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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Primary and secondary organic carbon downwind of Mexico City" *by* X.-Y. Yu et al.

X.-Y. Yu et al.

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RESPONSE TO REVIEWERS' COMMENTS We address the reviewers' comments in the order that they were published.

Referee #3 (Received and published: 2 February 2009) General Comments:

This paper describes measurements of elemental carbon (EC) and organic carbon (OC) made at the T1 and T2 sites during the MILAGRO campaign. Using these measurements, various ratios (e.g., OC/EC) are presented. The paper also attempts to quantify the percentage of the OC that is SOC, etc. This paper only modestly advances science; its primary value is as a reference for the OCEC data. My opinion is that for a big field campaign such as MILAGRO, These data description papers serve a distinct and useful purpose and should be published, because others can use the sum-

marized information to advance their own scientific agendas. Therefore I recommend publication, subject to consideration of the following specific comments.

Reply: We thank Reviewer 3 for the comments. We were able to get access to the Aerodyne Aerosol Mass Spectrometer (AMS) data collected simultaneously at T1 after the paper was reviewed. In order to increase the science impact of this paper, comparison of POC and SOC derived from the Sunset OCEC measurement with POA and SOA from the AMS was added. The specific comments from Reviewer 3 are addressed below.

Specific comments: 1. The uncertainties in some of this work seem very large and are not discussed in the paper. For example, the method used to derive the SOC/TC ratio seems fraught with uncertainty. Might the author provide error bounds for the SOC/TC percentages? If these errors cannot be quantified, then the authors should state this in the paper.

Reply: The uncertainty of SOC was discussed originally on p554. More discussion is added on this matter in the revised section 3.4. We also clarified the definition of SOC%. The SOC% previously used in the manuscript is SOC/OC*100%. In the revision, we differentiated the SOCTC*100% and SOCOC% as the SOC% to facilitate comparison with others. We clarified the definition and updated the figures which illustrate this quantity. The uncertainty of the EC-tracer method to derive SOC and POC is discussed with more details. Comparison between Deming regression and linear least-squares regression is added especially for the key parameter OC/ECpri. In addition, an estimate of errors in SOCTC% and SOCOC% are provided based on the RSD determined on TC and OC and assuming SOC bearing the same degree of uncertainty as that of OC during measurement and additional error from the EC-tracer method.

2. In Sect. 3.7, an EC/CO ratio is given, 0.0045. Baumgartner et al. (2002) has done a comprehensive study of this ratio for the Mexico City area, and they get a much lower number, about 0.001. There are many possible reasons for this difference, including the

ACPD

9, S2939–S2951, 2009

measurements of carbon; for example, the paper under review uses an OCEC instrument, while Baumgartner et al. mostly uses absorption measurements (aethelometer, PSAP) to measure BC. I suggest that at the very least the authors cite Baumgartner et al., and speculate why Baumgartner et al.;s BC/OC ratio is different than their EC/OC ratio. Baumgartner et al. (2002), JGR, 107, D21, 8342, doi:10.1029/2001JD000626.

Reply: Reference to the paper by Baumgardner et al. is added. Discussion about EC/CO ratio determined by Baumgardner in Mexico City and the reason why difference exists between results from this paper and Baumgartner et al. is added. The calculation of EC/CO was checked and a minor correction was made; the EC/CO is rounded to 0.004 when using gC/m3 for EC and g/m3 for CO.

3. If this paper is going to be a useful reference for others, the authors should exert every effort to make the paper user friendly;. For example, the time axes in Fig. 3, Figs. 10a, 10b., are given in UT, but the discussion in the paper is in LST. If LST is going to be referred to in the text, I suggest making the time axes LST.

Reply: The axes are changed to LST in these figures. Captions and text were corrected to reflect this change. In addition to Fig. 3, 10a and 10b, the time stamp on other figures are changed to LST including the following Fig.4, 5a, 5b, 11a, and 11b.

Technical comments: 1. Page 554, paragraph starting on line 7: this paragraph seems out of place and maybe should be deleted, or placed a the beginning of section 3.4

Reply: This paragraph is moved to start section 3.5 where we compare with the PMF analysis results from AMS.

