Atmos. Chem. Phys. Discuss., 7, S5455–S5461, 2007
www.atmos-chem-phys-discuss.net/7/S5455/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment of fine organic aerosol in Mexico City during the MILAGRO Experiment 2006" *by* E. A. Stone et al.

E. A. Stone et al.

Received and published: 28 September 2007

Response to referee 2

General comments: *This paper describes the characterization and source reconciliation of organic compounds content in fine particulate matter in Mexico City. This kind of studies are very scarce in Mexico and the characterization of organic compounds in this research is indeed the most detailed carried out until today. The discussion about the source apportionment is very interesting and the results presented in this paper will contribute to the understanding of the polluting aerosols in the atmosphere of Mexico City. Generally speaking, the paper is very good, but it sometimes is very brief thus giving rise to doubts that tend to remain. I would like to over the following comments*:

Reply: See specific comments below.

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Individual comments:

Reviewer comment 1.1: *Page 9640, It is not very clear how the extract from the soxhlet was divided, how many derivatizations, only two? which was used for PAH analyses?*

Reply: We agree with the reviewer that additional description of the extraction would benefit the interested reader. This portion of the methods section will be elaborated upon.

The description in section 2.2, page 9640, line 5 previously read: [Filters were]8230; extracted with methanol and methylene chloride using Soxhlets.

The text will be changed to read: Filters were extracted with methanol and methylene chloride using Soxhlets. The extracts were combined then concentrated using a rotary evaporator then a nitrogen evaporator. The combined extract was derivatized using diazomethane8230; This aliquot was used for quantification of PAH, alkanes, hopanes, steranes, and carboxylic acids.

Reviewer comment 1.2: *Page 9640, How many and which internal standards were used?*

Reply: We agree with the reviewer that this information should be included in the paper. It was an oversight that it was not included in the original manuscript.

The text in section 2.2, page 9640, line 4 previously read: Filters were spiked with isotopically-labelled internal recovery standards8230;

The will read: Filters were spiked with the following isotopically-labelled internal recovery standards which were used in quantification: pyrene-D10, benz(a)anthracene-D12, coronene-D12, cholestane-D4, eicosane-D42, tetracosane-D50, triacontane-D62, dotriacontane-D66, hexatriacontane-D74, tetracosanoic acid-D59, and galactosan-C13.

Reviewer comment 1.3: *Page 9640, I understand that n-alkanes were measured, how*

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many and which ones? Because table 1 doesn8217;t report any.

Reply: It was an oversight of the authors that the alkanes used in the chemical mass balance (CMB) model were not reported in Table 1. This table will be reformatted to include all of the species used in the CMB model and all of the species included in the CMB model will be clearly marked with a star. Specifically, aromatic dicarboxylic acids and select PAH which are not discussed in this paper will be removed from Table 1. In their place, C35-C36 n-alkanes and pinonic acid will be reported.

Reviewer comment 2.1: Page 9640, Although it was explained that profiles were taken from the literature, it is not clear how many profiles were used and which ones, there is very little detail provided. I assume the authors applied at least 5 profiles: woodsmoke, vehicles, gasoline vehicles, smoke vehicles (that is, by the way, a new concept in source apportionment), diesel engines and vegetative detritus, but it is not clear if there were several profiles for each source. For example Fine et al. (2004) have many profiles for woodsmoke. Did the authors apply one or several in each reconciliation or develop one as an average? The same situation occurs with the other sources; each mentioned in the paper has several profiles. A more detailed description about the profiles applied would be necessary for future studies and comparisons.

Reply: We agree with the reviewer that it is necessary for the interested reader to be able to easily access the source profiles used in this paper. The text will provide a more direct and comprehensive reference.

The following text will be added to section 2.3, page 9641, line 2: All of these profiles are reported in (Sheesley, et al., 2007) under the titles vegetative detritus, natural gas combustion, diesel exhaust, gasoline exhaust, gasoline non-catalyzed, and region 5 profile, respectively.

The text pertaining to the woodsmoke profile to section 2.3, page 9641, line 1 will be elaborated upon. This section previously read: and woodsmoke based on the average reported in (Sheesley et al., 2007) with data from (Fine et al., 2004a).

