

## Reply to Anonymous Referee #2

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following the suggestion, as described below.

Li Xing et al. present a modeling study of SOA formation pathways and contribution of heterogeneous HONO sources in the BTH region focusing on wintertime haze. This is an important study. I have several suggestions for strengthening the Manuscript, and I recommend that the following points need to be addressed before publication:

**1 Comment:** Introduction line 43: Please clarify if biogenic POA refers to POA from biomass burning and/or biological particles like bacteria, fungi etc.?

**Response:** In the present study, biogenic POA refers to the POA from biomass burning. Biological particles like bacteria, fungi, pollen, and viruses are usually termed as primary biological aerosol particles, or bioaerosols. We have clarified in Section 1: “*POA are directly emitted into the atmosphere as particles by various anthropogenic and biomass burning sources*”

**2 Comment:** Line 46: In addition to Robinson and Hallquist, suggest citing the recent review paper on SOA by Shrivastava et al. 2017 (1)

**Response:** We have included the reference in Section 1: “*Some species of POA evaporate into the atmosphere and are oxidized further, re-partition into aerosols, and form SOA (Robinson et al., 2007; Hallquist et al., 2009; Shrivastava et al., 2017).*”

**3 Comment:** Line 85: Also cite the global modeling paper using VBS by Shrivastava et al. 2015.

**Response:** We have included the reference in Section 1: “*CTMs using the VBS approach have remarkably improved the SOA simulations against observations (e.g., Li et al., 2011; Shrivastava et al., 2013, 2015; Feng et al., 2016).*”

**4 Comment:** Line 100: The difference between the 2-product model and VBS is also because the VBS accounts for semi-volatile and intermediate volatility organics emitted from fossil fuel and biomass burning sources in addition to traditional SOA. This needs to be mentioned here.

**Response:** We have rephrased the sentence as suggested in Section 1: “*Additionally, the predicted ratio of secondary OC to total OC in the VBS approach is about 33%, much higher than that (around 5%) in the two-product model and also close to observation-based estimation (32%), suggesting a more realistic representation of the SOA formation by the VBS approach through accounting for the semi-volatile and intermediate volatility organics emitted from fossil fuel and biomass burning sources.*”

**5 Comment:** Line 115: Please mention the different SOA sources being represented by VBS: e.g., anthropogenic, biomass burning, biogenic. Also, was gas-phase fragmentation of organic vapors included during multigenerational aging of organic vapors in the VBS? Please see the following papers for reference: (References 2,4,5 listed below)

**Response:** We have rephrased the model description about the SOA formation as suggested in Section 2.1: “*The POA components from traffic-related combustion and biomass burning are represented by nine surrogate species with saturation concentrations ( $C^*$ ) ranging from  $10^{-2}$  to  $10^6 \mu\text{g m}^{-3}$  at room temperature (Shrivastava et al., 2008), and assumed to be semi-volatile and photochemically reactive (Robinson et al., 2007). The SOA formation from each anthropogenic or biogenic precursor is calculated using four semi-volatile VOCs with effective saturation concentrations of 1, 10, 100, and  $1000 \mu\text{g m}^{-3}$  at 298 K. Previous studies have demonstrated that the fragmentation reactions of semi-volatile VOCs also play an important role in the SOA formation (Shrivastava et al., 2013, 2015, 2016). However, the fragmentation reactions have not been incorporated in the version of the WRF-CHEM model, and further studies need to be performed to include the contribution of those reactions to improve the SOA simulation.*”

**6 Comment:** Section 3.1. POA simulations and Figure 2: It is confusing why POA and HOA are on separate panels. POA is generally compared against the HOA factor derived from PMF analysis of HR-Tof-AMS data. Please clarify what is model POA being compared to in panel 2(a) and what is PMF AMS HOA being compared to in panel 2(b)? Also I do not see a comparison for PMF OOA and model SOA.

**Response:** Elser et al. (2016) have resolved five components of OA using a novel PMF method, which are HOA, BBOA, CCOA, COA, and OOA, respectively. HOA, BBOA, CCOA, and COA represent the POA related to the traffic combustion, biomass burning, coal combustion, and cooking emissions, respectively, and OOA is a surrogate for SOA. HOA in the study only represents the POA related to the traffic combustion emission, which is different from that used by Shrivastava et al. (2011), which represents the total urban POA and is not separated into different POA components. We have clarified in Section 2.3: *“Five components of OA are classified by their mass spectra and time series, including traffic-combustion hydrocarbon-like OA (HOA), cooking OA (COA), biomass burning OA (BBOA), coal combustion OA (CCOA), and oxygenated OA (OOA).”*

In Figure 2(a), the modeled POA is compared to the sum of HOA, BBOA, CCOA, and COA of AMS data resolved by PMF method. We have clarified in Section 2.1: *“Figure 2 presents the temporal profiles of the model-simulated and observed POA (sum of HOA, BBOA, CCOA, and COA), HOA, BBOA+COA, and CCOA concentrations from 9 to 26 January 2014 at IRSDE site in Beijing.”*

The comparison between modeled SOA and PMF-derived OOA is shown in Figure 4(b).

