



# Characterization of *n*-alkanes in PM<sub>2.5</sub> of the Taipei aerosol

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## Abstract

Ambient concentrations of *n*-alkanes with carbon number ranging from 17 to 36 were determined for PM<sub>2.5</sub> samples collected in Taipei city during September 1997–February 1998. The measured concentrations of particulate *n*-alkanes were in the range of 69–702 ng m<sup>-3</sup>, considerably higher than the concentration levels observed in Los Angeles and Hong Kong. The concentration distributions of *n*-alkanes homologues obtained in this study exhibited peaks at C<sub>19</sub>, C<sub>24</sub> or C<sub>25</sub>. This suggests that fossil fuel utilization, such as vehicular exhaust and lubricant residues, was an important contributor to the Taipei aerosol. Source apportionment of PM<sub>2.5</sub> was conducted using carbon preference index (CPI, defined as the ratio of the total concentration of particulate *n*-alkanes with odd carbon number to that with even carbon number) and U : R ratio (the concentration ratio of unresolved components to resolved components obtained from chromatograms). The low CPI value (0.9–1.9) and high U : R ratio (2.6–6.4) for each sample further confirmed that fossil fuel utilization was the major source of *n*-alkanes in ambient PM<sub>2.5</sub> of Taipei city. Estimates from these results showed that 69–93% of the *n*-alkanes in PM<sub>2.5</sub> of the Taipei aerosol originated from vehicular exhaust. The higher concentration level of particulate *n*-alkanes in the Taipei aerosol was mainly a result of vehicular emissions. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Urban aerosols; Fine particles; Carbon preference index; Vehicular exhaust; Source apportionment

## 1. Introduction

*n*-Alkanes, a group of nonpolar and relatively stable organic compounds, are primary pollutants of relatively high concentrations in urban areas. Gaseous and particulate *n*-alkanes, ranging from C<sub>2</sub> to C<sub>36</sub>, were quantitated during a severe photochemical smog episode in the Los Angeles area (Fraser et al., 1997). Ambient *n*-alkanes come from two major source categories: fossil fuel utilization and the contemporary biological sources (i.e., plant wax). Particulate *n*-alkanes in vehicular emissions are derived from incomplete combustion of fuel and from lubricant oil (Rogge et al., 1993). *n*-Alkanes of biological origin are produced by mechanical processes (mainly in coarse particles) and combus-

tion of biomass (in fine particles) (Kadowaki, 1994). The bulk characteristics of *n*-alkanes are source-specific and therefore provide much information about their origins (Mazurek et al., 1989; Schauer et al., 1996). The CPI value of *n*-alkanes homologues and the U : R ratio have been successfully applied to source apportionment in several studies (Kadowaki, 1994; Zheng et al., 2000).

According to the results reported by Simoneit (1984) and Mazurek et al. (1989), a CPI value greater than 3 suggests that the *n*-alkanes come from contemporary biological sources, while a CPI of about unity is indicative of incomplete combustion of fossil fuel. Similarly, a U : R ratio greater than 2 indicates contaminations from fossil fuel residues.

Taipei, a densely populated city (9735 inhabitants km<sup>-2</sup>), has an extremely high density of passenger cars (2200 vehicles km<sup>-2</sup>) and motorbikes (3300 vehicles km<sup>-2</sup>). Ambient concentrations of *n*-alkanes in total suspended particles and vapor have been determined for

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Taipei aerosols in an earlier study (Lin et al., 1997). In view of the fact that vehicular emissions represent a major source of fine particles in urban aerosols, chemical characterization and source apportionment for PM<sub>2.5</sub> are more useful for assessing health risk of air pollution and planning effective control measures. The primary objectives of this study were to determine the concentrations of *n*-alkanes and to use the bulk characteristics of *n*-alkanes for source apportionment of ambient PM<sub>2.5</sub> in the Taipei aerosol.

## 2. Method and materials

### 2.1. Sampling

A Model 310 Universal Air Sampler (MSP Corp., Minneapolis, MN, USA) was used to collect particles smaller than 2.5 µm in aerodynamic diameter (PM<sub>2.5</sub>) on quartz fiber filters (Pallflex, 8 × 10 in). Organic impurities were removed from the quartz fiber filters before sampling by annealing them at 700°C for 4 h. The sampler was placed on the rooftop, 15.7 m above the street level, of a school building in Taipei city. The sampling site was located at the vicinity of the Chung-Shan Air Quality Monitoring Station operated by the Taiwan Environmental Protection Administration. PM<sub>2.5</sub> samples were collected once every 10 days during September 1997–February 1998. On each run, the sampler was operated for 10 min in each quarter of an hour at a flow rate of 285 l min<sup>-1</sup> for 24 h. A field blank was placed at the sampling site to monitor any contamination during the sampling process.

