

Response to Reviewer #1

We gratefully thank you for your constructive comments and thorough review. Below are our point-by-point responses to your comments.

(Q=Question, A=Answer, C=Change in the revised manuscript)

General Comments:

Hu and coauthors describe a set of field experiments designed to investigate the gas/particle partitioning of glyoxal and methylglyoxal in Beijing as a function of season. Gas phase dicarbonyls were collected using DNPH-doped cartridges and particle phase dicarbonyls were collected using a filter assembly. Both reversible and irreversible uptake pathways are considered using supporting measurement data and irreversible pathways are found to be dominant for both dicarbonyls in all seasons, although reversible uptake (self-reaction, oligomerization) becomes more relevant in the winter. As expected, the field data demonstrate particle phase concentrations that are orders of magnitude higher than those expected based solely on absorptive partitioning theory. This study, however, is particularly useful in demonstrating the estimated dominance of the irreversible pathway in all seasons, and in presenting real-world SOA contributions for these dicarbonyls at this urban location (approximately 25% of Beijing SOA is assigned to glyoxal/methylglyoxal uptake processes). Overall, I find the manuscript to be well written with comprehensive consideration of the relative importance of reversible and irreversible uptake pathways and their impact on SOA production. These data should be useful for optimizing dicarbonyl uptake in SOA modeling efforts.

A: We highly appreciate your comments and suggestions. The questions you mentioned are answered as follows.

Major Comments:

Q1: Line 86: How were positive artefacts from direct deposition of gas phase glyoxal/methylglyoxal on the filter surfaces accounted for? This could bias the partitioning result from Equations 1 and 3 and should be discussed in the text.

A1: Thanks for your suggestion. Collecting particulate glyoxal/methylglyoxal by quartz filter without denuders might lead to positive artifacts as gaseous dicarbonyls could be adsorbed to the filter (Hart and Pankow, 1994; Mader and Pankow, 2001;

Liggio, 2004). In field observations, Odabasi and Seyfioglu (2005) revealed that about 36% of the measured particulate formaldehyde was caused by adsorbed formaldehyde on quartz filters, and Shen et al. (2018) found that the fractions of gaseous glyoxal/methylglyoxal in particulate samples were usually lower than 20%. To evaluate the possible adsorption artifacts, throughout our field observations, we placed a backup quartz filter after the particle sampling quartz filter using an independent filter holder. The first filters would collect the particles and adsorbed gaseous dicarbonyls, while the second filter would only collect gaseous carbonyls. And the ratio of measured dicarbonyls in second filter to that in the first were lower than 20%. The particulate concentrations of dicarbonyls used in this study were already corrected by the possible adsorption artifacts. And the partitioning results from Equations 1 and 3 were all calculated by calibrated concentrations of dicarbonyls and the artifacts caused by filter adsorption would not change our conclusions. We have expanded the methods of field sampling in the revised manuscript.

C1: Lines 105-110 in Sect. 2.1:

To estimate the positive artifacts by adsorption of gas-phase dicarbonyls onto the filter (Hart and Pankow, 1994; Mader and Pankow, 2001; Liggio, 2004; Odabasi and Seyfioglu, 2005), throughout our previous field observations, we placed a backup quartz filter after the particle sampling quartz filter using an independent filter holder. The sampling filters would collect the particles and adsorbed gaseous dicarbonyls, while the backup filter would only collect gaseous dicarbonyls. And the ratio of measured dicarbonyls in second filter to that in the first were lower than 20%, which was equal to the previous study (Shen et al., 2018). And the particulate concentrations of dicarbonyls used in this study were already corrected by the possible adsorption artifacts.

Q2: I think the manuscript would benefit from an expanded discussion of assumptions used to calculate the reversible and irreversible pathways. Calculations of the irreversible pathway involve the particle phase and gas phase monomer dicarbonyl concentrations to be known and these data are derived from analysis of the extracts. But the particle phase monomer extract concentration will also include the contributions from the reversibly formed products present in the extract. Expanding the

discussion of deriving the c_p term in the formulas and what exactly it represents would be useful for readers.

A2: Thanks for your suggestion. The c_p term in the formulas referred to the measured particulate carbonyls which was derived from the analysis of the extracts and it included the dissolved dicarbonyls monomers and their reversibly formed products (the reversible formed products could easily revert to their original monomer form during extraction and derivation). The concentrations of dissolved dicarbonyl monomers were estimated using theoretical Henry's law coefficients, which are used to determine the physical solubility of carbonyls (e.g., $K_H=5 \text{ M}\cdot\text{atm}^{-1}$ for glyoxal) (Schweitzer et al., 1998). The results were negligible compared to the concentrations of carbonyls in hydrate and oligomer forms. In section 3.2, we have calculated the product distribution of reversible reactions based on reversible reaction mechanisms, which could help to understand what exactly the c_p term represented. The c_p term included hydrates with proportion of 10%-50%, oligomers with proportion of 50%-90%, and monomers with proportion of ~1%. We have expanded the discussion of deriving c_p term in the formulas in the revised manuscript.

