

# COLUMBIA UNIVERSITY

IN THE CITY OF NEW YORK

DEPARTMENT OF CHEMICAL ENGINEERING

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Dear Manabu,

We thank you for the opportunity to respond to the reviewers' comments and submit a revised version of our manuscript acp-2018-51, entitled "Technical note: Updated parameterization of the reactive uptake of glyoxal and methylglyoxal by atmospheric aerosols and cloud droplets." We have revised the manuscript based on the reviewers' comments and we feel that it has become stronger as a result. Our conclusions remain the same.

The most significant change to the manuscript, which was requested by both reviewers, is that we have expanded our discussion of the dependence on the reactive uptake coefficients on particle composition, and the apparent dependence on calculated aerosol pH. Aerosol pH is not an independent parameter in our calculations, but rather a calculated output of ISORROPIA II as a function of input aerosol composition and RH. Furthermore, the mass transfer and reactive loss processes considered in our calculations are not explicitly pH dependent. Therefore, we interpret this apparent dependence on pH to be reflective of pH being a proxy for variations in solute concentration in the aerosol with varying aerosol liquid water content. For these reasons, we changed the wording in the abstract and elsewhere in the manuscript where it was previously said that  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  were calculated as a function of pH since this is not strictly correct, and may be misleading for readers. We include a parameterization for the dependence of  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  on pH at the request of the reviewers, but we have kept it in the Supporting Information. We note that all variations in  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  as a result of varying SNA aerosol composition or pH are incorporated in the error bars shown in the top panels of Figures 1 and 2, and therefore accounted for in the weighted least squares fits, and the uncertainty ranges provided in the parameterizations in Tables 4 and 5.

We attach our point-by-point response to the reviewers' comments, along with versions of the revised manuscript and supporting information with changes highlighted. I note that, since the manuscript was finalized after the responses to the reviewers were uploaded on 6/7/2018, there are some minor differences between the final revised manuscript and the descriptions of the changes made to the manuscript in the response documents.

We hope that you find this revised manuscript suitable for publication in *ACP*.

Best Regards,

*Faye*

Prof. V. Faye McNeill ([vfm2103@columbia.edu](mailto:vfm2103@columbia.edu))

Reviewer comments are copied below. Our responses are written below each comment in blue font.

### REVIEWER 1

General comments: Curry et al. present updated values for reactive uptake of glyoxal and methylglyoxal for use in models. These are based on RH parameterizations of maritime and remote aerosols and clouds that are comprised of sodium chloride or mixtures of ammonium nitrate and ammonium sulfate. These parameterizations are based on recent (bulk and aerosol) laboratory data that have probed gas-particle partitioning as a function of pH and aerosol or bulk solution chemical composition. This work will result in a more accurate reflection of SOA formed from the water-soluble aldehydes glyoxal and methylglyoxal. I have a few comments, but recommend publication in ACP after minor changes.

We thank the reviewer for the overall positive comments.

Specific comments:

1. Methods and Data: Statistical analysis and parameter estimation: It should be clarified in this section (rather than 3.2) that the authors also tested pH and aerosol chemical composition and the results of those are in the SI.

Thanks for this suggestion. The title of the subsection "Particle types" has been modified to "Particle types and composition" and we have inserted the sentence "Calculated results for  $\gamma_{\text{GLY}}$  and  $\gamma_{\text{MGLY}}$  as a function of S:A and S:N are available in the Supporting Information" after the sentence describing the particle types and composition and RH ranges considered. As discussed below, the results as a function of pH are now discussed separately in section 3.

2. Methods and Data: Calculating the Henry's constant: clarify that the  $K_{\text{H,w}}$  values are the effective Henry's law constants that incorporate hydration.

The sentence "Note that the  $K_{\text{H}}$  values are effective Henry's constants which account for hydration of the carbonyl species upon uptake." has been added after the introduction of  $K_{\text{H}}$  in equation (3).

3. Section 3.2: It looks as though there is a strong correlation of  $\gamma_{\text{GLY}}$  with pH in Fig. S1 so it is not clear how the authors determined that pH is not necessary.

The reviewer is correct, there is a correlation of  $\gamma_{\text{GLYX}}$  with pH in figure S1. In this study, variation in aerosol pH was not controlled independently, but rather it developed from the variation in S:N and S:A. Since the correlation with S:N and S:A was not strong, and aerosol pH is not a variable in GEOS-Chem, we chose not to address this dependence in the original manuscript. Since we see the value of providing this information despite its lack of direct applicability to GEOS-Chem simulations, we now discuss this data in more detail and include parameterizations for  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  as functions of pH.

4. Figure 1 and Figure 2: The "average  $\gamma_{\text{GLYX}}$ " and "average  $\gamma_{\text{MGLY}}$ " values are recommended due to large scatter and lack of correlation with RH. What "average" are the authors referring to? The black line does not appear to be the mean of the  $\gamma_{\text{GLYX}}$  or  $\gamma_{\text{MGLY}}$  values.

The statistical analysis and parameter estimation is described in section 2. The averages were obtained via weighted linear least squares regression, so points with lower uncertainty were given more weight in

the average, and the average does not lie in the middle of all of the points. We have added a parenthetical note to make this more clear: “The scatter in the calculated  $\gamma_{\text{GLYX}}$  led to a low-confidence result from the weighted least squares regression. For this reason, we recommend use of the average  $\gamma_{\text{GLYX}}$  value (obtained via weighted linear least squares regression, with slope = 0) in lieu of a parameterization (Table 4).”

Minor comments:

5. Introduction: Work by David De Haan’s group should also be cited for brown carbon formation, e.g.: Powelson et al. (2014) ES&T “Brown carbon formation by aqueous-phase aldehyde reactions with amines and ammonium sulfate”

This reference, as well as a reference to De Haan et al. ES&T 52 (7) 4061-4071 (2018) have been added.

6. Atmospheric Implications: Consider citing Sareen et al. (2017) ES&T, “Potential of Aerosol Liquid Water to Facilitate Organic Aerosol Formation: Assessing Knowledge Gaps about Precursors and Partitioning” as salting constants were included in this work and they do find that methylglyoxal is a minor contributor as Curry et al. predict.

