



# Source apportionment of particulate organic compounds in a rural area of Spain by positive matrix factorization

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## ABSTRACT

This study was conducted in order to identify possible sources and to estimate their contribution to particulate matter in a rural area. For this purpose, a commonly used receptor model, positive matrix factorization (PMF), was applied to a PM<sub>2.5</sub> data set collected in a rural area of Madrid (Spain) between May 2004 and April 2005. A total of eighty nine samples were gathered. Chemical composition of particulate matter including major components, trace elements, total carbon, alkanes, PAHs, alcohols and acids were analyzed to study sources of atmospheric aerosols using the positive matrix factorization model. This work is characterized by including some organic tracers within PMF analysis, through which we can get a more accurate source apportionment. To our knowledge, this is the first work employing organic tracers for source apportionment by PMF model in a rural area of Spain. To assign PMF factor with a possible source, authors have based on the presence of tracer species. PMF apportioned the PM<sub>2.5</sub> mass into nine factors. The factors included (1) even n-alcohols/acids factor, (2) n-alkanes factor, (3) secondary nitrate factor, (4) secondary sulfate factor, (5) secondary organic aerosol, (6) palmitic/stearic factor, (7) PAHs factor, (8) crustal factor and (9) low molecular weight alcohols/acids factor. Six of these factors are related to primary emissions and three of them are categorized as secondary aerosol. PMF identified two mixed sources, factor 6 identified as cooking /microbial source and factor 9 identified as a mixed source.

### Keywords:

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## 1. Introduction

Organic fraction is a major component of atmospheric particulate matter, being more significant in rural areas (Alves et al., 2001; Bi et al., 2005; Sharma and Maloo, 2005). As a result, during last years the number of works related to organic fraction has been increased significantly. This increase was due to the growing concern about atmospheric aerosol because their hazardous effects on human health (WHO, 2003; Perez et al., 2008; Woelz et al., 2010) and as far as its role in global climate change (IPCC, 2007; Haywood et al., 2008; Xu et al., 2010).

Organic fraction of atmospheric aerosol includes thousands of compounds, showing some of them a higher interest from the research community. In fact, alkanes and PAHs have been widely studied and there are numerous worldwide works about them (Lao et al., 1973; Lee et al., 1976; Simoneit and Mazurek, 1982; Mendez et al., 1993). Over the years, studies become more widespread, characterizing a larger number of compounds (Gogou et al., 1998; Pio et al., 2001a; Guo et al., 2004). Currently, some authors have characterized more than 300 organic compounds associated to particulate matter (Oliveira et al., 2007).

In order to reduce harmful effects of particulate matter, and therefore to increase air quality, two premises are needed: The composition of the particulate matter must be fully disclosed and emissions of particulate matter must be controlled in their origin. Thereby we can identify the most hazardous compounds to human health, identifying their origin and reducing emissions where possible. During the last years, the organic fraction of aerosols has been widely analyzed and as a result, a greater number of species

has been identified (Kourtchev et al., 2008; Agarwal et al., 2010; Alves et al., 2010; Ladji et al., 2010). On the other hand, many sources of organic aerosols have also been identified. Among them, anthropogenic sources include fossil fuel combustion, coal and wood burning, meat cooking, cigarette smoke, agriculture debris and resuspension of soil particles, while emission of plants wax, fungi, bacteria, pollen, algae and natural combustion processes as wildfires and volcano eruptions are the main natural sources (Bi et al., 2002; Brown et al., 2002; Cincinelli et al., 2003; Bi et al., 2005; Dutton et al., 2010; Harrison and Yin, 2010; Pey et al., 2010).

Many studies have been conducted using statistical methods, such as factor analysis (FA), principal component analysis (PCA), chemical mass balance (CMB) and lately, positive matrix factorization (PMF) with the only aim of identifying sources of particulate matter. However, few studies have performed a source apportionment methodology incorporating organic molecular marker data due to the time and effort required to collect a long enough time series of detailed measurements and uncertainties associated.

One of the most important advantages of PMF is the inclusion of uncertainties in the model that allows us to apply different weights to different variables, taking into consideration the lack of precision of the analytical methods; thus it selects only rotated solutions with positive contributions from the sources. Other advantage is that PMF can identify particulate matter sources and provide the contribution of each source in absence of prior information on sources. Also PMF identifies and quantifies sources relatively faster than other models such as CMB and PCA.

In light of the above, this study has two different aims: firstly to characterize the particulate fraction of atmospheric aerosol in a rural area and secondly to identify sources of PM according to chemical characterization. PMF model was chosen because this is the first study accomplished in this area and therefore there is no prior information about sources. Thus, chemical composition of 89 samples of PM<sub>2.5</sub> collected over 1 year has been used in order to estimate the fine aerosol sources and their contributions. Also, meteorological parameters and gaseous species were included to assist interpretation of the source factors.

## 2. Experimental

### 2.1. Samples collection and analysis

Sampling took place in Chapinería (altitude: 675 meters over sea level; latitude: 40° 22' 45" North; longitude: 4° 12' 15" West). Chapinería is a little town located 50 km from Madrid and has less than 2 000 inhabitants (Figure 1). Sampling area is surrounded by *Quercus ilex* forest and there are not significant industrial activities around it. For these reasons, this site is considered as a rural area. This region, as same as all Iberian Peninsula, is influenced by long-range transport processes of desert dust from North Africa.

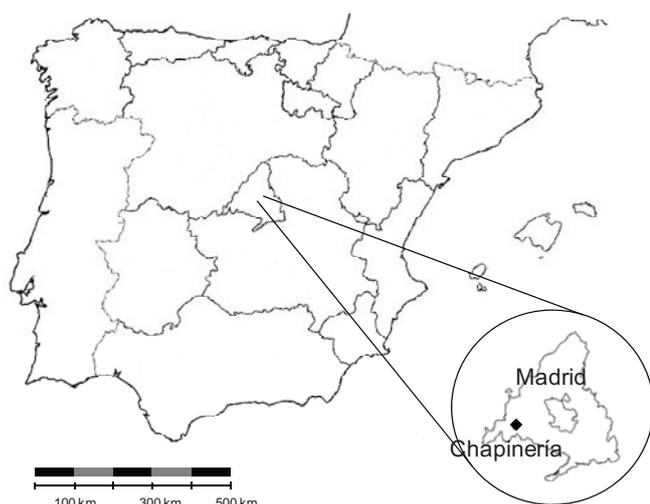


Figure 1. Map of the sampling site.

Particulate matter was collected using a high volume sampler with quartz filters, previously baked out. Measurements were taken between May 2004 and April 2005. Two samples were consecutively collected each seven days. Sampling duration was 24 h. Eighty nine samples were collected. Field blank filters were also collected to subtract concentrations due to adsorption of gas-phase organic components onto the quartz filter during and after sampling. Concentrations measured in blanks were negligible except for stearic acid and palmitic acid.