2. Page 554, line 25, deferred should be inferred?

Reply: corrected.

3. The authors should ensure that the final figures are big enough to be legible. In the ACPD article, some of the figures were so small that I could barely read this axes labels.

ACPD

9, S2939–S2951, 2009

Reply: Modification was made to all figures. For instance, the legend for each figure is enlarged, and resolution increased.

Referee #2 (Received and published: 13 February 2009)

This paper presents measurements of organic and elemental carbon (OC and EC) at ground sites T1 and T2 downwind of Mexico City during the MILAGRO experiment. Although the OCEC data are analyzed and presented in many ways, as the title indicates the main focus of the paper is to calculate primary and secondary OC, which is done by using the EC tracer method. The topic of primary and secondary sources of the organic aerosol are of interest, however, in my view the analysis performed in this paper is overly simplistic. First, there is no assessment of uncertainties associated with the method and if the results are realistic. A much more careful analysis might reveal unique limitations or new insights that can be gained by the application of this method to the MILAGRO data set, instead the paper does not present anything significantly novel. For example, why not explore why periods of 100% SOC are predicted; is this an artifact of the method or is there a valid physical reason (eg, time of day, unique meteorology, etc). Secondly, although the authors note that other measurements were made at T1 that could be used to compare with their predicted POC and SOC, no attempt was made to undertake this comparison. Critical details are also missing, such as was the OC data blank corrected (this could lead to significant bias if not considered) and is the data reported at standard temperature and pressure or ambient? I recommend that the paper needs a much tighter focus that involves a more detailed and critical analysis before publication in ACP.

Reply: EC tracer method is a measurement based technique to derive SOC and POC. These results are now compared with the deconvoluted SOA and POA results from the Aerodyne AMS (see Fig10). The agreement with the AMS measurements supports the analysis results by the EC tracer method. Being a relatively simple method does not invalidate its usefulness and applicability in data analysis. As to the uncertainties of the EC tracer method, discussion is added. Several recent papers have discussed

ACPD

9, S2939–S2951, 2009

the differences of linear regression techniques for use in the EC tracer method of secondary organic aerosol estimation. The 100% SOC points are caused by the EC points that are lower than the detection limit, i.e., $<$0.2 ugC/m3. These points should not be included in the first place, therefore they are removed in the revision. The determination of OC and EC was described in the experimental section. The system blank is determined daily at midnight. The blank OC and EC values are zeros. Since this is a real-time measurement, we did not subtract the blank as in the off-line analysis. However, if the blank OC and EC values were above the detection limit, the blank correction suggested by the reviewer will be useful. In addition, we use a denuder upstream of the OCEC analyzer, this reduces the bias caused by volatile and semivolatile organics in other integrated filtration techniques. These data are corrected to ambient pressure and pressure. This description is added in the experimental section.

Other comments to Consider 1. Instrumentation: no details are provided on the methods used to measure many compounds, instead the institution of the investigators is provided. A discussion of the measurement technique is of more interest than who made the measurement. Furthermore, no info is given on the PM2.5 mass method.

Reply: The trace gas measurements are well established, therefore, only references were given in the description. More details are not necessary. Additional references are added for the TEOM [Patashnick, 1991] and NO2 [Fehsenfeld, 1987)] measurements.

2. Blanks Pg 547, what is a 0-min sampling blank (no blank?). If blanks were measured, what were the concentrations, how did they vary, how do they compare with other studies, etc?

Reply: As described above and in the experimental section, the zero minute blank is a system blank where the Sunset OCEC analyzer samples for 0 min and then conduct an analysis. These blank values are zeros. Therefore, no additional subtraction is needed. These blank values rarely vary from location to location based on our results in different locations such as northeastern US or southern US in past studies.

ACPD

9, S2939–S2951, 2009

3. Fig 3 showing diurnal profiles in UTC, yet the text mainly uses LST. UTC data in the figure is hard to interpret, LST is preferred.

