

**Interactive comment on “Formation and sink of glyoxal and methylglyoxal in a polluted subtropical environment: observation-based photochemical analysis and impact evaluation” by Zhenhao Ling et al.**

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Response to Reviewers

Reviewer #2

The paper investigates the importance of glyoxal (GLY) and methylglyoxal (MGLY) on SOA formation in the PRD region. The importance of GLY and MGLY on the SOA formation has been previously studied but this study investigated several different methods of modeling GLY and MGLY SOA, which provides additional information on how to model this important process. I have a few suggestions for the authors when they revise their paper:

Reply: Thank a lot for the reviewer’s positive comments and helpful suggestions. We have addressed all the comments/suggestions in the revised manuscript. Detailed responses to the individual specific comment/suggestion are as follows. All the revision is highlighted in the revised manuscript.

- 1. The gas-phase concentrations of OH/HO<sub>2</sub> are not constrained in the box model simulations. Instead, they are calculated using the box model. However, GLY and MGLY can be removed in the gas phase reactions with OH. Thus, it is necessary to evaluate the predicted OH/HO<sub>2</sub> concentrations to make sure the competing between gas/particle partitioning, which forms SOA, and the gas phase decay processes that reduce the SOA formation is correctly captured.*

Reply: The reviewer’s comment is highly appreciated. In this study, the OH and HO<sub>2</sub> radicals were simulated based on the measured mixing ratios of O<sub>3</sub>, NO<sub>x</sub>, CO, and NMHCs, together with meteorological parameters, as the direct measurement of OH and HO<sub>2</sub> radical was not available (Xue et al., 2014a, b). Furthermore, the photolysis rates adopted in the model were determined from the photon fluxes from the Tropospheric Ultraviolet and Visible Radiation (TUV-v5) model (Madronich and Flocke 1997) according to the sampling location and modeling period. Previous studies have demonstrated that the observation-based model coupled with Master Chemical Mechanism (MCM), such as the PBM-MCM model in the present study, could perform well in the simulation of O<sub>3</sub>, photochemical reactivities and

atmospheric radical chemistry (e.g., the budgets, variations of OH and HO<sub>2</sub> radicals and contributions from varied production and destruction pathways) in different environments/regions in China (Huang et al., 2020 and references therein; Ling et al., 2014; Liu et al., 2019; Wang et al., 2018; Xue et al., 2014a, b; Yang et al., 2018).

To better evaluate the model performance on the simulation of OH and HO<sub>2</sub> abundance and variations, we also compared our simulation results with the previous observations conducted in PRD and other regions in the world (Table 1 as seen below). In this study, the simulation on the diurnal variations of OH and HO<sub>2</sub> was performed well, with peak values at noon, consistent with those measured and simulated in PRD (Hofzumahaus et al., 2009 and related papers; Tan et al., 2019). The simulated mean mixing ratios of OH and HO<sub>2</sub> radicals from the model in the present study were  $\sim 1.6 \times 10^6$  molecule·cm<sup>-3</sup> and  $\sim 3 \times 10^7$  molecule·cm<sup>-3</sup>, which are comparable to the winter observations at Beijing, Tokyo, and New York (Kanaya et al., 2007; Ren et al., 2006; Ma et al., 2019), and lower than the measurement and simulation values in summer (e.g., July) or autumn (e.g., October to November) in the PRD region (Table S3 in the supplementary) (Hofzumahaus et al., 2009; Tan et al., 2019). Note that the variations of simulation results in the present study and those observation results in previous studies in PRD may be associated with differences in the levels of O<sub>3</sub> and its precursors, different photolysis rates, and to a lesser extent, meteorological conditions (Hofzumahaus et al., 2009). The higher OH and HO<sub>2</sub> mixing ratios were expected in summer and autumn than winter due to the stronger solar radiation and higher temperature, as well as the variations of O<sub>3</sub> and its precursors in different sites, though the measurement of OH/HO<sub>2</sub> radicals has been very challenging, and significant uncertainties still exist in the measurement values of the radicals (Hofzumahaus et al., 2009; Tan et al., 2019). Furthermore, the comparison between the simulation of a box model and observation results suggested that the higher observed mixing ratios of OH and HO<sub>2</sub> radicals were related to an unidentified source of OH at the backgarden site of PRD in summer of 2006, while the comparison between the observed OH/HO<sub>2</sub> variations and those calculated from the parameterization of HO<sub>x</sub> (HO<sub>x</sub> = OH + HO<sub>2</sub>) production and destruction indicated a missing OH source of 4-6 ppbv·h<sup>-1</sup> and an

unknown RO<sub>2</sub> loss at the Heshan site in autumn of 2014.

Overall, the above comparison suggested that the model simulation for the variations of OH and HO<sub>2</sub> radicals, and related atmospheric photochemical reactivities was appropriate at Heshan in this study.

