

Reversible and irreversible gas-particle partitioning of dicarbonyl compounds observed in the real atmosphere

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Abstract. Glyoxal and methylglyoxal are vital carbonyl compounds in the atmosphere and play substantial roles in radical cycling and ozone formation. The partitioning process of glyoxal and methylglyoxal between the gas and particle phase via reversible and irreversible pathways could efficiently contribute to secondary organic aerosol (SOA) formation. However, the relative importance of two partitioning pathways still remains elusive, especially in the real atmosphere. In this study, we launched five field observations in different seasons and simultaneously measured glyoxal and methylglyoxal in the gas and particle phase. The field-measured gas-particle partitioning coefficients were 5–7 magnitudes higher than the theoretical ones, indicating the significant roles of reversible and irreversible pathways in the partitioning process. The particulate concentration of dicarbonyls and product distribution via the two pathways were further investigated using a box model coupled with the corresponding kinetic mechanisms. We recommended the irreversible reactive uptake coefficient γ for glyoxal and methylglyoxal in different seasons in the real atmosphere, and the average value of 8.0×10^{-3} for glyoxal and 2.0×10^{-3} for methylglyoxal best represented the loss of gaseous dicarbonyls by irreversible gas-particle partitioning processes. Compared to the reversible pathways, the irreversible pathways played a dominant role, with a proportion of more than 90% in the gas-particle partitioning process in the real atmosphere and the proportion was significantly influenced by relative humidity and inorganic components in aerosols. However, the reversible pathways were also substantial, especially in winter, with a proportion of more than 10%. The partitioning processes of dicarbonyls in reversible and irreversible pathways jointly contributed to more than 25% of SOA formation in the real atmosphere. 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.

1 Introduction

Glyoxal and methylglyoxal, the simplest α -dicarbonyls, are recognized as being of great importance in atmospheric chemistry due to their unique physicochemical properties. The α -dicarbonyl functionality leads to higher water solubility and reactivity

29 of dicarbonyls than expected, as the α -dicarbonyl functionality is hydrophilic and contributes to hydrate formation. The hydrate
30 form of carbonyls is less volatile and more water-soluble than the unhydrated form (EPA., 2012), owing to the strong effect of
31 the two hydrogen-bonding groups in the hydrated form (Elrod et al., 2021). Moreover, hydrates can easily participate in
32 continuous radical reactions with higher reactivity by H-abstraction to form higher-molecular-weight oligomers (Michailoudi
33 et al., 2021). The traditional opinion is that methylglyoxal is less reactive compared to glyoxal due to its unreactive methyl
34 substitution, while a very recent study noted that methylglyoxal could be more reactive under an atmospheric-relevant
35 concentration (Li et al., 2021). Overall, both of them play crucial roles in radiation balance, air quality, brown carbon formation,
36 and SOA formation (Laskin et al., 2015; Qiu et al., 2020). Moreover, as major carcinogenic and genotoxic compounds,
37 dicarbonyls can cause serious damage to human health. They have relatively limited primary sources, except for biomass
38 burning and biofuel combustion (Zarzana et al., 2017; Zarzana et al., 2018), compared to secondary formation that occurs with
39 photooxidation of both biogenic volatile organic compounds (VOCs), such as isoprene, and anthropogenic VOCs, such as
40 aromatic hydrocarbons (Lv et al., 2019). Considering the atmospheric sink, glyoxal and methylglyoxal can be lost in the gas
41 phase by self-photolysis, oxidation by active radicals (such as OH radicals, NO₃ radicals) and wet/dry deposition; however,
42 there is still a missing sink for the two dicarbonyls (Volkamer et al., 2007), that's the gas-particle partitioning process, which
43 would be fully discussed in this study.

44 Gas-particle partitioning was recently found to be the most important removal pathway for both glyoxal and methylglyoxal,
45 especially in regions like Beijing with high particulate matter (PM) pollution that provides sufficient aerosol surface area.
46 Although they have relatively high vapor pressure, glyoxal and methylglyoxal can efficiently partition into the particle phase
47 due to their α -dicarbonyl functionality. The surface-adsorbed dicarbonyls could alter the properties of the particle's surfaces
48 and the organic surface films could act as a kinetic barrier to gas-aerosol mass transport and thereby influence particle
49 equilibration and water/gas uptake (Donaldson and Vaida, 2006). Upon physical adsorption, besides desorption or reaction at
50 the surface, dicarbonyls could undergo solvation and incorporation into the bulk liquid, and then they could go through
51 diffusion and chemical reactions in the bulk phase. The product may return into surfaces and gas phase, or stay in the bulk
52 phase (Paul et al., 2011). Moreover, chemical reactions occurred at the surface or in the bulk phase could in turn accelerate the
53 physical adsorption and greatly contribute to the formation and growth of atmospheric particulate matter. Whereas, as it is
54 difficult to distinguish the surface reactions and bulk reactions in field observations, we regard both of them as particle-phase
55 reactions in this study. The chemical reactions occurring in the gas-particle partitioning processes can be divided into reversible
56 pathways, including reversible hydration and self-oligomerization, and irreversible pathways, which can be driven by oxidative
57 compounds. These processes can also efficiently explain observed aerosols properties – including relatively high oxygenation
58 levels, compositions such as organic acids and oligomers, and higher light absorption – that cannot be explained by traditional
59 absorptive models of gas-particle partitioning (Pankow, 1994; Pankow and James, 1994; Odum et al., 1996).

60 Many laboratory and model studies have made a great effort to investigate the reversible and irreversible pathways of
61 dicarbonyls to further understand their gas-particle partitioning mechanisms and reveal their contribution to SOA formation.
62 Fu et al. (2008) found that the modeled SOA concentrations were largely increased when accounting for irreversible uptake of
63 dicarbonyls in the GEOS-Chem model. Considering the surface-controlled reactive uptake of dicarbonyls into the CMAQ
64 model, the aerosol uptake of dicarbonyls accounted for more than 45% of total SOA in the eastern US (Ying et al., 2015);
65 similarly, the contribution of glyoxal and methylglyoxal to SOA formation in China was 14% to 25% and 23% to 28%,
66 respectively (Hu et al., 2017). Although reversible and irreversible pathways of dicarbonyls have been separately investigated
67 in previous studies, solely incorporating just one pathway into models could lead to a large discrepancy between model results
68 and observational data, highlighting the importance of comprehensively considering both reversible and irreversible pathways
69 when quantifying the gas-particle partitioning process of dicarbonyls (Li et al., 2014; Hu et al., 2017; Ling et al., 2020).
70 Despite increasing interest in dicarbonyls and their gas-particle partitioning processes, the detailed chemical mechanisms of
71 two partitioning pathways remain poorly understood. First, previous studies have exposed seed particles to high concentration
72 levels of dicarbonyl vapors, from hundred ppb to ppm levels, or used bulk samples; thus, their applicability to the real
73 atmosphere requires further validation. Second, prior studies always used one constant coefficient to present all heterogeneous
74 processes occurring on the aerosol, which neglects the influencing factors in real atmospheric partitioning processes. Further
75 studies have shown that the two pathways in the gas-particle partitioning process for glyoxal and methylglyoxal are rather
76 complex, and their relative contribution to the partitioning process can be influenced by many factors such as relative humidity
77 (Curry et al., 2018; Shen et al., 2018), particle acidity (Liggio et al., 2005b; Shi et al., 2020), and particle organic/inorganic
78 components (Kampf et al., 2013). However, there persist controversies in the specific partitioning mechanisms of glyoxal and
79 methylglyoxal, especially conflicting views on their role in SOA formation, which urgently warrants further investigation.
80 In this study, five field observations were launched over urban Beijing in four seasons, and glyoxal and methylglyoxal in the
81 gas and particle phase were simultaneously measured. Beijing, as the political center of China, is the most prosperous city with
82 numerous key environmental issues. Chen et al. (2021) found that the average concentration of dicarbonyls in Beijing is lowest
83 among the key regions that have relatively higher PM_{2.5} concentrations, indicating there is a more efficient partitioning process
84 of dicarbonyls. Thus, it is more environmentally significant to discuss the gas-particle partitioning processes in urban Beijing.
85 These processes are divided into reversible pathways and irreversible pathways, which is based on the reversibility of chemical
86 reaction of dicarbonyls occurred on condensed phase (Galloway et al., 2008; Ervens and Volkamer, 2010; Kampf et al., 2013;
87 Ling et al., 2020). On the basis of field-measured data, we could estimate the product distribution, main influencing factors,
88 and relative importance of the two gas-particle partitioning pathways for glyoxal and methylglyoxal in the real atmosphere.

89 **2 MATERIALS AND METHOD**

90 **2.1 Field sampling**

91 We performed field observations on the roof of a six-story teaching building (26 m above the ground) on the Peking University
92 campus (39.992°N, 116.304°E) in northwest urban Beijing. The field observations in this study were launched during four
93 different seasons from 2019 to 2021.

