

Slowik et al report the application of a field-deployable Toronto Photo-Oxidation Tube (TPOT) technique to provide *in situ* OH oxidation of ambient organic aerosols during the Whistler Aerosol and Cloud Study. The TPOT produces OH radicals via UV photolysis of O₃ in the presence of water vapor. The TPOT is used to simulate the heterogeneous oxidation of organics over 1 - 10 days of atmospheric oxidation. Aerosol chemical composition is measured with an Aerodyne compact time-of-flight aerosol mass spectrometer. Control measurements were performed to isolate OH-initiated changes in chemistry from: (1) exposure to UV light, which also results in a ~4 deg C temperature relative to the “lights off” condition (2) O₃ exposure in the absence of UV light, which does not appreciably change the AMS spectra. The authors present AMS time series and discuss their results in the context of the Ng et al. f_{44} - f_{43} triangle (fraction of AMS organic signal at $m/z = 43$ and 44) and the Van Krevelen diagram (H/C ratio versus O/C ratio). They apply Positive Matrix Factorization to identify five source factors: one factor influenced by biomass burning (BBOA) and four oxygenated organic aerosol (OOA) factors spanning a range of oxidation level, reactivity, and volatility. The OOA factors, which are principally identified by TPOT-induced oxidation of the ambient OA, suggest the importance of OH oxidation in organic aerosol aging.

This application of flow tubes to provide oxidative aging of ambient organic aerosols is original. It addresses an important issue in the atmospheric sciences regarding oxidative aging – induced changes in organic aerosol chemistry. Of particular relevance is the ability to simulate oxidation over multiple days in the atmosphere, which, to my knowledge, is a unique capability of flow tubes such as the TPOT and related techniques. I support eventual publication of this manuscript in ACP. However, there are several issues that should be addressed in the ACPD manuscript before I would recommend publication in ACP. The main issues are related to TPOT wall losses, presentation of PMF results, and TPOT-AMS kinetic/chemistry information.

MAIN COMMENTS

TPOT wall losses

1. The authors do not discuss any control experiments that were performed to measure particle wall losses through the TPOT mixing tube and/or the reaction zone (e.g. p. 8192, line 23), and/or post-correction of the data for wall losses. This is a significant omission, as it may affect interpretation of results, particularly in regards to the TPOT “AmbHt” and “AmbHtOH” conditions relative to “Amb”.
 - (a) The Lambe et al. 2011a reference suggests that flow tube wall losses can be significant, particularly as a result of large-scale, thermal convection-induced dispersion in flow tubes (e.g. following turning on UV lamps). This convection-induced dispersion is presumably more significant in the TPOT reaction zone than in the TPOT bypass flow tube, and might explain the 10-25% decrease in mass observed through the reaction zone.
 - (b) Furthermore, Figure 2 in Lambe et al. (2011a) suggests wall losses on the order of

10-20% for 150-300 nm diameter particles, which presumably encompasses the size range of particles sampled in this work. This result even includes the TPOT flow tube used by the authors in this study. Unless the data has already been corrected for TPOT wall losses (in which case this should be explicitly stated in the paper), it seems to me that this is a very plausible explanation for the 10-25% mass loss observed with turning on the TPOT lamps.

- (c) Do the authors have any additional evidence or references to support their expectation that changes in “AmbHt” spectra and loadings are driven by volatility rather than UV irradiation (p. 8193, lines 2-3)? For example, if the TPOT is heated by 4 deg C without turning the lights on, is the same 10-25% mass loss observed?