Table 1 The mean measured OH and HO<sub>2</sub> concentrations in the previous studies and our model results (in molecule cm<sup>-3</sup>)

Location	season	OH (× 10 <sup>6</sup> )	HO <sub>2</sub> (× 10 <sup>8</sup> )	year	Reference
PRD, China	Summer	15	-	2006	(Hofzumahaus et al., 2009)
Shanghai, China		10.2	-	2013	(Nan et al., 2017)
north-western Greece		8	4.7	1997	(Creasey et al., 2001)
PRD, China	Autumn	4.5	3.0	2014	(Tan et al., 2019)
Tokyo, Japan	Winter	1.5	-	2004	(Kanaya et al., 2007)
New York, America		1.4	-	2004	(Ren et al., 2006)
Beijing, China		1.5	0.3	2017	(Ma et al., 2019)
PRD, China		1.6	0.3	2017	This study

To clarify the model performance on the simulation of OH and HO<sub>2</sub> abundance and variations, the above analysis and comparison have been added in the revised manuscript:

“In this study, the simulation on the diurnal variations of OH and HO<sub>2</sub> was performed well, with peak values at noon, consistent with those measured and simulated in PRD (Hofzumahaus et al., 2009 and related papers; Tan et al., 2019). The simulated mean mixing ratios of OH and HO<sub>2</sub> radicals from the model in the present study were  $\sim 1.6 \times 10^6$  molecule·cm<sup>-3</sup> and  $\sim 3 \times 10^7$  molecule·cm<sup>-3</sup>, which are comparable to the winter observations at Beijing, Tokyo, and New York (Kanaya et al., 2007; Ren et al., 2006; Ma et al., 2019), and lower than the measurement and simulation values in summer (e.g., July) or autumn (e.g., October to November) in the PRD region (Table S3 in the supplementary) (Hofzumahaus et al., 2009; Tan et al., 2019). Note that the variations of simulation results in the present study and those observation results in previous studies in PRD may be associated with differences in the levels of O<sub>3</sub> and its precursors, different photolysis rates, and to a lesser extent, meteorological conditions

(Hofzumahaus et al., 2009). The higher OH and HO<sub>2</sub> mixing ratios were expected in summer and autumn than winter due to the stronger solar radiation and higher temperature, as well as the variations of O<sub>3</sub> and its precursors in different sites, though the measurement of OH/HO<sub>2</sub> radicals has been very challenging, and significant uncertainties still exist in the measurement values of the radicals (Hofzumahaus et al., 2009; Tan et al., 2019). Furthermore, the comparison between the simulation of a box model and observation results suggested that the higher observed mixing ratios of OH and HO<sub>2</sub> radicals were related to an unidentified source of OH at the backgarden site of PRD in summer of 2006, while the comparison between the observed OH/HO<sub>2</sub> variations and those calculated from the parameterization of HO<sub>x</sub> (HO<sub>x</sub> = OH + HO<sub>2</sub>) production and destruction indicated a missing OH source of 4-6 ppbv·h<sup>-1</sup> and an unknown RO<sub>2</sub> loss at the Heshan site in autumn of 2014.”

For details, please refer to Lines 380-403, Page 14 in the revised manuscript and Table S3 in the supplementary.

- 2. The impact of O<sub>3</sub> on GLY and MGLY is not discussed. Looking at Figure 2, it is obvious that GLY and MGLY must decrease at night. GLY and MGLY can also react with O<sub>3</sub>. This is likely an import process that reduces GLY and MGLY at night, in addition to SOA formation from gas-to-particle partitioning and aqueous reactions. Since GLY and MGLY data are collected throughout the entire 24 hour period, it might be interesting to see how well the box model predicts GLY and MGLY at night with different SOA modeling approaches. The nighttime behavior of GLY and MGLY and their roles in SOA formation is not as clear as the daytime and should not be ignored in this study.*

Reply: Thanks for the reviewer’s comment. By investigating the relative contributions of different loss pathways of Gly and Mgly, it was found that during the daytime, the heterogeneous processes were the most important pathway for the destruction of Gly and Mgly (both with contributions of ~62%), followed by photolysis, OH reactions and dry deposition. We also examined the loss pathways of Gly and Mglys during nighttime, and only the heterogeneous processes make notable contribution to Gly and Mgly destruction, accounting for more than 90% of the total destruction (Table 2 as seen below), which was consistent with previous studies (Washenfelder et al., 2011; Gomez et al., 2015). The lower contributions of Gly and Mgly with radicals were mainly because of the low concentration of OH at night and their relatively lower

reactivities with NO<sub>3</sub> radical (Calvert et al., 2011; Mellouki et al., 2015).

