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Atmospheric Chemistry and Physics Discussions

Interactive comment on “The time evolution of aerosol composition over the Mexico City plateau” *by* L. I. Kleinman et al.

Anonymous Referee #1

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Review of Kleinman et al.

The paper by Kleinman and coworkers presents the results of a study carried out using the G-1 DOE aircraft during March 2006, as part of the large MILAGRO campaign. It focuses on the evolution of urban aerosol composition with photochemical age. A number of assumptions and statistical analyses are performed to extract the urban signal from other influences in the dataset (industrial emissions, forest fires, etc.). These complex filtering and analyses appear to have been done very carefully, as far as I can tell from the information presented. The conclusion of rapid formation of urban SOA about an order of magnitude higher than predicted by current models confirms previous results in Mexico City and other regions. The paper is very well written and certainly appropriate for ACP and its MILAGRO special issue. I recommend the paper

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Discussion Paper

for publication in ACP after a few issues are addressed:

1) Evolution of sulfate aerosol

- P14447, line 20, plus Table 5 and Figure 10a. Although this is not discussed in the manuscript, this figure and table could be interpreted by a reader as very rapid production of sulfate in the urban plume, even faster than for SOA. This would be surprising given the known slower gas-phase kinetics of SO2 oxidation. Salcedo et al. (2006) concluded that the sulfate had more of a regional character in Mexico City, with large plumes at times, presumably arising from Tula and the Popocatepetl volcano. Those authors estimated (their Fig 12) that sulfate formation was of the order of 0.1-0.2 ug m-3 hr-1 inside Mexico City during the day. Compared to an average concentration of 3 ug m-3 in that study (and similar levels in Fig. 11 in the present paper), this rate could not possibly increase the concentration of sulfate by a factor of 10 in one day. Aqueous-phase oxidation is faster than gas-phase oxidation of SO2, but it is unlikely to have played a major role over the short timescales and given the low humidities reported in this study. The actual sulfate concentration is indeed relatively constant in Fig. 11.

Since the sulfate is more regional and not correlated with the CO sources in the city, ratioing its relatively constant regional concentration to the rapidly decreasing CO away from the city gives rise to the misleading impression that sulfate is the particle-phase species that is formed most effectively in the MC plume. The authors do not suggest this in the text and are more than likely aware of these issues. However this lack of discussion could prove very confusing for some readers. It is imperative that the different dynamics and character of sulfate are described in the manuscript. I also strongly suggest that sulfate, plus the fraction of ammonium that is associated with sulfate, are removed from Table 5 and Figure 10a. Since these are known from prior research and the C-130 measurements to be regional pollutants with no major urban sources, this would present a clearer picture of the evolution of the major urban secondary species, ammonium nitrate and SOA.

2) Correction of m/z 57 as a tracer of HOA

P14467, line 17: all of m/z 57 is attributed to the C4H9+ ion. However studies using the high resolution version of the AMS have shown that in aged air with high SOA content, a significant fraction of the signal at m/z 57 can originate from the oxygenated ion C3H5O+. Figure 8 of DeCarlo et al. (2006) presents a high-resolution AMS spectrum acquired in a summer afternoon in Riverside, CA, with a high fraction of OOA, where C3H5O+ is about 1/3 of the signal at m/z 57, or 7% of total m/z 44. One can expect that the oxygenated ion at 57 will be correlated with 44, and a better tracer for the HOA fraction of 57 would be:

m/z 57_corrected = m/z 57_total - 7% * m/z 44

Similar numbers have been observed in other studies with the HR-ToF-AMS. I suggest that this corrected 57 is used instead of total 57 in figure 12, as a better indicator of the HOA fraction of the aerosol.

3) Other Issues

- P14464, line 13: the de Gouw et al study was conducted on a ship, not a fixed ground site

- P14464, line 17: I suggest replacing "known" with "estimated." Trajectories or VOC ratios have significant uncertainties, as is discussed later in the paper.

- P14465, line 3 and in several other places later: the expression "amu/z" is used to describe the mass-to-charge ratios detected by the AMS. This expression is incorrect. An amu is a unit of mass, while z is a symbol for charge. The correct symbol used in the mass spectrometry literature is m/z. For example see the use in the Guide for Authors of the Journal of the American Society of Mass Spectrometry: http://www.elsevier.com/wps/find/journaldescription.cws_home/505727/authorinstructions .

- P14468, line 13: "regression" should be "regressions"

- P14469, line 1: perhaps differences in size distributions may also cause changes in the apparent CE?

- P14479, line 10: is aqueous-phase chemistry likely to be important in Mexico City, given the predominantly low RH conditions mentioned earlier in the paper?

- P14479, line 14: it is stated that "NH4+ and NO3+ are volatile." This is not quite correct. The NH4+ measured by the AMS includes that present in (NH4)2SO4, which is effectively completely non-volatile. Only the NH4+ chemically associated with NH4NO3 is semivolatile. Thus I recommend referring to ammonium nitrate and not the separate inorganic ions.

- P14480, line 16: toluene reacts relatively rapidly with OH, so I would be worried about using equation 10 using data for all photochemical ages. Has this equation been applied only to air with the lowest ages? If yes, please make it clear in the manuscript, if not, I recommend doing so.

- P14483, line 13: oxidation of biogenic VOCs may be a more important source of CO in the Northeast US than previously estimated (Hudman et al., in prep.).

- P14483, lines 24-26: I believe this definition of PILS WSOC is incorrect. It is not the fraction of the OA in particles that activate and grow to a collectible size in the PILS. The supersaturations in the PILS collector are very large, and effectively all particles beyond 20 nm or so (and effectively all the OA mass) are activated and collected into the liquid. The "water-soluble" qualifier arises because of the use of a liquid filter in the water line before entering the carbon analyzer: only carbonaceous species that are soluble in water get past this filter, while species that remain in insoluble particles do not get past the filter. For details see Sullivan et al. (2004).

References

P.F. DeCarlo et al. Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer. ANALYTICAL CHEMISTRY, 78: 8281-8289, 2006.

Hudman, R.C. et al.: Anthropogenic and biogenic CO sources over the United States: implication for CO as a tracer of pollution, in prep.

D. Salcedo et al. Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite. ATMOSPHERIC CHEM. PHYS., 6, 925-946, 2006

A. P. Sullivan et al. A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: Results from an urban site. GEOPHYSICAL RESEARCH LETTERS, VOL. 31, L13105, doi:10.1029/2004GL019681, 2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14461, 2007.