

Responses to Reviewers

We would like to thank the reviewers for your constructive comments. We have carefully revised this manuscript according to your comments, and the revisions in the revised manuscript were presented in red font. Enclosed please find the point-by-point responses to the reviewers' comments.

Responses to Referee #2's comments

General comment: I would like to thank the authors for the response and their efforts to improve and clarify this manuscript. The supplementary data is very useful and the discussion about the influence of the aerosol microphysics to the SOA formation provides a better understanding of the processes happening during guaiacol oxidation in the presence of SO₂ and seed aerosols. I still have a few comments about some of the updated paragraphs.

Response to comment: Many thanks for your constructive comments and valuable suggestions, which would be much helpful to improve the scientific merits of this manuscript. Your concerns have been carefully addressed in the revised manuscript.

Comment 1: l. 309 please provide the definition of CHO_{gt1}

Response to comment 1: The definition of CHO_{gt1} ion group has been added in the revised manuscript as follows.

Revision in the manuscript:

Line 311, Add: “containing more than one oxygen atom”

Comment 2: 1. 332 I would recommend to clarify this quantification by saying that these values were obtained if considering that all S-containing compounds are organosulfates and having the same response factor and fragmentation as methyl sulfate

Response to comment 2: According to your valuable suggestion, the descriptions of organosulfates concentration have been modified in the revised manuscript, shown in the following revisions.

Revisions in the manuscript:

Lines 335-336, Add: “assuming that all organic S-containing compounds are organosulfates and have the same response factor and fragmentation as methyl sulfate”

Lines 336-339, Change: “the conservative lower-bound concentration of organosulfates increased with the increase of SO₂ concentration, and was in the range of (2.1 ± 0.8) to (4.3 ± 1.7) ng m⁻³, calculated using the method described by Huang et al. (2015), shown in the Supplement.” **To** “the conservative lower-bound concentration of organosulfates was calculated to be in the range of (2.1 ± 0.8) to (4.3 ± 1.7) ng m⁻³ using the method described by Huang et al. (2015) shown in the Supplement, and increased with the increase of SO₂ concentration.”

Comment 3: 1. 340 Is SO₂ favorable for the uptake of low-MW species or at the contrary, sulfuric acid + SOA retain low-MW in the aerosol phase? It could be both.

Response to comment 3: According to your valuable suggestion, this sentence has been rewritten in the revised manuscript as follows.

Revision in the manuscript:

Lines 343-346, Change: “sulfuric acid formed from SO₂ may be favorable of the uptake of water-soluble low-MW species (e.g., small carboxylic acids and aldehydes)”

To “sulfuric acid formed from SO₂ may be favorable for the uptake of water-soluble low-MW species (e.g., small carboxylic acids and aldehydes) and also be helpful to retain them in aerosol phase”

Comment 4: l. 390 add value of O:C ratios in parenthesis

Response to comment 4: The O/C ratios have been added in parenthesis in the revised manuscript as follows.

Revisions in the manuscript:

Line 394, Add: “(0.94–0.99)”

Line 395, Add: “(0.90–0.93)”

Comment 5: l. 507 I would add “physic” and chemistry of SOA formation

Response to comment 5: According to your valuable suggestion, “chemistry” has been changed to “physics and chemistry” in the revised manuscript.

Revision in the manuscript:

Line 513, Change: “chemistry” **To** “physics and chemistry”

Comment 6: Figure 3. I would reverse the colors. Red more SOA and blue less SOA.

Response to comment 6: Colors in Figure 3 have been modified in the revised manuscript according to your valuable suggestion, shown as Figure R1.

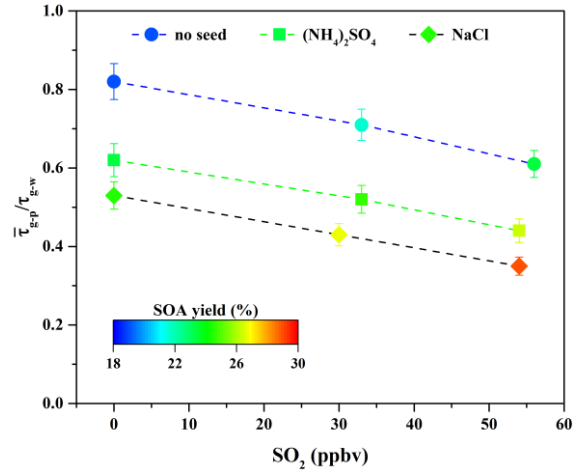


Figure R1. Variations in $\bar{\tau}_{g-p} / \tau_{g-w}$ ratio in the presence of various seed particles as a function of SO₂ concentration.

