

Response to Reviewer #2

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:

Jingcheng Hu and co-authors have measured the gas-particle partitioning of dicarbonyl compounds, especially glycol and methylglyoxal, at field sites in China. This is a highly relevant topic for the readership of ACP. As far as I can tell (being a computational chemist, not an experimentalist), the study is well carried out, and the manuscript is well written. I can thus recommend publication subject to some fairly minor revisions.

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

Major Comments:

Q1: The authors spend a lot of time pointing out that the measured partitioning is much higher than what they call the “theoretical” values - the latter seem to correspond to values obtained for the partitioning coefficient (or Henry’s law constant) of pure molecular glyoxal and methylglyoxal. However, as evident from their own introduction section, it is already very well known that the partitioning of these compounds is driven mainly by various reactions. For example, hydration alone is well-known to increase the Henry’s law coefficient of glyoxal by about five orders of magnitude (as discussed e.g. in Ip et al 2009, <https://doi.org/10.1029/2008GL036212>, or Kampf et al 2013 cited in the manuscript). The authors contribution to separating reversible and irreversible pathways is substantial and valuable - but just reporting that partitioning is much stronger than the “theoretical” values is not really novel (or even that interesting), and this aspect of the abstract and discussion should be toned down. For example, the speculation about “misidentification” or “discrepancies” around lines 175-180 is not really warranted: we already know mechanisms which can easily explain at least most of the observed deviations from the “theoretical” pure-compound values.

A1: Thanks for your suggestion. We have toned down the discussion of discrepancy between the field-measured partitioning coefficients and the theoretical ones in Section 3.1.2 in our revised manuscripts, which had been fully discussed in previous studies (Ip

et al., 2009; Kampf et al., 2013). And we would focus on and expand the discussions of reversible and irreversible pathways, which is relatively substantial and valuable.

Q2: Concerning the saturation vapour pressures discussed around line 190: are there any estimates of the relative saturation vapour pressures of the reversible vs irreversible products? Both are of course much lower than the saturation vapour pressures of the parent dicarbonyls (this is quite well-known and obvious), but how do the two product sets compare with each other? This would be a very interesting parameter to know in terms of evaluating the atmospheric impact of the "reversible vs irreversible" competition.

A2: Thanks for your suggestion. We have expanded the discussion of saturation vapor pressures of the two product sets in our revised manuscript as follows.

C2: Lines 257-262 in Section 3.1.2:

Take glyoxal for example, the effective saturation vapor pressures of the product set in reversible pathways are $\sim 10^{-5}$ Torr in the real atmosphere (Shen et al., 2018). And the products of the irreversible pathways had much lower vapor pressure values than those of reversible pathways, for example, the vapor pressure of oxalic acids and ammonium oxalates are $\sim 10^{-5}$ Torr (Saxena and Hildemann, 1996) and 5.18×10^{-8} Torr (EPA, 2011), respectively, and those of glyoxal trimer dihydrates are $\sim 10^{-11}$ Torr at 20 °C (SPARC, 2003), indicating the irreversible pathways make larger contributions to the underestimation of partitioning processes of dicarbonyls.

Q3: Line 208: "strong and positive dependence on particle acidity (pH)". Please be clear here: did the concentration increase with acidity (i.e. with decreasing pH), or did it increase with pH? These are opposite things.

A3: Thanks for your suggestion. In this study, the particulate concentration of dicarbonyls via reversible pathways had a strong dependence on particle acidity under high RH conditions, which increased with increasing pH values (decreasing aerosol acidity) and reached highest when pH was close to 4. Whereas, as the other reviewers suggested, there is no gas-phase measurements to constrain the partitioning of the semi-volatile gases, which can lead to large deviations in the calculated pH by the thermodynamic model ISORROPIA-II from real world observations. Thus, we would not focus on the pH dependence of gas-particle partitioning processes in our revised manuscript.

Reference

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