Temporal patterns of \( n \)-alkanes at traffic exposed and suburban sites in Vienna

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Abstract

Temporal and spatial trends of particulate \( n \)-alkanes \( C_{24} - C_{33} \) have been investigated at urban-fringe and traffic exposed inner urban sites of a larger European city. The annual average sum of \( n \)-alkanes at the four sampling sites ranged from 21 to 31 ng m\(^{-3}\). The urban impact factor was \( \sim 30\% \) averaged over the year. The seasonal biogenic emissions of the uneven \( n \)-alkanes cause a considerable seasonal variation in the distribution pattern of the alkanes in PM10 both in the city and at the suburban sites. The trends in the distribution pattern can be summarized using the odd carbon preference index CPI\textsubscript{odd} and the plant wax number \%WNA, both of which show clear maxima in summer pointing to important biogenic sources of \( n \)-alkanes. The biogenic contributions to the total \( n \)-alkanes were around 9\% in winter (DJF), and 37\% in summer (JJA) at the urban-fringe sites. At the inner city sites, the urban impact is dominated by \( n \)-alkanes from combustion sources at all seasons. A comparison of two approaches to determine the contribution of the “plant debris” source to ambient PM10 indicates two different mechanisms to form atmospheric “plant debris”. The observed relative contributions of plant debris to PM10 are well in the same range but exhibit differences in the seasonal trend. Considering the different underlying concepts, the agreement of the derived plant debris contributions to PM10 is noteworthy.

Keywords: \( n \)-Alkanes; PM10; Particulate matter; Source analysis; Biogenic particles

1. Introduction

In Europe, the ambient air quality standard for particulates is currently defined for PM10 as a yearly average of 40 \( \mu \)g m\(^{-3}\), and a daily average of 50 \( \mu \)g m\(^{-3}\), not to be exceed \( \sim 35 \) times a year. However, the short-term standard is actually exceeded in many urban areas of Europe (e.g., Querol et al., 2004; Van Dingenen et al., 2004; Houthuijs et al., 2001).

According to the directives 1999/30/EG and 96/62/EG of the European Commission, PM10 concentrations have to be radically reduced by the year 2010 and so the identification of the sources of the
particulates becomes important. Major groups of substances in the particulate matter comprise inorganic ions, carbonaceous material, and mineral species. n-Alkanes are a subgroup of the carbonaceous material, which can originate from both man-made and natural sources and the distribution patterns of the homologous constituents can help one to assess the contributors (e.g., Rogge et al., 1993a).

Particulate n-alkanes have been determined in vehicle exhaust (e.g., Rogge et al., 1993b; Schauer et al., 1999a, 2002a), tyre abrasion and brake lining dust as well as in road dust (Rogge et al., 1993c). Particulate n-alkanes are emitted in natural gas combustion (Rogge et al., 1993d), from boilers (Rogge et al., 1997a), and are contained in smoke from coal combustion (Oros and Simoneit, 2000). Hot asphalt roofing tar gives off copious amounts of higher hydrocarbons (Rogge et al., 1997b). The smoke of wood and synthetic logs burning is another source of particulate n-alkanes (e.g., Rogge et al., 1998; Schauer et al., 2001; Simoneit et al., 2000; Fine et al., 2001, 2002), and also cigarette smoke (Rogge et al., 1994; Kavouras et al., 1998). Paticulate n-alkanes were observed in cooking emissions from meat or vegetables (Rogge et al., 1991; Schauer et al., 1999b, 2002b; He et al., 2004). Vegetative detritus ranks as a “strong” n-alkanes source and particulate n-alkanes were reported in “leave” abrasion (Rogge et al., 1993e). From biosphere, pollens and micro-organisms such as bacteria and fungal spores, and insects are known to contribute n-alkanes (Simoneit and Eglinton, 1977).

