Atmos. Chem. Phys. Discuss., 15, C9594–C9600, 2015
www.atmos-chem-phys-discuss.net/15/C9594/2015/

Atmospheric Chemistry and Physics Discussions

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

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 PM2.5 and O3 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 not any 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 con-

tribution 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. Page 17976. Line 17. Correct "The values listed: : :".

R: Done.

Page 17986. Line 15. Correct "in in 80%...".

R: Done.

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