Response to reviewers’ comments

We thank the reviewers for their thoughtful comments. We have carefully revised the manuscript accordingly. Our point-to-point responses to the reviewers’ comments, which are repeated in italic, are given below.

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Reviewer #1

Yu et al studied the formation of non-volatile organic compounds through two aqueous mechanisms: oxidation via OH radical initiated by HOOH photolysis, and oxidation through 3C* initiated by photolysis of an aromatic aldehyde (which also includes OH oxidation due to the formation of HOOH via this route). The authors used a variety of analytical methods to describe the composition of the SOA at the half-way reaction mark. This study builds upon Sun et al (2010), adding a molecular-composition analysis based on both positive and negative ion mode high-resolution nano-DESI MS. The authors conclude that hydroxylation and various oligomerization reactions (e.g., coupling of phenoxy and aromatic alkyl radicals) are responsible for the aqueous SOA formation. This is an interesting analytical study that offers insight into a class of poorly-understood reaction mechanism in the aqueous phase, and should be published as such. There are areas that would benefit from clarification and further discussion, which I outline in the specific comments. In particular, it would be valuable to discuss mechanistic differences in guaiacol, syringol, and phenol in terms of the additional methoxy groups as activating substituents in the OH/3C* or abstraction vs. addition pathways of these radicals.

Authors’ reply #1: We have added some discussions on the influence of additional methoxy group on the reactivity of phenols in Sect. 3.1: “The reactivity differences among the three precursors are likely due to the electron-donating effect of the o-methoxy substituents, which may significantly increase the rate of electrophilic reactions on the benzene ring.”

Reviewer’s comment:
1. Including structures of guaiacol, syringol, and phenol would be helpful for understanding the discussion in the introduction and much of the text.

Authors’ reply #2: As suggested, we added the structures of syringol, guaiacol, and phenol in Table 1.

Reviewer’s comment:
2. The authors state in several areas a consistency with Smith et al that the aromatic species react “faster” with 3C* than OH. What does this mean exactly? Are the reaction rate coefficients $k_{3C^*} > k_{OH}$ or the effective rates $k_{3C^*}[3C^*] > k_{OH}[OH]$? If the former, what is the ratio? If the latter, can the authors make such a meaningful comparison without knowing $[3C^*]$ that is
Authors’ reply #3: Our statement of phenols reacting faster with $\text{^3C*}$ than with •OH is based on the effective, or pseudo first-order rate constants for phenol loss ($k'_{\text{ArOH}}$) measured in our experiments, i.e., $k_{\text{^3C*}}[\text{^3C*}] > k_{\text{•OH}}[\text{•OH}]$. Since the pseudo first-order rate is the product of the bimolecular rate constant and the steady state concentration of the oxidant: $k'_{\text{ArOH}} = k_{\text{ArOH}}[\text{Oxidant}]$, it is true that $k'_{\text{ArOH}}$ is dependent on oxidant concentrations. However, since the steady state concentrations of •OH and $\text{^3C*}$ in our reaction systems are comparable to the concentrations of these oxidants in atmospheric drops, the comparison of $k'_{\text{ArOH}}$ is meaningful. Based on the average $k'_{\text{ArOH}}$ values from our syringol experiments ($2.5 \times 10^{-4}$ s$^{-1}$ for syringol + $\text{^3C*}$ and $1.0 \times 10^{-4}$ s$^{-1}$ for syringol + •OH), and the bimolecular rate constants determined by Smith et al. (in preparation for PCCP), we calculate that steady state concentrations of $\text{^3C*}$ and •OH during our experiments are $6.9 \times 10^{-14}$ mol L$^{-1}$ and $5.1 \times 10^{-15}$ mol L$^{-1}$, respectively. Thus, the •OH steady state concentration in our solution is similar to the aqueous [•OH] measured in fog and cloud waters (Anastasio and McGregor, 2001; Arakaki et al., 2013). Although there are no reported literature values for [$\text{^3C*}$] in ambient fog/cloud waters, recent, not-yet published results from Anastasio’s group suggest a similar order of magnitude of [$\text{^3C*}$] in Davis fog water. These points are now clarified in Sect. 3.1.

