RESPONSE TO COMMENTS

Ms. No.: acp-2015-282

Title: Chemical characterization of fine organic aerosol for source apportionment at
Monterrey, Mexico
Submitted to: Atmospheric Chemistry and Physics

Anonymous Referee #2
Received and published: 28 July 2015

The subject manuscript presents new data about the chemical composition of organic
aerosol in the third largest city in Mexico. Organic tracers, measured by GCMS, are
used to identify source types and to drive chemical-mass-balance (CMB) source
apportionment modeling. The approach has been used previously in Mexico City and by
the authors in a range of locations. To a large extent, the limitations of the resulting
data are noted. A major shortcoming is a lack of discussion of the source apportionment
results in the text. A stronger presence in the text and through tables and figures
is warranted. A number of improvements are needed prior to publication.

C: We really appreciate the time spent for reviewing this manuscript. We attended every
comment and correction the best way. Thank you.

Specific comments:

1) Given the emphasis on source apportionment in the title, introduction, methods, and model
performance metrics; it was strongly anticipated that source apportionment would have a
strong presence in Section 3. In the current version, the only presence of these results is a
single sentence pertains to organic carbon apportioned to primary is as a multi-year and
season average in Fig. 6 and one sentence reference to this figure. Relative and absolute
abundances are neither presented, nor discussed and compared. A paragraph or two of text
needs to be added to discuss these results more rigorously in section 3.6. In addition, a Table
should be added that summarizes source contributions in different years, seasons, and day v.
night (if warranted). Comparison to other source apportionment studies in the region in terms of the gas/diesel split, fraction of BB, vegetative detritus, etc. is warranted.

R: This is a very important observation that we widely appreciate. We attend these comments in the following way:

Firstly, we summarized the whole results obtained for the 32 samples run in the CMB in the Table 5. In addition, this Table was added in the manuscript and discussed in section 3.6.

Table 5. Contributions and uncertainty of primary sources to seasonal average ambient PM$_{2.5}$ for daytime and nighttime in the MMA (in µg m$^{-3}$)

<table>
<thead>
<tr>
<th>Source category</th>
<th>Spring 2011</th>
<th>Fall 2011</th>
<th>Spring 2012</th>
<th>Fall 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Daytime</td>
<td>Nighttime</td>
<td>Daytime</td>
<td>Nighttime</td>
</tr>
<tr>
<td>Gasoline-powered vehicles</td>
<td>2.37 ± 0.56</td>
<td>2.46 ± 0.46</td>
<td>2.40 ± 0.57</td>
<td>2.46 ± 0.46</td>
</tr>
<tr>
<td>Diesel-powered vehicles</td>
<td>7.34 ± 0.86</td>
<td>3.81 ± 0.53</td>
<td>13.67 ± 1.59</td>
<td>13.10 ± 1.55</td>
</tr>
<tr>
<td>Vegetative detritus</td>
<td>0.22 ± 0.04</td>
<td>0.22 ± 0.04</td>
<td>0.13 ± 0.03</td>
<td>0.27 ± 0.05</td>
</tr>
<tr>
<td>Meat-cooking operations</td>
<td>8.24 ± 1.54</td>
<td>11.13 ± 1.85</td>
<td>3.26 ± 0.71</td>
<td>3.86 ± 0.71</td>
</tr>
<tr>
<td>Natural gas combustion</td>
<td>0.01 ± 0.01</td>
<td>N.I.</td>
<td>0.05 ± 0.03</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.20 ± 0.05</td>
<td>0.17 ± 0.05</td>
<td>0.17 ± 0.05</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>Fuel oil combustion</td>
<td>N.I.</td>
<td>N.I.</td>
<td>4.18 ± 3.55</td>
<td>3.60 ± 1.20</td>
</tr>
</tbody>
</table>

N. I. means Not Important. * samples were discarded due to poor CMB performance.

Secondly, we added the following discussion for Table 5.

Page 17989, Line 7, “The average contributions of primary sources are shown in Table 5. The vehicle exhaust and meat-cooking operations emissions for all monitoring campaigns were the highest. In analysis of the seasonal variation, the gasoline- and diesel-powered vehicles in falls were up to five times higher than in springs, when cold weather increases the demand of petroleum products due to low temperatures. The opposite occurred for meat-cooking operations, their spring emissions were three times higher than in fall seasons. The natural gas combustion, vegetative detritus and biomass burning emissions were very low and more
constant throughout the springs and falls. In analysis of the daytime and nighttime variations, the vehicle exhaust were much higher during daytime when traffic is heavier. For the meat-cooking operations, the emissions were some higher in nighttime during spring and more constant between daytime and nighttime during fall. For the rest of the sources, the daytime and nighttime emissions were relatively constant. There are not similar studies conducted in the MMA, this is the first source apportionment study based on molecular organic markers for this region. However, these results were similar to those obtained for the MMA using a factor analysis based on trace elements (Martinez et al., 2012) and those for the Mexico City based on molecular organic markers (Stone et al., 2008).”

Finally, we added a detailed Table with the CMB performance parameters for each sample in the Supplemental material. In addition, we added the following text in the manuscript.

Page 17989, Line 6, “A detailed description of the CMB performance and relative contributions for each sample can be found in Table S2.”

2) The lengthy discussion of molecular markers in sections 3.2-3.5 should be edited and shortened. For example, pages 17982-17984 and Tables 3 and 4 are devoted to using diagnostic ratios to identify PAH sources. These data really boil down to PAH implicating a mixture of combustion sources that require a more advanced tool (i.e. CMB modeling) in order to distinguish between their sources. The present discussion over-interprets the PAH data, suggesting that diagnostic ratios can be used for source apportionment and that correlations of PAH with OC and indicate the presence of “noncombustion sources.” It is best to use the CMB model for source apportionment, which should be discussed in an expanded section 3.6.

R: We really appreciate this comment. We are agree with the reviewer that sections 3.2-3.5 are long, however, one of the objectives of this study is also to show the organic composition and used these sections to discuss the organic composition and identify possible primary emission sources and then complement the conclusions derived from these sections with the use of CMB. For example, , the following is written on page 17982, line 27, “Then, these qualitative conclusions will be considered for the source apportionment to estimate the relative contribution of primary emission sources.” to highlight that all in section 3.3 will be confirm by CMB.
In addition, the following text was added on page 17980, line 10, “In the following sections will be analyzed the organic composition of the fine organic aerosols using several diagnostic ratios to identify the primary emission sources. Then the relative contribution of each primary source to the PM2.5 will be calculated by using the CMB receptor model.

In relation with the weak correlation between PAH and OC, the following was deleted on page 17984, line 14, “With regard to OC, the weak correlation was an indicator that other non-combustion sources exist.”

Finally, the section 3.6 (CMB) was expanded given this and further comments.

3) The very low levoglucosan levels observed in this study are surprising, and among the lowest reported for a heavily urbanized location. It would be valuable to corroborate the levoglucosan data with other biomass burning tracers. Page 17988 lines 5-10 should be expanded to a quantitative discussion of dehydroabietic acid, pimparic acid, and isopimaric acid concentrations. Please address whether or not these levels support a very small role for biomass burning?

R: We really agree with the reviewer, it is very important to support the levoglucosan emissions with other biomass burning tracers. The following was added and modified:

Page 17988, Line 5, “The resin acids such as dehydroabietic acid, pimparic acid, and isopimaric acid (Table S1) are secondary tracers from biomass burning (Schauer et al., 2001a). Dehydroabietic acid was the most abundant resin acid, ranging from 1.94 to 4.39 ng m⁻³ and 1.95 to 3.69 ng m⁻³ for spring and fall, respectively. Then, pimparic acid ranged from not detectable levels to 0.09 ng m⁻³ and from 0.15 to 0.35 ng m⁻³ for spring and fall, respectively. Finally, isopimaric acid ranged from not detectable levels to 0.03 ng m⁻³ and from 0.06 to 0.12 ng m⁻³ for spring and fall, respectively. The results for resin acids are in line with those obtained for the levoglucosan. These results support the low impact from biomass burning emissions in the MMA, especially from softwood burning (e.g., conifer wood) during
the spring and fall campaigns. In addition, the higher concentrations of resin acids in fall than in spring are associated with photochemical activity due to stagnation events in fall.”

4) As less than 10% of PM2.5 organic carbon is attributed to individual chemical species in this study, the results should not be presented as a “broad characterization” as done on page 17969 (line 1) and in the title. These should be revised to clarify that only molecular markers were targeted.

R: We completely agree with this comment. We change in line 1 on page 17969 “the broad chemical characterization of fine organic aerosol in Mexico and the first for the MMA” by “the organic composition and source apportionment of fine organic aerosol based on molecular markers in Mexico and the first for the MMA. Particularly molecular marker were quantified by solvent extraction with dichloromethane, derivatization, and gas chromatography with mass spectrometry (GC/MS)”’. In addition, we modify the title of this work by “Organic composition and source apportionment of fine organic aerosol at Monterrey, Mexico, based on organic markers”

5) The method by which the authors refer to the study periods as “first year” and “second year” in section 3.2 makes it difficult to connect the text and figures. Instead, it is suggested to use the years of sampling (e.g. “spring 2011”).

R: We really appreciate it the observation and we agree. All the expressions for “first sampling year” were replaced by “spring 2011 and fall 2011”, while all the expressions for “second sampling year” were replaced by “spring 2012 and fall 2012”. This was applied for section 3.2 and other sections.

6) The nature of biomass burning that occurs in and around the sampling site should be discussed. A relevant source is the surveys of fires conducted by Yokelson et al. (ACP pp 5569-5584, 2007). The authors should clearly discuss the limitations of the profiles utilized in CMB modeling in representing regional biomass burning.
R: We really appreciate this comment from the reviewer because it is very important to clarify that the MMA is mainly affected by types of biomass burning. The following was added:

Page 17989, line 23, “The MMA as well as other urban areas can be affected by types of biomass burning, especially, when they are not surrounded by forests. For examples, several studies have demonstrated that Mexico City has large contribution from biomass burning (Moffet et al., 2008; Stone et al., 2008; Yokelson et al., 2007) because it is affected by forests fires (Yokelson et al., 2007). Conversely, the MMA has not forests around, therefore, the contribution from biomass burning in the MMA might be higher because the source profile used for the CMB was only for wood combustion instead of using a source profile for garbage, industrial, and urban residues open fires (Simoneit et al., 2005). In addition, here is…”

We added the following references to the reference section:


7) In the introduction, the historical review of molecular-marker based source apportionment on page 7970 (lines 22-26) is inadequate. To accurately represent the development and advancement of this approach, further discussion is needed with respect to profiling sources, identifying elemental and molecular markers, and developing source apportionment methods. To suggest only “sparse efforts” in the 1990’s is not representative of a decade when
extensive source testing occurred within the Los Angeles Air Basin, allowing for assessment of the sources of photochemical smog.

R: Yes. We agree with the reviewer. We cited some relevant references associated with the source profile development and new methods in order to show a better overview.

Firstly, the following references were cited on page 17970, line 22 and added to the reference section:


Secondly, on page 17970, Line 25, the text “with sparse efforts” was deleted and on page 17970, Line 26, the following text was added: “... especially, with the development of organic source profiles for primary emission sources (Rogge et al., 1991; Rogge et al.,1993a; Rogge et al., 1993b; Rogge et al., 1993c; Rogge et al., 1994; Rogge et al., 1997; Fraser et al., 1999; Schauer et al., 1999) and alternative receptor models (Paatero 1997; Wold et al., 2001).

Furthermore, improved source apportionment methods have been developed (Antony Chen et al., 2011; Kelly et al., 2013; Watson et al., 2015) while other methods have been suggested to be dropped as a receptor model (Hopke 2015). More detailed information about source apportionment methods can be found elsewhere (Reff et al., 2007; Lin et al., 2010; Nozière et al., 2015).”

Finally, the following references were added to the reference section:

• Hopke, P. K.: It is time to drop principal components analysis as a “receptor model”, J. Atmos. Chem. 72, 127-128, 2015.

8) The description of analytical methodologies is quite lengthy. The authors should remove all redundancies with Brown et al. (2002) to shorten this section. If no redundancies exist, then the additional information that can be accessed in Brown et al. (2002) should be stated.

R: We agree with reviewer. Too specific steps about the extraction and derivatization process are detailed as well as the equipment specifications. In addition, as the reviewer mentioned, many of those are already detailed in Brown et al., 2002. Therefore, the section 2.3 (ambient
measurements) was shortened and additional information or redundancies were referenced to Brown et al., 2002. The section 2.3 was shortened to the half.

9) What are the expected accuracy and precision of organic species measurements?

R: We are conscious about the accuracy and precision, especially, when studies quantify organic species present in the particulate material. Their concentrations are naturally low (eg. ng m\(^{-3}\)), which promote the wide variations of the concentrations measured in different studies or laboratories for the same samples. Therefore, it is very difficult to determine the accuracy and precision in ambient samples. Data for several classes of compounds has shown a wide variation (NIST 2005). This variation is probably due to number of factors, including modifications needed in the extraction and isolation methods used for more polar compounds, mass spectral fragmentation, and chromatographic interference (NIST 2005). Efforts have been conducted to produce more information about the accuracy and precision in this field of study. In addition, to support this information:

- Firstly, there are not certified reference materials available for the measurement of aerosol organic compounds. Using the NIST 1649a as a material, many values are only indicative but not certified. Even, in the NIST 1649b few concentrations are only indicative and many values for other organic compounds are referenced. These documents were analyzed in the past and the accuracy was around 20% for most species with the exception of some PAH where it is known that GC/MS is biased (Coelution problems). However, the latter is less of an issue as all molecular marker work is based on these species; the same occurs for source profiles. Most of the studies use solvent extraction for GC/MS and hence all studies see the same bias towards accuracy. Overall no atmospheric studies besides a few very select pollutants (e.g. PAH) address accuracy failure to have appropriate reference materials due to classes of compounds showed a wide variation (NIST [Schantz et al., 2005]). Past work showed close correlation between out techniques for levoglucosan and other methods (Garcia et al., 2005).

