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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Microscopic characterization of carbonaceous aerosol particle aging in the outflow from Mexico City" *by* R. C. Moffet et al.

Anonymous Referee #1

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General Comments:

The authors have characterized single particles collected at three sites in Mexico City in order to better understand ageing processes, in particular with respect to organic carbon. The paper is generally well written and I suggest publication after the following specific comments are addressed. In particular, some sort of uncertainty analysis associated with the spectral deconvolution methods is needed as is some discussion of how the particles, as observed using the microscopy methods, may have been altered from their state in the atmosphere.

Specific Comments:

p. 17002: For the STXM measurements it is stated that the optical density depends on, among other factors, the material thickness. It is my understanding that the STXM method cannot directly get at particle thickness and so some assumption must be made in order to properly determine optical density. What assumption was made here? Spherical particles with a diameter determined based on the spatial extent of the particles in the other two dimensions? How are non-spherical particles treated?

p. 17003, line 23 (and throughout in general): The EDX line scan data provide evidence that for particles at T0 many of the particles can be generally described as having sulfate cores surrounded by organic material. However, it is reasonable to think that the exact nature of the particles as they exist in the atmosphere is modified by the collection technique, transport to the analysis location and the removal of water from the particles. Can the authors comment on how in particular this last aspect (no water) might bias the results?

p. 17003, line 24: The authors show that in addition to having sulfate cores with organic coatings, some particles have potassium cores with organic coatings. In Figure 4 it appears that the S and K cores are observed in the same particles, suggesting that the K and S are internally mixed. Presumably, K is from primary emissions and S is from secondary formation. Why then would these be so well internally mixed? Does this have anything to do with "missing" water during analysis (see the above comment)?

p. 17003, line 24: From the STXM images below, it would appear that EC behaves quite differently than the inorganics in terms of how it mixes in the particles. Here, the inorganics are present as "cores". But EC appears to be scattered throughout the particles. Why would this be the case? Presumably, EC would not mix with OC any better than the inorganics?

Figure 5: It appears from the images shown in figure 5 that not only is the amount of OC increasing, but that the carbonaceous inorganic phase (IN) is decreasing in going from T0 to T1 to T2 (i.e. there are fewer/smaller "blue" areas in B and C compared to

A). Can the authors comment on why this might be the case? Does it have anything to do with the 3D structure of the particles? In other words, where did the IN go?

p. 17004, Line 11 and Figure 6: Are the presented spectra averages over the three sites? Why not make a 9 panel figure breaking out the different sites as in Figure 5?

p. 17005, Line 27: The authors estimate the COOH as the difference between the C 1s–>pi* transition and the pre-edge intensity. Why not use the fits (as in Figure 11) to deduce the COOH fraction rather than the difference method used here? Additionally, I am not convinced that the difference between the T0 and T1/T2 COOH vs. distance plots necessarily provides clear information on the physical mixing within the particles. Presumably, the results shown in this figure are averages from a number of particles. But in Figure 9 it is shown that the fraction of particles at T1 and T2 that contain OC and S is smaller than at T0 (similar information can be gleaned from Figure 8). So is this difference in the COOH distribution just a sampling issue (i.e. the number of particles looked at using STXM at T1/T2 were less likely to contain OC and S than at T0)? For particles at T1/T2 that did contain significant amounts of S was the core/shell morphology also observed? Or did these specific particles show generally different behavior than at T0? This would suggest something important about mixing. As it stands, I am concerned that this conclusion arises more from the statistics of the sampling.

p. 17006, line 18: The authors suggest that oxidation of soot could have led to the formation of carbonyl moieties within the EC phase. However, given the timescale of the plume evolution (a few hours), would heterogeneous oxidation have been fast enough to explain the magnitude of the observed carbonyl fraction within the EC phase? Since the EC phase was identified by empirically (arbitrarily?) setting an sp2 threshold of 35%, could the observation of a significant carbonyl component have more to do with the spectral deconvolution?

p. 17006, line 26: Since the STXM technique looks through the particle, to what extent might the sorting into groups be driven by differences in the vertical structure of the

particles (e.g. OC-EC-OC or OC-IN-OC)? It would be extremely useful if the authors were to provide some sort of uncertainty estimate here.

p. 17008, line 24: The authors observed an increase in the total carbon mass per particle. How does this single particle result compare with the co-located bulk measurements (e.g. AMS)?

p. 17008, line 26: Again, some sort of uncertainty estimate for the deduced fractions of COOH, O-CH2, etc. would be extremely useful. Without knowing the uncertainty in the estimates, it is very difficult to know whether the observed changes in the particle COOH, etc. fractions are to be believed.

p. 17008, line 26: The authors state that the fraction of OCH2 groups (identified as being from sugars) increases downwind from T0. If the biomass sources are in the city (or part of the aerosol background) why would this fraction (the O-CH2 group) increase downwind since it is presumably derived from primary emissions. It would seem that the fraction should actually decrease as the amount of secondary material increased. I would naively think that the O-CH2 group would track with the %SP2 hybridization (since this is in some ways a marker for primary emissions).

p. 17009, line 12: I don't agree. I think if these were both normalized to the value at T0, the decrease would appear similar in magnitude. Or at least reasonably similar. Again, uncertainty estimates would help here. I would also recommend pointing out more clearly that the variability in going from T0-T1-T2 for the EC and OC sp2 bonds is quite similar. This would support your conclusion that the relative decrease in both is due to condensational growth. However, this still doesn't address the question of where the sp2 bonds in the OC phase come from. Can the authors comment on the source of the OC sp2 bonds (oligomers?)?

Figure 2: minor note: the bars indicating the additional transport days appear more blue than they do gray.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 16993, 2009.