TPOT – AMS kinetics / chemistry

2. The OH exposure calibration method using oxidized BES particles is an interesting idea (pp. 8189-8190, lines 28-9). However, I suggest that the authors more fully discuss some of the details regarding this calibration, because it has some limitations relative to the use of a gas-phase tracer. This would also help others that may be interested in adopting a similar calibration method in related studies.
- (a) A calibration curve relating the TPOT OH exposure (derived from MEK decay) to the f_{44} of oxidized BES particles should be presented, perhaps in the Supplement.
 - (b) Somewhere in the Experimental section, I think that the authors should explicitly state any assumptions or limitations used in this calibration relative to a more traditional gas-phase tracer, especially because the associated heterogeneous oxidation kinetics are different. For example,
 - (c) What OH uptake coefficient is assumed for BES particles?
 - (d) Over what range of OH exposure is the response in f_{44} linear / nonlinear?
 - (e) Is there a maximum f_{44} attainable for oxidized BES beyond which increases in OH do not change f_{44} ?
 - (f) What additional uncertainties are present, if any?
 - (g) It may also be worth emphasizing that specific operating parameters of the AMS (e.g. vaporizer temperature, fragmentation table coefficients) can affect f_{44} and need to be accounted for in using this calibration procedure.
3. The authors should estimate an OH rate constant or uptake coefficient (p. 8196, lines 23 – 25) for representative AMS spectral markers (e.g. $m/z = 91$ or related species) and/or the less-oxidized PMF factors (BBOA, $OOA_{R,V}$, $OOA_{R,NV}$). If possible, this should be calculated as a function of OH exposure. While this requires assumptions about particle size, density, and molecular weight, at the very least the authors can bound the range of measured OH reactivity/uptake. This would help place these results in the context of previous laboratory oxidative aging studies (e.g. references cited on p. 8187, lines 5-7), and might also augment the discussion of PMF species reactivity on pp. 8200-8201.

4. There are a few issues that should be cleared up regarding the presentation and discussion of results in the context of the Van Krevelen diagrams (p. 8198, lines 15-23; Figure 7):

- (a) By themselves, the calculated Van Krevelen slopes (-0.1 to -0.2) do not corroborate the observed formation of carboxylic acids, which, as described by Heald et al. (GRL, 2010), result in a Van Krevelen slope of -1.0. The only way (that I am aware of) to reconcile observations of carboxylic acid formation ($m/z = 44$ in AMS spectra) and Van Krevelen slopes of -0.1 to -0.2 is significant fragmentation (e.g. Ng et al., ACP, 2011) with preferential loss of carbon relative to oxygen. This was postulated on line 23 but, in my opinion, needs to be stated more emphatically.
- (b) I thought it was useful to place TPOT results in the context of simple oxidation reaction steps (p. 8198, lines 24-28). The authors might also consider placing relevant oxidation products such as *cis*-pinonic acid, *cis*-pinic acid, and 3-methyl-1,2,3-butanetricarboxylic acid in Fig. 7 to see if this aids in interpretation of results. See Chhabra et al. (ACP, 2011) for an example.
- (c) If the aerosols sampled in this study are predominately influenced by biogenic sources, then the dashed line from Heald et al. (intercept: H/C = 2) shown in Fig. 7 is probably irrelevant. The intercept on a Van Krevelen diagram should have some relation to precursor(s) associated with the OOA. An intercept of H/C = 2 was chosen by Heald et al. to represent large alkanes. Here, I think an intercept of H/C = 1.6 (terpenes) may have more relevance.

5. I suggest that the discussion regarding organonitrates (p. 8199, lines 1-9; Fig. 8) be removed from this paper, for the following reasons:

- (a) The decrease in f_{30}/f_{46} with OH exposure is not very convincing evidence of organonitrate observation. For example, these trends could also be due to changes in $\text{CH}_2\text{O}^+:\text{CH}_2\text{O}_2^+$ with oxidation (in addition to, or instead of, $\text{NO}^+:\text{NO}_2^+$). These ions may not have anything to do with organonitrates.
- (b) Even if there is definitive proof of organonitrate measurements, the authors did not relate them to any of the 5 PMF factors. Thus, while it might be an interesting observation, it doesn't seem to have anything to do with the main premise of the paper (and, moreover, distracts from that main point).