- Secondly, precision is again challenging to assess as sample material (filter) is limited and typically does not allow for split sample analysis in areas that are not very highly
polluted. However in past studies using reference material, internally we achieved typically reproducibilities of better than 25%, frequently better than 10% on replicate samples. These results are consistent with the few indications in the literature of actual uncertainties in these measurements, for example in Fraser et al. (2002) who states: “Known quantities of the quantification standard were repeatedly analyzed to provide an estimate of the precision of the analysis technique. While this precision varied between organic compounds, we estimate a precision of quantification by GC-MS of +/-23%.”

Finally, the review from Noziere et al., 2015 mentioned an interlaboratory comparison to assess and demonstrate their performance in a particular test associated with the quantifications or organic compounds present in particulate material. In this review, was mentioned that has been recently organized an interlaboratory comparison within the European ACTRIS project. In spite of the results showed small standard deviations between the measurements of selected organic compounds, it is not realistic to propose such intercomparison activities for a large number of compounds. However, this would be desirable for major markers in ambient aerosol.

To complement this in the manuscript, we cited some references on page 17978, line 24: “For individual organic compound quantification, an uncertainty of ±20% of the measured concentration was used for all ambient samples and source profiles (Schauer et al., 2000; SRM 1649a, 2007; SRM 1649b, 2009; Fraser et al., 2003; Schantz et al., 2005).” In addition, we added these references to the reference section.

References:


Noziere, B., Kalberer, M., Claeys, M., Allan, J., D’Anna, B., Decesari, S., Finessi, E.,
Glasius, M., Grgic, I., Hamilton, J. F., Hoffmann, T., Linuma, Y., Jaoui, M., Kahnt,
molecular identification of organic compounds in the atmosphere: state of the art and
Schantz, M., Poster, D., Kucklick, J., Wise, S., McDow, S., Lewtas, J.: NISTIR 7303,
Intercomparison program for organic speciation in PM2.5 air particulate matter:
description and results for tiral III. NIST, 2005.
Schauer, J. J., and Cass, G. R.: Source apportionment of wintertime gas-phase and
SRM 1649a; Urban Dust/Organics; National Institute of Standards and Technology; U.S.
Department of Commerce: Gaithersburg, MD (06 December 2007)
SRM 1649b; Urban Dust/Organics; National Institute of Standards and Technology; U.S.
Department of Commerce: Gaithersburg, MD (23 February 2009)
10) What are the analytical uncertainties in organic species measurements? This is an
important consideration when comparing day/night, inter-annual, and seasonal differences.
Further, these uncertainties are key inputs to the CMB model. Their calculation should be
clearly presented.
R: As stated in comment 9, the uncertainty could exhibit wide variation. For Table S1 we did
not report uncertainties for each chemical species, nor have other authors such as:

  Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, Environ.
  Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and


• SRM 1649a; Urban Dust/Organics; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (06 December 2007)

• SRM 1649b; Urban Dust/Organics; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (23 February 2009)


However, from several evidence, described in comment 9, we used ±20% of the measured concentration for each organic species as its uncertainty for the CMB receptor model (Schauer et al., 2000).

11) References for PAH diagnostic ratios should be integrated into Table 3 in the same row as the corresponding information. This will clarify to the reader which information is drawn from which reference. Then, these refs may be removed from the figure caption.

R: We appreciate the comment from the reviewer and we totally agree with the suggestion. The references were removed from the Table caption and were listed in the Table. In addition, the following reference was added to the reference list.


12) Throughout section 3.4, in particular, nomenclature should be consistent and conform to IUPAC standards. Eladic acid is not commonly known, and switching between C18:1, and octadecanoic acid is confusing.

R: We really appreciate the comment from the reviewer. Firstly, we review the whole section and we modified all not common names to the IUPAC standards. Secondly, for the case of
oleic acid and elaidic acid we switched these names by cis-9-Octadecenoic acid and trans-9-octadecenoic acid, respectively; the “C18:0” and “C18:1” were deleted, we decided to use the IUPAC standards. Finally, the name of the section 3.4 “Carboxylic acids” was replaced by “n-alkanoic acids”.

13) The non-cooking sources of cholesterol should be stated (page 17986 line 23).

R: The following was added in text (page 17986 line 23), “…non-cooking related sources such as soil and prescribed burns”. In addition the following references were cited in this part.


Lee et al., 2005 was added to the reference list.

14) Throughout the manuscript, the meaning of +/- is not clear.

R: We really appreciate this observation. The meaning of +/- is the standard deviations of the means that we calculated for each concentration and contribution from each organic marker as well as for any other parameters such as CPI, diagnostic ratio, etc. Sometimes we describe the range of the values in parenthesis. We added the following text on page 17979, line 8, “In this section, averaged values for concentrations and other parameters are given ± one standard deviation.”

15) Are any day/night trends statistically significant?
This is a valuable observation. As part of this study, Mancilla et al. (2015) showed that OC/EC data exhibited mainly variability between nighttime and daytime, but not much variability between individual days. However, individual daytime/nighttime concentrations of the carbonaceous species (OC and EC) were statistically significant different. This trends were identified by an ANOVA analysis.

16) How many CMB results were averaged to create Fig. 6 versus how many data were discarded due to poor model performance (page 17989, line 4).

R: We appreciate the observation. We modified the following:

Page 17989, line 4, “The rest of the samples…” was replaced by “Finally, 11 samples…”

In this way the balance of the balance of the total representative samples is clear (18 + 14 + 11 = 43).

17) With so much OC collected, what is the need for sample compositing?

R: We really understand the concern of this question. We have a justification for having carried out the sample compositing.

According to Brown et al. (2002), at least 400 µg of OC is necessary for a detailed organic speciation by GC/MS. Therefore, for the first campaign (Spring 2011), analyses for each 12-hour sample were carry out individually as discussed by Mancilla et al. (2015). OC in the samples during spring 2011 varied from 3,897 to 12,310 µg per filter.

• Even though the samples collected for the spring of 2011 exhibited high levels of OC, the quantification of molecular markers were very low. This is consistent with the high contributions of SOA as Mancilla et al. (2015) shows.

• In spite of many studies report a minimum of 400 µg per sample of OC as absolute minimum for the quantification of molecular marker species, some of these (e.g. Brown et al., 2002) point out that in the case of substantial SOA contribution to OC
and PM, molecular marker species might still not be detected in the samples as concentrations are too low.

- As part of the present study, SOA contributions were estimated (Mancilla et al., 2015) and the results showed high contributions of SOA to the total OC and PM2.5: 59–87% (EC-Tracer method), and 32–45% (minimum observed OC/EC ratio).

- Therefore, we expected to require at least the double of the carbon, which was not available on individual samples. Based on these findings, composites were formed for the following three campaigns (Fall 2011, Spring 2012 and Fall 2012) to ensure higher levels of collected mass used to identify the molecular markers.

- Weekday/weekend and daytime/nighttime differences of fine OC levels were investigated and considered to pool sample filters into weekday and weekend composites for the last three campaigns. Sample groups for composites varied from two to six sample filters with a total of OC varying from 5,019 to 62,536 µg per composite.

- Thereafter, the number of individual samples (or filters) was reduced from 111 to 43 representative samples. The composites made for this study are described in Table 2.

For the fall 2011, spring 2012 and fall 2012 we had a higher temporal resolution. In addition, we increase the OC to obtain better quantification and minimize the number of analysis which is quite time consuming. In addition OC/EC data on that study showed that there is mainly variability between nighttime and daytime but not much variability between individual days if they were day time/nighttime and weekend/weekday. Therefore, not much could be learned that justified the effort to analyze individual samples and analytical challenges and consequently we decided to make composited samples.

18) Further, what is the rationale for compositing non-consecutive time periods (day/night) and days (e.g. 30 May, 9 Jun, 11 Jun)?

R: This observation is very important because it is not quite clear in the manuscript. Firstly, as part of this study, Mancilla et al. (2015) showed that OC/EC data exhibited mainly variability between nighttime and daytime, but not much variability between individual days. However, individual daytime/nighttime concentrations of the carbonaceous species (OC and EC) were statistically significant different. This trends were identified by an ANOVA analysis.
Therefore, we decided to formed composites using only daytime or nighttime samples (never mixed), and if the pooling samples come from weekdays or weekend, it was not significant, but we decided to segregate the composites in weekdays and weekend. However, all this need to be clarified in the text, therefore, the following comments were added in the text:

- Page 17973, Line 19, Mancilla et al. (2015) was cited.

- Page 17973, Line 19. The following was added “Each composite included only daytime or nighttime samples collected during weekdays (Mon-Thu) or weekend (Fri-Sun).”

- For the case of the example that suggest the reviewer “30 May, 9 Jun, 11 Jun” there was a misunderstanding due to it is not pretty clarified in the Table 2 what it is means. In this case, the dates included refers to that filters collected on May 30, Jun 9 and Jun 11 were analyzed individually. Therefore, we made the following modifications in the footnote of the Table 2: “I represents an individual sample” was replaced by “I indicates that dates included were analyzed individually” and “C represents a composite sampling” was replaced by “C indicates that dates included were pooled to form a composite”.

19) Mass of OC collected is defined by air flow rates and sampling times. The last column of Table 2 is not useful and should be removed.

R: we agree with the comment. Therefore, the last column (OC in μg) was removed from Table 2.

20) Also in Table 2, the columns containing of D/N and the subsequent number need to have column headers.

R: we agree with the reviewer. We merged the D/N and number columns with the I/C column; the new column was named “Description” and it refers to the description of the composite or samples.

21) All multi-part figures should have parts A, B, C, etc. clearly labeled.
R: We agree with the reviewer. The following figures were clearly labeled.

Page 18006, Figure 2 was edited:

Figure 2. Concentrations of the resolved organic compound classes in the MMA. For (a) the n-Alkanoic and Alkenoic acids and wood smoke tracer were not included in the chemical analysis. For (b), (c) and (d) the n-alkanoic acids are divided by a factor of 10.
Figure 3. Carbon number distribution of $n$-alkanes in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. The black line is the daytime concentrations while the dot line is the nighttime concentrations.
Figure 4. Mass concentration distribution of PAHs in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. Coronene was included in all monitoring campaigns, except in the spring 2011.

Page 18009, Figure 5 was edited:
Figure 5. Carbon number distribution of $n$-alkanoic acids in the Monterrey Metropolitan Area (MMA) for (a) fall 2001, (b) spring 2012 and (c) fall 2012. The black line represents the daytime concentrations while the dot line represents the nighttime concentrations.
22) “Other OC” should be added to Fig. 6 so that 100% of the circle is equal to measured OC. This will visually clarify the fact that a large fraction of OC was not apportioned and is likely due to secondary or uncharacterized primary sources.

R: We really appreciate the comment. The Figure 6 was modified. We added a second chart to show the difference between the contributions to the identified and measured concentrations of PM$_{2.5}$.

![Figure 6](image)

Figure 6. CMB contributions to the (a) average identified ambient PM$_{2.5}$ in the MMA and to the (b) overall PM$_{2.5}$ including the unidentified mass of the measured PM$_{2.5}$ concentrations.

23) Figure 2 should have the same chemical species in each panel for easy comparison.
We agree with the reviewer. The comparison is not easy. We attended all these corrections in comment 21. We modified the Figure 2 to have the same chemical species for easy comparison. In addition, we labeled each part of the figure and we edited its caption.

Minor comments:
A) Suggest revising page 17970 line 4 to: “diagnostic ratios between homologs in series of biomolecules. For n-alkanes and carboxylic acids, the odd- and even- carbon preferences are indicators of biogenic sources (ref). A lack of carbon preference is indicative of fossil sources.”

R: Done. We really appreciate the suggestion provide by the reviewer. We considered the text suggested by the reviewer.

B) Page 17984 line 9, p < .1 and p < 0.05 is unusual. Suggest reporting p values for each.

R: Done.

C) Page 17984 line 9, report r with sign to indicate if these are positive or negative correlations. The direction of the correlation is lost when squaring.

R: Done. We report the average correlation r with positive sings.

D) Figure 4 – rescale panel A so PAH can be compared in vertical columns.

R: Done.
Anonymous Referee #3

Received and published: 17 September 2015
Journal: ACP Title: Chemical characterization of fine organic aerosol for source
apportionment
at Monterrey, Mexico Author(s): Y. Mancilla et al. MS No.: acp-2015-282 MS
Type: Research Article

Anonymous Referee comments.

General comments.

