

Characterization of aliphatic hydrocarbons in deep subsurface soils near the outskirts of Beijing, China

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Abstract: Thirty-nine deep subsurface soils (150—180 cm depth) near the outskirts of Beijing were investigated. The concentrations including *n*-alkanes from C₁₃ to C₃₆, pristane and phytane were in the range of 0.60 to 170.10 µg/g, with a median value of 4.26. Carbon preference index values for *n*-alkanes ranged from 1.08 to 2.98, with a median value of 1.48. The percentage contribution of “wax” *n*-alkanes was in the range of 6.03%—46.22%. A predominance of odd/even carbon *n*-alkanes and unresolved complex mixtures with different shapes and ranges were frequently observed. Factor analysis reduced the data set into three principal components and confirming contributions from low (19.58%), medium (20.49%) molecular weight species and long-chain *n*-alkanes (43.41%), respectively. Molecular biomarkers such as pristane, phytane, hopanes and steranes were detected. Based on the principal component analysis, the concentration profiles and molecular markers, it was found that the aliphatic hydrocarbons were from both biogenic and anthropogenic sources.

Keywords: deep subsurface soil; *n*-alkanes; spatial distribution; molecular markers; diagnostic indices

Introduction

Aliphatic hydrocarbons are introduced into soil through natural and anthropogenic sources. With increasing consumption of fossil fuel, hydrocarbon soil contamination is often associated with accidental spillage during storage and distributions of fuels, and deposition of stock emission. Aliphatic hydrocarbon analysis can be used to fingerprint spilled oils and provide additional information on the source of hydrocarbon contamination and the extent of degradation of the spilled oil. In addition, aliphatic hydrocarbons can be used as geochemical biomarkers reflecting geological environment to some extent. The origins of aliphatic hydrocarbons were often identified by concentration diagnostic indices together with molecular markers, and multivariate methods (Kavouras, 2001; Colombo, 1989). This paper studied the aliphatic hydrocarbons in deep subsurface soils near the outskirts of Beijing.

1 Materials and method

1.1 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. Deep subsurface samples (150—180 cm depth) were collected for every 16 km² soil region. The map of soil survey and sampling sites in 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-drying under a hood at room temperature and sieved to 35 meshes sieve.

All samples were refrigerated at -4°C until chemical analysis.

1.2 Materials

All solvents obtained from the Beijing Chemical Factory were of analytical grade and were redistilled in all-glass system before use. The *n*-alkane standards were purchased from Chem Service, Inc. Silica gel (100—200 mesh; Qingdao Haiyang Chemical Co., Shangdong, China) was activated for 16 h at 130°C and kept in a desiccator before use.

An aliquot (5 g) of soil sample was weighed accurately and ground with 5 g anhydrous sodium sulfate. The samples were extracted with petroleum ether/acetone, 1/1 (v/v), by

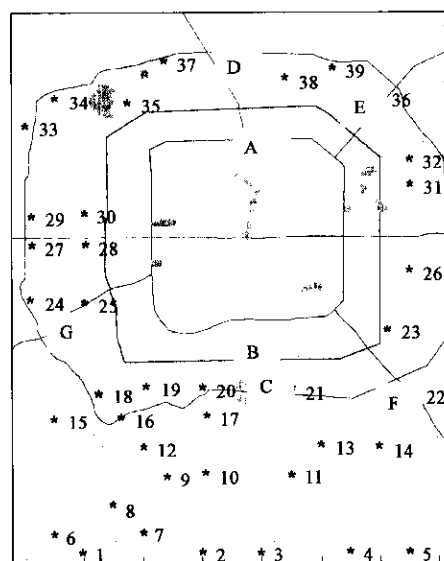


Fig. 1 Map of soil survey and sampling sites in the Beijing outskirts

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

ultrasonication for 3 min and then centrifuged. This procedure was repeated three times. The extracts were combined and the solvent was reduced to about 1 ml by using a K-D concentrator in a water bath.

For isolation of the alkane fraction, 10 g of activated silica gel was packed into a glass column with 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 the column and eluted with 25 ml of petroleum ether to obtain the alkane fraction. The fraction was concentrated by using a K-D concentrator in a water bath and finally under a gentle stream of nitrogen to 0.2 ml.

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. GC conditions were: injector and detector temperature 280°C 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. 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 standards and were quantified using peak area integration.

