<u>**Response to Reviewer 2**</u>

We appreciate the reviewer's thoughtful discussion and provide a point-by-point response below.

<u>**Comment 1**</u>

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?

Response

Although the TPOT system is conceptually based on that described in Lambe et al. (2011a), the present version has been significantly upgraded in terms of geometry and material. The new system is described in the current manuscript, however the changes were not emphasized; this will be corrected. Particle transmission in the improved TPOT is greatly improved compared to the Lambe et al. study. Wall loss experiments using size-selected BES particles show approximately 100% transmission for particles with 100 to 300 nm mobility diameter (larger sizes were not tested), with 90% transmission at 50 nm. Transmission is measured as the ratio of particle counts from CPCs located upstream and downstream of the reaction zone. Based on these measurements, it is unlikely that wall losses can account for the observed mass loss. As well, the bypass and reactor flow tubes were designed to be as similar as possible.

<u>**Comment 2**</u>

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 using this calibration procedure.

Response

There appears to be some confusion regarding the purposes of the MEK and BES calibrations. The MEK calibration is used to determine the TPOT OH exposure, while the BES "calibration" is intended only as a check on system stability during the campaign (because an MEK detector (PTR-MS) was not routinely available). The BES system is NOT used for an *a priori* determination of OH exposure. Thus, while the reviewer's points in (b-g) are well-taken, they do not influence our use of the BES "calibration" provided that particle generation, TPOT configuration, and AMS operation are consistent between experiments. We will note the limitations of the BES system and clarify the purposes of the MEK calibrations and BES stability checks in the revised manuscript.

Comment 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 assumption 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.

Response

A rate constant for m/z 44 production is already included. A table containing estimated rate constants for the other spectral markers will be added.

Comment 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 acides, 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 steps (p. 8198, lines 24-28). The authors might also consider placing relative oxidation products such as *cis*-pinonic acid, and 3-methyl-1,2,3-butanetricarboxylic acid in Fig. 7 to see if this aides in interpretation of results. See Chhabra et al. (ACP, 2011) for an example.

(c) If the aerosols sampled in this study are predominantly 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.

Response

We agree on all points and will incorporate the suggested changes. Simultaneous measurement with an HR-ToF-AMS on ambient aerosol show that the Van Krevelen intercept is indeed ~1.6. This will be presented in a future publication.

Comment 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 $CH_2O^+:CH_2O_2^+$ with oxidation (in addition to, or instead of, $NO^+:NO_2^+$). 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).

Response

(a) The WACS 2010 study also included a HR-ToF-AMS operated in parallel to the TPOT system. This instrument also observed organonitrate signal, and estimated that approximately 50-75% of the total "nitrate" could be attributed to organonitrates (manuscript in preparation). This supports the validity of the 30/46 ratio as a proxy for organonitrate content.

(b) The focus of this paper is not only on the PMF results, but more generally on the nature and timescale of OA processing by OH. Within this framework, organonitrate processing is of interest, as are other changes in the organic mass spectrum (e.g. production/reaction timescales of organic *m/z* in Fig. 6).

Comment 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 be 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.

Response

Sulfate and ammonium increase during the AmbHtOH condition, while nitrate decreases. As the reviewer notes, this is likely due to H_2SO_4 formation in the TPOT. This H_2SO_4 is quickly neutralized by reaction with gas-phase ammonia, yielding the ammonium increase. The decrease in nitrate may be due to oxidation of organonitrate species and/or reaction of HNO_3 with OH. These changes will be discussed in the revised manuscript.

Comment 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 FPEAK = -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 FPEAK 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.

Response

(a) Q/Q_{exp} = 1.13. The average residual, here calculated as abs(residual) / total, is 0.083. (b) This is governed by the PMF2 software algorithm and the precise cause is unknown. While it is possible to achieve convergence by relaxing the convergence criteria, this approach produces solutions with higher Q/Q_{exp} and was therefore rejected. (c) We will add residual time series and mass spectra to the Supplement.

Comment 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 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.

Response

The intended comparison was with the factors reported by Ng et al.(ES&T, 2011), however the reference was mistakenly not included. We will also add a graphical comparison as suggested by the reviewer.

<u>**Comment 9**</u>

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} ~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} ~1% - 4% (Cubison et al., ACP, 2011). If this factor truly represents BBOA, then (1) the "BBOA" factor may respresent a heavily aged biomass burning sources 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.