In this study the results obtained from the analysis of a data set of chemical composition (OC,
EC and organic molecular markers) in PM2.5 samples recorded during sampling campaigns
at Monterrey (Mexico) are shown. The sampling campaigns were carried out in the Spring
and Autumn seasons during 2 consecutive years. PM samples were obtained for day and night
12 hours consecutive periods. Molecular diagnostic ratios and a chemical mass balance
model were the main techniques used to analyses the data sets with the aim to identify sources
and origins of the fine organic aerosol and estimate mass contributions.

C: We appreciate the suggestions made by the reviewer. We have revised the content of the
manuscript aiming to clarify the findings set forth in the paper.

In my opinion the design of the study was not the best possible. It is not clear the reason why
the authors performed the sampling campaigns in spring and autumn. It would have been
better to obtain samples in winter and summer, when the emissions from anthropogenic
sources and the formation of secondary organic aerosols, respectively, are usually more
intense.

R: It is a good point. Typically winter and summer seasons are better to perform sampling
campaigns, however, a PM$_{2.5}$ and O$_3$ time series analysis for previous years were conducted.
From this analysis, it was observed high concentrations during the sampling campaign
selected for this study. This behavior can be by the meteorology and geography of the region.

The CMB was not performed for the spring and autumn periods, separately. Otherwise, the
collection of day and night samples is not justified taken into account the main results of the
paper, where the CMB was not performed for both groups of samples, too. In fact, there was no significant result in the conclusions section, in relation with the source apportionment of fine organic aerosol in the day and night periods.

R: We agree with the reviewer that CMB performance was limited. The same suggestions were made from other reviewers. Therefore, the section 3.6 was expanded; results for CMB performance by season, daytime and nighttime periods were discussed. In addition, a Table that summarize these results were added as well as a Table with specific detail for each run was added in the supplemental material. In the latter Table it can be found the performance parameters obtain for each CMB run.

Moreover, sampling periods longer than 12 hours could probably avoid the need to composite many samples to obtain higher concentrations of the organic compounds. This is one of the main shortcomings of the study. The resulting low number of representative samples (43) has probably hampered the identification of sources and the estimation of PM contributions to a certain extent. The number of representative samples used to perform the CMB, was even lower than 43. This number was not specified in the section 3.6.

R: We appreciate the comment from the reviewer and this comment were also made from another reviewer. We decided to conduct the sampling campaigns collecting 12-hour ambient samples due to a parallel study associated with carbonyls and VOC in order to do a further analysis considering daytime and nighttime periods. In addition, a daytime and nighttime analysis was desirable due to urban variations of the primary emission sources in the MMA. From preliminary results for the OC mass collected in 12-hour ambient samples seems to be enough for chemical characterization of the OC (Brown et al., 2002). However, given the high levels of secondary organic aerosol composites were made in order to increase the primary OC mass (Mancilla et al., 2015). In addition, for the fall 2011, spring 2012 and fall 2012 we had a higher temporal resolution. In addition, composites increased the OC to obtain better quantification and minimize the number of analysis which is quite time consuming. Furthermore OC/EC data for this study showed that there is mainly variability between nighttime and daytime but not much variability between individual days if they were day time/nighttime and weekend/weekday (Mancilla et al., 2015).
Not much could be learned that justified the effort to analyze individual samples and analytical challenges and consequently we decided to make composited samples. Finally, it section 3.6 was added the total samples ran in the CMB.

Finally, it should be stressed that a lower number of organic compounds were determined in the first (spring 2011) than in the other sampling campaigns.

R: This is very important. On page 17980, line 5, the following was added “These contributions were much lower than the following three campaigns due to some compounds classes were not included.”

In brief, I think that the present work does not show any significant and/or novel contribution to the global scientific community in relation with the source apportionment of fine organic aerosol. I agree with one of the conclusions reported by Referee #1 in his/her preliminary review: “the findings and the interpretations throughout the paper cannot convince me that such a study could be published in high-quality journals such as ACP”. For these reasons I must recommend the rejection of the paper acp-2015-282 to be published in ACP.

C: We understand the decision from the reviewer and we really appreciate the time of revising the whole manuscript. The reviewer provided a very important and helpful recommendations and corrections to improve the manuscript before get published.

Specific comments.
The authors should justify the relevance for the global scientific community of an urban site at the Monterrey Metropolitan Area, to perform a source apportionment study of fine organic aerosol. What are the specific features of this area in relation with other urban areas that justify this study?.

R: The Monterrey Metropolitan Area is among the twenty largest urban areas in the world. In addition, it is a large urban area that comprises several municipalities with different kind of emissions. This urban area is one the most polluted urban areas by particles suspended in the air. This urban area has an air quality monitoring system that is comprises of nine monitoring
stations up to date. All this comments were pointed out by all corrections suggested from other reviewers.

More details on the characteristics of the MMA car fleet (% of diesel and gasoline vehicles, % of passenger cars, trucks,: :) and the industrial activity should be included in the text.

R: This information was added and modified on page 17971, line 19, “The MMA has a population of 4.2 million inhabitants (INEGI, 2011) and it is considered the largest urban area in Northeastern Mexico and the third-largest urban center in the country. The MMA is composed of 12 municipalities that overall cover an area of 6,680 km² (SEDESOL et al., 2007), as shown in Fig. 1. The MMA has a vehicular fleet of 1.7 million vehicles (INEGI, 2010) with a composition of approximately 73% gasoline-powered vehicles (car passengers), 25% diesel-powered vehicles (buses and trucks) and 3% motorcycles. In addition, the MMA has an industrial activity dominated by manufacturing industries, construction and electricity, transport, restaurants and other local services.”

The occurrence of occasional biomass burning events due to regional transport should be confirmed, instead of being suggested, by means of a comprehensive analysis of meteorological data sets. The occurrence of stagnation events, which are supposed to influence the formation of carboxylic acids, as it was mentioned in the text, should be also characterized.

R: We totally agree with the reviewer. The reviewer #2 suggest the same comments for the biomass burning sources. Firstly, we supported the levoglucosan emissions with other biomass burning tracers. Then, we added a discussion for the dehydroabietic acid, pimaric acid, and isopimaric acid, it was clarified that the MMA is mainly affected by types of biomass burning. Finally, we cited that in Mancilla et al. (2015) was conducted a detail meteorological analysis for the sampling periods of this study.

Taking into account that, as stated by the authors in page 17982, lines 23-25, the diagnostic ratios should be interpreted with caution because many of the organic molecular markers are emitted from a variety of sources, it is really surprising that most of the paper was devoted to
the interpretation of these ratios. Otherwise the discussion of the CMB results is much more reduced.

R: We agree with reviewer that we devoted the analysis and discussion of diagnostic ratios over CMB results. We clarified these reasons through the text by making clear the idea of using the organic composition and diagnostic ratios as a preliminary analysis for identify the main primary emission sources and then run the CMB to corroborate the presence of these primary sources as well as the estimations of their relative contribution to the PM2.5.

The relative high contribution levels of the meat-cooking source (which are even higher than the gasoline-traffic contribution) to the measured PM2.5 mass obtained by the CMB, has not been discussed in detail in the text.

R: This is important. We added the following on page 17989, line 23 “The relative high contribution of the meat-cooking operations was expected given the high traditional restaurant activity in the MMA which contribute with the 16% of the local growth domestic product.”

The interpretation of Figure 6 is somewhat confusing. Does it represent the source contributions to the PM2.5 mass or to the OC mass in PM2.5?. Since the sum of contributions was 100%, where is the 35% of the unidentified mass?.

R: We agree with reviewer that Figure 6 is somewhat confusing. Therefore, we added in the same Figure two charts, one for the identified mass contributions and another for the contributions to the total PM2.5 mass. In the latter you can see the 35% of the unidentified mass.

It is really surprising that the authors highlighted the “potential of industrial sources” in the study area taking into account that they could not obtain an estimation of their contribution to the PM2.5 mass.

R: On page 17978, line 10, we mentioned that natural gas and fuel oil combustion profiles were considered for industrial emissions. We highlighted the potential of industrial sources given that probably the nature of the MMA industries is quite different of this source profiles.
We obtained a very low contribution from industries, however, this value might be higher if we used a source profile derived for the MMA.

**Technical corrections/Typing errors.**


R: Done.

Page 17986. Line 15. Correct “in in 80%...”.

R: Done.
The authors reported organic molecular markers (tracers) of various OA sources in the Monterrey region of Mexico. They collected daytime and nighttime samples in spring and autumn of 2011 and 2012. They attempted to apportion aerosol sources based on diagnostic ratios and CMB model. The report provides a referable dataset in the region where studies on aerosol sources were limited. They concluded that local anthropogenic emissions, mostly dominated by vehicle exhausts, are the major sources of PM. Before recommending publication, the authors are suggested to consider the following concerns.

C: We appreciate the time spent for revising this manuscript. We addressed the comments in the best way.

Major concerns

1. The development of the manuscript. The authors focused on the diagnostic ratios when discussing tracer and OC sources. However, “such ratios should be used with caution” as being pointed out by themselves in P17982, L23. They then attempted to quantify the source fraction of PM using CMB model, but with very little development. To make the manuscript more readable and consistent, the authors are suggested to consider one of the two possible ways to revise it.

The first way is to discuss PM sources focusing on the tracers, make extensive comparisons with up-to-date studies in the community. More detailed data profiles and analyses are needed. Statistical analyses on the daytime/nighttime differences and seasonal differences, and the implications are also needed.

The second way is to focus on the model results, as were suggested by other referees. In either case, the authors are suggested to provide clear research purposes in the Introduction section.

R: We agree with the reviewer. Here the main objective is the use of diagnostic ratios as a preliminary analysis to identify primary emission sources and then use the CMB receptor model to estimate the relative contributions of primary emission sources. We tried to
complement these approaches to each other. However, the second way is very important, but is poorly discussed in the manuscript. Therefore, from we attend these concerns in the following way:

- Firstly, we summarized the whole results obtained for the 32 samples run in the CMB in the Table 5. In addition, this Table was added in the manuscript and discussed in section 3.6.

- Secondly, we added the following discussion for Table 5 on page 17989, line 7, “The average contributions of primary sources are shown in Table 5. The vehicle exhaust and meat-cooking operations emissions for all monitoring campaigns were the highest. In analysis of the seasonal variation, the gasoline- and diesel-powered vehicles in falls were up to five times higher than in springs, when cold weather increases the demand of petroleum products due to low temperatures. The opposite occurred for meat-cooking operations, their spring emissions were three times higher than in fall seasons. The natural gas combustion, vegetative detritus and biomass burning emissions were very low and more constant throughout the springs and falls. In analysis of the daytime and nighttime variations, the vehicle exhaust were much higher during daytime when traffic is heavier. For the meat-cooking operations, the emissions were some higher in nighttime during spring and more constant between daytime and nighttime during fall. For the rest of the sources, the daytime and nighttime emissions were relatively constant. There are not similar studies conducted in the MMA, this is the first source apportionment study based on molecular organic markers for this region. However, these results were similar to those obtained for the MMA using a factor analysis based on trace elements (Martinez et al., 2012) and those for the Mexico City based on molecular organic markers (Stone et al., 2008).”

- Finally, we added a detailed Table with the CMB performance parameters for each sample in the Supplemental material. In addition, we added the following text in the manuscript on page 17989, line 6, “A detailed description of the CMB performance and relative contributions for each sample can be found in Table S2.”

2. Methods. Using the method of solvent extraction followed by GC/MS to determine organic compounds, the recovery, precision, and repeatability are key parameters to assure the data...
quality. Specifically, the uncertainty information is needed in model inputs. The authors are suggested to provide such information.

R: We are totally agree with the reviewer. We received the same comment from the reviewer #2. We are conscious about the accuracy and precision, especially, when studies quantify organic species present in the particulate material. Their concentrations are naturally low (e.g. ng m$^{-3}$), which promote the wide variations of the concentrations measured in different studies or laboratories for the same samples. Therefore, it is very difficult to determine the accuracy and precision in ambient samples. Data for several classes of compounds has shown a wide variation (NIST 2005). This variation is probably due to number of factors, including modifications needed in the extraction and isolation methods used for more polar compounds, mass spectral fragmentation, and chromatographic interference (NIST 2005). Efforts have been conducted to produce more information about the accuracy and precision in this field of study. In addition, to support this information:

- Firstly, there are not certified reference materials available for the measurement of aerosol organic compounds. Using the NIST 1649a as a material, many values are only indicative but not certified. Even, in the NIST 1649b few concentrations are only indicative and many values for other organic compounds are referenced. These documents were analyzed in the past and the accuracy was around 20% for most species with the exception of some PAH where it is known that GC/MS is biased (Coelution problems). However, the latter is less of an issue as all molecular marker work is based on these species; the same occurs for source profiles. Most of the studies use solvent extraction for GC/MS and hence all studies see the same bias towards accuracy. Overall no atmospheric studies besides a few very select pollutants (e.g. PAH) address accuracy failure to have appropriate reference materials due to classes of compounds showed a wide variation (NIST [Schantz et al., 2005]). Past work showed close correlation between out techniques for levoglucosan and other methods (Garcia et al., 2005).

- Secondly, precision is again challenging to assess as sample material (filter) is limited and typically does not allow for split sample analysis in areas that are not very highly polluted. However in past studies using reference material, internally we achieved
typically reproducibilities of better than 25%, frequently better than 10% on replicate samples. These results are consistent with the few indications in the literature of actual uncertainties in these measurements, for example in Fraser et al. (2002) who states: “Known quantities of the quantification standard were repeatedly analyzed to provide an estimate of the precision of the analysis technique. While this precision varied between organic compounds, we estimate a precision of quantification by GC-MS of +/-23%.”

