

1 **Observational constraints on glyoxal production from isoprene**
2 **oxidation and its contribution to organic aerosol over the Southeast**
3 **United States**

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45 **Key Points**

- 46 • Box model simulated glyoxal production from three isoprene oxidation
47 mechanisms differ greatly
 - 48 • Aerosol uptake of glyoxal was constrained using airborne *in situ* measurements
49 and a global model
 - 50 • Model results show that glyoxal contributes 0-14% of SOA in the Southeast U.S.
51 during summer
- 52

53 **Abstract**

54 We use a 0-D photochemical box model and a 3-D global chemistry-climate model,
55 combined with observations from the NOAA Southeast Nexus (SENEX) aircraft
56 campaign, to understand the sources and sinks of glyoxal over the Southeast United
57 States. Box model simulations suggest a large difference in glyoxal production among
58 three isoprene oxidation mechanisms (AM3ST, AM3B, and MCM v3.3.1). These
59 mechanisms are then implemented into a 3-D global chemistry-climate model.
60 Comparison with field observations shows that the average vertical profile of glyoxal is
61 best reproduced by AM3ST with an effective reactive uptake coefficient γ_{glyx} of 2×10^{-3} ,
62 and AM3B without heterogeneous loss of glyoxal. The two mechanisms lead to 0-0.8 μg
63 m^{-3} secondary organic aerosol (SOA) from glyoxal in the boundary layer of the Southeast
64 U.S. in summer. We consider this to be the lower limit for the contribution of glyoxal to
65 SOA, as other sources of glyoxal other than isoprene are not included in our model. In
66 addition, we find that AM3B shows better agreement on both formaldehyde and the
67 correlation between glyoxal and formaldehyde ($R_{GF} = [\text{GLYX}]/[\text{HCHO}]$), resulting from
68 the suppression of δ -isoprene peroxy radicals ($\delta\text{-ISOPO}_2$). We also find that MCM v3.3.1
69 may underestimate glyoxal production from isoprene oxidation, in part due to an
70 underestimated yield from the reaction of IEPOX peroxy radicals (IEPOXOO) with HO_2 .
71 Our work highlights that the gas-phase production of glyoxal represents a large
72 uncertainty in quantifying its contribution to SOA.

73 **1 Introduction**

74 Glyoxal (CHOCHO) is one of the most abundant dicarbonyl compounds in the
75 atmosphere. Its sources include direct emissions from biofuel use and biomass burning,

76 and secondary production from oxidation of various volatile organic compounds (VOCs)
77 [*Fu et al.*, 2008; *Hays et al.*, 2002; *Myriokefalitakis et al.*, 2008]. Glyoxal has a lifetime
78 of about 1-3 hours against photolysis and oxidation by OH at midday [*Feierabend et al.*,
79 2009; *Volkamer et al.*, 2005; *Washenfelder et al.*, 2011]. It is highly water-soluble, with a
80 Henry's Law constant of $3.0 - 4.2 \times 10^5 \text{ M atm}^{-1}$ at 298 K [*Sander*, 2015]. In aerosol
81 water, the solubility increases rapidly at low salt concentrations (up to $5.0 \times 10^8 \text{ M atm}^{-1}$)
82 [*Kampf et al.*, 2013; *Waxman et al.*, 2015], due to the formation of glyoxal hydrate -
83 sulfate complexes ("salting-in") [*Kurtén et al.*, 2015]. However, this increase is inhibited
84 at high salt concentrations by the kinetic limitation of gas-particle partitioning [*Kampf et*
85 *al.*, 2013; *Knote et al.*, 2014]. Laboratory and field studies showed that glyoxal readily
86 undergoes heterogeneous uptake to aerosols and cloud droplets to form secondary
87 organic aerosol (SOA) [*Carlton et al.*, 2007; *Ervens et al.*, 2011; *Galloway et al.*, 2009;
88 *Galloway et al.*, 2011b; *Liggio et al.*, 2005a; b; *Lim et al.*, 2005; *Volkamer et al.*, 2007].

89 Glyoxal can provide important constraints on quantifying VOC emissions and
90 oxidation mechanisms. Observations from aircraft, ground and satellite show that glyoxal
91 is often highly correlated with formaldehyde (HCHO), another product of VOC oxidation
92 [*DiGangi et al.*, 2012; *Kaiser et al.*, 2015; *MacDonald et al.*, 2012; *Miller et al.*, 2014;
93 *Stavrakou et al.*, 2009; *Vrekoussis et al.*, 2010]. The ratio of glyoxal to formaldehyde
94 (surface or tropospheric column concentrations), R_{GF} , varies for different biogenic and
95 anthropogenic VOC precursors, so it can be used to quantify the source strength of local
96 VOC emissions [*DiGangi et al.*, 2012; *Kaiser et al.*, 2015; *Miller et al.*, 2014; *Vrekoussis*
97 *et al.*, 2010]. The NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) dependence of R_{GF} , although it varies greatly
98 for different VOCs and may offer additional information on VOC oxidation [*DiGangi et*

99 *al.*, 2012; *Kaiser et al.*, 2015; *Vrekoussis et al.*, 2010]. Thus, it is important to evaluate
100 model performance on R_{GF} and its NO_x dependence on regional and global scales,
101 providing critical information for present and future satellite validation [*Vrekoussis et al.*,
102 2010].

103 Sources and sinks of glyoxal remain largely uncertain [*Ervens et al.*, 2011; *Fu et al.*,
104 2008; *Galloway et al.*, 2011a; *Myriokefalitakis et al.*, 2008; *Stavrakou et al.*, 2009;
105 *Volkamer et al.*, 2007; *Washenfelder et al.*, 2011]. Production from isoprene oxidation
106 represents a major source of glyoxal on the global scale [*Fu et al.*, 2008]. Chamber
107 experiments suggest a significant yield (up to 3%) of glyoxal from the first generation of
108 isoprene oxidation under high NO_x conditions (500 ppbv NO) [*Galloway et al.*, 2011a;
109 *Volkamer et al.*, 2006]. As we show below, this high yield may not reflect the distribution
110 of β - and δ -isoprene peroxy radicals (ISOPO_2) as a function of their lifetimes under
111 ambient conditions [*Peeters et al.*, 2014]. Another large uncertainty lies in the
112 heterogeneous loss of glyoxal to aerosols and cloud droplets, which contributes to SOA
113 mass. Laboratory studies indicate that the uptake of glyoxal depends on aerosol and cloud
114 composition [*Corrigan et al.*, 2008; *Jang et al.*, 2002; *Kroll et al.*, 2005; *Liggio et al.*,
115 2005a; b; *Nozière et al.*, 2009; *Volkamer et al.*, 2009; *Waxman et al.*, 2015], ambient
116 relative humidity (RH) [*Corrigan et al.*, 2008; *Hastings et al.*, 2005; *Kampf et al.*, 2013;
117 *Liggio et al.*, 2005a] and temperature [*Gomez et al.*, 2015]. By assuming irreversible
118 reactive uptake with an uptake coefficient $\gamma_{\text{glyx}} = 2.9 \times 10^{-3}$, *Fu et al.* [2008] found that
119 this process accounts for 14% of glyoxal loss globally. *Volkamer et al.* [2007] estimated
120 γ_{glyx} of 3.7×10^{-3} in Mexico City, where glyoxal contributes about 15% of ambient SOA.
121 A much lower γ_{glyx} (0.8×10^{-4} for the day and $(2 \pm 1) \times 10^{-4}$ for the night) was derived in