We now mention and cite this study: “The reduced contribution of MGLY to aqueous SOA formation due to salting out is consistent with the calculations of Sareen et al. (2017).”

7. Figure S1: consider changing y-axis to  $\gamma_{\text{GLYX}}$  for consistency with the main text.

The change has been made.

8. References: check for formatting issues (e.g. “Henry ‘s Law” in Aster et al., “ChemPhysChem” in Herrmann et al., “(NH<sub>4</sub>(+))” in Nozière et al., etc.)

We have checked the reference list and made corrections where necessary. ChemPhysChem is the correct name of the journal in the Herrmann et al. (2010) reference.

Reviewer comments are copied below. Our responses are written below each comment in blue font.

## REVIEWER 2

This technical note describes the calculation of uptake coefficients for glyoxal and methylglyoxal based on measured values for Henry's Law coefficients as a function of various salt concentrations and on modeled values for OH radical concentrations in cloudwater and aqueous aerosol. These uptake coefficients are sorely needed, and this note is sure to be of value to the field. The results and methods are clearly described and presented.

We thank the reviewer for this overall positive assessment.

The authors at one point compare their calculated uptake coefficients for glyoxal on SNA aerosol at 50% RH to laboratory measurements on ammonium sulfate aerosol at 55% RH by Liggio et al.(1). The new, calculated results are high by a factor of three, which seems like reasonable agreement in this field.

We actually had not done the comparison mentioned by the reviewer, and it is an interesting suggestion. Since the dependence on relative humidity is strong near 50% RH (see Figure 1 top panel), if you use our SNA parameterization for glyoxal from Table 4 and plug in 55% RH, the result is  $\gamma_{\text{GLYX}} = 3.6 \times 10^{-3}$ , which is only 24% higher than the experimental value of Liggio et al. We now mention this in the Atmospheric Implications section: "The values we calculated under many conditions are lower than those currently used in large-scale models such as GEOS-Chem. However, we note that the parameterization presented in Table 4 at the experimental conditions of Liggio et al. (2005), 55% RH, yields  $\gamma_{\text{GLY}} = 3.6 \times 10^{-3}$ , which is within 24% of their experimental value ( $2.9 \times 10^{-3}$ )."

However, values used for certain parameters are not given, and I have two concerns about the scope of the conclusions.

### Specific Comments

This study appears to take into account only one kind of irreversible reactivity: oxidation by dissolved OH radicals. Can the authors justify that this reaction is more important than all other irreversible aqueous-phase reactions involving dissolved dicarbonyls, such as organosulfate formation, or the non-radical reactions with ammonium sulfate that the authors have studied in the past? I think it is unlikely that using effective Henry's law coefficients, even ones that include salting in / salting out effects, accounts for all of these processes, and the authors allude to this problem in the final paragraph. Given this problem, could the authors be getting reasonably accurate results for glyoxal uptake for the wrong reasons (due to a second error pushing the results in the opposite direction of the first)? It would be helpful to discuss this limitation and the magnitude of the uncertainties more thoroughly to help readers better interpret the results.

We chose to focus on reactive uptake driven by OH oxidation since this is the dominant irreversible loss process for GLYX and MGLY in aqueous aerosols and cloud droplets. This reaction is the initiation step for most radical-based chemistry of GLYX and MGLY in the aqueous phase, including organic acid formation and organosulfate formation (McNeill et al., 2012; Perri et al., 2010). Other irreversible loss processes such as imidazole formation occur at much longer timescales (Teich et al., 2016; Yu et al., 2011). The consistency of our calculations with the experimental reactive uptake coefficient of Liggio at

al., a system in which the multiple aqueous-phase processes mentioned here were active, provides support for our approach. We have expanded our discussion of this matter in the text.

Finally, as we note in the final paragraph of the manuscript, “This representation of aqueous SOA formation by GLYX and MGLY, with the treatment of Henry’s constants described here, does not take into account the contribution of reversible uptake of GLYX, which could be a significant, although transient, source of aerosol mass under some conditions (McNeill et al., 2012; Woo and McNeill, 2015). The use of this parameterization together with simpleGAMMA (Woo and McNeill, 2015) would give representation of both aqSOA formation types by GLYX.”

Second, the authors have chosen to ignore the effects of sulfate / nitrate ratios, sulfate / ammonium ratios, and pH on glyoxal uptake coefficients and focus exclusively on the effects of relative humidity. Based on Figure S1, I acknowledge that RH appears to be more important than these other three factors. However, Figure S1 shows that sulfate / nitrate ratios, sulfate / ammonium ratios, and pH all have non-linear effects on glyoxal uptake that are as large as the effects of increasing the RH from 70 to 99%. In addition, the laboratory experiments of Liggio et al.<sup>1</sup> showed that glyoxal uptake coefficients depend on aerosol acidity. Just because these effects are non-linear does not mean that they can or should be ignored. In the manuscript, the single statement on p. 5 line 18 that discusses Figure S1 (“no clear correlation is apparent”) is at best an oversimplification, and might even be seen as misleading.

We agree with the reviewer that more discussion of the dependence of  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  on pH, S:N, and S:A is required. In this study, variation in aerosol pH was not controlled independently but rather it developed from the variation in S:N and S:A. Since the correlation with S:N and S:A was not strong, and aerosol pH is not a variable in GEOS-Chem, we chose not to address this dependence in the original manuscript. However, since we see the value of providing this information despite its lack of direct applicability to GEOS-Chem simulations, and we agree with the reviewer that not doing so may lead to misunderstanding, we now discuss this data in more detail and include parameterizations for  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  as functions of pH.

The dependence of  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  on S:N and S:A is, as the reviewer noted, weak compared to the dependence on RH and pH. Furthermore, the plots in Figure S1 show scatter and a lack of monotonicity in the dependence that suggest a lack of a mechanistic basis for the variation observed. As a result, we choose not to include these variables in the parameterization. The variation as a function of S:N and S:A is included in the error bars on the RH fits. We now discuss this in more detail in section 3.

