Response to Reviewer #3

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

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

General Comments:

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 paritioning/reverisible 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.

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

Major Comments:

Q1: 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:

A1: Thanks for your suggestions and we have expanded the discussion of methods in our revised manuscript. The questions or suggestions you mentioned about the methods are answered as follows.

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.

1a): Thanks for your suggestion. Additional field-sampling were launched to estimate the sampling efficiency during the collection of gas-phase dicarbonyls. Two blank DNPH cartridges were connected in tandem to sample the gas-phase dicarbonyls and the sampling conditions were similar to the field observations. Sampling efficiency (SE) were the ratio of dicarbonyl concentrations in the first cartridge to the total concentrations in the two cartridges. And the results were more than 95% for both glyoxal and methylglyoxal, which were equal to the official sampling efficiency provided by Waters Corporation, which is the authoritative corporation to produce DNPH cartridges.

Recovery tests were also conducted using two methods, that was adding standard solutions and repeated extraction. We added additional mixed standard solutions at three spiked levels of 0.025, 0.25 and 2.5μg (namely 50 μL of 0.5 $\mu g \cdot mL^{-1}$, 5 $\mu g \cdot mL^{-1}$ and 50 $\mu g \cdot mL^{-1}$ analytical standards) into the blank DNPH cartridges to determine the carbonyl lost during the extraction and analysis. Then the cartridges were extracted in the same way as the ambient samples. Each group were set with five parallel. The recoveries ranged from 88% to 96% for gas-phase method. Moreover, we also estimated the recovery efficiency by repeated extraction and the recoveries were the ratios of dicarbonyl concentrations in the first extraction to the total concentrations in the two extractions. The results ranged from 92.8% to 99.9%.

1b) Similarly, the authors should have a discussion about the percent collected / percent lost for the dicarbonyl aerosol on filters.

1b): Thanks for your suggestion. Additional field-sampling were also launched to estimate the sampling efficiency during the collection of particle phase of dicarbonyls. We placed a backup Teflon filter after the particle sampling Teflon filter using an independent filter holder to estimate the particle collection efficiency. Both Teflon filters were weighed by a semimicro balance (Sartorius, Germany) to obtain the mass concentration of collected particles. The mass concentrations of particles collected on the backup filters were closed to zero, indicating that the sampling efficiency of particle were more than 99%.

Similar to gas-phase methods, recovery tests were also conducted using two methods. We adding additional mixed standard solutions at three spiked levels of 0.025, 0.25 and 2.5μg into the blank quartz filters to determine the carbonyl lost during the extraction and analysis. Then the filters were extracted in the same way as the ambient samples. Each group were set with five parallel. The recoveries ranged from 85% to 96% for particle-phase method. Moreover, we also estimated the recovery efficiency by repeated extraction and the recoveries ranged from 90% to 99.9%.

1a), 1b): Lines 147-162 in Sect. 2.3:

Additional field-sampling were launched to estimate the sampling efficiency during the collection. Two blank DNPH cartridges were connected in tandem to assess the sampling efficiency of gas-phase carbonyls. The sampling efficiency of the cartridges were the ratios of dicarbonyl concentrations in the first cartridge to the total concentrations in the two cartridges and the results were more than 95% for both glyoxal and methylglyoxal. Similarly, a backup Teflon filter were placed after the particle sampling Teflon filter using an independent filter holder to estimate the particle collection efficiency. Both Teflon filters were weighed by a semimicro balance (Sartorius, Germany) to obtain the mass concentration of collected particles. The mass concentrations of particles collected on the backup filters were closed to zero, indicating that the sampling efficiency of particle were more than 99%.

Moreover, recovery tests were also conducted using two methods - adding standard solution and repeated extraction. We added the standard solution at three spiked levels of 0.025, 0.25 and 2.5 μg (namely 50 μL of 0.5 μg·mL-1, 5 μg·mL-1 and 50 μg·mL-1 analytical standards) into blank DNPH cartridges and blank quartz filters to determine the carbonyl lost during the extraction and analysis. And then the cartridges and filters were extracted in the same way as the ambient samples. Each group were set with five parallel. The recoveries were ranged from 88% to 96% for gas-phase method and ranged from 85% to 96% for particle-phase method. Moreover, we also estimated the recovery efficiencies by repeated extraction and the recoveries were the ratios of dicarbonyl concentrations in the first extraction to the total concentrations in the two extractions. The results ranged from 92.8% to 99.9% for gas-phase method and ranged from 90% to 99.9% for particle-phase method.