Finally, the review from Noziere et al., 2015 mentioned an interlaboratory comparison to assess and demonstrate their performance in a particular test associated with the quantifications or organic compounds present in particulate material. In this review, was mentioned that has been recently organized an interlaboratory comparison within the European ACTRIS project. In spite of the results showed small standard deviations between the measurements of selected organic compounds, it is not realistic to propose such intercomparison activities for a large number of compounds. However, this would be desirable for major markers in ambient aerosol.

To complement this in the manuscript, we cited some references on page 17978, line 24: “For individual organic compound quantification, an uncertainty of ±20% of the measured concentration was used for all ambient samples and source profiles (Schauer et al., 2000; SRM 1649a, 2007; SRM 1649b, 2009; Fraser et al., 2003; Schantz et al., 2005)”. In addition, we added these references to the reference section.


- Noziere, B., Kalberer, M., Claeys, M., Allan, J., D’Anna, B., Decesari, S., Finessi, E., Glasius, M., Grgic, I., Hamilton, J. F., Hoffmann, T., Linuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-


- SRM 1649a; Urban Dust/Organics; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (06 December 2007)
- SRM 1649b; Urban Dust/Organics; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (23 February 2009)

However, from several evidence, described in comment 9, we used ±20% of the measured concentration for each organic species as its uncertainty for the CMB receptor model (Schauer et al., 2000). For Table S1 we did not report uncertainties for each chemical species, nor have other authors such as:


SRM 1649a; Urban Dust/Organics; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (06 December 2007)

SRM 1649b; Urban Dust/Organics; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (23 February 2009)


3. The biogenic sources. The authors found that the carboxylic acids are the most abundant identified OA components, while they are mainly from biogenic sources (Section 3.4). However, of most of the discussions and the corresponding conclusions, the authors emphasized the anthropogenic sources. The application of CMB model with very small sample size may not assure a reliable output. Although the samples were collected in an urban site, the regional sources should not be ignored. The authors are suggested to examine the general (seasonal) air circulation pattern, as well as those with respect to episodic events if any.

R: We agree with reviewer. Some comments from reviewer #2 also suggested the consideration of regional sources. In addition, in Mancilla et al. (2015) a detailed description of air circulation patterns and backward trajectories were discussed. Finally, on page 17985, line 29, the following text was added: “Air circulation patterns (Hysplit backward trajectories) during these monitoring campaigns suggested a long-range transport from the northeast and southeast (Mancilla et al., 2015).”

4. The biomass burning sources. Similar with those of biogenic sources, regional input of biomass burning emissions should also be considered. Moreover, domestic burning, such as the burning of woods for heating and cooking might also contribute to the elevation of levoglucosan. Levoglucosan of being several tens of ng m$^{-3}$ was not low. These episodes worth being deeply analyzed.

R: We totally agree with the reviewer. The reviewer #2 suggest the same comments for the biomass burning sources.
Firstly, we supported the levoglucosan emissions with other biomass burning tracers. Therefore, the following was added and modified: on page 17988, line 5, “The resin acids such as dehydroabietic acid, pimaric acid, and isopimaric acid (Table S1) are secondary tracers from biomass burning (Schauer et al., 2001a). Dehydroabietic acid was the most abundant resin acid, ranging from 1.94 to 4.39 ng m\(^{-3}\) and 1.95 to 3.69 ng m\(^{-3}\) for spring and fall, respectively. Then, pimaric acid ranged from not detectable levels to 0.09 ng m\(^{-3}\) and from 0.15 to 0.35 ng m\(^{-3}\) for spring and fall, respectively. Finally, isopimaric acid ranged from not detectable levels to 0.03 ng m\(^{-3}\) and from 0.06 to 0.12 ng m\(^{-3}\) for spring and fall, respectively. The results for resin acids are in line with those obtained for the levoglucosan. These results support the low impact from biomass burning emissions in the MMA, especially from softwood burning (e.g., conifer wood) during the spring and fall campaigns. In addition, the higher concentrations of resin acids in fall than in spring are associated with photochemical activity due to stagnation events in fall.”

Secondly, it was clarified that the MMA is mainly affected by types of biomass burning by adding the following text: on page 17989, line 23, “The MMA as well as other urban areas can be affected by types of biomass burning, especially, when they are not surrounded by forests. For examples, several studies have demonstrated that Mexico City has large contribution from biomass burning (Moffet et al., 2008; Stone et al., 2008; Yokelson et al., 2007) because it is affected by forests fires (Yokelson et al., 2007). Conversely, the MMA has not forests around, therefore, the contribution from biomass burning in the MMA might be higher because the source profile used for the CMB was only for wood combustion instead of using a source profile for garbage, industrial, and urban residues open fires (Simoneit et al., 2005). In addition, here is…”

Finally, the following references were added to the reference section:

o Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C.,
Crounse, J. D., Wennberg, P. O., Fisher, M. E., Wold, C. E., Campos, T. L.,
Adachi, K., Buseck, P. R., and Hao, W. M.: Emissions from forest fires near

Minor concern

Wood smoke markers. What compounds were used as wood smoke markers were not given.

R: Done. The levoglucosan and resin acids were used as wood smoke markers. The
methoxyphenols such as guaiacol and vanillin are other markers that were not discussed in the
manuscript due to they were quantified only for the last monitoring campaign. Therefore, they
were not representative for the whole study. The same happened for the retene, a PAH that is
characteristic for wood smoke.

Technical correction

Term of alkanoic acids/carboxylic acids should be uniformed.

R: Done. All terms of “carboxylic acids” were changed to “n-alkanoic acids”.

Chemical characterization of fine organic aerosol for source apportionment at Monterrey, Mexico, based on organic markers

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Abstract

Primary emissions from anthropogenic and biogenic sources as well as secondary formation are responsible for the pollution levels of ambient air in major urban areas. These sources release fine particles into the air that negatively impact human health and the environment. Organic molecular markers, which are compounds that are unique to specific PM$_{2.5}$ sources, can be utilized to identify the major emission sources in urban areas. In this study, 43 representative PM$_{2.5}$ samples, for both daytime and nighttime periods, were built from individual samples collected in an urban site of the Monterrey Metropolitan Area (MMA) during the spring and fall of 2011 and 2012. The samples were analyzed for organic carbon, elemental carbon, and organic molecular markers. Several diagnostic tools were employed for the preliminary identification of emission sources. Organic compounds for eight compound classes were quantified. The $n$-alkanoic acids were the most abundant, followed by $n$-alkanes, wood smoke markers, and levoglucosan/alkenoic acids. Polycyclic aromatic hydrocarbons (PAHs) and hopanes were less abundant. The carbon preference index (0.7–2.6) for $n$-alkanes indicate a major contribution of anthropogenic and mixed sources during the fall and the spring, respectively. Hopanes levels confirmed the contribution from gasoline and diesel engines. In addition, the contribution of gasoline and diesel vehicle exhaust was confirmed and identified by the PAH concentrations in PM$_{2.5}$. Diagnostic ratios of PAH showed
emissions from burning coal, wood, biomass, and other fossil fuels. The total PAH and elemental carbon were correlated ($r^2 = 0.39-0.70$) across the monitoring periods, reinforcing that motor vehicles are the major contributors of PAH. Cholesterol levels remained constant during the spring and fall, showing evidence of the contribution of meat cooking operations, while the isolated concentrations of levoglucosan suggested occasional biomass burning events. Finally, source attribution results obtained using the CMB model indicate that emissions from motor vehicle exhausts are the most important, accounting for the 64% of the PM$_{2.5}$, followed by meat cooking operations with 31%. The vegetative detritus and biomass burning had the smallest contribution (2.2% of the PM$_{2.5}$). To our knowledge, this is the second study to explore the organic composition and source apportionment of fine organic aerosol based on molecular markers in Mexico and the first for the MMA. Particularly molecular marker were quantified by solvent extraction with dichloromethane, derivatization, and gas chromatography with mass spectrometry (GC/MS), the broad chemical characterization of fine organic aerosol in Mexico and the first for the MMA.

1 Introduction

Fine organic aerosol (OA) has a major role in environmental and human health impacts (Peng et al., 2009). Some researchers have recently estimated that fine OA constitutes 23–38% of the PM$_{2.5}$ mass in urban areas (Qin et al., 2006; Viana et al., 2006; Duan et al., 2007; Upadhyay et al., 2011). In addition, OA along with elemental carbon (EC) can account for up to 31–57% of the PM$_{2.5}$ mass (Duan et al., 2007; Upadhyay et al., 2011; Martínez et al., 2012).

Atmospheric fine OA is a complex mixture of hundreds of organic compounds that are directly emitted or are generated by atmospheric chemical processes. Many of these organic compounds are toxic or carcinogenic (Spurny, 2000; Pope et al., 2002), but can be useful as markers to identify the source of the aerosols being measured at a specific site. Organic markers that have been used in the past include levoglucosan, cholesterol, nicotine, n-alkanes, hopanes (pentacyclic triterpanes), and polycyclic aromatic hydrocarbons (PAHs). Levoglucosan is a pyrolysis decomposition and combustion product of cellulose; therefore, it can be used as a tracer for biomass burning sources (Fraser et al., 2000; Robinson et al., 2006a; Alves et al., 2011; Gonçalves et al., 2011). Cholesterol and nicotine are good markers for meat cooking operations (Rogge et al., 1991; Schauer et al., 2001b; Robinson et al.,...
and cigarette smoke (Eatough et al., 1989; Hildemann et al., 1991; Rogge et al., 1994; Kavouras et al., 1998), respectively. Hopanes are biomarkers of fuel oil combustion, coal combustion and lubricants, and are useful to identify engine emissions (Rogge et al., 1993a; Oros and Simoneit, 2000; Simoneit et al., 2004; Schnelle-Kreis et al., 2005). PAHs are semi-volatile compounds formed from fossil fuel incomplete combustion processes (Rogge et al., 1993a; Marr et al., 2004; Sklorz et al., 2007). Finally, \( n \)-alkanes are indicators of fossil fuel utilization and biogenic emissions (Simoneit et al., 2004; Young and Wang, 2002). Additional details about specific organic markers and their emission sources can be found elsewhere (Simoneit et al., 1991; Simoneit, 1999; Lin et al., 2010; Blanchard et al., 2014).

Another feature used to identify the origin of fine OA are the diagnostic ratios between homologs in series of biomolecules. For \( n \)-alkanes and alkanoic acids, the odd- and even-carbon preferences are indicators of biogenic sources (Tsapakis et al., 2002). A lack of carbon preference is indicative of fossil sources, diagnostic ratios between some organic compounds, such as the case of \( n \)-alkanes, carboxylic acids, and PAHs. For the \( n \)-alkanes and carboxylic acids, the odd-to-even carbon ratio is an indicator used to determine whether fine OA come from biogenic or anthropogenic emission sources (Tsapakis et al., 2002). For the case of PAHs, some ratios can be used to identify emissions from fossil fuel combustion (Zhang et al., 2005).

Source apportionment studies based on organic molecular markers have accomplished a better understanding of the emission sources in urban areas. This approach considers two main principles: (1) that organic molecular markers are present in relatively high concentrations in emissions from a specific source and in lower concentrations in the remaining sources, and (2) that they react slowly enough in the atmosphere to be conserved during transport from the source to the observation/receptor site (Schauer et al., 1996; Lin et al., 2010). The use of organic molecular markers in the last decade has proven to be a powerful method to identify and attribute emission sources in urban areas (Alves et al., 2001; Fraser et al., 2003; Abas et al., 2004; Kalaitzoglou et al., 2004; Zheng et al., 2005; Feng et al., 2006; Huang et al., 2006; Li et al., 2006; Park et al., 2006; Alves et al., 2007; Chow et al., 2007; Ke et al., 2007; Stone et al., 2008; Amador-Muñoz et al., 2010; Yin et al., 2010; Pietrograndi et al., 2011; Perrone et al., 2012; Giri et al., 2013; Villalobos et al., 2015; Watson et al., 2015; Zheng et al., 2015).

In spite of recent research interest on organic molecular markers for source apportionment, the application of this approach started in the 80s (Simoneit, 1985; Simoneit, 1986; Eatough et al., 2006b).
1989; Simoneit and Mazurek, 1989) and continued in the 90s with sparse efforts (Simoneit et al., 1990; Simoneit et al., 1991; Schauer et al., 1996; Simoneit, 1999; Schauer and Cass, 2000). Especially, with the development of organic source profiles for primary emission sources (Rogge et al., 1991; Rogge et al., 1993a; Rogge et al., 1993b; Rogge et al., 1993c; Rogge et al., 1994; Rogge et al., 1997; Fraser et al., 1999; Schauer et al., 1999) and alternative receptor models (Paatero, 1997; Wold et al., 2001). Furthermore, improved source apportionment methods have been developed (Antony Chen et al., 2011; Kelly et al., 2013; Watson et al., 2015) while other methods have been suggested to be dropped as a receptor model (Hopke, 2015). More detailed information about source apportionment methods can be found elsewhere (Reff et al., 2007; Lin et al., 2010; Nozière et al., 2015).

