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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Spectro-microscopic measurements of carbonaceous aerosol aging in Central California" *by* R. C. Moffet et al.

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This is the response to referees 1 and 3. The original referee comment is in italic and our response is in normal font.

Referee 1

This manuscript contrasts aerosol composition measurements at two sites along a Lagrangian trajectory during the CARES campaign in California. The authors combine observations from OC/EC, electron microscopy, and X-ray microscopy. For the last technique, they apply a reduced set of X-ray energies to determine total organic carbon content (relative to the inorganic fraction) for a large number of individual

particles and contrast these results, along with descriptions of soot-like character, to particles previously analyzed from the MILAGRO campaign in Mexico City. This manuscript is recommended for publication in Atmospheric Chemistry and Physics after the following comments are addressed

We thank the reviewer for commenting on our paper. We have addressed the reviewer's comments as indicated below.

Some logistical details are difficult to locate in the manuscript. For instance: How many particles were analyzed by CCSEM/EDX vs STXM/NEXAFS? Figure S1 and S2 contains the derivative of this information but should be stated up front.

This information is in figures 6 and 7. We have modified the captions of these figures to highlight the information. We have also included this information in the experimental section (last sentence of section 2.4).

For STXM/NEXAFS, how many images/spectra were obtained with great detail (p. 9192 line 26: what is "numerous"?) vs. the quicker method with reduced number of energy levels?

The following was added after the sentence on p. 9192:

"For this dataset, 73 full stacks and 151 stacks were acquired."

Also, in each of the analyses sometimes it is unclear which spectra was used to derive the results or metrics.

We have modified the text starting at p. 9193, line 2 to read:

"The four mixing states described below were identified in a manner consistent with previously published method of determining mixing state from STXM/NEXAFS data (Moffet et al., 2010a) with some minor changes to accommodate four energy image maps. The same algorithm was used to analyze both stacks and maps."

Were some TEM grids and silicon nitride windows sampled on concurrently or in sequentially within the same time window? Cannot tell if there is overlap in the vertical lines in Figure 3.

We think that the reviewer may be under the impression that only silicon nitride windows are used solely for STXM and that TEM grids are used only for CCSEMEDX. We have deleted the "for electron microscopy" from p. 9183, line 19.

We have also added the sentence:
"Each substrate was sequentially subjected to the particle beam for 20 minutes."
to highlight the fact that the substrates were not exposed to the particle beam in a parallel fashion.

The relationship between the CCSEM/EDX and STXM/NEXAFS particle categories are unclear following the discussions in Sections 3.2 and 3.3.

We think this is an important point. We have added the following paragraph to the end of section 3.4.1

"It is difficult to speculate exactly what clusters STXM classified particles belong to because the two techniques are sensitive to different chemical species. However, there is some correspondence between the STXM mixing states and the clusters derived from CCSEM/EDX (Section 3.3). Any particle defined to have the "IN" phase will have an inclusion of non-carbonaceous material that is more abundant (by mass) than the organic phase. Therefore, many of the INOC particles likely consist of dust and sea salt, which correspond to SEM clusters 3, 5, and 6. Submicron INOC particles likely contain sulfate, possibly corresponding to SEM clusters 1 and 6; these clusters have elevated sulfur. The homogenous OC particles identified by STXM probably belong to SEM clusters 1 and 4 due to the slightly lower sulfur content. Lastly, the particles identified as EC by STXM probably also belong to SEM clusters 1 and 4 due to their high carbon content. EDX spectroscopy cannot be used to identify soot because it is only sensitive to elemental composition whereas STXM can readily be used to identify soot based on the C=C sp2 content."

Regarding the elucidation of mechanisms discussed in the abstract and introduction in the results section: Small particles with potassium cores possibly indicative of biomass burning: Tivanski et al. 2007 (previous work by one of the co-authors) studied the spectral signature of the NEXAFS K-edge of biomass burning particles. Is there any resemblance of these particles with these tarballs? Tivanski, A. V.; Hopkins, R. J.; Tyliszczak, T. Gilles, M. K. Oxygenated interface on biomass burn tar balls determined by single particle scanning transmission X-ray microscopy, Journal of Physical Chemistry A, 2007, 111, 5448-5458

There was no obvious resemblance between these particles and tar balls. We did not specifically "look" for the tar ball spectral signature in the individual particles. This comment was based solely on potassium.

Were there biomass burning events reported during these periods at the CARES study?
Fast et al. looked into the prevalence of fires using MODIS hotspot data. Only a few fires were observed during the study and particles from such fires are not expected to have much of an influence on the dataset here.

Referee 2

General Comments: The paper presents a new data set utilizing detailed single-particle analysis techniques, and it is generally well written. However, I believe that major changes are needed prior to publication in ACP. The main conclusion, that organic content on particles increases as they age, is rather mundane, especially considering that the case study was especially chosen to be a period when the total organic mass increased over time. The most potentially interesting section, comparison of California to Mexico City organics, is too brief to provide much useful information.