C2: Lines 170-172 in Sect. 2.3:

$C_p (\mu\text{g}\cdot\text{m}^{-3})$ is the concentrations of dicarbonyls in the particle phase, which is derived from the analysis of extracts, including monomers and their reversibly formed products (the product distribution is discussed in Section 3.2).

Minor and Technical Comments:

Q3: Figure 2c: Change the color of one of the grey traces

A3: We have changed the color of the traces in Figure 2c as follows.

C3:

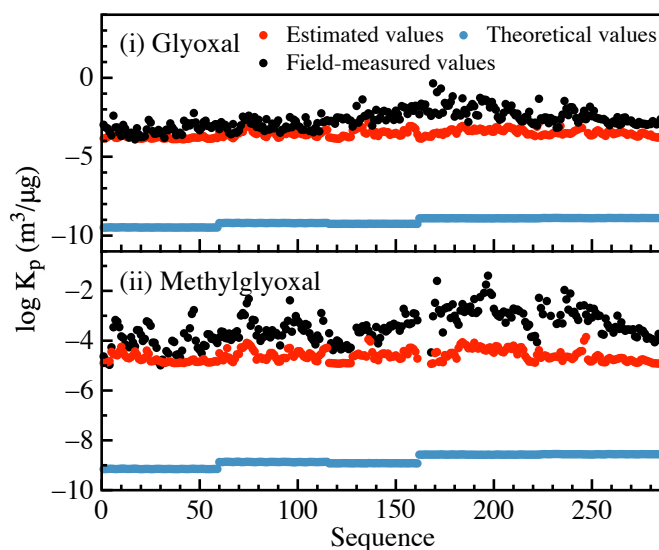


Figure 2c: The gas-particle partitioning coefficients for (i) glyoxal and (ii) methylglyoxal. The black, red, and blue circles refer to field-measured values, estimated values by the proposed mechanism, and theoretical values calculated by Pankow's absorptive model, respectively.

Q4: Figure 3: Define SNA in caption

A4: We have defined SNA in caption in Figure 3.

Q5: Figures throughout: Colorscales should go from lower values in blue to higher values in red to be consistent with general uses in the literature. It is counterintuitive for the reader for these to be the other way around. Also the axis scale in the colorscale legends has numbers increasing from right to left which is also confusing.

A5: Thanks for your suggestion. We have revised the color scales in all figures, which now consistently go from lower values in blue and to higher values in red. And we also revised the axis scale in the legends of color scale, the numbers of which now increase from bottom to top. The revised figures are presented as follows (take Figure 4 for example):

C5:

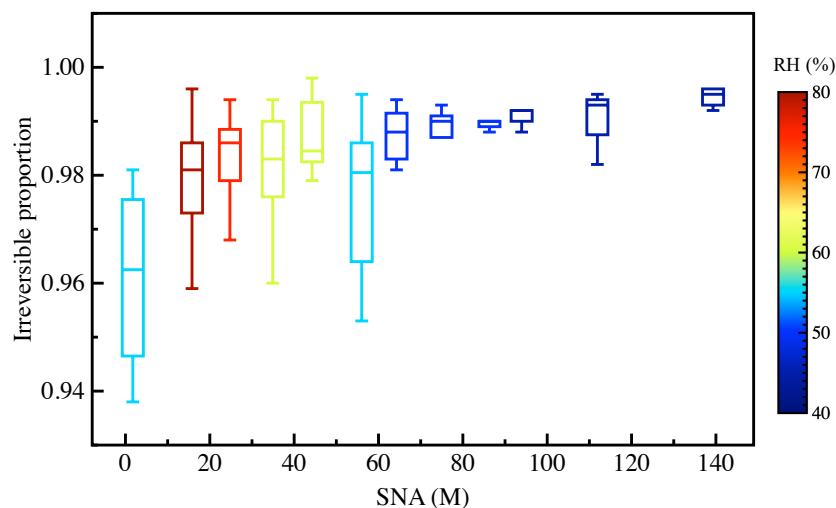


Figure 4: Correlation between the proportion of the irreversible pathway in gas-particle partitioning process for dicarbonyls and aqueous sulfate, nitrate, and ammonia (SNA) concentration in ambient aerosols under different relative humidity conditions.

Q6: Abstract, change last line to present tense. eg “To our knowledge, this article is the first to...”

A6: Thanks for your suggestion. We have changed last line to present tense.

C6: Lines 22-25 in Abstract:

To our knowledge, this study is the first to systemically examine both reversible and irreversible pathways in the ambient atmosphere, strives to narrow the gap between model simulations and field-measured gas-particle partitioning coefficients, and reveals the importance of gas-particle processes for dicarbonyls in SOA formation.

Q7: Line 33: reorder the two references

A7: Thanks for your suggestion. We have reordered the two references.

Q8: Line 36: consider rephrasing to “lost in the gas phase by photolysis, oxidation by OH radicals, and dry deposition” as OH oxidation is a photochemical reaction

A8: Thanks for your suggestion. We have rephrased the sentences as follows.