Cooper and Bray (1963) introduced the term carbon preference index (CPI_odd) which is used to identify the origin of the n-alkanes origin. The information obtained from CPI_odd and n-alkanes distributions in different sources is discussed in detail in Gogou et al. (1998), Rogge et al. (1993a), and Simó et al. (1991). Fossil petroleum deposits show a CPI_odd value near unity and are accompanied by a shift of the most abundant homologues in the range C_{22}–C_{25}. As a result, the emissions from utilization of fossil fuel exhibit CPI_odd values close to 1.0. While the homologues with <20 carbons may have a mixed origin, the presence of homologues with >21 carbons, with CPI_odd>1 and maxima at C_{29}–C_{31}, does suggest a predominant biomass input from plants. The organic matter (OM) of recent biogenic origin shows CPI_odd values of 6–9. Urban environments, with large contribution from anthropogenic emissions, generally have CPI_odd ranging from 1.0 to 2.0 (Brown et al., 2002). In addition, Simoneit et al. (1991) introduced the plant wax number (%WNA) which is deduced mainly for the directly emitted material from the vegetation rather than from resuspended soil detritus. The %WNA and CPI_odd has been observed to correlate positively at urban areas, e.g., by Lin and Lee (2004) and Zheng et al. (2000). In this paper, we use the %WNA to derive a quantitative estimate of plant debris contributions to PM levels.

The plant debris contribution to atmospheric organic carbon (OC) and PM levels has been assessed in Europe also using cellulose as “macro-tracer” (Puxbaum and Tenze-Kunit, 2003; Sánchez-Ochoa et al., 2007).

In this paper, we report the concentrations and distribution patterns of the higher n-alkanes in airborne particulate samples collected at four sites in Vienna, Austria, over a period of a year (2004). We investigate the concentrations of n-alkanes over a northwest to southeast transect across Vienna at sites more and less impacted by traffic sources, which allows us to derive an “urban impact” from the n-alkanes. We use the bulk characteristics of n-alkanes for deriving information on direct biogenic vs. anthropogenic combustion derived contributions to the n-alkanes. Then we compare two approaches—the plant debris derived from cellulose and derived from the wax number as proposed in this paper—to determine the contribution of the “plant debris” source (also named vegetative detritus by other authors) to ambient PM10, yielding a remarkable agreement.

2. Experimental

2.1. Sampling

PM10 sampling was conducted from January to December 2004 at four air quality measurement stations of the Vienna air quality network (Fig. 1). Sampling was organized by the local authorities. Two of the four sites have urban-fringe characteristics. Schaerbergbad is located in a park-type residential area (16°18′10″E, 48°14′09″N, 320 m a.s.l.). The Lobau sampling site is in the area of the Donau Auen National Park (16°31′37″E, 48°09′45″N, 150 m a.s.l.). The other two sampling stations are located close to busy roads. The A23 highway runs nearby the Rinnbökstrasse sampling site (16°24′28″E, 48°11′05″N, 160 m a.s.l.), while the
fourth sampling site at Kendlerstrasse is beside a busy street (16°18'39"E, 48°12'20"N, 230 m a.s.l.).

The PM10 samples were collected with high volume samplers (DHA-80, DIGITEL Electronik AG, Switzerland) on quartz fiber filters (Pallflex™ 2500QAT-UP, diameter 150 mm, PALL Life Sciences, USA) for 24-h sampling periods, with volumes of approximately 700 m³ per filter. The filters were conditioned for around 48 h in a clean room at a temperature of 20 ± 1 °C and a relative humidity of 50 ± 5% and were weighed before and after sampling. The gravimetric measurements were performed by the local authorities.

2.2. Chemical analyses

Analytes to be determined were \( n \)-alkanes C\(_{20}\)–C\(_{35}\). One quarter of a quartz fiber filter (or an aliquot area from pooled filters) was taken for the extraction. The filter was cut into small pieces (≈1.5 cm\(^2\)) which were spiked with recovery standards (perdeuterated tetra-cosane C\(_{24}D_{50}\) and benzo[\( a \)]pyrene-d\(_{12}\)). The filter pieces were transferred into a glass tube and extracted twice with 5 mL of cyclohexane in a mild ultrasonic bath at room temperature each time for 5 min. The internal standard (1-bromopentadecane) was then added to the combined extract, and the volume was reduced to 200 μL under a gentle stream of pure nitrogen at 35 ± 5 °C. After that the extract was analyzed by GC–MS.

