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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.

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Response to referee 1

General comments: *This paper describes the application of organic molecular markers to the source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment. The methods are now becoming relatively conventional and have been widely applied by some of the authors of this paper. In general, the results appear convincing and give a good quantitative description of the sources of organic aerosol at two sites in Mexico City, one in the downtown area, the other on the periphery. Whilst the paper does not break any major new ground in terms of methods or insights into atmospheric processes, results of the kind presented are not otherwise readily available and the paper will be of significant interest to an international audience.*

Reply: We agree with the reviewer that this paper does not break new ground in terms of methods or insights into atmospheric processes. It is significant, however, that this paper presents a novel comparison of modeled to measured water-soluble organic carbon which provides evidence that the methods used in this paper are reasonable and that OC unapportioned by the CMB model is likely from secondary sources.

Individual comments:

Reviewer comment 1a: *As noted above, some of the authors of this paper have been associated with a number of previous publications using the organic molecular marker techniques to identify sources of organic aerosol. However, there are issues which the paper does not address, which in the view of the reader should have been covered. These include the following*: *(a) There is insufficient description of the sampling sites and possible local influences. For example, the results suggest an appreciable influence of biomass burning but the site descriptions give no indication that this is conducted locally. What and where are the likely sources? Influences on the peripheral site are particularly difficult to discern. According to the Methods section, this site was subject to significant resuspension of dust. What is the evidence for this? Also, a peripheral site could be influenced mainly by very local emissions or alternatively by air advected from the central parts of the city, or as a further possibility, air from surrounding the rural areas, obviously depending upon wind direction. No insights into this matter at all are given. It is suggested that as a minimum some analysis of meteorological data including local wind directions and airmass back trajectories is conducted for the period over which the results of daily samples are reported. This would help the reader understand the influences upon this site.*

Reply: We agree with the reviewer that a more detailed description of primary aerosol sources and meteorological conditions at the peripheral site would provide important context for the discussion of source apportionment results and the urban influence on the peripheral site. The descriptions of the sampling sites are based upon the observations of the authors of this paper made during the field campaign and those

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reported in the scientific literature.

The text in section 2.1, page 9639, line 5 previously read: This site was located in a rural agricultural area where significant resuspension of road dust occurred.

It will be changed to read: This site was located in a rural agricultural area where local primary aerosol sources were observed to include wind-blown dust and soil and motor-vehicle emissions.

Furthermore, the following text will be added in section 2.1, page 9639, line 7: The Mexico City basin is believed to have been influenced by emissions from forest fires in the pine-savannas in the mountains surrounding the city; other potential combustion sources included agricultural waste burning or fires in grasslands and forests, all of which were observed in south-central Mexico during March 2006 (Yokelson et al., 2007).

Additionally, meteorological data will be expanded upon. A new paragraph will be added to section 2.1, page 9639, at line 8. It will read: Transport of aerosols from the urban to the peripheral site was highly dependant on the prevailing wind direction; for such transport to occur the dominant wind direction would have to be westerly or south-westerly. A meteorological study reported that transport was considered likely on 18-22, 24-25, and 30 March and possible on other days (Fast et al., 2007). Aerosols at the peripheral site were likely influenced by local sources and by the surrounding region in addition to the variable urban influence. Precipitation events that would cause a washing-out of aerosols from the atmosphere occurred on 23-30 March 2006 (Fast et al., 2007).

The following text will be omitted: Rain events occurred on 23 and 25-30 March 2006.

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

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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 no 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 during 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.

Further, we agree with the reviewer that, in light of the conclusion that the urban site and peripheral site aerosol are isolated from each other, possible sources the do affect the peripheral site should be acknowledged in the discussion.

The following text will be added to section 3.2, page 9642, line 21: The peripheral site, then, was likely affected by aerosols generated locally or those generated in surrounding rural areas.

Reviewer comment 1b: *(b) Table 1 lists the specific organic compounds analysed as part of this work. This is a shorter list than that in some other papers by the same authors. Can some explanation be given as to why this particular set of components was selected and not the longer list used in other studies?*

Reply: The reviewer is correct that Table 1 contains an abbreviated list of the analytes measured in this study. The intention of the authors was to present this data in a clear and concise manner on a single page. The compounds included in Table 1 were selected because they were important molecular marker species used in the chemical mass balance (CMB) model or have been reported in previous studies such that they were considered to be useful for comparison. In light of the reviewer8217;s comments, the authors plan to revise this table so that species included in the CMB model are

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clearly marked with a star. Furthermore, 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.

The caption for Table 1 will be changed to read: Summary of organic carbon analyses and organic species, based on a 24-h sampling time. Molecular markers used in CMB modeling are marked with a star.