Revision in the manuscript:

Figure R1 has been added in the revised manuscript.

Comment 7: In the supplement:

- (1) 1.54 In Zhang et al., 2014, Avogadro was misspelled to Avagadro. Change to Avogadro and also Boltzman to Boltzmann.
- (2). Figure S7: make sure that the trace (NH₄)₂SO₄ blue triangles is not actually the NaCl data. Because SO₂ concentrations for ammonium sulfate seeds is 33 ppbv and for NaCl is 30 ppbv while in the figure the NaCl trace is higher than the (NH₄)₂SO₄ trace.
- (3). 1. 36 change to mass accommodation coefficient of vapors deposition to the wall
- (4). 1. 38 the coefficient of eddy diffusion will be chamber dependent. The k_e used here is the one corresponding to the chamber used in Zhang et al., 2014. Please explain your choice for this value that may or may not be the best fit for your study.
- (5). Please provide the same discussion for the choice of the mass accommodation

values (to the walls and particles).

Response to comment 7: Thank you very much. The detailed responses to these comments are listed as follows.

(1). “Avagadro” and “Boltzman” have been changed to “Avogadro” and “Boltzmann”, respectively.

(2). Figure traces in Figure S7 have been corrected in the revised Supplement, shown as Figure R2.

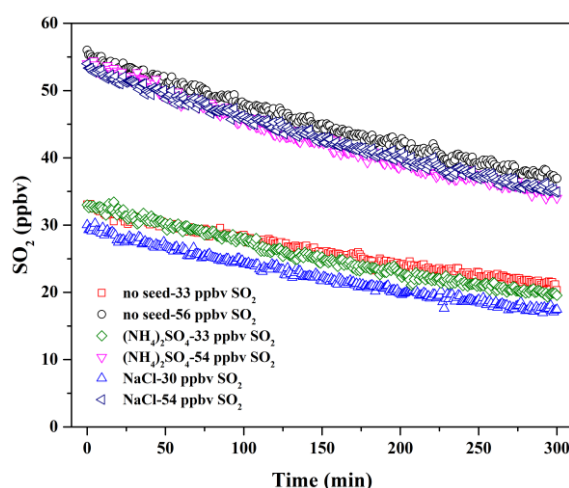


Figure R2. Decays of SO₂ as a function of irradiation time with different seed particles.

(3). “Mass accommodation coefficient of eddy diffusion” has been changed to “mass accommodation coefficient of vapors deposition to the wall”.

(4) and (5). We agree that the values of k_e and α_w are chamber dependent. In this work, considering that the chamber volume (30 m³) is very close to that (28 m³) used by Zhang et al. (2014), thus the values of k_e and α_w reported by them were selected to calculate the overall wall loss rate of organic vapor (k_w).

Revisions in the manuscript:

(1). **Line 64, Change:** “Avagadro” and “Boltzman” To “Avogadro” and “Boltzmann”,

respectively.

(2). Figure R2 has been added in the revised Supplement.

(3). Lines 36-37, Change: “mass accommodation coefficient of eddy diffusion” To “mass accommodation coefficient of vapors deposition to the wall”

(4) and (5). Lines 39-41, Add “Considering that the chamber volume in this work (30 m³) is very close to that (28 m³) used by Zhang et al. (2014), thus the values of k_e and α_w reported by them were applied to calculate k_w .”

Comment 8. The authors are not considering the vapor wall loss as a reversible process. Can you explain this choice? I would expect this process to be reversible.

Response to comment 8: Thank you very much. We agree that the vapor wall loss is a reversible process. In this work, we considered that the equilibrium was established for vapor wall losses after four hours photooxidation, because Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014) reported the rapid equilibrium established within less than an hour for vapor wall losses in Teflon chambers. In addition, assuming that the chamber wall was essential an absorbing medium of infinite extent, the overall wall loss rate of organic vapor (k_w) could be calculated using Eq. (S3) (Zhang et al., 2015), shown in the Supplement. Since this method could not separate the evaporation of adsorbed organic materials from the wall, the effect of vapor wall loss in this calculation might be overestimated. The detailed descriptions have been added in the revised Supplement.

