

## ***Interactive comment on “Aqueous-phase photochemical oxidation and direct photolysis of vanillin – a model compound of methoxy-phenols from biomass burning” by Y. J. Li et al.***

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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

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important cloud processing reactions were studied: oxidation by aqueous OH radicals and direct photolysis. Vanillan 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 H<sub>2</sub>O<sub>2</sub> 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

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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...

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Last paragraph of section 3.6: The authors state that the measured decay rate of  $2.3 \times 10^{-4} \text{ s}^{-1}$  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 vanillin 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 methoxy 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.

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## 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.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 27641, 2013.