122 Los Angeles [*Washenfelder et al.*, 2011], where kinetic limitations at the high salt
123 concentrations likely reduce the rate of SOA formation [*Kampf et al.*, 2013; *Knote et al.*,
124 2014].

125 The Southeast Nexus (SENEX) aircraft campaign, which took place in June–July of
126 2013, aimed to improve the understanding of the interactions between biogenic and
127 anthropogenic emissions over the Southeast U.S. It provided a detailed characterization
128 of tropospheric photochemistry (gas and aerosol), including ozone, NO_y (NO , NO_2 and its
129 atmospheric oxidation products), biogenic VOCs (isoprene, terpene), isoprene oxidation
130 products and organic aerosols [*Warneke et al.*, 2016]. In particular, glyoxal was measured
131 on board the NOAA WP-3D aircraft using a cavity enhanced absorption spectroscopy
132 technique [*Min et al.*, 2015], and formaldehyde was measured using laser induced
133 fluorescence technique [*Cazorla et al.*, 2015]. These measurements provide an
134 unprecedented opportunity to examine the sources and sinks of glyoxal in this region, as
135 well as its contribution to SOA mass.

136 Here we first examine the glyoxal yield from isoprene oxidation in a box model with
137 three chemical mechanisms (AM3ST, AM3B, and the Master Chemical Mechanism
138 v3.3.1 [*Jenkin et al.*, 2015]). We then use field observations from the SENEX field
139 campaign, interpreted with a chemistry-climate model, to understand the sources and
140 sinks of glyoxal over the Southeast U.S. The comparison of the model to high resolution
141 aircraft data for both glyoxal and formaldehyde provides important new constraints on
142 the potential for glyoxal to form SOA, but also highlights uncertainty in the mechanism
143 for isoprene oxidation, the single largest source of glyoxal in the Southeast U.S.

144 **2 Methods**

145 AM3 is the atmospheric component of the Geophysical Fluid Dynamics
146 Laboratory (GFDL) coupled model CM3. The dynamical core, physical
147 parameterizations, cloud and precipitation processes, and cloud-aerosol interactions in
148 AM3 are described in detail in *Donner et al.* [2011]. Chemistry in a previous version of
149 AM3 has been described by *Naik et al.* [2013]. In this work, we nudge the horizontal
150 wind field in the model toward values from the NCEP Global Forecast System (GFS),
151 allowing the model to simulate synoptic conditions corresponding to those sampled
152 during field campaigns [*Lin et al.*, 2012]. We also apply finer vertical grids for
153 convection plumes than the standard AM3 to improve the wet removal of tracers during
154 summer time [*Paulot et al.*, 2015]. The photolysis module has been updated to Fast-JX
155 v7.1 (<ftp://128.200.14.8/public/prather/Fast-J>), to compute the impacts from aerosols and
156 clouds interactively. Dry deposition velocities prescribed in the model reflect rapid dry
157 deposition of oxidized organic compounds [*Nguyen et al.*, 2015].

158 Biogenic emission of isoprene is computed using the Model of Emissions of Gases
159 and Aerosols from Nature (MEGAN) inventory [*Guenther et al.*, 2006], with a total 15.9
160 Tg C in North America in June-August of 2013, which is slightly higher than previous
161 estimates of 12.2-14.6 Tg C (June-August of 2006) in the same region [*Millet et al.*,
162 2008]. We reduce the isoprene emissions estimated by MEGAN by 20% (to 12.7 Tg C),
163 to be consistent with other estimates of isoprene emission over the Southeast U.S.
164 [*Warneke et al.*, 2010]. We do not consider glyoxal production from oxidation of terpenes
165 and aromatics in this work, as their contribution is relatively small compared to isoprene
166 over the Southeast U.S. [*Kaiser et al.*, 2015]. Inclusion of larger isoprene emissions and

167 other VOC sources would proportionally increase the magnitude of glyoxal sinks derived
168 in the analysis below. Anthropogenic emissions in 2013 follow the Representative
169 Concentration Pathway 8.5 (RCP 8.5) projection [Lamarque *et al.*, 2011]. We applied
170 diurnal variation anthropogenic NO_x emissions in North America following Mao *et al.*
171 [2013b]. Anthropogenic NO_x emissions in RCP 8.5 are 0.34 Tg N/month over North
172 America, comparable to the estimate from NEI 2011 of 0.29 Tg N/month [Travis *et al.*,
173 2015]. We reduce these anthropogenic NO_x emissions by 25% to 0.26 Tg N/month, to be
174 consistent with recent estimates in this region [Anderson *et al.*, 2014].

175 2.1 Isoprene chemistry

176 The standard isoprene mechanism used in AM3, “AM3ST”, is largely based on Mao
177 *et al.* [2013b] following chamber observations from Paulot *et al.* [2009a; 2009b] and
178 Crouse *et al.* [2011]. The main features of this mechanism include: (1) substantial yield
179 (7%) of first generation organic nitrates from δ -ISOPO₂, compared to 4.7% from β -
180 ISOPO₂; (2) detailed assignment of the fate of first- and second-generation organic
181 nitrates; and (3) isomerization of ISOPO₂ using the laboratory-determined rate constants.
182 We further update this chemistry in several aspects. First, we assume a 25% molar yield
183 of glyoxal from ISOPO₂ isomerization as the first-generation product [Marais *et al.*,
184 2016]. Second, the reaction of ISOPO₂ with HO₂ is updated following St. Clair *et al.*
185 [2016a] to reflect a higher yield of unsaturated hydroxy hydroperoxides (ISOPOOH)
186 (94%). Third, we adopt a new methylvinyl ketone (MVK) oxidation chemistry in which
187 the glycolaldehyde molar yield is increased from 0.53 to 0.72 under high NO_x conditions
188 [Praske *et al.*, 2015]. Fourth, we include fast photolysis of carbonyl organic nitrates
189 [Miller *et al.*, 2014]. Fifth, we adopt a substantially slower ozonolysis rate of isoprene β -