#### Technical comments

While the reported parameter values seem reasonable, I was unable to find the values used for two key parameters: the accommodation coefficient ( $\alpha$ ) and the aqueous diffusion coefficients. Are the terms that include these parameters not very influential on the overall values calculated for the uptake coefficients?

Thank you for catching this omission, we have now included this information in section 2. The aqueous-phase diffusion coefficient used for glyoxal was  $D_{\text{aq}} = 10^{-9} \text{ m}^2/\text{s}$  and the accommodation coefficient used was  $\alpha = 0.02$ .  $D_{\text{aq}}$  does not vary much for small species, and this value is typical for small organics (Bird et al., 2006). This value of  $\alpha$  is an estimate based assuming that  $\alpha$  for GLY and MGLY are similar to that

of formaldehyde uptake to water (Jayne et al., 1992). As the reviewer suggests, the calculation is insensitive to within 10% for a 50% variation in  $\alpha$  for values of  $\gamma < 10^{-3}$ .

Abstract (line 12): I think that the statement “We take into account . . . aqueous-phase chemical kinetics” should be modified given the first concern described above. Only the chemical kinetics of oxidation reactions with OH are taken into account in this study, not the chemical kinetics of other irreversible reactions.

In response to this suggestion, we have modified this sentence to be more specific and accurate, replacing “aqueous-phase chemical kinetics” with “irreversible reaction of the organic species with OH in the aqueous phase”

### References

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# Technical note: Updated parameterization of the reactive uptake of glyoxal and methylglyoxal by atmospheric aerosols and cloud droplets

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## Abstract

We present updated recommendations for the reactive uptake coefficients for glyoxal and methylglyoxal uptake to aqueous aerosol particles and cloud droplets. The particle and droplet types considered were based on definitions in GEOS-Chem v11, but the approach is general. Liquid maritime and continental cloud droplets were considered. Aerosol types include sea salt (fine and coarse) with varying relative humidity and particle size, and sulfate/nitrate/ammonium as a function of relative humidity, and particle composition, ~~and aerosol pH~~. We take into account salting effects, aerosol thermodynamics, mass transfer, and ~~aqueous phase chemical kinetics~~ irreversible reaction of the organic species with OH in the aqueous phase. The new recommended values for the reactive uptake coefficients in most cases are lower than those currently used in large-scale models, such as GEOS-Chem. We expect application of these parameterizations will result in improved representation of aqueous secondary organic aerosol formation in atmospheric chemistry models.

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## 1 Introduction

The uptake and reaction of water soluble volatile organic compounds (VOCs) in cloud droplets and aerosol liquid water is likely a significant source of secondary organic aerosol (SOA) material (Carlton et al., 2008; Fu et al., 2009, 2008; McNeill, 2015; McNeill et al., 2012). These processes may be referred to, collectively, as aqueous SOA (or aqSOA) formation.

20 Glyoxal (CHOCHO, GLYX) and methylglyoxal (CH<sub>3</sub>C(O)CHO, MGLY) are both atmospherically abundant gas-phase oxidation products of multiple VOC precursors, including isoprene and toluene. Both GLYX and MGLY are water-soluble, GLYX more so than MGLY (Betters and Hoffmann, 1988; Zhou and Mopper, 1990). Taking into account salting effects, the effective Henry's Law constant for GLYX in aerosol water can be several orders of magnitude higher than that of MGLY, depending on the aerosol ionic content (Kampf et al., 2013; Waxman et al., 2015). As  $\alpha$ -dicarbonyl species, GLYX and MGLY exhibit similar aqueous-phase chemistry: they undergo reversible hydration and self-oligomerization (Ervens and Volkamer, 2010; Hastings et al., 2005; Sareen et al., 2010; Shapiro et al., 2009), they can be oxidized by aqueous-phase radicals to form organic acids or organosulfates (Carlton et al., 2007; Lim et al., 2013; Perri et al., 2010; Schaefer et al., 2012, 2015), and they can react with nitrogen-containing species to form brown carbon (De Haan et al., 2018; Lee et al., 2013; Maxut et al.,

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2015; Nozière et al., 2009; Powelson et al., 2014; Sareen et al., 2010; Schwier et al., 2010; Shapiro et al., 2009; Yu et al., 2011a).

GLYX and MGLY received significant attention in the atmospheric chemistry modelling community (Carlton et al., 2008; Fu et al., 2009, 2008) following early experimental demonstrations of their potential significance as aqSOA precursors (Carlton et al., 2007; Hastings et al., 2005; Kroll et al., 2005; Loeffler et al., 2006). Fu and co-workers predicted that uptake of GLYX and MGLY to low-level clouds was a significant source of organic aerosol over North America, with MGLY producing more than three times more SOA than GLYX (Fu et al., 2009). Carlton et al. (2008) found that including in-cloud aqSOA production by GLYX in CMAQ improved agreement with aircraft observations.

Since these initial studies, more information has become available regarding the gas-particle partitioning of glyoxal and methylglyoxal (Ip et al., 2009; Kampf et al., 2013; Waxman et al., 2015; Yu et al., 2011a) and their chemical processing in the aqueous phase, allowing a refinement of their representation in models.

Here, we calculate reactive uptake coefficients for glyoxal and methylglyoxal for several cloud and aerosol types for application in large-scale atmospheric chemistry modelling. We take into account salting effects, aerosol thermodynamics, mass transfer considerations, and aqueous phase chemical kinetics. We base our calculations on the cloud and aerosol types used in GEOS-Chem v11, so these recommendations can be applied directly to that model, but the approach is general.

