

Interactive comment on “Enhancement of Secondary Organic Aerosol Formation and its Oxidation State by SO₂ during Photooxidation of 2-Methoxyphenol” by Changgeng Liu et al.

Anonymous Referee #2

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This work describes the effect of the composition and presence of seed aerosol and gas-phase SO₂ (NO_x) on the SOA formation from guaiacol photooxidation. The topic is of great interest as methoxyphenols are largely emitted by biomass burning (BB) emissions and the evolution of these compounds in the atmosphere in a more complex environment is not fully understood yet. Some paragraphs of the discussion could be improved (in a quantitative way) in order to better appreciate the results provided by the authors.

General comments:

The influence of SO₂ in the gas-phase as a source of seed aerosol should be ad-

C1

dressed. The sulfate aerosol arising from SO₂ conversion has the potential to impact the surface area available for condensation and therefore enhance SOA formation. This question needs to be addressed in a more quantitative way. SOA yields could be corrected from this estimation and would help the reader to know whether the increase of SOA concentrations is due to the aerosol microphysics or chemical reactions. The AMS used in this study can provide a lot of information about the evolution of the aerosol all along the experiment. The evolution of the seed aerosol concentration for each experiment would help understanding and estimating the influence of both micro-physics and chemistry on SOA formation.

I would expect more details in the experimental section specifically for the instruments used (PTR and AMS). Also, it would be worth adding a section for the AMS data analysis (quantification, PMF...)

The authors used the AMS which is an instrument known to highly fragment molecules and does not allow molecular level chemical characterization for organics. Organosulfates and organonitrates can be positively identified only using appropriate instrumentation. I would suggest to use: organic sulfur-containing compounds and organic nitrogen-containing compounds (or something similar).

For some results, an evaluation of the uncertainties would help knowing if the variability is due to the uncertainty of the measurement or really represents a difference in a physico-chemical process. It would be worth providing uncertainties for Mo, SOA yields and OSc. In Figure 7, the larger SOA mass in the first 2 hours of the experiment with NaCl only comparing with NaCl + 30 ppb of SO₂ could be due to the uncertainty of the experiment. If not, this behavior needs to be discussed by the authors.

Specific comments:

I-51 and elsewhere in the introduction → Specify the type of fuel used for the given emission factors

C2

I-62 SOA formation from guaiacol photooxidation in the presence of NOx has been studied in the past (Lauraguais et al., 2014; Yee et al., 2013). See your discussion paragraph. Experimental section Iú The experimental section could be improved by adding details about the the AMS/PTR-MS instrumental settings (experimental conditions) and data analysis (N:C, O:C, H:C, sulfur and nitrogen-containing compounds concentrations, PMF).

I. 165-167 Do you see any low volatility products in the gas phase based on the PTR-MS data?

I.171 and all the paper Iú What is the estimated uncertainties of the reported SOA yields?

I.170 How would you explain the difference in SOA yield between your study and Lauraguais et al., 2014? The SOA formation in their study is 3 times higher with the same guaiacol and OH concentrations and without seed particles.

I. 179 Sun et al., 2010 presented results of aqueous-phase oxidation of guaiacol with and without an added source of OH. Their results are not really comparable to this study.

I. 189-197 Organonitrates (-ONO₂) are different than nitro-organics (nitro-aromatics, nitro-compounds...) containing a (-NO₂) chemical group. The formation of nitro-aromatics from the photooxidation of guaiacol under high NOx conditions has already been reported (i.e. nitroguaiacol, nitrocatechol) (Ahmad et al., 2017; Lauraguais et al., 2014).

In this study, the reported NO₊/NO₂⁺ is clearly different from the ammonium nitrate standard. This difference could be explained by the presence of both nitro and nitrate organics (Sato et al., 2010; Farmer et al., 2010). I would suggest to use organic nitrogen-containing compounds (or something similar) instead of “organonitrates” unless the authors provide molecular chemical characterization clearly showing the for-

C3

mation of organonitrates.

I. 224 The results in Figure 3 arise from one specific condition or represent an average of MS for the three different conditions? Unclear. In the MS in Figure 3, we can see a large contribution of the m/z 44 in the factor 1. At t=0 min, the factor 1 dominates the aerosol fraction which means that before the photooxidation experiment there is already a large fraction of m/z 44 in the aerosol. Is there already oxidized organics and SOA in the aerosol before the photooxidation experiments? Does it correspond to guaiacol condensation on the aerosol phase? Something else? To illustrate these experiments, I would recommend to provide the evolution of the organics, sulfate, nitrate, over the course of an experiment (before and after lights on and corrected with wall loss). This would help visualizing the change in sulfate an organics concentrations. The impact of sulfate formation on SOA formation due to an increase of condensation or due to chemical processes needs to be addressed in a more quantitative way.

I 243-248 From the MS presented in Figure S5 we clearly see that in the presence of SO₂, low-MW compounds are more abundant. It also appears that high-MW compounds are in higher abundance in the presence of SO₂ (33 ppb vs no SO₂ and 56 ppb vs 33 ppb). Do you have an idea of the role of SO₂ in the formation of these compounds?

I. 254 Do you see water soluble low-MW compounds in the gas-phase using the PTR-MS and an increase of the uptake of these compounds with increasing SO₂ concentrations?

L 253 How did you quantify the amount of organosulfates? In Figure S6: Is this MS from a standard or from smog chamber experiment? Unclear. In Huang et al., 2015, they quantified using a commercial standard. What is the uncertainty in your measurement considering that the C₅H₃O and C₅H₃O₂ are highly abundant (and the resolution seems lower comparing to Huang et al. 2015) and can induce error during the peak fitting?

C4

L 261 Would it be possible to provide a potential chemical mechanism that could lead to the formation of organosulfate (or organic sulfur containing compounds) through heterogeneous uptake of SO₂?

L 323 Do you see chlorine containing compounds (organics) or fragments using the AMS or the PTR-MS? Do you think they could participate to SOA formation?

I-362 Do you see a higher SO₂ uptake in the presence of NaCl comparing with (NH₄)₂SO₄? This could illustrate the enhance SO₂ uptake and explain the higher SOA formation.

I. 368 Do you see a difference in the PTR-MS signal for low MW compounds in the presence of SO₂ for NaCl and (NH₄)₂SO₄? (a larger uptake of these molecules in the presence of NaCl?).

Typing errors: I. 164 values I. 166 partitioned I. 335 inorganic SII. 31 Formation Figure S5: signal

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C5

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C6