Reply: All figures showing UTC are now using LST.

4. Fig 6a; The point of this plot is not clear; why would one expect OC/EC ratio to depend on the date of the measurement during the study.

Reply: Fig 6a is to show that there was no clear daily pattern of the OC/EC ratio. It is stated that the global fit could not really explain the complex data set. There is no expectation that the OC/EC ratio should depend on time.

5. Fig 6b; I do not understand this plot. The slope of the OC vs EC graph is the OC/EC ratio, so why are the data points colored by OC/EC ratio (thus it is not surprising that data corresponding to lower slopes have colors associated with lower OC/EC ratios, or am I missing something)? Why not give statistics (mean, median, stdev, range etc) in OC/EC for each site.

Reply: Statistics information of OC/EC ratio for T1 and T2 is added in Table 3. Fig 6b is to illustrate that although the OC/EC ratio has a very wide range at both sites, most of the particles observed at T1 have an OC/EC ratio in the range of 0 – 10 at T1, whereas it is 0-50 at T2.

6. Pg 552, Line 8, avoid the use of the phrase other big cities, what does big mean?

Reply: The word big is deleted in this paragraph, a couple of other places in the text, and in the conclusions. We use metropolitan area instead.

7. Page 554 line 25, what does deferred mean here? Also, explain why the instruments that directly measure SOA provide on an approximation (line 26).

Reply: The word inferred is now used. The PILS-TOC and AMS do not directly measure SOA. The quantity that may relate to SOA by either measurement results from analysis. Since we are able to compare with the AMS deconvoluted HOA and OOA results, this

ACPD

9, S2939–S2951, 2009

Interactive Comment

discussion is revised. A new figure replaces the old Figure 11. More references are added in this discussion.

8. Tables 6 and 7. How do you account for the large intercept? Is this primary OC from non-combustion sources? Can you just ignore it in the POC and SOC calculation?

Reply: The intercepts of these linear regression fits are usually used to estimate non-combustible OC influence. A brief discussion is added. In addition, comparison with Deming fit and discussion about uncertainty are added.

9. Page 555, how is it possible to a have 100% SOC in a region dominated by anthropogenic emissions?

Reply: The high SOC was caused by including data points that should have been excluded, i.e., those with EC below the Sunset OCEC detection limit. The data are reviewed carefully and only data points above the detection limit for OC and EC are used in the revision.

10. Page 557, Can wind directions measured at the sampling site really be used to predict influences from possible sources over 70 and 129 km away?

Reply: Doran and Fast’s paper in 2008 has more detailed discussion on the meteorology and its influence on the observation at T1 and T2 using modeling approach. This paper does not intend to repeat these results. Their paper is cited and a brief discussion added to refer to their findings on meteorological influences.

11. Figure 10. Again the use of UTC for diurnal plots makes little sense. Furthermore, when the data were delineated into weekday vs weekend, was UTC used or local time used (eg, is this weekend/weekday UTC or LST)?

Reply: The original plots all used UTC. However, all plots were plotted using LST in the revision.

12. Figures 11, 12, 13 I believe are all from TI; this should be stated in the figure

ACPD

9, S2939–S2951, 2009

caption.

Reply: Added. These plots are revised for better comparison.

13. Page 560 lines 6 and 7, regarding the correlation between EC and NO confirming EC is primary; what else would it be, is there secondary EC ?

Reply: This sentence is revised to avoid confusion.

Anonymous Referee #1 (Received and published: 24 February 2009) General comment This paper presents measures of EC, OC and TC taken at supersites T1 and T2 during the experimental campaign of MILAGRO project, also a descriptive analysis of the campaign. Also shows results about methods to obtain primary organic carbon (POC) and secondary organic carbon (SOC).

An interesting paper from the experimental point of view, gives useful data for future health studies on population exposed to EC, OC and TC. Nevertheless, contribution to scientific knowledge is small.

My recommendation is: The paper needs more work to be published in ACP journal. Improve data analysis for a more detailed interpretation of the origin variables measured (EC, OC, gasses, etc.)