In terms of the question of whether the phenol loss in reactions with $\text{^3C*}$ can be entirely attributed to $\text{^3C*}$, we believe the •OH contribution was minor. While Anastasio et al. (1997) showed that HOOH, a precursor for •OH, is produced from reactions of phenols with $\text{^3C*}$, the amount of HOOH produced is small and •OH oxidation in the triplet experiments appears to be negligible (Smith et al., 2014). Approximately 4-7 molecules of phenol are destroyed for every molecule of HOOH produced under the experimental conditions similar to those used in this study, suggesting that a majority of the photodestroyed phenol leads to products other than HOOH. In response to the reviewer’s comments, we now added the sentence in Sect 3.2: “Note that the amount of HOOH produced in the reactions of phenols + $\text{^3C*}$ is small and •OH oxidation appears to be negligible compared to $\text{^3C*}$ oxidation (Smith et al., 2014).”

Reviewer’s comment:
3. Additional to the above comment, can the authors provide estimates of steady-state [Oxidant] from HPLC-UV decay trace of the aromatic precursors?

Authors’ reply #4: The steady state concentrations of •OH and $\text{^3C*}$ during this study are estimated at $5.1 \times 10^{-15}$ mol L$^{-1}$ and $6.9 \times 10^{-14}$ mol L$^{-1}$, respectively, for syringol, $1.4 \times 10^{-15}$ mol L$^{-1}$ and $2.6 \times 10^{-14}$ mol L$^{-1}$, respectively, for guaiacol, $4.4 \times 10^{-16}$ mol L$^{-1}$ and $7.4 \times 10^{-14}$ mol L$^{-1}$, respectively, for phenol. This information is now provided in Sect. 3.1.

Reviewer’s comment:
4. [Experimental methods] The authors explain later in the text that the reason they blow dry one sample (then later reconstitute in water) and freeze dry the other is to remove the semivolatile from the blow dry case. Why not explicitly state this in the experimental methods?

Authors’ reply #5: Done as suggested. By the way, we did not freeze dry samples. The flash-frozen samples were prepared by rapidly freezing the solutions using liquid nitrogen. These
samples were stored in the dark under -20 °C and were thawed inside a refrigerator (~ 4°C) prior to analysis. The procedures for AMS analysis of the thawed flash-frozen sample and the reconstituted blown-down samples are exactly the same.

**Reviewer’s comment:**
5. [Experimental methods] If Milli-Q water served as the analytical blank, did the mass of 3,4DMB count towards the mass yield of the $^3$C* oxidation system? Were controls performed in the photolysis of 3,4DMB alone and evaporated in the same way?

**Authors’ reply #6:** The mass of 3,4-DMB was removed from the calculation of the aqSOA mass yields. Control experiments were performed to examine the photolysis of 3,4-DMB alone and the resulting solutions were evaporated in the same way as treating the aqSOA samples. No formation of aqSOA was observed. The results of the control experiments are shown in Smith et al. (2014) (Figure S8 in the Supporting Information). In response to reviewer’s comments, we added the sentence: “In addition, no formation of aqSOA was observed in control experiments in which 3,4-DMB was illuminated alone under the same condition and the resulting solution evaporated in the same way.” at the end of Sect. 2.1.

**Reviewer’s comment:**
6. [21158, line 1] What is the significance of “near 100%” mass yield, when this value can be exceeded from oxygen incorporation into the phenolic structure?

**Authors’ reply #7:** Assuming no carbon losses, i.e., no formation of volatile and semivolatile species that evaporate during the experiments or the drying processes, the mass yields of phenol, guaiacol, and syringol should be 201%, 161%, and 143%, respectively, for $^3$C*-mediated reactions, and 214%, 184% and 142%, respectively, for •OH-mediated reactions, based on comparing the OM/OC ratios of the aqSOA and the corresponding precursors. We added this information in Sect. 3.1: “Based on comparing to the OM/OC of the precursors, the mass yields of the aqSOA should be 142-214% assuming all reacted phenols were converted into low volatility species. However, the measured values are 16-38% lower, indicating that approximately 16-38% of the reacted phenols were converted into volatile and semi-volatile species that evaporated during illumination and/or drying.”

**Reviewer’s comment:**
7. [21158, lines 26-29] I find this speculation strange. Why would ESI efficiency (in both pos/neg mode) be reduced for “highly oxidized species” when the positive mode ionization is partially cluster formation and the negative mode ionization is deprotonation? Also, more support is needed if one is to claim that ESI alone causes decarboxylation of organic acids – as this ionization mechanism should be excellent for the detection of organic acids in the negative mode without extensive fragmentation. Do authors have evidence that certain carboxylic acids standards undergo this instrument-assisted decomposition in standard ESI? Levens et al 2007 that is cited is not appropriate here, as Levens and coauthors studied losses of neutrals from precursor ions through collision-induced dissociation in an ion trap (e.g., energy was supplied to purposefully fragment ions) as opposed to this study.
Authors’ reply #8: We agree with the reviewer’s comments, and removed related discussions in the revised manuscript.