For each sample, PM<sub>2.5</sub> mass concentration and chemical composition were obtained. The analysis was separately performed for organic and inorganic fractions. For this purpose, filters were cut into two subsamples. The analytical procedures followed for the analysis of these species has been already published (Pindado et al., 2009). Briefly, ionic components, such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were leached with water and analyzed by ion chromatography (IC). On the other hand, an acid digestion with HNO<sub>3</sub> and HCl was performed and 24 trace elements were analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) and Atomic Absorption. Total carbon was determined by combustion elemental analysis. In order to analyze organic composition, filters were Soxhlet extracted with CH<sub>2</sub>Cl<sub>2</sub>/Acetone 3:1 mixture, extracts were purified via sequential elution through a glass column packed with 1.5 g of silica gel using

solvents of increasing polarity. Four fractions were eluted to provide a separate chromatographic analyses; alkanes, alcohols and acids were subject to gas chromatographic–mass spectrometric (GC–MS) analysis, performing a derivatization with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) for polar compounds, meanwhile PAHs were submitted to high performance liquid chromatography (HPLC) with fluorescence detector. Also, two gaseous species, NO<sub>x</sub> and ozone, were continuously measured by Chemiluminescence and UV absorption respectively, and included into PMF analysis.

Uncertainties associated with organic compounds were calculated individually. Briefly, five sources of uncertainties were identified: sampling, extraction, clean-up, derivatization and analysis, being extraction stage the highest contributor to uncertainty, mainly for polar species. As a result, combined uncertainty ranged from 10 to 18% for alkanes, 12 – 16% for PAHs, 10 – 18% for alcohols and 9 – 21% for acids (Pindado et al., 2010). Uncertainties of inorganic compounds were calculated identifying three main sources: sampling, extraction and analysis. For these variables, uncertainties ranged from 5 to 10%.

### 2.2. PMF description

The PMF model was developed by Paatero at the University of Helsinki in Finland in the mid 1990s (Paatero, 1997; Paatero, 1999). PMF assumes that concentrations at receptor sites are impacted by linear combinations of source emissions, which are derived as factors in the model. Thus, model supposes there are  $p$  sources impacting a receptor, and linear combinations of the impacts from the  $p$  sources give rise to the observed concentrations of the various species. Mathematically can be written as:

$$X_{ij} = \sum_{k=1}^p G_{ik}F_{kj} + E_{ij} \quad (1)$$

where  $X_{ij}$  is the ( $i \times j$ ) matrix of ambient concentrations of  $j$  species on the  $i$  days,  $G_{ik}$  is the ( $i \times k$ ) matrix of sources contributions of  $k$  factors on  $i$  days,  $F_{kj}$  is the ( $k \times j$ ) matrix of source profiles of  $k$  factors that is species  $j$ , and  $E_{ij}$  is the ( $i \times j$ ) matrix of residuals not fitted by the model. The task of PMF model is to minimize the  $Q$  function using constrained, weighted least-squares. This function is defined as:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{X_{ij} - \sum_{k=1}^p G_{ik}F_{kj}}{S_{ij}} \right)^2 \quad (2)$$

where  $S_{ij}$  is an uncertainty estimate in the  $j$  species measured on the  $i$  days.

To perform the PMF model, a qualitative knowledge of the sources is only required, however PMF model also has limitations such as inability to clearly separate covariant sources. It is remarkable that PMF factors only reveal species temporally covary and thus the model will group them. However, temporal variability of a pollutant concentration is not solely determined by changes in emissions, as PMF model assumes, so we should not link the factors to source profiles directly, although many studies refer the PMF factors as sources.

PMF requires two input files, one file with the concentrations and one with the uncertainties associated with those concentrations. The selection of modelling parameters and number of factors is not straightforward and is still largely affected by the experience of authors (Paatero and Hopke, 2003).

EPA PMF1.1 was downloaded from the US EPA website (<http://www.epa.gov/heads/products/pmf/pmf.html>) and used for the current analysis. This first version of the model determines signal-to-noise ratio (s/n) statistics for every input species.

Moreover, the model generates regression diagnostics, including the intercept, slope, root mean squared error and *r*-square. This information will help to optimize the solution. A good fit will provide intercept values near 0, slope values near 1 and *r*-squares greater than 0.6.

### 3. Results and discussions

#### 3.1. Characterization of particle fraction of atmospheric aerosol

More than 90 organic compounds, including alkanes, PAHs, alcohols and acids, were separately determined. In addition, the inorganic fraction (main ionic components and metals) was quantified (Pindado et al., 2009). The  $\Sigma n$ -alkane and  $\Sigma$ PAHs ranged from 3 to 81 ng/m<sup>3</sup> and 0.1 to 6 ng/m<sup>3</sup> respectively, being the higher concentrations during colder months. Diagnostic parameters suggested that alkanes were predominantly from anthropogenic origin. However, there are evidences that some alkanes were originated from wax plants. Ambient concentrations of  $\Sigma n$ -alcohols and  $\Sigma n$ -acids ranged from 21 to 184 ng/m<sup>3</sup> and 39 to 733 ng/m<sup>3</sup>, respectively. The highest values for alcohols were reached during summer, while acids showed highest values during winter. In both cases, CPI values are higher in summer and lower in winter, showing that plant waxes emissions are the main source of alcohols and fatty acids. Also, several components of secondary organic aerosol have been quantified; thus, identification of  $\alpha$ -pinene degradation products confirms the biogenic contribution to aerosol. Generally, concentrations of organic compounds were above to other rural areas, confirming the anthropogenic contribution to the rural area of Chapineria (Oliveira et al., 2007).

#### 3.2. PMF results

In order to simplify the model, some compounds were not included in the PMF analysis. Those species of each family that do not provide essential information related to its sources and also showed low concentrations, for instance alkanes higher than C<sub>33</sub>, and alcohols and acids with odd number of carbons have been omitted. On the other hand, some compounds were grouped according to the categorization previously made by Shrivastava et al. (2007). For instance pinonic acid, pinic acid and norpinonic acid were grouped because of their recognized biogenic secondary origin. Oleic, linoleic and palmitoleic acids have mainly a primary source, and azelaic acid is a degradation product of unsaturated acids (Vesna et al., 2009). For this reason, azelaic, oleic, linoleic and palmitoleic acids were grouped. Thus, finally we chose 66 species for PMF analysis. Table 1 summarizes average concentrations of chemical components of fine particles from a year-long study included in the model.

The most critical step in PMF analysis is the determination of the number of factors. One indicator is the goodness of fit of the model, Q value that is approximately equal to the number of data points. In this study the final selection was based on the evaluation of the source profiles obtained as well as the quality of the fit for the chemical species. Thus Q value was used to select the number of factors and assisted for solution interpretation.

Missing values, which were 6% in this study, were established as the geometric mean of all the concentrations measured for each species and uncertainty was set 4 times the geometric mean (Polissar et al., 1998). Among the 66 species chosen, 14 were removed from the computation because they were frequently present at concentrations below the detection limit and 6 species were considered "weak". Hence, fifty-two variables have been chosen to develop PMF, including alkanes, PAHs, alcohols, saturated acids, unsaturated acids,  $\alpha$ -pinene degradation products, metals, main inorganic ions, gaseous species and total carbon. Finally, a 9-factor solution was proved to be the best choice, in terms of both quality of the fit and physical sense for the

studied system. The statistics of each of the 52 variables are listed in Table 2.

