

Interactive comment on “Chemical characterization of fine organic aerosol for source apportionment at Monterrey, Mexico” by Y. Mancilla et al.

Y. Mancilla et al.

y.mancilla@itesm.mx

Received and published: 20 November 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.

C9567

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 ug m⁻³)"

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

C9568

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 "non-combustion 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

C9569

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 PM_{2.5} 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, 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

C9570

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 PM_{2.5} 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.

C9571

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:

Moffet, R. C., de Foy, B., Molina, L. T., Molina, M. J., and Prather, K. A.: Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry, *Atmos. Chem. Phys.* 4499-4516, 2008.

Simoneit, B. R. T., Medeiros, O. M., and Didyk, B., M.: Combustion products of plastics as indicators for refuse burning in the atmosphere, *Environ. Sci. Technol.* 39, 6961-6970, 2005.

Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C., Crouse, 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 Mexico City, *Atmos. Chem. Phys.*

C9572

5569-5584, 2007.

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:

Watson, J. G, Chow, J. C., Lowenthal, D. H., Antony Chen, L.-W., Shaw, S., Edgerton, E. S., and Blanchard, C. L.: PM2.5 source apportionment with organic markers in the southeastern aerosol research and characterization (SEARCH) study, *J. Air Waste Manage. Assoc.*, 65, 1104-1118, 2015.

Zheng, M., Cass, G. R., Ke, L., Wang, F., Schauer, J. J., Edgerton, E. S., and Russell, A. G.: Source apportionment of daily fine particulate matter at Jefferson Street, Atlanta, GA, during summer and winter, *J. Air Waste Manage. Assoc.*, 57, 228-242, 2015.

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;

C9573

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:

Antony Chen, L.-W., Watson, J. G., Chow, J. C., DuBois, D. W., and Herschberger, L.: PM2.5 source apportionment: reconciling receptor models for U. S. nonurban and urban long-term networks, *J. Air Waste Manage. Assoc.* 61, 1204-1217, 2011.

Kelly, K. E., Kotchenruther, R., Kuprov, R., and Silcox, G. D.: Receptor model source attributions for Utah’s Salt Lake City airshed and the impacts of wintertime secondary ammonium nitrate and ammonium chloride aerosol, *J. Air Waste Manage. Assoc.* 63, 575-590, 2015.

Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere, *Atmos. Environ.* 33, 2715-2724, 1999.

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

Nozière, 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-Kreis, J., Surratt, J. D., Szidat, Sönke, Szmigielski, R., and Wisthalder, A.: The molecular identification of organic compounds in the atmosphere: state of the art and challenges, *Chemical Reviews*, 115, 3919-3983, 2015.

Paatero, P.: Least squares formulation of robust non-negative factor analysis. *Chemometr. Intell. Lab.*, 37, 23-35, 1997.

Reff, A., Eberly, S. I., and Bhave, P. V.: Receptor modeling of ambient particulate

C9574

matter data using positive matrix factorization: review of existing methods, *J. Air Waste Manage. Assoc.* 57, 146-154, 2007.

Wold, S., Sjöström, M., and Eriksson, L., 2001. PLS-regression: a basic tool of chemometrics. *Chemometr. Intell. Lab.* 58, 109-130.

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:

C9575

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 of organic compounds present in particulate material. In this review, was mentioned that has been recently organized an interlaboratory comparison within

C9576

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 $\pm 20\%$ 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:

Fraser, M. P., Yue, Z. W., Tropp, R. J., Kohl, S. D., and Chow, J. C.: Molecular composition of organic fine particulate matter in Houston, TX, *Atmos. Environ.*, 36, 5751–5758, 5 doi:10.1016/s1352-2310(02)00725-2, 2002.

García, C.D., Engling, G., Herckes, P., Collett, J.L., and C. S. Henry, Determination of Levoglucosan from Smoke Samples Using Microchip Capillary Electrophoresis with Pulsed Amperometric Detection, *Environmental Science and Technology*, 39, 618-623, 2005.

Nozriere, 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., Kourttchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, Sönke, Szmigielski, R., and Wisthalder, A.: The molecular identification of organic compounds in the atmosphere: state of the art and challenges, *Chemical Reviews*, 115, 3919-3983, 2015.

Schantz, M., Poster, D., Kucklick, J., Wise, S., McDow, S., Lewtas, J.: NISTIR 7303, Intercomparison program for organic speciation in PM_{2.5} air particulate matter: description and results for trial III. NIST, 2005.