94 Gaseous carbonyls were collected by adsorption reactions in a 2,4-dinitrophenyl hydrazine (DNPH) cartridge (Sep-Pak; Waters
95 Corporation). The air samples were first passed through an ozone scrubber (Sep-Pak; Waters Corporation) to eliminate
96 interference by ozone and then trapped in the DNPH cartridge. To prevent deliquescence of the potassium iodide in the ozone
97 scrubber, the air samples were mixed with ultrapure nitrogen before pumped into the sampling tubing. Air samples were
98 continuously collected every 3 h in daytime and 9 h in nighttime. The total flow rate was $0.8 \text{ L} \cdot \text{min}^{-1}$.

99 Particulate carbonyls were collected by a four-channel ambient particles sampler (TH-16A, Wuhan Tianhong) with Teflon
100 filter and quartz filter (47 mm, Whatman). The Teflon filter was used to measure the mass concentration of collected $\text{PM}_{2.5}$
101 and water-soluble inorganic compounds (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}). The quartz filters were used for
102 carbonyl analysis. The flow rate was set at $16.7 \text{ L} \cdot \text{min}^{-1}$ and particle samples were continuously collected every 12 h daily.
103 Detailed information about field sampling and analysis were provided in the previous studies (Rao et al., 2016; Qian et al.,
104 2019). To estimate the positive artifacts by adsorption of gas-phase dicarbonyls onto the filter (Hart and Pankow, 1994; Mader
105 and Pankow, 2001; Liggio, 2004; Odabasi and Seyfioglu, 2005), throughout our previous field observations, we placed a
106 backup quartz filter after the particle sampling quartz filter using an independent filter holder. The sampling filters would
107 collect the particles and adsorbed gaseous dicarbonyls, while the backup filter would only collect gaseous dicarbonyls. And
108 the ratio of measured dicarbonyls in second filter to that in the first were lower than 20%, which was equal to the previous
109 study (Shen et al., 2018). And the particulate concentrations of dicarbonyls used in this study were already corrected by the
110 possible adsorption artifacts.

111 The meteorological station was co-located at our sampling site and provided meteorological parameters. Common trace gases,
112 such as NO/NO_2 , SO_2 , CO , and O_3 , were detected online by Thermo 42i, 43i, 48i, and 49i analyzers, respectively. A TEOM
113 1400A analyzer was applied to measure the mass concentrations of $\text{PM}_{2.5}$ and PM_{10} , the results of which were consistent with
114 the $\text{PM}_{2.5}$ weighing results (Fig. S1). The time resolution for all of the above data was 1 min. Detailed information about these
115 five observations is shown in Table S1.

116 **2.2 Sample extraction and analysis**

117 The gaseous carbonyl samples were eluted with acetonitrile (HPLC/GC-MS grade) at a flow rate of less than $3 \text{ mL}/\text{min}$ (higher
118 flow rates can result in reduced recovery). And the particulate carbonyl samples on quartz filter were eluted with acidic DNPH
119 solutions in the flask and then were shaken for 3 h at $4 \text{ }^\circ\text{C}$ with a rotation rate of 180 rpm in an oscillator (Shanghai Zhicheng

120 ZWY 103D). The derived solutions were placed in darkness for 12-24 h to ensure complete derivatization, and then they were
121 analyzed by high-performance liquid chromatography-ultraviolet (HPLC-UV) for separation and detection. Carbonyls were
122 separated effectively with each other (Fig. S2) in this method. They were calibrated using a mixing standard solution with a
123 concentration range of 0.1–10 μM , and the linearity was indicated by a correlation of determination (r^2) of at least 0.999. The
124 detailed analysis method was presented in the previous study (Wang et al., 2009).

125 The Teflon samples were also extracted by deionized water using an ultrasonic bath for 30 min at room temperature. The
126 extracted solutions were analyzed by ion chromatography (IC Integriion and Dionex ICS 2000, USA) to measure the water-
127 soluble inorganic compounds (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) and low-molecular-weight organic acids
128 (formate, acetate, and oxalate) in aerosols.

129 **2.3 Quality assurance / quality control**

130 As carbonyl compounds are ubiquitous in environmental media, following measurements were conducted during the sample
131 collection, pretreatment and analysis to ensure the accuracy of results: (1) Before sampling, flow calibration and airtightness
132 tests of sampling devices were conducted, and flow difference were less than 10%; (2) After sampling, the gas-phase samples
133 were resealed by its end cap and plug, and stored in the provided pouch under cool environment ($<4^\circ\text{C}$); the particle-phase
134 samples were stored in the sealed boxes wrapped by pre-baked aluminum foils under freezing environment ($<-18^\circ\text{C}$), both
135 gas-phase and particle-phase samples were extracted and analyzed within a week; (3) The extraction processes were conducted
136 in fume hood with glassware, which was rinsed with acetonitrile for at least three times; (4) A calibration run was performed
137 each day to determine the response factor of the detector and recalibration was performed if the relative deviation of the RF
138 was beyond 5%.

139 Blank samples were collected every three days and then were stored and extracted by the same procedure as that for ambient
140 samples. The blank gas-phase samples were collected by placing blank DNPH cartridges near the gas inlet for the same
141 duration without artificial pumping. And the blank particle-phase samples were collected by placing blank quartz filter on the
142 $\text{PM}_{2.5}$ inlet with flow rate of 0 L/min. All data used in this study were all calibrated by blanks.

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

147 Additional field-sampling were launched to estimate the sampling efficiency during the collection. Two blank DNPH cartridges
148 were connected in tandem to assess the sampling efficiency of gas-phase carbonyls. The sampling efficiency of the cartridges
149 were the ratios of dicarbonyl concentrations in the first cartridge to the total concentrations in the two cartridges and the results

150 were more than 95% for both glyoxal and methylglyoxal. Similarly, a backup Teflon filter were placed after the particle
 151 sampling Teflon filter using an independent filter holder to estimate the particle collection efficiency. Both Teflon filters were
 152 weighed by a semimicro balance (Sartorius, Germany) to obtain the mass concentration of collected particles. The mass
 153 concentrations of particles collected on the backup filter were closed to zero, indicating that the sampling efficiency of particle
 154 were more than 99%.

155 Moreover, recovery tests were also conducted using two methods - adding standard solution and repeated extraction. We added
 156 the standard solution at three spiked levels of 0.025, 0.25 and 2.5 μg (namely 50 μL of 0.5 $\mu\text{g}\cdot\text{mL}^{-1}$, 5 $\mu\text{g}\cdot\text{mL}^{-1}$ and 50 $\mu\text{g}\cdot\text{mL}^{-1}$
 157 1 analytical standards) into blank DNPH cartridges and blank quartz filter to determine the carbonyl lost during the extraction
 158 and derivation. And then the cartridges and filters were extracted in the same way as the ambient samples. Each group were
 159 set with five parallel. The recoveries were ranged from 88% to 96% for gas-phase method and ranged from 85% to 96% for
 160 particle-phase method. Moreover, we also estimated the recovery efficiencies by repeated extraction and the recoveries were
 161 the ratios of dicarbonyl concentrations in the first extraction to the total concentrations in the two extractions. The results
 162 ranged from 92.8% to 99.9% for gas-phase method and ranged from 90% to 99.9% for particle-phase method.

163 2.3 Estimation of effective partitioning coefficient

164 To estimate the effective partitioning process of gas-phase carbonyls to the particle phase, we could use Pankow's absorptive
 165 partitioning theory for the gas-organic phase (Eqs. (1), (2)) (Odum et al., 1996) and Henry's law for the gas-liquid phase (Eq.
 166 (3)):

$$167 K_p^f = \frac{C_p}{C_g \times \text{TSP}} \quad (1)$$

$$168 K_p^t = \frac{RTf_{om}}{10^6 MW_{OM} \zeta p_L^0} \quad (2)$$

$$169 \text{eff } K_H = 10^3 \frac{c_p}{c_g \times M \times \text{ALWC} / \rho_{\text{water}}} \quad (3)$$

170 In Eq. (1), K_p^f ($\text{m}^3 \cdot \mu\text{g}^{-1}$) is the field-measured gas-particle partitioning coefficient; C_p ($\mu\text{g} \cdot \text{m}^{-3}$) is the concentrations of
 171 dicarbonyls in the particle phase, which is derived from the analysis of extracts, including monomers and their reversibly
 172 formed products (the product distribution is discussed in Section 3.2); C_g ($\mu\text{g} \cdot \text{m}^{-3}$) is the concentration of dicarbonyls in the
 173 gas phase; and TSP ($\mu\text{g} \cdot \text{m}^{-3}$) is the mass concentration of suspended particles (mass concentrations of $\text{PM}_{2.5}$ were used in this
 174 study). In Eq. (2), K_p^t ($\text{m}^3 \cdot \mu\text{g}^{-1}$) are the theoretical gas-particle partitioning coefficients determined by Pankow's absorptive
 175 model, f_{om} is the absorbing fraction of total particulate mass, MW_{OM} ($\text{g} \cdot \text{mol}^{-1}$) is the mean molecular weight of the organic
 176 phase, and ζ is the activity coefficient of target compounds. In the estimation of K_p^t in this study, f_{om} and ζ are unity and MW_{OM}
 177 = 200 $\text{g} \cdot \text{mol}^{-1}$, as used in previous studies (Healy et al., 2008; Williams et al., 2010; Xie et al., 2014; Shen et al., 2018), and
 178 p_L^0 (Pa) is the supercooled vapor pressure of compounds as a pure liquid at temperature T, which is calculated by the extended

179 aerosol inorganic model (E-AIM, http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php) (Clegg et al., 1998). The possible
 180 uncertainty in K_p^l calculation were fully discussed in Supporting Information. In Eq. (3), $\text{eff } K_H$ ($\text{M}\cdot\text{atm}^{-1}$) is the field-derived
 181 effective Henry's law coefficient; c_p ($\mu\text{g}\cdot\text{m}^{-3}$) and c_g (atm) are particle- and gas-phase concentrations of carbonyls, respectively;
 182 ALWC ($\mu\text{g}\cdot\text{m}^{-3}$) is the aerosol liquid water content calculated by the thermodynamic model ISORROPIA-II(forward model,
 183 metastable state), the results of which are comparable to the actual measured contents confirmed by previous studies (Guo et
 184 al., 2015).