Gas chromatographic measurements were carried out with a model HP-6890 equipped with an HP-7683 autosampler and a split/splitless injector (300 °C) was operated in splitless mode (2 min). The separation was performed on a DB-5 MS capillary column (J&W Scientific) with 5% phenyl, 95% polydimethylsiloxane stationary phase (30 m × 0.25 mm i.d. × 0.25μm film thickness) and preceded by a 1 m × 0.32 mm uncoated fused silica pre-column. The temperature programme started at 50 °C for 2 min, followed by 8 °C min\(^{-1}\) to 98 °C, then 6 °C min\(^{-1}\) to 290 °C for 20 min. As carrier gas helium (Messer, Vienna, Austria) suitable for trace analysis (purity of 99.999%) was used with a constant flow of 1.5 mL min\(^{-1}\). The gas chromatograph was coupled to a quadrupole mass spectrometer (HP-5973) operated at 70 eV in the electron ionization (EI) mode. Mass spectra were recorded in the full scan mode (\( m/z \) range: 50–550) and sensitive detection was carried out in the selected ion monitoring (SIM) mode. Temperature of source, quadrupole and transfer line were 230, 150, and 300 °C, respectively.

For identification and quantification of \( n \)-alkanes (from SIM mode) standards of \( n \)-alkanes C\(_{20}\), C\(_{22}\), C\(_{24}\), C\(_{26}\), C\(_{28}\), C\(_{29}\), C\(_{30}\), and C\(_{32}\) (Fluka, min. 99% (GC)) were used.

The other alkanes were identified based on their EI mass spectra and comparison with spectra from the NIST library, and quantified using the calibration
curve of the nearest lower carbon number \( n \)-alkane. The method detection limit defined as three times noise level, ranged from 2.6 \( \mu \text{g m}^{-3} \) for \( n \)-eicosane (C\(_{20}\)) to 22.4 \( \mu \text{g m}^{-3} \) for \( n \)-dotriacontane (C\(_{32}\)), when calculated with the average sampling volume of 700 \( \text{m}^3 \). For practical purposes, the double of the limit of detection or quantification was assigned to samples below the limits when computing mean and sum.

3. Results and discussion

3.1. PM10 and filter pooling

The concentrations of PM10 in the samples (on a daily base) at Rinnböckstrasse ranged from 7.8 to 124 \( \mu \text{g m}^{-3} \) with an average of 33 \( \pm 18 \mu \text{g m}^{-3} \). At the other city station, Kendlerstrasse, the values varied from 6.1 to 125 \( \mu \text{g m}^{-3} \) with an average of 28 \( \pm 17 \mu \text{g m}^{-3} \). From the urban-fringe sampling sites PM10 concentrations were in the range 4.4–95 \( \mu \text{g m}^{-3} \), average 20 \( \pm 12 \mu \text{g m}^{-3} \) at the Schafbergbad station, and 4.1–79 \( \mu \text{g m}^{-3} \), 20 \( \pm 16 \mu \text{g m}^{-3} \) at Lobau. Thus, while the annual means were acceptable in terms of the European Directive, there were many days showing exceedances in the periods 1 January–1 April 2000 and 7 October–31 December 2004, with 54 at Rinnböckstrasse, 36 at Kendlerstrasse, 15 at Schafbergbad, but only 9 at the Lobau sampling site.

For the chemical analyses, the daily samples were grouped into pools. The main criteria were the PM10 concentrations in time periods of similar temporal behavior. The same time synchronized pools were prepared for each sampling site. Some pools focused on high-PM10 “episodes”, defined as periods when the PM10 mass concentrations were above the EU short-term limit. The further pools combined samples from “non-episode” days.

Altogether 52 pooled samples were obtained: 14 in January, 2 in February, 4 in March, 2 in April, 2 from May–August, 3 in September, 8 in October, 5 in November, and 6 in December. One pool was missing from Schafbergbad (from December) and 15 pools form Lobau (8 from January, 1 from September, 6 from October), because of lack of samples.