**7 Comment:** Also, can the authors compare their glyoxal and methylglyoxal to some of the AMS factors? If not, can AMS total organic signal – (sum of HOA+BBOA+CCOA+COA) be used as an estimate of glyoxal/methylglyoxal? If not, please explain. For example, are there any distinct AMS makers for glyoxal/methylglyoxal SOA or aqueous SOA formed during Haze? What was the overall O:C ratio of AMS organic aerosol?

**Response:** HOA, BBOA, CCOA, and COA are the primary OA, which cannot be used as an estimation of the glyoxal/methylglyoxal SOA. Sun et al. (2016) have resolved aqueous SOA factors from the AMS measurement and reported that the aqueous SOA (aq-SOA) is correlated well with several specific fragment ions, including  $C_2H_2O_2^+$  (m/z 58),  $C_2O_2^+$  (m/z 56) and  $CH_2O_2^+$  (m/z 46), which are typical fragment ions of glyoxal and methylglyoxal (Chhabra et al., 2010). In addition, aq-SOA is also highly correlated with several sulfur-containing ions, e.g.  $CH_3SO^+$ ,  $CH_2SO_2^+$  and  $CH_3SO_2^+$ , which are typical fragment ions of methanesulfonic acid (MSA), a secondary product from the oxidation of dimethyl sulfide (DMS). Also sulfate is

mainly formed in the aqueous phase during wintertime haze days (G. Li et al., 2017), which is compared with the simulated HSOA in Beijing. We have extracted the concentrations of those specific fragment ions reported in Sun et al. (2016) and compared with the simulated HSOA concentrations in Beijing. We do not use the concentrations of  $\text{CH}_2\text{O}_2^+$  (m/z 46) for comparisons, as  $\text{NO}_2^+$  ion has the same m/z value with  $\text{CH}_2\text{O}_2^+$ , which cause some biases. The concentrations of  $\text{CH}_2\text{SO}_2^+$  cannot be extracted from the AMS data, which is not used for comparisons.

We have clarified in Section 3.3: “Sun et al. (2016) have resolved aqueous SOA (aq-SOA) factors from the AMS measurement, and reported that the aq-SOA is correlated well with several specific fragment ions, including  $\text{C}_2\text{H}_2\text{O}_2^+$  (m/z 58),  $\text{C}_2\text{O}_2^+$  (m/z 56) and  $\text{CH}_2\text{O}_2^+$  (m/z 46), which are typical fragment ions of glyoxal and methylglyoxal (Chhabra et al., 2010). Additionally, aq-SOA is also highly correlated with several sulfur-containing ions, e.g.  $\text{CH}_3\text{SO}^+$ ,  $\text{CH}_2\text{SO}_2^+$  and  $\text{CH}_3\text{SO}_2^+$ , which are typical fragment ions of methanesulfonic acid (MSA). Sulfate is also mainly formed in the aqueous phase during wintertime haze days (G. Li et al., 2017).  $\text{CH}_2\text{O}_2^+$  (m/z 46) is not used to compare with the simulation, as it has the same m/z value with  $\text{NO}_2^+$  ion, causing some biases. In addition, the concentrations of  $\text{CH}_2\text{SO}_2^+$  cannot be extracted from the AMS measurement, so is not used for comparisons. Figure 10 shows the scatter plot of the simulated HSOA concentration and the AMS measured sulfate and several specific fragment ions concentration during the episode. The simulated HSOA exhibits good correlations with those specific fragment ions with correlation coefficients exceeding 0.50, especially with regard to the  $\text{C}_2\text{H}_2\text{O}_2^+$  and  $\text{C}_2\text{O}_2^+$  ions with correlation coefficients of 0.59 and 0.58, respectively, showing reasonable simulation of the HSOA formation. The correlation of sulfate with the HSOA is not as good as those of the fragment ions, indicating that non-heterogeneous sources also play a considerable role in the sulfate formation. All the correlations are statistically significant with p-value smaller than 0.01. Furthermore, the average observed OM/OC and O/C ratio during the simulation period are 1.42 and 0.21, respectively.”