The distribution factors for all studied compounds by the PMF model are presented in Figure 2. Figure 3 shows the time series of contributions associated with the factor, where the contribution average to 1. In order to identify source types, the resolved sources profiles from PMF analysis were compared with known profiles obtained from previous works (Rogge et al., 1998; Schauer et al., 2001; Hays et al., 2002; Zheng et al., 2002; Landis et al., 2007; Shrivastava et al., 2007) and the identification of sources was based on the presence of key species.

**Interpretation of factor profiles.** The first factor is characterized by alcohols C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub>, C<sub>30</sub> and acids C<sub>24</sub>, C<sub>26</sub> and C<sub>28</sub>. These key species have been associated with primary biogenic emissions such as plant waxes by several authors (Simoneit, 1989; Huang et al., 2006; Oliveira et al., 2007). This factor explains 60% of the >C<sub>20</sub> alcohols and 90% of the >C<sub>20</sub> fatty acids. It is well known that odd alkanes are associated with biogenic emissions; mainly related to plant waxes (Pio et al., 2001a). Thus the slight contribution of odd alkanes suggests wax plant emissions. Time series of contributions show a clear seasonal behaviour with higher autumn and winter values, due to leaves fall. Furthermore, this factor showed similar pattern for weekdays and weekends, being consistent with biogenic emissions.

Second factor grouped 50%–90% of aliphatic hydrocarbons between n-C<sub>24</sub> and n-C<sub>33</sub>. Alkanes have been associated to any combustion processes (Bi et al., 2002; Bi et al., 2003; Lin and Lee, 2004; Feng et al., 2005). The slight presence of odd n-alkanes is also consistent with primary biogenic emissions as wax plants. The rest of variables comprise less than 10%, uniquely is remarkable 20% of NO<sub>x</sub> involved in this factor. NO<sub>x</sub> is related with combustion processes. These results may suggest it should come from mixed sources. However a slight weekly pattern, with higher values in weekdays implied an anthropogenic origin. Also, the time series show higher contributions during winter. This may reveal a residential burning contribution (Karanasiou et al., 2009). Thus results lead us to associate this factor with a combustion process rather than a mixed source.

Factor 3 grouped the highest contributions of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> so it was identified as secondary nitrate. The secondary nitrate particles contain high concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. Also NO<sub>x</sub>, which is a precursor of nitrate, has a large contribution to this factor. The main sources of NO<sub>x</sub> in the atmosphere are traffic and stationary sources. The secondary nitrate do not shows a weekly variation, which might indicate a relationship with traffic emissions. Moreover, secondary nitrate showed an important content of TC, which could be attributed to the semi-volatile organic compounds condensing onto surface of ammonium nitrate particles (Amato et al., 2009). In addition, the seasonal evolution shows higher concentrations in winter, when low temperature and high relative humidity help to the formation of secondary nitrate particles (Kim and Hopke, 2008; Nicolas et al., 2008). In our study, secondary nitrate showed the highest contribution during 22/Nov and 12–13/Jan. On this period, low temperature and high humidity conditions favoured an accumulation of atmospheric pollutants.

The species contributing to fourth factor are sulfite, nitrate, Na, Cl and ozone. Sulfate ion is formed through different oxidation reactions of SO<sub>2</sub>, which is released to the atmosphere by several combustion processes. This factor has also shown a high contribution for ozone, suggesting sulphur dioxide can react with ozone to create sulphate. Typically, secondary sulphate tends to be abundant in warmer days due its formation from photochemical oxidation of SO<sub>2</sub>. Thus, the secondary sulfate shows seasonal variations with higher concentrations in summer when photochemical activity is highest. It is well known that secondary

**Table 1.** Average, standard deviation, maximum and minimum for each of the variables used in the PMF analysis

Species		Average	Standard deviation	Maximum	Minimum	BDL (%) <sup>b</sup>	Missing value (%)
Particles ( $\mu\text{g}/\text{m}^3$ )	PM <sub>2.5</sub>	16.9	11.0	64.1	3.1	0	0
	TC	4.0	2.7	16.6	0.03	0	0
Ion components ( $\mu\text{g}/\text{m}^3$ )	NO <sub>3</sub> <sup>-</sup>	1.1	2.7	17.6	0.02	0	0
	SO <sub>4</sub> <sup>2-</sup>	1.8	0.9	4.3	0.02	0	0
	Cl <sup>-</sup>	0.05	0.04	0.31	0.01	3	0
	Na <sup>+</sup>	0.1	0.0	0.3	0.02	0	0
	NH <sub>4</sub> <sup>+</sup>	0.9	0.9	6.5	0.02	0	0
Elements ( $\mu\text{g}/\text{m}^3$ )	K	0.1	0.1	0.5	0.02	2	0
	Ca	0.3	0.3	1.5	0.04	0	0
	Mg	0.0	0.0	0.1	0.02	18	0
	Al	0.1	0.2	0.8	0.02	0	0
	Fe	0.2	0.2	1.0	0.02	0	0
	Pb <sup>a</sup>	5.5	6.2	43.8	0.8	1	30
	Sr <sup>a</sup>	1.3	1.4	6.0	0.2	1	0
	Zn <sup>a</sup>	28.7	17.3	85.0	7.7	0	0
	Ba <sup>a</sup>	4.5	4.0	23.4	0.8	0	0
	Cu <sup>a</sup>	38.2	25.9	149.0	4.0	0	0
	Ni <sup>a</sup>	2.1	1.8	7.1	0.4	18	30
Gases ( $\mu\text{g}/\text{m}^3$ )	NO <sub>x</sub>	13.8	11.1	65.7	1.04	0	0
	Ozone	64.9	23.6	116.4	8.89	0	0
AHS ( $\text{ng}/\text{m}^3$ )	Alkane C <sub>23</sub>	2.0	1.5	7.9	0.1	0	0
	Alkane C <sub>24</sub>	2.0	1.5	8.3	0.2	0	0
	Alkane C <sub>25</sub>	2.1	1.5	9.1	0.1	0	0
	Alkane C <sub>26</sub>	1.7	1.3	6.1	0.0	0	0
	Alkane C <sub>27</sub>	1.8	1.4	6.5	0.1	0	0
	Alkane C <sub>28</sub>	1.3	1.1	6.8	0.1	2	0
	Alkane C <sub>29</sub>	2.0	1.8	9.2	0.1	1	0
	Alkane C <sub>30</sub>	1.0	1.2	10.6	0.0	6	0
	Alkane C <sub>31</sub>	1.6	1.7	11.0	0.1	8	0
	Alkane C <sub>32</sub>	0.6	1.0	8.7	0.0	10	0
	Alkane C <sub>33</sub>	0.9	1.1	5.3	0.0	17	0
	Fitane	1.1	0.5	2.9	0.4	14	17
	Pristane	0.8	0.5	3.4	0.1	4	17
PAHs ( $\text{pg}/\text{m}^3$ )	F	3	3	21	0.2	24	14
	Ph	74	53	366	4	2	14
	An	8	25	214	0.2	11	14
	Fl	96	67	391	10	7	14
	Py	190	209	1 054	9	3	14
	BaA	98	122	621	7	2	14
	Chr	217	211	941	18	2	14
	BbF	162	171	844	3	1	14
	BkF	59	69	344	4	6	14
	BaP	115	179	1 056	3	2	14
	DBA	19	22	102	0.4	26	14
	BghiPe	256	339	1 871	6	1	14
	Alcohols ( $\text{ng}/\text{m}^3$ )	Alcohol C <sub>14</sub>	25.4	13.2	65.1	0.3	0
Alcohol C <sub>15</sub>		4.7	5.3	19.8	0.3	50	2
Alcohol C <sub>16</sub>		9.9	9.0	43.2	0.2	18	2
Alcohol C <sub>18</sub>		7.2	5.1	19.5	0.3	9	2
Alcohol C <sub>24</sub>		3.1	5.1	27.2	0.1	36	2
Alcohol C <sub>26</sub>		4.3	7.2	46.5	0.2	41	2
Alcohol C <sub>28</sub>		3.3	3.4	18.3	0.3	51	2
Alcohol C <sub>30</sub>		1.7	1.6	6.9	0.1	73	2
Acids ( $\text{ng}/\text{m}^3$ )	Acid C <sub>12</sub>	15.6	8.9	47.6	1.4	0	4
	Acid C <sub>13</sub>	5.1	5.0	25.2	0.1	11	4
	Acid C <sub>14</sub>	18.0	9.5	59.1	2.6	0	4
	Acid C <sub>15</sub>	10.7	6.4	26.2	0.1	9	4
	Acid C <sub>16</sub>	56.5	57.0	404.4	0.1	1	4
	Acid C <sub>17</sub>	4.7	4.5	19.3	0.1	37	4
	Acid C <sub>18</sub>	25.8	27.9	203.4	0.1	13	4
	Acid C <sub>24</sub>	16.4	20.4	101.8	0.7	47	4
	Acid C <sub>26</sub>	8.1	7.4	35.0	0.6	58	4
	Acid C <sub>28</sub>	3.8	3.0	14.9	1.3	61	4
	Acid C <sub>30</sub>	2.9	2.0	8.3	1.1	73	4
	Unsaturated <sup>c</sup>	14.6	20.3	114.5	0.1	32	7
	Pinene products <sup>d</sup>	27.3	31.2	179.0	1.6	9	7