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It will be changed to read: The woodsmoke profile used was a region 5 average (Sheesley et al., 2007) based on a more comprehensive study (Fine et al., 2004a).

Reviewer comment 2.2: *Page 9640, How many fitting species were used in the CMB model?*

Reply: We agree that including the specific number of fitting species would clarify the modeling methods for the reader.

Section 2.3, page 9641, line 2 previously read: The chemical species included in the model were 8230;

It will be changed to read: The seventeen chemical species marked with a star in Table 1 were included in the model.

Reviewer comment 3: *Page 9641, first paragraph talks about the chemical species 3 hopanes, 5 PAH, EC, levoglucosan, and C28-C34 alkanes. (Which alkanes and how many?). Which were the criteria for the selection of PAH and alkanes?*

Reply: We agree with the reviewer that the methods section could be made clearer by clearly stating that a continuous series of C28-C34 n-alkanes were used. This issue will also be treated by the reformatting of Table 1 such that the molecular marker species used in the CMB study are clearly marked.

The text in section 2.3, page 9641, line 2 previously read: EC, C28-C34 n-alkanes, levoglucosan8230;

It will be changed to read: EC, a continuous series of n-alkanes from C28-C34, levoglucosan8230;

Further, references that provided the basis for compound selection will be cited.

The following text will be added to section 2.3, page 9641, line 5: The series of C28-C34 n-alkanes were selected because this range has been shown to demonstrate the greatest of the odd-carbon preference that is specific to biogenic sources (Rogge et al.,

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1993). These particular PAH were used based upon the recommendations of previous studies (Lough et al., 2007; Sheesley al., 2007).

Reviewer comment 4: *Page 9643. Results Line 21 Regarding figure 3, it doesn8217;t seem that on weekend, hopanes concentrations were lower with the exception of day 19. On the other hand, March 21 should be included in this category because it was a holiday that allowed the circulation of all vehicles.*

Reply: We agree with the reviewer that 21 March should be considered a holiday in this context. It is also noted by the authors that the difference between weekday and weekend hopanes concentrations is difficult to discern visually by Figure 3. The paragraph has been reorganized and reworded to improve clarity.

Section 3.2, page 9643, line 21 previously read: The ambient concentrations of these three hopanes were consistently lower on the weekends compared to the weekends over the course of this study. Weekends are defined as Saturday and Sunday and include March 18, 19, 25, and 26; the average of all weekend samples was compared to the average of all weekday samples. The average weekday hopane concentration exceeded the average weekend concentration by 13

It will be updated to read: In this study, hopanes were considered primarily to originate from motor vehicle emissions and not other fossil-fuel source categories. Picene was not detected at either site over the course of the study which further eliminated coal-fired power plants as a major source of both OC and hopanes at the urban or peripheral sites. A temporal trend was observed in which the average weekend concentration was lower than the average weekend concentration for the three hopanes presented in Figure 3. Weekends were defined as Saturday, Sunday, and holidays and included 18-19, 21 and 25-26 March. The average weekday hopane concentration exceeded the average weekend concentration by 9

Reviewer comment 5: *Page 9646. Results Line 12 The suggestion could be ventured that urban woodsmoke events that affect urban atmosphere do not affect the periphery.*

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Most of the days the wind did not blow to the north (peripheral site), so that could be the reason of the apparent lack of influence. Although the discussion could be true, it will be better supported with the analyses of direction and speed of the wind. This is one of the advantages of the MILAGRO study because there are meteorological data available from other researches.

Reply: We agree with the reviewer that it would be important to discuss transport of aerosol from the urban to the peripheral site in the context of meteorological data.

Section 3.2 pave 9642, line 18 previously read: There was little correlation between levoglucosan concentrations at the urban site and the peripheral site (R2=0.07) and this data suggests that primary biomass combustion at the urban and peripheral sites were isolated from each other.

It will be expanded upon to read: There was little correlation between levoglucosan concentrations at the urban site and the peripheral site as shown by a linear regression analysis (R2=0.07). When this regression analysis was limited to days for which transport from the urban to the peripheral site was considered to be meteorologically favorable (Fast et al., 2007), correlation did not improve (R2=0.05). This data suggests that primary biomass combustion at the urban and peripheral sites were isolated from each other.

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