**8 Comment:** Section 3.3: The authors include glyoxal SOA, but seems they do not include isoprene epoxydiol (IEPOX SOA) which is also formed by aqueous chemistry. Is the IEPOX-SOA contribution expected to be insignificant?

**Response:** We have clarified in Section 3.3: *“It is worth noting that isoprene epoxydiol (IEPOX SOA) formed by aqueous chemistry also plays a considerable role in the SOA formation. However, Hu et al. (2017) have shown that, during the wintertime, the IEPOX SOA contribution to the SOA formation in BTH is insignificant due to the very low biogenic isoprene emissions and the elevated NO<sub>x</sub> concentrations which substantially suppress the production of IEPOX SOA from the isoprene oxidation.”*

**9 Comment:** Line 270-275: What sources contribute to residential living? Are these biofuel burning? Also, could glyoxal and methylglyoxal also be emitted from wildfires and agricultural waste burning?

**Response:** We have clarified in Section 3.3: *“The residential living sources include biofuel and coal combustion, and attain peak emissions in winter for heating purposes in Northern China. M. Li et al. (2017) have estimated that residential sector contributes about 27% of non-methane VOCs emissions in 2010 in China and biofuel combustion contributes a large part of oxygenated VOCs, alkynes, and alkenes to residential sector emissions. Laboratory and field studies have shown that wildfires and agricultural waste burning also emit glyoxal and methylglyoxal. Hays et al. (2002) have detected glyoxal and methylglyoxal emissions from six kinds of biomass in US and measured their emission rates for different kinds of biomass. Zarzana et al. (2017) have observed glyoxal and methylglyoxal emissions from agricultural biomass burning plumes by aircraft. Koss et al. (2018) have measured the emission factors of glyoxal and methylglyoxal by burning biofuels characteristic of western US. Fu et al. (2008) have estimated that 20% of glyoxal comes from biomass burning and 17% from biofuel use on a global scale, and 5% and 3% of methylglyoxal comes from biomass burning and biofuel use, respectively.”*

**10 Comment:** Figure 3: In addition to observed average diurnal cycle, also include modeled diurnal cycle average for O<sub>3</sub> and HONO. For HONO please include both the base and HOMO cases from Figure 4.

**Response:** We have included the modeled O<sub>3</sub> and HONO diurnal cycle in Figure 3 as suggested and clarified in Section 3.2: *“Additionally, the WRF-CHEM model also generally yields the observed HONO diurnal cycle, but the underestimation is substantial during nighttime (Figure 3a). The simulated O<sub>3</sub> diurnal cycle is in agreement with the observation at IRSDE site, but the*

*model underestimates the O<sub>3</sub> concentration against the measurement in the morning (Figure 3b).”*

### References from the referee:

- 1 Shrivastava, M. et al. Recent advances in understanding secondary organic aerosol: Implications for global climate forcing. *Rev. Geophys.* 55, 509-559, doi:10.1002/2016RG000540 (2017).
- 2 Shrivastava, M. et al. Global transformation and fate of SOA: Implications of low- volatility SOA and gas-phase fragmentation reactions. *J. Geophys. Res.-Atmos.* 120, 4169-4195, doi:10.1002/2014jd022563 (2015).
- 3 Shrivastava, M., Lane, T. E., Donahue, N. M., Pandis, S. N. & Robinson, A. L. Effects of gas particle partitioning and aging of primary emissions on urban and re- gional organic aerosol concentrations. *J. Geophys. Res.-Atmos.* 113, doi:D18301 10.1029/2007jd009735 (2008).
- 4 Shrivastava, M. et al. Implications of low volatility SOA and gas-phase fragmentation reactions on SOA loadings and their spatial and temporal evolution in the atmosphere. *J. Geophys. Res.-Atmos.* 118, 3328-3342, doi:10.1002/jgrd.50160 (2013).
- 5 Shrivastava, M. et al. Sensitivity analysis of simulated SOA loadings using a variance-based statistical approach. *Journal of Advances in Modeling Earth Systems* 8, 499-519, doi:10.1002/2015ms000554 (2016).