185 The irreversible reactive uptake coefficient γ could efficiently describe the irreversible pathways of the gas-particle partitioning
 186 process of dicarbonyls driven by OH radicals. We could estimate the reactive uptake coefficients γ based on the effective
 187 Henry's constant via theory calculation (Hanson et al., 1994; Curry et al., 2018) and then calculate the effective uptake rate
 188 $k_{\text{eff, uptake}}$, following Eqs. (4)–(7):

$$189 \quad \frac{1}{\gamma} = \frac{1}{\alpha} + \frac{v}{4RT \text{ eff } K_H \sqrt{k^l D_{\text{aq}}}} \times \frac{1}{[\text{coth}q - 1/q]} \quad (4)$$

$$190 \quad v = \sqrt{\frac{8RT}{\pi M_X}} \quad (5)$$

$$191 \quad q = R_p / l = R_p / \sqrt{\frac{D_{\text{aq}}}{k^l}} \quad (6)$$

$$192 \quad k_{\text{eff, uptake}} = \frac{1}{4} v \times \gamma \times A_{\text{surf}} \quad (7)$$

193 where γ is the dimensionless uptake coefficient, v ($\text{m}\cdot\text{s}^{-1}$) is the gas-phase thermal velocity of glyoxal/methylglyoxal, D_{aq}
 194 ($\text{m}^2\cdot\text{s}^{-1}$) is the diffusion coefficient in the liquid phase, α is dimensionless mass accommodation coefficient, $\text{eff } K_H$ ($\text{M}\cdot\text{atm}^{-1}$)
 195 is the effective Henry's law constant calculated by field-measured data in Table 2, R is the universal gas constant, k^l (s^{-1}) is the
 196 first-order aqueous loss rate, M_X ($\text{kg}\cdot\text{mol}^{-1}$) is the average molar mass of gas-phase dicarbonyls, q is the parameter for
 197 measuring in-particle diffusion limitations, R_p (m) is the particle radius, l (m) is the diffusion reactive length, $k_{\text{eff, uptake}}$ (s^{-1}) is
 198 the effective uptake rate, and A_{surf} ($\text{m}^2\cdot\text{m}^{-3}$) is the aerosol surface area density. This formulation is based on the effective Henry's
 199 law constant under high RH conditions ($\text{RH} > 40\%$). Moreover, the formulation describes the reactive uptake due to irreversible
 200 multiple-phase loss processes in the presence of OH. The uncertainty in the γ calculation is mainly attributed to the uncertainty
 201 in OH concentration, which was 3×10^{-12} M on average and varied from 5.5×10^{-14} to 8×10^{-12} M (Herrmann et al., 2010).

202 3 RESULT AND DISCUSSION

203 3.1 Observation results and partitioning coefficients calculation

204 3.1.1 Dicarbonyls in the gas and particle phase

205 We launched five field observations in different seasons. Table S1 details the information about the field observations,
 206 including observation periods, sample volume, and meteorological parameters. We totally collected 387 gas-phase samples

207 and 130 particle-phase samples in four seasons. In these samples, carbonyls were simultaneously measured in both gas phase
208 and particle phase. Ten carbonyls were measured in the gas phase, including formaldehyde, acetaldehyde, acetone,
209 propionaldehyde, methacrolein, butyraldehyde, methyl vinyl ketone, benzaldehyde, glyoxal, and methylglyoxal; and six
210 carbonyls were measured in the particle phase, including formaldehyde, acetaldehyde, acetone, propionaldehyde, glyoxal, and
211 methylglyoxal. In this study, we mainly discuss the gas-particle partitioning processes of glyoxal and methylglyoxal because
212 of their significant roles in atmospheric chemistry.

213 Figure 1 and Table 1 show the temporal characteristics and seasonal variation of glyoxal and methylglyoxal, respectively.
214 Gaseous dicarbonyls showed obvious seasonal variation. Concentrations in summer (0.99 ± 0.59 ppbv) were generally much
215 higher than in other seasons, followed by autumn and spring, and the concentrations in winter were the lowest. This seasonal
216 variation could be partly attributed to the higher temperature and more intensive radiation in summer, which could greatly
217 enhance the secondary formation of gaseous carbonyls via photochemical reactions. The diurnal variation in the dicarbonyls
218 during summer support this interpretation of the data; gas-phase dicarbonyls exhibited obviously diurnal variations in summer,
219 whereas this variation was irregular in other seasons (Fig. S3). The concentration levels of gaseous dicarbonyl in summer
220 rapidly increased after sunrise, remained relatively high during the daytime (12:00–14:00), and then decreased at dusk.
221 Although methylglyoxal has a shorter lifetime compare to glyoxal (glyoxal 2.9 h vs. methylglyoxal 1.6 h) (Fu et al., 2008), its
222 gas-phase concentration levels were generally higher than those of glyoxal, consistent with previous studies (Rao et al., 2016;
223 Mitsubishi et al., 2018; Qian et al., 2019), mainly due to the relatively larger production from isoprene and acetone for
224 methylglyoxal.

225 The concentrations of particulate dicarbonyls were an order of magnitude smaller than the gaseous concentrations using the
226 unit of nanogram per cubic meter of air (ng/m^3 air). The average particulate glyoxal and methylglyoxal were 19.37 and 11.24
227 ng/m^3 , respectively, which were slightly higher than previously reported values (Zhu et al., 2018; Shen et al., 2018; Qian et al.,
228 2019; Cui et al., 2021). Dicarbonyls measured in the particle phase also showed obvious seasonal variation. The particulate
229 concentrations of the two dicarbonyls in winter (43.38 ± 32.42 ng/m^3 air) were 2–2.3 times higher than those in other seasons,
230 suggesting that the dicarbonyls were more favored into the particle phase in winter. Moreover, particulate dicarbonyls in
231 different seasons exhibited the same diurnal variation (Fig. S3). The particulate concentrations of dicarbonyls in daytime were
232 generally higher than those in nighttime, especially in winter.

233 3.1.2 Gas-particle partitioning coefficient

234 Dicarbonyls could partition between gas and aerosol phases or the liquid phase, following Pankow's absorptive partitioning
235 theory or Henry's law, respectively, as listed in Table 2. Both gas-particle partitioning coefficient (K_p^f) and effective Henry's
236 law coefficient (K_H^f) were calculated on the basis of field-measured data and were in the range of 10^{-4} – 10^{-2} $\text{m}^3 \cdot \mu\text{g}^{-1}$ and 10^6 –

237 $10^8 \text{ M}\cdot\text{atm}^{-1}$, respectively. The partitioning coefficient values of the two dicarbonyls exhibited the same seasonal variation, as
238 winter and spring > autumn > summer. A higher aerosol concentration accompanied by higher aerosol surface area
239 concentration and lower relative humidity resulted in a higher partitioning coefficient in winter and spring, when heavy
240 pollution and sandstorms always occurred. In the case of temperature variation varied from 265.53 K to 310.75 K in different
241 seasons, lower temperature promoted the gas-to-particle partitioning processes as K_p^f values for the dicarbonyls and
242 temperature showed negative correlation with significant difference ($p < 0.001$) (Fig. S4). Moreover, The K_p^f and K_H^f values
243 of glyoxal were always higher than those of methylglyoxal, implying the former was more likely to partition to the particle
244 phase; this could be attributed to their different structures. Glyoxal were more soluble and reactive because of the adjacent
245 electron-poor aldehydic carbons, whereas methylglyoxal was more stable due to the reduced electron-deficient ketone moiety
246 (Kroll et al., 2005).

247 Both K_p^f and K_H^f were relatively close to those found in previous field-measured studies (Shen et al., 2018; Qian et al., 2019;
248 Cui et al., 2021). However, compared with the theoretical partitioning coefficients K_p^t calculated by Pankow's absorptive
249 theory, K_p^f values were approximately 5–7 orders of magnitudes higher than the corresponding K_p^t values. Similarly, K_H^f values
250 were approximately 2–5 orders of magnitudes higher than the theoretical Henry's law coefficient K_H^t calculated in pure water,
251 which could be attributed to salting effects in wet aerosol (Figure S5). K_p^f/K_p^t values in this study were close to but slightly
252 higher than the values published in previous literature (Table S2) and the discrepancy between field-measured partitioning
253 coefficients and the theoretical ones was fully discussed in Supporting Information.