## 2 Methods and Data

Following Hanson et al. (1994), the reactive uptake coefficient,  $\gamma$ , is calculated according to:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4H^*\mathbb{R}T\sqrt{k^l D_{aq}}} \left( \frac{1}{\coth q - 1/q} \right) \quad (1)$$

where  $\alpha$  is the mass accommodation coefficient,  $\omega$  is the gas-phase thermal velocity of the organic species,  $H^*$  is the effective Henry's Law constant (Schwartz, 1986),  $\mathbb{R}$  is the universal gas constant, T is temperature in Kelvin,  $k^l$  is the first order aqueous loss rate, and  $D_{aq}$  is the aqueous-phase diffusion coefficient for the organic. Particle radius,  $R_p$ , and in-particle diffusion limitations are taken into account through the parameter  $q = R_p/l$ , where  $l$  is the diffuso-reactive length:

$$l = \left( \frac{D_{aq}}{k^l} \right)^{1/2} \quad (2)$$

The aqueous-phase diffusion coefficient used for both GLYX and MGLY was  $D_{aq} = 10^{-9}$  m<sup>2</sup>/s.  $D_{aq}$  does not vary much for small species, and this value is typical for small organics (Bird et al., 2006). The mass accommodation coefficient used was  $\alpha = 0.02$ . This value of  $\alpha$  is an estimate based on the assumption that  $\alpha$  values for GLYX and MGLY are similar to that of



formaldehyde uptake to water (Jayne et al., 1992). Following equation (1), the calculation is insensitive to within 10% for a 50% variation in  $\alpha$  for values of  $\gamma < 10^{-3}$ .

**Particle types and composition.** Although the approach described here is general, we applied it to the liquid cloud and aerosol particle types in GEOS-Chem v11. A complete listing can be found in the Supporting Information. Briefly, we considered marine and remote continental liquid cloud droplets, coarse and fine sea salt aerosol particles as a function of relative humidity, and sulfate/nitrate/ammonium (SNA) aerosols as a function of relative humidity, ~~pH~~, and composition. Calculated results for  $\gamma_{\text{GLY}}$  and  $\gamma_{\text{MGLY}}$  as a function of S:A and S:N, and calculated pH are available in the Supporting Information. Sea salt aerosols are assumed to be composed of 100% NaCl. The Windows stand-alone executable for ISORROPIA-II (Fountoukis and Nenes, 2007) was used in forward mode to calculate the equilibrium inorganic ion composition of the aerosols, in order to calculate the Henry's constant. The temperature was held constant at 280 K and calculations were performed for each of the desired relative humidities (99, 95, 90, 80, 70, 50 and 0%). Solid formation was suppressed (metastable mode). For the SNA aerosols, the amount of  $\text{NO}_3^-$  was held constant at  $2 \mu\text{mol}/\text{m}^3$  air, while the  $\text{SO}_4^{2-}$  and  $\text{NH}_3$  amounts were each varied from 1-8  $\mu\text{mol}/\text{m}^3$ .

**Aqueous-phase reaction.** The formulation in eq (1) and (2) describes uptake due to irreversible aqueous-phase loss processes only. Based on our previous analysis of the system using the multiphase photochemical box model GAMMA, the dominant irreversible atmospheric aqueous-phase reactive process for GLYX and MGLY is reaction with OH (McNeill, 2015; McNeill et al., 2012). This reaction is the initiation step for most radical-based chemistry of GLYX and MGLY in the atmospheric aqueous phase, including organic acid formation and organosulfate formation (McNeill et al., 2012; Perri et al., 2010). Other irreversible loss processes, such as imidazole formation, occur on much longer timescales (Teich et al., 2016; Yu et al., 2011). Therefore, the aqueous loss is represented by the pseudo first order rate constant for the reaction between the organic species of choice and OH (i.e.,  $k^l = k_{\text{OH}}[\text{OH}]$ ). Reversible reactive processes, e.g. spontaneous hydration and self-oligomerization of glyoxal and methylglyoxal, which substantially promote uptake of GLYX and MGLY to the aqueous phase, may be taken into account by the use of an effective Henry's Law constant (McNeill et al., 2012). However, we note that the form of eq. 1 implies no uptake (reversible or irreversible) in the absence of OH.

Considerable uncertainty exists in the aqueous concentration of OH in cloudwater and especially aerosol particles. In order to calculate  $k^l$ , we use OH concentrations for maritime and remote continental clouds and aerosols following Herrmann et al. (2010) (Table 1). They reported a range of [OH] for each scenario calculated using the CAPRAM 3.0 model. This [OH] range was used to calculate the uncertainty in  $\gamma$ .

**Table 1. Mean values and range of in-particle hydroxyl radical concentrations, as reported by Herrmann et al., (2010).**

Cloud/aerosol type	Mean [OH] (M)	Max [OH] (M)	Min [OH] (M)
Maritime aerosols	$10^{-13}$	$3.3 \times 10^{-12}$	$4.6 \times 10^{-15}$
Remote aerosols	$3.0 \times 10^{-12}$	$8 \times 10^{-12}$	$5.5 \times 10^{-14}$
Maritime clouds	$2.0 \times 10^{-12}$	$5.3 \times 10^{-12}$	$3.8 \times 10^{-14}$
Remote clouds	$2.2 \times 10^{-14}$	$6.9 \times 10^{-14}$	$4.8 \times 10^{-15}$

5 **Calculating the Henry's constant.** The solubility of glyoxal and methylglyoxal in aqueous solutions depends on the salt content (Ip et al., 2009; Kampf et al., 2013; Waxman et al., 2015; Yu et al., 2011a). Glyoxal becomes more soluble with increasing salt concentration (i.e., it exhibits "salting in"), whereas the opposite is true for methylglyoxal (it "salts out"). Therefore, the Henry's constants for glyoxal and methylglyoxal are a function of particle type and liquid water content (and therefore relative humidity).

