₇ and n -C₂₇ alkanes, respectively (Doskey and Andren, 1986). In the present study, UCMs with different shapes and range were observed in most samples, suggesting a petroleum input to the soils in the Beijing area. The presence of a major UCM derived from petroleum residues was further confirmed by the presence of molecular

Fig. 3. (a) Loading and (b) score plots of the principal component analysis.

markers as described below. In addition, bacteria may also be a source for small amount of UCM (Simoneit et al., 1991). The degree of petroleum contamination can be expressed as the ratio of the unresolved to resolved hydrocarbon compounds (U/R; Simoneit, 1984).

U/R values were in the range of 0.29–10.44 with a median of 2.08, confirming the presence of a petroleum component.

The concentration profiles reflect the relative contribution of different sources. The distribution pattern

Fig. 4. Representative gas chromatographic patterns of alkane fraction. Numbers in the figure refer to the chain length of *n*-alkanes. Pr, pristane; Ph, phytane.

from aliphatic hydrocarbons in our study can be basically divided into four types, and representative GC profiles are presented in Fig. 4:

Type A, with a bimodal C_{max} pattern for the UCM, a minor maximum at about C_{17} and a major one at C_{27} , together with a predominance of odd/even carbon numbers in the high molecular homologues, is the most prevalent. The UCM is considered to have an anthropogenic source, while the higher molecular weight n -alkanes with a strong preference of odd to even carbon numbers result from the epicuticular waxes of higher plants (e.g. Schneider et al., 1983); this means that the aliphatic hydrocarbons in soils from the Beijing area are from mixed sources, i.e., petroleum and higher plant waxes.

Type B, with the UCM peak with a maximum at C_{16} – C_{20} and a minor odd/even predominance, was probably caused by both a microbial hydrocarbon contribution and a slight higher plant wax contribution. A small “hump” and preference for odd/even carbon numbers found in type C gas chromatograms indicated the least fossil fuel input. A significant UCM with maximum at C_{27} – C_{33} was observed in the type D distribution, which is characteristic of strong anthropogenic impact.

The CPI has been a useful parameter for estimating biogenic or anthropogenic contributions since it was first put forward (Bray and Evans, 1961). The n -alkanes from epicuticular waxes of higher plants show a pronounced odd carbon number predominance, while fossil fuel and microbial hydrocarbons exhibit $CPI \sim 1$. The carbon number ranges used for calculations are different among different researchers (Kavouras et al., 2001; Colombo et al., 1989; Simoneit and Mazurek, 1982). In the present study, the CPI for n -alkanes was calculated as follows: CPI_1 (whole range for n -alkanes) = $\sum(C_{13}-C_{35})/\sum(C_{14}-C_{36})$; CPI_2 (petrogenic n -alkanes) =

$\sum(C_{13}-C_{23})/\sum(C_{14}-C_{24})$; CPI_3 (higher plant wax n -alkanes) = $\sum(C_{25}-C_{35})/\sum(C_{26}-C_{36})$. CPI_1 values were in the range of 0.86–4.26 with a median value of 1.64, comparable to the aerosol values for Beijing (Li et al., 2001), indicating a similar origin. The contour map of CPI_1 is presented in Fig. 5. It was found that the highest CPI_1 value was located at the southwest site of the city, indicating a higher relative proportion of vascular plant n -alkanes in these samples and the lowest anthropogenic source input because the sampling areas were on agricultural land. In addition, CPI_2 values ranged from 0.38 to

Fig. 5. The contour map of CPI_1 in soil samples from the Beijing outskirts.

Fig. 6. Four types of $WaxC_n$ vs. carbon number plots.

1.39 with a median of 1.05, typical of a petroleum origin. CPI_3 values varied between 0.59 and 21.84 with a median of 2.69, suggesting leaf epicuticular waxes as the predominant source for this *n*-alkane range in most samples.

The MH index in most samples was at C_{29} , C_{31} , and C_{27} , indicating that vascular plants sources played a very important role. A lower molecular weight C_{max} around C_{17} and C_{21} was also observed in several samples. Studies of aerosols in the Beijing area found that MH indices in most winter and spring samples were at C_{29} , C_{31} , while in summer and autumn, lower molecular weight C_{max} around C_{23} and C_{25} were observed (Li et al., 2001).