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.

1c): Thanks for your suggestions. We have expanded the discussion about potential artifacts for both methods. Following measurements were conducted during the sample collection, pretreatment and analysis to ensure the accuracy of results: (1) Before sampling, flow calibration and airtightness tests of sampling devices were conducted, and flow difference were less than 10%; (2) After sampling, the gas-phase samples were resealed by its end cap and plug, and stored in the provided pouch under cool environment (<4°C), the particle-phase samples were stored in the sealed boxes wrapped by pre-baked aluminum foils under freezing environment (<-18°C), both gas-phase and particle-phase samples were extracted and analyzed within a week; (3) The extraction processes were conducted in fume hood with glassware, which was rinsed with acetonitrile for at least three times; (4) A calibration run was performed each day to determine the response factor of the detector and recalibration was performed if the relative deviation of the RF was beyond 5%.

As for aerosol filter collection, we used a four-channel ambient particles sampler (TH-16A, Wuhan Tianhong) with $PM_{2.5}$ cutters (D_{a50}=2.5 ± 0.2 μm, σ_g=1.2 ± 0.1) for size selection. The filters were pre-baked at 550 °C in muffle furnace (Meicheng Corporation) for 6 h to remove impurities before sampling and were continuously collected every 11.5-12 h daily. During the sampling of particle-phase dicarbonyls, we didn't use denuders and the lack of denuders may lead to positive artifacts by adsorption of gas-phase dicarbonyls on the quartz filters. To evaluate and eliminate the adsorption artifacts, we followed the same method described in the artifact experiments by (Shen et al., 2018), which placed a backup quartz filter after the sampling filter using an independent filter holder. During the sampling, the sampling filters would collect the particles and adsorbed gaseous dicarbonyls, while the backup filters would only collect gaseous dicarbonyls. And the ratio of measured dicarbonyls in second filters to that in the first were lower than 20%, which was equal to the previous study (Shen et al., 2018). Particulate concentration of dicarbonyls used in this study were all corrected by the adsorption artifacts.

As for gas-phase dicarbonyls, besides environmental contamination, ozone in urban air could degrade the hydrazone derivatives and we placed an ozone scrubber cartridge (Waters Corporation) on the inlet of the DNPH cartridge. Moreover, the elution flow could affect the extraction efficiency, which should be less than 3 mL/min.

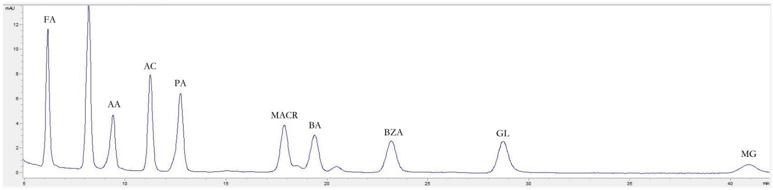
We have fully discussed the potential artifacts for both methods in Section 2 Materials and Method in our revised manuscript.

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 beneificial)?

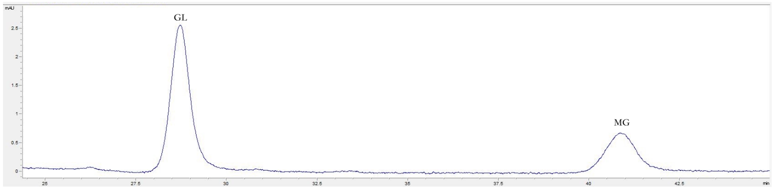
1d): Thanks for your suggestion. We presented an example chromatogram in SI and the retention time for glyoxal and methylglyoxal were 29 min and 41 min, respectively. The peaks for glyoxal and methylglyoxal were separated effectively with each other. And the peaks for glyoxal and methylglyoxal in extraction of sampling filters were corresponding to those in standard solution.