Reply: The authors do not agree with the reviewer’s assessment in terms of the scientific significance of this paper. It is not clear how small is defined, while the paper is interesting and provides useful data as a measurement paper. The focus of this paper is about the POC and SOC determined using the EC tracer method. The analysis between EC and OC vs. trace gases at T1 is provided to validate the usefulness of the EC tracer method. Other papers have already reported findings on emissions and sources during the MILAGRO study, such as Doran and Fast et al. in their ACP publication in 2008. Their paper is cited and a brief discussion is added. As mentioned earlier, we were able to get access to the analyzed AMS data by PMF during the paper revision. Therefore, a comparison between the SOA and POA is added. This

ACPD

9, S2939–S2951, 2009

should add more impact of this paper to the community.

Specific comments 1. It is important that every 6 hours data be given for OC; EC and TC, helping to understand the evolution of aerosols in both sites, and also to associate with local emissions or transport from other areas.

Reply: Table 5 has summarized comparison with past measurements including 6-hour data by Querol et al at T1 in 2006 and Chow et al in Mexico City in 2002. Additional discussion is added to compare the 6 hr average of the Sunset data with those of Querol et al. besides what is in the original discussion. A comparison table is added in the supplemental materials.

2. Characterize well T1 and T2 respect to EC and OC concentrations, compare with results by Marley et al, 2008, Paredes et al, 2009 and Querol et al, 2008 (every 6 hours).

Reply: Querol et al.’s results were already compared in Table 5. Discussion was in section 3.3. The measurements by Marley et al. and Paredes et al. are not directly comparable with those by the Sunset OCEC, because different quantities are measured due to different physical principles used in each technique. For comparison with 6 hr data by Querol et al and Chow et al, please see response above.

3. Make a better use of meteorological data (wind speed and direction) trying to identify the origin of EC and OC in both sites. Take into account, for example, that during March there were fires at a municipal dump (located at South West of site T1), as well as in farm fields near both sites.

Reply: Discussion on biomass influence is added. Comparison of POA vs. HOA and SOA vs. OOA are added in the new Figure. 10. We also revised the section title from EC, POC, SOC emissions to EC, OC, POC, SOC vs. trace gases to better focus this part of discussion as validation of the results by the EC-tracer method.

4. At sites T1 and T2 differentiate days with or without influence from Mexico City

ACPD

9, S2939–S2951, 2009

(according to Fast et al, 2007) and compare behaviors of EC, OC. Gasses, temperature and boundary layer. Report important differences.

Reply: Doran and Fast et al. in 2008 have reported the findings of meteorology influence using modeling approaches in their paper. A brief discussion of their findings is added. The influence with and without influence from Mexico City is illustrated in Figure 9. More plots of EC, OC vs. trace gases etc. were in the supplemental materials. Adding these in the main text will make this paper more unfocused. We also moved the original Figure 11 to supplemental material in this revision following the same consideration.

Detailed comments 1. Table 3. According to the authors TC=OC+EC. Reported values of TC do not add up.

Reply: The results in Table 3 are statistical summaries. At each individual datum point, TC=OC+EC.

2. Fig.3. The authors say: "A distinctive diurnal pattern is observed for OC, EC and TC at T1. OC arrived at the first maximum at 8 a.m. (LST) at T1. A second peak of OC occurred at 2 p.m.. EC reached its first peak at 6 a.m. Then it reached its second maximum at much reduced amplitude between 8-11 p.m. TC peaked first at 6 p.m., then at 2 p.m. during the early afternoon rush hour". The figure is not well explained in the text, for example, a correlation of EC and TC with the boundary layer is no apparent. The 6 a.m. peaks for EC and TC are not to be seen.

Reply: This confusion is probably caused by the different time stamp used in the discussion and that in the figures. This is fixed. Now all figures use LST as in discussion.

3. The authors say: "The boundary layer height remained shallow at night and early morning until approximately 8.30 a.m. (LST) it then began to grow and reached its maximum of 3300m above ground between 4-5 p.m." But according to their figure, it starts growing around 3 p.m. and reaches the 3300 maximum around 11 p.m.