Reviewer’s comment:
8. [21159, lines 1-5] After considering the 1 – 4% of organic acids that were not analyzed in nano-DESI, what would the corrected O/C be? My assumption is that it does not make much of a difference in the O/C.

Authors’ reply #9: By considering 1-4% of organic acids that were not analyzed in nano-DESI the O/C would increase by 0.03-0.05. The sentence now reads: “According to IC analysis, these small organic anions together represent 0.8-3.8% of the TOC of aqSOA (Table 1). Therefore accounting them for these species would only increase the nano-DESI O/C values by 0.03-0.05”.

Reviewer’s comment:
9. [21160, lines 6-7] Specifically which kind of functional groups in phenol aqSOA would not be well-ionized by both the positive and negative mode nano-DESI that was used here? If there is an aromatic group intact, (+) nano-DESI should ionize these compounds well.

Authors’ reply #10: In negative ion mode nano-DESI analysis, phenol and carboxyl groups should be readily ionized while aldehyde, ketone, and methoxy groups are ionized less efficiently. In positive ion mode nano-DESI analysis, larger oligomers containing multiple carbonyl groups form sodium adducts. All other groups in phenolic compounds are not very well ionized in positive ion mode.

Reviewer’s comment:
10. [21164, line 3] The AMS results are only quantitative if the specific ion (e.g., C16H18O6+) does not show up as smaller fragments, thus dispersing the signal of the molecule. Do authors have evidence that this is the case from calibrations with standards? Further, this is nitrate-equivalent mass which has its own assumptions about ionization and line-transfer efficiency.

Authors’ reply #11: Since the fragment pattern of 70 eV EI mass spectrometry is reproducible (McLafferty and Turecek, 1993), unique ions can be used as tracer species to quantify the concentration of the parent compound. We will examine the quantification of individual compounds using AMS in details in future studies. We added the sentences “Since the fragmentation pattern from 70 eV electron ionization is reproducible (McLafferty and Turecek, 1993), unique ions can be used as tracer species to quantify the concentration of the parent compound.” in Sect. 3.3.

Reviewer’s comment:
11. [21165, lines 1-4] Can the authors expand on why the structures of guaiacol and syringol would lead to these observed mechanistic differences?

Authors’ reply #12: It is unclear to us why guaiacol aqSOA are composed of more oligomers and derivatives than syringol aqSOA are. One possible reason is that guaiacol oligomers are more stable than syringol oligomers. This is a topic that will be subjected to future research.
Reviewer's comment:
12. [21166, lines 5-6] The authors mention that they examined the optical properties of “phenolic aqSOA” but only discuss syringol? Do phenol and guaiacol follow the same general behavior? Why not show their spectra?

Authors’ reply #13: The aqSOA of phenol and guaiacol also show enhanced absorption in the UV-Vis region. The optical properties of phenolic aqSOA will be reported in detail in a publication in the near future (Smith et al., in preparation). We added the sentence in Sect. 3.4: “Phenol and guaiacol aqSOA also show enhanced absorption in the tropospheric sunlight wavelengths (> 300 nm), while phenol and guaiacol themselves do not.”

Reviewer's comment:
13. [21166, line 18] Again, this is an interesting point, i.e., that the t_1/2 reactivities is higher for compounds with fewer methoxy groups within one oxidation system, that should be expanded to discuss structure-activity relationships.

Authors’ reply #14: Precursors with fewer methoxy groups react more slowly with the oxidant, and have longer half-lives under illumination. We attribute the positive correlation between the reactivities and methoxy groups to the electron-donating effect of the o-methoxy substituents, which can increase the rate of electrophilic reactions on the benzene ring by large factors. We mentioned this point in Sect. 3.1

Reviewer's comment:
14. [21167, lines 15-end] While the particular AMS ions listed appear to be useful in this single-precursor system study, I disagree that these nominal mass assignments can be “signatures” in the ambient environment. Concerns about EI fragmentation aside, nominal mass resolution at a high m/z as 306 produces a large array of possible molecular formula candidates when sources are unknown. In the atmosphere, there is little evidence that these molecular formulas are unique to a particular chemical system. The authors should also consider the possibility that nominal even-mass ions like 306 can be assigned to either a CxHyOz aromatic ion radical or CxHyOzN cation in the atmosphere. For identifying the impact of phenolic aqSOA, it seems more promising to apply nano-DESI, as the authors have done, to field samples than AMS.