<sup>a</sup> ( $\text{ng}/\text{m}^3$ )<sup>b</sup> Below Detection Limit<sup>c</sup> Unsaturated:  $\Sigma$  palmitoleic acid, linoleic acid, oleic acid, azelaic acid<sup>d</sup> Pinene products:  $\Sigma$  pinic acid, pinonic acid, norpinonic acid

Table 2. Statistics of species used as variables in PMF

Species	Categorization	Intercept	Slope	RMSE	r <sup>2</sup>	Residuals (%)
TC	Strong	0.18	0.86	0.93	0.86	2
NO <sub>3</sub> <sup>-</sup>	Strong	0.11	0.79	0.32	0.98	0
SO <sub>4</sub> <sup>2-</sup>	Strong	0.19	0.81	0.44	0.75	1
Cl <sup>-</sup>	Strong	0.01	0.65	0.02	0.71	0
Na <sup>+</sup>	Strong	0.05	0.05	0.01	0.02	2
NH <sub>4</sub> <sup>+</sup>	Strong	0.02	0.93	0.16	0.97	0
K	Strong	0.04	0.75	0.07	0.82	2
Ca	Strong	0.04	0.76	0.07	0.88	0
Mg	Strong	0.02	0.51	0.02	0.71	1
Al	Strong	0.06	0.75	0.11	0.91	0
Fe	Strong	0.01	0.88	0.06	0.92	1
Sr	Strong	0.29	0.42	0.37	0.67	0
Ba	Strong	1.73	0.28	1.39	0.39	4
Alkane C <sub>23</sub>	Strong	0.15	0.79	0.62	0.78	1
Alkane C <sub>24</sub>	Strong	0.13	0.86	0.39	0.92	0
Alkane C <sub>25</sub>	Strong	0.23	0.82	0.43	0.90	0
Alkane C <sub>26</sub>	Strong	0.07	0.89	0.36	0.91	0
Alkane C <sub>27</sub>	Strong	0.08	0.91	0.39	0.91	0
Alkane C <sub>28</sub>	Strong	0.28	0.71	0.53	0.67	0
Alkane C <sub>29</sub>	Strong	0.36	0.72	0.73	0.76	0
Alkane C <sub>30</sub>	Weak	0.52	0.29	0.56	0.29	0
Alkane C <sub>31</sub>	Strong	0.45	0.53	0.76	0.59	0
Alkane C <sub>32</sub>	Weak	0.32	0.23	0.40	0.25	0
Alkane C <sub>33</sub>	Strong	0.15	0.48	0.36	0.65	3
BaA	Strong	0.01	0.75	0.03	0.90	1
Chr	Strong	0.01	0.89	0.06	0.91	0
BbF	Strong	0.00	0.95	0.04	0.94	0
BkF	Strong	0.00	0.99	0.01	0.95	0
BaP	Strong	0.02	0.72	0.04	0.89	1
DBA	Strong	0.00	0.70	0.01	0.76	3
BghiPe	Strong	0.02	0.84	0.08	0.92	0
Alcohol C <sub>15</sub>	Weak	3.08	0.33	2.00	0.44	0
Alcohol C <sub>16</sub>	Strong	4.03	0.38	3.51	0.49	1
Alcohol C <sub>18</sub>	Strong	2.73	0.48	2.30	0.54	0
Alcohol C <sub>24</sub>	Strong	0.20	0.54	0.92	0.87	0
Alcohol C <sub>26</sub>	Strong	0.10	0.51	1.03	0.75	0
Alcohol C <sub>28</sub>	Strong	0.13	0.56	1.09	0.68	1
Alcohol C <sub>30</sub>	Strong	0.21	0.32	0.17	0.79	0
Acid C <sub>12</sub>	Weak	6.77	0.41	5.20	0.34	0
Acid C <sub>14</sub>	Weak	8.58	0.40	5.65	0.31	0
Acid C <sub>15</sub>	Strong	1.87	0.77	3.05	0.72	0
Acid C <sub>16</sub>	Strong	4.54	0.80	14.11	0.75	2
Acid C <sub>17</sub>	Weak	3.01	0.36	1.76	0.46	0
Acid C <sub>18</sub>	Strong	5.05	0.65	8.56	0.72	1
Acid C <sub>24</sub>	Strong	-0.63	0.81	5.79	0.84	10
Acid C <sub>26</sub>	Strong	-0.37	0.95	2.61	0.82	7
Acid C <sub>28</sub>	Strong	-0.9	1.10	0.81	0.92	3
Acid C <sub>30</sub>	Strong	0.16	0.05	0.07	0.57	16
Unsaturated	Strong	5.83	0.28	6.60	0.28	2
Pinene products	Strong	7.50	0.41	9.70	0.51	0
NO <sub>x</sub>	Strong	-0.08	0.83	5.49	0.74	6
Ozone	Strong	9.80	0.77	16.07	0.53	3
No. of Factors: 9	Q (robust) = Q (true) = 4 666.61					

sulfate is a tracer of long-range transport, so presence of NaCl, which is related to marine aerosol, confirms there is a regional transport (Chan et al., 2006). For these reasons, secondary sulphate particles may have been formed elsewhere and then transported to the sampling area. The age of the aerosol has been evaluated through the parameter C<sub>18</sub>/C<sub>18:1</sub> by several authors (Guo et al., 2003; He et al., 2006; Oliveira et al., 2007). Elevated values of this parameter indicate that the aerosol has been emitted in other areas and was subject to transport processes. Average value calculated at Chapineria was 11.9, confirming a transport phenomenon.