C9577

Schauer, J. J., and Cass, G. R.: Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environ. Sci. Technol.* 34, 1821-1832, 2000.

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:

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, 25, 1112-1125, doi: 10.1021/es00018a015, 1991.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and Heavy-duty diesel trucks, *Environ. Sci. Technol.*, 27, 636-651, 1993a.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants, *Environ. Sci. Technol.*, 27, 2700-2711, doi: 10.1021/es00049a008, 1993b.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Sources of fine organic aerosol. 5. Natural gas home appliances, *Environ. Sci.*

C9578

Technol., 27, 2736-2744, 1993c.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Sources of fine organic aerosol. 6. Cigarette smoke in the urban atmosphere, Environ. Sci. Technol., 28, 1375-1388, 1994.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil, Environ. Sci. Technol., 31, 2731-2737, 1997.

Schantz, M., Poster, D., Kucklick, J., Wise, S., McDow, S., Lewtas, J.: NISTIR 7303, Intercomparison program for organic speciation in PM_{2.5} air particulate matter: description and results for trial III. NIST, 2005.

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)

Schauer, J. J. and Cass, G. R.: Source apportionment and particle-phase air pollutants using organic compounds as tracers, Environ. Sci. Technol., 34, 1821-1832, 2000.

Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.: Source apportionment of airborne particulate matter using organic compounds as tracers, Atmos. Environ., 30, 3837-3855, 1996.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 1. C₁ through C₂₉ organic compounds from meat charbroiling, Environ. Sci. Technol., 33, 1566-1577, 1999.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 3. C₁–C₂₉ Organic Compounds from Fireplace Combustion of Wood, Environ. Sci. Technol., 35, 1716-1728. doi: 10.1021/es001331e,

C9579

2001a.

Schauer, J. J., Kleeman, M. J., Cass, G. R. and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 4. C₁–C₂₇ Organic Compounds from Cooking with Seed Oils, Environ. Sci. Technol., 36, 567-575, doi: 10.1021/es002053m, 2001b.

Schauer, J. J., Kleeman, M. J., Cass, G. R. and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 5. C₁–C₃₂ Organic Compounds from Gasoline-Powered Motor Vehicles, Environ. Sci. Technol., 36, 1169-1180, doi: 10.1021/es0108077, 2002.

However, from several evidence, described in comment 9, we used $\pm 20\%$ 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.

Yunker, M.B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., Sylvestre, S.: PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33, 489-515.

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-

C9580

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, S., Baumann, K., Schauer, J. J., Sheesley, R. J., Naeher, L. P., Meinardi, S., Blake, D. R., Edgerton, E. S., Russell, A. G., Clements, M.: Gaseous and particulate emissions from prescribed burning in Georgia. *Environ. Sci. Technol.*, 39, 9049-9056, 2005.

Sheesley, R. J., Schauer, J. J., Bean, E., and Kenski, D.: Trends in secondary organic aerosol at a remote site in Michigan’s Upper Peninsula, *Environ. Sci. Technol.*, 38, 6941-6500, 2004.

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 \pm one standard deviation.”

15) Are any day/night trends statistically significant?

R: 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

C9581

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.

C9582

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 PM_{2.5}: 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

C9583

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.

C9584

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.

Page 18007, Figure 3 was edited: 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.

Page 18008, Figure 4 was edited: 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 2011, (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. 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. "

C9585

23) Figure 2 should have the same chemical species in each panel for easy comparison.

R: 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 signs.

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

R: Done.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/15/C9567/2015/acpd-15-C9567-2015-supplement.pdf>