For the Monterrey Metropolitan Area (MMA), the third largest urban center of Mexico, there is a growing concern to determine the emission sources of fine OA. It was recently determined that fine OA accounts for 36–71% of PM$_{2.5}$ mass in this urban center (Mancilla et al., 2015). Previously, Martínez et al. (2012) estimated an OA fraction of ~40% of the PM$_{2.5}$ for the MMA. According to a recent tunnel study, PM$_{2.5}$ emissions from gasoline-powered vehicles (one of the major emission sources in the MMA) contain as much as 55% of carbonaceous material (Mancilla and Mendoza, 2012). To date, only one study has addressed the chemical characterization of fine OA in the MMA, but it focused exclusively on the levels of PAHs (González-Santiago, 2009). More importantly, the present study would be the second of this kind in Mexico and the first one for the MMA; previously, Stone et al. (2008) reported an evaluation of molecular organic markers for source apportionment at the Mexico City. This city has a temperate and wet climate while the MMA has a dry and extreme climate with scarce rains. It is well-known that climate conditions can affect the air quality in urban areas. Extreme climates, including high temperatures, could increase the concentrations of air pollutants. For example, warm and dry climates promote photochemical reactions in the atmosphere producing secondary OA. The unique geography and the changeable climate as well as its typical industries of the region make of the MMA unique and different from other Mexican cities.

2 Methodology
2.1 Sampling site

The MMA has a population of 4.2 million inhabitants (INEGI, 2011) and it is considered the largest urban area in Northeastern Mexico and the third-largest urban center in the country. The MMA is composed of 12 municipalities that overall cover an area of 6,680 km² (SEDESOL et al., 2007), as shown in Fig. 1. The MMA has a vehicular fleet of 1.7 million vehicles (INEGI, 2010) with a composition of approximately 73% gasoline-powered vehicles (car passengers), 25% diesel-powered vehicles (buses and trucks) and 3% motorcycles. In addition, the MMA has an industrial activity dominated by manufacturing industries, construction and electricity, transport, restaurants and other local services, and 4.2 million inhabitants (INEGI, 2011) and is considered the largest urban area in Northeastern Mexico and the third-largest urban center in the country. In addition, the MMA has a network of air quality monitoring stations (Sistema Integral de Monitoreo Ambiental, SIMA). For this study, PM$_{2.5}$ samples were collected at only one site placed in the facilities of the downtown monitoring station of the SIMA network (25° 40’ 32” N, 100° 20’ 18” W), 556 meters above sea level. The sampling site is affected mainly by traffic and emissions from a wide range of industrial activities (e.g., steel and cement production). The vegetation around the sampling site includes dispersed and scarce grass, shrubs, and street tree systems in the immediate vicinity as well as in the periphery. The sampling site selection was based on coefficients of divergence (COD) analysis using the 24-hour average PM$_{2.5}$ concentrations recorded in 2009 by the SIMA network. Details about this analysis can be found elsewhere (Mancilla et al., 2015).

2.2 Sampling periods and instruments

The samples were collected during the spring and fall of 2011 and 2012 (Table 1). For every sampling day two consecutive twelve-hour samples were taken to obtain information for daytime and nighttime periods. The daytime sampling was performed from 06:00 a.m. to 06:00 p.m. (local time), while nighttime samples were collected from 06:00 p.m. to 06:00 a.m. the next day. For the spring and fall 2011 campaigns, sampling periods were performed on alternate days. For example, for the spring of 2011, the first sampling day was on May 28, the second on May 30, and so on. For the campaigns of 2012, both were conducted for 14 consecutive sampling days.
Carbonaceous aerosol samples were collected using high-volume filter-based instruments with PM$_{2.5}$ inlet (TE-6001-2.5, Tisch Environmental Inc), operating at a flow of 1.13 m$^3$/min. The flow rates for the high-volume samplers were calibrated at the start and end of each monitoring campaign. For each high-volume sampler, the calibration was carried out using a calibration orifice (NIST Traceable Calibration Certificate). The samplers were mounted on the rooftop of the monitoring station three meters above the ground. One high-volume sampler was used for each campaign, except for the campaign of fall 2012, in which two high-volume samplers were deployed and operated simultaneously to collect pairs of samples for each diurnal and nighttime sampling period. Fine particles were collected in 8”×10” quartz microfiber filters (Whatman QMA). Filters were previously pre-fired for 8 hrs at 600°C in a furnace to remove residual carbon and stored in baked aluminum foil within sealed plastic bags (Ziploc®) until they were used. After sampling, loaded 8”×10” filters were stored in tall 8 oz. glass jars (VWR, IR221-0250). Loaded filters were placed in a cooler with blue ice for immediate transport from the sampling site to the laboratory. All loaded filters were stored in a freezer at −20°C to prevent the evaporation of volatile compounds until they were analyzed. A total of 111 samples and 10 field blanks were collected throughout the study.

### 2.3 Ambient measurements

According to Brown et al. (2002), at least 400 µg of OC is necessary for a detailed organic speciation by GC/MS. For the first campaign (Spring 2011), analyses for each 12-hour sample were carried out as discussed by Mancilla et al. (2015). OC in the samples of this first campaign varied from 3,897 to 12,310 µg per filter. Even though the samples collected for the spring of 2011 exhibited high levels of OC, some concentrations for different organic compounds of interest were low (0.03 to 0.16 ng m$^{-3}$). In addition, the OC concentrations for the last three campaigns (the fall of 2011, the spring of 2012, and the fall of 2012) were on average up to 35% lower than OC concentrations of the first campaign (spring 2011). Based on these findings, composites were formed for the last three campaigns to ensure higher levels of collected mass used to identify the organic molecular markers. Weekday/weekend and daytime/nighttime differences of fine OC levels were investigated and considered to pool sample filters into weekday and weekend composites for the last three campaigns (Mancilla et al., 2015). Each composite included only daytime or nighttime samples collected during weekdays (Mon-Thu) or weekend (Fri-Sun). Sample groups for composites varied from two to six sample filters with a total of OC varying from 5,019 to 62,536 µg per composite.
Thereafter, the number of individual samples (or filters) was reduced from 111 to 43 representative samples. The composites made for this study are described in Table 2.

Solvent-extractable molecular markers were quantified using gas chromatography mass spectrometry (GC/MS) using dichloromethane (DCM), and methanol (MeOH). The solvents used were optima grade (high purity 99.9%, Fisher Scientific), and included isopropanol (IPA), dichloromethane (DCM), and methanol (MeOH). The chemical reagents and authentic deuterated standards (Sigma Aldrich) were used. In addition, the glassware and laboratory tools were cleaned using detergent and water, rinsed with deionized water and isopropanol, and baked overnight at 450°C. MeOH was used in the preparation of some stock solutions. Organic molecular markers were determined by (GC/MS). The preparation of each individual filter or composite described in Table 2 was conducted over a clean surface covered properly with aluminum foil. Stored sample jars containing the loaded filters were thawed until they equilibrated with the room temperature. Then, the filters were removed from the sample jars using clean tweezers. Next, filters were cut into pieces and placed into pre-baked glass jars. Finally, filters were spiked with 50 µL of the following deuterated internal standards (Sigma Aldrich): n-hexadecane-d34, n-hexatriacontane-d74, n-eicosane-d42, n-triacontane-d62, vanillin-d3, benzophenone-d5, chrysene-d12, dibenz(a,h)anthracene-d14, naphthalene-d8, pyrene-d10, benzo(e)pyrene-d12, coronene-d12, decanoic acid-d19, palmitic acid-d31, stearic acid-d35, levoglucosan-13c6, and cholesterol-d6. Each individual filter (the spring of 2011 campaign) or sample composite (rest of the campaigns) was extracted three times with DCM. During each extraction, enough DCM was added to cover the filters, and then the jars were subjected to ultrasonic agitation for 20 min using a sonicator (Branson® model 5510R-DTH). The extracts were combined into a new pre-baked jar and then concentrated by evaporation under a gentle flow ultra-high purity nitrogen until the extract reached a volume of ~5 mL. The extracts were filtered through a pre-fired quartz filter, subsequently reduced in volume to 250 µL, and then separated into three fractions. One fraction was a direct portion of the 250 µL extract for direct analysis by GC/MS, and the other two fractions were used for chemical derivatizations. All fractions were put into vials and kept in a freezer until they were analyzed.

Two fractions of each concentrated extract (250 µL extract) were used for chemical derivatizations. One fraction was methylated using diazomethane (CH2N2) to convert carboxylic acids to their respective methyl esters. The another fraction was silylated using a
combination of BSTFA (N, O-bis(trimethylsilyl)trifluoroacetamide) and TMCS (trimethylchlorosilane) to convert sterols and sugars to their respective trimethylsilyl esters. For methylation, 50 µL of a Diazomethane (CH₂N₂) solution was combined in a vial with 50 µL of extract. For the silylation, 50 µL of BSTFA+TMCS (molar ratio 99:1) was combined with 50 µL sample extract. Then, the mixture was allowed to react for 3 h at 65°C.

Filter extracts were analyzed on an Agilent 6890N Gas Chromatograph (Agilent Technologies) coupled with an Agilent 5973N Mass Selective Detector (MSD) (Agilent Technologies). Separation was carried out using a non-polar 30 m × 250 µm × 0.25 µm HP-5MS Agilent ultra-inert capillary column coated with 5% phenyl methyl siloxane. Injections of 2 µL aliquots were performed using an Agilent 7683 Autosampler (Agilent Technologies) in splitless mode and using helium (ultra high purity, 99.999%) as the carrier gas. The MSD was operated in ion scan mode and ions were produced using an electron impact (EI) ion source. The GC/MS operating conditions included an initial hold of 5 min at 65 °C, followed by a temperature ramp rate of 10 °C min⁻¹ that was held constant for 25 min until the GC oven reached 300 °C. The quantification and identification of organic compounds was based on comparisons with authentic standards, retention times, literature mass spectra, and fragmentation patterns using HP chemstation. A detailed description of the extraction and analysis procedures as well as the chromatograph and column used can be found in elsewhere (Brown et al., 2002).

### 2.4 Molecular diagnostic ratios

To investigate the origin of fine organic aerosols, the following diagnostic ratios were used:

#### 2.4.1 Carbon Preference Index (CPI)

The CPI is an indicator of the measure of odd or even carbon homologues series of organic compounds within a sample. Based on several studies (Abas and Simoneit, 1996; Tsapakis et al., 2002; Harrad et al., 2003), the CPI for n-alkanes (odd to even ratio) was calculated as follows:

\[
\text{CPI} = \frac{\sum (C_{17} \text{ to } C_{33})}{\sum (C_{16} \text{ to } C_{32})}
\]  

(1)

and for n-alkanoic acids (even to odd ratio), as:
The CPI is an important indicator that is used to determine whether emissions come from natural or anthropogenic sources. For both \( n \)-alkanes and \( n \)-alkanoic acids, values of CPI > 1 indicate that hydrocarbons and carboxylic acids are emitted from natural sources. In contrast, values of CPI ≤ 1 (or close to one) indicate that they are emitted from anthropogenic sources (Gogou et al., 1996; Alves et al., 2001; Gelencsér, 2004).

Another useful indicator that is used to specify the origin of the emissions is the carbon number with maximum concentration \( (C_{\text{max}}) \). Hydrocarbons and carboxylic acids of high molecular weight (> C\text{25}) are emitted from biogenic sources, while those with lower molecular weight (≤ C\text{25}) are mainly emitted from fossil fuel combustion processes (Alves et al., 2001; Young and Wang, 2002; Gelencsér, 2004).

### 2.4.2 Diagnostic ratios of PAHs

Other indicators that have been used as markers of different source emissions of OA are the PAHs diagnostic ratios (DRs) (Dvorská et al., 2011; Katsoyiannis et al., 2011). The DRs calculated in this study are shown in Table 3. The values listed in this table can be found elsewhere (Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012).

### 2.5 Chemical Mass Balance model

The CMB is a single-sample receptor model that can be stated in terms of the contribution from \( p \) independent sources to all chemical species as follows:

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)
\]

where \( x_{ij} \) is the measured concentration of species \( j \) in sample \( i \), \( f_{kj} \) is the concentration of species \( j \) in the emissions of source \( k \), \( g_{ik} \) is the contribution of source \( k \) to sample \( i \), and \( e_{ij} \) is the model error. This model considers a prior knowledge of the source profiles and that the components of the source emissions do not undergo changes during their transport from the source to the receptor. CMB provides an effective variance-weighted least-squares solution to the over determined set of mass balance equations (Eq. 1). CMB takes into account the known...
uncertainties in the ambient measurements and the source emission data to minimize the chi-square ($\chi^2$) goodness-of-fit parameter for each sample $i$:

$$\chi^2 = \sum_{j=1}^{m} \left[ \frac{x_j - \sum_{k=1}^{p} g_{jk} f_k}{\sigma_{xj}^2 + \sum_{k=1}^{p} \sigma_{jk}^2 f_k} \right]$$

where $\sigma_{xj}$ is the standard deviation of the concentration of species $j$, $\sigma_{gjk}$ is the standard deviation of the $g_{jk}$, and $m$ the total number of species. The U.S. EPA-CMB8.2 software has been successfully used to apportion source contributions to ambient PM$_{2.5}$ (Ke et al., 2007; Stone et al., 2008; Watson et al., 2008; Kleeman et al., 2009; Schneidemesser et al., 2009; Yin et al., 2010; Perrone et al., 2012; Villalobos et al., 2015). More details about CMB can be found elsewhere (e.g., Henry et al., 1984; Watson et al., 2008).