190 hydroxy nitrate (ISOPNB, 3.7×10^{-19} molec⁻¹cm³s⁻¹ [Lee *et al.*, 2014]) than the previous
191 value from Lockwood *et al.* [2010] (1.06×10^{-16} molec⁻¹cm³s⁻¹). Lastly, we update the
192 NO₃-initiated chemistry of isoprene following MCM v3.2 [Jenkin *et al.*, 1997; Saunders
193 *et al.*, 2003]. As illustrated in Figure S1, glyoxal is produced in the first generation of
194 isoprene oxidation, both from the decomposition of alkoxy radical (DIBOO shown in
195 Figure S1) through the δ -channel under high NO_x conditions [Peeters and Nguyen, 2012],
196 and from isomerization of ISOPO₂ under low NO_x conditions [Stavrakou *et al.*, 2010].
197 Glyoxal is further produced in later generations from oxidation of carbonyl compounds
198 including glycolaldehyde and isoprene epoxydiol (IEPOX).

199 In this work, we introduce an additional mechanism, “AM3_beta” (AM3B), to reflect
200 more recent updates to the understanding of isoprene oxidation. Both theoretical and
201 experimental studies indicate that β - and δ -ISOPO₂ undergo fast interconversion [Bates *et*
202 *al.*, 2014; Crouse *et al.*, 2011; Peeters *et al.*, 2014]. One important implication is that
203 oxidation products observed in experimental chambers at ~500 ppbv NO may not reflect
204 the products in ambient air where NO is several orders of magnitude lower. This is due to
205 a higher fraction of δ -ISOPO₂ loss via bimolecular reactions than interconversion back to
206 β -ISOPO₂ under high NO_x conditions. To reflect this change, we only allow β -ISOPO₂ to
207 react with NO because δ -ISOPO₂ is believed to only account for < 3% of total ISOPO₂
208 under ambient conditions [Peeters *et al.*, 2014]. The yield of β -hydroxyl isoprene nitrate
209 (ISOPNB) is assumed to be 0.1, an average of the suggested values 0.09 [Xiong *et al.*,
210 2015] and 0.16 [Teng *et al.*, 2015]. The yields of HCHO, MVK and methacrolein
211 (MACR) from β -ISOPO₂ + NO are adjusted accordingly for carbon balance. As we show

212 below, this update changes the production of formaldehyde and glyoxal under high NO_x
213 conditions.

214 The Leeds Master Chemical Mechanism (MCM) is a near-explicit chemical
215 mechanism that describes gas-phase VOC chemistry. The latest revision, v3.3.1, includes
216 recent updates for OH-initiated isoprene chemistry [Jenkin *et al.*, 2015], such as isoprene-
217 peroxy radical interconversion and isomerization pathways [Peeters *et al.*, 2014], and the
218 chemistry of IEPOX [Bates *et al.*, 2014; Paulot *et al.*, 2009b]. Consequently, these
219 updates show significant differences in simulated HO_x (HO_x = OH + HO₂), NO_x and
220 major oxidation products compared to earlier versions of MCM. To evaluate the
221 performance of MCM v3.3.1 in our global model, we implement a MCM-like mechanism
222 (‘AM3M’) by adjusting the production of glyoxal from major pathways in the AM3B
223 mechanism, to approximate the glyoxal and HCHO yields of MCM v3.3.1 in a highly
224 condensed chemical mechanism suitable for use in a global model (Figure S2).

225 2.2 Heterogeneous loss of glyoxal and methylglyoxal

226 Heterogeneous loss onto aerosols and cloud droplets plays an important role in the
227 fate of dicarbonyls. Here we assume this process is irreversible and can be represented by
228 a first-order reactive uptake rate constant k [Mao *et al.*, 2010]

$$k = \left(\frac{a}{D_g} + \frac{4}{v\gamma} \right)^{-1} A$$

229 where a is the effective radius of aerosols or cloud droplets, D_g is the gas phase
230 diffusion constant, γ is the reactive uptake coefficient, A is the surface area of aerosols
231 or cloud droplets, and v is the mean molecular velocity of the gas molecule.

232 We allow this process to take place on five types of aerosols including sulfate, black
233 carbon (BC), primary organic carbon (POC), sea salt, mineral dust and SOA, with
234 hygroscopic growth included [Mao *et al.*, 2013a]. Given the large uncertainties associated
235 with the uptake of glyoxal, we use field observations to assess the possible range of γ_{glyx} .
236 We do not include glyoxal uptake by cloud droplets in this work, because the uptake
237 coefficient by aerosols is much greater, and because large uncertainties are associated
238 with mixing of cloudy and no-cloud volumes within a grid box [Huijnen *et al.*, 2014;
239 Jacob, 2000]. We include heterogeneous loss of methylglyoxal with an uptake coefficient
240 of 7.6×10^{-3} [Zhao *et al.*, 2006], to produce better closure with total organic aerosol (OA)
241 in the model.

242 The irreversible surface uptake coefficient, γ_{glyx} applied here should be viewed as an
243 “effective reactive uptake coefficient”, to simply represent the net heterogeneous loss of
244 glyoxal that does not revert back to the gas-phase, and provide an estimate for its
245 contribution to SOA mass on the regional scale. Previous studies have indicated that this
246 process is likely reversible to some extent [Galloway *et al.*, 2009; Kroll *et al.*, 2005]. We
247 show below that the values of γ_{glyx} are dependent on the choice of gas-phase chemistry.

248 **3 NO_x-Dependent Glyoxal and HCHO Yields**

249 We first conduct box model simulations to quantify the yield of glyoxal and HCHO
250 from isoprene oxidation as a function of NO_x levels, using the Dynamically Simple
251 Model of Atmospheric Chemical Complexity (DSMACC) [Emmerson and Evans, 2009].
252 We test three mechanisms (AM3ST, AM3B, and MCM v3.3.1) in the model. The model
253 is initialized at 8:00 local time (LT) for mid-latitude summer conditions, with 1 ppbv of

254 isoprene, 60 ppbv of ozone, 150 ppbv of CO, and a choice of 0.01, 0.1 or 1 ppbv of NO_x.
255 While NO_x is held constant, isoprene is allowed to decay over time. Figure 1 shows the
256 cumulative yields of glyoxal and HCHO per unit carbon from isoprene oxidation at
257 various NO_x levels after three days of model integration with their loss processes turned
258 off [Palmer *et al.*, 2003]. We also use tagged tracers for individual pathways (β/δ -
259 ISOPO₂ + NO, ISOPO₂ + HO₂, isomerization of ISOPO₂) to compute their contribution in
260 each mechanism.