C9586

C9587

Source category	Spring 2011		Fall 2011		Spring 2012		Fall 2012	
	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime
Gasoline-powered vehicles	2.37 ± 0.56	2.46 ± 0.46	3.70 ± 0.78	2.24 ± 0.51	1.43 ± 0.41	*	7.51 ± 1.27	3.19 ± 0.54
Diesel-powered vehicles	7.34 ± 0.86	3.81 ± 0.53	13.67 ± 1.59	13.10 ± 1.55	2.93 ± 0.41	*	13.85 ± 1.58	5.15 ± 0.62
Vegetative detritus	0.22 ± 0.04	0.22 ± 0.04	0.13 ± 0.03	0.27 ± 0.05	0.40 ± 0.06	*	0.42 ± 0.07	0.31 ± 0.05
Meat-cooking operations	8.24 ± 1.54	11.13 ± 1.85	3.26 ± 0.71	3.86 ± 0.71	9.74 ± 1.20	*	3.22 ± 0.53	3.37 ± 0.47
Natural gas combustion	0.01 ± 0.01	N.I.	0.05 ± 0.03	0.03 ± 0.01	0.01 ± 0.01	*	0.10 ± 0.02	0.04 ± 0.01
Biomass burning	0.20 ± 0.05	0.17 ± 0.05	0.17 ± 0.05	0.07 ± 0.02	0.16 ± 0.04	*	0.01 ± 0.01	0.01 ± 0.01
Fuel oil combustion	N.I.	N.I.	4.18 ± 3.55	3.60 ± 1.20	N.I.	*	N.I.	0.22 ± 0.48
N. I. means Not Important. * samples were discarded due to poor CMB performance								