10 The Henry's constants are calculated for sea salt aerosols following Waxman et al. (2015) using the equation:

$$\log\left(\frac{K_{H,w}}{K_{H,NaCl}}\right) = K_{s,NaCl}c_{NaCl} \quad (3)$$

15 where  $K_{H,w}$  is the Henry's constant for pure water,  $K_{H,NaCl}$  is the Henry's constant for the salt-containing aerosol,  $c_{NaCl}$  is the NaCl concentration in molality as calculated using ISORROPIA-II, and  $K_{s,NaCl}$  is the salting constant (Table 2). **Note that the  $K_H$  values are effective Henry's constants, which account for hydration of the carbonyl species upon uptake.** Waxman and coworkers showed that salting constants were additive for a mixed  $(NH_4)_2SO_4/NH_4NO_3$  system, following:

$$\log\left(\frac{K_{H,w}}{K_{H,salt}}\right) = K_{s,(NH_4)_2SO_4}c_{(NH_4)_2SO_4} + K_{s,NH_4NO_3}c_{NH_4NO_3} \quad (4)$$

20 where  $K_{H,salt}$  is the Henry's constant for the salt mixture,  $c_{(NH_4)_2SO_4}$  and  $c_{NH_4NO_3}$  are the concentrations in molality and  $K_{s,(NH_4)_2SO_4}$  and  $K_{s,NH_4NO_3}$  are the salting constants. The sum of sulfate and bisulfate was used to calculate  $c_{(NH_4)_2SO_4}$ .

For cloud droplets,  $K_{H,w}$  is used due to the low ion concentrations in cloudwater (Ervens, 2015; McNeill, 2015).

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**Table 2. Reaction and mass transfer parameters**

Species	$k_{OH}$ ( $M^{-1} s^{-1}$ )	$K_{H,w}$ ( $M atm^{-1}$ )	$K_{s, NaCl}$ [1/m]	$K_{s, (NH_4)_2SO_4}$ [1/m]	$K_{s, NH_4NO_3}$ [1/m]
Glyoxal	$1.1 \times 10^9$ <sup>a</sup>	$3.5 \times 10^5$ <sup>c</sup>	-0.10 <sup>e</sup>	-0.24 <sup>d</sup>	-0.07 <sup>e</sup>
Methylglyoxal	$7 \times 10^8$ <sup>b</sup>	$3.71 \times 10^3$ <sup>c</sup>	0.06 <sup>e</sup>	0.16 <sup>e</sup>	0.075 <sup>e</sup>

a (Schaefer et al., 2015)

b (Schaefer et al., 2012)

c (Betterton and Hoffmann, 1988)

5 d (Kampf et al., 2013)

e (Waxman et al., 2015)

**Statistical analysis and parameter estimation.** The calculated reactive uptake coefficient,  $\gamma$ , for MGLY and GLYX and each  
 10 particle type was parameterized as a function of relative humidity via weighted least squares regression. Assuming that the  
 errors in the reactive uptake coefficients are log-normally distributed, a covariance matrix for the model parameters was  
 calculated based on the mean square errors of the data and the design matrix of the linear regression. The standard deviations  
 of the model parameters were then determined from the diagonal of the covariance matrix (Aster et al., 2005). Student's t-tests  
 were then performed on each model parameter for the hypothesis that the model parameter in question is equivalent to zero in  
 15 order to assess the necessity of each parameter. The nonzero model parameter was kept for t-tests in which there was at least  
 98% confidence that the hypothesis of the model parameter being zero could be rejected.

### 3 Results and Discussion

The reactive uptake coefficient,  $\gamma$ , was calculated for MGLY and GLYX as a function of [OH], RH, particle size, and in the  
 case of SNA aerosol, particle composition. Calculated values of  $\gamma$  varied over several orders of magnitude. In most cases these  
 20 values are lower than those previously used to model reactive uptake of these species in large-scale models.

#### 3.1 Liquid cloud droplets.

The results for marine and remote continental cloud droplets are shown in Table 3 with the mean value and error bars given.  
 The uncertainty reflects the uncertainty in [OH].  $\gamma_{MGLY}$  is lower than  $\gamma_{GLYX}$  by a factor of roughly 100 in each case, consistent  
 25 with its lower  $K_{H,w}$  and  $k_{OH}$ .

**Table 3. Recommended  $\gamma$  for liquid cloud droplets.** Cloud types and size as defined in GEOS-Chem v11.

Cloud type	$R_{\text{eff}}$ ( $\mu\text{m}$ )	$\gamma_{\text{GLYX}}$	$\gamma_{\text{MGLY}}$
Marine	10	$7.5 \times 10^{-4}$ (+0.001, $-7.4 \times 10^{-4}$ )	$5.7 \times 10^{-6}$ (+ $9.4 \times 10^{-6}$ , $-5.6 \times 10^{-6}$ )
Remote continental	6	$4.3 \times 10^{-6}$ (+ $9.2 \times 10^{-6}$ , $-3.4 \times 10^{-6}$ )	$3.2 \times 10^{-8}$ (+ $6.7 \times 10^{-8}$ , $-2.5 \times 10^{-8}$ )

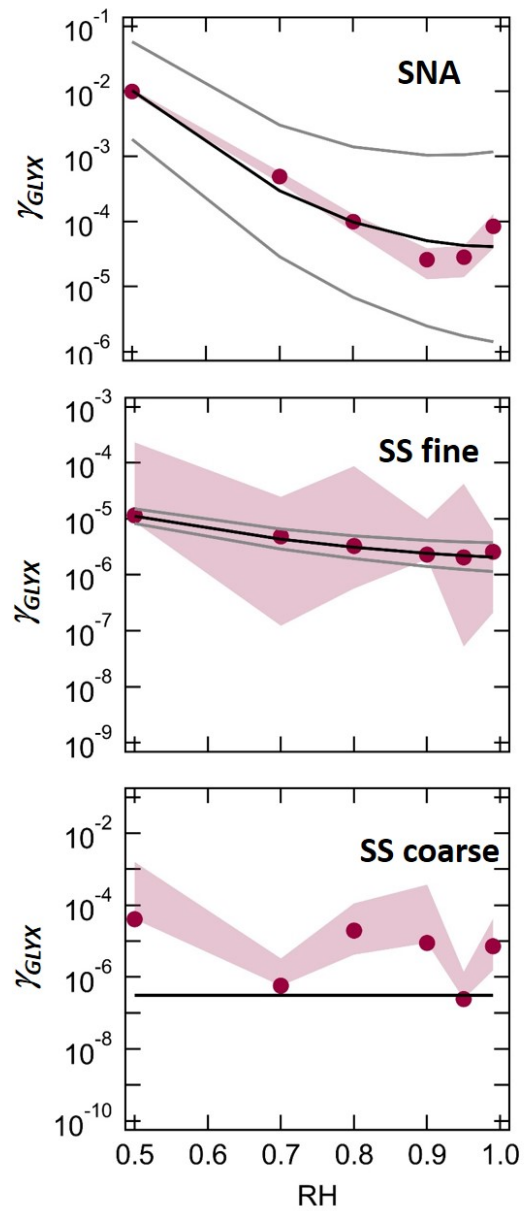
### 3.2 Aerosols.