3.2. \( n \)-Alkanes

There is no single accepted group of \( n \)-alkanes which should be considered for characterization of PM10 material. Alkanes with <20 carbons are generally considered too volatile and so would be lost to varying extents from the particulate matter even before as well as during sampling, depending on the sampling procedure. On the other hand, those with >36 carbons can be difficult to determine at the low levels present. In pooled samples collected in this study, \( n \)-alkanes ranging from \( n \)-eicosane (C\(_{20}\)) to \( n \)-pentatriacontane (C\(_{35}\)) were determined to give estimates of the particulate \( n \)-alkanes present.

The concentration of total \( n \)-alkanes C\(_{20}\)–C\(_{35}\) in pools sampled at the four Vienna stations varied from 6.88 to 127 \( \text{ng m}^{-3} \). The concentrations of individual \( n \)-alkanes showed values up to 18.7 \( \text{ng m}^{-3} \) (Table 1).

The sums of \( n \)-alkanes reported in the past for PM10 collected at European sampling sites are difficult to compare as different homologue selections were investigated. However, the concentrations observed at urban sites were of a similar order of magnitude to those observed at clean rural sites. For example, 37–205 \( \text{ng m}^{-3} \) were reported from an industrialized area in Prato (Italy, sampling period May 2000–January 2001, \( n \)-alkane range C\(_{13}\)–C\(_{34}\) (Cincinelli et al., 2003), 16–262 \( \text{ng m}^{-3} \) at an urban/industrial influenced grassland location in Melpitz (Germany, April–May 2001, C\(_{16}\)–C\(_{34}\) (Alves et al., 2006), and 7.2–95 \( \text{ng m}^{-3} \) at Hytiälä, a forest site (Finland, August 2001, C\(_{16}\)–C\(_{34}\) (Alves et al., 2006).

Normal alkanes are released from anthropogenic and biogenic sources in the range C\(_{12}\)–C\(_{40}\) and the concentration range of a particular compound can be wide, e.g., the mean concentrations of tricosane (C\(_{23}\)) determined by Kubátová et al. (2002) in Ghent were 8.6 \( \pm 14.1 \text{ ng m}^{-3} \) in winter and 1.2 \( \pm 2.0 \text{ ng m}^{-3} \) in summer 1998. The concentration variation of organic species in the aerosols is generally considered to be a consequence of the semi-volatile nature of some components, meteorological conditions (may influence the particle-gas phase partitioning and deposition of aerosols), chemical characteristics after emission, as well as by changes in the source contributions.

The distribution pattern of the \( n \)-alkanes in the airborne particulates over Vienna is shown in Fig. 2. In all four cases, summer (April–September) and winter (January–March, October–December), city and suburban there can be seen peaks superimposed on a smooth curved background. The smooth background distribution is much higher in the urban samples than in the suburban samples, and
is at a maximum in winter. This is likely a result of emissions from urban “winter” sources, such as domestic heating (e.g., natural gas, oil, and wood combustion). The main components are always C_{27}, C_{29}, and C_{31} considered to originate from plant material. However, in the summer samples than in those from winter. The predominance of n-alkanes C_{27}, C_{29}, or C_{31} has been reported for other sites in Europe, e.g., in Portugal (Alves et al., 2001), Germany (Alves et al., 2006), and Finland (Alves et al., 2006; Rissanen et al., 2006).

Since the C_{10}–C_{23} n-alkanes are semi-volatile (e.g., Kadowaki, 1994), they are not further considered in the analysis.
here. \(n\)-Alkanes > C\textsubscript{33} generally occur at very low concentrations (Fig. 2), thus we also excluded them from the long term study. The range of C\textsubscript{24}–C\textsubscript{33} is called the higher plant wax range. In this range, \(n\)-alkanes originate from both natural and man-made sources, and it is possible to discriminate the influence from those two groups of sources by investigating the uneven/even relationships of the samples.

Table 1 shows the annual mean concentrations of \(n\)-alkanes, as well as sum of \(n\)-alkanes C\textsubscript{24}–C\textsubscript{33}, and standard deviations of monthly means. The two inner city sites do have higher concentrations than the two urban-fringe sites, and the difference is taken as the urban impact for the \(n\)-alkanes which in this case is 28.6%.

The total \(n\)-alkanes C\textsubscript{24}–C\textsubscript{33} concentration varied in individual pools from 16.8 to 86.9 ng m\textsuperscript{-3} at traffic exposed sampling sites, and from 3.9 to 77.9 ng m\textsuperscript{-3} at sampling sites with urban-fringe characteristics (Table 1). The maximum values were observed in the pool from January (8 January 2004).