The fifth factor explains 80% of  $\alpha$ -pinene products degradation and unsaturated acids. The three measured species categorized as  $\alpha$ -pinene products degradation were *cis*-pinonic acid,

*trans*-norpinonic acid and pinic acid. These compounds are components of secondary organic aerosol and were measured in smog chambers from the oxidation of monoterpenes (Fick et al., 2004). Unsaturated acids involve oleic, linoleic, palmitoleic and azelaic acid. Most of the species associated with this factor are related to organic secondary components, although some of them (palmitoleic, linoleic and oleic acids) have other primary sources such as meat cooking; therefore we may conclude that this factor represents the secondary aerosol but there are also mixed sources due to the grouping of the species. This factor showed a slight seasonal pattern, exhibiting higher contribution during summer. This fact is in agreement with the known trend of secondary organic aerosol (SOA) to be mainly formed during warm days, when there are higher temperatures that encourage atmospheric reactions.

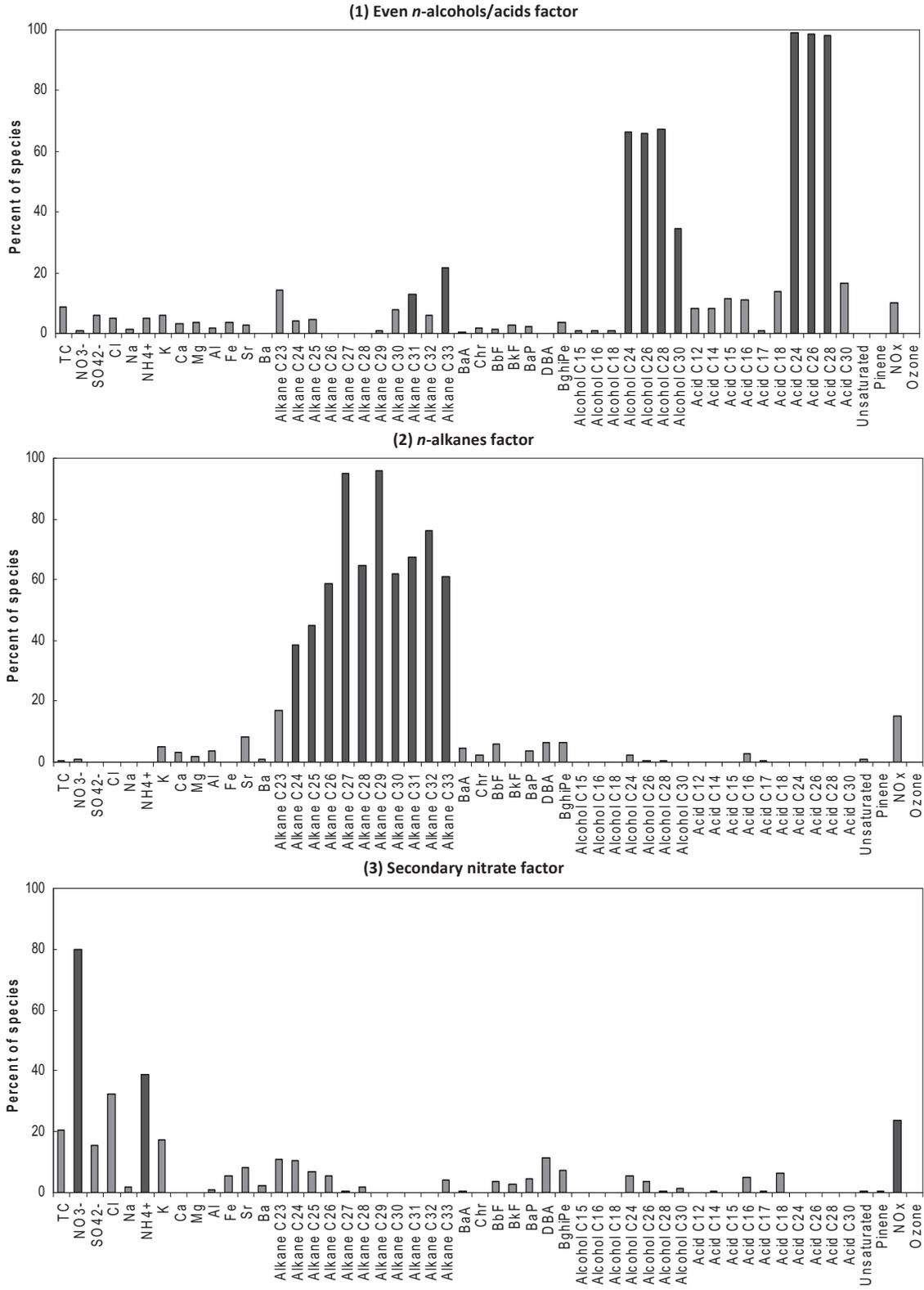


Figure 2. Source profiles resolved from PM<sub>2.5</sub> samples analysed by PMF.