ACPD

9, S2939–S2951, 2009

Reply: Again, this is caused by the different time stamp used. Figures are corrected using LST to avoid confusion.

4. Figures in 5b should be made clear.

Reply: The data points are colored at a function of TC to illustrate that high OC/EC ratio is not necessarily corresponding to high TC. This is added in the discussion for clarification.

Additional Comments from Jose Jimenez received on March 5, 2009

Dear Xiao-Ying,

I have a comment on your ACPD paper "Primary and secondary organic carbon down-wind of Mexico City". I was meaning to submit it as a comment on the public discussion but I didn't get to it on time.

The comment is that the EC-tracer method was developed to separate POC from SOC in polluted urban areas where urban POC and SOC were assumed to be the main OC sources. Biomass burning POC has very large OC/EC ratios (often 5-10, see e.g. the review of Reid et al., ACP 2005) and when there is strong influence from BB you cannot separate POC from SOC with the EC-tracer method. You can only separate urban POC from the sum of urban SOC plus biomass burning (POC + SOC). This is a very well established fact, e.g. see the review about SOA from Hallquist et al., currently in ACPD:

http://www.atmos-chem-phys-discuss.net/9/3555/2009/acpd-9-3555-2009-print.pdf

in p. 3602 says: "Furthermore, in areas where both wood (or other biomass) burning and traffic emissions are significant, it becomes almost impossible to estimate SOA using the OC/EC method because of the very different OC/EC ratios of these particle sources (Szidat et al., 2006)."

Clearly in Mexico City both urban SOA and BB are important, so you can only separate

ACPD

9, S2939–S2951, 2009

the sum of those sources from urban POC with the EC-tracer method there. I think this is still valuable, but it needs to be explained more clearly.

Finally, I think the OC/EC ratio that you are using for traffic is a little low for Mexico City, e.g. from Fig 1 of Dzepina et al. (ACPD, see http://www.atmos-chem-phys-discuss.net/9/4417/2009/acpd-9-4417-2009.pdf) we estimate HOA/EC ~ 1.1, equivalent to POC/EC ~ 0.9 or so for average Mexico City POC. We summarized POC/EC ratios in a recent paper in ES&T, see Fig. 1a and associated discussion:

http://pubs.acs.org/cgi-bin/sample.cgi/esthag/2008/42/i20/pdf/es8008166.pdf

Let me know if something is not clear, and good luck with the paper.

Cheers, -Jose

Reply

There are two comments from Jose: 1) better discussion on the EC-tracer method on the biomass contribution to organic matter; and 2) the OC/EC pri ratio.

We can’t derive BBOA from the EC-tracer method, this is due to the assumptions used in the EC-tracer method. We added a brief discussion to clarify this point. Jose’s first comment is also addressed by adding discussion and comparison with the AMS OOA, HOA, OM at T1 in Figure 10. The meaningful comparison is to compare the Sunset determined SOA and POA with the AMS two component PMF analysis suggested by Manjula Canagaratna. The two component PMF analysis results from T1 was recently published by de Gouw et al. (de Gouw et al., ACP, 9 (10), 3425-3442, 2009). The same data set is used in the comparison between the AMS results and those of the Sunset measurements. We conducted Deming fit of OOA vs. SOA, HOA vs. POA, and AMS OM vs. Sunset OM (POA+SOA).

As to his second comment, the OC/ECpri ratio varies from location to location. It also depends on seasons as discussed in the manuscript line 5 – line 10 on p555. Therefore, the relatively higher OC/ECpri determined during a campaign in Riverside,

ACPD

9, S2939–S2951, 2009

CA is reasonable. However, this does not invalidate the OC/ECpri determined at T1. As to the estimated slightly higher HOA/EC values by Dzepina et al., this perhaps indicates there is a difference between the EC-tracer method and the AMS PMF analysis. Future study should look into inter-comparison among different methods and determine the uncertainties. A brief discussion is added to reflect this point.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 541, 2009.

ACPD

9, S2939–S2951, 2009

Interactive Comment