Atmos. Chem. Phys. Discuss., 7, S8714–S8723, 2008
www.atmos-chem-phys-discuss.net/7/S8714/2008/

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.

L. I. Kleinman et al.

Received and published: 23 January 2008

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

We would like to thank the reviewers for their encouraging comments and useful suggestions. For the readers convenience, the 3 reviews are repeated here along with a point by point response.

Anonymous Referee #1 Received and published: 14 November 2007 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 for publication in ACP after a few issues are addressed:

Response: Thank you for your encouraging review

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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.

Response: The Reviewer brings up some interesting questions that have helped bring our sulfate numbers into better focus. I agree that text should be added to describe the difference in dynamics and character of sulfate as compared to aerosol constituents whose sources are co-located with urban CO. My reason for including sulfate was not so much to show growth rates but rather to specify the aerosol composition aerosol that was observed. Regardless of the source of sulfate (and associated ammonium) it is still important to provide concentrations that can be compared with other constituents such as in Fig 10a. Inclusion in Table 5 also serves a purpose as sulfate is the prototypical example of a secondary aerosol constituent that does not partition back into the gas phase. I agree that it is important to distinguish what a growth factor means for sulfate as opposed to organics. A paragraph has been added discussing the different nature of sulfate in Section 5-1 "Non-uniform sources" with a reference to Salcedo et al. (2006). The different nature of sulfate is also noted below Eq. (6).

Some additional info: In order to get sulfate concentrations representative of the urban plume, limits on SO2 concentrations were imposed (Table 4). These criteria eliminate the more concentrated plumes, in particular those from Tula.

The sulfate concentrations and their change with photochemical age are actually quite reasonable for gas phase oxidation of SO2. Here is one way of looking at the numbers: In the manuscript, boundary layer background CO is estimated to be about 130 ppb. This is clearly not clean air but rather represents an accumulation of dilute aged pollutants from various sources. In the range CO = 120 to 140 ppb, average sulfate aerosol is 0.74 ug m-3. (The median is slightly lower, 0.6 ug m-3). From these background estimates and data in the paper we have:

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

Young = average of bins 1 and 2 Aged = average of bins 9 and 10

Sulfate (young, aged, background) = 2.15, 1.63, 0.74 ug/m3

CO (young, aged, background) = 857, 170, 130 ppb

Assume dilution of the Young air with Background air. The dilution factor = (857-130)/(170-130) ˜ 18. After dilution the sulfate concentration will be (2.15+17*0.74)/18 = 0.82. The actual sulfate concentration is 1.63 giving a change in sulfate due to chemical production of 0.81 ug m-3. This additional sulfate could be formed in less than a day at a rate of 0.1 to 0.2 ug m-3 h-1. A large growth factor for sulfate (9.5 in Table 5) is expected. The growth factor pertains to a change in sulfate concentration above background. Primary emissions of aerosol sulfate are very small, so the large growth factor is expressing the fact that most of the aerosol sulfate is secondary.

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.

Response: I have seen presentations of high resolution AMS spectra from Mexico City and as you say C3H5O+ is a significant component of the m/z = 57 signal. I have re-done Fig 12 using m/z 57 corrected as suggested (not included in revised manuscript). The problem is that above a photochemical age of 0.6, the corrected M57 (surrogate for HOA) is zero or slightly negative. I assume that the problem is that the 7% figure is too

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

high for Mexico City. On the other hand, M57 is clearly not a perfect choice for HOA. An age graph of HOA/CO vs. photochemical age (not in manuscript) shows a factor of 2 growth which is due to the problem that you bring up. I was waiting for a PMF analysis of the AMS spectra before doing anything more sophisticated than presenting M44 and M57. I have changed the text to indicate that M57 is an approximate surrogate for HOA, that it includes $C_3H_5O^+$, and that HOA should decrease faster with photochemical age than the M57 age dependence shown in Fig. 12. A citation to DeCarlo et al (2006) has been added.

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

Response: So noted.

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

Response: Changed as suggested

- 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

Response: amu/z changed to m/z

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

Response: changed

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Response: Probably true, but I'm not aware of a literature reference

- 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?

Response: This was meant to be a general statement about sulfate production pathways – not specific to Mexico City.

- 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.

Response: Changed as suggested to NH4NO3.

- 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.