C8: Lines 40-41 in Sect.1:

Considering the atmospheric sink, glyoxal and methylglyoxal can be lost in the gas phase by self-photolysis, oxidation by active radicals (like OH radicals, NO₃ radicals) and wet/dry deposition.

Q9: Line 40: “Although they have relatively high...”; Line 90: “common”; Line 94: “time resolution”; Line 167: “soluble”; Line 170: “close to”; Line 180: “real atmosphere”; Table 4: “Particulate matter”; Line 270: “close to”

A9: Thanks for your suggestion. We have revised that.

Q10: Line 41: How relevant is adsorption to surfaces vs absorption into the bulk particle phase material? Worth discussing here

A10: Thanks for your suggestion. We have discussed the relevance of adsorption to surfaces vs adsorption into the bulk particle phase material as follows.

C10: Lines 47-55 in Sect.1:

The surface-adsorbed dicarbonyls could alter the properties of the particle’s surfaces and the organic surface films could act as a kinetic barrier to gas-aerosol mass transport and thereby influence particle equilibration and water/gas uptake (Donaldson and Vaida, 2006). Upon physical adsorption, besides desorption or reaction at the surface, dicarbonyls could undergo solvation and incorporation into the bulk liquid, and then they could go through diffusion and chemical reactions in the bulk phase. The product may return into surfaces and gas phase, or stay in the bulk phase (Paul et al., 2011). Moreover, chemical reactions occurred at the surface or in the bulk phase could in turn accelerate the physical adsorption and greatly contribute to the formation and growth of atmospheric particulate matter. Whereas, as it is difficult to distinguish the surface reactions and bulk reactions in field observations, we regard both of them as particle-phase reactions in this study.

Q11: Line 206: Worth noting that the observed RH dependence for the reversible pathway is consistent with the Healy et al 2009 chamber study reference

A11: Thanks for your suggestion. We have added the reference as follows.

C11: Lines 290-293 in Sect. 3.2:

The results exhibited a similar pattern to a previous study, in which the partitioning of glyoxal and methylglyoxal gradually increased as RH increased to 40%, peaked sharply around 50%, and subsequently decreased as RH increased towards 80% (Healy et al., 2009).

Q12: Line 284: Define SNA

A12: We have defined SNA in the revised manuscript.

Q13: Line 285: rephrase

A13: Thanks for your suggestion. We have rephrased the sentences as follows.

C13: Lines 382-386 in Sect. 3.3.2:

The total particulate concentration of glyoxal and methylglyoxal via irreversible pathway varied from several to more than 100 nanograms per microgram PM_{2.5} (ng/μg PM_{2.5}), and it was strongly dependent on RH, as shown in Fig. 3c, which generally decreased with increasing RH. Concentrated inorganic solutions and relatively higher ionic strength in aerosol water under low RH conditions (Fig. S8) could jointly contribute to the hydration of dicarbonyls, the products of which could easily participate into the following irreversible radical reactions via H-abstraction.

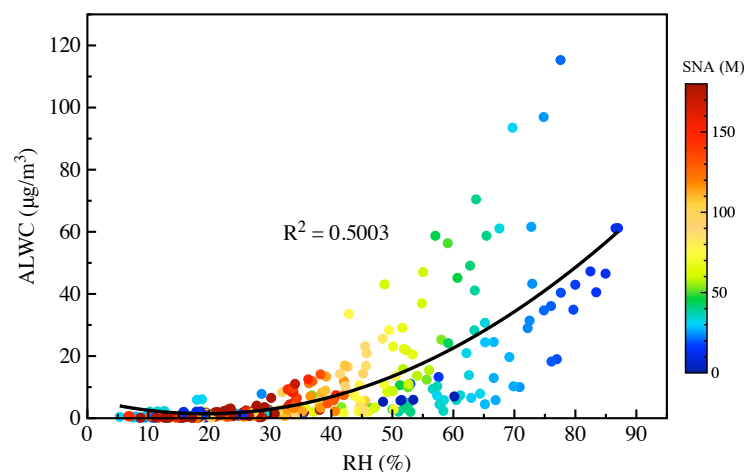


Figure S8: The dependence of aerosol liquid water contents (ALWC) on the relative humidity (RH) with different SNA (sulfate, nitrate and ammonia) concentrations.

Q14: Line 339: rephrase

A14: Thanks for your suggestion. We have rephrased the sentences as follows.

C14: Lines 424-425 in Sect. 3.4:

Comprehensively considering the contribution of both reversible pathways and irreversible pathways occurred in gas-particle partitioning processes could benefit the ambient dicarbonyls simulations.

Reference:

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- Odabasi, M. and Seyfioglu, R.: Phase partitioning of atmospheric formaldehyde in a suburban atmosphere, *Atmospheric Environment*, 39, 5149-5156, 10.1016/j.atmosenv.2005.05.006, 2005.
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- Shen, H., Chen, Z., Li, H., Qian, X., Qin, X., and Shi, W.: Gas-Particle Partitioning of Carbonyl Compounds in the Ambient Atmosphere, *Environmental Science & Technology*, 52, 10997-11006, 10.1021/acs.est.8b01882, 2018.