261 A striking difference between the MCM v3.3.1 and AM3 mechanisms is the glyoxal
262 production under low NO_x conditions. While the AM3 mechanisms show a large yield of
263 glyoxal from isomerization of ISOPO₂ and the oxidation of IEPOX (via the ISOPO₂ +
264 HO₂ pathway), MCM v3.3.1 shows very little production of glyoxal from these channels.
265 For the isomerization pathway, MCM v3.3.1 assumes 50% of 1,6-H shift isomerization
266 flux produces hydroperoxy-aldehydes (HPALDs), with another 50% produces complex
267 dihydroperoxy formyl peroxy radicals, referred as “di-HPCARPs” by *Peeters et al.*
268 [2014]. MCM v3.3.1 includes low production of glyoxal from the degradation of
269 HPALDs and di-HPCARPs. On the other hand, the AM3 mechanisms do not include di-
270 HPCARPs, and assume fast photolysis as the only loss process of HPALDs, with prompt
271 yield of glyoxal following *Stavrakou et al.* [2010].

272 Another large difference in glyoxal yield comes from the treatment of the ISOPO₂ +
273 HO₂ pathway, particularly regarding the fate of IEPOX. MCM v3.3.1 assumes a major
274 production of organic peroxides from the reaction of IEPOX peroxy radicals (IEPOXOO)
275 (α -carbonyl peroxy radicals) with HO₂, while AM3 mechanisms follow *Paulot et al.*
276 [2009b] and assume full radical propagation for this reaction, with a 28% yield of glyoxal.

277 As a result, a much higher yield of glyoxal is predicted from the ISOPO₂ + HO₂ pathway
278 in the AM3 mechanisms compared to MCM v3.3.1. In fact, several studies have
279 confirmed significant OH production from the reaction of HO₂ with α-carbonyl peroxy
280 radicals [Dillon and Crowley, 2008; Hasson et al., 2004; Jenkin et al., 2007]. This is also
281 consistent with recent studies of IEPOX kinetics, which show very little formation of
282 peroxides under low NO_x conditions [Bates et al., 2014; Jacobs et al., 2013].

283 Under high NO_x conditions, the three mechanisms show better agreement for glyoxal
284 production, though with different pathways contributing. MCM v3.3.1 shows a dominant
285 production from the β-ISOPO₂ + NO pathway, mainly due to a higher yield of glyoxal
286 from oxidation of glycolaldehyde (20%), based on Niki et al. [1987]. An even higher
287 yield of glyoxal (29%) was adopted by Galloway et al. [2011a]. In contrast, the AM3
288 mechanisms apply a lower yield of glyoxal (13%) following Butkovskaya et al. [2006].
289 Surprisingly, both AM3ST and AM3B show significant production from isomerization of
290 ISOPO₂ and the ISOPO₂ + HO₂ pathway, suggesting the potential importance of these
291 channels for glyoxal production even under high NO_x conditions. AM3ST has a major
292 production from the δ-ISOPO₂ + NO pathway, leading to 60% higher glyoxal yield than
293 AM3B. MCM v3.3.1 shows a small contribution from the δ-ISOPO₂ + NO channel, due
294 to a small fraction of δ-ISOPO₂ in the radical pool of ISOPO₂ (< 3%). This reflects a
295 different distribution of δ-ISOPO₂ and β-ISOPO₂ under ambient conditions vs. very high
296 NO chamber conditions [Peeters et al., 2014], consistent with our assumption in AM3B.
297 Overall, the AM3 mechanisms show decreasing glyoxal production with increasing NO_x
298 concentration, whereas MCM v3.3.1 shows the opposite.

299 The HCHO yield and its NO_x dependence appear to be more consistent across the
300 different mechanisms. Under low NO_x conditions, isomerization of ISOPO₂ and the
301 ISOPO₂ + HO₂ pathway contribute most to HCHO. At NO_x = 1 ppbv, the ISOPO₂ + NO
302 pathway becomes the primary source of HCHO. The HCHO yield in AM3B is 17%
303 higher than AM3ST and comparable to MCM v3.3.1, mainly due to a higher HCHO yield
304 from the β-ISOPO₂ + NO pathway than the δ-ISOPO₂ + NO pathway. It should be noted
305 that the cumulative yields shown in Figure 1 represent the potential glyoxal and HCHO
306 produced from sufficient oxidation of 1 ppbv isoprene and the intermediate VOCs. This
307 is different from ambient conditions that isoprene is continuously emitted and the
308 production of glyoxal and HCHO are dependent on OH levels (i.e. the production rate of
309 ISOPO₂). Chemical loss of HCHO and glyoxal are similar across the mechanisms (Table
310 S1).

311 The NO_x dependent yields of glyoxal and HCHO from box model results are useful to
312 identify their major production pathways at different NO_x levels. This knowledge can be
313 translated to 3D model outputs and help evaluate model performance from these
314 pathways using aircraft observations.

315 **4 Observational Constrains on Glyoxal Production**

316 4.1 Vertical profiles of gaseous and particulate species

317 We compare the AM3 model predictions for glyoxal, formaldehyde, and isoprene
318 oxidation products to measurements of these species acquired during the SENEX field
319 campaign. All measurements are averaged to 1 minute time resolution. The measurement
320 accuracies for isoprene, formaldehyde, NO_x, glyoxal, organic aerosol and aerosol surface

321 area are 25%, 10%, 5%, 5.8%, 50%, and 36% respectively ([*Warneke et al.*, 2016] and
322 the references therein). Although other carbonyl compounds have recently been found to
323 suffer from inlet artifacts arising from catalytic conversion of organic hydroperoxides on
324 metal inlet surfaces [*Rivera-Rios et al.*, 2014], we do not expect such interferences for
325 glyoxal since no metal surfaces are present in the glyoxal sampling line [*Min et al.*, 2015],
326 and since there are currently no known mechanisms for conversion of hydroperoxides to
327 glyoxal. We also expect little interferences for formaldehyde since its residence time
328 during exposure to metal surfaces is very small [*Cazorla et al.*, 2015], This is confirmed
329 by recent laboratory tests, suggesting the interference is < 5% for this specific instrument
330 [*St. Clair et al.*, 2016b]. We exclude biomass burning, urban plumes, stratospheric air
331 ($\text{CH}_3\text{CN} \geq 225$ pptv, $\text{NO}_x/\text{NO}_y > 0.4$ or $\text{NO}_2 > 4$ ppbv or $\text{O}_3/\text{CO} > 1.25$ mol/mol,
332 respectively) from our analysis following *Hudman et al.* [2007], and omit data from the
333 Ozark Mountains, where the model shows a significant positive bias for isoprene (Figure
334 S3). We also exclude nighttime flights from our analysis.