Selected samples were further analyzed by a Hewlett Packard 6890 GC coupled to a 5973 MSD and a DB-5 MS(25 m × 0.25 mm i. d., 0.25 µm film thickness) capillary column. GC oven program 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°C and 200°C, respectively. Helium was used as carrier gas. Data acquisition and processing were controlled by 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—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(September 4, 2003, SPSS Inc., 1989—2003).

2 Results and discussion

2.1 General comments on concentrations

Thirty-nine subsoil samples were analyzed, and 26 compounds(*n*-alkanes from C₁₃ to C₃₆, pristane (Pr) and phytane (Ph)) were quantitatively determined. The concentrations and indices of aliphatic hydrocarbons for deep subsurface samples are presented in Table 1. The residue levels were in the range of 1.90—170.10 µg/g (median 6.56 µg/g). The spatial distribution of the total concentrations of aliphatic hydrocarbons(Fig. 2) shows that relatively higher levels were located at the northeast, southeast, and southwest sites of the city. No correlation between soil organic matter content and clay content with the concentrations was found.

Table 1 Concentrations and compositional indices of aliphatic hydrocarbons in the deep subsurface soils

Sites	OC, %	Clay, %	CEC	ΣC _n	U/R	C _n /C ₁₆	C ₁₇ /Pr	C ₁₈ /Ph	Pr/Ph	CPI ₁ ^a	CPI ₂ ^a	CPI ₃ ^a	Wax, %	L/H ^b	C _{max}
1	0.44	9.2	8.35	3.32	—	11.48	2.01	1.73	0.90	1.36	0.96	4.12	22.48	3.05	C ₂₉
2	0.34	8.1	6.01	22.20	3.17	67.57	1.53	1.18	0.90	1.36	1.13	1.41	15.54	0.19	C ₁₇
3	0.24	6.7	6.48	6.56	2.98	60.04	1.87	1.48	0.92	1.71	0.99	1.94	27.30	0.28	C ₃₁
4	0.59	15.9	12.46	66.96	1.46	146.59	1.85	1.35	1.08	1.11	0.98	1.22	8.09	0.06	C ₂₉
5	0.74	19.8	14.18	37.14	4.87	157.35	2.29	1.81	0.87	1.25	0.82	1.25	11.82	0.13	C ₃₁
6	0.27	2.2	2.98	5.71	4.57	59.13	1.92	1.55	0.95	1.53	1.27	1.60	18.61	0.35	C ₃₁
7	1.02	31.8	19.69	5.66	5.36	35.20	2.01	1.43	1.05	2.83	1.19	3.59	46.22	0.28	C ₂₅
8	0.30	8.8	6.8	33.99	—	154.04	2.20	1.57	0.98	1.21	1.01	1.26	11.51	0.06	C ₂₉
9	0.62	18.4	14.17	52.15	1.81	334.54	2.14	1.71	0.97	1.10	0.82	1.18	7.68	0.04	C ₃₁
10	0.78	17.8	12.58	1.92	—	15.18	2.29	1.61	0.92	1.24	0.95	1.72	17.91	1.48	C ₁₄
11	0.57	18.5	10.66	2.29	—	19.97	2.09	1.52	0.79	1.24	0.97	1.91	19.20	1.96	C ₁₄
12	0.46	10.6	8.37	8.66	2.08	86.04	1.99	1.43	0.90	1.20	1.13	1.29	10.33	0.11	C ₂₉
13	0.68	13.4	10.21	170.14	0.83	479.71	15.78	1.26	0.84	1.08	2.54	1.14	6.91	0.05	C ₂₉
14	0.22	11.7	8.1	4.04	11.69	10.50	1.93	1.25	0.95	1.63	1.11	3.11	21.98	1.95	C ₃₁