The mass content of \(n\)-alkanes in PM10 calculated as the ratio of mass of \(n\)-alkanes C\textsubscript{24}–C\textsubscript{33} to the mass of PM10 is, for individual pools, usually in the range 0.05–0.15%. Somewhat higher values appeared in the warm season from May to September with a maximum of 0.34% for Kendlerstrasse (Fig. 3a).

Similarly, the mass content of \(n\)-alkanes in OM was calculated (see Fig. 3b). \(n\)-Alkanes C\textsubscript{24}–C\textsubscript{33} accounted for 0.37–0.43% of the total OM as an average of individual pools, at all four sites, with the lowest contribution at Rinnböckstrasse which could be explained by the higher proportion of OM from nearby traffic. OM was calculated from OC as

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**Table 1**

<table>
<thead>
<tr>
<th>Pool</th>
<th>C\textsubscript{24}–C\textsubscript{33} (ng m\textsuperscript{-3})</th>
<th>Sample Mean (ng m\textsuperscript{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rinnböckstrasse</td>
<td>16.8</td>
<td>35.2</td>
</tr>
<tr>
<td>Kendlerstrasse</td>
<td>86.9</td>
<td>101.4</td>
</tr>
<tr>
<td>Schafbergbad</td>
<td>12.3</td>
<td>28.6</td>
</tr>
<tr>
<td>Lobau</td>
<td>3.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

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**Fig. 3.** (a) Total \(n\)-alkanes C\textsubscript{24}–C\textsubscript{33} as a % of PM10 mass. (b) Total \(n\)-alkanes C\textsubscript{24}–C\textsubscript{33} as a % of organic matter.
OM = \(1.7 \times OC\) (Bauer et al., 2006) where OC was determined according method described earlier by Salam et al. (2003). Thus, the \(n\)-alkanes of interest represent only minor constituents of OM, at the most of 1.05% in the Vienna area. The interest in analysing the samples for these compounds stems therefore more from the information which they could reveal than from their importance as individual components of the PM10.

Higher concentrations of total \(n\)-alkanes C\(_{24}\)–C\(_{33}\) were found in the samples with higher concentrations of PM10 in the atmosphere. Fig. 4 shows that the total C\(_{24}\)–C\(_{33}\) \(n\)-alkane values correlate with the PM10 mass concentrations.

### 3.3. Seasonal variation and origin of \(n\)-alkanes

Fig. 5 shows the variation in total \(n\)-alkanes at the different sites throughout the year on a month-by-month basis. The first impression is that the seasonal variation is small, with slightly higher values in the winter period. The urban impact is remarkably constant. The monthly mean concentrations of total \(n\)-alkanes C\(_{24}\)–C\(_{33}\) at the Vienna sampling sites varied from 12.6 to 39.3 ng m\(^{-3}\). The lowest urban impact was observed in May and June, when the concentrations of total \(n\)-alkanes C\(_{24}\)–C\(_{33}\) at the inner city sampling sites were very similar to concentrations at sampling sites with urban-fringe...

![Correlation between total \(n\)-alkanes C\(_{24}\)–C\(_{33}\) concentrations and PM10 concentrations in individual pools.](image1)

![Monthly averages of total \(n\)-alkanes at Vienna sampling sites (2004).](image2)
characteristics. On the other hand, the highest urban impact was observed in April.

The CPI_{odd} is expressed as concentration ratio of n-alkanes with odd and even carbon number:

\[ \text{CPI}_{\text{odd}} = \frac{\sum \text{odd carbon number n-alkanes}}{\sum \text{even carbon number n-alkanes}} \]

In our case, the CPI_{odd} is calculated for the so-called higher plant wax CPI split range. The values are higher than those obtained for whole range as, for example, C_{17–C_{35}} (e.g., Alves et al., 2001, 2006; Harrad et al., 2003). The CPI_{odd} for the Vienna samples shows a considerable seasonal variation (Table 2). The values are in range of 0.93–1.31 in the cold season (January, February, and December 2004) for all sampling sites. The maximum was observed in July, when the CPI_{odd} was around 2.67 at Rinnböckstrasse and Kendlerstrasse and around 3.43 at Schaalberg and Lobau. We can also see a different CPI_{odd} index for the near traffic sampling cites in comparison to the sampling sites on the Vienna urban-fringe sites.