1d):

(a) Chromatogram for standard solution of ten carbonyls



(b) Chromatogram for standard solution of glyoxal and methylglyoxal



(c) Chromatogram for extraction of sampling filters

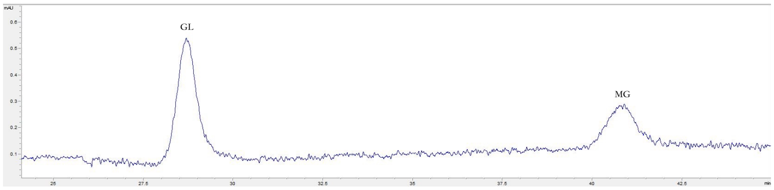


Figure S2: The chromatogram for the measured carbonyls. (a) chromatogram for standard solutions of ten measured carbonyls; (b) specific chromatogram for standard solutions of glyoxal and methylglyoxal; (c) chromatogram for extraction of sampling filters (FA: formaldehyde; AA: acetaldehyde; AC: acetone; PA: propionaldehyde; MACR: methacrolein; BA: butyraldehyde; MVK: methyl vinyl ketone; BZA: benzaldehyde; GL: glyoxal; MG: methylglyoxal).

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 chromatagram).

1e): Thanks for your suggestion. By adding excess derivatization agent (like 2,4-dinitrophenylhydrazone in this study), dicarbonyls as well as their reversibly formed hydrates and oligomers are efficiently transformed into dicarbonyl-bis-2,4-dinitrophenylhydrazone, which was quantified by means of analysis techniques (Kampf et al., 2013). Moreover, Healy et al.(2008) have confirmed that derivatization agent was found to efficiently dissolve a trimeric glyoxal standard and convert the resulting monomers to oxime derivatives, and oligomers were not detected in the extracts of filter samples by GC-MS analysis, indicating the use of excess derivatization agent could convert the hydrates and oligomers back to the monomeric species by removing dicarbonyl monomers from the extract as soon as they are formed. We have discussed it in Section 3.2 (3.2 Reversible pathways) in our revised manuscript. And we prepare to have the reversible products on a filter or extracts to provide a further proof in our future study.

1e): Lines 271-277 in Sect. 3.2:

By adding excess derivatization agent (like 2,4-dinitrophenylhydrazone in this study), dicarbonyls as well as their reversibly formed products are efficiently transformed into dicarbonyl-bis-2,4-dinitrophenylhydrazone, which are quantified as monomers by means of analysis techniques (Kampf et al., 2013). Moreover, Healy et al.(2008) have confirmed that derivatization agent was found to efficiently dissolve a trimeric glyoxal standard and convert the resulting monomers to oxime derivatives, and oligomers could not be detected in the extracts of filter samples by GC-MS analysis, also indicating the use of excess derivatization agent could efficiently convert the hydrates and oligomers back to the monomeric species by removing dicarbonyl monomers from the extract as soon as they are formed.

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

1f): We have moved the irreversible uptake calculation to the methods.

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

1g): We have collected the blanks in both gas-phase samples and particle-phase samples. The blank gas-phase samples (blank DNPH cartridge samples) were collected every 3 days by placing it near the gas inlet for the same duration without artificial pumping. And the blank particle-phase samples (blank quartz filters) also were collected every 3 days by placing it on the $PM_{2.5}$ inlet with flow rate of 0 L/min. The data used in this study were all calibrated by blanks.

The LOD are approximately 1 ng/m^3 for particle-phase samples and ~50 pptv for gas-phase samples.

1g): Lines 139-146 in Sect. 2.3:

Blank samples were collected every three days and then were stored and extracted by the same procedure as that for ambient samples. The blank gas-phase samples were collected by placing blank DNPH cartridges near the gas inlet for the same duration without artificial pumping. And the blank particle-phase samples were collected by placing blank quartz filters on the $PM_{2.5}$ inlet with flow rate of 0 L/min. All data used in this study were all calibrated by blanks.

The limit of detection (LOD) of two methods was 50 pptv for gaseous carbonyls and 1 $ng \cdot m^{-3}$ for particulate carbonyls, which is similar to our previous literature (Shen et al., 2018). Sample amount to limit of detection ratios were significantly higher than 1.0 for both gas- and particle-phase samples, indicating that the sensitivity of the methods was sufficient to analyze the samples.

1h) What is the uncertainty associated with the assumptions made to calculate Kp? 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.