We have added to this section as detailed below.

In addition, the authors hypothesize changes due to new particle formation, coagulation or condensation, but never show complete size distributions over time to help support these concepts. These data would add value to the paper, and presumably they are available for the CARES experiment.

STXM size distributions are shown in Figure S1 and S2. Size distributions from the scanning mobility particle sizer and aerodynamic particle sizer have been published elsewhere (Setyan et al., Zaveri et al, and Mei et al. (Setyan et al., 2012;Zaveri et al., 2012;Mei et al., 2013). We have added a discussion based on these sources as detailed below.

Specific or Minor Comments: Abstract: Suggestions for those who haven't read the whole paper: Line 20: Do you mean for equivalent particle sizes?

We have revised this to read "circular equivalent diameters".

Line 22: "Less" should be "fewer", since you are talking about discrete features.

Corrected.

p. 9182, lines 9-25: Suggest you refer to these locations on Fig. 1, for the uninitiated reader.

We have added reference to figure 1.

p. 9182, lines 28-29: If data from this case are being supplied to models, how representative is it? Based on the Meteorology section, it seems it is not very typical of conditions in general. A better argument should be made that this unusual case is important, and modelers should be cautioned that it is not typical for the region.

We believe this is a common case for aerosol formation and aging when high summertime temperatures are realized. We have thus added the following sentence:

"Events such as these are representative of stagnant conditions during the summertime in the California central valley. These conditions are conducive to the upslope and down slope flows that carry the urban plume from source to receptor and allow us to characterize changes in mixing state due to SOA formation."

p. 9183: "Fixed-site microscopy sampling" is an odd phrase. I think you mean that samples were taken at fixed sites for later analysis, but as it reads, one might assume the microscopy was done at that site.

We have deleted "fixed-site".

Fig. 2: Axis and scale lettering needs to be enlarged. Figure description is too brief to fully describe the complexity of the figure–i.e., what tracer? Units? How was it determined?

We have corrected the problems with the figure and have added the following description to the figure caption:

"Simulated distribution of CO tracer (ppb) from all anthropogenic sources in the vicinity of the Bay Area and Sacramento at two times on June 27 and 28, 2010."

2.2: This sub-section seems a little out of place; suggest moving it down to just before the Results section.

We have moved section 2.2 to the end of the experimental section. It is now section 2.5.

2.3: p. 9184, line 25: Approximately what percent of fine-mode particles does the 0.3 micron size limit represent? Presumably optical size distribution measurements are

available, and typically this would be a small fraction of the total number or even of those expected to act as CCN.

This is a typo. With the CCSEM EDX we considered particles larger than 100 nm. According to the published size distributions in Setyan et al., this corresponds over 50

p. 9189, lines 3-4: It should be mentioned that at T0 site, soot seems to be attached to the edges of particles while at the T1 site, soot is nearer the center of the particle (assuming these images are representative.) This presumably relates to different mixing processes, affects the absorption properties of the soot, and also gives information onhow appropriate the typical "soot core" model is.

These particles are not necessarily representative of the whole particle population. We are in the process of doing a statistical analysis of the morphology of soot containing particles to be published in a future publication.

Fig. 4: How is "dominance" determined here? Is it qualitative or quantitative?

As stated in the text on lines 9188, lines 7 8, the mapping of the organic "dominant" phase was covered in (Moffet et al. 2010a).

p. 9194, discussion: Obviously, gas-phase reactants is likely to condense on existing particles when organic aerosol mass increases. This section could be made more interesting, however, if complete aerosol particle size distributions (not just those measured by STXM) were used to clearly separate condensation on existing particles from formation of new particles, for example.

We have obtained complete size distributions from the CARES campaign website. Nucleation of particles is clearly present on the days prior to and during our focus period. These size distributions have been published in (Setyan et al., Zaveri et al, and Mei et al.). From the size distributions, it is clear that nucleation mode particles contribute to the overall mass concentration at sizes above 100 nm through condensational growth. The contribution of these nucleation mode particles to the mass of accumulation mode particles through coagulation cannot be separated without an extensive modeling study, which we believe is beyond the scope of the current paper. Nevertheless, we have addressed the reviewer's comment by adding the following discussion based on the previously published size distributions:

"Submicron size distributions show that nucleation events are frequent at both the T0 and T1 sites (Mei et al., 2013 ;Setyan et al., 2012;Zaveri et al., 2012). From these observations, it is clear that nucleation mode particles contribute to the overall aerosol population on a daily basis. At T0, nucleation events were initiated daily at sunrise, while at T1, the events seemed to happen later in the afternoon (around 12 PM local time). How much of a contribution these atmospherically nucleated organic particles make to the accumulation mode population via condensation and coagulation can be estimated using a modeling study with accurate emissions. It is expected that the homogeneous organic dominant particles are due to condensational growth of nucleation mode particles or coagulation of organic rich nucleation mode particles with each other. Particles with ammonium sulfate cores would likely be identified as INOC, so these inorganic/organic mixed particles could be isolated in a model as long as the source and phase of ammonium sulfate is adequately represented"

Fig. 6 and Fig. 7 show different category types. This reflects the different analysis techniques, but can the types be unified to the extent possible?