### 2.2. Chemical analysis

#### 2.2.1. Extraction

Each particle sample was Soxhlet-extracted with 300 ml of CH<sub>2</sub>Cl<sub>2</sub> for 24 h with at least 4 cycles h<sup>-1</sup>. The entire process of extraction was carried out in a darkened hood to prevent photochemical reactions of *n*-alkanes. The extract was concentrated under reduced pressure to approximately 3–5 ml by a rotary evaporator and then filtered through a pipette packed with glass wool to remove suspended solids. Following evaporation by nitrogen blowdown and addition of internal standard solutions, the volume of each sample extract was adjusted to 1 ml by adding CH<sub>2</sub>Cl<sub>2</sub>.

#### 2.2.2. Instrumental analysis

The concentrated extracts were analyzed using a Hewlett Packard Model 5890 gas chromatograph system with a 30 m CP-Sil 8 CB (Crompack, 25 µm film thickness, 0.32 mm i.d.) fused silica capillary column and a flame ionization detector. In each run, 2 µl of each extract was injected in splitless mode. The temperature

was 300°C at the injector and 325°C at the detector. The temperature programming for the oven was: (1) isothermal hold at 50°C for 3 min, (2) temperature ramp of 25°C min<sup>-1</sup> to 200°C, (3) temperature ramp of 3°C min<sup>-1</sup> to 320°C, and (4) isothermal hold at 320°C for 8 min. Data acquisition and analysis were performed with the SISC-LAB Chromatography Data System (Version 1.0) software.

#### 2.2.3. Identification and quantification

The retention time of each peak in the chromatogram of a sample was compared with those of a standard solution, and *n*-alkanes were identified by matching retention times. Quantitation was made using the internal standard method. Standard solutions of *n*-alkanes (C<sub>17</sub>–C<sub>36</sub>) in CH<sub>2</sub>Cl<sub>2</sub> were prepared in the concentration range of 0.1–15 µg ml<sup>-1</sup>. Predetermined volumes of 250 µg ml<sup>-1</sup> C<sub>18</sub>H<sub>30</sub> (dodecyl benzene) and 100 µg ml<sup>-1</sup> C<sub>28</sub>H<sub>56</sub>O<sub>2</sub> (heptacosanoic acid methyl ester) were added to standard solutions and sample extracts as the internal standards for compound identification and quantification. To account for day-to-day instrumental variations, retention time windows (RTWs) and calibration curves were determined from chromatograms of authentic standard solutions prior to each analysis session. RTWs were determined from the 99% confidence interval of retention time (i.e., mean ± 3 × standard deviations) obtained in seven successive analyses of standard solutions. The relative standard deviation of the RTW for each *n*-alkane was less than 0.1%. The use of RTWs for compound identification in GC/FID analysis was verified by GC/MS analysis (*m/z* 57, 71 and 99). A calibration curve was obtained for each *n*-alkane by plotting the concentration of a standard solution against the corresponding peak area ratio, defined as the ratio of the peak area of the *n*-alkane to that of an internal standard on the chromatogram. The regression coefficient for each calibration curve was higher than 0.995.

To evaluate possible losses of *n*-alkanes during the processes of extraction, concentration, and cleaning, recovery studies were conducted by spiking each blank filter with predetermined amounts of C<sub>17</sub>–C<sub>36</sub> *n*-alkanes as recovery standards. Four different amounts of recovery standards (1, 5, 10 and 15 µg) corresponding to the concentrations of standard solutions for calibration curves were used. The recovery of each *n*-alkane was calculated as

$$\text{Recovery (\%)} = [(A_r/A_{is})/(A_{std}/A_{is})] \times 100\%$$

where  $A_r$  is the peak area of a recovery standard obtained from a spiked filter,  $A_{std}$  the peak area of a recovery standard obtained directly from a standard solution, and  $A_{is}$  the peak area of an internal standard.

The average recovery for all *n*-alkanes was estimated to be 84%. The method detection limits of individual

*n*-alkanes in solutions were in the range of 3.6–25.4 ng ml<sup>-1</sup>. All concentration data were corrected for blank contamination and the losses during extraction, concentration, and cleaning.