335 Figure 2 shows the mean vertical profiles of observed and modeled isoprene, glyoxal,
336 HCHO and other related species during SENEX. Model output is sampled along the
337 flight tracks and at the flight time with 1 hour time resolution. We include two model
338 simulations (AM3ST and AM3B). MCM v3.3.1 is not included because of its complexity.
339 Instead, we show AM3M in our global model as a proxy to MCM v3.3.1 in the following
340 sections. Simulated NO_x agrees with the observations at all altitudes except for a slight
341 overestimate (~20%) near the surface. Observed isoprene concentration peaks near the
342 surface at 1.2 ppbv and decreases gradually with altitude. Both AM3ST and AM3B show
343 a positive bias of isoprene below 1 km, but no such bias is evident for HCHO. As HCHO

344 in this region is dominantly produced from isoprene and has a relatively longer lifetime
345 than that of isoprene (4 h vs. < 1 h), we attribute this positive bias of modeled isoprene
346 partly to sampling bias and partly to shallow boundary layer and slow vertical mixing in
347 the current model. We further examine modeled OH and J values using ICARTT (2004)
348 [Mao *et al.*, 2013b] and NOMADSS (2013)
349 (https://www.eol.ucar.edu/field_projects/nomadss) field observations over the eastern
350 U.S., and we find that the model agrees with observed OH and J values within 20%
351 (Figure S4 and S5).

352 Like isoprene, both HCHO and glyoxal decrease with altitude, reflecting their short
353 photochemical lifetimes (4 h and 3.5 h) and their dominant source from isoprene. Our
354 model is able to reproduce their vertical gradients, although the vertical profiles of
355 HCHO and glyoxal appear to be sensitive to the choice of photochemical mechanisms.
356 AM3ST underestimates HCHO by 32% and overestimates glyoxal almost by a factor of
357 two near the surface. With the suppression of δ -ISOPO₂ in AM3B, HCHO is increased by
358 17% and glyoxal is decreased by 38% near the surface, leading to better agreement with
359 observations for both species.

360 The abundance of glyoxal is also dependent on its heterogeneous loss. By assuming
361 an irreversible reactive uptake on aerosols, an optimal value of γ_{glyx} is selected to
362 minimize the difference between modeled and observed glyoxal in the boundary layer.
363 We find that the best agreement is achieved for AM3ST with γ_{glyx} of 2×10^{-3} and for
364 AM3B with γ_{glyx} of zero (Table S2); we adopt those values in the following analysis.

365 γ_{glyx} derived with AM3B is lower than the value from previous laboratory
366 experiments (2.9×10^{-3} by *Liggio et al.* [2005b]), likely due to two reasons. First, there
367 could be a missing source of gas-phase glyoxal in the current mechanism, which can be
368 compensated by aerosol uptake and lead to a higher contribution to SOA formation. We
369 find that approximate 30% increase of glyoxal production in AM3B would be required to
370 compensate aerosol uptake of glyoxal with $\gamma_{\text{glyx}} = 2.9 \times 10^{-3}$. Second, the effective aerosol
371 uptake coefficient, as we assumed here to represent the net heterogeneous loss of glyoxal,
372 is indeed smaller than the value from the previous study. One possibility is that the
373 aerosol uptake of glyoxal is to some extent reversible [*Galloway et al.*, 2009; *Kroll et al.*,
374 2005], which would lead to a lower estimate of γ_{glyx} . Another possibility is the
375 suppression of glyoxal loss to ambient aerosols that are internally mixed with organic and
376 inorganic components, resulting from its organic coating [*Galloway et al.*, 2011b]. It is
377 also possible that additional production of glyoxal in the particle-phase from other
378 organic compounds reduces the net loss of glyoxal to the aerosol surface. In fact, the
379 negligibly small uptake coefficients of glyoxal ($0-8 \times 10^{-4}$ during the daytime and (2 ± 1)
380 $\times 10^{-4}$ during the nighttime) have also been determined from analysis of glyoxal
381 observations in a previous field study in Los Angeles during the CalNex field campaign
382 [*Washenfelder et al.*, 2011].

383 Overall, the resulting average contribution of glyoxal to organic aerosols is about 0.8
384 $\mu\text{g m}^{-3}$ for AM3ST (Figure S7) and negligible for AM3B in the boundary layer over the
385 Southeast U.S. We emphasize that this is likely the lower limit of glyoxal SOA, as other
386 glyoxal sources such as anthropogenic VOCs and monoterpenes, are not included in our
387 model. Accounting for these additional sources would require a higher sink of glyoxal,

388 and therefore results in higher glyoxal SOA. The estimate from AM3ST is comparable to
389 previous model studies over the same region assuming reversible or irreversible reactive
390 uptake of glyoxal onto aerosols [*Knote et al.*, 2014; *Li et al.*, 2015; *Ying et al.*, 2015],
391 while AM3B is not. We also find that the inclusion of IEPOX aerosol uptake may reduce
392 glyoxal in the boundary layer by less than 15% over the Southeast U.S. (Figure S8). This
393 would lead to an even lower estimate of glyoxal SOA.

394 4.2 R_{GF} and its dependence on NO_x

395 Comparison of modeled and observed R_{GF} provides additional constraint on the gas-
396 phase chemistry for glyoxal production. Figure 3 shows the co-variation of glyoxal and
397 formaldehyde in the boundary layer during SENEX. The linear regression slope (R_{GF})
398 derived from observations is 2.4% ($R^2=0.61$) in the boundary layer over the Southeast US,
399 suggesting that the dominant source of both glyoxal and formaldehyde in this region is
400 isoprene [*Kaiser et al.*, 2015]. The AM3ST mechanism overestimates R_{GF} by a factor of
401 two, while better agreement is achieved by the AM3B mechanism, due to the suppressed
402 production of glyoxal and enhanced production of HCHO. Simulations with both
403 mechanisms significantly underestimate the range of HCHO concentrations observed.
404 Without heterogeneous loss of glyoxal, the model with AM3ST significantly
405 overestimates R_{GF} but predicts a similar result as assuming no heterogeneous loss of
406 glyoxal with AM3B.