15	0.68	15.9	14.3	7.04	4.07	22.82	1.86	1.28	0.89	1.55	1.11	1.73	20.16	0.58	C ₂₉
16	0.32	8.1	6.04	2.79	6.91	13.19	2.33	1.59	0.96	1.96	1.18	3.70	29.86	1.24	C ₃₁
17	0.35	16.5	12.75	32.53	3.47	107.52	2.03	1.47	0.98	1.15	0.62	1.22	11.76	0.15	C ₁₇
18	0.44	14.4	9.66	136.54	0.56	454.38	1.86	1.37	0.88	1.09	1.01	1.18	6.75	0.02	C ₃₁
19	0.26	3.2	3.41	11.00	3.30	39.94	1.16	1.61	1.47	1.29	1.03	1.52	14.77	0.28	C ₂₉
20	0.48	15.1	12.35	2.62	—	33.55	2.05	1.65	0.87	1.19	0.86	1.44	18.16	0.60	C ₂₉
21	1.13	15.1	14.18	2.58	—	13.00	2.71	2.07	0.85	1.83	0.99	3.84	31.04	1.14	C ₃₁
22	0.22	20.0	13.02	3.94	5.10	13.39	1.72	1.47	1.24	1.48	1.24	1.71	17.92	1.22	C ₁₇
23	0.50	12.5	11.34	4.70	5.23	19.96	2.52	1.61	0.86	2.29	1.24	3.63	36.12	0.79	C ₃₁
24	0.35	7.4	5.82	9.24	3.31	32.94	0.97	1.52	0.92	1.35	0.97	1.56	18.04	0.34	C ₂₉
25	0.25	5.7	5.83	2.39	5.87	17.33	1.97	1.59	0.91	1.92	1.16	3.39	28.33	1.17	C ₃₁
26	0.93	13.1	10.46	27.89	3.57	104.18	2.00	1.43	0.83	1.55	0.99	1.63	22.52	0.12	C ₃₁
27	0.34	12.7	6.04	42.40	3.57	151.88	2.10	1.54	0.82	1.16	0.87	1.23	9.46	0.11	C ₂₉
28	0.84	6.9	10.21	4.84	6.86	18.31	2.02	1.47	0.89	1.66	1.12	2.65	24.72	0.90	C ₃₁
29	1.05	9.9	19.42	2.08	3.37	25.87	1.85	1.29	0.89	2.86	2.38	3.07	45.65	1.12	C ₂₁
30	1.06	21.2	11.94	2.27	4.76	18.34	1.78	1.29	0.90	2.18	1.14	4.09	33.70	0.97	C ₃₁
31	0.52	13.5	6.96	7.39	2.48	30.04	2.16	1.45	0.87	1.69	1.13	1.91	24.86	0.37	C ₂₉
32	0.87	9.2	8.45	126.43	0.85	368.82	1.82	1.41	0.99	1.08	0.97	1.15	6.03	0.03	C ₂₉
33	0.63	10.9	13.86	1.89	3.50	41.30	0.34	1.32	3.91	1.25	1.11	1.25	12.19	0.32	C ₃₁
34	0.57	18.2	11.04	4.89	7.52	25.32	1.86	1.46	1.03	1.51	1.05	1.67	19.05	0.57	C ₃₁
35	1.10	10.3	11.66	13.02	3.13	51.77	1.87	1.57	0.72	2.22	1.05	2.89	37.75	0.34	C ₂₉
36	0.30	22.0	14.41	2.82	3.45	17.51	2.00	1.39	0.99	2.34	1.17	3.86	36.88	0.74	C ₁₅
37	0.16	6.7	5.6	3.43	7.83	14.27	2.20	1.35	0.97	2.98	3.04	2.16	46.08	4.25	C ₂₉
38	0.92	14.1	10.58	8.34	3.36	43.86	1.90	1.35	1.02	1.48	1.13	1.55	18.82	0.20	C ₂₉
39	0.58	14.9	14.33	7.31	3.90	20.06	1.83	1.35	0.99	2.96	1.12	5.57	46.14	0.53	C ₃₁
Median	0.52	13.1	10.58	6.56	3.37	33.55	1.99	1.47	0.92	1.48	1.11	1.71	19.05	0.35	

Notes: ^a CPI₁ (whole range for *n*-alkanes) = Σ(C₁₃—C₃₅)/Σ(C₁₄—C₃₆); CPI₂ (petrogenic *n*-alkanes) = Σ(C₁₃—C₂₃)/Σ(C₁₄—C₂₄); CPI₃ (higher plant wax *n*-alkanes) = Σ(C₂₅—C₃₅)/Σ(C₂₆—C₃₆); ^b L/H₁: the ratios of low(C₁₀—C₂₄) to high(C₂₀—C₃₆) MW *n*-alkanes

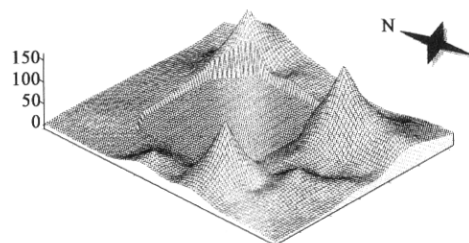


Fig.2 The spatial distribution of aliphatic hydrocarbons in deep layer soils near the Beijing outskirts