Table 2. The relative contributions of different loss pathways of Gly and Mgly at nighttime

Loss pathways	Gly	Mgly
NO <sub>3</sub> ,OH-reaction, %	2.44	3.56
dry deposition, %	1.04	0.74
dilution, %	1.92	1.60
heterogeneous <sup>a</sup> , %		
Irreversible processes, %	57.9	55.9
Reversible processes, %	36.7	38.2

<sup>a</sup> Considered both irreversible and reversible parameterizations of the aerosol sinks (*i.e.*, scenario 4 and M2).

Furthermore, we agree with the reviewer that Gly and Mgly may be also removed by the reaction with O<sub>3</sub>, and incorporation of more possible reaction mechanisms in addition to oxidation of Gly and Mgly by NO<sub>3</sub> and OH radicals are reasonable. The previous study reported that kinetic data of O<sub>3</sub> reactions with Gly and Mgly are of negligible atmospheric importance, with the reaction rate constants of  $< 3$  and  $< 6 \times 10^{-21} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , respectively, which are 6 order of magnitude lower than the reaction rate constants with NO<sub>3</sub> (which  $> 1$  and  $> 2 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , respectively), and are 9 order of magnitude lower than the reaction rate constants with OH (which = 9 and  $13 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ ) (Mellouki et al., 2015). Due to the much lower reaction rates, we believe that the influence of O<sub>3</sub> on the removal of Gly and Mgly was negligible. Furthermore, there were few parameterizations for the reaction mechanism of Gly/Mgly with O<sub>3</sub> due to their low reaction rates with O<sub>3</sub>. Therefore, the present study did not include the pathway of O<sub>3</sub> oxidation on Gly and Mgly.

To explain the exclusion of the oxidation of Gly and Mgly by O<sub>3</sub>, and to clarify the contributions of different pathways to the removal of Gly and Mgly during nighttime, the following text has been added in the revised manuscript:

“It should be noted that the oxidation of Gly and Mgly by O<sub>3</sub> was not considered in

this study as the reaction rate constants of Gly and Mgly with O<sub>3</sub> are  $< 3$  and  $< 6 \times 10^{-21} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , respectively, which are 6 order of magnitude lower than the reaction rate constants with NO<sub>3</sub> (which  $> 1$  and  $> 2 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , respectively), and are 9 order of magnitude lower than the reaction rate constants with OH ( $9$  and  $13 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  for the reactions of Gly and Mgly with O<sub>3</sub>, respectively) (Mellouki et al., 2015). Therefore, we believe that the influence of O<sub>3</sub> on the removal of Gly and Mgly was negligible (Mellouki et al., 2015). Furthermore, there were few parameterizations for the reaction mechanism of Gly/Mgly with O<sub>3</sub> due to their low reaction rates with O<sub>3</sub>.

On the other hand, at nighttime, only the heterogenous processes made the main contribution to Gly and Mgly destruction, with contributions higher than 90% to the total destruction of Gly and Mgly at night (Table S9 in the supplementary), consistent with previous studies (Washenfelter et al., 2011; Gomez et al., 2015). The lower contributions of Gly and Mgly with radicals were mainly because of the low OH concentration at night and their relatively lower reactivities with NO<sub>3</sub> radical (e.g., the reaction rate constants of Gly/Mgly with NO<sub>3</sub> are  $\sim 1000$  times lower than those with OH radical) (Calvert et al., 2011; Mellouki et al., 2015).”

For details, please refer to Lines 544-562, Pages 19-20 in the revised manuscript and Table S9 in the supplementary.

3. *The other issue that I think should be addressed is the primary emissions of GLY and MGLY, since not all are produced secondarily. It seems that no emissions of primary GLY and MGLY are included in the box model simulations. The authors might want to discuss how this omission can impact their conclusions.*

Reply: We thank the reviewer’s valuable comment. Indeed, not all the Gly and Mgly in the atmosphere are produced secondarily. However, many previous studies have suggested that the dicarbonyls such as Gly and Mgly have limited primary sources except biomass burning and biofuel combustion (Grosjean et al., 2001; Zhang et al., 2016). The primary emissions of Gly and Mgly were much less significant than those secondarily from photochemical reactions (Lv et al., 2019). Fu et al. (2008) estimated

that the primary emissions only accounted for about 4% and 17% to the total emissions of Mgly and Gly, respectively.