1h): Thanks for your suggestion and we have added the discussion of uncertainties in K_p^t calculations in our revised Supporting Information as follows:

1h): Lines 13-31 in Supporting Information:

According to Eq.2, there would be uncertainty in temperature (T), activity coefficient (ζ), vapor pressure(p_L^0), absorbing fraction of the total particulate matter (fom), and molecular weight of the organic phase (MWOM) to calculate the theoretical partitioning coefficients (K_p^t). The K_p^t values could increase with increasing temperature T, which ranged from 265.53 K to 310.75 K in our observations. We calculate the K_p^t at the two extreme temperature and the ratios $K_{p,\,310.75K}^t/K_{p,\,265.53K}^t$ are always lower than 3 for both glyoxal and methylglyoxal. Aerosol phase activity coefficients ζ are a function of the aerosol composition (Jang et al., 1997; Seinfeld et al., 2001) but are thought to modify K_p^t by less than one order of magnitude (Bowman and Melton, 2004). And fom was little changed during our observations and was usually within ~0.3-0.6 in urban Beijing (Huang et al., 2014; Ma et al., 2022). As for MW_{OM}, previous laboratory experiments have shown that the molecular weight of individual constituents in isoprene SOA and 1,3,5-TMB SOA ranges from 100 to 1000 and that the average molecular weight increases with aerosol age due to oligomerization (Kalberer and M., 2004; Dommen et al., 2006). We used a MWOM value of 200 g·mol-1, which is used in previous work (Barsanti and Pankow, 2004; Williams et al., 2010; Shen et al., 2018) and increasing MWOM even to 500 g·mol-1 would only reduce K_p^t by a factor of 4. Moreover, we calculated the vapor pressure by the extended aerosol inorganic model (E-AIM, http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php) (Clegg et al., 1998), the results of which were close to those of other methods, such as the SPARC online calculator (Version 3.1) (Hilal et al., 1995; Healy et al., 2008). Overall, the uncertainties associated with K_p^t calculation were within one order of magnitude. However, as discussed in our study, the discrepancy between field-measured partitioning coefficients and the theoretical ones was more than five orders of magnitude and the uncertainty in the K_p^t calculation would not change the interpretations and conclusions of this work.

Q2: 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.

A2: Thanks for your suggestion. We compared the K_p^f/K_p^t values (field-measured partitioning coefficients/theoretical partitioning coefficients) in this study and the values published in previous literatures in a new table in Supplement Information as follows.

C2:

Table S2: Comparison between K_p^f / K_p^t values (field-measured partitioning coefficients/theoretical partitioning coefficients) in this study and the values published in previous literatures.

Dicarbonyls	Seasons	K_p^f	K_p^f/K_p^t	Reference
Glyoxal	summer	3.23×10^{-4}	8.90×10^{5}	Qian et al.(2019)
		6.31×10^{-4}	1.32×10^{6}	Cui et al.(2021)
		1.02×10^{-1}	/	Ortiz et al.(2013)
		8.11×10^{-4}	2.48×10^{6}	This study
	winter	1.44×10^{-3}	1.13×10^{6}	Shen et al.(2018)
		1.71×10^{-3}	1.05×10^{6}	Cui et al.(2021)
		1.30×10^{-2}	1.02×10^{7}	This study
	spring	1.33×10^{-3}	1.80×10^{6}	Cui et al.(2021)
		1.43×10^{-2}	3.55×10^{7}	This study
	autumn	1.05×10^{-3}	1.26×10^{6}	Cui et al.(2021)
		2.14×10^{-3}	3.41×10^{6}	This study
Methylglyoxal	summer	4.07×10^{-5}	5.22×10^{4}	Qian et al.(2019)
		1.40×10^{-4}	1.31×10^{5}	Cui et al.(2021)
		7.41×10^{-2}	/	Ortiz et al.(2013)
		1.49×10^{-4}	2.10×10^{5}	This study
	winter	4.19×10^{-4}	1.53×10^{5}	Shen et al.(2018)
		4.27×10^{-4}	1.16×10^{5}	Cui et al.(2021)
		2.60×10^{-3}	9.93×10^{5}	This study
	spring	3.48×10^{-4}	2.10×10^{5}	Cui et al.(2021)
		1.06×10^{-3}	8.77×10^{5}	This study
	autumn	2.07×10^{-4}	1.11×10^{5}	Cui et al.(2021)
		9.55×10^{-4}	7.07×10^{5}	This study

Q3: 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.

A3: Thanks for your suggestion. We have removed the discussion of discrepancy between the field measured coefficients and the theoretical ones to Supplement Information.