254 To narrow the large discrepancy between field-measured partitioning coefficients and theoretical ones, we needed to further
255 investigate the mechanism and product distribution of chemical reactions occurring in the aerosols during the partitioning
256 processes. The products of the reversible and irreversible pathways mostly have lower saturated vapor pressure, and thus
257 leading to higher partitioning coefficients compared to monomer dicarbonyls. Take glyoxal for example, the effective
258 saturation vapor pressures of the product set in reversible pathways are $\sim 10^{-5}$ Torr in the real atmosphere (Shen et al., 2018).
259 And the products of the irreversible pathways had much lower vapor pressure values than those of reversible pathways, for
260 example, the vapor pressure of oxalic acids and ammonium oxalates are $\sim 10^{-5}$ Torr (Saxena and Hildemann, 1996) and $5.18 \times$
261 10^{-8} Torr (EPA, 2011), respectively, and those of glyoxal trimer dihydrates are $\sim 10^{-11}$ Torr at 20 °C (SPARC, 2003), indicating
262 the irreversible pathways make larger contributions to the underestimation of partitioning processes of dicarbonyls. The
263 following sections further discuss the mechanism and product distribution of reversible and irreversible pathways to explain
264 the partitioning process of dicarbonyls.

265 **3.2 Reversible pathways**

266 Gas-particle partitioning of dicarbonyls via reversible pathways mainly consists of hydration and self-oligomerization. Since

267 glyoxal and methylglyoxal had high water solubility and reactivity, they could easily dissolve into aerosol liquid water, and
268 then form hydrates and oligomers. Hemiacetal/acetal formation (Loeffler et al., 2006) and aldol condensation (Haan et al.,
269 2009) are the most thermodynamically favored oligomer reactions for glyoxal hydrates and methylglyoxal hydrates,
270 respectively. The proposed mechanism for the reversible formation of glyoxal and methylglyoxal in aerosols is shown in Fig.
271 S6. By adding excess derivatization agent (like 2,4-dinitrophenylhydrazine in this study), dicarbonyls as well as their
272 reversibly formed products are efficiently transformed into dicarbonyl-bis-2,4-dinitrophenylhydrazine, which are quantified
273 as monomers by means of analysis techniques (Kampf et al., 2013). Moreover, Healy et al. (2008) have confirmed that
274 derivatization agent was found to efficiently dissolve a trimeric glyoxal standard and convert the resulting monomers to oxime
275 derivatives, and oligomers could not be detected in the extracts of filter samples by GC-MS analysis, also indicating the use
276 of excess derivatization agent could efficiently convert the hydrates and oligomers back to the monomeric species by removing
277 dicarbonyl monomers from the extract as soon as they are formed. Both dissolves dicarbonyl monomers and reversibly formed
278 production are efficiently transformed into carbonyl-bis-2,4-dinitrophenylhydrazine, which was quantified by means of
279 HPLC-UV in this study. The concentrations of dissolved dicarbonyl monomers were estimated using Henry's law coefficients,
280 which is 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
281 results were negligible compared to the concentrations of carbonyls in hydrate and oligomer forms. Thus, the concentrations
282 of particle-phase dicarbonyl in reversible partitioning pathways were close to the measured concentration of carbonyls by
283 HPLC-UV.

284 As glyoxal and methylglyoxal have similar trend under different conditions, we focused on the total concentration of the two
285 dicarbonyls in the following discussion. As shown in Fig. 2a, the particulate concentration of dicarbonyls via a reversible
286 pathway was strongly dependent on RH. It increased significantly when RH increased from <10% to 60%, as dicarbonyls were
287 more favorable to dissolve into hygroscopic aerosols during their growth (Mitsuishi et al., 2018; Xu et al., 2020). However,
288 from 60% to 80% RH, it exhibited the opposite trend and decreased with increasing RH, as higher water concentrations at
289 elevated RH levels may dilute the monomer concentration in the particle phase and hinder oligomerization reactions (Healy et
290 al., 2009), and the product distribution of the reversible formation could also well explain this phenomenon. The results
291 exhibited similar partten to a previous study, in which the partitioning of glyoxal and methylglyoxal gradually increased as
292 RH increased to 40%, peaked sharply around 50%, and subsequently decreased as RH increased towards 80%(Healy et al.,
293 2009). Moreover, ionic strength could also influence the reversible partitioning process as it is closely related to aerosol liquid
294 water and RH conditions. The presence of inorganic ions could catalyze and participate in oligomerization reactions via salting
295 effects (Sareen et al., 2010; Mcneill, 2015). Whereas, increasing viscosity of particles with increasing ionic strength could
296 slow down all particle-phase reactions, and the reversible nucleophilic addition of inorganic ions (e.g., sulfate ions) at carbonyl
297 carbons deactivates the molecule for further oligomerization (Kampf et al., 2013).

298 To roughly estimate the product distribution of the reversible pathway in the real atmosphere, we simplified reaction
299 mechanisms and calculated the product distribution on the basis of the kinetic mechanisms listed in Table S3 using a 0-D box
300 model with a steady-state approach. Generally, more dicarbonyls existed in oligomer forms than in hydrate forms in the
301 reversible formation. Moreover, their distribution exhibited obvious seasonal variations. Summer had the highest proportion
302 of hydrate forms, while winter had the highest proportion of oligomer forms. Detailed information is shown in Table S4. The
303 seasonal variation could be attributed to the RH in different seasons – relatively high in summer and low in winter. As shown
304 in Fig. 2b, the product distribution of the reversible formation has a strong dependence on RH. The proportion of dicarbonyls
305 in hydrate forms increased with increasing RH and could reach more than 75% in high RH, while the proportion of dicarbonyls
306 in oligomer forms exhibited the opposite trend. Hydrates play a dominant role in dilute solutions under high RH conditions
307 with a relatively high aerosol liquid water concentration, which might hinder oligomer formation. And large quantities of
308 oligomers, including dimers and trimers, would form until the aerosol liquid concentration became greater than 1 M (Liggio
309 et al., 2005b) when RH decreased. However, the product distribution here was simulated based on the bulk-phase mechanisms
310 and higher ionic strength in aerosol phase would influence reaction equilibria and rate constant (Ervens and Volkamer, 2010;
311 McNeill, 2015). The lack of quantitative reaction rate in aerosol phase could contribute more uncertainties to the simulation,
312 whereas, the RH dependence of product distribution and the order of magnitude of estimated K_p values were close to those in
313 aerosol-phase and the roughly simulation could help to understand the reversible partitioning pathways of dicarbonyls.
314 Combined with the vapor pressure of dominant products published in previous studies (Hastings et al., 2005; Axson et al.,
315 2010), their gas-particle partitioning coefficient can be roughly estimated and can effectively fit the field-measured values, as
316 shown in Fig. 2c. The estimated gas-particle partitioning coefficients in this study are five orders of magnitude higher than the
317 theoretical ones but still 1–2 orders of magnitude lower than the field-measured coefficients, especially in winter. The
318 difference between the estimated partitioning coefficients and the field-measured ones suggests that the current understanding
319 of the equilibrium in reversible formations cannot reasonably explain the gas-particle partitioning processes of dicarbonyls.
320 There still exist extra pathways of reversible formation. Cross-oligomerization of glyoxal and methylglyoxal is nonnegligible
321 and could form similar molecular structure products and contribute to SOA yield (Schwier et al., 2010). Esterification and
322 amination of diols also occur in aerosol liquid water but are negligible compared to hydration and polymerization (Zhao et al.,
323 2006). However, these reactions are not further discussed here. The hydrates and oligomers mentioned above are the dominant
324 forms of glyoxal/methylglyoxal in the particle phase, while the higher molecular oligomers up to nonamer could also exist
325 with a relatively smaller but still significant fraction at equilibrium. Although the reactions are thermodynamically reversible,
326 upon evaporation of the aerosol liquid water, the oligomer formation is faster than the evaporation of dehydrated dicarbonyls,
327 and the dicarbonyl evaporation is limited (Liggio et al., 2005b; Loeffler et al., 2006). This results in relatively stable oligomers
328 and yielding SOA. Moreover, other nucleophilic species may also form oligomers with glyoxal and methylglyoxal and

329 effectively prevent their evaporation. Besides reversible pathways, higher carbon number products with lower volatility were
330 mainly formed through irreversible pathways, such as radical reactions (e.g., OH radicals), which are fully discussed in the
331 next section.

332 **3.3 Irreversible pathways**

333 **3.3.1 Irreversible pathways driven by hydroxyl radicals**

334 Reactive uptake driven by hydroxyl radicals (OH) is the dominant process for glyoxal and methylglyoxal in their irreversible
335 gas-particle partitioning pathways. Compared to other irreversible pathways, such as imidazole formation,
336 glyoxal/methylglyoxal + OH chemistry occurs on much shorter timescales (Teich et al., 2016). The reaction is the initial step
337 for most radical-based chemistry of glyoxal/methylglyoxal and has been proven to be an important source of SOA in both
338 cloud/fog droplets and wet aerosols (Tan et al., 2012; Lim et al., 2013), producing low-volatility products such as organic acids,
339 large multifunctional humic-like substances, and oligomers. The proposed mechanism for the irreversible pathway of glyoxal
340 and methylglyoxal driven by hydroxyl radicals in aerosols is shown in Fig. S7. The OH radicals in aerosol liquid water are
341 mainly from the direct uptake of gas-phase OH radicals with a Henry's law constant of 30 M/atm (Faust and Allen, 1993) and
342 Fenton reactions, and Fenton reactions are closely related to hydrogen peroxide, iron ions, and manganese ions in the particle
343 phase. The sources of OH radicals are one of the major uncertainties in SOA formation (Ervens et al., 2014).