To investigate the spatial difference of *n*-alkane pattern in soil, principal component analysis (PCA) was used. A data set containing 39 samples and 26 compounds (Table 2) was used for the principal component analysis. The first three principal components (PCs) account for 43.41%, 20.49%, and 19.58% of the total variance, with eigenvalues > 1, and are associated with high, medium, and low molecular weight *n*-alkanes, respectively (Table 3). The relationships among the samples are displayed in the score plots (Fig. 3), and it was found that (1) the samples No. 13, 18, and 32 with highest concentrations containing the highest amount of PC₁, (2) the samples 5, 17, and 27 characterized by the highest values of PC₂, (3) the samples such as 2, 4, 39, etc. that have positive scores on PC₃, and (4) dense clusters containing the remaining samples that have the lowest values for PCs.

Table 2 Compounds analyzed Unit: $\mu\text{g/g}$

Compounds	Minimum	Maximum	Mean	SD ($n = 39$)
<i>n</i> -C ₁₃	nd	0.16	0.06	0.03
<i>n</i> -C ₁₄	nd	0.72	0.10	0.11
<i>n</i> -C ₁₅	0.04	1.35	0.21	0.20
<i>n</i> -C ₁₆	0.05	0.46	0.23	0.10
<i>n</i> -C ₁₇	0.07	4.09	0.40	0.62
Pr	0.04	0.69	0.17	0.08
<i>n</i> -C ₁₈	0.07	0.45	0.25	0.11
Ph	0.05	0.33	0.17	0.08
<i>n</i> -C ₁₉	0.05	0.33	0.19	0.09
<i>n</i> -C ₂₀	0.03	0.29	0.13	0.07
<i>n</i> -C ₂₁	0.03	0.42	0.15	0.10
<i>n</i> -C ₂₂	0.03	0.42	0.13	0.10
<i>n</i> -C ₂₃	0.03	0.68	0.17	0.15
<i>n</i> -C ₂₄	0.03	1.09	0.21	0.26
<i>n</i> -C ₂₅	0.05	4.62	0.86	1.18
<i>n</i> -C ₂₆	0.03	5.58	0.79	1.22
<i>n</i> -C ₂₇	0.09	8.23	1.17	1.75
<i>n</i> -C ₂₈	0.03	13.12	1.54	2.86
<i>n</i> -C ₂₉	0.13	18.96	2.67	4.41
<i>n</i> -C ₃₀	0.03	20.00	2.37	4.79
<i>n</i> -C ₃₁	0.11	22.98	3.13	5.70
<i>n</i> -C ₃₂	nd	19.80	2.38	5.03
<i>n</i> -C ₃₃	nd	17.58	2.18	4.47
<i>n</i> -C ₃₄	nd	13.34	1.46	3.33
<i>n</i> -C ₃₅	nd	10.74	1.10	2.61
<i>n</i> -C ₃₆	nd	10.36	0.65	1.54

2.2 Diagnostic indices

Unresolved complex mixture (UCM) is one of the indicators of petrogenic inputs (Fryzinger, 2003). One or two raised baseline humps, usually appearing near the *n*-C₁₇ and *n*-C₂₇ peaks, respectively, can be observed in the gas chromatograms (Doskey, 1986). The degree of petroleum contamination can be expressed as the ratio of the unresolved to resolved hydrocarbon compounds (U/R) (Simoneit, 1984). In our study, UCMs with different shapes and range were observed in the most samples. U/R values were in the range

of 0.56–11.69 (median 3.37), confirming the petroleum component, which will be further confirmed by the presence of molecular makers. In addition, bacteria may also be a source for small amount of UCMs (Simoneit, 1991).