407 We further examine the NO_x dependence of HCHO, glyoxal and R_{GF} during SENEX
408 (Figure 4). A prominent feature of Figure 4 is the high similarity between the observed
409 NO_x -dependence of HCHO and glyoxal. Both HCHO and glyoxal are observed to

410 increase with NO_x concentrations and to start to level off at 1 ppbv of NO_x . Remarkably,
411 R_{GF} shows little variation across NO_x concentrations, consistent with *Kaiser et al.* [2015].
412 Both AM3ST and AM3B are able to reproduce the NO_x dependence of HCHO, although
413 they tend to underestimate HCHO by 1-2 ppbv across NO_x regimes, consistent with
414 *Wolfe et al.* [2016]. AM3B shows better agreement with observations than AM3ST at
415 high NO_x level, indicating δ -channel is suppressed under ambient conditions. Using the
416 optimized γ_{glyx} values described above (2×10^{-3} for AM3ST and zero for AM3B), our
417 model can roughly capture the NO_x dependence of glyoxal. In contrast to Figure 1,
418 neither AM3ST nor AM3B shows high glyoxal concentrations under low NO_x conditions,
419 reflecting slower production of glyoxal under such conditions due to low OH radical
420 concentrations and slow ISOPO_2 production rate in the ambient atmosphere [*Wolfe et al.*,
421 2016]. Although the NO_x dependent HCHO and glyoxal are individually captured
422 qualitatively, a large positive bias in R_{GF} is apparent for AM3ST across NO_x regimes and
423 for AM3B at $\text{NO}_x < 0.5$ ppbv. We attribute the bias in AM3ST to the overestimate of
424 glyoxal under low NO_x and underestimate of HCHO across NO_x regimes. The bias in
425 AM3B is mainly due to the underestimate of HCHO.

426 To examine the NO_x dependence of HCHO, glyoxal and R_{GF} from MCM v3.3.1, the
427 AM3M mechanism that mimics MCM v3.3.1 is then tested in our AM3 global model.
428 Comparison to the SENEX data (Figure 4) shows that AM3M can also well reproduce the
429 NO_x dependence of HCHO, similar to the performance of other AM3 mechanisms.
430 However, AM3M largely underestimates glyoxal and R_{GF} across all NO_x levels,
431 suggesting additional sources of glyoxal needed in the current MCM mechanism.
432 Inclusion of heterogeneous loss of glyoxal would further reduce glyoxal in AM3M and

433 worsen the comparison. One possible reason for the underestimate of glyoxal in AM3M
434 is the lack of a radical propagating channel for the IEPOXOO + HO₂ reaction in MCM
435 v3.3.1, as described above.

436 R_{GF} provides a useful tool to estimate global production of glyoxal from isoprene
437 oxidation. In particular, the fact that R_{GF} is insensitive to NO_x allows us to directly
438 compute its global production rate. Assuming 0.4 HCHO yield per isoprene C (Figure 1,
439 also consistent with *Palmer et al.* [2003]) and a global constant R_{GF} of 2.4% (according to
440 the measurements during SENEX), we can derive the global production of 23 Tg glyoxal
441 with 500 Tg isoprene emitted annually [*Guenther et al.*, 2006]. This is similar to a
442 previous estimate of 21 Tg yr⁻¹ glyoxal from isoprene [*Fu et al.*, 2008].

443 **5 Budget of Glyoxal in North America**

444 Table 1 summarizes the monthly averaged glyoxal budget over North America
445 (20°~55°N, 60°~130°W) in the boundary layer (0-1.5 km) during June-July of 2013 for
446 AM3ST and AM3B. The total chemical production of glyoxal varies with the chemical
447 mechanisms, from 0.32 Tg/month with AM3B to 0.44 Tg/month with AM3ST. The
448 major sink of glyoxal with both mechanisms is photolysis, followed by aerosol uptake
449 and OH oxidation for AM3ST and OH oxidation and aerosol uptake for AM3B, although
450 the contribution of each pathway varies with mechanisms and γ_{glyx} . For example, in
451 AM3ST, heterogeneous loss is an important sink, accounting for 26% of the total
452 chemical loss of glyoxal; however, the contribution is negligible in the AM3B
453 simulations. Deposition accounts for only 1-2% of total glyoxal loss in the model. We

454 show in this work that the estimates of sources and sinks of glyoxal are dependent on the
455 choice of gas-phase chemistry.

456 **6 Conclusions and Discussion**

457 A 0-D photochemical box model and a 3-D chemistry-climate model applied to data
458 from the Southeast U.S. during the SENEX field campaign provide the first model
459 evaluation of *in situ* glyoxal aircraft observations.

460 We find that the three mechanisms (AM3ST, AM3B, and MCM v3.3.1) show
461 similarity in HCHO but large differences in glyoxal, leading to opposite NO_x dependence
462 of R_{GF} . Under low NO_x conditions, the AM3 mechanisms predict much higher glyoxal
463 yields than MCM v3.3.1, largely due to the significant contribution from isomerization of
464 ISOPO₂ and oxidation of IEPOX via the ISOPO₂+HO₂ pathway. Although the three
465 mechanisms agree better under high NO_x conditions, they show different pathways
466 contributing to glyoxal production.

467 With the constraints from field measurements during SENEX, AM3ST with an
468 effective reactive uptake coefficient γ_{glyx} of 2×10^{-3} and AM3B without heterogeneous
469 loss of glyoxal can best reproduce the observed vertical profile. The latter shows better
470 agreement with observed R_{GF} in the boundary layer. These two choices lead to less than
471 $0.8 \mu\text{g m}^{-3}$ or negligible of glyoxal SOA in the boundary over the Southeast U.S.,
472 accounting for 0-14% of the total SOA in this region (Figure S7). These are likely the
473 lower limit of glyoxal SOA due to missing sources of glyoxal that are not included in our
474 model. Over North America, glyoxal sinks are dominated by photolysis, followed by

475 aerosol uptake and OH oxidation for AM3ST and OH oxidation and aerosol uptake for
476 AM3B. Dry and wet deposition are negligible for both AM3 versions (Table 1).

477 In the boundary layer, observations suggest a very similar NO_x dependence for
478 HCHO and glyoxal, resulting in a nearly constant R_{GF} across NO_x levels [Kaiser *et al.*,
479 2015]. Both AM3ST and AM3B can roughly capture the NO_x dependence of HCHO and
480 glyoxal, although AM3ST tends to overestimate R_{GF} at all NO_x regimes, likely due to the
481 overestimate of glyoxal at low NO_x and underestimate of HCHO across NO_x regimes.
482 AM3B shows a positive bias in R_{GF} at $\text{NO}_x < 0.5$ ppbv due to insufficient production of
483 HCHO. The MCM v3.3.1 like mechanism (“AM3M”) shows a large underestimate of
484 glyoxal across all NO_x levels. One possible reason is the lack of a radical propagating
485 channel for the IEPOXOO + HO₂ reaction in MCM v3.3.1.