### 2.6 Source profiles

The source profiles used in this work were taken from the most comprehensive studies available. The selection of the source profiles was based on previous source apportionment studies carried out for Mexican urban areas. Firstly, Stone et al. (2008) used CMB with organic molecular markers profiles to estimate contributions from gasoline- and diesel-powered vehicles, vegetative detritus and biomass burning in Mexico City. Secondly, Martinez et al. (2012) based on trace elements identified primary sources such as industrial sources, motor vehicle exhaust and biomass burning in the MMA. Finally, from these studies, seven primary source profiles were selected.

The source profile for gasoline- and diesel-powered vehicles were taken from Schauer et al. (2002) and Fraser et al. (2002), respectively. In the MMA, the gasoline vehicle fleet seems to be rather well maintained and of a recent model year, while diesel vehicle fleet is composed by heavy duty vehicle trucks and buses. Therefore, the profiles reported for catalyst-equipped gasoline-powered motor vehicles emissions and heavy duty trucks from dynamometer tests were used.

From evidence of industrial sources in Mexican urban atmospheres, a source profile for natural gas combustion and fuel oil combustion were taken from Rogge et al. (1993c) and Rogge et al. (1997), respectively.
Finally, source profiles for meat cooking operations, vegetative detritus, and biomass burning were taken from Schauer et al. (1999), Rogge et al. (1993b) and Schauer et al. (2001a), respectively. Most traditional restaurants activities of the region of study include meat charbroiling operations. For biomass burning, given the existence of softwood and hardwood sources in the region (Zurita, 2009), the softwood pine and hardwood oak profiles were used in this study. These last profiles were used separately because they are highly collinear. Regarding vegetative detritus, a source profile was included based on the contributions determined by Stone et al. (2008) in Mexico City along with the fact that the MMA is surrounded by rural areas with vast green covers. Therefore, it is possible to have an impact from transport of biogenic emissions.

For individual organic compound quantification, an uncertainty of ±20% of the measured concentration was used for all ambient samples and source profiles (Schauer et al., 2000; SRM 1649a, 2007; SRM 1649b, 2009; Fraser et al., 2003; Schantz et al., 2005). A detailed description of source profiles and settings used to perform the CMB in this study can be found in Fraser et al. (2003). For the current application, the fitting species for CMB included 20 organic compounds along with EC and overall OC. The molecular markers included seven n-alkanes (C27–C33), four petroleum biomarkers (17a(H),21b(H)-29-norhopane, 17a(H),21b(H)-hopane, 22R+S 17a(H),21b(H)-30-homohopane, and 22R+S 17a(H),21b(H)-30-bishomohopane), five polycyclic aromatic hydrocarbons (benzo[a]anthracene, benzofluoranthenes, benzo[a]pyrene, indeno[123-cd]pyrene and benzo[ghi]perylene), two saturated fatty acids (C16:0 and C18:0), cholesterol and levoglucosan.

3 Results and discussion

3.1 Resolved organic aerosols

The results for the chemical characterization of the fine organic aerosol for the MMA are summarized in Table S1. In this and other sections, averaged values for concentrations and other parameters are given ± one standard deviation. Most of the PM$_{2.5}$ daytime concentrations were 20% higher than nighttime concentrations. The concentrations of OC and EC were on average 32% higher during the daytime than the nighttime. In addition, the OC and EC accounted together for 28–49% and 46–55% of the PM$_{2.5}$ for spring and fall, respectively. In the spring, the daytime carbonaceous fraction was 1.6–1.8 times higher than the corresponding nighttime fraction, whereas during the fall, it was 1.1–1.2 times higher. The
average OC/EC ratios ranged from 7.4 to 12.6 during this study. A detailed information and analysis of the carbonaceous aerosol for this study can be found in Mancilla et al. (2015).

All the samples collected during this study were analyzed for eight organic compound classes except those samples collected in the spring of 2011 campaign, for which carboxylic acids, wood smoke markers, and nitro-PAH compounds were not included for the chemical analysis. Therefore, the overall contribution of the resolved organic compounds to OC in the spring of 2011 is not directly comparable to the last three campaigns. For the eight resolved compound classes in the last three campaigns (Fig. 2), the n-alkanoic acids were the most abundant, followed by n-alkanes, wood smoke markers, and levoglucosan/alkenoic acids. The PAHs and triterpanes hydrocarbons were less abundant. The same tendency was observed in the spring of 2011, except that the n-alkanes were the most abundant. The concentrations of nitro-PAH were neglected because their levels were below the detection limit of the method.

The daytime and nighttime concentrations of the resolved organics for the spring of 2011 accounted for 0.49±0.52% and 0.46±0.41% of the ambient OC, respectively. These contributions were much lower than the following three campaigns due to some compounds classes were not included. For spring 2012 and all fall campaigns, the total daytime concentrations of the resolved organics accounted for 7.58±4.89% and 2.64±1.82% to 4.67±1.76%, respectively, while the total nighttime concentrations accounted for 11.0±6.3% and 3.2±2.4% to 8.0±4.0%, respectively. These observations are consistent with the findings that typically, around 84% of the fine OC is either non-extractable or will not elute from the GC column (Schauer and Cass, 2000). In the following sections will be analyzed the organic composition of the fine organic aerosols using several diagnostic ratios to identify the primary emission sources. Then the relative contribution of each primary source to the PM$_{2.5}$ will be calculated by using the CMB receptor model.

### 3.2 n-Alkanes and Hopanes

The n-alkanes have two main sources: petroleum product utilization and natural vegetation waxes. The latter source consists of the longer chain plant lipids (>C$_{20}$) as n-alkanes (Simoneit and Mazurek, 1982). In this study, the n-alkanes in the range of C$_{17}$–C$_{33}$ were detected. For the samples obtained collected for the first year campaigns, spring 2011 and fall 2011, the average daytime and nighttime concentrations of n-alkanes were 1.6 and 2.3 times higher for the fall than the spring, respectively. This is consistent with the high contribution of the OC to
PM$_{2.5}$ and the lowest OC/EC ratios exhibited during the fall (Mancilla et al., 2015). In addition, the average temperature in the fall was 18.7–22.1°C versus 27.8–29.4°C in the spring. Low temperatures typically promote the utilization of petroleum products. In Mexico, the government sets the tariff-rates for the electric energy consumption with regard to the temperature; during the cold seasons the government removes the subsidy to the domestic electric energy due to the demand on fossil fuels in those seasons, and the sampling years of this study were not the exception (SENER, 2013). The average CPI values of n-alkanes in the spring were 1.5±0.3 (range: 1.1–1.9) in the daytime and 1.7±0.5 (range: 1.1–2.6) in the nighttime, while the CPI values in the fall were 1.0±0.3 (range: 0.7–1.2) in the daytime and 0.9±0.1 (range: 0.7–1.0) in the nighttime. The CPI values in the spring suggest the mixed contribution of anthropogenic and biogenic emissions sources, whereas those values in the fall indicated a dominance of anthropogenic emissions. In addition, the contribution of anthropogenic emission sources is confirmed by the presence of petroleum biomarkers (hopanes: range of 0.06 to 2.36 ng m$^{-3}$) and n-alkanes ≤ C$_{25}$ (Fig. 3). For the fall, the average daytime and nighttime concentrations of hopanes were 2.3 and 4.2 times higher than in the spring, respectively. Similarly, the presence of biogenic emissions due to $C_{max}$ was found at $C_{27}$, $C_{29}$, or $C_{31}$ (Fig. 3). These carbons’ number dominance and trace levels of hopanes are characteristics of plant wax emissions and urban traffic emissions, respectively (Standley and Simoneit, 1987; Cass, 1998; Simoneit et al., 2004). For the second sampling years, spring 2012 and fall 2012, the behavior of n-alkanes was the opposite of the first year 2011. The average daytime and nighttime concentrations of n-alkanes were 1.5 and 2.0 times higher in the spring than in the fall, respectively. The EC levels remained similar to those of the 2011 previous year, but the OC levels were higher during the fall 2012 increasing the OC/EC ratios. Some of these ratios exhibited high peaks suggesting a contribution from primary emission sources with elevated OC/EC ratios like biomass burning (Mancilla et al., 2015). The average temperature in the fall was 23.5–26.4°C versus 28.0–30.7°C in the spring. The average fall temperatures were not consistent with the average of the previous year 2011. In the fall of 2012, the warmer temperatures might have promoted less utilization of some fuels compared to the previous year 2011 in which lower temperatures could have promoted their utilization, increasing the n-alkanes’ concentrations in that fall 2011. The average CPI values of n-alkanes in the spring 2012 were 0.9±0.1 (range: 0.8–1.1) in the daytime and 1.2±0.1 (range: 1.2–1.3) in the nighttime, while the CPI values in the fall
2012 were 1.3±0.1 (range: 1.0–1.4) in the daytime and 1.5±0.2 (range: 1.3–1.6) in the nighttime. From these CPI values, it appears that biogenic emissions are relevant in all sampling periods. For spring 2012 daytime, the emissions appear to be heavily dominated by anthropogenic emissions due to the low CPI value exhibited. The presence of petroleum biomarkers supports the relative contribution of anthropogenic emissions. However, in 2012 the hopanes levels were ~35% lower at daytime and ~43% lower at nighttime than those in the previous year. The low hopane levels (range of 0.10 to 1.49 ng m⁻³) highlight the possible presence of biogenic emissions (Fig. 2).

3.3 PAHs

Twelve PAH compounds, fluoranthene (FLT), acephenanthrylene (ACE), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CRY), benzo(k)fluoranthene + benzo(b)fluoranthene (BFA), Benzo(a)pyrene + Benzo(e)pyrene (BaP+BeP), perylene (PER), indeno(123cd)pyrene (IP), benzo(ghi)perylene (BgP), dibenz(ah)anthracene (DaA), and coronene (Cor), were identified in the MMA fine OC samples. For both sampling years, the average daytime and nighttime concentrations of PAHs were 1.4–5.9 and 1.4–2.4 times higher in the fall than in the spring, respectively. This is consistent with the high contribution of the OC to the PM₂.₅ during the falls. Independently of the season, the daytime concentrations were 1.3–1.6 times higher than nighttime concentrations. These seasonal differences are consistent with the results of Guo et al. (2003) and Li et al. (2006), where PAH levels were 2–4 and 14.4 times higher in the cold seasons than in the warm seasons, respectively.

As illustrated by Fig. 4, the high molecular weight (HMW) PAHs were the most abundant for the MMA. The presence of HMW PAHs such as BaP+BeP, IP, and BgP is an indication of gasoline-powered vehicle emissions (Katsoyiannis et al. 2011; Tobiszewski and Namieśnik, 2012). In addition, a possible contribution of diesel-powered vehicles is indicated by the low concentrations of the low molecular weight (LMW) PAHs such as FLT, PYR, and CRY. To identify the emission sources of PAH, diagnostic ratios were calculated (Table 4). These ratios should be used with caution due to PAHs are emitted from a variety of emission sources, particularly combustion sources, and their profiles can be modified due to their reactivity (Tsapakis et al., 2002). From these ratios, it can be determined the source origin (e.g. pyrogenic and petrogenic sources). Then, these qualitative conclusions will be considered for the source apportionment to estimate the relative contribution of primary emission sources.
The average ratios of IP/(IP+BgP) indicate that ambient PAHs in the MMA originated from gasoline and diesel combustion, whereas the ratios of BAA/(BAA+CRY) show the presence of petrogenic sources as well as vehicle emissions. To complement these results, the ratios of (BaP+BeP)/BgP identified a marked contribution of non-traffic sources for the spring of 2011, traffic source for the fall of 2011 and the spring of 2012, and mixed-sources for the fall of 2012. Presence of gas-phase PAHs was not evaluated and thus no information on gas/particle partitioning of these semivolatile species is available. Thus, only diagnostic ratios for HMW PAHs were calculated for this study because those PAHs exhibit low volatility (Kavouras et al, 1999).

In this study, the average total concentrations of the quantified PAHs (TPAHs) were 2.42±2.45 ng m⁻³ (range: 0.65–8.31 ng m⁻³) and 4.11±2.62 ng m⁻³ (range: 1.42–11.97 ng m⁻³) during 2011 and 2012, respectively, whilst those quantified by González-Santiago (2009) at two different sites in the MMA were 1.30±1.64 ng m⁻³ (range: 0.05–6.93 ng m⁻³) and 1.70±1.88 ng m⁻³ (range: 0.07–9.14 ng m⁻³). The lowest concentrations were obtained during the spring because its average temperature was statistically higher than during the fall seasons (p<0.05). The volatility of PAH increases with temperature; as a result low concentrations are obtained in comparison with fall and winter seasons. For this study the concentrations of PAH were lower during the spring than concentrations during fall; this pattern was exhibited during the two sampling years. González-Santiago (2009) identified only six PAHs, while in this study were identified twelve. In the current study, the total concentrations calculated for the six common PAHs were from 3 to 8 times higher than those estimated by González-Santiago (2009). Similar concentrations (between 0.04 ng/m³ and 1.78 ng/m³) were also reported for six individual PAHs in urban samples collected in Mexico City (Stone et al., 2008). Of the same PAHs identified among these studies, their levels were in the same concentration range.