344 The calculated γ and $k_{\text{eff, uptake}}$ values for different seasons are listed in Table 3. The reactive uptake coefficients of glyoxal were
345 in the range 10^{-4} – 10^{-2} , and the average value of 8.0×10^{-3} in this study was close to the ones representing the loss of glyoxal by
346 surface uptake during the KORUS-AQ campaign in a very recent studies (Kim et al., 2022). And the value slightly exceeded
347 the one commonly used in model simulations ($\gamma = 2.9 \times 10^{-3}$), which was based on an experimental study for $(\text{NH}_4)_2\text{SO}_4$ aerosols
348 at 55% RH (Liggio et al., 2005a), and also far outweighs the uptake coefficients of glyoxal on clean and acidic gas-aged
349 mineral particles ($\gamma = 10^{-6}$ – 10^{-4}) (Shen et al., 2016), implying that a real atmospheric aerosol provides a far more reactive
350 interface for physiochemical processes than that of mineral particles. Moreover, uptake coefficients for methylglyoxal were
351 with an average value of 2.0×10^{-3} and were higher than those reported in other experimental studies, which varied from 10^{-6}
352 to 10^{-3} (Curry et al., 2018; De Haan et al., 2018). On the one hand, conflicting with previous experimental results (Waxman et
353 al., 2015), methylglyoxal exhibited an unexpected salting-in effect in real atmosphere due to much more complex compositions
354 and higher ionic strength in ambient particles, which was also reported in other observational studies (Shen et al., 2018; Cui
355 et al., 2021). And the higher Henry's law coefficient values in Eq.4 could lead to higher uptake coefficient values. On the
356 other hand, a recent study also provided direct experimental evidence to confirm that methylglyoxal is more reactive and have
357 larger uptake coefficients on seed particles under atmospherically relevant concentrations (Li et al., 2021). The γ values for
358 both glyoxal and methylglyoxal exhibited similar seasonal variations, which were lowest in summer and reached their highest

359 in winter. This seasonal variation could be attributed to RH variation and particle composition. Moreover, the effective uptake
360 rate ($k_{\text{eff, uptake}}$), which is regarded as a pseudo-first-order reaction rate, is a net result of competition between reversible and
361 irreversible processes, and it varied from 10^{-4} s^{-1} to 10^{-5} s^{-1} in the real atmosphere in this study. As shown in Fig. 3a, the negative
362 dependence of $k_{\text{eff, uptake}}$ on RH also confirmed that the irreversible uptake of dicarbonyls could be inhibited in high RH
363 conditions. What's more, as we can see in Figure 3b, the irreversible uptake increased exponentially with increasing SNA
364 (SNA: Sulfate, Nitrate and Ammonia) concentrations, mainly because that higher SNA concentrations always occurred in
365 lower RH conditions with lower aerosol liquid water content (Figure S8) and the irreversible uptake was promoted by
366 combined efforts of RH effects and ion effects. Whereas, for a given RH, uptake coefficients γ for both glyoxal and
367 methylglyoxal showed a weak dependence on the ratio of SNA (Sulfate:Ammonia and Sulfate:Nitrate) with significant scatter
368 (Fig. S9).

369 Moreover, it was worth noting that under extremely low RH (<40%), the aerosol was not completely deliquescent, and the
370 uptake coefficients based on Henry's law could not explain the irreversible pathways. Previous research indicated that the
371 irreversible uptake of dicarbonyls could still occur under a low RH condition (Liggio et al., 2005a; De Haan et al., 2018), and
372 that these uptake values were generally lower due to the inefficient reactive uptake process onto the crystallized aerosols.

373 **3.3.2 Reactive uptake of dicarbonyl compounds**

374 We could not directly measure the particulate concentration of dicarbonyls via an irreversible pathway, as the dicarbonyls
375 irreversibly reacted with oxidative radicals on aerosols. To quantitatively evaluate the contribution of the irreversible pathway
376 of dicarbonyls, we calculated their average concentration based on Eqs. (S3)–(S7) in the Supplement with the calculated γ
377 values in this study. The samples estimated here were collected under high RH conditions (RH > 40%) because of the
378 calculation limitation of irreversible uptake coefficients. Although the products of irreversible pathways could not be directly
379 detected in particle phase and didn't directly contribute to the increase of particulate dicarbonyls, the irreversible pathways
380 could contribute to the decrease of gaseous dicarbonyls and well explain the overestimation of modeled dicarbonyl mixing
381 ratios, which is about 3-6 times higher than the observed ones (Volkamer et al., 2007; Ling et al., 2020).

382 The total particulate concentration of glyoxal and methylglyoxal via irreversible pathway varied from several to more than
383 100 nanograms per microgram $\text{PM}_{2.5}$ ($\text{ng}/\mu\text{g PM}_{2.5}$), and it was strongly dependent on RH, as shown in Fig. 3c, which generally
384 decreased with increasing RH. Concentrated inorganic solutions and relatively higher ionic strength in aerosol water under
385 low RH conditions could jointly contribute to the hydration of dicarbonyls, the products of which could easily participate into
386 the following irreversible radical reactions via H-abstraction.

387 To further discuss the product distribution of the reaction of glyoxal/methylglyoxal with hydroxyl radicals, we used the kinetic
388 mechanisms of glyoxal/methylglyoxal + OH chemistry proposed by Lim et al.(2013) on the basis of a 0-D box model with a

389 steady-state approach. The average OH radical concentration setting in the modeling was 3.2×10^{-12} M, which is based on the
390 hypothesis of the Henry equilibrium of OH radicals between the gas and particle phase (Sander, 2015; Shen et al., 2018).
391 Oxalate can be considered as a tracer for this aqueous chemistry, since it does not have any other significant chemical sources.
392 Oxalate was detected in the particle-phase samples by ion chromatography. The modeling results of oxalate concentration
393 agreed well with the measured values, and their deviations were in the considered range (Fig. S10). Meanwhile, we can
394 estimate the distribution of major products in irreversible glyoxal/methylglyoxal-OH radical chemistry under different RH
395 conditions, as illustrated in Figure 3d. Generally, oxalate is the major product in wet aerosols, contributing ~60%, and its
396 proportion increases with increasing RH. Besides oxalate, oligomers also play significant roles in glyoxal/methylglyoxal-OH
397 radical chemistry with a contribution of ~30%, and their proportion is maximum under relatively low RH conditions. The RH
398 dependence of the product distribution could mainly be attributed to the particulate concentration of glyoxal/methylglyoxal,
399 which significantly affects the OH radical chemistry. With relatively high carbonyl concentrations (0.1–10 M) in aerosol liquid
400 water, self-reactions of organic molecules become more favorable, resulting in new carbon–carbon bonds and high molecular
401 weight oligomers via radical–radical chemistry (Lim et al., 2013). Moreover, besides OH radical chemistry, reaction with
402 sulfate and ammonium also contribute to the oligomer formation and irreversible uptake of gaseous dicarbonyls (Ortiz-
403 Montalvo et al., 2014; Lin et al., 2015; Lim et al., 2016). The oligomer proportion could be more than 30% in concentrated
404 carbonyl solutions (~0.1 M) and only account for 1% in diluted solutions (~0.01 M).

405 **3.4 Relative importance of two partitioning pathways**

406 Table 4 summarizes the particulate concentration of glyoxal and methylglyoxal via reversible and irreversible pathways in
407 different seasons. The average particulate concentrations of glyoxal (0.43 ng/ μ g in the reversible pathway and 24.26 ng/ μ g in
408 the irreversible pathway) were generally higher than those of methylglyoxal (0.25 ng/ μ g in the reversible pathway and 16.53
409 ng/ μ g in the irreversible pathway), mainly due to the relatively higher water solubility and reactivity of glyoxal. Comparing
410 two gas-particle partitioning processes, the irreversible pathway played extremely dominant roles and generally accounted for
411 96.7% and 95.0% for glyoxal and methylglyoxal, respectively. The proportion of the irreversible pathway varied from 90% to
412 99.9% and reached its highest in summer for glyoxal (98.8%) and in autumn for methylglyoxal (99.2%), while it was minimum
413 in winter (92.9% for glyoxal and 92.8% for methylglyoxal). Overall, the irreversible pathway played a dominant role in the
414 gas-particle partitioning process for both glyoxal and methylglyoxal in the real atmosphere, while the reversible pathway was
415 also substantial and nonnegligible, especially in winter, with an proportion of ~10%. Furthermore, as discussed above, the
416 particulate concentrations of dicarbonyls and their relative importance were influenced by environmental factors such as
417 relative humidity and particle composition, which could jointly influence both the reversible and irreversible pathways of
418 dicarbonyls. As shown in Figure 4, the proportion of irreversible pathways in the gas-particle partitioning process for

419 dicarbonyls increased with aqueous SNA concentrations, and reached maximum when SNA concentrations were more than 100
420 M under low RH conditions. Moreover, higher organic concentrations in aerosol may lead to an OH-limit environment,
421 hindering the irreversible pathways driven by radicals and influencing the relative importance of the two pathways (Waxman
422 et al., 2013; Ervens et al., 2014). But the OH limitations are still elusive due to the uncertainties in the sources of OH in
423 aerosol particles (Herrmann et al., 2010).