The ratios of the sum of all *n*-alkanes to C_{16} were also estimated and were from 10.34 to 147.64 with a median of 27.72. High and low values can be interpreted to be derived from biogenic and oily sources, respectively (Colombo et al., 1989).

Fossil fuel characteristics are $CPI > 1$, $L/H > 1$, $U/R > 1$ and presence of fossil hopanoids, while characteristic diagnostic indices for urban dust and vegetation fires are $CPI \sim 1.5$ and $L/H < 1$, but urban dust shows a relatively higher U/R value, about 4.5 (Fernandes and Brook, 2003). Minor homologues $< n-C_{20}$ may have an origin from microbial detritus (Simoneit et al., 1991). In the soil samples studied, the ratio of L/H was quite varied, suggesting complicated sources.

Fig. 7. Examples of mass fragmentograms: (a) m/z 191 for triterpanes, solid peaks are the 17α (H), 21β (H)-hopane series, G stands for gammacerane; (b) m/z 217 and (c) m/z 218 key ion for steranes, solid peaks: $\alpha\alpha\alpha = 5\alpha$ (H), 14α (H), 17α (H)-steranes, $\alpha\beta\beta = 5\alpha$ (H), 14β (H), 17β (H)-steranes, R and S = C-20R and S configuration.

Another important parameter to reconcile sources is WaxC_n . This is calculated as follows: $\text{WaxC}_n = C_n - 0.5(C_{n+1} + C_{n-1})$ and negative values are taken as zero (Kavouras et al., 1999). The relative concentrations of WaxC_n vs. carbon number were plotted. These plots show a quite different *n*-alkane distribution pattern. Figure 6 shows four main types. Type A was the most frequently observed, followed by type D. The percentage of concentration of biogenic wax *n*-alkanes to the total *n*-alkane concentration ranged from 10.52% to 59.02%, with a median value of 26.58%. The wax composition signature was large, compared with data for aerosols from Santiago de Chile (4.55–20.83%; Kavouras et al., 1999) and Guangzhou (5.2–19.4%; Bi et al., 2002), suggesting a higher relative proportion of vascular plant waxes in the Beijing soil samples.

4.2. Molecular markers

The presence of Pr and Ph, indicative of petrochemical use (Simoneit, 1984), was observed in all samples. The levels of Pr and Ph were both in the range of 0.02–0.87 $\mu\text{g/g}$. C_{17}/Pr and C_{18}/Ph were used to indicate microbial degradation. Biodegradation rates for *n*-alkanes are faster than those of Pr and Ph (Chaineau et al., 1995); therefore, the lower indices suggested the presence of degraded oil and the higher values fresh oil input. The median values of C_{17}/Pr and C_{18}/Ph were 1.62 and 1.47, respectively. Pr/Ph ratios for almost all samples were close to 1, higher than the data for aerosols from Beijing (Simoneit et al., 1991). Sample No. 16–11 had the lowest C_{17}/Pr value (0.19) and the highest Pr/Ph ratio (7.63) due to low amounts of C_{17} and Ph, rather than a high amount of Pr.

Examples of the petroleum biomarker distribution patterns are shown in Fig. 7. The $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopane series, characteristic of a petroleum input, was detected in almost all samples using GC–MS. The series maximizes at C_{30} and also exists in Beijing aerosols (Simoneit et al., 1991). Gammacerane is also present due to most Chinese crude oils being derived from lacustrine sources (Fu et al., 1990; Jiang et al., 1988; Philp and Fan, 1987). Steranes were detected using the m/z 217 and m/z 218 ion peaks in the GC–MS data. They are common in crude oils from China.

5. Conclusions

Aliphatic hydrocarbons in soils from the Beijing area were mainly from anthropogenic and biogenic sources, based on the distribution patterns, compositional indices and molecular markers. The highest total concentrations of aliphatic hydrocarbons were clustered at the north and northeast sites of the city. The anthropogenic com-

ponents comprise mainly petroleum residues, confirmed by UCMs, U/R, Pr, Ph and the $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopane series, gammacerane, $5\alpha(\text{H})$, $14\alpha(\text{H})$, $17\alpha(\text{H})$ and $5\alpha(\text{H})$, $14\beta(\text{H})$, $17\beta(\text{H})$ -sterane series. Multivariate statistical analysis reduced the data set to two principal components explaining 82.82% of the total variance.