Table 3 Factor loadings of principal component analysis

Compounds	Component		
	1	2	3
<i>n</i> -C ₃₄	0.969	0.119	0.171
<i>n</i> -C ₃₆	0.968	0.123	0.173
<i>n</i> -C ₃₅	0.967	0.100	0.181
<i>n</i> -C ₃₂	0.961	0.164	0.173
<i>n</i> -C ₃₀	0.961	0.205	0.154
<i>n</i> -C ₃₃	0.960	0.152	0.178
<i>n</i> -C ₃₁	0.954	0.202	0.181
<i>n</i> -C ₂₉	0.939	0.246	0.192
<i>n</i> -C ₂₈	0.934	0.308	0.140
<i>n</i> -C ₂₇	0.861	0.449	0.165
<i>n</i> -C ₂₆	0.752	0.622	0.112
<i>n</i> -C ₁₇	0.677	0.141	0.224
<i>n</i> -C ₂₄	0.401	0.877	0.148
<i>n</i> -C ₂₃	0.349	0.873	0.277
<i>n</i> -C ₂₂	0.349	0.837	0.371
<i>n</i> -C ₂₅	0.542	0.803	0.118
<i>n</i> -C ₂₁	0.310	0.647	0.311
<i>n</i> -C ₂₀	0.357	0.626	0.624
<i>n</i> -C ₁₄	-0.122	0.449	-0.010
Ph	0.288	0.231	0.908
<i>n</i> -C ₁₈	0.221	0.299	0.889
<i>n</i> -C ₁₆	0.262	0.173	0.878
Pr	0.248	0.092	0.863
<i>n</i> -C ₁₉	0.278	0.518	0.776
<i>n</i> -C ₁₃	0.031	0.196	0.385
<i>n</i> -C ₁₅	-0.030	-0.123	0.340

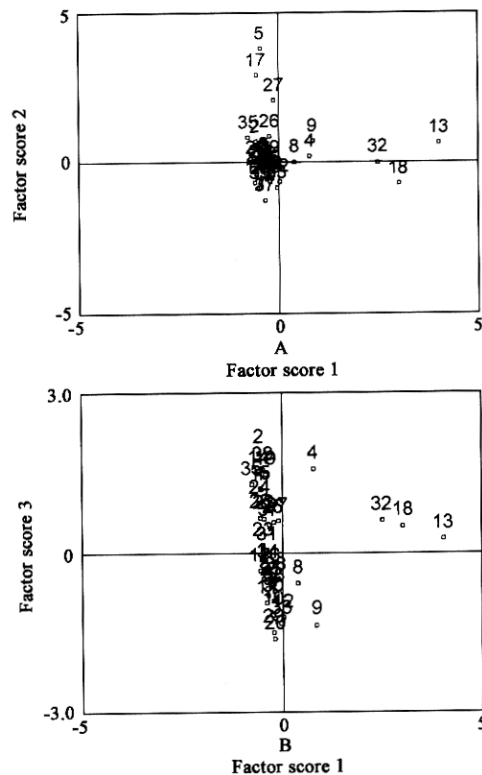


Fig.3 Score plots of the principal components analysis

The concentration profiles reflect the relative contribution of different sources to some extent. The distribution pattern of aliphatic hydrocarbons in our study can be basically divided into four types, and representative gas chromatographic profiles are presented in Fig. 4:

Type a, with bimodal C_{\max} pattern for the UCM, with a minor maximum at about C₁₇ and a major one at C₂₇, together

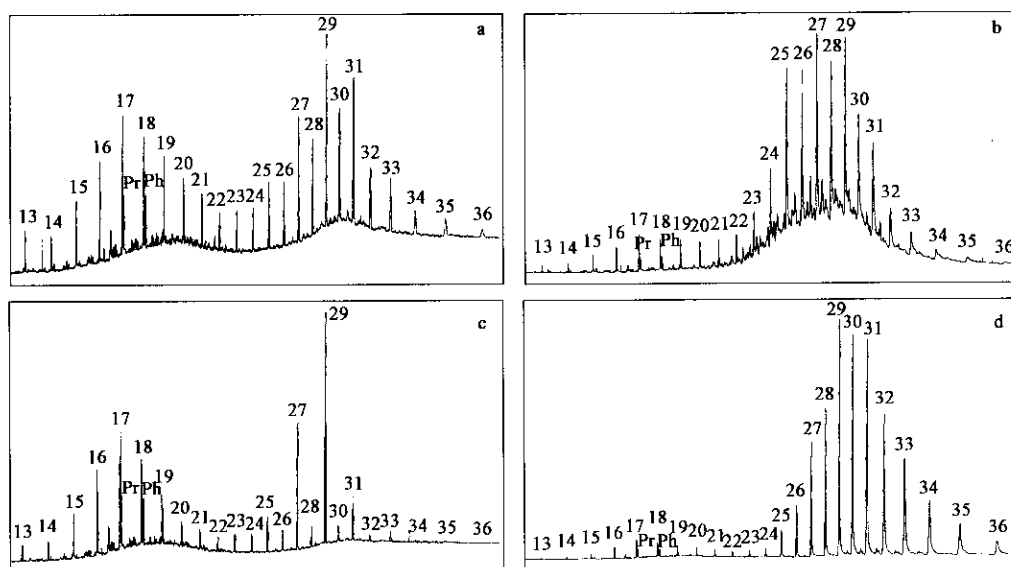


Fig.4 Representative gas chromatographic patterns of alkane fraction
(numbers refer to *n*-alkane chain lengths)