Q4: 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?

A4: Gas-particle process of dicarbonyls in this study is separated into reversible and irreversible pathways, and the separation is based on the reversibility of chemical reaction of dicarbonyls occurred on condensed phase (Ervens and Volkamer, 2010; Kampf et al., 2013; Ling et al., 2020; Galloway et al., 2008). The reversible pathways here include hydration, dimerization and oligomerization, the product of which could revert to their parent compounds during extraction and could be directly detected in particle-phase samples. And the irreversible pathways here refer to irreversible uptake, which is driven by oxidative compounds in aerosols. As glyoxal/methylglyoxal + OH chemistry plays a dominant role in irreversible pathways, we use uptake coefficients γ (Eq. 4-7) to estimate and quantify the processes. Although the products of irreversible pathways could not be directly detected in particle phase and don't contribute to the c_p term in partitioning coefficient calculation (Eq.1), the irreversible pathways can well explain the overestimation of modeled dicarbonyl mixing ratios, which is about 3-6 times higher than the observed ones (Volkamer et al., 2007; Ling et al., 2020). Moreover, the reversible pathways were 10% or less the process the dicarbonyls undergone and the associated uncertainties in the calculations were ~5%, indicating the minimal reversible lost was closed to 1-2%.

C4: Lines 85-86 in Sect.1:

These processes are divided into reversible pathways and irreversible pathways, which is based on the reversibility of chemical reaction of dicarbonyls occurred on condensed phase (Ervens and Volkamer, 2010; Kampf et al., 2013; Ling et al., 2020; Galloway et al., 2008).

Although the products of irreversible pathways could not be directly detected in particle phase and didn't directly contribute to the increase of particulate dicarbonyls, the irreversible pathways could contribute to the decrease of gasous dicarbonyls and well explain the overestimation of modeled dicarbonyl mixing ratios, which was about 3-6 times higher than the observed ones (Volkamer et al., 2007; Ling et al., 2020).

Q5: 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.

A5: Thanks for your suggestion. Gas-phase dicarbonyls could partition into aerosol liquid water by dissolution, and then reversibly form hydrates and oligomers. Both dissolves dicarbonyl monomers and reversibly formed production are efficiently transformed into glyoxal-bis-2,4-dinitrophenylhydrazone, which was quantified by means of HPLC-UV in this study. The concentrations of dissolved dicarbonyl monomers were estimated using Henry's law coefficients, which is used to determine the physical solubility of carbonyls (e.g., K_H=5 M·atm^{-1} for glyoxal) (Schweitzer et al., 1998). The results were negligible compared to the concentrations of carbonyls in hydrate and oligomer forms. Therefore, the data in Figure 2, which referred to particle-phase concentration of dicarbonyls in reversible partitioning pathways, were equal to the measured concentration of carbonyls by HPLC-UV. We have described it in our manuscript.

C5: Lines 277-283 in Sect. 3.2:

Both dissolves dicarbonyl monomers and reversibly formed production are efficiently transformed into carbonyl-bis-2,4-dinitrophenylhydrazone, which was quantified by means of HPLC-UV in this study. The concentrations of dissolved dicarbonyl monomers were estimated using Henry's law coefficients, which is used to determine the physical solubility of carbonyls (e.g., K_H=5 M·atm^{-1} for glyoxal) (Schweitzer et al., 1998). The results were negligible compared to the concentrations of carbonyls in hydrate and oligomer forms. Thus, the concentrations of particle-phase dicarbonyl in reversible partitioning pathways were close to the measured concentration of carbonyls by HPLC-UV.

Q6: 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 inherant 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.

A6: Thanks for your suggestion. The pH values used in this study indeed contains large inherent uncertainty and we have deleted the discussion of pH in our revised manuscript.

Q7: 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 porduct to product in 2b) distribution to the potential product distribution with uncertainty due to bulk vs aerosol phase.