5 For aerosols, the reactive uptake coefficients were found to vary significantly with RH due to salting effects. ~~No clear correlation of  $\gamma$  with S:A, S:N or aerosol pH is apparent (see Supporting Information). Therefore, in developing the parameterization, we examine the dependence of each reactive uptake coefficient on RH only.~~

Figure 1 shows calculated values of  $\gamma_{\text{GLYX}}$  for the three particle types as a function of RH. The range of uncertainty in the calculated values, indicated by the red shading, is due to the uncertainty in [OH] (Table 1), and in the case of SNA aerosols,  
 10 variations due to the different aerosol compositions tested. The black lines indicate the weighted least squares fit to the data, and the grey lines indicate the confidence interval for the fit. The average values and the results of the least squares fits are summarized in Table 4.

$\gamma_{\text{GLYX}}$  decreases with increasing RH, due to salting in. Therefore, the maximum  $\gamma_{\text{GLYX}}$  ( $10^{-2}$  for SNA, 50% RH) exceeds the dilute (cloudwater) case. It also exceeds the general case used by Fu et al. (2008) ( $\gamma_{\text{GLYX}, \text{Fu}} = 2.9 \times 10^{-3}$ ), which was based  
 15 on the experimental observations of Liggio et al. (2005) for  $(\text{NH}_4)_2\text{SO}_4$  aerosols at 55% RH. The parameterization presented in Table 4 yields  $\gamma_{\text{GLY}} = 3.6 \times 10^{-3}$  at 55% RH.

In the case of coarse sea salt, in-particle diffusion limitations led to smaller  $\gamma_{\text{GLYX}}$  at the mean [OH] than at the minimum [OH] for some RH values. The scatter in the calculated  $\gamma_{\text{GLYX}}$  led to a low-confidence result from the weighted least squares regression. For this reason, we recommend use of the error-weighted average  $\gamma_{\text{GLYX}}$  value in lieu of a parameterization  
 20 (Table 4).



**Figure 1.** Calculated reactive uptake coefficients for uptake of glyoxal to sulfate/nitrate/ammonium (SNA) aerosols, and fine and coarse sea salt (SS) aerosols, as defined in GEOS-Chem v11. Red shading indicates the uncertainty in  $\gamma_{\text{GLYX}}$ . The black lines show the results of weighted least squares regression, with the confidence intervals in grey.

5

**Table 4. Summary of  $\gamma_{\text{GLYX}}$  recommendations for aerosols.** Aerosol types and specifications as defined in GEOS-Chem v11.

Aerosol type	$\gamma_{\text{GLYX}}$ average value	$\gamma_{\text{GLYX}}$ Parameterization x: RH as fraction
SNA	$1.0(\pm 0.1) \times 10^{-2}$ (RH = 50%) $4.9(\pm 1.0) \times 10^{-4}$ (RH = 70%) $1.0(\pm 0.3) \times 10^{-4}$ (RH = 80%) $2.6(\pm 1.3) \times 10^{-5}$ (RH = 90%) $2.8(\pm 1.4) \times 10^{-5}$ (RH = 95%) $8.5(\pm 4.6) \times 10^{-5}$ (RH = 99%)	$\gamma = \exp(a + bx + cx^2)$ $a = 12.1 (\pm 0.6)$ $b = -44.5 (\pm 1.7)$ $c = 22.3 (\pm 1.1)$ conf = 0.9997
Sea salt (fine)	$2.6 \times 10^{-6}$ (+0.04, $-2.6 \times 10^{-6}$ )	$\gamma = \exp(a + bx + cx^2)$ $a = -7.5 (\pm 0.1)$ $b = -10.0 (\pm 0.3)$ $c = 4.4 (\pm 0.2)$ conf = 0.9998
Sea salt (coarse mode)	$4.8 \times 10^{-7}$ (+0.013, $-4.8 \times 10^{-7}$ )	Average value recommended

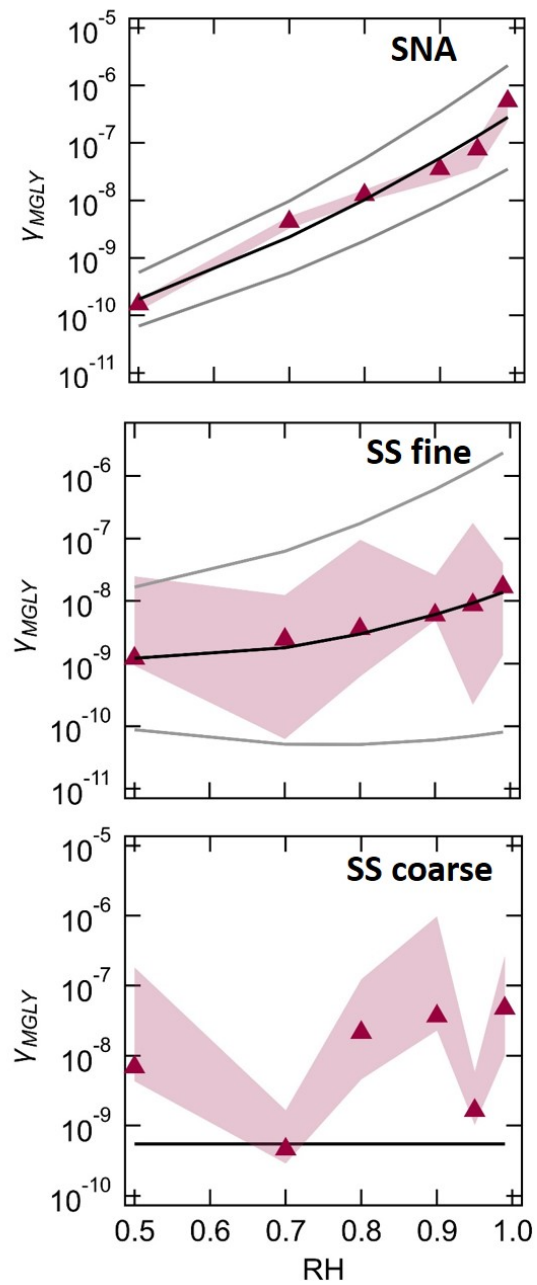
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Figure 2 shows calculated values of  $\gamma_{\text{MGLY}}$  as a function of RH. The average values and the results of the least squares fits are summarized in Table 5. In contrast to glyoxal, methylglyoxal salts out, so  $\gamma_{\text{MGLY}}$  increases with increasing RH. All calculated values ( $10^{-10} < \gamma_{\text{MGLY}} < 10^{-6}$ ) are much smaller than the general case used by Fu et al. (2008) ( $\gamma_{\text{MGLY, Fu}} = 2.9 \times 10^{-3}$ ). Those investigators had assumed that the reactive uptake coefficient for methylglyoxal would be equal to that for glyoxal as measured