#### 2.2.4. Source attribution

The carbon number distribution, CPI and U:R ratio were used for source attribution of *n*-alkanes by comparing them with those reported by Mazurek et al. (1989) for a variety of *n*-alkanes sources.

### 3. Results and discussion

#### 3.1. Mass concentrations of ambient *n*-alkanes

Table 1 shows the total mass concentrations of C<sub>17</sub>–C<sub>36</sub> *n*-alkanes for 15 PM<sub>2.5</sub> samples collected in Taipei city during September 1997–February 1998. The meteorological data on sampling days are given in Table 2. The 24-h average total concentrations of particulate *n*-alkanes were in the range of 69–702 ng m<sup>-3</sup>. Since the source emission rates remained relatively constant throughout the year, changes in meteorological conditions were likely the causes for variations in ambient concentrations of *n*-alkanes. Comparison of concentration data with the corresponding meteorological data shows that heavy rains significantly reduced the concentration of particulate *n*-alkanes (see, for example, the data for February 20, 1998). The concentration

Table 1

The total mass concentrations of particulate *n*-alkanes, CPI values, U:R ratios and percentages of plant wax *n*-alkanes in PM<sub>2.5</sub> samples collected in Taipei during September 1997–February 1998

Date	Conc. <sup>a</sup>	CPI <sup>b</sup>	U:R ratio	Wax (%) <sup>c,b</sup>
10-09-97	100	1.7	3.8	22
20-09-97	80	1.9	4.3	27
30-09-97	122	1.3	3.5	17
10-10-97	115	1.3	2.6	19
20-10-97	290	1.7	4.4	24
30-10-97	112	1.8	3.6	31
09-11-97	104	1.6	3.8	9
20-11-97	702	1.1	5.9	10
29-11-97	95	1.3	3.9	10
09-12-97	118	1.1	6.4	14
19-12-97	466	1.1	5.2	18
29-12-97	91	1.1	4.1	7
10-01-98	164	1.3	5.5	20
20-01-98	119	1.2	2.8	9
20-02-98	69	0.9	3.9	24

<sup>a</sup> Unit of concentration: ng m<sup>-3</sup>.

<sup>b</sup> In carbon number range of C<sub>17</sub>–C<sub>36</sub>.

<sup>c</sup> Total plant wax *n*-alkanes(%):  $\{\Sigma[\text{Plant wax } C_m]/\Sigma[C_n]\} \times 100\%$ , [C<sub>*n*</sub>]: Concentration of *n*-alkane with carbon number *n* (*n*: an integer from 17 to 36).

Table 2

Meteorological data on sampling days during September 1997–February 1998<sup>a</sup>

Date	Atmospheric pressure (hPa)	Ambient temperature (°C)	Relative humidity (%)	Precipitation (mm)	Wind velocity (m s <sup>-1</sup> )
10-09-97	1012	29.7	75.7	0.0	1.3
20-09-97	1014	25.6	62.1	0.0	3.6
30-09-97	1013	25.0	87.2	0.0	3.0
10-10-97	1015	22.8	86.0	7.3	1.2
20-10-97	1010	26.6	78.0	0.3	4.3
30-10-97	1023	20.8	68.1	0.0	2.8
09-11-97	1021	23.7	62.4	0.0	3.9
20-11-97	1018	24.3	67.1	0.0	1.7
29-11-97	1020	21.2	80.8	3.0	3.9
09-12-97	1026	13.3	76.0	1.7	1.7
19-12-97	1016	22.9	76.7	0.0	1.1
29-12-97	1017	21.6	78.4	2.9	1.4
10-01-98	1014	21.3	77.1	0.0	1.2
20-01-98	1022	15.2	87.1	2.0	2.0
20-02-98	1013	19.9	89.9	61.4	1.6

<sup>a</sup> All data are 24-h averages except the precipitation which is the rainfall in 24 h.