To preliminarily estimate the contributions of primary and secondary sources to measured Gly and Mgly, a correlation-based source apportionment method suggested by previous studies was used, as described by equation 1 (Friedfeld et al., 2002; Yuan et al., 2013).

$$[\text{dicarbonyls}] = \beta_0 + \beta_1[\text{C}_2\text{H}_2] + \beta_2[\text{O}_3] \quad (1)$$

where  $\beta_0$ ,  $\beta_1$ , and  $\beta_2$  are the coefficients derived from the linear regression analysis. For every unit increase in  $\text{C}_2\text{H}_2$  concentration there is a  $\beta_1$  unit increase in dicarbonyls. Similarly, for every unit increase in  $\text{O}_3$  concentration there is a  $\beta_2$  unit increase in dicarbonyls.  $\beta_0$  can be considered the background carbonyls level (in units of ppbv). Relative contributions from primary emissions, secondary formation, and background dicarbonyl concentrations can be computed according to the tracer concentrations and corresponding  $\beta$ -values by the following equations:

$$P_{\text{primary}} = \frac{\beta_1[\text{C}_2\text{H}_2]i}{(\beta_0 + \beta_1[\text{C}_2\text{H}_2]i + \beta_2[\text{O}_3]i)} \times 100\% \quad (2)$$

$$P_{\text{secondary}} = \frac{\beta_2[\text{O}_3]i}{(\beta_0 + \beta_1[\text{C}_2\text{H}_2]i + \beta_2[\text{O}_3]i)} \times 100\% \quad (3)$$

$$P_{\text{background}} = \frac{\beta_0}{(\beta_0 + \beta_1[\text{C}_2\text{H}_2]i + \beta_2[\text{O}_3]i)} \times 100\% \quad (4)$$

Table 3 shows linear regression coefficients and relative source contributions of Gly and Mgly. It was found that the contributions from primary sources is significantly lower than those from secondary sources (96.14% and 96.44% for Gly and Mgly, respectively), confirming that Gly and Mgly in the present study were mostly related to secondary formation.

Table 3. Linear regression coefficients and relative contributions of primary, secondary, and background sources of Gly and Mgly.

	Linear regression coefficients			Source Contribution			
	$\beta_0$	$\beta_1$	$\beta_2$	Background	Primary	Secondary	R
Gly	0.001	0.066	0.042	0.40%	3.46%	96.14%	0.77
Mgly	0.002	0.108	0.081	0.05%	3.51%	96.44%	0.75

To highlight the potential significance of secondary formation on the abundance of Gly and Mgly, the following text was added:

“It has been well documented that Gly and Mgly have limited primary sources except biomass burning and biofuel combustion (Grosjean et al., 2001; Zhang et al., 2016). Furthermore, the primary emissions of Gly and Mgly were much less significant than those secondarily from photochemical reactions (Lv et al., 2019). Fu et al. (2008) estimated that primary emissions only accounted for about 4% and 17% to the total emissions of Mgly and Gly, respectively.”

For details, please refer to Lines 80-85, Page 3 in the revised manuscript.

Furthermore, the following text for the preliminary estimation of primary and secondary sources of Gly and Mgly was added in the revised manuscript:

“In this study, the simulated Gly and Mgly were secondarily formed from the oxidation of their VOC precursors. Therefore, before the comparison between the simulation and observation results, the contributions of primary and secondary sources to the measured Gly and Mgly were preliminarily estimated by a correlation-based source apportionment method suggested by previous studies (Friedfeld et al., 2002; Yuan et al., 2013). Table S5 in the supplementary shows linear regression coefficients and relative source contributions of Gly and Mgly. It was found that the contributions from primary sources (3.46 % and 3.51% for Gly and Mgly, respectively) were significantly lower than those from secondary sources (96.14% and 96.44%, respectively), confirming that observed Gly and Mgly in the present study were mostly related to secondary formation.”

For details, please refer to Lines 440-450, Page 16 in the revised manuscript and Table S5 in the supplementary.

4. *Modeling SOA formation from GLY and MGLY using the Master Chemical Mechanism has been discussed in a more complete regional air quality model that considers the transport and emissions of GLY and MGLY (Li et al. 2015). Another paper that discusses the importance of the GLY and MGLY on SOA formation is Ying et al 2015, which shows that including SOA from uptake of GLY/MGLY leads to significant improvement in predicated SOA in these southeast United States.*



*These references appear to be neglected by the authors.*

Reply: Thanks for the reviewer's suggestions. It has been revised accordingly in the revised manuscript.

“For example, Li et al (2015) constructed a Master Chemical Mechanism with an equilibrium partitioning module and coupled it in a Community Air Quality Model (CMAQ) to predict the regional concentrations of SOA from VOCs in the eastern United States (U.S). It was found that those SOA formed from Gly and Mgly were accounted for more than 35% of total SOA. Similarly, Ying et al. (2015) used a modified SAPRC-11 (S11) photochemical mechanism, considering the surface-controlled reactive uptake of Gly and Mgly, and incorporated the mechanism in the CMAQ model to simulate ambient SOA concentrations during summer in the eastern U.S. The results showed that the uptake of Gly and Mgly resulted in the significant improvement in predicted SOA concentration, and the aerosol surface uptake of isoprene-generated Gly, Mgly and epoxydiol accounted for more than 45% of total SOA.”

For details, please refer to Lines 68-78, Page 3 in the revised manuscript.

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