Response: This is an interesting point. The regression in the paper includes all data. The regression is heavily dominated by young, high concentration points. Repeating the regression for low age points, one gets a virtually identical slope (difference $<$ 1%) as long as the intercept is forced to give zero toluene at 100 ppb CO. Otherwise the slope is slightly lower (5%) – not greater as expected from toluene reactivity. Such is the precision of the data. The aged air mass points by themselves do give a lower slope as expected. Text has been added stating that all points are used – but results are essentially the same as obtained for fresh emissions.

- 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.).

Response: I have not seen results from this study. It is an interesting possibility that

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

for a low SOA yield compound such as isoprene, the addition of SOA and CO could actually lower the urban SOA/CO ratio. I'll look for this paper when it appears.

- 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).

Response: I did not realize that there was a filter. My explanation of the water soluble component is incorrect and has been removed. I've added the Sullivan et al (2004) citation.

References P.F. DeCarlo et al. Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer. ANALYTICAL CHEMISTRY, 78: 8281-8289, 2006. S6871 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. S6872

Anonymous Referee #2 Received and published: 14 November 2007 This paper discusses the evolution of aerosol composition over the Mexico City Plateau based on measurements from multiple DOE flights covering a range of photochemical ages. Air

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

masses analyzed range from freshly emitted to approximately 1 day old according to NOx/NOy ratio. The authors performed a thoughtful analysis of their data and report important findings such as the substantial underestimation of OA production using chamber yields and VOC measurement data and the lack of correlation between SOA production rates and pollution level. This paper is extremely well written, on a topic that clearly suits the scope of ACP. I highly recommend its publication.

Response: Thank you for your kind comments

One suggestion I want to make is to show the scatter plots of aerosol species vs. CO for the entire dataset (color by photochemical age). These figures will provide good overviews. They can be included in the supplementary info if limited by space.

Response: I've shown that type of figure in presentations. While it is a good visual in some respects, it is difficult to extract quantitative information because lots of data points lie on top of each other. Instead, I've added supplementary information consisting of the 20 graphs showing linear regressions of organic aerosol vs. CO and total aerosol vs. CO.

I am curious about how the organic-equivalent mass concentrations of m/z 44 and 57 vary as a function of photochemical age. It will be interesting to see if there is any trend in HOA concentration vs. photochemical age.

Response: As I mentioned in my response to Reviewer 1, there is a factor of 2 growth in M57/CO as a function of increasing photochemical age. As Reviewer 1 noted, high resolution spectra show that M57 contains an oxygenated peak, C3H5O+, which should account for the increase with age. The prescription offered to construct an HOA component out of M44 and M57 should be an improvement on just using M57 – but it resulted in zero and slightly negative HOA at high photochemical ages. A proper treatment of this topic awaits a PMF analysis.

Minor comments: Replace amu/z with m/z (e.g. Page 14465, line 3) Page 14473, line

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

14, extra -a- after -we- 14479, 21, replace -loose- by -loss- 14484, 26, massed- with -mass- 14496, footnote 1,

Response: Typos corrected.

Age Growth factor was defined in Eq. (7) Fig. 9 can be expanded to include the plots of SO4 /CO and NO3/CO vs. Age.

Response: Reviewer 1 correctly points out differences between sulfate and organics and I have changed the text accordingly. I am hoping that the age dependence of NO3-/CO will be a topic of another study.

————————————————————————-

Anonymous Referee #3 Received and published: 15 November 2007 This manuscript describes the results of airborne measurements of aerosol composition downwind from the Mexico City metropolitan area. The study looks at the aerosol composition as a function of photochemical processing, characterized by NOx/NOy ratios. This is really an excellent paper. The DOE G-1 data set from Milagro is eminently suited for an analysis of this kind. In addition, the authors do a commendable job of describing the treatment of the data in detail and placing the observations in the proper perspective provided by the recent literature. The main conclusions are that the growth of organic aerosol in the urban plume is rapid and cannot be accounted for by the removal of aromatic precursors These conclusions agree with those from multiple other studies -all are properly referenced- and as a result this work places all of these findings on an even firmer basis. The authors end by noting that OA/CO ratios after day of processing are similar between Mexico City and the northeastern U.S. This is a very interesting finding that was maybe not entirely expected. Future research should be aimed at explaining these similarities, and may give further insights into the pre- cursors and mechanisms that are responsible for SOA formation in urban plumes. The manuscript can be published as is. The authors clearly did a very careful job describing these results and there is no need to burden them with more work in order to get this study

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

accepted to ACP.

Response: Thank you for your kind comments

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper