Response to Reviewer #1

We thank Reviewer #1 for the comments. Below we address those comments point-by-point. Our responses are denoted by "R". The original text to be changed is denoted by "O" and the changed text is denoted by "M".

Reviewer #1

General impressions: This is a nice paper that will be valuable to the community and should be accepted after a few relatively minor modifications. The paper very nicely highlights the importance of particle phase chemistry on aerosol mass yields / composition. Results suggest that a "one size fits all" approach falls short, and detailed understanding of cloud/fog water composition and photochemistry is important to predict the atmospheric fate and lifetime of molecules produced in biomass burning events. The paper could be improved by additional experiments on other model compounds within the same class, and additional efforts to oxidatively age aerosol produced under condition "B." My suspicion is this experiment would result in a very similar pattern to "A." In addition, the concentration of H2O2 in condition "A" appears to be far too high to really be interesting. The chosen conditions really represent "all" or "nothing" - that is the H2O2 concentration is so high that all of the organic will quickly decompose, or the concentration is so low that the other processes will be favored. In addition, the authors atomize an aqueous phase reaction mixture. While this is interesting, to a certain degree it eliminates the need for a AMS. Why not probe the chemistry of particles when they react in the aerosol phase and use the AMS to measure the particles? Heterogeneous phase chemistry may yield very different results. This is speculative, however, the authors have been provided with this fine measurement instrument to answer such questions.

R: The reviewer raised a few possibilities for further investigation. Specifically, the reviewer suggested four points for further experiments: a) to study other model compounds; b) to prolong experiments under condition (B) to see whether it results in a similar pattern as in condition (A); c) to study lower H2O2 concentration (although a misunderstanding may exist, see below); and d) to probe heterogeneous chemistry with suspended particles instead of aqueous solution. They are useful suggestions that are all interesting and worth exploring. For the current manuscript, we feel that it already involved a number of aspects including reactions, on-line/off-line characterizations, chemical information and hygroscopic property. We will consider these additional experiments for future studies.

Nevertheless, we will address Points a) – c), with necessary changes made to the revised manuscript, in the related specific comments later. We now address point d), i.e.,

heterogeneous chemistry, here.

Heterogeneous oxidation involves reactions between gas-phase oxidants (O3 and OH etc.) and particle-phase organics. This is definitely an important process that would lead to changes of OA properties and even OA mass (decrease if oxidation forms more volatile products by fragmentation and increase if oxidation leads to functionalization only). To study heterogeneous oxidation of submicron organic particle and gaseous oxidants, an aerosol flow tube or a smog chamber would be needed. At the moment, we are not equipped with these facilities. On the other hand, the atomization coupled with AMS measurements in this study provided results useful in understanding cloud/fog evaporation. That is, some slightly volatile and slightly water soluble species such as vanillin can exist in aqueous droplets but would evaporate after drying. With aqueous-phase oxidation, however, the evaporative loss of this type of organics would be strongly reduced by forming less volatile products. This important feature cannot be revealed without measurements of organic in the bulk solution and real-time measurements of atomized and dried particles by the AMS.

Top of page 27646 – concentration of H2O2 – It lists 34.5 – 36.5 wt %. Is this correct? It seems this experiment is then somewhat dangerous, so I encourage the authors to include a section on safety measures. In addition, this is much, much higher than relevant atmospheric conditions. At such a high concentration of H2O2 it is not surprising most of the organic is quickly degraded - treatment with high conc. of H2O2 is a known wastewater treatment strategy and the literature on kinetics / mechanisms of organic degradation is very large. I feel that experiments at much lower concentration of H2O2 are warranted to better understand the chemistry of this system.

R: This might be a misunderstanding (related to point c) in the general expression above) due to our unclear statement. The 34.5-36.5 wt% is the concentration for the stock chemical as purchased. During the experiments, we used 11.8 mM (indicated in Table 1). We have included this concentration of H2O2 actually used in the experiments in the revised manuscript. Now the sentence reads as below.

O: … with or without H_2O_2 (Sigma-Aldrich, 34.5-36.5 wt%) …

M: …with or without 11.8 mM H_2O_2 (Sigma-Aldrich, 34.5-36.5 wt%)…

Page 27650, line 5-10. The authors discuss conditions A and B and draw conclusions regarding the OH mediated mechanisms vs direct photolysis of vanillin. Can the authors present a justification for this assumption? It seems the reality may be more complicated. For instance, is the 'branching ratio' H2O2 conc. dependent? Is OH generated during photolysis rxns? The authors later seem to allude to the fact that the conc. ratio may be

important (bottom of 27659), so it seems this is important issue to clear up. Again, additional experiments in which the H2O2 conc. is varied could be quite valuable.

R: We respond to this comment in relation to point b) in the general impression above. For condition (B), we referred to a previous study (Anastasio et al., 1997) that a small amount of H2O2 might be formed during the direct photolysis of phenolic compounds. It was also our interest to see whether it is the case and attempt has been made to measure the H2O2 during reactions under condition (B). It was not successful, however, because the method for H2O2 measurement that we adopted (Allen et al., 1952) is a colorimetric method but light-absorbing materials formed under condition (B) interfered the detection. From the experiments, the H:C to O:C data in the Van Krevelen plot (Heald et al., 2010) do not show exactly the same trend for the first 60 min of (A) and the 3-hour experiments of (B), as shown in Figure R1. Without direct evidence, we do not want to go too far to speculate that condition (B) was just a slow version of condition (A) with lower concentrations of H2O2 (thus lower concentrations of OH).

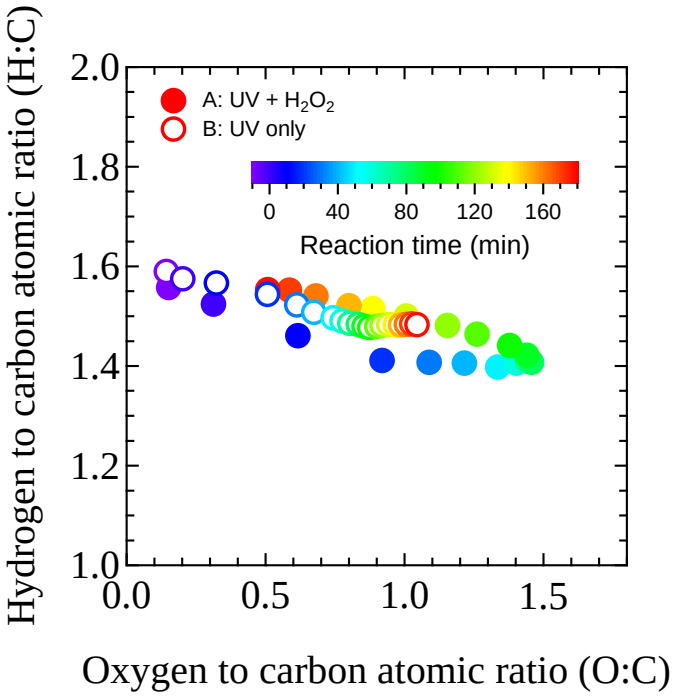

Figure R1. H:C vs. O:C ration under conditions (A) and (B).

We referred to OH oxidation under condition (A) and direct photolysis under condition (B) in a relative term. Under condition (A), photolysis of H2O2 and vanillin occurred simultaneously. But photolysis of H2O2 generated a high concentration of OH radicals, which are responsible for the fast vanillin oxidative decay (Figure 4 in the manuscript). Under condition (B), even if a small amount of H2O2 was generated and OH oxidation contributed partially, the main pathway was still photolysis. At least it was photolysis

of vanillin that triggered the radical formation for further reactions. The observation that high vanillin/H2O2 ratio in a trial experiment also led to yellow coloration hints that a competition between polymerization (leading to highly conjugated and high-molecular-weight products) and fragmentation (leading to small oxygenates). Again, we do not want to speculate on whether there is a "branching ratio" between these two pathways based solely on results from a trial experiment.

Varying H2O2 concentrations for condition (A) is a topic that worth exploring but for current study, we only use one concentration to demonstrate the reactivity. Further study would be needed for more detailed study on the dependence of the reactions on H2O2 concentration.

General comment – it would be nice if authors could pursue measurements on other phenolic compounds produced in biomass burning. With only one model compound, it is not clear if results should serve as guidance for the entire class of materials or just vanillin.

R: This is related to point a) in the general expression above. It is definitely worthwhile to try more on methoxy phenols with similar structure and we plan to do so in future studies. As we noted in the last paragraph of the manuscript (Page 27660), the choice of vanillin is just to demonstrate reactivity of this class of compound and results may be different for other methoxy phenols.

General comment: the authors consider cases A (with H2O2) and B (without H2O2). Several times, they refer to the "final" product or the "final" condition of the experiment when comparing cases. Is it possible that data shown in figure 3B or 2 for that matter would begin to appear very similar to case "A" if sufficient oxidative aging occurred? As a general theme, it seems to be important how we define "final" condition with regards to aerosols in Earth's atmosphere. Are the results here simply suggesting the aerosol of case "B" simply has not experienced the oxidative aging case "A" has? It seems to me this is the case.

R: We have modified it to correctly reflect the products (or other properties) at the highest organic mass or highest O:C ratio (60-80 min). This is because we believe that the first 40-60 min of reactions under condition (A) may be more relevant to atmospheric conditions (see discussion in Section 4). Some changes are made accordingly as follow.

Page 27651, line 23

O: … under these two conditions indicate that the final products that retained in the particle phase formed under these two conditions were substantially different.

M: … under these two conditions indicate that the retainable products observed were substantially different.

Page 27652, line 20

O: Therefore, the final organic products that retained in the particle phase under condition (B) are believed to be less oxygenated than those under condition (A).

M: Therefore, the organic products that retained in the particle phase at the time of highest O:C ratio under condition (B) (~3 hours) are believed to be less oxygenated than those under condition (A) (~80 min).

Page 27659 line 21 – the work cited (Chang and Thompson) would clearly be of relevance to this study, however they did not report observations of brown carbon in ambient samples. Their conditions seem to be somewhere between case A and B reported here.

R: Agreed. A more relevant reference (Andreae and Gelencser, 2006) has been cited here.

FIgure 2 - a major point of this paper is that differences exist between case A and B. Can you enlarge the mass spectra of figure 2 in an attempt to really make this point? Addition discussion in the text is also warranted.

R: Figure 2 in the manuscript has been enlarged. A more detailed discussion is provided at the end of Section 3.1 as below.

M: The differences in the evolution of mass spectral features under these two conditions indicate that the retainable products observed were substantially different within the experimental time scale of 3 hours. The disappearance of high-molecular-weight ions and emergence of ions representing small oxygenates (e.g., CO^+ and CO_2^+) under condition (A) suggested that fragmentation might dominate over functionalization. Fragmentation was very likely via ring-opening pathways, leading to the formation of carboxylic acids which generated high intensity of m/z 44 (CO_2^+) in AMS mass spectra. Under condition (B), on the other hand, the preservation of the methoxy-phenolic structure was evidenced by the presence of m/z 137 ($C_7H_5O_3^+$). Reactions might have proceeded mainly via functionalization with the ring retained. Note that even under condition (B), the intensities of high-molecular-weight ions decreased but those of m/z 18 and m/z 44 increased too, which suggested that fragmentation has occurred, albeit at a less extent than that under condition (A).

References

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Anastasio, C., Faust, B. C., and Rao, C. J.: Aromatic carbonyl compounds as aqueous-phase photochemical sources of hydrogen peroxide in acidic sulfate aerosols, fogs, and clouds .1. Non-phenolic methoxybenzaldehydes and methoxyacetophenones with reductants (phenols), *Environ. Sci. Technol.*, 31, 218-232, 1997.

Andreae, M. O., and Gelencser, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, 6, 3131-3148, 2006.

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Response to Reviewer #2

We thank Prof. Collett for the comments to help improve the manuscript. Below we address those comments point-by-point. Our responses are denoted by "R". The original text to be changed is denoted by "O" and the changed text is denoted by "M".

Reviewer #2

Li et al. report very interesting results concerning the aqueous phase oxidation of vanillin, an important biomass burning emission. Oxidation by UV and by OH are both tested and the generation of secondary organic aerosol (SOA) mass and its composition examined. The experiments are well designed and the data analysis is robust and insightful. The findings are highly relevant to ACP readers and fill a current gap in knowledge concerning aqueous SOA formation from cloud processing of prescribed and wild fire emissions. I commend the authors on this impressive piece of work and have only a few suggestions and comments to improve a final version of the manuscript.

1. The authors use UPLC/ESI-TOFMS to report the composition of some product species. More information is needed regarding how the authors went from the elemental formulae provided by the TOFMS to the structures they present. Mention is made of fragmentation loss, but the analytical description provided in the supplement does not address the fragmentation approach used. I assume in-source fragmentation was employed, but this should be explicitly stated and relevant details provided.

R: Yes, the fragmentation was in-source fragmentation without pre-selecting a particular ion for fragmentation. Collision energy of -10.0 eV was set to perform the in-source collision induced dissociation. Those details of the ToF-MS operation are now included into Sect. 5.2 in the Supplementary Information as below.

M: The capillary voltage was 4000 V, with an end plate offset of -500 V. The nebulizer pressure was 3.0 bar and the dry gas was at 4.0 L/min with dry heater operating at 220 °C. In-source collision induced dissociation, with a collision energy of -10.0 eV, was used to generate some fragments for structural elucidation.

R: In addition to the last entry in Table S3, where proposed fragmentation losses leading to the observed fragment peaks are listed, a paragraph of structural elucidation is added in Sect. 5.2 in the Supplementary Information, as below.

M: Fragmentation information induced by in-source collision was used for structural elucidation. For example, we observed three peaks in the chromatogram (Figure S11) with m/z 167 ± 0.5 Da ($[M - H]^-$). The mass spectra of these three peaks are shown in Figure S12 (panel a-c). The spectrum in Figure S12-b has a loss of CO_2 (see also Table

S3), a characteristic loss of carboxylic acids (Li et al., 2011). This product is therefore believed to be a carboxylic acid, formed by oxidation in the carbonyl group of VL. The other two isobaric products do not have this CO_2 loss (Figures S11-a and -c, and Table S3), thus they are believed to be formed with one oxygen atom added to the aromatic ring as OH group. The positions of the OH group in these two products are not known at this point. Likewise, two isobaric products with a molecular weight of 184 ($[M-H]^-$ = 183) are believed to be formed by adding one more oxygen atom to the above products. One of them (B184_a, Figure S12-d) is believed to be a carboxylic acid with one more OH group than B168_b, while the other has two OH groups added to the aromatic ring (Figure S11-e). The product B302_a is believed to be a dimer of VL by radical polymerization based on two reasons. First, the molecular formula ($C_{16}H_{14}O_6$) is double of that of VL ($C_8H_8O_3$) with two hydrogen atoms less, supporting a radical polymerization process (Sun et al., 2010). Second, the loss of two CH_3 groups (Table S3) suggests that there are two building blocks with VL structure that bears two OCH_3 groups contributing to the CH_3 losses. There is little information of other dimers for structural elucidation and their structures are not proposed.

2. On a related note, is there a reason the authors did not scan below m/z 50 in the ESI-TOFMS analyses to look for the presence of smaller product molecules?

R: If the scan range was set to below m/z 50, ions from the solvent (H_2O and MeOH) adducts would be detected and their abundance would be very high and might dominate the mass spectra. We want to avoid this for two reasons. First, as we used elution program in the LC part, the ratio between H_2O and MeOH changed during an LC run. This would give a drifting background as relative abundance of the adduct ions would change according to the H_2O/MeOH ratio. Second, too high intensities of solvent adduct ions almost continuously getting into the detector would probably shorten the lifetime of the detector.

Furthermore, scanning from m/z 50 does not provide any advantage in providing evidence of fragments of the $[M - H]^-$ of oxalic acid ($C_2HO_4^+$, m/z = 89), while derivatization GC-MS clearly has confirmed the presence of oxalic acid. As mentioned in the main text (Section 3.4), the two major reasons of low sensitivity of LC-MS in detecting small oxygenates are 1) poor separation of those small oxygenates in reversed phase LC and 2) inefficient ionization in ESI for those very hydrophilic organics.

3. Please mention the volume of solution used for the reactor experiments.

R: information about the solution volume (300 mL) is now included in Sect. 2.1, as below.

O: An aqueous solution of…

M: A volume of 300 mL aqueous solution of…

4. The authors conclude in section 3.6 that vanillin loss through aqueous oxidation by

UV light can be as important as vanillin oxidation in the gas phase. This claim needs to be better justified. In particular, I question whether the UV exposure (both wavelengths and intensity) utilized in the lab experiments is comparable to atmospheric conditions. If it is not comparable, the authors should explain how they scaled their aqueous results for comparison to atmospheric gas phase oxidation rates. They did a good job of this for vanillin's aqueous oxidation by OH but did not address it for the UV exposures.

R: This section is modified in the Supporting Information to provide the justification.

O: This decay rate is at least comparable to the gas-phase loss rate (1×10^{-4} s^{-1}) for VL, assuming a gas-phase oxidation rate constant of 10×10^{-11} cm^3 $molecules^{-1}$ s^{-1} (Coeur-Tourneur et al., 2010) and a gas-phase OH concentration of 1×10^6 molecules cm^{-3} (Ervens et al., 2013). Therefore, even without H_2O_2 in the aqueous phase, the loss of methoxy-phenolic compounds like VL through the aqueous-phase process (with UV light) can be as important as that through gas-phase oxidation.

M: This decay rate is at least comparable to the gas-phase loss rate (1×10^{-4} s^{-1}) for VL, assuming a gas-phase oxidation rate constant of 10×10^{-11} cm^3 $molecules^{-1}$ s^{-1} (Coeur-Tourneur et al., 2010) and a gas-phase OH concentration of 1×10^6 molecules cm^{-3} (Ervens et al., 2013). Note that this decay rate was measured with a UV lamp of 254 nm, lower than wavelength with significant actinic flux in the troposphere (>290 nm). A simple calculation shows that with the absorption cross section of VL estimated from its molar absorption coefficient and an assumed quantum yield of 0.28 (resulting in the measured decay rate at 254 nm), the photolysis rate in the wavelength range of tropospheric importance (295-425 nm) is 7.06×10^{-4} s^{-1}. The details of the calculation are provided in Section 7 in the Supporting Information. Therefore, even without H_2O_2 in the aqueous phase, the loss of methoxy-phenolic compounds like VL through the aqueous-phase process (with UV light) can be as important as that through gas-phase oxidation.

R: A justification is provided in detail in the Supporting Information as Section 7.

M:

7. Estimation of photolysis rate in 295-425 nm

Wavelength-dependent photolysis rate (J) can be estimated from the absorption cross section ($\sigma(\lambda)$), the quantum yield ($\phi(\lambda)$), and the solar actinic flux ($I(\lambda)$), all of which are wavelength dependent (Seinfeld and Pandis, 2006). The first two parameters, $\sigma(\lambda)$ and $\phi(\lambda)$, are also compound specific and are not readily available in the literature for VL. The last parameter, $I(\lambda)$, can be estimated from the energy output of the UV lamp (UVP, Pen-ray 254 nm 9", model 97606-08) used in the experiments and from literature for typical tropospheric environments (Finlayson-Pitts and Pitts, 1986).

We first estimate J_{VL} in our experiments under condition (B), assuming that the decay

of VL under condition (B) was solely due to direct photolysis. Then we have (Seinfeld and Pandis, 2006):

$$\frac{d[VL]}{dt} = -k_{decay} \times [VL] = -J_{VL} \times [VL]$$

$$J_{VL} = \int \sigma_{VL}(\lambda)\phi_{VL}(\lambda)I(\lambda)d\lambda = \sum \bar{\sigma}_{VL}(\lambda)\bar{\phi}_{VL}(\lambda)\bar{I}(\lambda)\Delta\lambda$$

where k_{decay} is our measured decay rate (s^{-1}) under condition (B), J_{VL} is the first-order photolysis rate (s^{-1}) of VL, $\sigma_{VL}(\lambda)$ is the wavelength-dependent absorption cross section (cm^2) of VL, $\phi_{VL}(\lambda)$ is the wavelength-dependent quantum yield of VL, and $I(\lambda)$ is the solar actinic flux, or the photo flux from the UV lamp in our experiments. The integration is simplified by summing the photolysis rates in finite "bins" (with $\Delta\lambda = 5\ nm$), calculated from the average values of the required parameters (denoted by a bar over the symbols).

Absorption cross section can be estimated from molar absorption coefficient:

$$\sigma_{VL}(\lambda) = \frac{10^3 \times \varepsilon_{VL}(\lambda)}{N_A}$$

where $\varepsilon_{VL}(\lambda)$ is the molar absorption coefficient (dm^3/mol/cm) and N_A is the Avogadro constant (6.02×10^{23} mol^{-1}). Figure S14-a shows the molar absorption coefficient (from NIST) of VL from 220-350 nm in a red line (Talrose et al., 2007), and the calculated absorption cross section ($\sigma_{VL}(\lambda)$, 290-425 nm, $\Delta\lambda$=5 nm) is shown as blue open symbols in Figure S14-a. The molar absorption coefficient beyond 350 nm, which is not included in NIST database, was assumed to decrease exponentially from 330 nm without major absorption band in this region for VL.

Absorption cross section for experiments under condition (B) is thus calculated.

$$\bar{\sigma}_{VL}(254) = 2.35 \times 10^{-20} cm^2$$

The quantum yield during experiments under condition (B), $\bar{\phi}_{VL}(254)$, is first assumed to be unity. Photon flux is calculated from the energy output (F_{UV}, specified by the manufacturer) of the UV lamp, F_{UV} = 5.4 mW/cm^2 = 5.4×10^{-3} J cm^{-2} s^{-1}, at 0.75 inch (approximately half of the bottle radius), by:

$$\bar{I} = \frac{F_{UV}}{E_{h\nu}} = \frac{F_{UV}}{\frac{h \times c}{\lambda}} = \frac{5.4 \times 10^{-3} J cm^{-2} s^{-1}}{\frac{6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^8\ m\ s^{-1}}{254 \times 10^{-9}\ m}}$$

$$= 6.92 \times 10^{15} photons\ cm^{-2} s^{-1}$$

Here $E_{h\nu}$ is the energy of one photon, h is the Planck constant and c is the speed of light. The estimated J_{VL} at 254 nm in our experiments is (assuming quantum yield of 1 $photon^{-1}$ and wavelength width of 5 nm):

$$J_{VL}(254) = \bar{\sigma}_{VL}(\lambda)\bar{\phi}_{VL}(\lambda)\bar{I}(\lambda)\Delta\lambda$$
$$= 6.92 \times 10^{15}\ photons\ cm^{-2}s^{-1} \times 2.35 \times 10^{-20}cm^2 \times 1 \times 5$$
$$= 8.13 \times 10^{-4}s^{-1}$$

This estimated $J_{VL}(254)$ is 3.5 times of the measured k_{decay} (2.3×10^{-4} s^{-1}) in our experiments under condition (B). We attribute this difference to the quantum yield of VL photolysis and hence assume a non-unity quantum yield for the whole wavelength:

$$\bar{\phi}_{VL}(\lambda) = \frac{2.3 \times 10^{-4}}{8.13 \times 10^{-4}} = 0.28.$$

Using this quantum yield, we then estimate the photolysis rates of VL in the UV region of tropospheric importance (290-425 nm). The wavelength-dependent solar actinic flux in typical tropospheric environments (ground level, July 1, noon, 40°N, 298 K) is taken from (Finlayson-Pitts and Pitts, 1986) and is shown in red open symbols in Figure S14-b.The estimated photolysis rates are believed to be upper limits since wavelength-dependent quantum yields normally decrease, most likely exponentially, as wavelength increases.

Table S4 showed the estimated photolysis rates of VL in different wavelength "bins". The photolysis rates of VL range from 10^{-5} to 10^{-4} s^{-1} for wavelength where VL has a strong absorption band, i.e., 300-350 nm. Beyond 350 nm, the photolysis rates become too small to be important due to low absorption cross section for VL. The overall J_{VL} is 7.06×10^{-4} s^{-1}, a few times higher than the k_{decay} measured (2.3×10^{-4} s^{-1}) and the gas-phase loss rate due to OH reactions (1×10^{-4} s^{-1}). Therefore, we believe that the decay rate due to UV photolysis of VL in the troposphere is at least comparable to that of OH reactions in gas phase. Note that the same UV photolysis can occur in gas phase too.