424 Comprehensively considering the contribution of both reversible pathways and irreversible pathways occurred in gas-particle
425 partitioning processes could benefit the ambient dicarbonyls simulations. Ling et al. (2020) found that the observation and
426 simulation of the gas-phase concentration level of dicarbonyls could reach reasonable agreement when the irreversible uptake
427 and reversible partitioning were incorporated into the model, as these jointly contribute ~62% to the sink of dicarbonyls.
428 Moreover, the contribution of gas-particle partitioning processes of dicarbonyls to SOA formation were higher as the two
429 partitioning pathways were jointly considered. In this study, gas-particle partitioning processes of dicarbonyls accounted for a
430 relatively large proportion of total particle mass (PM_{2.5}), on the average of ~5% considering both reversible and irreversible
431 gas-particle partitioning pathways. Since a large fraction of PM_{2.5} mass in Beijing consists of SOAs (~30%) (Huang et al.,
432 2014), we could roughly estimate the contribution of gas-particle partitioning processes of dicarbonyls to SOA yields (by
433 mass). There were approximately 25% SOAs formed from glyoxal and methylglyoxal in this study. However, the particulate
434 dicarbonyls calculated here only contained simple reversible pathways and irreversible pathways driven by OH radicals. More
435 complicated chemical processes, such as NO₃ radical chemistry, were not considered, which still resulted in the
436 underestimation of their contribution to SOA formation.

437 **4 Conclusions**

438 We simultaneously measured glyoxal and methylglyoxal concentration in the gas and particle phase in different seasons over
439 urban Beijing. Based on field-measured data, the field-derived gas-particle partitioning coefficients were calculated and found
440 to be 5–7 magnitudes higher than the theoretical values. Such a large discrepancy provides field evidence that the gas-particle
441 partitioning process does not occur by physical absorption alone but also results from the combined and simultaneous effects
442 of reversible and irreversible pathways. Hydration and oligomerization occurred in the reversible pathway, producing
443 compounds with lower volatility in the condensed phase, and the irreversible pathway could accelerate the uptake of gaseous
444 dicarbonyls. The two pathways jointly contributed to the underestimation of gas-particle partitioning of dicarbonyls.
445 This study systemically considers both reversible and irreversible pathways in the ambient atmosphere for the first time.
446 Compared to the reversible pathways, the irreversible pathways play a dominant role in the gas-particle partitioning process
447 for dicarbonyls, accounting for ~90% of this process. We recommend the irreversible reactive uptake coefficient for glyoxal

448 and methylglyoxal in different seasons in the real atmosphere. The values we calculated here are higher than those used in
449 model simulations to date, especially for methylglyoxal which exhibits an unexpected salting-in effect under an atmospheric-
450 relevant concentration. We expect the application of these parameterizations will increase the calculated contribution of
451 irreversible uptake of dicarbonyls to SOA formation and narrow the gap between model predictions and field measurements
452 of ambient dicarbonyl concentrations. Moreover, relative humidity and inorganic particle compositions are defined as the most
453 important factor influencing particulate concentration and product distribution of dicarbonyls via both reversible and
454 irreversible pathways, implying the significance of considering different RH conditions in dicarbonyl SOA simulations.
455 Furthermore, we note that there may be other potential explanations for the increase in particle mass caused by dicarbonyls
456 and the uncertainty in the gas-particle partitioning process, including physical adsorption, reversible pathways and irreversible
457 pathways. Physical adsorption of dicarbonyls could be enhanced by water-soluble organics and mineral dust. Other reversible
458 pathways, such as adducts formed from glyoxal with inorganic species, could also promote the gas-particle partitioning process.
459 Irreversible pathways driven by other oxidants, such as NO₃ radicals, can also perform a substantial role. Shen et al. (2016)
460 found that glyoxal could irreversibly produce formic acid, glycolic acid, and oligomers on particles without illumination or
461 extra oxidants. Besides gas-particle partitioning, particulate dicarbonyls formed via the heterogeneous reaction of VOCs could
462 contribute to the uncertainty in partitioning research. Dong et al. (2021) recently revealed that aqueous photooxidation of
463 toluene could yield glyoxal and methylglyoxal via a ring-cleavage process. Overall, the real gas-particle partitioning process
464 of glyoxal and methylglyoxal is more complicated and their contribution to SOA formation is still indistinct; thus, more
465 laboratory experiments and field measurements are urgently needed to improve our understanding of the gas-particle
466 partitioning process for glyoxal and methylglyoxal.

467

468 *Data availability.* The data are accessible by contacting the corresponding author (zmchen@pku.edu.cn).

469

470 *Author contributions.* In the framework of the five field measurements in different seasons, ZC and JH designed the study, and
471 JH performed all carbonyl measurements used in this study, analyzed the data, and wrote the paper. ZC helped interpret the
472 results, guided the writing, and modified the manuscript. XQ and PD contributed to the methods of sampling and analyzing
473 gas- and particle-phase carbonyls. All authors discussed the results and contributed to the final paper.

474

475 *Competing interests.* The authors declare that they have no conflict of interest.

476

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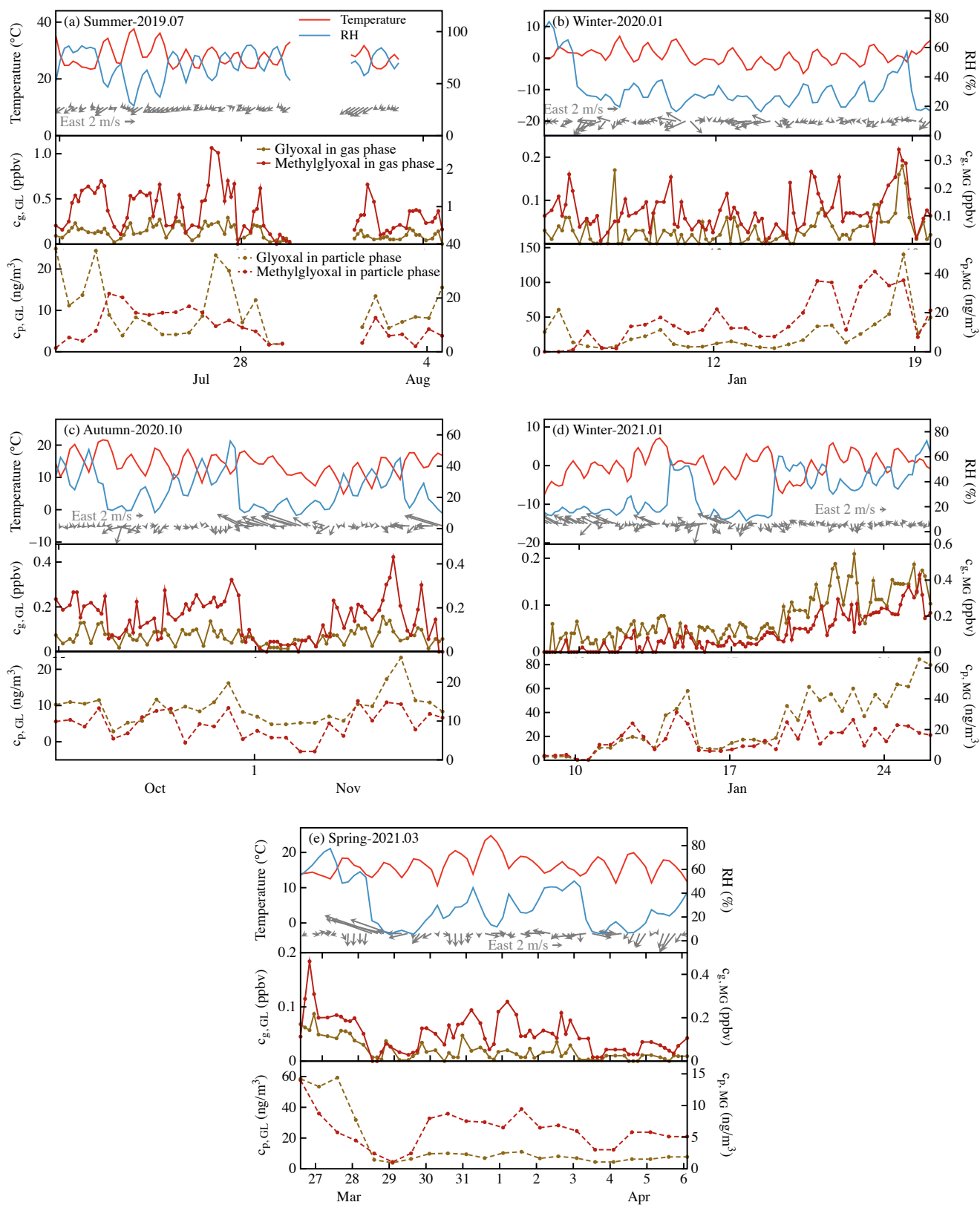
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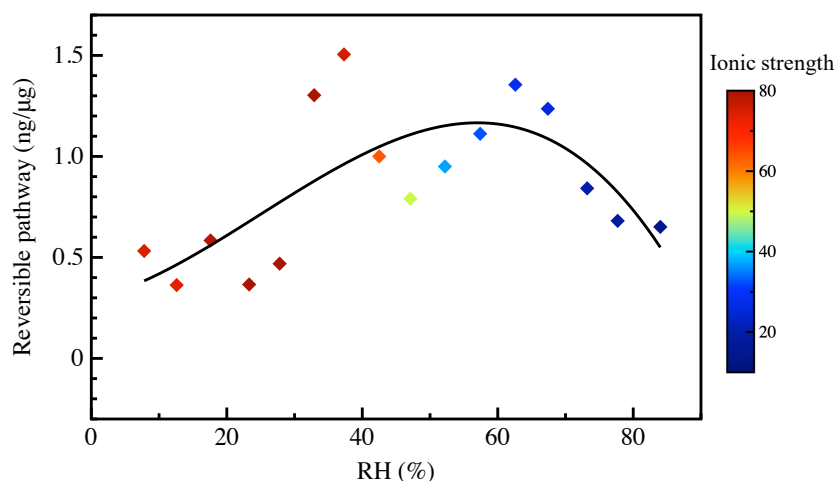
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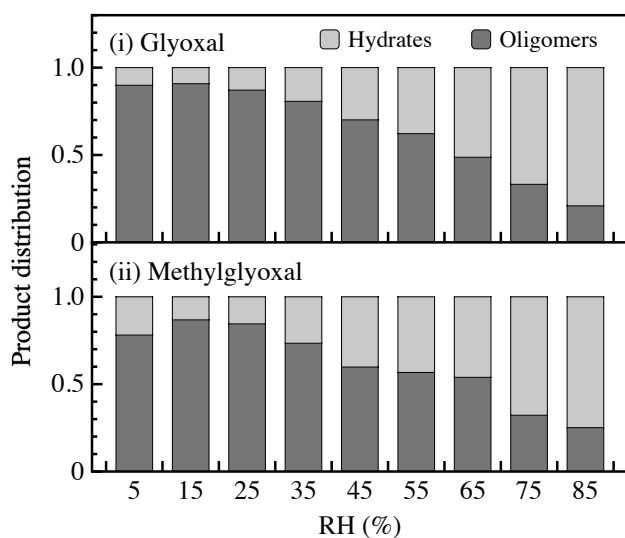
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684 Figure 1: Time series of meteorological parameters and gas- and particle-phase glyoxal and methylglyoxal observed in different
 685 seasons: (a) summer, 2019.07.20-2019.08.04; (b) winter, 2020.01.05-2020.01.19; (c) autumn, 2020.10.24-2020.11.07; (d)
 686 winter, 2021.01.08-2021.01.26; (e) spring, 2021.03.26-2021.04.06.