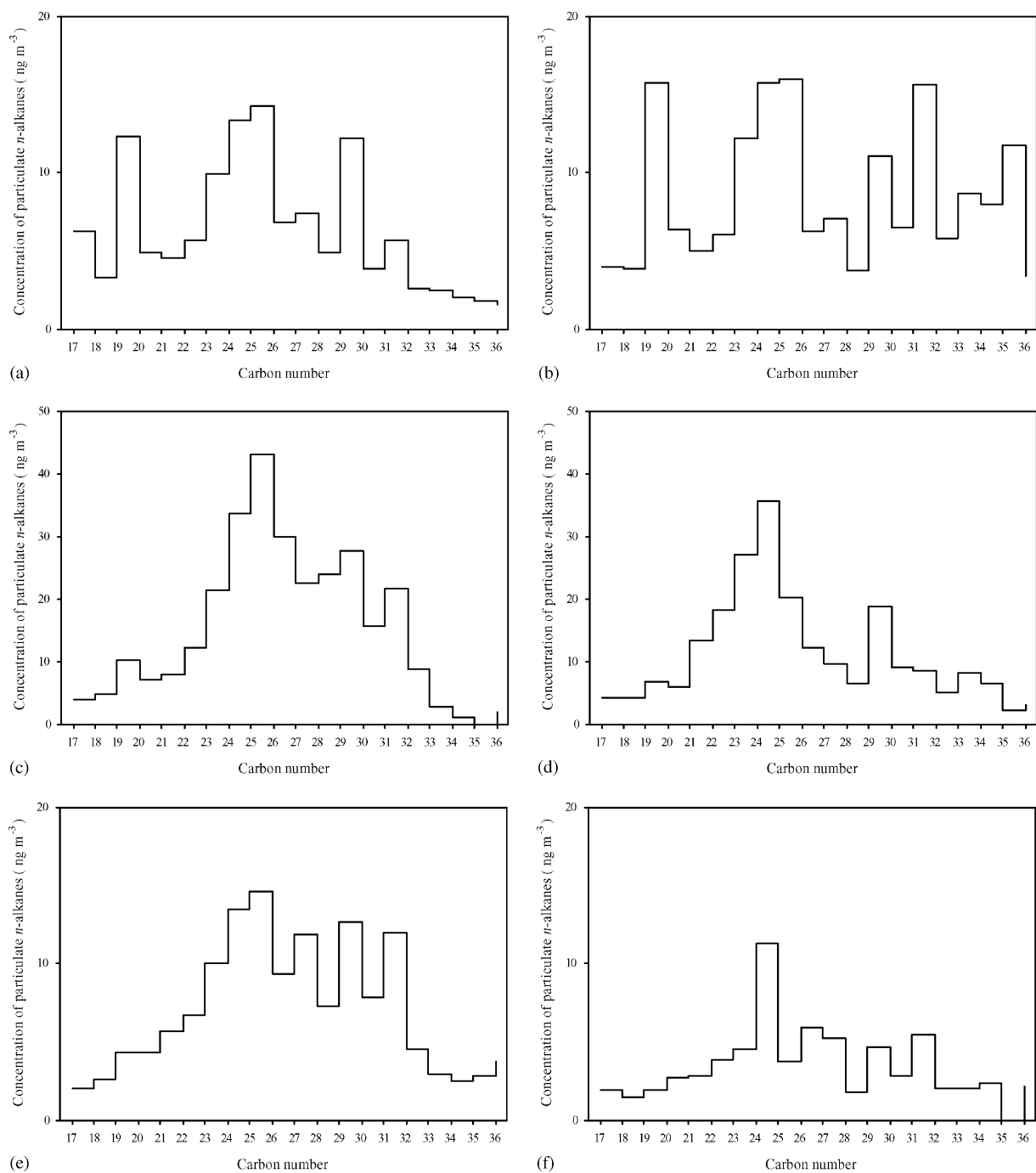


Fig. 1. Carbon number distributions of the concentration of particulate *n*-alkanes in  $PM_{2.5}$  of the Taipei aerosol averaged over samples obtained during each month. (a) September 1997, (b) November 1997, (c) October 1997, (d) December 1997, (e) January 1998, (f) February 20, 1998.

levels of particulate *n*-alkanes during days of average air quality in Taipei city were significantly higher than those observed during a severe photochemical smog episode in

Los Angeles ( $2.42\text{--}72.62\text{ ng m}^{-3}$  for  $C_{17}\text{--}C_{36}$  *n*-alkanes in fine particles, Fraser et al., 1997), and Hong Kong ( $6.5\text{--}41.1\text{ ng m}^{-3}$  for  $C_{14}\text{--}C_{36}$  *n*-alkanes in  $PM_{2.5}$ , Zheng

et al., 2000), indicating that the emissions of particulate *n*-alkanes in Taipei were considerably greater than in the other two areas.