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 results from the epicuticular waxes of higher plants (Schneider, 1983), which means that aliphatic hydrocarbons in soils from the Beijing area are from mixed sources, i.e., petroleum and higher plant wax.

Type b, a UCM peak with maxima at C_{24} – C_{32} and a minor odd/even predominance, was probably caused by both anthropogenic contribution and a slight higher plant wax contribution. A small “hump” with maxima around C_{17} – C_{19} and a significant preference for odd/even carbon number found in type c gas chromatograms, indicating slight microbial hydrocarbon contribution and strong higher plant wax contribution. Neither UCM nor preference for odd/even carbon number were observed in the type d distribution, which is characteristic of strong anthropogenic impact.

The carbon preference index (CPI) is a very useful parameter for estimating biogenic or anthropogenic contributions. CPI_1 values were in the range of 1.08–2.98 (median 1.48), comparable to the aerosol values of Beijing (Li, 2001), indicating the similar origins. The contour map of CPI_1 was presented in Fig. 5. In addition, CPI_2 values ranged from 0.62–3.04 (median 1.11), typical petroleum origin. CPI_3 values varied between 1.14–5.57 (median 1.71), indicating relatively low contribution of high plant for the most samples.

The MH index in most samples was C_{29} and C_{31} , indicating the vascular plants sources. Lower molecular weight C_{max} around C_{17} and C_{14} were also observed in several samples. The ratios of the sum of all *n*-alkanes to C_{16} were various, in the range of 10.50–479.71 (median 33.55). High and low values can be interpreted to be derived from biogenic and oily sources, respectively (Colombo, 1989). The ratios of I/H, ranging from 0.03 to 3.05, exhibit spatial variation.

Another important parameter to reconcile the relative importance of biogenic and petrogenic sources is $WaxC_n$. This is calculated as follows: $WaxC_n = C_n - 0.5(C_{n-1} +$

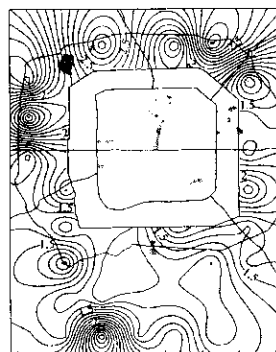


Fig.5 The contour map of CPI in the deep layer samples near the Beijing outskirts

C_{n-1}) and negative values are taken as zero (Kavouras, 1999). The contribution of plant wax ranged from 6.03%–46.22% (median 19.05%). The difference of relative concentrations of $WaxC_n$ vs. carbon number reflects differences in *n*-alkane distribution pattern (Fig. 6). There are four main types. Type a was the most frequently observed, in which C_{29} is the major compound; whereas type b, c, and d had high portions of C_{31} , C_{21} , and C_{25} , respectively.

2.3 Molecular markers

The presence of Pr and Ph, indicative petrochemical use (Simoneit, 1984), was observed in all samples. The levels of Pr and Ph were in the range of 0.04–0.36 $\mu\text{g/g}$ and 0.05–0.33 $\mu\text{g/g}$, respectively. Biodegradation preferentially removes C_{17} , C_{18} and other normal alkanes over isoprenoid compounds; therefore, the low values of C_{17}/Pr and C_{18}/Ph suggested the presence of degraded oil and high indices indicated fresh oil input. The median values of C_{17}/Pr (0.34–15.78) and C_{18}/Ph (1.18–2.07) were 1.99 and 1.47, respectively. Pr/Ph 0.72–3.91 (0.92) ratios for almost all the samples were close to 1. Samples No. 33 had the lowest C_{17}/Pr value (0.34) and the highest Pr/Ph ratio (3.91) due to low amounts of C_{17} and Ph, rather than high amount of Pr.