Acknowledgements

This project was supported by the Ministry of Science and Technology of China (G1999045707). We acknowledge the Agilent Company for technical support. The authors would like to express thanks to Dr. Wenjian Lao, Dr. Huiming Chen, and Dr. Xuetong Wang for help during the experiments. Our special thanks go to Professor Phil Mayers, Dr. Maowen Li, Professor J.O. Grimalt and an anonymous reviewer for comments.

Associate Editor—Maowen Li

References

- Aceves, M., Grimalt, J.O., 1993. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environmental Science and Technology* 27, 2896–2908.
- Bi, X., Sheng, G., Peng, P., Zhang, Z., Fu, J., 2002. Extractable organic matter in PM_{10} from LiWan district of Guangzhou city, PR China. *The Science of the Total Environment* 300, 213–228.
- Bray, E.E., Evans, D.E., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* 22, 2–15.
- Chaineau, C.H., Morel, J.L., Oudot, J., 1995. Microbial degradation in soil microcosms of fuel oil hydrocarbons from drilling cuttings. *Environmental Science and Technology* 29, 1615–1621.
- Colombo, J.C., Pelletier, E., Brochu, C., Khalil, M., Catoggio, J.A., 1989. Determination of hydrocarbon sources using *n*-alkane and polyaromatic hydrocarbon distribution indices. Case study: Rio de La Plata estuary, Argentina. *Environmental Science and Technology* 23, 888–894.
- Doskey, P.V., Andren, A.W., 1986. Particulate and vapor-phase *n*-alkanes in the northern Wisconsin atmosphere. *Atmospheric Environment* 20, 1735–1744.
- Fernandes, M.B., Brook, P., 2003. Characterization of carbonaceous combustion residues: II. Nonpolar organic compounds. *Chemosphere* 53, 447–458.
- Frysinger, G.S., Gaines, R.B., Xu, L., Reddy, C.M., 2003. Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science and Technology* 37, 1653–1662.
- Fu, J.M., Sheng, G.M., Xu, J.Y., Eglinton, G., Goward, 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.

- Gagosian, R.B., Peltzer, E.T., Zafiriou, O.C., 1981. Atmospheric transport of continentally derived lipids to the tropical north Pacific. *Nature* 291, 312–314.
- 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., Lawrence, J., Koutrakis, P., Stephanou, E.G., Oyola, P., 1999. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. *Atmospheric Environment* 33, 4977–4986.
- Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Bear, 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.
- Leuenberger, C., Czuczwa, J., Heyerdahl, E., Giger, W., 1988. Aliphatic and polycyclic aromatic hydrocarbons in urban rain, snow and fog. *Atmospheric Environment* 22, 695–705.
- Li, R.Q., Zhang, Z.Q., Shi, J.H., Liu, X.D., Yu, T., 2001. The analysis of organic compounds of atmospheric aerosols in Beijing. *Research of Environmental Sciences* 14, 21–23 (in Chinese).
- Marty, J.C., Saliot, A., 1982. Aerosols in equatorial Atlantic air: *n*-alkanes as a function of particulate size. *Nature* 298, 144–147.
- Maldonado, C., Bayona, J.M., Bodineau, L., 1999. Sources, distribution, and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the northwestern Black sea water. *Environmental Science and Technology* 33, 2693–2702.
- Philp, R.P., Fan, Z., 1987. Geochemical investigation of oils and source rocks from Qianjing Depression of Jianhan Basin, a terrigenous saline basin, China. *Organic Geochemistry* 11, 549–562.
- Prahl, F.G., Crecellus, E., Carpenter, R., 1984. Polycyclic aromatic hydrocarbons in Washington coastal sediments: an evaluation of atmospheric and riverine route of introduction. *Environmental Science and Technology* 18, 687–693.
- Schneider, J.K., Gagosian, R.B., Cochran, J.K., Trull, T.W., 1983. Particle size distributions of *n*-alkanes and ²¹⁰Pb in aerosols off the coast of Peru. *Nature* 304, 429–432.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere-II. Nature background of biogenic lipid matter in aerosols over the rural western United States. *Atmospheric Environment* 16, 2139–2159.
- Simoneit, B.R.T., 1984. Organic matter of the troposphere-III. 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., 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmospheric Environment* 25A, 2111–2129.
- Tolosa, I., Bayona, J.M., Albaiges, J., 1996. Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in northwestern Mediterranean sediments: spatial and temporal variability, fluxes, and budgets. *Environmental Science and Technology* 30, 2495–2503.