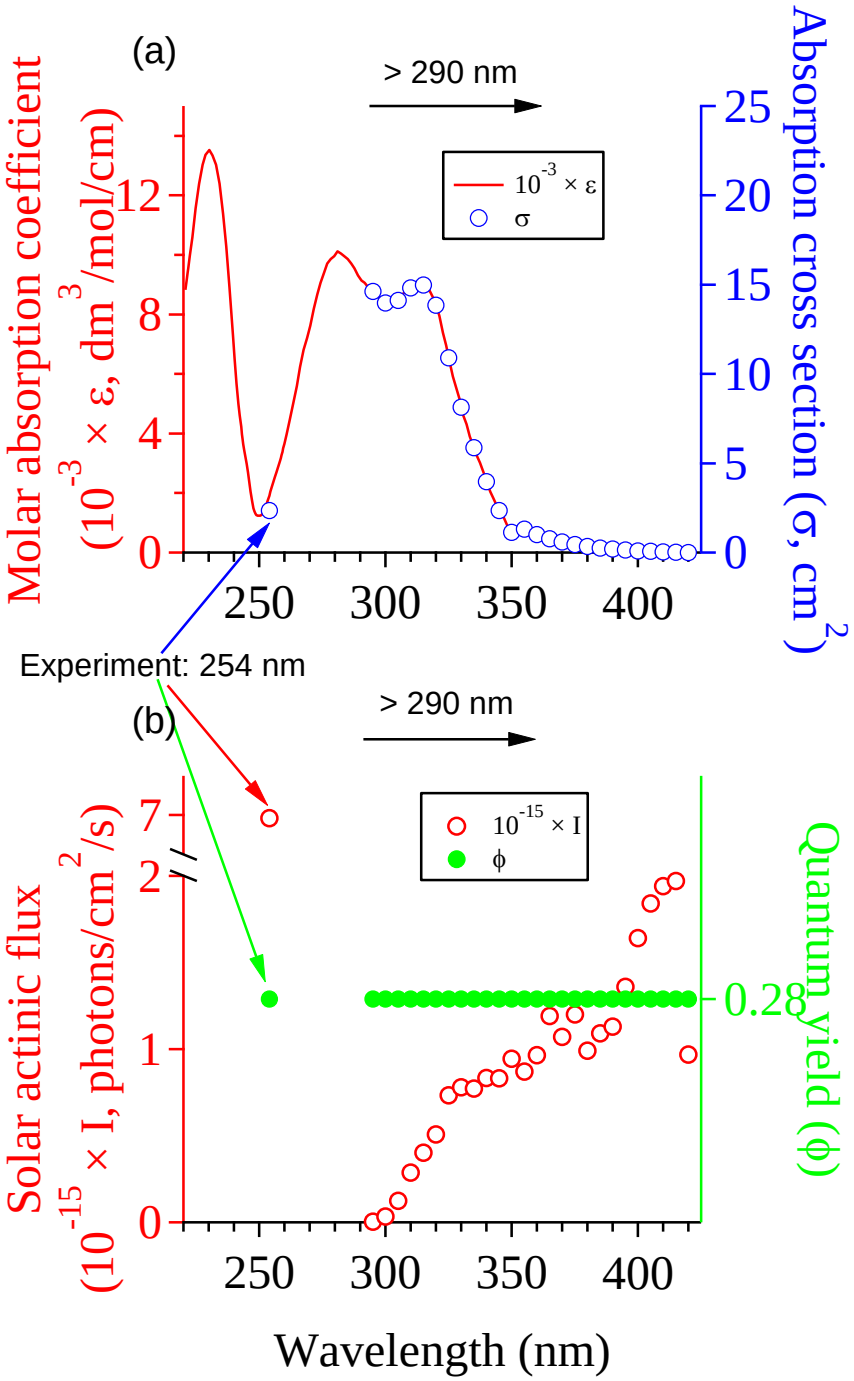

Figure S14. (a) molar absorption coefficient (from NIST database) and estimated absorption cross section of VL; (b) solar actinic flux in typical tropospheric environments: ground level, July 1, noon, 40°N, 298 K (Finlayson-Pitts and Pitts, 1986) and assumed quantum yield (0.28) for VL.

Table S4. Estimation of wavelength-dependent photolysis rates of VL.

Wavelength λ (nm)	$\bar{I}$ (photons cm^{-2} s^{-1})	$10^{20} \times \bar{\sigma}_{VL}$ (cm^2)	$\bar{\phi}_{VL}$	J_{VL} (s^{-1})
254 (condition B)	**6.92×10^{15}**	**2.35**	**0.28**	**2.3×10^{-4}**
295-300	3.14×10^{12}	15	0.28	6.42×10^{-7}
300-305	3.35×10^{13}	14	0.28	6.56×10^{-6}
305-310	1.24×10^{14}	14	0.28	2.45×10^{-5}
310-315	2.87×10^{14}	15	0.28	5.96×10^{-5}
315-320	4.02×10^{14}	15	0.28	8.43×10^{-5}
320-325	5.08×10^{14}	14	0.28	9.85×10^{-5}
325-330	7.34×10^{14}	11	0.28	1.12×10^{-4}
330-335	7.79×10^{14}	8.1	0.28	8.88×10^{-5}
335-340	7.72×10^{14}	5.9	0.28	6.34×10^{-5}
340-345	8.33×10^{14}	4	0.28	4.63×10^{-5}
345-350	8.32×10^{14}	2.4	0.28	2.74×10^{-5}
350-355	9.45×10^{14}	1.1	0.28	1.49×10^{-5}
355-360	8.71×10^{14}	1.3	0.28	1.59×10^{-5}
360-365	9.65×10^{14}	1	0.28	1.36×10^{-5}
365-370	1.19×10^{15}	0.78	0.28	1.30×10^{-5}
370-375	1.07×10^{15}	0.6	0.28	8.95×10^{-6}
375-380	1.20×10^{15}	0.46	0.28	7.67×10^{-6}
380-385	9.91×10^{14}	0.35	0.28	4.81×10^{-6}
385-390	1.09×10^{15}	0.26	0.28	3.97×10^{-6}
390-395	1.13×10^{15}	0.19	0.28	3.05×10^{-6}
395-400	1.36×10^{15}	0.14	0.28	2.66×10^{-6}
400-405	1.64×10^{15}	0.099	0.28	2.26×10^{-6}
405-410	1.84×10^{15}	0.066	0.28	1.71×10^{-6}
410-415	1.94×10^{15}	0.041	0.28	1.11×10^{-6}
415-420	1.97×10^{15}	0.021	0.28	5.85×10^{-7}
420-425	9.69×10^{14}	0.0057	0.28	7.78×10^{-8}
	Total (295-425 nm)			**7.06×10^{-4}**

5. As mentioned by another commenter, the authors should include information about the pH of reaction solutions in their experiments. Ideally this should be monitored throughout aqueous aging. At a minimum, it should be measured at the beginning and end of each experiment, if not controlled. Please provide pH information and discuss the possible role of varying pH in more realistic atmospheric clouds on the aqueous chemical processing observed here.