Reviewer comment 1c: *(c) The results of the chemical mass balance modeling will depend critically upon the use of appropriate source profiles. Those adopted appear to have come largely from work in California published in the early 1990s supplemented by some more recent currently unpublished studies. The question is not addressed of how relevant these profiles are to emissions in Mexico City in 2006. There are both spatial and temporal issues that need to be considered in addressing this question.*

Reply: The reviewer is correct that the results of the CMB modeling depend on the appropriate use of source profiles. It is clearly unreasonable to individually characterize primary aerosol sources in every location where ambient aerosol is measured, especially over various time scales. It is crucial, however, that researchers use the best profiles available at the time of the study and that steps are taken to ensure that reasonable profiles used. It is the opinion of the authors of this study utilizes the best available source profiles to date. The mobile source profiles are drawn from the most recent and comprehensive study on this topic (Lough et al., 2007). Similarly, the woodsmoke profile used in this study is an average from a recent and comprehensive study (Fine et al., 2004). The vegetative detritus and natural gas source profiles used in this study were drawn from literature published in 1993 by researchers in California; these profiles are the only ones published for these source categories and they remain widely used and accepted.

In response to the reviewer8217;s question of the temporal relevancy of the profiles used in this study, source profiles, with the exception of motor vehicles, do not change

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significantly on the decadal time scale. Mobile source emissions are the only source category subject to change with improved emission controls and the introduction of alternative fuels. The use of a recent and comprehensive mobile source study would account for such temporal changes.

In response to the reviewer8217;s question of the spatial relevancy of the profiles used in this study, source profiles do not change significantly from country to country. This is expected to be particularly true for mobile sources which use fuels that are ubiquitous. A previous source apportionment study of aerosol at three sites in Hong Kong showed that the use of American source profiles provided reasonable results (Zheng et al., 2006). Further, the uncertainty associated with the use of biomass profiles can be reduced by using regional average profiles rather than a profile generated from combustion of a single type of biomass (Sheesley et al., 2007). The region 5 woodsmoke average profile is a particularly reasonable for use in Mexico City because of its similarities to the pine tree woodsmoke (Sheesley et al., 2007); pine is the dominant type of tree in the Mexico City region. The authors conclude that the source profiles used in this study, although they were not measured in the Mexico City region, are reasonable for use in apportionment of Mexico City aerosol.

In order to improve clarity on the subject of selection of source profiles in this study, the following text will be added to section 2.3, page 9640 line 22: The source profiles used were drawn from the most recent and comprehensive studies available at the time of this experiment. They include8230;

The following text will be omitted: Detailed chemical profiles for primary sources were compiled from available literature8230;

Reviewer comment 1d: *(d) Section 3.4 contains a considerable discussion of measurements of pinonic acid. This substance is not listed amongst the analytes in Table 1. Is the table therefore incomplete?*

Reply: The reviewer is correct that pinonic acid was not originally included in the list of

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analytes presented in Table 1. This table will be revised to include pinonic acid.

Reviewer comment 1e: *(e) The reviewer found the way in which the WSOC data were used particularly useful. However, no use appears to have been made of the measurements of aromatic carboxylic acids. Did any of these correlate with the estimated SOC concentrations?*

Reply: The reviewer is correct that this paper does not include analysis of aromatic carboxylic acids as potential markers for secondary organic carbon. Such a comparison was made by the authors but a good relationship was not observed. For example, a linear regression of phthalic acid and OC unapportioned by CMB yielded weak correlation, R2 values of 0.45 and at the urban site. The authors chose to focus on the correlation of water-soluble organic carbon (WSOC) and OC unapportioned by CMB for several reasons. First, WSOC measurements are analytically much easier to make and therefore more reliable. Second, the direct comparison of aromatic acids to modeled secondary organic carbon is confounded in that aromatic acids may arise from primary sources. For the peripheral site, a linear regression of phthalic acid and WSOC showed a fair correlation with an R2 value of 0.65, however the correlation of phthalic acid to modeled secondary OC was 0.38. These results are consistent with aromatic acids having many possible sources ranging from primary biogenic or anthropogenic sources like motor vehicle exhaust to secondary formation in the atmosphere by various pathways (Ray McDow, 2005). As previously discussed in the reply to Reviewer comment 1b, these compounds are to be removed from Table 1.

Technical corrections:

Reviewer comment 2a: *One of the author8217;s names is misspelt in the footnote to page 9641.*

Reply: The reviewer is correct that one of the author8217;s names was misspelled in the footnote. This misspelling was an oversight of the authors; this footnote will be omitted for a full citation is now available.

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Reviewer comment 2b: *In the legend to table 1, sites rather than sties.*

Reply: This misspelling was also an oversight of the authors; this correction will be made to the manuscript.

Reviewer comment 2c: *In Table 1, benzo(ghi)perylene rather than benzo(GHI)perylene.*

Reply: The reviewer is correct that benzo(ghi)perylene is the appropriate notation; this correction will be made to the manuscript.

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