However, the TPAH levels in the MMA compared to those calculated by Marr et al. (2006) (20–100 ng m⁻³) in Mexico City were found at appreciably lower concentrations. In addition, Marr et al. (2006) suggest that vehicles are the major source of PAHs. They demonstrated that PAHs and carbon monoxide (CO) concentrations are well correlated in Mexico City and, given that 99% of CO emissions are emitted by motor vehicles, this source is a major contribution of PAH emissions. For the current study, daytime correlations ($r^2$) of 0.56–0.60+0.76 ($p \leq 0.054$) were found between TPAH and CO, reinforcing the conclusion that
motor vehicles are one major source of PAH emissions for the MMA. The concentrations of CO during this study were obtained from the SIMA network.

The total PAH (TPAH) concentrations were compared with the EC and OC levels. TPAH concentrations measured in the MMA exhibited fair daytime correlations with EC ($r^2 = 0.60 - 0.67 + 0.79; p < 0.05$), but low correlations with OC ($r^2 = 0.11 - 0.66 + 0.57; p > 0.05$). According to Marr et al. (2004), the strong correlation between TPAH and EC indicated the relative contribution of diesel-powered vehicle exhaust, while weak correlations may be due to the low concentrations of EC determined during this study (Mancilla et al., 2015). Furthermore, the weak correlation between TPAH and EC suggests the presence of emission sources with an elevated OC/EC. With regard to OC, the weak correlation was an indicator that other non-combustion sources exist.

### 3.4 Carboxylic acids $n$-Alkanoic acids

The carboxylic acids or $n$-alkanoic acids are mainly derived from biogenic emissions (Rogge et al., 1993b). However, these acids have also been identified in several primary sources such as cooking operations (Rogge et al., 1991; Schauer et al., 2001b) and fossil fuel combustion (Schauer et al., 2002). The $n$-alkanoic acids from C$_{10}$ to C$_{32}$ were identified quantified only for the three last monitoring campaigns. The $n$-alkanoic acids were the most abundant, accounting for 69±16% at daytime and 78±11% of the total resolved organics at nighttime for both spring and fall. The daytime and nighttime concentration levels were two times higher in the spring than in the fall. As can be seen in Fig. 5, the $n$-alkanoic acids measured in the MMA were dominated by hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid). This dominance is consistent with measurements in other locations (Fraser et al., 2002; Simoneit 2004; Li et al., 2006).

The average CPI values of $n$-alkanoic acids in the fall of 2011 were 4.3±1.0 (range: 3.3–5.3) during the day and 5.0±0.4 (range: 4.6–5.4) at night. For the second sampling the 2012 year the CPI values in the spring were 3.6±0.6 (range: 2.9–4.5) during the day and 4.7±0.8 (range: 3.9–5.8) at night, while the CPI values in the fall were 4.7±0.3 (range: 4.3–5.1) during the day and 5.3±1.1 (range: 4.0–6.8) at night. These elevated CPI values indicated the significant influence of biogenic sources such as microbial and plant wax sources. The $n$-alkanoic acids $<C_{20}$ are derived in part from microbial sources while those $>C_{20}$ are from vascular plant waxes (Guo et al., 2003; Yue and Fraser, 2004; Simoneit et al., 2004). Fig. 5 clearly shows
influence of long chain (>C20) plant wax particles for the MMA. The CPI values in this study were consistent with those obtained by Wang and Kawamura (2005) (CPI: 5.3–10) and Yue and Fraser (2004) (CPI: 3.2–11.2). Regardless of the elevated CPI values obtained for the MMA, the values were not as high as those reported by the other mentioned studies due to a scarcity of green vegetation covers in the MMA.

The n-alkenoic acids only included the cis-9-Octadecenoic acid (oleic acid) and trans-9-octadecenoic acid (elaidic acid). The concentrations of cis-9-Octadecenoic acid oleic acid ranged from 0.96 ng m⁻³ to 15.38 ng m⁻³, while the concentrations of trans-9-octadecenoic acid elaidic acid ranged from 2.11 ng m⁻³ to 13.35 ng m⁻³. The ratio of octadecanoic acid (C18:0) to cis-9-Octadecenoic acid oleic acid (C18:1) has been used as an indicator of the atmospheric chemical processing (aging) of aerosols, since the unsaturated acids are susceptible to atmospheric oxidation from gaseous precursors (Brown et al., 2002; Yue and Fraser, 2004). In this study, the average ratios of C18:0/C18:1 were 5.0 (range: 1.5–9.4) during the day and 3.8 (range: 2.5–4.9) at night for the spring, while 20.3 (range: 4.7–38.6) during the day and 21.0 (range: 10.5–29.1) at night for the fall. The transport of aerosols from local and rural sources can lead to the loss of cis-9-Octadecenoic acid oleic acid, producing high octadecanoic acid to cis-9-Octadecenoic acid C18:0/C18:1 ratios. By contrast, the stagnation of aerosols may reflect the impact of high oxidant concentrations in an urban atmosphere producing low C18:0/C18:1 ratios (Brown et al., 2002; Yue and Fraser, 2004). Therefore, these ratios suggest that the ambient organic aerosols for the MMA were aged and might be produced from transport and atmospheric oxidation. Air circulation patterns (Hysplit backward trajectories) during these monitoring campaigns suggested a long-range transport from the northeast and southeast (Mancilla et al., 2015). As expected, the lowest and highest octadecanoic acid to cis-9-Octadecenoic acid ratios of C18:0/C18:1 obtained for the MMA were consistent with the highest OC/EC ratios estimated for the MMA for the same campaign; high OC/EC ratios identified transport and stagnation scenarios for the spring and fall, respectively (Mancilla et al., 2015). In addition, these results are in line with those reported by Brown et al. (2002) and Yue and Fraser (2004), who obtained C18:0/C18:1 ratios of 5–11 and 1.0–21.5, respectively.

In addition, a minor biogenic contribution can be identified by the presence of terpenoic acids such as cis-pinonic acid and pinic acid. These acids are known to be a secondary, particle-phase product of pinene, which is emitted from plants, particularly conifers (Plewka et al.,
2006; Sheesley et al., 2004). The pinonic acid and pinic acid exhibited higher concentrations in the spring than in the fall (Table S1), indicating biogenic emissions from softwood sources.

### 3.5 Meat cooking and biomass burning tracers

The major tracers for meat cooking particles are the steroids, while for biomass burning are the anhydrosaccharides and methoxyphenols. All of these organic tracers were intermittent in only 80% of the total OA samples/composites collected during this study.

There was not a clear trend between spring and fall samples during the two sampling years for steroids (Table S1). However, the evidence of cooking operations’ impact on the MMA was confirmed by the presence of cholesterol and stigmasterol along with hexadecanoic acid, octadecanoic acid, and oleic acid. Although cholesterol is considered a good marker for meat cooking, studies have reported unexpectedly high levels of cholesterol from non-cooking related sources such as soil and prescribed burns (Sheesley et al., 2004; Lee et al., 2005; Robinson et al., 2006a).

Anhydrosaccharides are the tracers from burning cellulose and hemicelluloses, whereas the methoxyphenols the tracer from burning of lignin (Giri et al., 2013). Levoglucosan, a combustion and pyrolysis product of cellulose, is the main biomarker used to track biomass burning emissions (Schauer et al., 2001a). Levoglucosan was not detected in all collected samples. The levoglucosan found in the OC samples indicates that biomass burning is impacting the MMA to some extent (Table S1). The levoglucosan concentrations varied by sampling dates, ranging from not detectable levels to 54 ng m$^{-3}$ for spring. In contrast, levoglucosan was detected in all fall samples, ranging from 0.14 to 28 ng m$^{-3}$. The intermittent peaks of levoglucosan concentrations during the springtime can be explained by the fact that Northeastern Mexico’s atmosphere is highly influenced by forest wildfires and prescribed agricultural burnings during the spring (Mendoza et al., 2005); this is in line with the idea that high OC/EC ratios obtained, in a parallel study, were influenced in part by regional transport emissions (Mancilla et al., 2015). In the case of fall seasons, the levoglucosan levels can be associated with local biomass burning due to mild temperatures exhibited during these seasons; a local contribution can be associated with high OC/EC ratios and stagnation conditions determined for this period (Mancilla et al., 2015). The high OC/EC ratios during spring may have a contribution from primary sources with elevated OC/EC.
ratios. The low and variable levoglucosan concentrations in this study indicate that
wood/vegetation smoke episodes were occasional at the urban site. Average levoglucosan
concentrations of 112.9 ng m\(^{-3}\) and 151.3 ng m\(^{-3}\) were reported at urban and peripheral sites
for Mexico City, respectively (Stone et al., 2008). Based on an average concentration of
levoglucosan, Mexico City exhibited from 5 to 7 times higher levels than the MMA. These
results are consistent with the concentrations of OC and EC obtained in the Mexico City; the
EC concentrations were up to two times higher than those calculated in the MMA, whereas
the OC concentrations were from 2 to 6 times higher. A study conducted in Houston, TX,
during August-September reported elevated concentrations of levoglucosan: up to 234 ng m\(^{-3}\)
(Yue and Fraser, 2004). Similarly, a study conducted for 14 cities in China during summer
and winter, also reported elevated levoglucosan concentrations of 259 ng m\(^{-3}\) (Wang et al.,
2006). However, in those studies the vegetation around the sampling sites included a vast
number of parks and woody shrubs, suggesting a major biomass burning contribution contrary
to the MMA. Apart from those studies, Zheng et al. (2002) reported elevated levoglucosan
concentrations of 166–307 ng m\(^{-3}\) for urban areas of similar surroundings to the MMA. In this
case, it is also possible that the levoglucosan emissions reported come from industries that
have implemented biomass burning processes for energy generation. As can be seen from the
previous comparison, the contribution of biomass burning is minor for the MMA in
comparison with other urban locations. In addition, biomass burning contributions are
inconsistent with those reported in similar locations to the MMA.

The resin acids such as dehydroabietic acid, pimaric acid, and isopimaric acid (Table S1) are
secondary tracers from biomass burning (Schauer et al., 2001a). Dehydroabietic acid was the
most abundant resin acid, ranging from 1.94 to 4.39 ng m\(^{-3}\) and 1.95 to 3.69 ng m\(^{-3}\) for spring
and fall, respectively. Then, pimaric acid ranged from not detectable levels to 0.09 ng m\(^{-3}\) and
from 0.15 to 0.35 ng m\(^{-3}\) for spring and fall, respectively. Finally, isopimaric acid ranged
from not detectable levels to 0.03 ng m\(^{-3}\) and from 0.06 to 0.12 ng m\(^{-3}\) for spring and fall,
respectively. The results for resin acids are in line with those obtained for the levoglucosan.

These results support the low impact from biomass burning emissions in the MMA, especially
from softwood burning (e.g., conifer wood) during the spring and fall campaigns. In addition,
the higher concentrations of resin acids in fall than in spring are associated with
photochemical activity due to Stagnation events in fall. (Table S1), indicating softwood
burning (e.g., conifer wood) during the spring and fall campaigns in the MMA.
3.6 Source Apportionment

CMB was applied using the quantification of individual organic compounds found in the collected PM$_{2.5}$ samples. The relative contributions for gasoline-powered vehicles, diesel-powered vehicles, natural gas combustion, fuel oil combustion, meat cooking operations, vegetative detritus, and biomass burning were estimated. From the source categories selected, the ones corresponding to natural gas and fuel oil combustion were not determined as significant for some ambient samples. These two sources were determined to have contributions that were not statistically different from zero or were slightly negative and thus were excluded from the model. Model performance was determined by $r^2$ values ranging between 0.58 and 0.85 and chi-squared ($\chi^2$) values between 2.97 and 8.85. Similar values for $r^2$ and $\chi^2$ have been obtained in Fraser et al. (2003) and Schneidemesser et al. (2009). The latter study used composites to perform the CMB. Another performance metric calculated by EPA-CMB8.2 is the percent mass explained. Theoretically, values ranging from 80% to 120% are acceptable. This ideally can occur when ambient data is not impacted heavily by SOA because CMB is only able to account accurately for primary sources. In spite of this limitation, CMB results with low percent mass explained values have been reported by some studies. In these cases, the high levels of unexplained mass have been associated with secondary production (Fraser et al., 2003; Zheng et al., 2005). For the 43 ambient samples fed to CMB in this study, 18 samples exhibited low percent mass explained values (ranging from 20% to 77%), whilst 14 samples had values around 100%. These results are in line with the relative high and low OC/EC ratios obtained for spring and fall, respectively Mancilla et al. (2015). The rest of the samples were discarded due to poor performance parameters calculated. These samples were not exclusively from a particular monitoring campaign; there were samples from both springs and falls. A detailed description of the CMB performance and relative contributions for each sample can be found in Table S2.

The average contributions of primary sources are shown in Table 5. The vehicle exhaust and meat-cooking operations emissions for all monitoring campaigns were the highest. In analysis of the seasonal variation, the gasoline- and diesel-powered vehicles in falls were up to five times higher than in springs, when cold weather increases the demand of petroleum products due to low temperatures. The opposite occurred for meat-cooking operations, their spring
emissions were three times higher than in fall seasons. The natural gas combustion, vegetative detritus and biomass burning emissions were very low and more constant throughout the springs and falls. In analysis of the daytime and nighttime variations, the vehicle exhaust were much higher during daytime when traffic is heavier. For the meat-cooking operations, the emissions were some higher in nighttime during spring and more constant between daytime and nighttime during fall. For the rest of the sources, the daytime and nighttime emissions were relatively constant. There are not similar studies conducted in the MMA, this is the first source apportionment study based on molecular organic markers for this region. However, these results were similar to those obtained for the MMA using a factor analysis based on trace elements (Martinez et al., 2012) and those for the Mexico City based on molecular organic markers (Stone et al., 2008).