486 While glyoxal has been studied extensively over the past decade to understand the
487 magnitude of its heterogeneous uptake, we show here that its gas-phase production is a
488 large source of uncertainty that requires equal consideration. We find that its production
489 from isoprene oxidation varies greatly among different chemical mechanisms. This in
490 turn greatly impacts global estimates of glyoxal and in particular its contribution to SOA,
491 especially in regions with low to moderate NO_x levels (Figure 1). Under high NO_x
492 conditions, models differ significantly in the production of glyoxal from oxidation of
493 glycolaldehyde, as well as the fate of δ -ISOPO₂. Under low NO_x conditions, there is very
494 little laboratory evidence available on the production of glyoxal from IEPOX, HPALDs,
495 di-HPCARPs or other intermediate products. Although heterogeneous loss of IEPOX is
496 not included in current work, sensitivity tests show that inclusion of this uptake reduces
497 glyoxal concentrations by 10-20% for the mean vertical profile over the Southeast U.S.

498 Thus, the fate of IEPOX represents another mechanistic uncertainty for predicting
499 glyoxal. Also, there are missing sources that are not represented in our model [*Volkamer*
500 *et al.*, 2015] would increase modeled glyoxal and thus also inferred SOA. Future
501 laboratory measurements are urgently needed and may have important implications for
502 understanding the contribution of glyoxal to SOA in past and future atmospheres.

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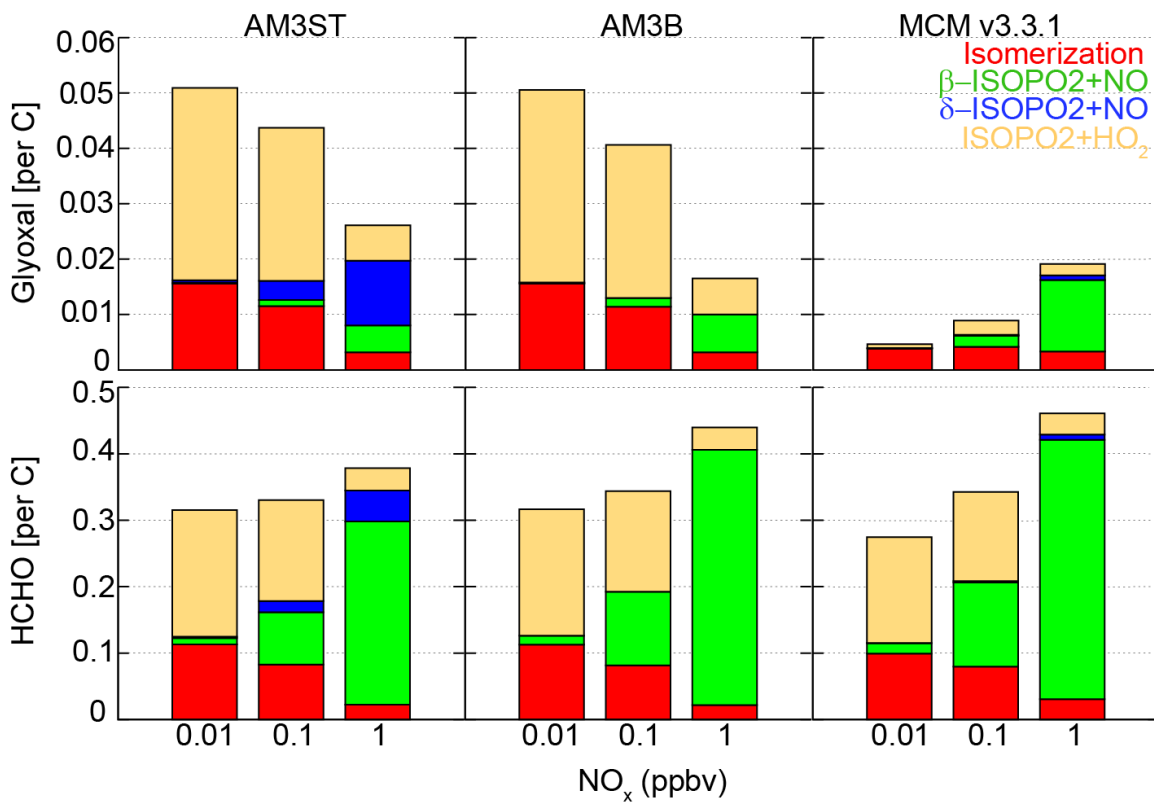
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832 **Table 1.** Budget of glyoxal over North America (20 ~55 °N, 60 ~130 °W) below 1.5 km
 833 in June-July of 2013. Percentage is the contribution of each pathway to the total chemical
 834 loss of glyoxal.

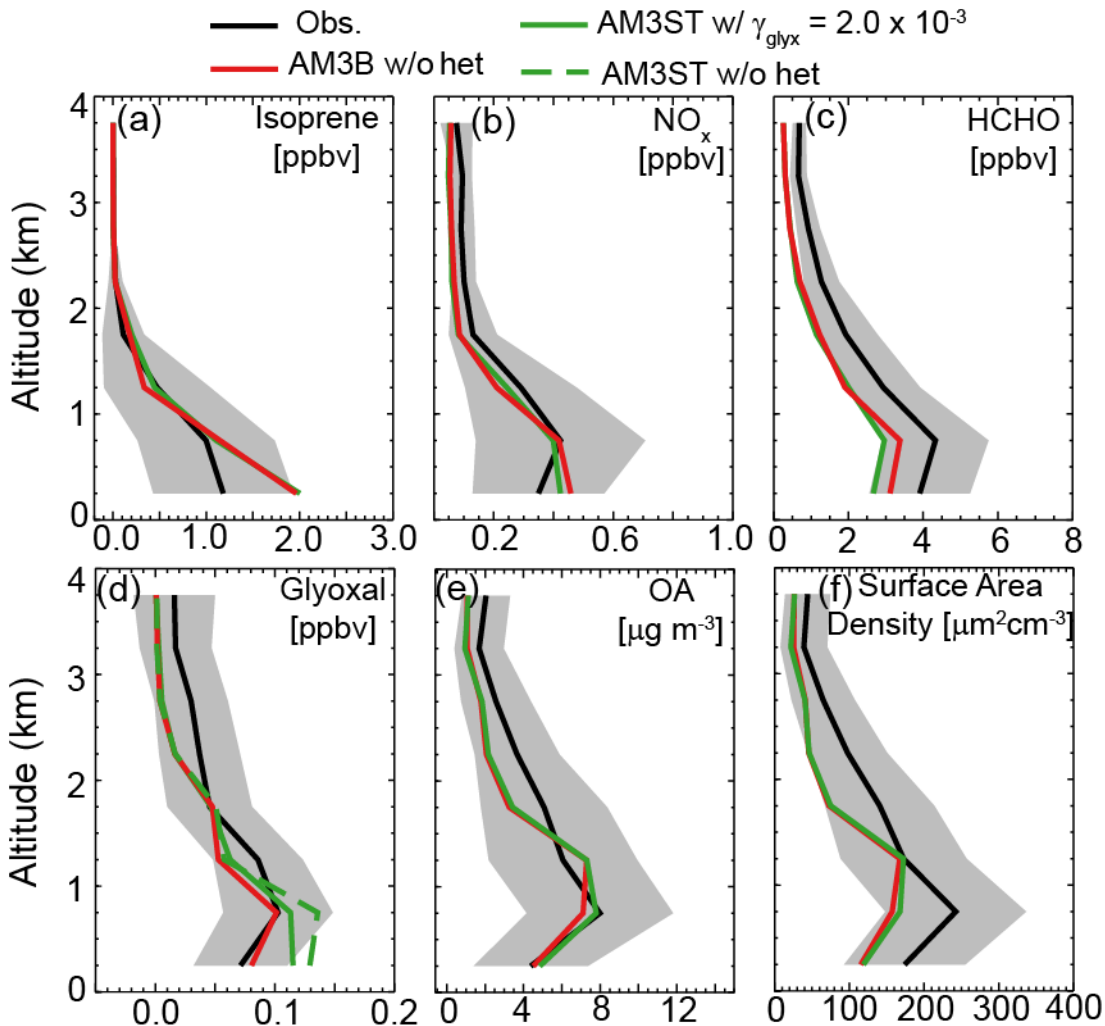
	AM3ST	AM3B
$\gamma_{\text{glyx}} (\times 10^{-3})$	2.0	0
Production (Tg/month)	0.44	0.32
Chemical Loss (Tg/month)	0.41	0.29
Photolysis	57%	77%
OH	17%	23%
Uptake by Aerosols	26%	–
Dry Deposition (Tg/month)	1.2×10^{-2}	1.2×10^{-2}
Wet Deposition (Tg/month)	1.1×10^{-2}	1.6×10^{-2}