10

by Liggio et al. (2005). Similar to the glyoxal case, the variability in  $\gamma_{\text{MGLY}}$  for the coarse mode sea salt aerosols due to in-particle diffusion limitations led to a low-confidence weighted least squares fit. The error-weighted average value is recommended.

15



**Figure 2.** Calculated reactive uptake coefficients for uptake of methylglyoxal to sulfate/nitrate/ammonium (SNA) and sea salt (SS) aerosols. See text for details.

**Table 5. Summary of  $\gamma_{\text{MGLY}}$  recommendations for aerosols.**

Aerosol type	$\gamma_{\text{MGLY}}$ average value	$\gamma_{\text{MGLY}}$ Parameterization x: RH as fraction
SNA	$1.6(\pm 0.4) \times 10^{-10}$ (RH = 50%) $4.3(\pm 1.0) \times 10^{-9}$ (RH = 70%) $1.3(\pm 0.3) \times 10^{-8}$ (RH = 80%) $3.5(\pm 1.5) \times 10^{-8}$ (RH = 90%) $7.7(\pm 4.1) \times 10^{-8}$ (RH = 95%) $5.3(\pm 2.9) \times 10^{-7}$ (RH = 99%)	$\gamma = \exp(a + bx + cx^2)$ $a = -25.7 (\pm 0.4)$ $b = 2.5 (\pm 1.0)$ $c = 8.3 (\pm 0.7)$ conf = 0.9990
Sea salt (fine)	$6.5 (\pm 1.3) \times 10^{-9}$	$\gamma = \exp(a + bx + cx^2)$ $a = -17.9 (\pm 0.9)$ $b = -10.4 (\pm 2.6)$ $c = 10.3 (\pm 1.7)$ conf = 0.9909
Sea salt (coarse mode)	$5.5 \times 10^{-10}$ (+0.016, -5.5 $\times 10^{-10}$ )	Average value recommended

For a given relative humidity,  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  show weak, nonmonotonic dependence on S:A and S:N, with significant scatter (see Supporting Information). Plotting  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  as a function of calculated aerosol pH shows a general positive trend, with  $\gamma$  increasing with increasing pH at a given RH. These plots can be found with Supporting Information along with a parameterization of the trend. We note that aerosol pH is not an independent parameter in our calculations, but rather a calculated output of ISORROPIA II as a function of input aerosol composition and RH. Furthermore, the mass transfer and reactive loss processes considered here are not explicitly pH dependent. Therefore, we interpret this apparent dependence on pH to be reflective of pH being a proxy for variations in solute concentration in the aerosol with varying aerosol liquid water content. All variations in  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  as a result of varying SNA aerosol composition or pH are incorporated in the error bars shown in the top panels of Figures 1 and 2, and therefore accounted for in the weighted least squares fits, and the uncertainty ranges provided in the parameterizations in Tables 4 and 5.

#### 4 Atmospheric Implications

We present revised recommendations for the reactive uptake coefficient for glyoxal and methylglyoxal for several cloud and aerosol types. The values we calculated in most cases under many conditions are lower than those currently used in large-scale



models such as GEOS-Chem, although we note that the parameterization presented in Table 4 at the experimental conditions of Liggio et al. (2005), 55% RH, yields  $\gamma_{\text{GLY}} = 3.6 \times 10^{-3}$ , which is within 24% of their experimental value ( $2.9 \times 10^{-3}$ ). We expect application of these parameterizations will result in a ~~dramatic~~ decrease in the calculated contribution of MGLY uptake to aqueous SOA formation and better representation of spatial variability in aqSOA formed from glyoxal. The reduced contribution of MGLY to aqueous SOA formation due to salting out is consistent with the calculations of (Sareen et al., (2017)).

Reactive uptake of glyoxal and methylglyoxal to other hygroscopic aerosols such as organics is possible, although given the importance of salting effects on this chemistry, and the low expected [OH] concentration in organic aerosols (McNeill, 2015), we expect the contribution of these processes to aqSOA formation to be minor.

This representation of aqueous SOA formation by GLYX and MGLY, with the treatment of Henry's constants described here, does not take into account the contribution of reversible uptake of GLYX, which could be a significant, although transient, source of aerosol mass under some conditions (McNeill et al., 2012; Woo and McNeill, 2015). The use of this parameterization together with simpleGAMMA (Woo and McNeill, 2015) would give representation of both aqSOA formation types by GLYX.

## 15 Acknowledgements

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## Supplementary Information

Details of the GEOS-Chem v11 cloud and aerosol specifications, plots of ~~the dependence of  $\gamma$  on~~ as a function of aerosol composition and calculated aerosol pH, a parameterization for  $\gamma$  as a function of calculated aerosol pH, and the MATLAB routine for calculating  $\gamma$  can be found in the supplementary information.