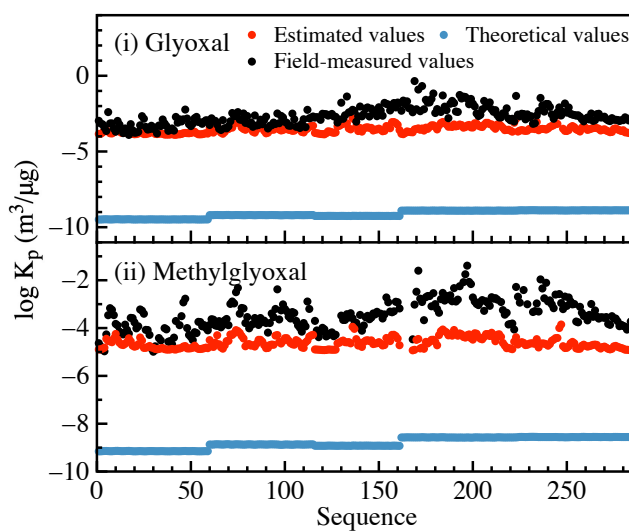
(a) RH dependence of dicarbonyl concentrations



(b) Product distribution

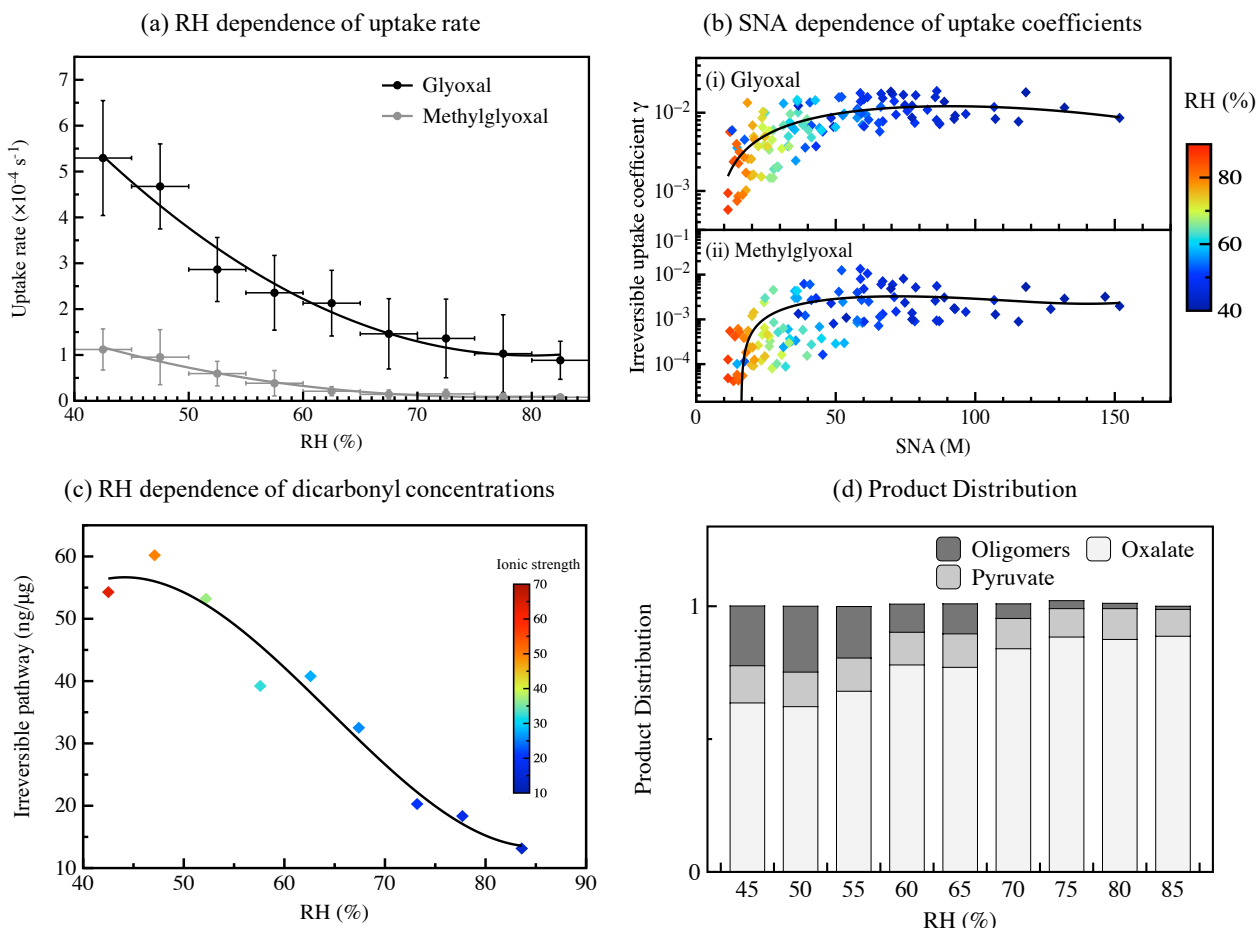


(c) Gas-particle Partitioning Coefficients



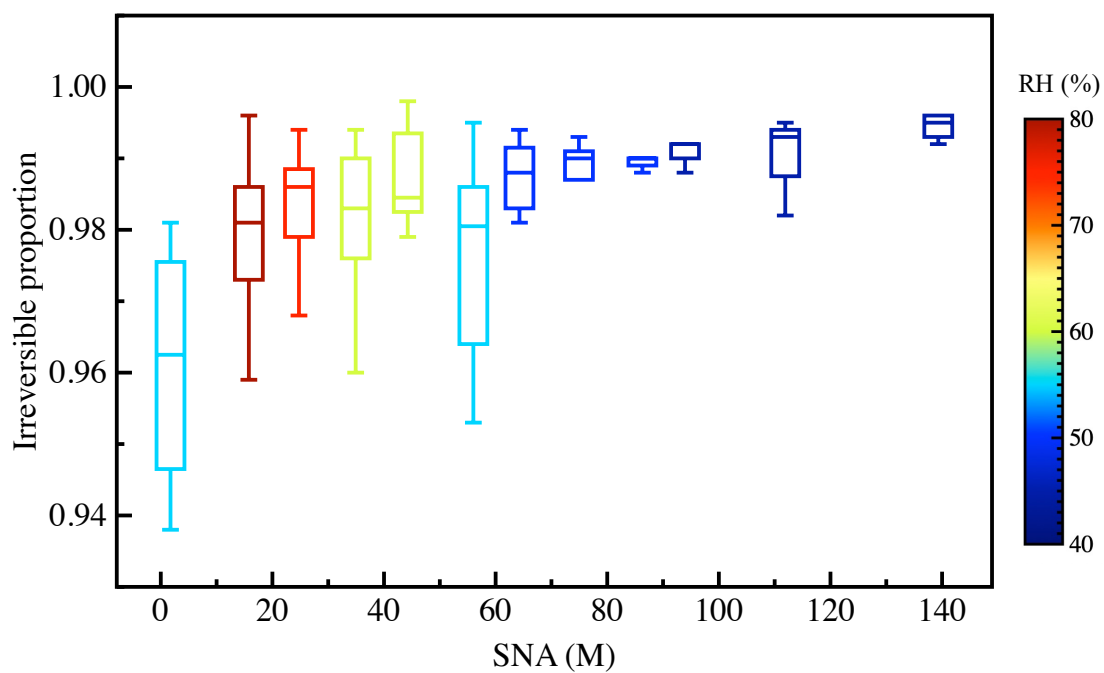
687

688 Figure 2: Gas-particle partitioning of dicarbonyls via reversible pathways. (a) The RH dependence of particulate
689 concentrations of dicarbonyl via reversible pathways. (b) The product distribution for (i) glyoxal and (ii) methylglyoxal under
690 different RH conditions. (c) The gas-particle partitioning coefficients for (i) glyoxal and (ii) methylglyoxal. The black, red,
691 and blue circles refer to field-measured values, estimated values by the proposed mechanism, and theoretical values calculated
692 by Pankow's absorptive model, respectively.



693

694 Figure 3: Gas-particle partitioning of dicarbonyls via irreversible pathways. (a) The RH dependence of irreversible uptake rate
 695 for glyoxal and methylglyoxal. (b) The SNA dependence of uptake coefficients for (i) glyoxal and (ii) methylglyoxal, SNA
 696 refers to the concentration of sulfate, nitrate and ammonia in wet aerosols. (c) The RH dependence of particulate concentrations
 697 of dicarbonyl via irreversible pathways. (d) The corresponding modeled product distribution in wet aerosols under different
 698 RH conditions.



699
 700 Figure 4: Correlation between the proportion of the irreversible pathway in gas-particle partitioning process for dicarbonyls
 701 and aqueous sulfate, nitrate, and ammonia (SNA) concentration in ambient aerosols under different relative humidity
 702 conditions.
 703

704 Table 1: Statistical data for the α -dicarbonyls in gas and particle phase in different seasons.

Season	Dates of the measurements	Gas phase (ppbv)		Particle phase (ng m ⁻³)	
		Glyoxal	Methylglyoxal	Glyoxal	Methylglyoxal
summer	2019.07.20-08.04	0.13 ± 0.07	0.87 ± 0.54	10.18 ± 6.63	9.50 ± 5.62
spring	2021.03.26-04.06	0.02 ± 0.02	0.12 ± 0.08	15.24 ± 17.50	6.07 ± 2.79
autumn	2020.10.24-11.07	0.07 ± 0.03	0.15 ± 0.09	9.33 ± 4.24	9.15 ± 3.62
winter	2020.01.05-01.19, 2021.01.08-01.26	0.06 ± 0.05	0.11 ± 0.09	28.77 ± 25.33	14.61 ± 10.15

705

706 Table 2: Comparison of the field-measured partitioning coefficient K^f values for the dicarbonyls and their corresponding
 707 theoretical K^t values in different seasons.

Coefficients	Dicarbonyl	Season	K^f		^a K^t	K^f / K^t
			Average	Range		
Gas-particle partitioning coefficients ($m^3 \cdot \mu g^{-1}$)	Glyoxal	summer	8.11×10^{-4}	$(1.25-58.6) \times 10^{-4}$	3.27×10^{-10}	2.48×10^6
		autumn	2.14×10^{-3}	$(2.61-224) \times 10^{-4}$	6.27×10^{-10}	3.41×10^6
		spring	1.43×10^{-2}	$(0.08-14.6) \times 10^{-2}$	5.59×10^{-10}	3.55×10^7
		winter	1.30×10^{-2}	$(0.067-44.2) \times 10^{-2}$	1.27×10^{-9}	1.02×10^7
	Methylglyoxal	summer	1.49×10^{-4}	$(0.833-169) \times 10^{-5}$	7.10×10^{-10}	2.10×10^5