Although all through along the year 2004 in Vienna the main components were n-alkanes with odd carbon number C_{27}, C_{29}, and C_{31}, the CPI_{odd} values show clearly seasonal differences in the n-alkanes composition. At Rinnböckstrasse and Kendlerstrasse, we can see a strong contribution from anthropogenic emissions. The influence of biogenic emissions became clear only in July, when the CPI_{odd} was >2.0. At sampling sites with urban-fringe characteristics, such values were observed in the warm season from May to August.

In spite of lower concentrations of n-alkanes in the atmosphere in the warm season, their contribution to PM10 (in percentage) is slightly higher and the CPI_{odd} increased. This implies a very strong contribution of biogenic sources during the warm season at all sampling sites. These deductions can be verified by plant wax number values.

The contribution of plant wax n-alkanes (%WNA) is calculated as follows (Simoneit, 1989):

\[ \% \text{WNA} = \frac{\sum (C_n - 0.5(C_{n+1} + C_{n-1}))}{\sum n - \text{alkanes}} \times 100\% \]

where negative values of the numerator are taken as zero. The plant wax number calculation assumes the wax n-alkanes are directly emitted from the vegetation and not in part from resuspended soil detritus (Simoneit et al., 1991).

The %WNA observed in this study show the same trend as CPI_{odd} (Table 2). The values are higher in the warm season than in the cold season, and the inner city sampling sites have lower wax numbers than the urban-fringe stations.

The %WNA number of 9% suggest that around 81% of n-alkanes C_{24–C_{33}} at Vienna sampling sites determined in PM10 ambient aerosol samples in winter months (December, January, February) were from petroleum residues rather than from higher plant wax, whereas it was only ~63% in summer months (June–August).

In our case, correlation coefficient \( r^2 \) between %WNA and CPI_{odd} of 0.93–0.94 was observed at traffic-exposed sites, while at sites with urban-fringe characteristics \( r^2 \) reached values of 0.86 for Schaferbad and of 0.91 for Lobau, because in July %WNA did not increased proportional to CPI_{odd}.

Values of urban impact CPI_{odd} and %WNA are listed in Table 2. Monthly values were calculated from monthly mean concentrations of individual n-alkanes. Negative values of urban impact which occurred for some analytes in February, May, and June were taken as zero. Carbon preference index of urban impact is relatively constant and typical values are in the range from 1.1 to 1.8. The %WNA values showed that 13–42% n-alkanes C_{24–C_{33}} emitted in Vienna should come from vegetation. In the urban impact, both characteristics are correlated with \( r^2 \) of 0.71, when “problematic” months are not considered. Analogously obtained yearly urban impact CPI_{odd} and %WNA clearly show that aerosols emitted at inner city sampling sites have anthropogenic character.

3.4. Biogenic emissions contribution to PM10

The contribution of plant debris, respectively vegetative detritus, to OC or PM levels has been derived in the past by use of CMB models (e.g., Schauer et al., 2002c; Zheng et al., 2002) and by using cellulose as macrotracer (Puxbaum and Tenze-Kunit, 2003; Sánchez-Ochoa et al., 2007). Here, we compare the results from the cellulose tracer with results obtained with a factor derived from the waxy contribution of n-alkanes combined with n-alkanes data from plant debris “profile” data from Rogge et al. (1993c).

The portion of the plant debris in the aerosol from the cellulose value (PD_{CEL}) is proposed to be estimated by the following equation, which takes in account the cellulose content in leaves and the way of cellulose determination:

\[ \text{PD}_{\text{CEL}} = \frac{\text{FC}}{0.72} \times 2, \]
where FC is concentration of “free cellulose” in atmospheric aerosol samples; for details see Puxbaum and Tenze-Kunit (2003).

