

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

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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.

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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 high-

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est. 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 (eg. ng m<sup>-3</sup>), which promote the wide variations of the concentrations measured in different studies or laboratories for the same samples. Therefore, it is very

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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

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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 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.

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.

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-Kreis, J., Surratt, J. D., Szidat, Sönke, Szmigielski, R., and Wisthalder, A.: The molecular

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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<sub>2.5</sub> air particulate matter: description and results for trial III. NIST, 2005.

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)

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). 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.

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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. 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<sub>2.5</sub> 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. C<sub>1</sub> through C<sub>29</sub> 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

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Emissions from Air Pollution Sources. 3. C<sub>1</sub>–C<sub>29</sub> Organic Compounds from Fireplace Combustion of Wood, *Environ. Sci. Technol.*, 35, 1716-1728. doi: 10.1021/es001331e, 2001a.

Schauer, J. J., Kleeman, M. J., Cass, G. R. and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 4. C<sub>1</sub>–C<sub>27</sub> 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. C<sub>1</sub>–C<sub>32</sub> Organic Compounds from Gasoline-Powered Motor Vehicles, *Environ. Sci. Technol.*, 36, 1169-1180, doi: 10.1021/es0108077, 2002.

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

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the elevation of levoglucosan. Levoglucosan of being several tens of ng m<sup>-3</sup> 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<sup>-3</sup> and 1.95 to 3.69 ng m<sup>-3</sup> for spring and fall, respectively. Then, pimaric acid ranged from not detectable levels to 0.09 ng m<sup>-3</sup> and from 0.15 to 0.35 ng m<sup>-3</sup> for spring and fall, respectively. Finally, isopimaric acid ranged from not detectable levels to 0.03 ng m<sup>-3</sup> and from 0.06 to 0.12 ng m<sup>-3</sup> 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 . . .”

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Finally, the following references were added 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.* 5569-5584, 2007.

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 alkanolic acids/carboxylic acids should be uniformed.

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

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 17967, 2015.

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