The average contribution of each emission category to the identified PM$_{2.5}$ mass is shown in Fig. 6. The unidentified mass was on average 35±24% of the measured PM$_{2.5}$ concentrations. This value is 1.5 times greater than the ∼23% of secondary organic aerosol contribution to the total PM$_{2.5}$ mass concentration (SOC/PM$_{2.5}$) estimated in Mancilla et al. (2015) for the MMA. The average secondary contribution used for this comparison was based on the minimum OC/EC ratios observed and reported in Mancilla et al. (2015). These ratios may take into account primary sources with elevated values of OC/EC ratios such as biomass burning and kitchen operations as well as fossil fuel combustion sources. The unidentified mass by CMB may include secondary organic and inorganic aerosol and trace elements. Thus, the levels of unidentified mass resolved by CMB are reasonable given that the secondary aerosol estimated in Mancilla et al. (2015) was in fact only SOA. Therefore, the 12% of difference between 35% and 23% might be attributed to the secondary inorganic aerosol and other chemical species. As indicated in Fig. 6, the emissions from motor vehicle exhausts (gasoline and diesel) are the most important, accounting for the 64% of the identified PM$_{2.5}$ emissions, followed by meat-cooking operations (31%) and industries (2.8%). The vegetative detritus and biomass burning were the less emitted with only 2.2% of the identified PM$_{2.5}$ emissions. The relative high contribution of the meat-cooking operations was expected given the high traditional restaurant activity in the MMA which contribute with the 16% of the local growth domestic product. The MMA as well as other urban areas can be affected by types of biomass burning, especially, when they are not surrounded by forests. For examples, several studies have demonstrated that Mexico City has large contribution from biomass burning (Moffet et al., 2008; Stone et al., 2008; Yokelson et al., 2007) because it is affected by forests fires.
Conversely, the MMA has not forests around, therefore, the contribution from biomass burning in the MMA might be higher because the source profile used for the CMB was only for wood combustion instead of using a source profile for garbage, industrial, and urban residues open fires (Simoneit et al., 2005). In addition, it is important to point out the potential of industrial sources due to prior studies conducted in the MMA and the rest of the country. The MMA is the third largest urban center of the country with approximately 9,700 industries (INEGI, 2005). In the MMA the main emissions from industrial sources come from the combustion of natural gas; low emissions come from the use of fuel oil. In this study the natural gas profile did not fit well and it was discarded from the CMB, but the fuel oil did it. The combustion of natural gas emits low amount of particles, therefore, its contribution to the airborne particles is not significant.

4 Conclusions

Spring and fall sampling campaigns were performed in 2011 and 2012 at one representative site to conduct a chemical characterization of the fine OC in PM$_{2.5}$ in the MMA. The identified organic compound classes represented a low fraction of the ambient OC: 0.5% for spring 2011 and 2.6 to 11% for the last three campaigns. The average CPI values derived from the $n$-alkanes (0.9–1.7) and $n$-alkanoic acids (2.9–6.8) demonstrated that anthropogenic (e.g., fossil fuel combustion) were dominant while biogenic (e.g. plant waxes, microbial origin) emission sources contribute at least some times to the fine OA in the MMA.

The PAH diagnostic ratios indicate that gasoline- and diesel-powered vehicles are the main emission sources of this class of organic compounds in PM$_{2.5}$. However, other pyrogenic sources such as coal, grass, and wood combustion were also identified as contributors to the fine OA. The quantified levels of cholesterol and levoglucosan confirm the high and low, but noticeable contribution of cooking operations and biomass burning, respectively. Low levoglucosan concentrations suggest low episodic or transport effects of emissions of biomass burning on PM$_{2.5}$ in the MMA.

In a parallel study, significant SOA formation was found in the MMA. The chemical speciation of the OC confirmed the aging of primary emissions and the SOA from biogenic volatile organic compounds. On one hand, the identified octadecanoic acid (C18:0) and cis-9-Octadecenoic acidoleic acid (C18:1) along with other secondary organic markers point out the SOA formation in the MMA atmosphere. The average ratios of octadecanoic acid to cis-9-
Octadecenoic acid C\textsubscript{18}:0/C\textsubscript{18}:1 (3.8–21) indicate aging of the fine OA due to photochemical activity and transport. On the other hand, the presence of the cis-pinonic and pinic acids confirmed the SOA derived from biogenic sources. This is in line with the transport and stagnation events that predominated during spring and fall, respectively.

The emissions from vehicle exhausts are the most important, accounting for the 64% of the identified PM\textsubscript{2.5} emissions. By contrast, the vegetative detritus and biomass burning were the less contributors with barely 2.2% of the identified PM\textsubscript{2.5} emissions.

Finally, the outcomes of a comparison with other studies were that the MMA exhibits similar concentrations patterns of the organic molecular markers identified in this study.

**Acknowledgements**

This work was supported by the Mexican National Council for Science and Technology (CONACYT) through grant number CB-2010-154122 and Tecnológico de Monterrey through grant number 0020CAT186. Yasmany Mancilla received additional support (a scholarship) through CONACYT. We appreciate the Integral System of Environmental Monitoring’s support of the MMA during the field campaigns conducted in this study.

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Table 1. Monitoring experiments conducted for this study.

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<td>2</td>
</tr>
<tr>
<td>Fall 2011</td>
<td>October 22 to November 3</td>
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\(^a\) Non-consecutive days.
Table 2. Characteristics of individual and composite samples for each monitoring campaign.

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<th>Dates included</th>
<th>PM$_{2.5}$ ($\mu g \ m^{-3}$)</th>
<th>SD</th>
<th>OC ($\mu g \ m^{-3}$)</th>
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<td>□ 10.8</td>
<td>1.0</td>
<td>5.3</td>
<td>0.6</td>
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1 Values in curly brackets are the mass ranges for the mass of OC collected per filter included.
2 Values for PM$_{2.5}$ are the averages obtained from the SIMA network. OC concentration values are the average values reported by Mancilla et al. (2015). SD represents standard deviation. I indicates that dates included were analyzed individually. C indicates that dates included were pooled to form a composite.
sampling, D represents daytime sampling, N represents nighttime sampling, 1 refers to weekday sampling, 2 refers to weekend sampling.

Table 3. PAH diagnostic ratios for different source categories (Katsoyiannis et al., 2011; Tobiszewski and Namieśnik, 2012).

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<th>Diagnostic Ratio</th>
<th>Value</th>
<th>Source</th>
<th>Reference</th>
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<td>Petrogenic</td>
<td>Katsoyiannis et al., 2011</td>
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<td>&gt; 0.20</td>
<td>Pyrogenic</td>
<td>Katsoyiannis et al., 2011</td>
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<td></td>
<td>0.20–0.50</td>
<td>Gasoline and diesel Petroleum</td>
<td>Yunker et al., 2005</td>
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<tr>
<td></td>
<td>&gt; 0.50</td>
<td>Coal, grass, and wood combustion</td>
<td>Yunker et al., 2005</td>
</tr>
<tr>
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<td>0.20–0.35</td>
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<td>Coal, grass, and wood combustion</td>
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<td></td>
<td>&gt; 0.40</td>
<td>Pyrogenic</td>
<td>Katsoyiannis et al., 2011</td>
</tr>
<tr>
<td></td>
<td>0.40–0.50</td>
<td>Gasoline and diesel Fuel</td>
<td>Katsoyiannis et al., 2011</td>
</tr>
<tr>
<td></td>
<td>&gt; 0.50</td>
<td>Coal, grass, and wood combustion</td>
<td>Ravindra et al., 2008</td>
</tr>
<tr>
<td>(BaP+BeP)/BgP</td>
<td>&gt; 0.60</td>
<td>Traffic</td>
<td>Katsoyiannis et al., 2011</td>
</tr>
<tr>
<td></td>
<td>&lt; 0.60</td>
<td>Non-traffic</td>
<td>Katsoyiannis et al., 2011</td>
</tr>
</tbody>
</table>

The PAH abbreviations are IP: Indeno(123cd)pyrene, BgP: Benzo(ghi)perylene, BAA: Benz(a)anthracene, CRY: Chrysene, FLT: Fluranthene, PYR: Pyrene, BaP: Benzo(e)pyrene, BaP: Benzo(a)pyrene.
Table 4. Average diagnostic ratios of PAHs in MMA

<table>
<thead>
<tr>
<th>Season</th>
<th>Period</th>
<th>IP/(IP+BgP)</th>
<th>BAA/(BAA+CRY)</th>
<th>FLT/(FLT+PYR)</th>
<th>(BaP+BeP)/BgP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring 2011</td>
<td>D</td>
<td>0.41±0.05</td>
<td>0.34±0.28</td>
<td>0.50±0.03</td>
<td>0.19±0.24</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.46±0.02</td>
<td>0.62±0.30</td>
<td>0.49±0.10</td>
<td>0.07±0.06</td>
</tr>
<tr>
<td>Fall 2011</td>
<td>D</td>
<td>0.35±0.10</td>
<td>0.50±0.03</td>
<td>0.55±0.12</td>
<td>2.67±0.75</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.51±0.26</td>
<td>0.17±0.29</td>
<td>0.66±0.25</td>
<td>4.63±4.49</td>
</tr>
<tr>
<td>Spring 2012</td>
<td>D</td>
<td>0.33±0.13</td>
<td>0.01±0.003</td>
<td>0.72±0.20</td>
<td>4.48±2.19</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.47±0.34</td>
<td>0.06±0.12</td>
<td>0.89±0.02</td>
<td>10.40±2.45</td>
</tr>
<tr>
<td>Fall 2012</td>
<td>D</td>
<td>0.34±0.04</td>
<td>0.35±0.07</td>
<td>0.60±0.06</td>
<td>0.55±0.08</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.36±0.02</td>
<td>0.40±0.09</td>
<td>0.68±0.05</td>
<td>0.52±0.13</td>
</tr>
</tbody>
</table>

D represents daytime, N represents nighttime

Table 5. Contributions and uncertainty of primary sources to seasonal average ambient PM$_{2.5}$ for daytime and nighttime in the MMA (in µg m$^{-3}$)

<table>
<thead>
<tr>
<th>Source category</th>
<th>Spring 2011</th>
<th>Fall 2011</th>
<th>Spring 2012</th>
<th>Fall 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Daytime</td>
<td>Nighttime</td>
<td>Daytime</td>
<td>Nighttime</td>
</tr>
<tr>
<td>Gasoline-powered vehicles</td>
<td>2.37 ± 0.56</td>
<td>2.46 ± 0.46</td>
<td>3.70 ± 0.78</td>
<td>2.24 ± 0.51</td>
</tr>
<tr>
<td>Diesel-powered vehicles</td>
<td>7.34 ± 0.86</td>
<td>3.81 ± 0.53</td>
<td>13.67 ± 1.59</td>
<td>13.10 ± 1.55</td>
</tr>
<tr>
<td>Vegetative detritus</td>
<td>0.22 ± 0.04</td>
<td>0.22 ± 0.04</td>
<td>0.13 ± 0.03</td>
<td>0.27 ± 0.05</td>
</tr>
<tr>
<td>Meat-cooking operations</td>
<td>8.24 ± 1.54</td>
<td>11.13 ± 1.85</td>
<td>3.26 ± 0.71</td>
<td>3.86 ± 0.71</td>
</tr>
<tr>
<td>Natural gas combustion</td>
<td>0.01 ± 0.01</td>
<td>N.I.</td>
<td>0.05 ± 0.03</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.20 ± 0.05</td>
<td>0.17 ± 0.05</td>
<td>0.17 ± 0.05</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>Fuel oil combustion</td>
<td>N.I.</td>
<td>N.I.</td>
<td>4.18 ± 3.55</td>
<td>3.60 ± 1.20</td>
</tr>
</tbody>
</table>

N. I. means Not Important. * samples were discarded due to poor CMB performance.
Figure 1. Location and municipalities of the Monterrey Metropolitan Area (MMA); the sampling site was set up in the downtown.
Figure 2. Concentrations of the resolved organic compound classes in the MMA. For (a) the $n$-Alkanoic and Alkenoic acids and wood smoke tracer were not included in the chemical analysis. For (b), (c) and (d) the $n$-alkanoic acids are divided by a factor of 10.
Figure 3. Carbon number distribution of $n$-alkanes in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. The black line is the daytime concentrations while the dot line is the nighttime concentrations.
Figure 4. Mass concentration distribution of PAHs in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. Coronene was included in all monitoring campaigns, except in the spring 2011.
Figure 5. Carbon number distribution of $n$-alkanoic acids in the Monterrey Metropolitan Area (MMA) for (a) fall 2001, (b) spring 2012 and (c) fall 2012. The black line represents the daytime concentrations while the dot line represents the nighttime concentrations.
Figure 6. CMB contributions to the (a) average identified ambient PM$_{2.5}$ in the Monterey Metropolitan Area MMA and to the (b) overall PM$_{2.5}$ including the unidentified mass on average 35\% of the measured PM$_{2.5}$ concentrations. This percentage include SOA, trace metals and other OC.