Response

(a) It is likely that PMF is unable to retrieve a "pure" BBOA factor because of the short temporal duration of biomass burning influences at the site (i.e only the last few days of the campaign). This is suggested by somewhat high residuals at m/z 60, and especially by higher residuals during the biomass burning period. The f_{60} values reach a maximum (0.72%) during the biomass burning periods (compared to background values of 0.2% +/- 0.05%). This indicates that the BBOA factor is unable to fully represent the variability at m/z 60 (note that the BBOA factor never accounts for more than 80% of the total OA, so the discrepancy between measured f_{60} and PMF-reconstructed f_{60} is larger than indicated by the BBOA factor mass spectrum). Additionally, slight increases in the BBOA factor are observed during periods that are not influenced by biomass burning (e.g Fig. 9a), consistent with mixing in the PMF solution.

(b) The suggested comparisons will be added to the Supplement.

Comment 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.

Response

We will add a graphical comparison of these factors to the Supplement.

Comment 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).

Response

The citation will be removed.

Comment 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).

Response

Particle time-of-flight (PToF) data was not collected due to mechanical failure of the chopper motor that modulates the particle beam in PToF mode early in the campaign. Because production of the motor has been discontinued, replacement of the part would have required a major upgrade of the control electronics, which was not feasible during the campaign.

Comment 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.

Response

These citations refer to the Ulbrich et al., 2009 paper included in the reference list. We apologize for the typo.

Comment 14

P. 8192, line 26: What is the linear correlation coefficient (r^2) between the mass spectra of unreacted aerosol and O_3-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 O_3 does not alter the AMS spectra.

Response

 The r^2 value for this comparison is 0.9995.

Comment 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.

Response

 We agree that the suggested figures would be useful and that the bulk of the m/z 45 discussion can be moved to the Supplement.

Comment 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?

Response

 This is a good point, and this caveat will be added to the manuscript.

Comment 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.

Response

 There is a critical distinction between m/z 44 enhancement (i.e ratio of oxidized to unreacted organic mass at m/z 44) and a change in f_{44} (i.e. ratio of organic mass at m/z 44 to total organic mass). It is quite possible for oxidation to cause a low (or, hypothetically, zero) enhancement in m/z 44 to result in a large change in f_{44} if the oxidation causes a reduction in the total organic mass.

One can see from Fig. 6 that the largest OH exposures yield a ~25% m/z 44 enhancement coupled with a ~20% decrease in total organics, while Fig. 4 shows an increase in f_{44} from ~0.12 to ~0.19, and these values are consistent, i.e. (0.12 + 0.12 x 0.25) / (1 – 1 x 0.8) = 0.19.

Comment 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 fragmentation reactions, especially because of the observed mass loss following heterogeneous oxidation.

Response

This is a typo: "functionalization" should be "fragmentation." This discussion will be clarified, the definitions included, and the Kroll et al. reference added.

Comment 19

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

Response

The citation will be added.

Comment 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.

Response

Here the "50 to 100%" increase was intended to compare the organic concentrations on the (warmer) 21 July vs. the (colder) 19 July, i.e. the concentrations are 50-100% higher (depending on time of day) on 21 July. This was not clear in the original manuscript. The reviewer correctly notes that the change during the day is much smaller (~30% on 21 June vs. ~15% on 19 June).

Comment 21

P. 8205, line 9, line 15, and elsewhere in references: Capitalize "aerodyne"

Response

This typo will be corrected.

Comment 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.

Response

The text is correct: the bypass system is identical to the reaction zone except that the lamp housing is empty. Fig. 1 will be amended to reflect this.

Comment 23

Figure 3: This figure doesn't 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).

Response

As noted in response to Comment 1, wall losses are unlikely to strongly influence the results in this figure. We feel the figure is useful for providing an overview and comparison of the organic mass loss for heating/photolysis vs. OH oxidation.

<u>Comment 24</u>

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

Response

The PMF factors will be added.

<u>Comment 25</u>

Figure 11: It may be worth including fits to "guide the eye", particularly for the $OOA_{RP,NV}$ trace, where the authors are claiming $Mass_{AmbHtOH}/Mass_{AmbHt}$ for $OOA_{RP,NV}$ increases and then decreases with OH exposure (p. 8202, lines 1-5).

Response

The suggested fits will be added.