A7: Thanks for your suggestion and we regret for the incomprehensive consideration. Compared to bulk phase, the higher ionic strength in aerosol phase could affect aerosol-phase reactions in the following ways: (1) change aerosol hygroscopicity, surface tension and viscosity (Kampf et al., 2013; Sareen et al., 2010); (2) the presence of inorganic ions and corresponding change in the activity of water could shift the hydration equilibrium of organics with multiple hydration states (Loeffler et al., 2006); (3) influence the partitioning process of organics to the condensed phase via salting effects, as the presence of inorganic ions could catalyze and participate in oligomerization reactions (Sareen et al., 2010; McNeill, 2015). However, the reversible aerosol-phase reactions of volatile organic compounds in aerosols have not been systematically explored due to the lack of suitable reaction parameters and mechanisms. Recently, many laboratory experiments and model simulations have been conducted to evaluate the oligomerization in different seed aerosols. Take glyoxal for example, the dimensionless equilibrium constant of oligomerization K_{olig} varied a lot in different seed aerosols with the values of 1000 on $(NH_4)_2SO_4$ seed particles (Ervens and Volkamer, 2010), >700 on Na_2SO_4 seed particles (Corrigan et al., 2008) and 3-5 on NaCl seed particles (Ip et al., 2009). All of these parameters were worth to be considered in reversible aerosol-phase reactions simulation. Moreover, Elrod et al.(2021) investigated the carbonyl hydration equilibria on aqueous atmospheric particles using nuclear magnetic resonance (NMR) spectroscopy coupled with the MG2MS electronic structure method and revealed that the hydration equilibrium constants were ~1000 for glyoxal and ~100 for methylglyoxal. However, the rate constants of glyoxal and methylglyoxal in aerosol-phase have not been accurately quantified and we have to roughly estimate the product distribution on the basis of mechanisms in bulk-phase. The RH dependence of product distribution and the order of magnitude of estimated K_p values were close to those in aerosol-phase. We have added the uncertainty description in product simulation and deleted the definitive numbers in our revised manuscript.

C7: Lines 309-313 in Sect. 3.2:

However, the product distribution here was simulated based on the bulk-phase mechanisms and higher ionic strength in aerosol phase would influence reaction equilibria and rate constant (Ervens and Volkamer, 2010; Mcneill, 2015). The lack of quantitative reaction rate could contribute more uncertainties to the simulation, whereas, the RH dependence of product distribution and the order of magnitude of estimated K_p values were close to those in aerosol-phase and the roughly simulation could help to understand the reversible partitioning pathways of dicarbonyls.

Q8: 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.

A8: Thanks for your suggestion and we regret for the unclear expression. Methylglyoxal always presents a “salting-out” effect because of its increasing steric hindrance in ion hydration shell in previous laboratory studies (Waxman et al., 2015). However, in this study, methylglyoxal exhibited an unexpected “salting-in” effect in ambient particles due to much more complex compositions and higher ionic strength in ambient particles, which was also reported in other observational studies (Shen et al., 2018; Cui et al., 2021). Figure S4 presents the Setschenow plot of dicarbonyls versus aqueous sulfate, nitrate, and ammonia (SNA) concentration in aerosol. The negative salting constant indicated the “salting in” effects, which could result in exponential solubility and higher Henry’s law coefficient values for methylglyoxal in the real atmospheric. Although the equations (Eq.4-7) calculating uptake coefficients don’t include the aerosol composition or ionic strength, the higher effective Henry’s law coefficient values (eff K_H) in Eq.4 could lead to higher uptake coefficient values in this study comparing to other experimental ones (Curry et al., 2018; De Haan et al., 2018). Moreover, Li et al.(2021) pointed out that methylglyoxal is more reactive and have larger uptake coefficient on seed particles under atmospherically relevant concentrations.

C8: Lines 350-357 in Sect. 3.3.1:

Moreover, uptake coefficients for methylglyoxal were with an average value of 2.0×10^{-3} and were higher than those reported in other experimental studies, which varied from 10^{-6} to 10^{-3} (Curry et al., 2018; De Haan et al., 2018). On the one hand, conflicting with previous experimental results (Waxman et al., 2015), methylglyoxal exhibited an unexpected salting-in effect in real atmosphere due to much more complex compositions and higher ionic strength in ambient particles, which was also reported in other observational studies (Shen et al., 2018; Cui et al., 2021). And the higher Henry’s law coefficient values in Eq.4 could lead to higher uptake coefficient values. One the other hand, a recent study also provided direct experimental evidence to confirm that methylglyoxal is more reactive and have larger uptake coefficients on seed particles under atmospherically relevant concentrations (Li et al., 2021).

Minor and Technical Comments:

Q1: 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.