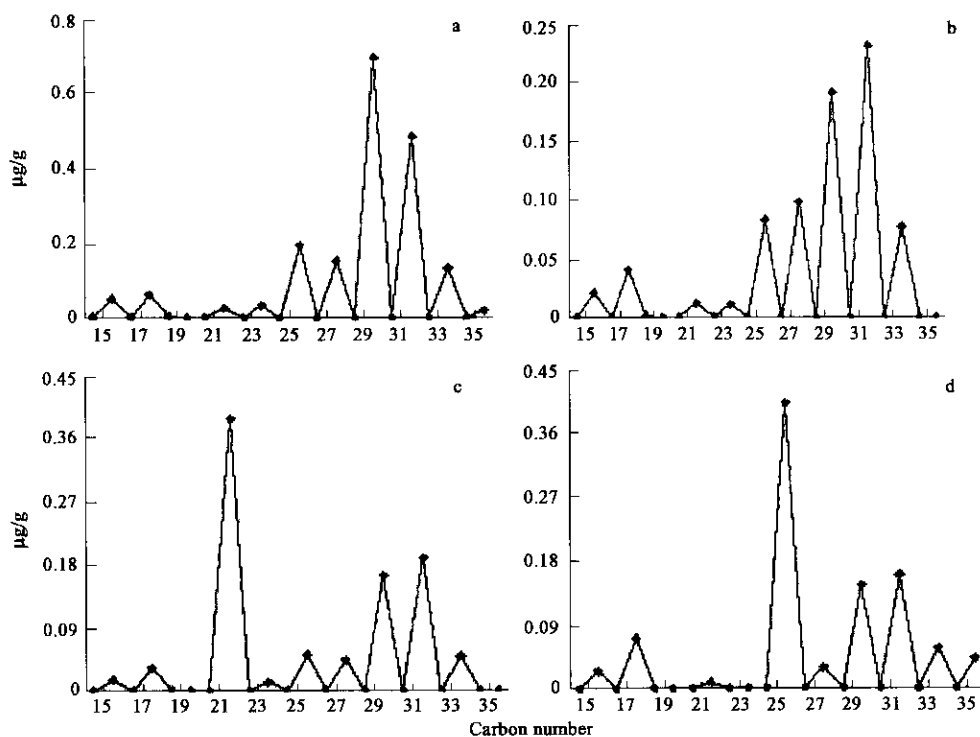


Fig. 6 Distribution diagrams of concentration vs. carbon number for *n*-alkanes attributable to vegetation epicuticular wax

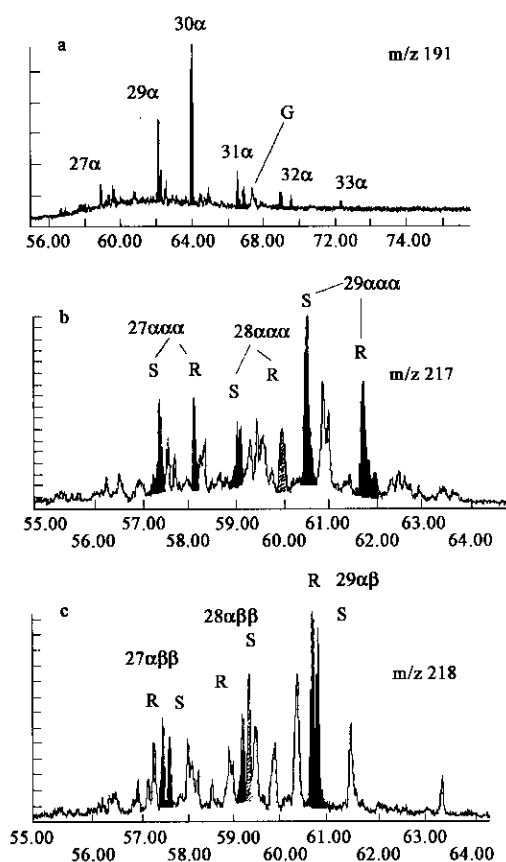


Fig. 7 Examples of mass fragmentograms

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

series are very useful in the organic geochemistry to infer the oil residues. Examples of the petroleum biomarker distribution patterns are shown in Fig. 7. The $17\alpha(H)$, $21\beta(H)$ -hopane series, typical of a petroleum input, was detected. The series also exists in Beijing aerosols (Simoneit, 1991). Gammacerane is also present due to the most Chinese crude oils being derived from lacustrine sources (Fu, 1990). 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.

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Biomarkers such as triterpane, sterane, and hopane