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837 **Figure 1.** Cumulative yields of glyoxal and HCHO in major pathways from isoprene
 838 oxidation at different NO_x levels. Glyoxal and HCHO from isoprene oxidized by O_3 and
 839 by NO_3 are not shown due to low production in all the mechanisms.



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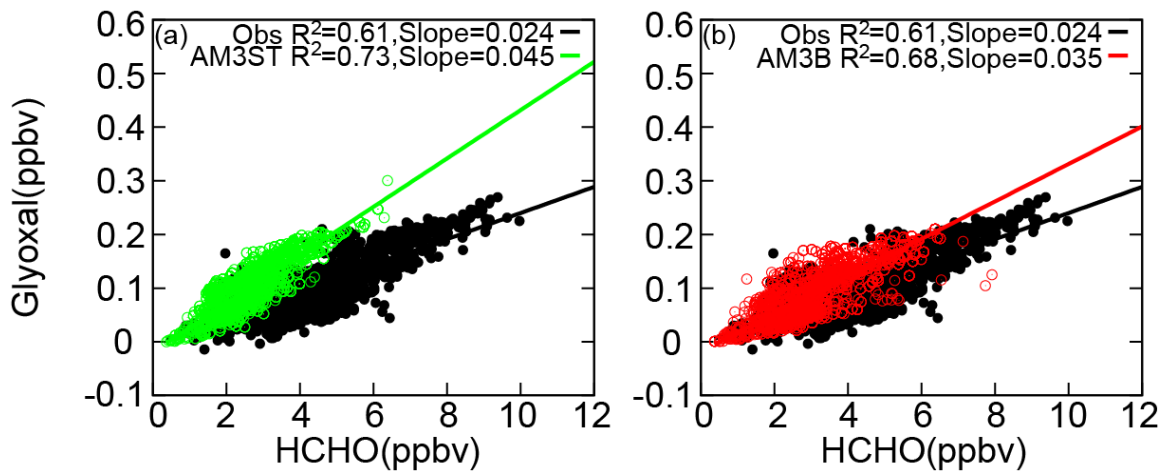
842 **Figure 2.** Mean vertical profiles of isoprene, formaldehyde, NO_x , glyoxal, organic

843 aerosol (OA) and surface area density of aerosol during SENEX. Grey shades are the

844 standard deviation (σ) of the averaged profiles of the measured tracers. Dashed green line

845 in panel (d) is model estimate without heterogeneous loss of glyoxal by AM3ST.

Observed organic aerosol mass and aerosol surface area density are from dry particles.



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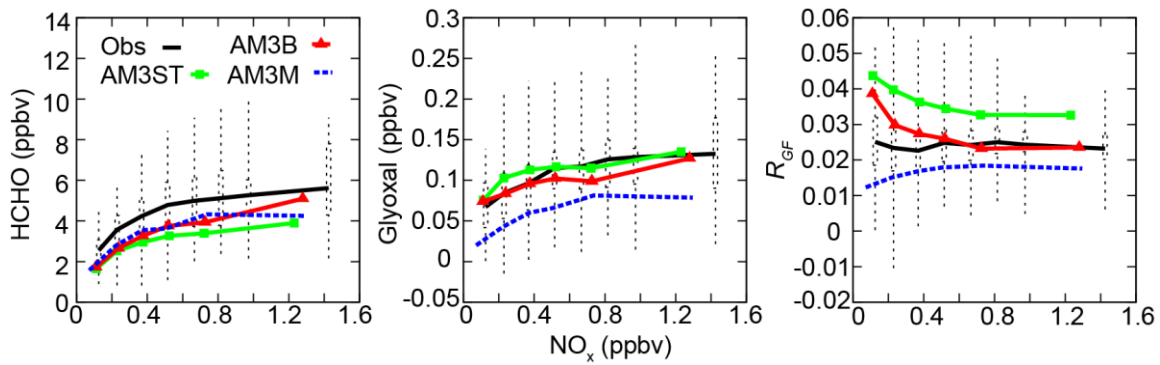
847

848 **Figure 3.** Correlation between glyoxal and formaldehyde below 1.5 km during SENEX.

849 Black dots represent observations, while green and red open circles show AM3ST with

850 $\gamma_{\text{glyx}} = 2.0 \times 10^{-3}$ (left) and AM3B without heterogeneous loss of glyoxal (right). Solid

lines are linear regression lines, with regression slopes calculated from least-squares fit.



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Figure 4. HCHO (ppbv), glyoxal (ppbv), and R_{GF} in each NO_x bin below 1.5 km during SENEX. Dots, dashed boxes and whiskers are the mean, interquartile range and lowest and highest of the observations; green squares and red triangles are the mean of AM3ST with $\gamma_{\text{glyx}}=2.0 \times 10^{-3}$ and AM3B without heterogeneous loss of glyoxal respectively; blue dashed lines are the mean of AM3M without heterogeneous loss of glyoxal.