		autumn	9.55×10^{-4}	$(0.65-86.9) \times 10^{-4}$	1.35×10^{-9}	7.07×10^5
		spring	1.06×10^{-3}	$(0.42-108) \times 10^{-4}$	1.21×10^{-9}	8.77×10^5
		winter	2.60×10^{-3}	$(0.34-410) \times 10^{-4}$	2.72×10^{-9}	9.93×10^5
Henry's law coefficients ($M \cdot atm^{-1}$)	Glyoxal	summer	1.96×10^8	$(1.71-167) \times 10^7$	3.29×10^5	6.11×10^2
		autumn	5.08×10^8	$(1.88-10.2) \times 10^8$	1.14×10^6	3.63×10^3
		spring	2.53×10^9	$(1.23-139) \times 10^8$	9.03×10^5	1.92×10^4
		winter	1.04×10^9	$(1.37-55.4) \times 10^8$	4.15×10^6	2.55×10^3
	Methylglyoxal	summer	4.92×10^7	$(1.70-363) \times 10^6$	2.73×10^3	1.88×10^4
		autumn	8.52×10^7	$(3.66-15.7) \times 10^7$	9.50×10^3	2.00×10^5
		spring	1.33×10^8	$(5.22-456) \times 10^6$	7.49×10^3	1.36×10^5
		winter	2.63×10^8	$(1.03-175) \times 10^7$	3.44×10^4	9.01×10^4

708 ^a Theoretical gas-particle partitioning coefficients were calculated on the basis of Eq. (3) and theoretical Henry's law
 709 coefficients here referred to the Henry's law constant in pure water, which were calculated on the basis of Eq.(S1)-(S2) (Ip et
 710 al., 2009; Sander, 2015).

711

712 Table 3: Summary of calculated uptake coefficients γ and effective uptake rate coefficient $k_{\text{eff, uptake}}$ in different seasons for
 713 glyoxal and methylglyoxal.

Dicarbonyl	Season	T (K)	RH (%)	$\gamma (\times 10^{-3})$			$k_{\text{eff, uptake}} (\text{s}^{-1})$ ($\times 10^{-4}$)
				Average	Min	Max	
Glyoxal	Summer	301.1	67.7	4.15	0.12	7.30	1.61
	Autumn	287.2	45.4	8.62	0.29	12.9	4.83
	Spring	289.4	54.0	11.7	1.24	14.9	6.85
	Winter	273.5	54.0	10.6	0.56	14.4	3.59
	^a General	287.8	59.0	8.0	0.46	11.4	3.38
Methylglyoxal	Summer	301.1	67.7	1.01	0.02	2.09	0.25
	Autumn	287.2	45.4	1.83	0.04	3.94	0.92
	Spring	289.4	54.0	2.36	0.06	4.34	0.69
	Winter	273.5	54.0	3.45	0.11	5.83	0.77
	^a General	287.8	59.0	2.0	0.05	3.8	0.55

714 ^aGeneral is the average value of all the samples observed in the five field observations.

715

716 Table 4: Calculated relative importance of reversible and irreversible pathways in the gas-particle partitioning processes and
 717 their contribution to the particulate matter.

Season	Glyoxal		Methylglyoxal		Contribution to particulate matters
	^a [X] _{P, rever}	^b [X] _{P, irrever}	^a [X] _{P, rever}	^b [X] _{P, irrever}	
Summer	0.17 (1.2%)	18.87 (98.8%)	0.25 (5.5%)	20.55 (94.5%)	3.98%
Autumn	0.14 (0.7%)	23.91(99.3%)	0.12 (0.8%)	17.02 (99.2%)	4.12%
Spring	0.26 (1.9%)	15.94 (98.1%)	0.09 (1.5%)	14.16 (98.5%)	3.05%
Winter	0.89 (7.1%)	34.70 (92.9%)	0.38 (7.2%)	12.59 (92.8%)	4.86%
^c General	0.43 (3.3%)	24.26 (96.7%)	0.25 (5.0%)	16.53 (95.0%)	4.15%

718 ^a [X]_{P, rever} is the concentration of particle-phase carbonyl via reversible pathway (ng·μg⁻¹) and its proportion (%).

719 ^b [X]_{P, irrever} is the concentration of particle-phase carbonyl via irreversible pathway (ng·μg⁻¹) and its proportion (%).

720 ^c General is the average value of all the samples observed in the five field observations.