Authors’ reply #15: We agree that it is interesting to apply nano-DESI to field samples in order to identify phenolic aqSOA in ambient air and we indeed plan to do so in the future. But it is challenging to use nano-DESI for quantification, although progress has been made in this aspect (Nguyen et al., 2013). On the other hand, AMS uses 70 eV electron impact ionization, and the EI fragmentation pattern is reproducible, which allows for the identification and quantification of individual molecule in the mixture (McLafferty and Turecek, 1993). The EI ionization may also generate unique ions that are representative of the parent molecules. It is therefore viable to apply AMS signature ions for identifying phenolic aqSOA species and analyzing. We have revised this paragraph to make these points clearer. It now reads: “Overall, our results indicate that aqueous-phase processing of phenols represents an important pathway for the production of low-volatility, highly oxygenated and high molecular weight species, which remain in the particle phase after water evaporation. Since phenolic aqSOA are both water soluble and light
absorbing, understanding the impacts of these reactions on the chemical and physical properties, and thus the climatic and health effects, of atmospheric particles may be important, especially in regions influenced by biomass burning emissions. An approach for evaluating the importance of phenolic aqSOA formation in the atmosphere is to systematically analyze the AMS mass spectra of ambient aerosol for signature ions representative of phenolic aqSOA. AMS has been broadly applied for chemical analysis of ambient aerosol and multivariate statistical approaches (e.g., positive matrix factorization) have been frequently used on organic aerosol mass spectral data to determine factors representing different sources and processes (Ulbrich et al., 2009; Zhang et al., 2011). An important criterion for validating the extracted factor is via examining the mass spectra of the factors for signature ions (Zhang et al., 2011). The fact that AMS uses 70 eV EI ionization, which ionizes and fragments molecules with reproducible pattern (McLafferty and Turecek, 1993), allows for the identification and quantification of certain compounds or compound classes in a mixture via signature ions. Indeed, previous studies have demonstrated the capability of using unique AMS ions to fingerprint species such as hydrocarbon-like and oxygenated organic aerosols (Zhang et al., 2005), polycyclic aromatic hydrocarbons (PAH) (Dzepina et al., 2007), methanesulfonic acid (MSA) (Ge et al., 2012), and certain nitrogen- and sulfur-containing organic aerosols (Farmer et al., 2010; Ge et al., 2014).

With this in mind, in this study, we identified several ions that are potentially representative of phenolic aqSOA, including C_{16}H_{18}O_{6}^+ (m/z = 306) for syringol dimer, C_{14}H_{14}O_{4}^+ (m/z = 246) for guaiacol dimer, C_{14}H_{14}O_{5}^+ (m/z = 262) and C_{14}H_{14}O_{6}^+ (m/z = 278) for hydroxylated guaiacol dimer, C_{12}H_{10}O_{2}^+ (m/z = 186) for phenol dimer, C_{21}H_{20}O_{6}^+ (m/z = 368) for guaiacol trimer, and C_{18}H_{14}O_{5}^+ (m/z = 278) for phenol trimer (Fig. 8). Since all these ions have odd number of electrons with relatively high m/z’s, their productions in the AMS are more directly linked to the specific parent compounds, meaning that they are less likely contributed by confounding molecules (McLafferty and Turecek, 1993). In addition, while large hydrocarbon molecules, e.g., those from vehicle emissions, may generate significant ion signals at m/z > 200, most of them are even-electron ions and contain no oxygen. They are therefore easily differentiated from the isobaric ions from phenolic aqSOA. Nevertheless, it is important to point out that the validity of using the signature ions identified in this study needs to be evaluated by examining ambient organic aerosol mass spectrometry data. In addition, analyzing field samples with nano-DESI may also provide important insights into the impacts of aqueous phase processing of phenolic compounds in the atmosphere.”

Reviewer #2

The authors present a detailed study of the products of aqueous-phase oxidation of phenol, guaiacol, syringol. They examine oxidation by the OH radical and by the triplet excited states of 3,4-DMB. This manuscript can be viewed as a companion paper to Smith et al., ES&T (2014). In that study the authors presented the kinetics and SOA yields of these processes, but the discussion is confined to product characterization here. The volatility and optical properties of the SOA are also examined, although these results are discussed only briefly in the manuscript.
Reviewer’s comment:
1. The $^3$C* pathway is very interesting and potentially important. I would like to hear more from the authors regarding their choice of 3,4-DMB as a photosensitizer. Why was this model compound chosen when other aromatic carbonyl compounds exist in biomass burning aerosol which might be more environmentally relevant? Could any of the reactants (or the aromatic carbonyl products they form) also act as photosensitizers? Were any control experiments performed to investigate this?