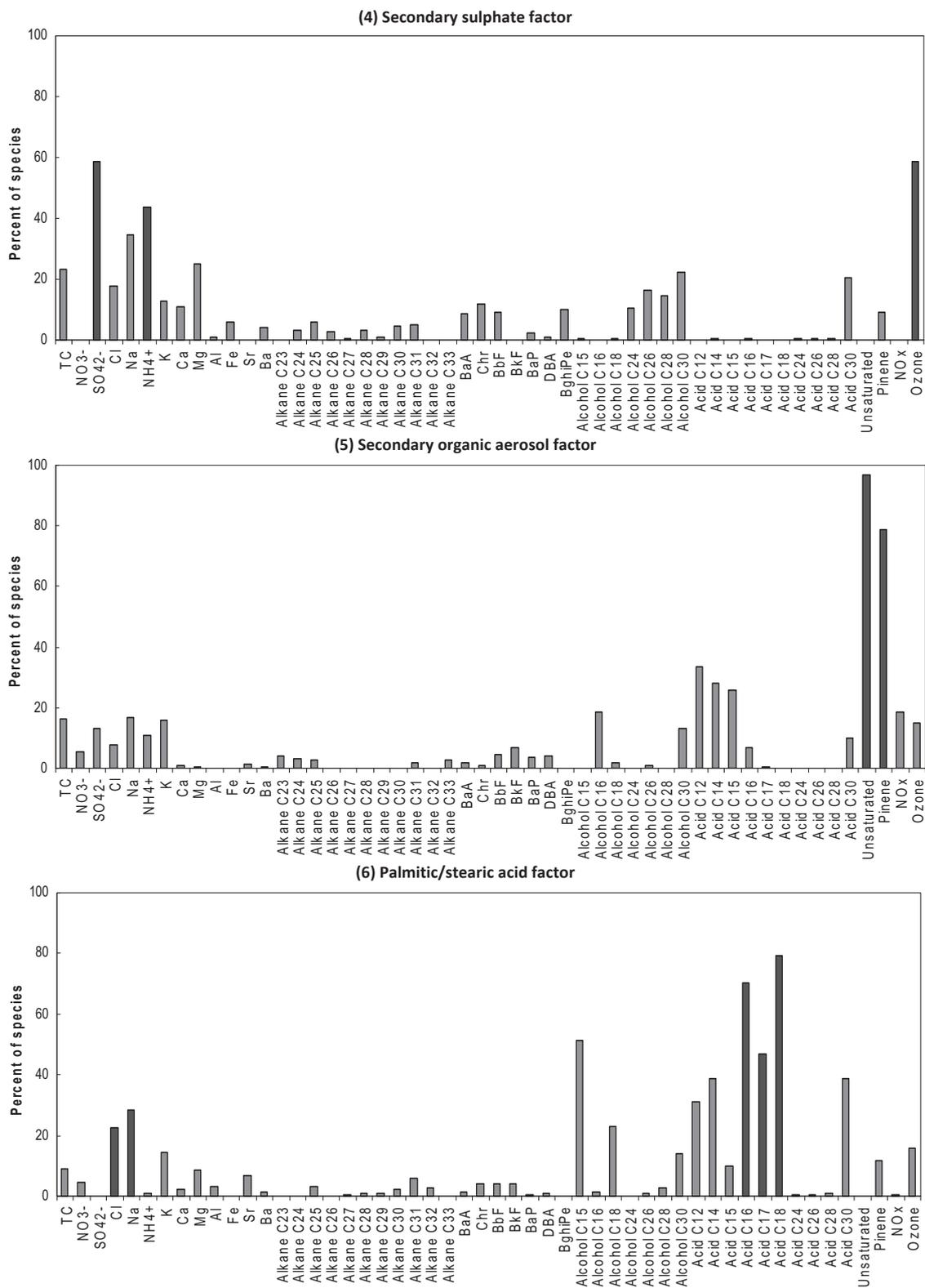


Figure 2. Source profiles resolved from PM<sub>2.5</sub> samples analysed by PMF (Continued).

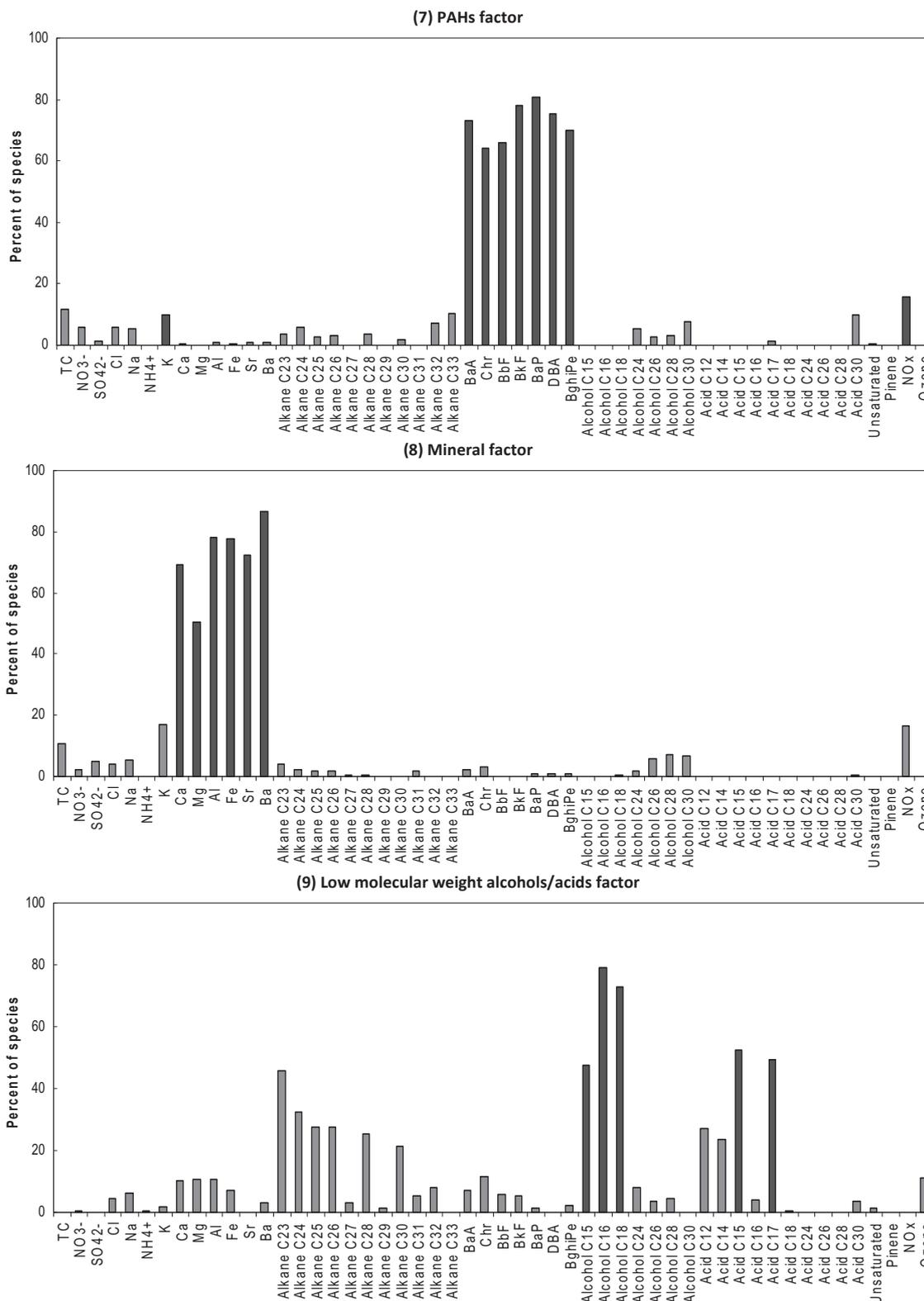


Figure 2. Source profiles resolved from PM<sub>2.5</sub> samples analysed by PMF (Continued).

The sixth factor was dominated by palmitic and stearic acids. Both compounds are elevated in source profiles such as seed oil, meat cooking (Dutton et al., 2010) and other primary sources as traffic emissions or microbial sources. Also, high contributions of acids and alcohols with less than 20 atoms of carbon are related to microbial sources (Simoneit and Mazurek, 1982; Yue and Fraser, 2004). The occurrence of NaCl in this factor might also confirm cooking emissions. This factor does not show a clear seasonality, which points to cooking emissions rather than traffic emissions. However, since important tracers to apportion cooking emissions

were not analyzed, it is very difficult to link this factor to cooking emission so authors have decided to assign this as a mixed factor: cooking and microbial sources.

Factor 7 describes 60%–80% of most PAHs included in the model. A contribution of 15% of NO<sub>x</sub> and K is also explained in this factor. PAHs are associated with incomplete combustion of fossil fuels meanwhile NO<sub>x</sub> and K are also related with combustion processes (Jeong et al., 2008). In accordance to these results, factor 7 is related to combustion processes, like the factor 2.

