

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2022-86

Anonymous Referee #3

Referee comment on "Reversible and irreversible gas–particle partitioning of dicarbonyl compounds observed in the real atmosphere" by Jingcheng Hu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-86-RC3>, 2022

Hu et al. present observations of glyoxal and methylglyoxal collected during four seasons in Beijing. The observations included gas-phase and aerosol-phase dicarbonyls. With these observations, the authors investigate the partitioning / reversible and irreversible uptake of the dicarbonyls. They find that theoretical values underpredict the real world observations. Further, they find that irreversible uptake dominates in all seasons, though reversible uptake becomes more important in winter time. This study provides an interesting data set and way to investigate this long standing question of the uptake of dicarbonyls to aerosol as other studies normally just have gas-phase measurements and use a steady state model to derive the first order uptake of glyoxal to aerosol.

Though this paper is of interest to the ACP community, there are some aspects of the paper the authors can improve upon to improve the overall study. With the clarifications suggested below, the manuscript would be acceptable for ACP.

- 1) One of the major areas that would benefit with expanded text would be the methods. Currently, there is not enough information in order to understand the measurements and discussions from the authors. The following discussions in methods should be added to improve the understanding of the paper:
 - 1a) As the authors are collecting the gas-phase dicarbonyls onto cartridges, a discussion on the percent collected / percent lost both during the collection and extraction / analysis period.
 - 1b) Similarly, the authors should have a discussion about the percent collected / percent lost for the dicarbonyl aerosol on filters.
 - 1c) Another reviewer commented, and I agree, a discussion about potential artifacts for both methods, but especially the aerosol filter collection, needs to be included. This includes if there was a cyclone for size selection, is there a denuder to prevent gas-phase from being collected onto the filters, how long the filters were collected, potential lost of dicarbonyls from the filters during sampling or preparation, and potential side reactions on the filters that may have led to biases.
 - 1d) Besides how much material is recovered for sampling, how well were these two dicarbonyls identified? E.g., as it is expected that there are other dicarbonyls, how well

were the peaks separated for glyoxal and methylglyoxal (an example chromatogram in the SI would be beneficial)?

1e) The authors state the assumption that all dicarbonyls that have done reversible partitioning to the aerosol-phase are extracted as the parent compound. A discussion showing this to be true either in the methods or in the results would be beneficial (e.g., if possible, having the reversible products on a filter, extract, and see if they come out as glyoxal/methylglyoxal in the chromatogram).

1f) The irreversible uptake calculation (page 9, line 252 - page 10, line 268) should be moved to the methods.

1g) Were blanks collected? What is the LOD for both methods?

1h) What is the uncertainty associated with the assumptions made to calculate K_p ? E.g., there would be high uncertainty in activity coefficient, vapor pressure, and potentially the absorbing fraction of the total particulate matter, depending on how well the methods measured total OA.

2) As the authors state different comparisons for the values they observed / calculated, it would be beneficial to either in their current tables or in a new table compare their results with literature.

3) I agree with the other reviewers that the discussion of theory (Section 3.1.2) does not add much to the paper as this is generally already known and would advise to either reduce this discussion or potentially remove it for more room to expand upon the reversible, irreversible, and methods.

4) It is currently unclear how the authors are separating irreversible and reversible. This is especially important in the partitioning calculations, as how much could the irreversible uptake be influencing the calculated value? Further, as the reversible was 10% or less the process the dicarbonyls undergone, is that within the associated uncertainty in the calculations, indicating potentially minimal reversible lost?

5) It is currently unclear how the authors derived the values in Fig. 2 (reversible pathway with units of ng/ug). If this is from one of the equations, please state and that will help better understand where the data from this figure originated from. If something else, please describe.

6) Another concern with Fig. 2 is the fact the authors are showing trends vs pH. As they are calculating their pH from only aerosol-phase measurements, there is large inherent uncertainty in the pH values as there is no gas-phase measurements to constrain the partitioning of the semi-volatile gases (NH_3 , HNO_3 , or HCl), which can lead to large deviations in the calculated pH from real world observations. I strongly advised the authors to not use the pH as it does not add much to the results.

7) I'm assuming the values listed in Table S2 are for bulk-phase reactions instead of aerosol-phase reactions. Recent studies have shown that these bulk-phase reactions may

not represent the aerosol-phase reaction rates due to the differences in the ionic strength. Therefore, for lines 210 - 222 and Fig. 2b, I would recommend the authors to be careful with those numbers in being the "definitive" product (also correct product to product in 2b) distribution to the potential product distribution with uncertainty due to bulk vs aerosol phase.

8) Lines 276 - 279: It's currently unclear how the authors are drawing the conclusion that methylglyoxal is exhibiting unexpected salting-in effects if they are using Eq. 4 - 7 to calculate the uptake coefficient. As these equations don't include the aerosol composition or ionic strength, further clarification on this conclusion would help this statement.

Minor

1) Since ionic strength is being calculated with the aerosol liquid water, it may be useful to look at how these parameters relate to ionic strength.

2) For Fig. 1, it is currently hard to following what is happening with the particulate-phase dicarbonyls. I would recommend including a thin-line connecting the points to better see the data and potential trends.

3) Line 287, it should be Fig. S8 instead of S7.

4) For Fig. S7, it is unclear what sequence number (x-axis) and what the grey shaded area are for.

5) For table 1, it would be useful to include the dates of the measurements.

6) For table 2, it is unclear how "theory" Henry's law constant is calculated compared to the "field" values.