6. Figure 2: There seems to be structure in the ammonium, nitrate and sulfate time series. Their concentrations increase when the TPOT-AMS is switched from "AmbHt" to "AmbHtOH" mode. The nitrate formation is discussed in the text, but the sulfate increase is not. A short description of this feature might worth including in the text. The authors imply that SOA formation in the TPOT is negligible. However, if I take this result at face value, it implies that significant amounts of SO_2 are present and are oxidized to form sulfuric acid in the TPOT. Perhaps this feature would be even more pronounced if the TPOT had a lower surface-area-to-volume ratio.

TPOT-AMS PMF results

7. As far as I can tell, the statistics for the authors' rotated 5-factor solution are not presented anywhere in the paper (e.g. p. 8191, line 28) or in the supplement. This is a significant omission that should be fixed.

(a) What is the normalized Q-value (Q/Q_{exp}) for the 5-factor solution with $F_{\text{PEAK}} = -0.5$? Also, what is the average residual (fraction or percentage)? While there is always some underlying subjectivity associated with interpretation of PMF factors, the authors should provide at least some of the statistical data from the various PMF solutions, and discuss those data in the context of justifying their choice of the 5-factor rotated solution as the "optimal" solution.

(b) Why do PMF solutions with F_{PEAK} between -0.5 and 0 not converge?

(c) A time series of the PMF residual should be added to Fig. 9 and/or briefly discussed in the text.

8. The comparison of TPOT factors to SV-OOA and LV-OOA PMF factors from the literature is not useful without (1) graphic presentation and/or (2) linear correlation of the pertinent SV-OOA and LV-OOA PMF factors (e.g. pp. 8200-8201, lines 28-2). There is also quite a bit of variance in literature SV-OOA and LV-OOA factors depending on the specific study (Ng et al., ES&T, 2011). This should be addressed by indicating which literature SV-OOA and LV-OOA factors are being intercompared with TPOT factors, and by providing a statistical indicator of the quality of comparison.

9. Page 8201, lines 2-8 and Figs. 9-10: I think that the "BBOA" factor identification should be clarified/improved. At the very least, identification of this factor from AMS data is not definitive in the current presentation.

(a) The reported $f_{60} \sim 0.5\%$ is barely above typical background levels of regions unaffected by biomass burning ($f_{60} = 0.2\% - 0.4\%$), compared to "fresh" BBOA sources with $f_{60} \sim 1\% - 4\%$ (Cubison et al., ACP, 2011). If this factor truly represents BBOA, then (1) the "BBOA" factor may represent a heavily aged biomass burning source or (2) $m/z = 60$ and $m/z = 73$ signals from the biomass burning source have been mixed into the other factors. I think that these issues should be mentioned in the discussion.

(b) The authors mention that acetonitrile is correlated with the "BBOA" plume. Why not show a time series or correlation plot of [BBOA] as a function of [acetonitrile] or the AMS $m/z = 39$ (K^+) signal? Either of these tracers seems like a more robust indicator that would support the identification of this factor as biomass-burning-influenced. K^+ has a large negative mass defect ($m/z = 38.964$) which may be possible to resolve from other masses at $m/z = 39$ (e.g. C_3H_3^+ , $m/z = 39.023$) using the c-ToF-AMS.

10. Page 8203, lines 23-28: In its current form, the comparison of TPOT factors to PMF factors from George et al. is also not useful to readers that are unfamiliar with the George et al. work. If this comparison is important, this should be rectified in a similar manner as outlined in Comment #8 above.

MINOR COMMENTS

11. P. 8187, lines 12-13: “Changes to particle CCN properties are described in a separate publication (Wong et al., 2011)”. I would remove this sentence, because this seems like an unnecessary place to cite this paper (especially because it is referenced later on page 8189, line 22). Also, ‘CCN’ is not defined earlier in the paper (Cloud Condensation Nuclei).