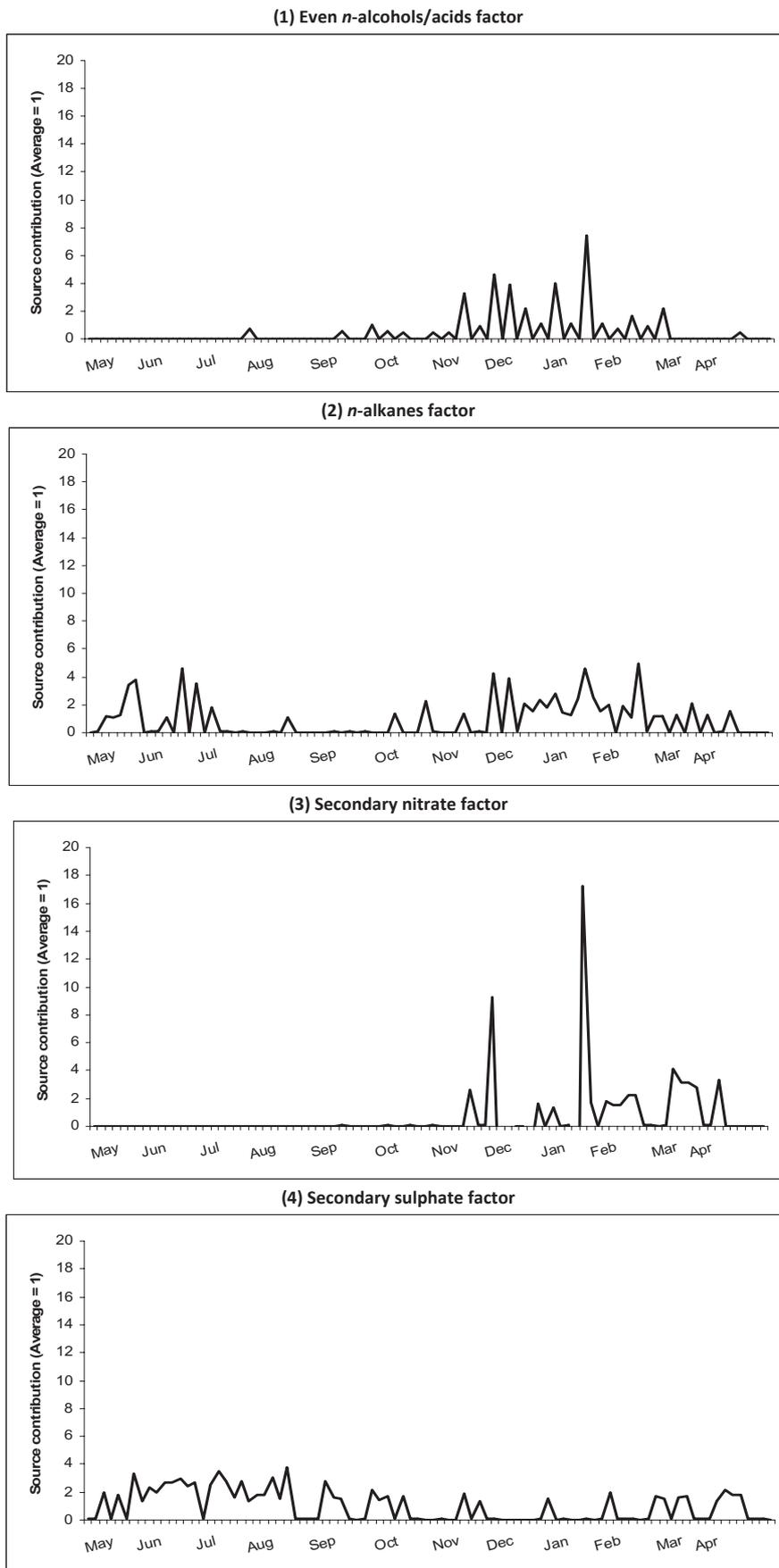


Figure 3. Source contributions (sampling period) associated with each factor, where the contribution average is 1.

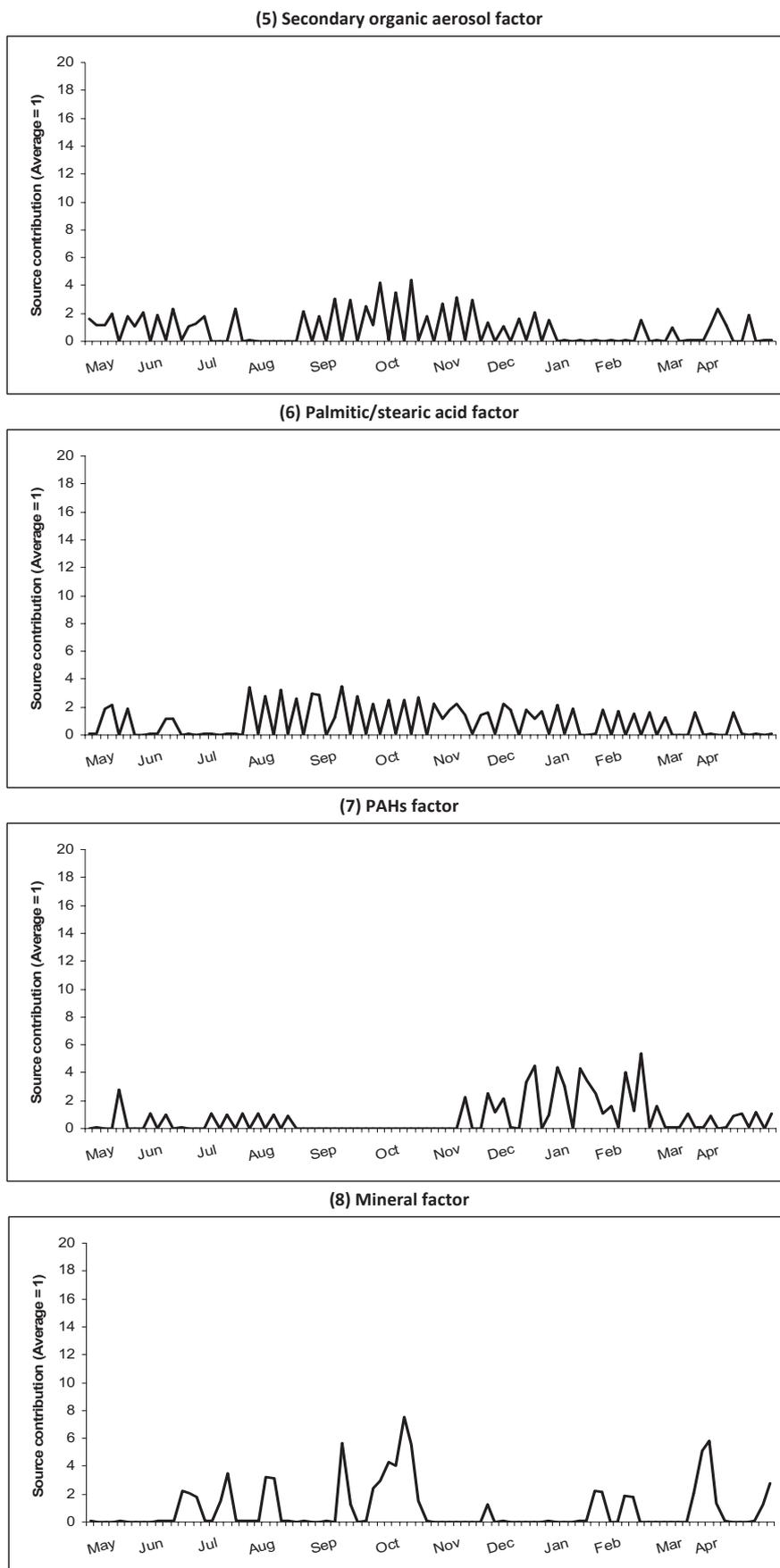
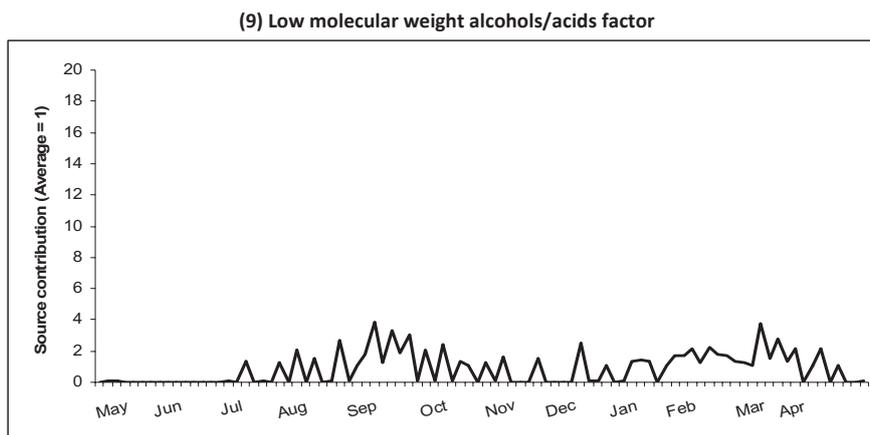


