Atmos. Chem. Phys. Discuss., 11, C2372–C2375, 2011
www.atmos-chem-phys-discuss.net/11/C2372/2011/

Atmospheric
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Discussions

Interactive comment on "Ozone-driven photochemical formation of carboxylic acid groups from alkane groups" *by* S. Liu et al.

Anonymous Referee #2

Received and published: 28 April 2011

This is a very interesting paper that offers a different approach to the problem of separating SOA from other OA sources with a focus on carboxylic acids. It is a complicated analysis of ambient aerosol measurements that combines FTIR and AMS techniques to study increases in OA as a function of change in ozone during transport of aerosols from large source regions. The central hypothesis, based on previous chamber studies, is that the secondary production of condensible carboxylic acids occurs via a two-step process beginning with the oxidation of alkanes by OH followed by the ozonolysis of dihydrofuran. The observations are used to demonstrate the feasibility of this hypothesis as well as estimate the fraction of OA contributed from SOA in this situation. The paper is well written and organized with a few exceptions. Specific comments follow.

1. The AMS is a great instrument, but it is not a PM1 instrument. All published reports

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of modelling, laboratory and field measurements indicate that it does not measure 50% of the 1 um geometric diameter particles. The 50% transmission efficiency of the AMS is approximately 0.7 um aerodynamic diameter. If you want to scale your AMS data to some filter-based PM1 measurement(s), then you might call that an estimate of PM1, but the PM1 designation as applied here is unacceptable.

2. What about the diurnal pattern of sulphate? Assuming no low cloud during the daytime, most sulphate is driven by OH. Based on the AMS, you have almost as much sulphate as OA, and since you estimate that <40% of the OA was secondary you could have a stronger photochemical signal in sulphate than OA. This would help with your discussion on page 7205 as well as with timing of OH reactivity. How fast is the two-step oxidation process, and would you expect to see a slight lag of the acids relative to ozone? It is not possible to tell anything about that from Figure 3.

3. Since combustion was the dominant factor (page 7204), I would expect a stronger correlation than r=0.5. To me, this suggests that there are other factor(s) controlling more of the variation in OM from FTIR and AMS than the source. Another possibility is there was a lag, as discussed above. One mechanism that might have significantly influenced the correlation is the sea-breeze. There is really little discussion of the impact of the sea breeze on the main aspects of the paper. There is reference to the impact on the marine component, but we do not know how the sea breeze may have affected the trajectories and your ability to treat this as a pseudo-Lagrangian scenario. Some discussion of these points is needed.

Minor comments:

4. Additions of CO along the trajectory path, without corresponding additions of OM, will perturb your use of CO as a dilution tracer. See Liggio et al., JGR, 2010 for a discussion of this. Also, Liggio et al. use measurements from a Hi-RES-AMS and a photochemical tracers to estimate about 40% of OA was from SOA approximately one photochemical day downwind of urban emissions. Besides comparing with this, there

are references in that paper to other SOA estimations that could be included here.

5. Comment about why the second oxidation step is by ozone rather than OH.

6. P7190, line 8 – define “tightly correlated”.

7. P7190, line 11 – “derived from” rather than “resulted from”

8. P7191, line 6 – “are found in” rather than “remain in”

9. P7191, line 14 – “radiative” rather than “physical”

10. P7194, lines 23-25 – The calibration of a TEI 49C does usually does not drift so much that the mixing ratios are that much in error. Some idea of the ozone levels would be useful.

11. P7194, line 25 – “are” rather than “were”

12. P7195 - first sentence grammar

13. Figure 3 and 6 – the print version is very small and difficult to read.

14. P7195, line 8 – maybe “consistent” rather than “stable”. The latter tends to imply something more when discussing temperatures.

15. P7195, line 22 – what do you mean by “consistent” number of days?

16. P7196, line 17 – mass concentration

17. P7196, line 20 – a single air mass

18. P7197, near end of first full paragraph, you say “This is consistent with the fact that the sulfate-based CE used here was developed for ambient samples associated with relatively high sulfate fractions that were about 40% on average”. Why then did you use that adjustment for the CE? In Figure 4, there is no correlation for points above 4 ug/m3. Which has more uncertainty in its OM concentration, the FTIR or the AMS?

19. P7197, line 23 - "insignificant relative to the ambient variations" or something like

that.

20. Figure 6 - Why is the ozone variation not shown for the overnight period?

21. P7204, line 16 – transmission efficiency rather than collection efficiency.

22. P7205, line 8 – “tightly” again.

23. P7205, lines 10-12 – A correlation of the carboxylic acid groups with odd oxygen (O3+NO2) would be preferable to just ozone, but NO2 measurements were unavailable during this study.

24. P7206, line 23 – The OM peaks about 300-500 nm, but OM/PM1 peaks below 200 nm. Clarify what you are plotting: OM/(total AMS mass) where both terms are for a particular size interval.

25. P7209, line 2 – “are MOSTLY secondary”. Even in your Figure 12, you show a background carboxylic acid level some of which at least can not be ruled out as primary.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7189, 2011.