### 3.2. Carbon number distribution of *n*-alkanes

Figs. 1(a)–(f) show the carbon number distributions of particulate *n*-alkanes concentrations averaged over each month for the ambient samples collected during September 1997–February 1998 (there was only one sample in February 1998). The particulate *n*-alkanes had considerably higher concentrations in the range from C<sub>23</sub> to C<sub>31</sub> with a peak at C<sub>24</sub> or C<sub>25</sub>. The distribution profiles exhibited a combination of two different patterns: (1) a very high concentration of C<sub>19</sub>, C<sub>24</sub> or C<sub>25</sub> *n*-alkanes, indicating contributions from vehicular exhaust and lubricant residues, and (2) higher concentrations of *n*-alkanes with odd carbon number (C<sub>27</sub>, C<sub>29</sub>, and C<sub>31</sub>), suggesting biological inputs. One distinctive feature of the carbon number distributions in Figs. 1(a)–(e) was that all the profiles showed a peak at C<sub>19</sub>, an indicator of lubricant oil used in gasoline- and diesel-powered engines (Simoneit, 1986). No other study of ambient *n*-alkanes has shown such an abundance of C<sub>19</sub> *n*-alkane. The peak at C<sub>19</sub> can be attributed to the high density of diesel vehicles and two-stroke motorbikes in Taipei.

### 3.3. Estimation of fossil fuel contribution

Table 1 also summarizes the CPI values, U : R ratios and estimated percentages of plant wax *n*-alkanes in the PM<sub>2.5</sub> samples. Most of the CPI values were approximately unity, very close to that for vehicular exhaust. The U : R ratios were in the range of 2.6–6.4, suggesting that fossil fuel contributions dominate over biological origins. Fig. 2 shows a hump in a typical chromatogram of resolved and unresolved components in solvent extractable organic compounds of the PM<sub>2.5</sub> samples. The hump under the peaks, termed the unresolved complex mixture (UCM), consists mainly of branched and cyclic hydrocarbons from fossil fuel residues (Aceves and Grimalt, 1993). The CPI values and the U : R ratios calculated from the concentration data showed an inverse linear relationship (Fig. 3). Although the correlation was only moderate, it did indicate a certain degree of consistency of these two indices in their applications in source attribution.

The concentrations of plant wax to the *n*-alkanes with odd carbon number were estimated by the following equation (Simoneit et al., 1991)

$$[\text{Plant wax } C_m] = [C_m] - \frac{[C_{m+1}] + [C_{m-1}]}{2},$$

where *m* is an odd number between 16 and to 36 and [C<sub>*m*</sub>] the concentration of the *n*-alkane with carbon

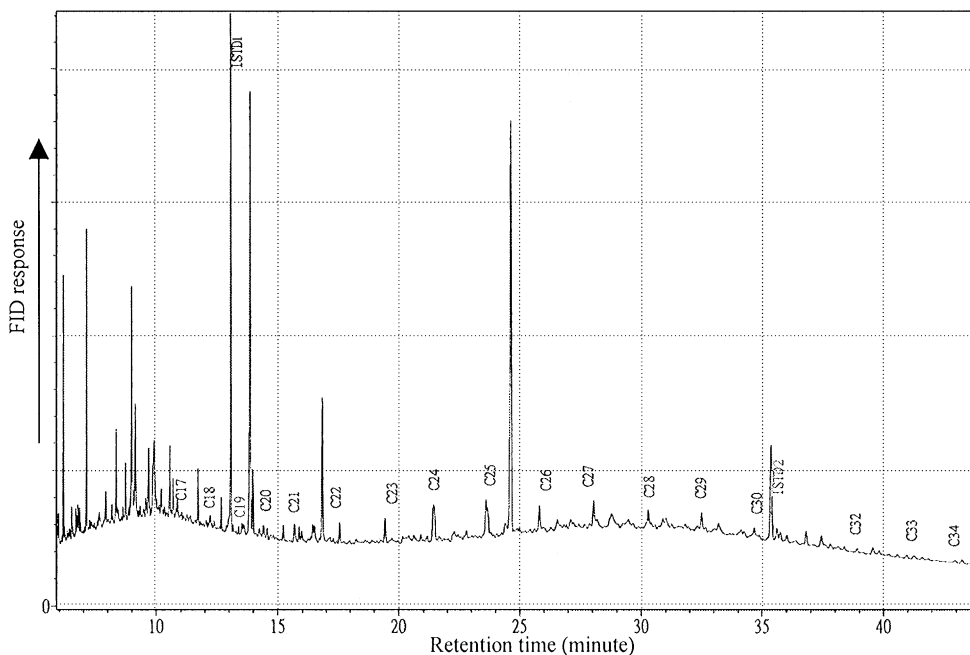


Fig. 2. A typical chromatogram of resolved and unresolved components in solvent extractable organic compounds of PM<sub>2.5</sub>; C<sub>*n*</sub> denotes the *n*-alkane with carbon number *n*; ISTD1 and ISTD2 are the internal standards (dodecyl benzene and heptacosanoic acid methyl ester, respectively).