## References:

- Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, *Atmos. Chem. Phys.*, 10, 4111–4131, doi:10.5194/acp-10-4111-2010, 2010.
- Elser, M., Huang, R.-J., Wolf, R., Slowik, J. G., Wang, Q., Canonaco, F., Li, G., Bozzetti, C., Daellenbach, K. R., Huang, Y., Zhang, R., Li, Z., Cao, J., Baltensperger, U., El-Haddad, I., and Prévôt, A. S. H.: New insights into PM<sub>2.5</sub> chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry, *Atmos. Chem. Phys.*, 16, 3207–3225, doi:10.5194/acp-16-3207-2016, 2016.
- Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *J. Geophys. Res.-Atmos.*, 113, doi: 10.1029/2007jd009505, 2008.
- Hays, M. D., Geron, C. D., Linna, K. J., and Smith, D.: Speciation of gas-phase and fine particle emissions from burning of foliar fuels, *Environ. Sci. Technol.*, 36, 2281-2295, doi: 10.1021/es0111683, 2002.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155-5236, 2009.
- Hu, J., Wang, P., Ying, Q., Zhang, H., Chen, J., Ge, X., Li, X., Jiang, J., Wang, S., Zhang, J., Zhao, Y., and Zhang, Y.: Modeling biogenic and anthropogenic secondary organic aerosol in China, *Atmos. Chem. Phys.*, 17, 77-92, doi: 10.5194/acp-17-77-2017, 2017.
- Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L. and Krechmer, J.: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, *Atmos. Chem. Phys.*, 18, 3299-3319, doi: 10.5194/acp-18-3299-2018, 2018.
- Li, G., Bei, N., Cao, J., Huang, R., Wu, J., Feng, T., Wang, Y., Liu, S., Zhang, Q., Tie, X., and Molina, L. T.: A possible pathway for rapid growth of sulfate during haze days in China, *Atmos. Chem. Phys.*, 17, 3301-3316, <https://doi.org/10.5194/acp-17-3301-2017>, 2017.
- Li, M., Zhang, Q., Kurokawa, J. I., Woo, J. H., He, K., Lu, Z., Ohara, T., Song, Y., Streets, D. G., Carmichael, G. R., Cheng, Y., Hong, C., Huo, H., Jiang, X., Kang, S., Liu, F., Su, H., and Zheng, B.: MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP, *Atmos. Chem. Phys.*, 17, 935-963, doi: 10.5194/acp-17-935-2017, 2017.
- Shrivastava, M. K., Lane, T. E., Donahue, N. M., Pandis, S. N., and Robinson, A. L.: Effects of gas particle partitioning and aging of primary emissions on urban and regional organic aerosol concentrations, *J. Geophys. Res.-Atmos.*, 113, doi: 10.1029/2007jd009735, 2008.
- Shrivastava, M., Fast, J., Easter, R., Gustafson Jr., W. I., Zaveri, R. A., Jimenez, J. L., Saide, P. and A. Hodzic: Modeling organic aerosols in a megacity: Comparison of simple and



complex representations of the volatility basis set approach, *Atmos. Chem. Phys.*, 11(13), 6639–6662, 2011.

Shrivastava, M., Zelenyuk, A., Imre, D., Easter, R., Beranek, J., Zaveri, R. A., and Fast, J.: Implications of low volatility SOA and gas-phase fragmentation reactions on SOA loadings and their spatial and temporal evolution in the atmosphere, *J. Geophys. Res.-Atmos.*, 118, 3328-3342, doi: 10.1002/jgrd.50160, 2013.

Shrivastava, M., Easter, R. C., Liu, X., Zelenyuk, A., Singh, B., Zhang, K., Ma, P. L., Chand, D., Ghan, S., Jimenez, J. L., and Zhang, Q.: Global transformation and fate of SOA: Implications of low-volatility SOA and gas-phase fragmentation reactions, *J. Geophys. Res.-Atmos.*, 120(9), 4169-4195, doi: 10.1002/2014JD022563, 2015.

Shrivastava, M., Zhao, C., Easter, R. C., Qian, Y., Zelenyuk, A., Fast, J. D., Liu, Y., Zhang, Q., and Guenther, A.: Sensitivity analysis of simulated SOA loadings using a variance-based statistical approach, *J. Adv. Model. Earth Syst.*, 8, 499-519, doi: 10.1002/2015MS000554, 2016.

Shrivastava, M., Cappa, C. D., Fan, J., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., Kuang, C., Laskin, A., Martin, S. T., Ng, N. L., and Petaja, T.: Recent advances in understanding secondary organic aerosol: Implications for global climate forcing, *Rev. Geophys.*, 55(2), 509-559, doi: 10.1002/2016RG000540, 2017.

Sun, Y. L., Du, W., Fu, P. Q., Wang, Q. Q., Li, J., Ge, X. L., Zhang, Q., Zhu, C. M., Ren, L. J., Xu, W. Q., Zhao, J., Han, T. T., Worsnop, D. R., and Wang, Z. F.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, *Atmos. Chem. Phys.*, 16, 8309–8329, doi: 10.5194/acp-16-8309-2016, 2016.