R: We agree with the reviewers that pH can be an important parameter on the reactions under study. That is why we measured the H_2O_2 decay rate in the ammonium sulfate (AS) and ammonium bisulfate (ABS) solutions to first confirm whether the pH affects H_2O_2 decay or not. As shown in Figure S6, it does not. One can thus investigate the effects of pH on the reactions between organics and OH radical (or direct photolysis). However, as we pointed out in the response to Reviewer #1, too many variables in the experiments might diverge from the current focus of the current manuscript. We plan to investigate the effect of pH on the reactions in future experiments. A discussion on possible pH effects is included in the section of Atmospheric Implications in the revised manuscript, as below.

O: Moreover, the OH radical concentration used was also one order of magnitude higher than typical ambient concentrations.

M: On the other hand, pH in the aqueous droplets will have an effect on the aqueous-phase reactions (Ervens et al., 2011). Commonly found acidic aqueous phase in the atmosphere may not affect the production of OH radical from H_2O_2 photolysis as shown in Figure S6, where ammonium bisulfate (ABS) was used as the medium for H_2O_2 UV photolysis at 254 nm, with negligible difference as compared to when AS solution was used as the medium. But the acidic environment may promote hydration of some carbonyl compounds, thus alter the kinetics and even branching ratios of aqueous-phase reactions. In the current study, the pH of the aqueous solution was not controlled, and a pH value was approximately 6 with 0.1 mM of AS. Further investigation is needed to ascertain the role of acidity in the aqueous-phase reactions of methoxy-phenolic compounds. Moreover, the OH radical concentration used was also one order of magnitude higher than typical ambient concentrations.

6. Please specify the “dry conditions” RH used in the growth factor experiments and discuss whether the tested particle types are likely to be completely free of water at that RH.

R: the “dry condition” refers to RH < 5% in the first DMA. For ammonium sulfate (AS) particles, crystallization is expected to occur at around RH=30%. Thus, it can be considered to be completely free of water for AS under this dry condition. For AS/organics mixed particles, however, small amounts of water might be retained even at RH < 5%. Using E-AIM II (Clegg et al., 1998), we show below that if the AS particles are mixed with 50% (by molar number) of oxalic acid, the most commonly found hygroscopic dicarboxylic acid in aerosols and surrogate of small oxygenates under condition (A) in this study, would retain a small amount of water even at RH = 5%. This estimation is uncertain because of the high concentrations of the electrolytes and the assumption that the organic portion comprises of oxalic acid only. Nevertheless, this small amount of water will cause only little difference in growth factor

measurements and will not affect the conclusion of the current study.

Table R1 E-AIM II inputs:

	Case I (solid formation allowed)	Case II (solid formation not allowed)
Temperature (K)	298.15	
Relative humidity (%)	5	
Ammonium sulfate (mole)	1E-6	
Oxalic acid (mole)	1E-6	
Solid formation	$(NH_4)_2SO_4$, $HOOCCOOH \cdot 2H_2O$	-

E-AIM II outputs:

Table R2. Output from E-AIM II with Cases I and II.

Species	**Mass (gram)**	
	Case I	Case II
H(aq)	4.80E-10	1.18E-10
NH4(aq)	4.07E-07	3.61E-05
HSO4(aq)	4.99E-07	3.30E-05
SO4(aq)	5.91E-07	6.34E-05
OH(aq)	2.73E-24	1.60E-28
HOxal-(aq)	4.92E-07	2.42E-05
Oxal2-(aq)	4.13E-09	2.99E-06
H2O(aq)	1.48E-06	7.99E-06
NH3(aq)	1.43E-16	1.08E-14
Oxalic(aq)	8.95E-05	6.25E-05
H2O(aq) m%[1]	1.59	3.47
H2O(aq) v%[2]	2.71	5.90
Diameter increase (%)[3]	0.9	1.9

Note [1]mass percentage of liquid water; [2] assuming AS and oxalic acid dihydrate have a similar density of 1700 kg/m^3 (1770 for AS and 1650 for oxalic acid dehydrate) and liquid water density of 1000 kg/m^3; [3]compared to completely dried particles.

In Case I, aqueous-phase water (H2O(aq)) is only 1.6% by mass of the condensed phase and 2.7% by volume. Translated to diameters, this little amount of water would cause <1% of difference compared to completely dry solid particles.

In case II, aqueous-phase water (H2O(aq)) is 3.5% by mass of the condensed phase and 5.9% by volume. Translated to diameters, this little amount of water would cause <2% of difference compared to completely dry solid particles.

A discussion on this has been added to Section 2.5 in the revised manuscript.

O: The hygroscopic growth factor, GF_{90}, defined as the ratio of the humidified (at 90% RH) particle diameter to the dry particle diameter, was then obtained.

M: The hygroscopic growth factor, GF_{90}, defined as the ratio of the humidified (at 90%

RH) particle diameter to the dry particle diameter, was then obtained. Note that under condition (A) when substantial amounts of small oxygenates were formed, the dried particles may not be completely water free. Although there is uncertainty in the estimation without the exact knowledge of the amounts of all the small oxygenates and high electrolyte concentrations, EIM-II (Clegg et al., 1998) predicted a <2% difference in the D_{dry}.

7. "bond" should be changed to "bound" in line 14 of the supplement

R: changed as suggested.

8. "maker" should be changed to "marker" in line 4 of p. 27644

R: changed as suggested.

9. I prefer the use of the term "saturation vapor pressure" to "saturated vapor pressure," but that may simply reflect a difference in British vs. American English

R: changed as suggested.

10. Change "form" to "formed" on line 17 of p. 27646

R: changed as suggested.