Authors’ reply #1: There are three reasons for choosing 3,4-DMB as the photosensitizer. First, 3,4-DMB has high molar absorptivities across the solar UV wavelengths and is an effective source of $^3$C* (Anastasio et al., 1997). Secondly, 3,4-DMB is emitted in large amounts from biomass burning (Schauer et al., 2001) and exists nearly exclusively in condensed phases in the atmosphere. Lastly, 3,4-DMB is commercially available. In response to the reviewer’s comments, we added the following sentence in Sect. 2.1: “3,4-DMB was chosen as the photosensitizer in this study to represent non-phenolic aromatic carbonyls, which are emitted in large quantities from wood burning (Schauer et al., 2001), exist nearly exclusively in condensed phases in the atmosphere, and rapidly form $^3$C* that efficiently oxidizes phenols (Anastasio et al., 1997).”

Phenols themselves have little or no light absorption in the solar range and are not effective photosensitizers. Some of the products formed during illumination absorb light at longer wavelengths and might be photosensitizers, but we do not think that they contributed significantly to phenol loss in our experiments since the kinetics of phenol loss out to one half-life all showed good first-order decays, indicating relatively stable oxidant concentrations. For this reason, it is unlikely that intermediate species are a significant source of $^3$C* during the initial stage of the reaction. However, there are indications that other reactions could have become important after prolonged illumination. For example, we found that the destruction rate of guaiacol deviates from first-order decay after ~ 1.3 hours of reaction (Yu et al., in preparation). Note that the $t_{1/2}$ of guaiacol + $^3$C* is 35 min and all the aqSOA studied in this work were acquired at $t_{1/2}$. We will explore the influence of intermediate phenol reaction products on photosensitized chemistry in future studies. In response to the reviewer’s comments, we have added relevant discussions in Sect. 2.1.

Reviewer’s comment:
2. The authors propose a mechanism in Figure 7 based on their product analysis. It wasn’t clear to me why the authors concluded that the $^3$C* exclusively oxidizes phenols directly, rather than also reacting with O$_2$ to producing singlet molecular oxygen (and therefore other oxidants) in the aqueous phase (e.g. Figure 4 of Smith et al. (2014))? 

Authors’ reply #2: The $^3$C* triplet can indeed react with O$_2$ to produce singlet oxygen (and perhaps other oxidants), which can oxidize phenols and possibly lead to the production of aqSOA. However, as we described in Smith et al. (2014), singlet molecular oxygen appears to be a negligible oxidant in our solutions because of the rapid triplet-mediated reactions. Thus we did not include this pathway in Fig. 7.

Reviewer’s comment:
3. The recent work of C. George and coworkers demonstrating SOA formation via photosensitizer chemistry (Aregahegn et al. (2013), Rossignol et al. (2014), Monge et al. (2012)) should be referenced in the introduction.

Authors’ reply #3: As suggested, we have added relevant discussions and cited these literatures in the introduction.

Reviewer’s comment:
4. Can the authors comment on the possible impacts of sample drying on the observed product distributions (e.g. oligomers and light-absorbing species)?

Authors’ reply #4: As discussed in Smith et al. (2014), there are some differences in the SOA mass yields determined gravimetrically from N₂ blowdown of solutions and those determined in real-time by HR-ToF-AMS. A possible reason is that some semi-volatile components may have reacted and formed low-volatility products during the N₂ blowdown procedure, probably because of the presence of small amount of sulfuric acid in the solution, which was added to adjust the pH of the solution (Smith et al., 2014). Despite this, according to our analysis, the ESI-MS spectra of the blown-down sample reconstituted in Milli-Q water and the flash-frozen sample for the aqSOA formed from syringol + ³C* are overall similar. For example, 65 - 70% of the molecules identified in these two sample types are common species and for both samples, oligomers and their derivatives account for ~ 50% of the total signal in the ESI spectra. In addition, the AMS spectra of the blown-down samples and those of the flash-frozen samples are overall similar. For these reasons, it appears that sample drying had relatively small influence on the observed product distribution. Nevertheless, it is important to conduct future studies to understand the reasons for these methodological differences in aqSOA yield, and evaluate the possible influence of sample drying process on aqSOA mass, composition, and light-absorbing species. In response to the reviewer’s comments, we have added relevant discussions in Sect. 3.1.

References


Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J. and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and