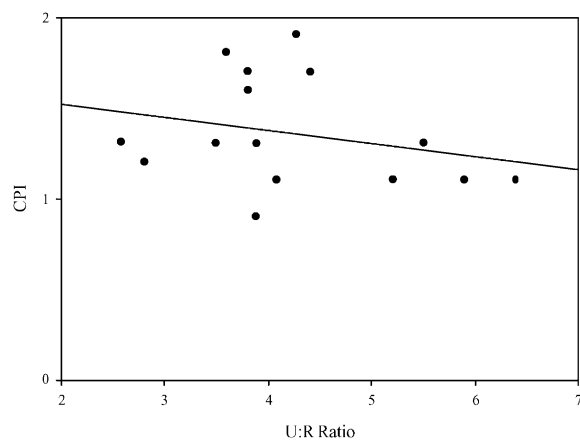


Fig. 3. Correlation between CPI values and U:R ratios of 24-h samples of Taipei aerosol obtained during September 1997–February 1998.

number  $m$  and [Plant wax  $C_m$ ] the portion of [ $C_m$ ] contributed from plant wax. Negative values of [Plant wax  $C_m$ ] obtained in calculations were replaced by zero. The contributions of plant wax to  $C_{17}$ – $C_{36}$   $n$ -alkanes were in the range of 7–31%.

#### 4. Conclusions

The concentration level of particulate  $n$ -alkanes in Taipei  $PM_{2.5}$  during days of average air quality was significantly higher than those in Los Angeles during a severe photochemical smog episode and in Hong Kong. The higher concentration level of particulate  $n$ -alkanes in Taipei City was mainly a result of vehicular emissions.

The  $n$ -alkanes distributions obtained in this study showed two common features: a very high concentration of  $C_{19}$ ,  $C_{24}$  or  $C_{25}$   $n$ -alkanes, which represented contributions from vehicular exhaust and lubricant residues, and an odd carbon number preference in the range of  $C_{27}$ – $C_{31}$ , suggesting inputs of biological sources. A combination of low CPI values with high U:R ratios indicated that vehicular exhaust was the major source of  $n$ -alkanes in ambient  $PM_{2.5}$  of Taipei. It was estimated that vehicular exhaust contributed 69–93% of the  $n$ -alkanes in  $PM_{2.5}$ . A moderate correlation between CPI values and U:R ratios indicated a certain degree of consistency between the two indices in their application in source apportionment.

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#### 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.
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T., Rasmussen, R.A., 1997. Air quality model evaluation data for organics—4.  $C_2$ – $C_{36}$  non-aromatic hydrocarbons. *Environmental Science and Technology* 31, 2356–2367.
- Kadowaki, S., 1994. Characterization of carbonaceous aerosols in Nagoya urban area—2. Behavior and origin of particulate  $n$ -alkanes. *Environmental Science and Technology* 28, 129–135.
- Lin, S., Young, L.H., Wang, C.S., 1997. Gaseous and particulate  $n$ -alkanes in the Taipei aerosol. *Journal of Aerosol Science* 28 (Suppl. 1), S133–S134.
- Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1989. Interpretation of high-resolution gas chromatography/mass spectrometry data acquired from atmosphere organic aerosol samples. *Aerosol Science and Technology* 10, 408–420.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T., 1993. Quantification of urban organic aerosols at molecular level: identification, abundance and seasonal variation. *Atmospheric Environment* 27A, 1309–1330.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837–3855.
- 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., 1986. Characterization of organic constituents in aerosols in relation to their origin and transport: a review. *International Journal of Environmental Analytical Chemistry* 23, 207–237.
- 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.
- Zheng, M., Fang, M., Wang, F., To, K.L., 2000. Characterization of the solvent extractable organic compounds in  $PM_{2.5}$  aerosols in Hong Kong. *Atmospheric Environment* 34, 2691–2702.