Fig. 1. Table 5

C9588

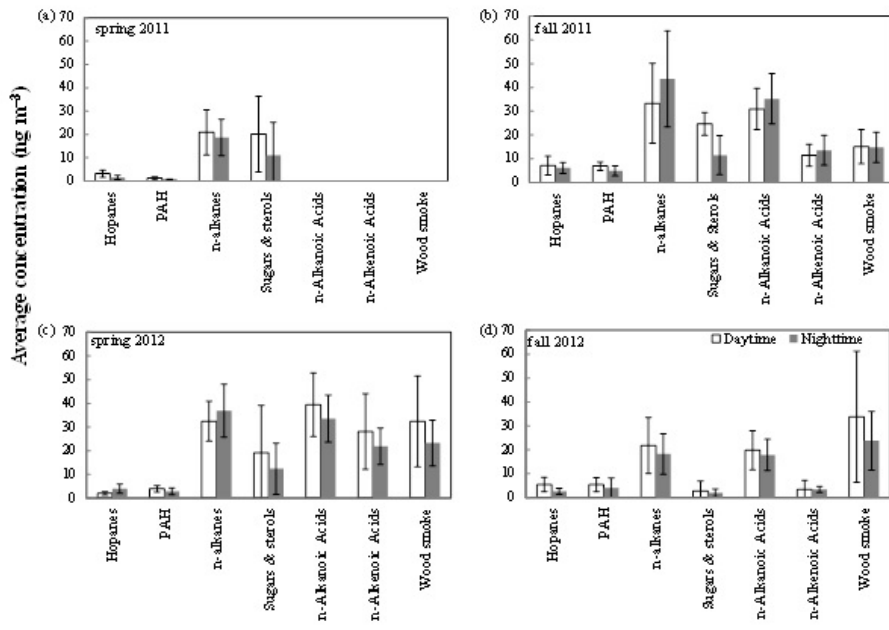


Fig. 2. Figure 2

C9589

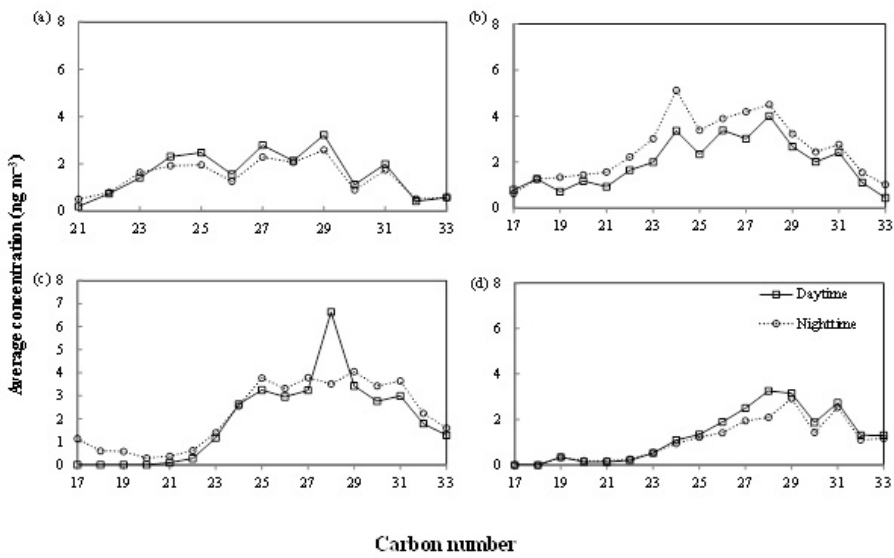


Fig. 3. Figure 3

C9590

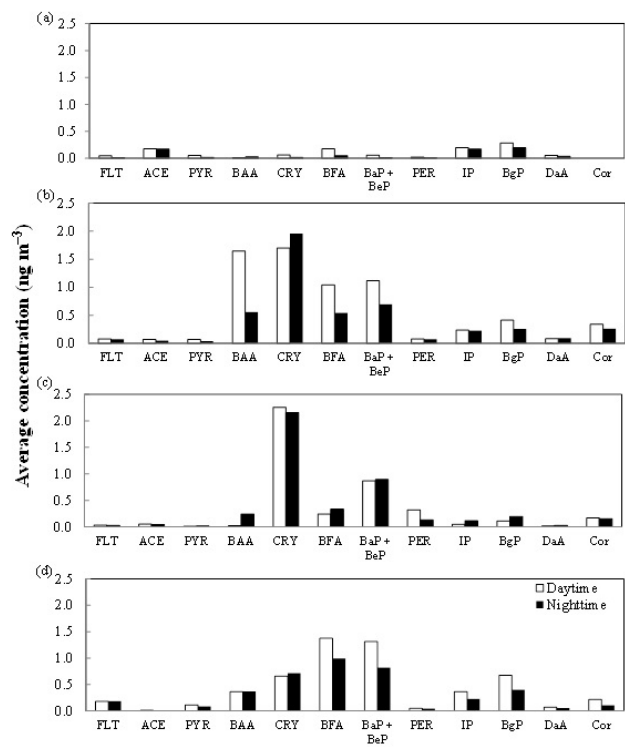


Fig. 4. Figure 4

C9591

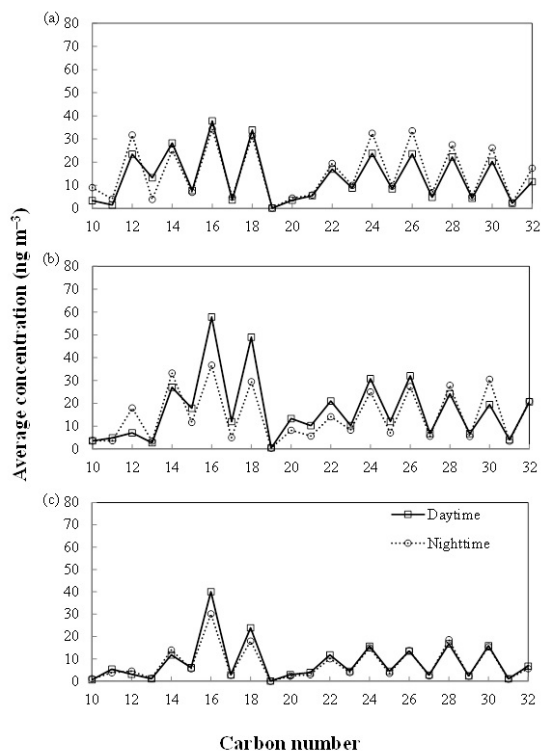


Fig. 5. Figure 5

C9592

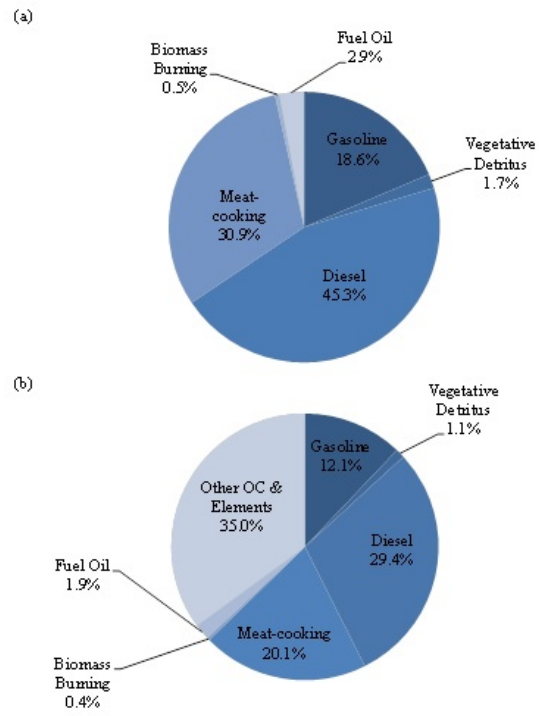


Fig. 6. Figure 6

C9593