Zarzana, K. J., Min, K. E., Washenfelder, R. A., Kaiser, J., Krawiec-Thayer, M., Peischl, J., Neuman, J. A., Nowak, J. B., Wagner, N. L., Dubè, W. P. and St. Clair, J. M.: Emissions of Glyoxal and Other Carbonyl Compounds from Agricultural Biomass Burning Plumes Sampled by Aircraft, *Environ. Sci. Technol.*, 51, 11761-11770, doi: 10.1021/acs.est.7b03517, 2017.

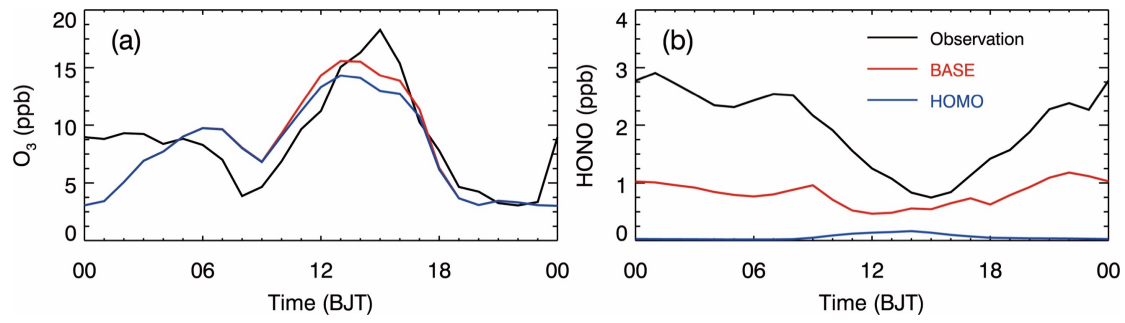


Figure 3 Diurnal cycle of observed (black line) and modeled (red line: BASE case; blue line: HOMO case) (a) O<sub>3</sub> and (b) HONO concentrations averaged from 9 to 26 January 2014 at IRSDE site in Beijing.

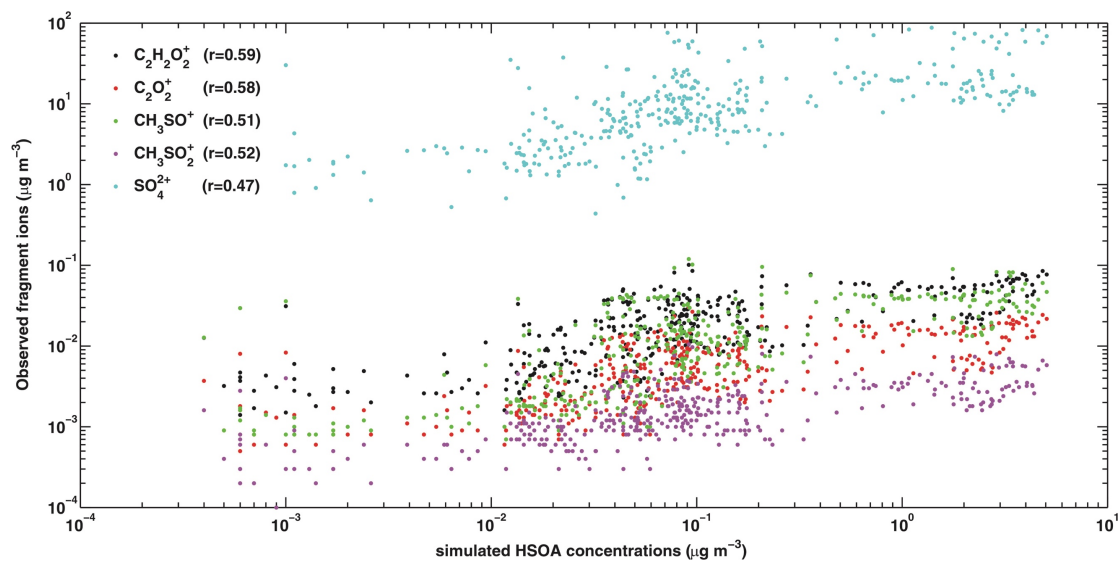


Figure 10 Scatter plot of the simulated HSOA concentration and the AMS measured  $SO_4^{2+}$ ,  $C_2H_2O_2^+$ ,  $C_2O_2^+$ ,  $CH_3SO^+$ , and  $CH_3SO_2^+$  concentrations from 9 to 26 January 2014 at IRSDE site in Beijing. All the correlations are statistically significant with  $p$ -value smaller than 0.01.