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Response to Reviewer #3

We thank Dr. Scott Epstein for the comments to improve the manuscript. Below we address those comments point-by-point. Our responses are denoted by "R". The original text to be changed is denoted by "O" and the changed text is denoted by "M".

Reviewer #3

General Comments

The manuscript presents an interesting and extremely comprehensive study of the fate of a methoxy-phenolic compound, vanillin, in the atmospheric aqueous-phase. Two important cloud processing reactions were studied: oxidation by aqueous OH radicals and direct photolysis. Vanillian was processed in the bulk-aqueous-phase and continuously atomized to produce secondary organic aerosol (SOA). The authors used a variety of on-line and off-line instrumentation to monitor product composition. The results of these exhaustive experiments yield several important conclusions related to the degree of oxygenation, cloud-condensation nuclei activity, and the specific compounds formed in the SOA. They conclude that SOA generation from cloud-processing of methyl-phenolic compounds is significant and should be included in chemical transport models. Both the breadth and depth of this paper are impressive. In addition, the authors do a nice job expanding and supporting the experimental results in the Supporting Information. The paper is also well-written. I recommend publication after the authors address the following comments:

Specific Comments

The authors use a 254 nm lamp to generate OH from H2O2 photolysis and to induce direct photolysis. However, using a 254 nm light to induce photolysis may not be atmospherically relevant. Actinic radiation is only present at wavelengths longer than _290 nm. There is the potential for this higher energy light to open up additional reaction channels that would not be available in the atmosphere. This should be addressed in the manuscript. I would be somewhat cautious when extrapolating experimental results from the laboratory to the atmosphere.

R: Agree. The short-wavelength and high energy UV lamp used in the experiments do differ from the actinic radiation in typical tropospheric environments. We did not recommend direct application of the product formation and kinetic data obtained in these experiments to ambient conditions without considering such differences; and we emphasized the wavelength of 254 nm in the experiments in a number of places in the manuscript.

The effects in the different light intensity and wavelengths can be in two folds. First, the reaction pathways might be different, as pointed out by this reviewer. This can be reflected in channel-specific quantum yields, i.e., breaking down wavelength dependent and pathway

dependent quantum yields. However, as pointed out in our response to Reviewer 2, the overall wavelength dependent quantum yields for VL decay are not available. Without additional information, we modify a sentence in the section of Atmospheric implication to reflect the caution suggested by the reviewer, as below.

O: This observation suggests that direct photolysis of methoxy-phenolic compounds could contribute to the light-absorbing "brown carbon" observed in ambient aerosol samples (Andreae and Gelencser, 2006).

M: This observation suggests that direct photolysis of methoxy-phenolic compounds could contribute to the light-absorbing "brown carbon" observed in ambient aerosol samples (Andreae and Gelencser, 2006), although differences between actinic radiation in typical tropospheric environments (> 290 nm) and the short UV wavelength (254 nm) used in the experiments need to be considered.

R: Second, the difference in wavelength range will affect the decay rate of VL. This is addressed in the response to Reviewer 2, with one additional section added to the Supporting Information.

Certain aqueous reactions may involve dissolved oxygen. Is the experimental setup oxygen limiting? Do the authors have any evidence that the reaction products are oxygen dependent? How does the availability of oxygen within the experiment compare to the availability of oxygen in a typical cloud or fog droplet?

R: We believe that the experimental setup was not oxygen limiting since cylinder compressed air was used during the experiments. Therefore, we do not have data to suggest oxygen dependence of the reactions. The usage of compressed air is stated in the revised manuscript.

O: …was continuously atomized to generate particles…

M: …was continuously atomized with compressed air to generate particles…

Last paragraph of section 3.6: The authors state that the measured decay rate of 2.3 x 10ˆ-4 sˆ-1 is comparable to the vanillin loss rates from gas phase oxidation by OH and the loss rate of common aqueous organic compounds. However, the measured decay rate in the experiment is a function of the wavelength dependence and power of the UV-lamp. If the lamp intensity (typically quantified with an actinometer) and the wavelength dependence (quantified with a UV-Vis) are determined, one can calculate the corresponding atmospheric loss rate constant after picking a solar zenith angle and ozone column depth.

R: Agree. This is addressed in the response to Reviewer 2, with one additional section added to the Supporting Information.

Last paragraph of section 3.6: When comparing rates of atmospheric processes, it is more helpful to compare the rate and not the rate constant. E.g. Even if the rate constant of aqueous photolysis is fast, concentrations in the aqueous phase could be so low that aqueous photolysis is not significant. The concentration of vanilin in the aqueous phase relative to the gas phase should be considered when determining the significance of aqueous photolysis.

R: We agree that if one wants to stress how much secondary organic aerosol can be produced from aqueous-phase reactions, one needs to consider the reaction rate by taking into account concentrations in aqueous droplets for VL (or other mehoxy phenols). Here in section 3.6, we tried to compare the loss rates of VL due to different processes, including gas-phase OH oxidation, aqueous-phase OH oxidation, and aqueous-phase photolysis. However, there is little data available in concentration in particle phase and gas phase for VL, and more generally methoxy phenols. Therefore, we do not have a proper aqueous-phase concentration of VL in aqueous droplets in the atmosphere when comparing the loss rates. We intend to keep using rate constants instead rates because of the lack of more detailed information on gas and particulate phase VL concentrations.

Reference

Andreae, M. O., and Gelencser, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, 6, 3131-3148, 2006.