For the determination of plant debris based on the concentration of biogenic n-alkanes concentrations in the atmospheric aerosols PDALK, the following formula was used:

\[
\text{PDALK} = \frac{\sum n - \text{alkanes} \times (% WNA/100)}{0.0236}
\]

The biological fraction of n-alkanes is expected to come exclusively from plant debris as the contributions from other source (e.g., pollen, bacteria, and insect) are supposed to be negligible. The content of n-alkanes material varies in a wide range from different plant species (e.g., Maffei et al., 2004; Maffei, 1996). For the determination of PDALK, the mean value of n-alkane concentrations of “green leaves” and “dead leaves” reported by Rogge et al. (1993e) was used (yielding a factor of 0.0236).

The PDCEL and the PDALK values were used to calculate the percentage of PM10 derived from plant debris. The %PD-cel, %PD-alk values are within the same range, but the absolute values and the patterns were not identical (Fig. 6). The %PD-alk values were lower in winter and higher in summer than the %PD-cel. A maximum of 3.6% of %PD-alk was found at the urban-fringe sampling site Lobau in May. The %PD-cel values were more similar for all Vienna sampling sites and did not exceed a value of 2% (with one exception for Schafbergbad in January). It can be concluded that, although plant debris contributions to PM10 are not high, it is a non-negligible source.

The differences between results obtained by calculation from cellulose and from n-alkanes could be caused by several factors. For the plant debris calculation with cellulose as tracer is has to be considered that cellulose originates from the bulk material of plant debris. For the conversion of measured “free cellulose” values to the PDCEL two factors are used which have to be considered when assessing the uncertainty of the results. A factor of 0.72 is used for conversion of “free cellulose” to “total cellulose” with a standard deviation of 0.16% (Puxbaum and Tenze-Kunit, 2003). A factor of 2 is taken for conversion of cellulose to plant material as derived from the cellulose content of “green leaves” of approximately 50% (Puxbaum and Tenze-Kunit, 2003; Kunit and Puxbaum, 1996). Moreover, “dead leaves” may contain less cellulose than green leaves, since cellulose is degraded faster than lignin. The cellulose might be partly resuspended to the atmosphere. Drewnik (2006) reported a high variability in cellulose degradation kinetics in soil when after 10 weeks 22–98%, and after 1 year 48–100% were decomposed. Sánchez–Ochoa et al. (2007) estimated the over all uncertainty of the plant debris values from cellulose by 37%. The plant debris calculation according to the n-alkane signal also used two factors. %WNA values should refer the n-alkanes percentage from plant debris. Simoneit et al. (1991) notice that the %WNA calculation assumes the wax n-alkanes are directly from vegetation and not in part from resuspended soil detritus. However, the