Reviewer 1 had a similar comment and we have added some discussion noting some similarities. In fact, our color scheme was meant to unify the two analyses. Any green SEM cluster represents what we believe would be a similar particle type as determined by STXM. To call the reader's attention to this, we have added the following sentence to the manuscript:

"To reflect these observations, the carbon rich organic clusters were colored green in Figure 6 to correspond to the OC STXM class shown in Figure 7. The refractory carbonaceous SEM/EDX cluster (Cluster 6) abundantly present at T0 significantly less abundant at T1, most likely due to a larger contribution from carbon compared to refractory elements (Na, K, Fe)."

This sentence follows the changes noted in response to reviewer 1's comment above. Changes to the text were made following P. 9193, line 21.

p. 9196: The MILAGRO data are discussed in the text, but too briefly to provide much of a useful comparison. For example, are time periods and particle sizes similar? Boundary layer thickness? Are total number concentrations similar?–this alone could affect how much mass condenses on individual particles. This comparison seems perfunctory, particularly since its conclusions are included in the Abstract.

To address these comments, we have added the following on p 9195, line 10:

"To compare the amount of organic carbon on the particles, number concentrations during the two field studies need to be considered. The size distributions measured with STXM were similar for both MILAGRO and CARES. Absolute number concentrations during CARES peaked at roughly 30,000 part cm-3 at T0 and 10,000 part cm-3 at T1 (Zaveri et al., ACP, 2012). In Mexico City, total particle concentrations peaked at roughly 50,000 part cm-3 (Klienman, ACP, 2009). Therefore, since the number concentrations in Mexico City are higher, it might be expected that there would be less condensed organic mass per particle. However, boundary layer height can also affect gas-particle partitioning. MILAGRO boundary layer heights started out at 500 m at sunrise (6:40 LST) and rose to 3000 m at approximately 15:00 LST (Doran et al., 2007;Shaw et al., 2007). The situation at T0 and T1 during CARES was somewhat different due to the elevation difference between T0 and T1. Nevertheless, the boundary layer heights were below 500 m at sunrise and rose as high as 2000 m in the evening (Fast et al., 2012)."

Specific MILAGRO data such as given for CARES in Figs. 9 and 10 would be helpful.

This information was presented in our previous article on Mexico City. We did examine the correlation of total carbon from the OCEC measurement with that from STXM. The correlation was not nearly as good. It is possible that some of the data is limited due to particle statistics. Furthermore, OCEC data was not available for the T0 site. The following has been added to the text (P. 9196, line 24):

"This analysis was carried out for the Mexico City dataset, however, OCEC measurements were not available for T0 and the number of particles analyzed was much lower. Although the correlation was positive, it was not as strong (R2=0.03)."

Also,I don't understand the statement "along the transport path for Mexico City there are anthropogenic precursor emissions along the way from T0 to T1", since the T0 and T1 sites apply to California, not Mexico, don't they? Perhaps some of this is already published, it but needs to be discussed in more detail to make this section viable.

We have clarified this sentence to emphasize that there were T0 and T1 sites in both Mexico City as well as during CARES. The sentence now reads:

"Furthermore, along the transport path for Mexico City there are anthropogenic precursor emissions along the way from the Mexico City T0 site to the Mexico City T1 site, but in CARES anthropogenic emissions drop off dramatically well before the CARES T1 site. This will lead to less exposure to precursors, resulting in particles having less anthropogenic organic content."

Also, the Abstract discusses soot number fractions for the two sites, but they don't seem to be in the text.

We believe this is an important point and we have discussed this further in the text. We have also added a discussion about the mixing state of soot. After P. 9194, line 16, we added:

"The number fraction of soot particles was observed to be slightly lower at T1 where 13.4

And we re-worded the abstract to read:

"The number fraction of soot particles at the Mexico City urban site (ranging from 16.6 to 47.3

Grammar: The author tends to omits commas to separate independent clauses and parenthetical elements. For more clarity, I suggest that some of these should be added.

We have re-read the manuscript and made corrections to address this comment.

The first text paragraph is one example. Typos: p. 9187 line 21: “a” should be “as”. p. 9190, line 4: “coarse” is misspelled. p. 9191, line 22: First “clusters” should be “cluster”. p. 9192, line 25: “function” is misspelled.

These typos have been corrected and we thank the Reviewers for their comments.

References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9179, 2013.