Figure 3. Source contributions (sampling period) associated with each factor, where the contribution average is 1 (Continued).



**Figure 3.** Source contributions (sampling period) associated with each factor, where the contribution average is 1 (Continued).

However, the model has separated both factors, because the factor 7 had a strong weekly variability, with higher values during the weekdays, a trend not clearly shown in factor 2. This weekly variability suggests anthropogenic origin and can be attributed to traffic emissions. The ratio of BaA/(BaA+Chry) was 0.31, which is very close to those reported in previous studies: 0.27 in diesel vehicles (Moon et al., 2008) and 0.40 in gasoline vehicle (Kavouras et al., 1999). This factor cannot differentiate between exhausts from diesel or gasoline engines.

The eighth factor grouped Ca, Mg, Al, Fe, Sr and Ba. The percentage apportioned for these species to this factor ranged from 50% to 80%. All species associated with this factor are related to crustal material. This factor showed a contribution six times higher than mean value in three periods; September 2004, October 2004 and March 2005. During these days, three long-range transport processes of desert dust from Sahara were registered (Gomez-Comino and Artinano, 2006; Salvador et al., 2008). Those dust episodes transported from Sahara Desert have been extensively analysed (Nicolas et al., 2008; Amato et al., 2009; Viana et al., 2010) In light of the above, factor 8 has been allocated as dust soil.

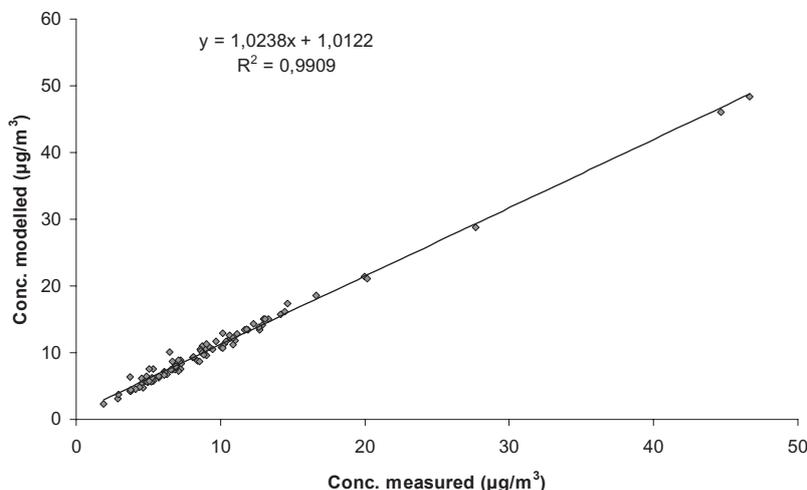
Factor 9 explains 50 – 70% of the alcohols and acids with less than 20 atoms of carbon. According to previous works, these alcohols are associated with microbiological emissions (Zheng et al., 2000; Alves et al., 2001; Pio et al., 2001b); meanwhile acids with less than 20 atoms of carbon are linked with microbiological emissions as well as anthropogenic emissions (Rogge et al., 1993; Pio et al., 2001a; Schauer et al., 2001; Azevedo et al., 2002; Hays et al., 2002; Radzi Bin Abas et al., 2004; Hays et al., 2005; Oliveira et

al., 2007). Thus factors 6 and 9 are closely related because both showed markers of cooking and microbial origin. However, PMF model have separated them due to the high contribution of even alkanes to factor 9. Even alkanes are characteristic from anthropogenic sources such as traffic and biomass burning (Bi et al., 2002; Bi et al., 2003; Lin and Lee, 2004; Feng et al., 2005). Since factor 2 grouped alkanes emitted from biomass burning, alkanes associated to factor 9 may be related to traffic emissions. In light of these, it is very likely that factor 9 represents a mixed source.

**Model performance.** The ability of the PMF model to reproduce the measured PM<sub>2.5</sub> concentration was evaluated by comparison between measured and predicted concentrations. Figure 4 shows the sum of concentration measured for all species included in the model (abscissa) versus the sum of concentrations calculated for all species by the model (ordinate). The correlation coefficient was 0.99, indicating that the 9 factor solution account for the variation in mass concentration of species. The slope of the correlation curve was 1.02, which implies the PMF model slightly overestimates concentrations.

#### 4. Conclusions

The chemical characterization of several organic and inorganic compounds associated to PM<sub>2.5</sub> fraction of aerosol present in the rural site has been performed along one year. The families of organic compounds consistently quantified were alkanes, PAHs, alcohols and carboxylic acids, meanwhile inorganic compounds quantified encompass ionic components and 24 trace elements. Moreover, TC was determined and gravimetric analysis for PM<sub>2.5</sub>



**Figure 4.** Correlation plot between measured and predicted concentrations by PMF model.

fraction was presented. Some of these data were analyzed by the PMF model to estimate and evaluate the contributions of possible emissions sources. Five major ions, 11 species of trace elements, TC and several organic compounds, including alkanes, PAHs, alcohols and acids were included. One of the achievements of this work is the inclusion of organic and inorganic components because it gives a better model fit. Association of PMF factors with source profiles was based on the presence of key species. As a result, nine factors were identified including even *n*-alcohols/acids, *n*-alkanes, secondary nitrate, secondary sulfate, secondary organic aerosol, palmitic/stearic acids, PAHs, mineral and low molecular weight alcohols/acids. Six of these factors are related to primary emissions and three of them are categorized as secondary aerosols. PMF identified two mixed sources, factor 6 identified as cooking/microbial and factor 9 identified as a mixed source. In light of these results, although the sampling area was considered a rural area, a clear influence of anthropogenic emissions was found, which points out clearly Chapinería as a semi rural area.

This work exhibited the usefulness of PMF to identify and interpret emission sources, although some evidence of uncertainties remains and further research is needed to ensure that sources identified are robust enough.

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