<table>
<thead>
<tr>
<th>Month</th>
<th>Rinnböckstrasse</th>
<th>Kendlerstrasse</th>
<th>Schafbergbad</th>
<th>Lobau</th>
<th>Urban impact</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CPI_odd %WNA</td>
<td>CPI_odd %WNA</td>
<td>CPI_odd %WNA</td>
<td>CPI_odd %WNA</td>
<td>CPI_odd %WNA</td>
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<tr>
<td>January</td>
<td>1.14 12.7</td>
<td>1.19 12.9</td>
<td>1.13 11.3</td>
<td>1.15 14.4</td>
<td>1.20 12.9</td>
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<td>February</td>
<td>1.08 6.8</td>
<td>0.93 9.7</td>
<td>1.06 3.8</td>
<td>1.03 3.4</td>
<td>1.14 16.7</td>
</tr>
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<td>March</td>
<td>1.33 15.4</td>
<td>1.28 12.6</td>
<td>1.17 7.8</td>
<td>1.05 10.3</td>
<td>1.73 24.1</td>
</tr>
<tr>
<td>April</td>
<td>1.78 26.0</td>
<td>1.42 16.2</td>
<td>1.54 18.0</td>
<td>1.77 25.3</td>
<td>1.47 18.9</td>
</tr>
<tr>
<td>May</td>
<td>2.00 29.3</td>
<td>1.90 27.5</td>
<td>2.65 42.8</td>
<td>2.78 44.4</td>
<td>1.42 39.7</td>
</tr>
<tr>
<td>June</td>
<td>2.10 36.9</td>
<td>2.09 31.3</td>
<td>2.62 42.2</td>
<td>2.29 44.3</td>
<td>0.76 37.7</td>
</tr>
<tr>
<td>July</td>
<td>2.63 39.0</td>
<td>2.70 41.2</td>
<td>3.56 40.4</td>
<td>3.29 47.8</td>
<td>1.53 31.4</td>
</tr>
<tr>
<td>August</td>
<td>2.07 31.0</td>
<td>1.73 24.5</td>
<td>1.94 30.3</td>
<td>2.52 39.3</td>
<td>1.17 13.2</td>
</tr>
<tr>
<td>September</td>
<td>1.69 22.1</td>
<td>1.86 31.8</td>
<td>1.58 18.8</td>
<td>2.04 36.2</td>
<td>1.72 26.1</td>
</tr>
<tr>
<td>October</td>
<td>1.62 21.3</td>
<td>1.61 20.3</td>
<td>1.61 20.0</td>
<td>1.60 20.2</td>
<td>1.65 22.6</td>
</tr>
<tr>
<td>November</td>
<td>1.45 15.0</td>
<td>1.26 17.0</td>
<td>1.27 10.3</td>
<td>1.44 19.3</td>
<td>1.36 24.0</td>
</tr>
<tr>
<td>December</td>
<td>1.31 11.1</td>
<td>1.23 8.7</td>
<td>1.14 6.1</td>
<td>1.00 6.7</td>
<td>3.89 41.6</td>
</tr>
<tr>
<td>Yearly average</td>
<td>1.57 20.9</td>
<td>1.49 19.4</td>
<td>1.56 19.6</td>
<td>1.81 28.7</td>
<td>1.23 13.1</td>
</tr>
</tbody>
</table>
\%WNA values dedicated from Rogge et al. (1993) gave very similar values for "green" and "dead leaves". The "emission" factor of 0.0236 carries uncertainty as it might be derived from a limited number of plant species. Its advantage is, however, that it covers emissions from "green" as well as "dead leaves" and included abrasive material from leaves, conifers, grasses, etc.

Thus, we conclude that cellulose is a substance representative for the "total" plant material while waxes originate from the plant surfaces.

The mechanism to form atmospheric cellulose is rather grinding and degradation, for \(n\)-alkanes, it seems to be the material rubbing off the surface of the leaves.

Since the mechanisms of forming atmospheric cellulose and atmospheric plant wax particles are different, it is not expected that the results will agree perfectly. However, considering two different underlying processes, the agreement observed is in the same range and still remarkable.

4. Conclusions

- The annual mean concentrations of total \(n\)-alkanes were higher at the inner city sampling sites than at urban-fringe sampling sites; the urban impact adds in average 30\% to \(n\)-alkanes levels at traffic exposed city sites.
- \(n\)-Alkanes represent up to 0.34\% of PM10 and 1.05\% of OM.
- There is a strong correlation \((r^2 > 0.63)\) between total \(n\)-alkane concentrations and mass concentrations of PM10 at the city sites.
- Individual \(n\)-alkanes exhibit a strong seasonal variation; relative composition of total \(n\)-alkanes...
is similar at sampling sites and varied more with time than with location; the predominant \( n \)-alkanes are C\(_{27} \), C\(_{29} \), and C\(_{31} \).

- CPI\(_{\text{odd}} \) and %WNA (plant wax) values showed predominant contributions of anthropogenic sources during the cold season, and of biogenic sources during the warm season; the influence of biogenic sources is higher at sampling sites with urban-fringe characteristics.

- Urban impact CPI\(_{\text{odd}} \) of 1.23 and urban impact %WNA of 13.1% calculated from yearly mean concentrations of \( n \)-alkanes C\(_{24} \)–C\(_{23} \) indicate that emissions in the area of Vienna city have mainly anthropogenic character.

- The comparison of two approaches to determine the contribution of the “plant debris” source to ambient PM10 indicates two different mechanisms to form atmospheric “plant debris”. The observed relative contributions of plant debris to PM10 are in the same range. The seasonality with higher values during the vegetative period is more pronounced for the data derived from the \( n \)-alkanes. However, considering the different underlying concepts, the agreement of the derived plant debris contributions to PM10 is remarkable.

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### References