12. P. 8190, lines 21-22: I assume that the authors did not collect particle time-of-flight data with the AMS because of signal-to-noise limitations. I suggest adding a few words to clarify the reason(s).

13. P. 8191, line 24 and P. 8192, line 5: The authors reference a paper by Ulrich et al. (2010), but the Ulrich et al. paper in the list of references was published in 2009. Either this is a typo or there is a reference missing.

14. P. 8192, line 26: What is the linear correlation coefficient (r^2) between the mass spectra of unreacted aerosol and O₃-exposed aerosol? I assume from Figure S1 that it is very close to unity. That information would be useful to include here, and would underscore the point the authors that O₃ does not alter the AMS spectra.

15. P. 8196, lines 5 – 14: I suggest that the authors remove most of the text here (“The peak intensity at $m/z = 45$ [...] and organonitrate consumption during oxidation, discussed below”). It is unnecessarily long and detracts from the rest of the discussion. Show a figure of the raw mass spectra at $m/z = 45$ (and 43 if desired) in the Supplement if these points need to be elaborated on.

16. P. 8197, lines 6-7: Isn’t it possible that ions of a specific m/z experience a fractional increase (as a function of OH oxidation) that is offset by a fractional decrease in another ion with the same integer mass but a different exact mass?

17. P. 8197, line 10: I am confused by the statement that $m/z = 44$ is only enhanced by ~25% following OH oxidation, because Fig. 4 suggests that the f_{44} increase is often much greater than 25%. Please explain.

18. P. 8197, lines 11-13: “For both aerosol types, production of m/z 44 occurs relatively rapidly, with most of the production occurring in less than ~ 3 days of OH exposure. This suggests a similar rate for functionalization reactions.”

I assume the authors define functionalization reactions as adding oxygen without loss of carbon, and fragmentation reactions as those resulting in net loss of carbon (Kroll et al., PCCP, 2009). The $m/z = 44$ production is more likely associated with fragmentation reactions than with functionalization reactions, especially because of the observed mass loss following heterogenous oxidation.

19. P. 8197, line 25: Cite Heald et al (GRL, 2010) here in addition to where it is currently cited later in the section.

20. P. 8202, line 24 and Fig. 12: It looks like the total organic mass changes by at most 0.5 ug/m^3 on July 21st, with a range of 3 to 3.5 ug/m^3 . How, then, do the authors determine a 50%-100% change in organics during the day? Please clarify.

21. P. 8205, line 9, line 15, and elsewhere in references: Capitalize “aerodyne”

22. Figure 1: Text on page 8189, lines 17-19 states that the reaction bypass system is a flow tube that is identical to the reaction zone (flow tube) except for the lamp. However, Fig. 1 is confusing because it suggests that the reaction zone bypass is a simple straight tube rather than a flow tube. Please fix the text, Fig. 1, or both to reflect the actual TPOT setup.

23. Figure 3: This figure doesn't seem to serve much of a purpose beyond the text; the authors might consider removing it, especially in the context of the wall loss issues I mentioned earlier (and even if it already accounts for wall losses).

24. Figure 4: Is it worth adding f_{43} & f_{44} from PMF factors (i.e. Fig. 10) to this plot?

25. Figure 11: It may be worth including fits to “guide the eye”, particularly for the OOARP,NV trace, where the authors are claiming $\text{Mass}_{\text{AmbHtOH}}/\text{Mass}_{\text{AmbHt}}$ for $\text{OOA}_{\text{RP,NV}}$ increases and then decreases with OH exposure (p. 8202, lines 1-5).

References

P. S. Chhabra et al. Elemental composition and oxidation of chamber organic aerosol, *Atmos. Chem. Phys.*, 11, 8827–8845, 2011.

M. J. Cubison et al. Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, 11, 12049–12064, 2011.

J. H. Kroll et al. Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol, *Phys Chem. Chem. Phys.*, 2009, 11, 8005–8014.

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