A1: Thanks for your suggestion. We have expanded the discussion about the relationship between reversible/irreversible pathways of dicarbonyls and ionic strength in wet aerosol as follows.

C1: Lines 293-297 in Section 3.2:

Ionic strength could also influence the reversible partitioning process as it is closely related to aerosol liquid water and RH conditions. The presence of inorganic ions could catalyze and participate in oligomerization reactions via salting effects (Sareen et al., 2010; Mcneill, 2015). Whereas, increasing viscosity of particles with increasing ionic strength could slow down all particle-phase reactions, and the reversible nucleophilic addition of inorganic ions (e.g., sulfate ions) at carbonyl carbons deactivates the molecule for further oligomerization (Kampf et al., 2013).

Lines 383-386 in Sect. 3.3.2:

The particulate concentration of dicarbonyls via irreversible pathways generally decreased with increasing RH. Concentrated inorganic solutions and relatively higher ionic strength in aerosol water under low RH conditions could jointly contribute to the hydration of dicarbonyls, the products of which could easily participate into the following radical reactions via H-abstraction.

Q2: 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.

A2: Thanks for your suggestion. We have added a thin-line to connect the points in Figure 1 in our revised manuscript as follows.

C2:

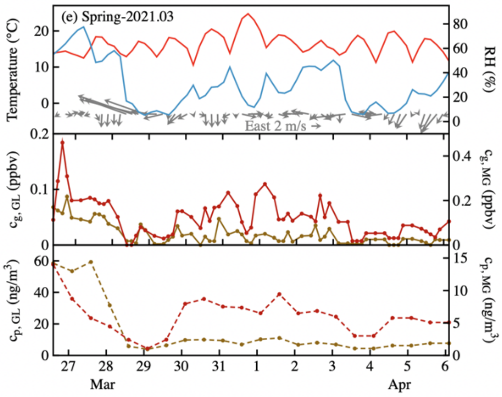


Figure 1e: Time series of meteorological parameters and gas- and particle-phase glyoxal and methylglyoxal observed in spring.

Q3: Line 287, it should be Fig. S8 instead of S7.

A3: Thanks for your suggestion. We have corrected it in our revised manuscript.

Q4: For Fig. S7, it is unclear what sequence number (x-axis) and what the grey shaded area are for.

A4: Thanks for your suggestion and we regret for the unclear expression. The sequence number (x-axis) refers to the serial number of samples. And the grey shaded area refers to the variation range of modeled oxalate concentrations, which is constrained by OH concentrations in aerosol liquid water. And we have specified it in the caption of Fig. S7 in our revised manuscript.

Q5: For table 1, it would be useful to include the dates of the measurements.

A5: Thanks for your suggestion and we have added the dates of the measurements in Table 1 in our revised manuscript.

Q6: For table 2, it is unclear how "theory" Henry's law constant is calculated compared to the "field" values.

A6: We regret for the unclear expression. The theoretical Henry’s law constant refers to the Henry’s law constant of dicarbonyls in pure water, which is calculated from Eq. 1-2 in previous studies (Sander, 2015). We have specified it in our revised manuscript.

$$\frac{d(\ln H)}{d(1/T)}=-\frac{-\Delta_{sol}H}{R} \qquad (1)$$

$$H(T)=H^{\Theta}\times\exp\left(\frac{-\Delta_{sol}H}{R}\times\left(\frac{1}{T}-\frac{1}{T^{\Theta}}\right)\right) \qquad (2)$$

Where H(T) ($mol \cdot m^{-3} \cdot Pa^{-1}$) is the Henry's law constant of dicarbonyls in pure water at different ambient temperature T(K); H^{Θ}($mol \cdot m^{-3} \cdot Pa^{-1}$) is the Henry's law constant of dicarbonyls in pure water at standard temperature T^{Θ}(298.15K); $\Delta_{sol}H$ (J/mol) is molar enthalpy of dissolution. For glyoxal, H^{Θ} is 4100 $mol \cdot m^{-3} \cdot Pa^{-1}$, $\frac{-\Delta_{sol}H}{R}$ is 7500 K (Ip et al., 2009); and for methylglyoxal, H^{Θ} is 34 $mol \cdot m^{-3} \cdot Pa^{-1}$, $\frac{-\Delta_{sol}H}{R}$ is 7500 K (Betterton and Hoffmann, 1988).

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