Revision in the manuscript:

Supplement, Lines 41-49, Add: “In addition, we considered that the equilibrium was established for vapor wall losses after 4 hours photooxidation, because Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014) reported the rapid equilibrium established within less than an hour for vapor wall losses in Teflon chambers. Meanwhile, it was assumed that the chamber wall was essential an absorbing medium of infinite extent. In this case, k_w could be calculated using Eq. (S3) (Zhang et al., 2015). Since this method could not separate the evaporation of adsorbed organic materials from the wall, the effect of vapor wall loss in this calculation might be overestimated.”

Comment 9: Typing errors: I would recommend that the authors read carefully their paper to make sure no typing errors remain in the paper.

l. 69 direct

l. 90 Smog

l. 269 trace of NH₃

l. 329 low-MW

l. 403, 404 change to “might explain”

l. 438 when SO₂ concentration raised from 0 to 30 ppbv for NaCl, M_o increased from 84.91 to 90.89 μg m⁻³ and not from 63.62 to 90.89. Change the percentage too and the same changes has to be done for (NH₄)₂SO₄.

l. 487 add parenthesis before 26.37

l. 501 attention

1. 576 mass spectrometer

Response to comment 9: We have carefully checked the grammar and typing errors.

The mistakes mentioned above have been corrected in the revised manuscript, listed as follows.

Revisions in the manuscript:

Line 69, Change: “direact” To “direct”

Line 90, Change: “Somg” To “Smog”

Line 270, Change: “trace NH₃” To “trace of NH₃”

Line 331, Change: “low-WM” To “low-MW”

Line 409, Change: “might be potentially explain” To “might explain”

Line 445, Change: “63.62 ± 1.71” To “84.91 ± 2.01”

Line 446, Change: “42.86% and 55.39%” To “7.04% and 16.43%”

Line 448, Change: “63.62 ± 1.71” To “79.44 ± 1.86”

Lines 449-450, Change: “32.58% and 41.34%” To “6.18% and 13.19%”

Line 493, Add: “(”

Line 507, Change: “attenion” To “attention”

Line 590, Change: “aass spectrometer” To “mass spectrometer”

Responses to Referee #3's comments

Comment 1: Thank you for a very careful and thorough response to the suggestions presented in the review. I have one remaining concern: the mass spectra are communicated as being normalized to a sum of intensities of 1. However, when they are subtracted, there is net more intensity on one side. This is especially clear in Figure S13, please also check Figure 7c. If the mass spectra are normalized as described, the sum of the difference intensities should equal zero. Please double check this and the corresponding conclusions drawn from these figures.

Response to comment 1: Thank you very much. We are very sorry not to accurately response your comment in the previous version. In this work, the mass spectra were normalized to the mass concentration of SOA while not the sum intensity, which were obtained directly from AMS data analysis software (ToF-AMS analysis toolkit SQUIRREL 1.57I/PIKA 1.16I version, in Igor Pro version 6.37). Considering that the product distribution and SOA composition were different under different experimental conditions, the sum of difference intensities would not equal to zero. The similar phenomena were also reported by Tuet et al. (2017).

References

- Matsunaga, A. and Ziemann, P. J.: Gas-wall partitioning of organic compounds in a Teflon film chamber and potential effects on reaction product and aerosol yield measurements, *Aerosol Sci. Technol.*, 44, 881-892, <https://doi.org/10.1080/02786826.2010.501044>, 2010.
- Tuet, W. Y., Chen, Y., Fok, S., Gao, D., Weber, R. J., Champion, J. A., and Ng, N. L.: Chemical and cellular oxidant production induced by naphthalene secondary organic aerosol (SOA): Effect of redox-active metals and photochemical aging, *Sci. Rep.*, 7, 15157, <https://doi.org/10.1038/s41598-017-15071-8>, 2017.
- Yeh, G. K. and Ziemann, P. J.: Alkyl nitrate formation from the reactions of C8-C14 n-alkanes with OH radicals in the presence of NO_x: measured yields with essential corrections for gas-wall partitioning, *J. Phys. Chem. A*, 118, 8147–8157, <https://doi.org/10.1021/jp500631v>, 2014.
- Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *Proc. Natl. Acad. Sci. U. S. A.*, 111, 5802-5807, <https://doi.org/10.1073/pnas.1404727111>, 2014.
- Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, *Atmos. Chem. Phys.*, 15, 4197-4214, <https://doi.org/10.5194/acp-15-4197-2015>, 2015.