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Supporting information for

## Technical note: Updated parameterization of the reactive uptake of glyoxal and methylglyoxal by atmospheric aerosols and cloud droplets

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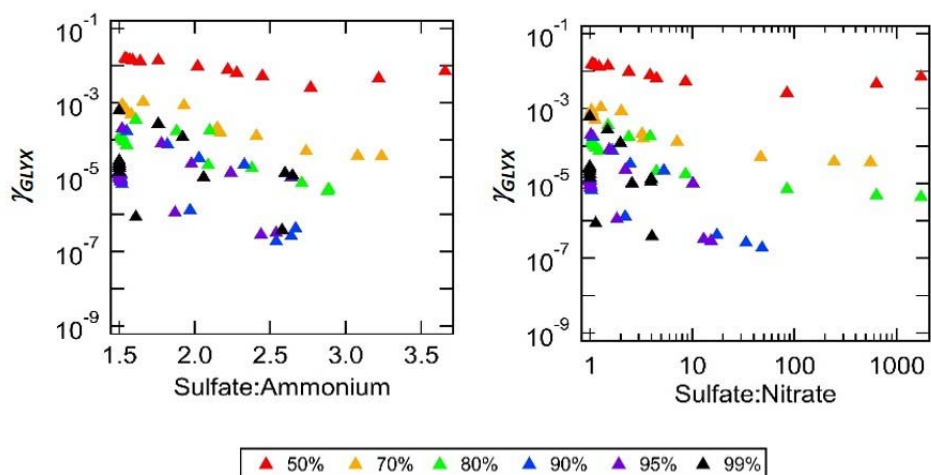
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**Table S1. GEOS-Chem cloud and aerosol parameters**

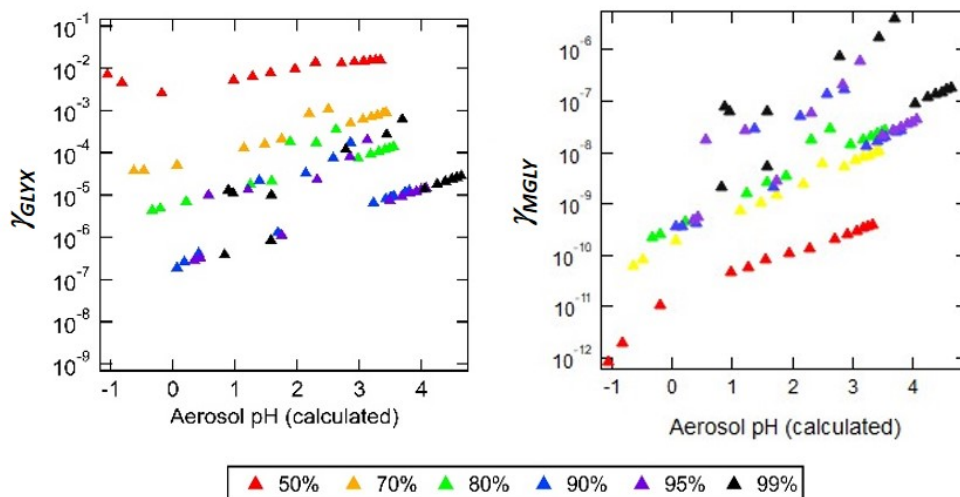
Cloud type	Effective radius ( $\mu\text{m}$ )
Liquid cloud droplet (marine)	10
Liquid cloud droplet (continental)	6

Aerosol type	Dry radius $R_{\text{dry}}$ ( $\mu\text{m}$ )	Effective radius $R_{\text{eff}}$ ( $\mu\text{m}$ )	Growth factor of $R_{\text{eff}}$ ( $R_{\text{eff}} / R_{\text{eff, RH=0\%}}$ )	Notes
Sulfate + nitrate + ammonium	0.069	0.121 (RH = 0%); 0.149 (RH = 50%); 0.162 (RH = 70%); 0.174 (RH = 80%); 0.198 (RH = 90%); 0.227 (RH = 95%); 0.304 (RH = 99%)	1.00 (RH = 0%); 1.23 (RH = 50%); 1.34 (RH = 70%); 1.44 (RH = 80%); 1.64 (RH = 90%); 1.88 (RH = 95%); 2.51 (RH = 99%)	So4.dat based on GADS (David Ridley)
Seasalt (accumulation mode)	0.085	0.129 (RH = 0%); 0.207 (RH = 50%); 0.233 (RH = 70%); 0.256 (RH = 80%); 0.306 (RH = 90%); 0.372 (RH = 95%); 0.613 (RH = 99%)	1.00 (RH = 0%); 1.60 (RH = 50%); 1.81 (RH = 70%); 1.98 (RH = 80%); 2.37 (RH = 90%); 2.88 (RH = 95%); 4.75 (RH = 99%)	Ssa.dat based on GADS (David Ridley)
Seasalt (coarse mode)	0.401	0.952 (RH = 0%); 1.534 (RH = 50%); 1.725 (RH = 70%); 1.899 (RH = 80%); 2.274 (RH = 90%); 2.780 (RH = 95%); 4.673 (RH = 99%)	1.00 (RH = 0%); 1.61 (RH = 50%); 1.81 (RH = 70%); 1.99 (RH = 80%); 2.39 (RH = 90%); 2.92 (RH = 95%); 4.91 (RH = 99%)	Ssc.dat based on GADS (David Ridley)
Dust Bin 1		0.7 (RH $\geq$ 35%)		Dust mod.F
Dust Bin 2		1.4 (RH $\geq$ 35%)		Dust mod.F
Dust Bin 3		2.4 (RH $\geq$ 35%)		Dust mod.F

Dust Bin 4		4.5 (RH >= 35%)		Dust mod.F
Organics, hydrophilic	0.021	0.127 (RH = 0%); 0.139 (RH = 50%); 0.145 (RH = 70%); 0.149 (RH = 80%); 0.159 (RH = 90%); 0.171 (RH = 95%); 0.203 (RH = 99%)	1.00 (RH = 0%); 1.09 (RH = 50%); 1.14 (RH = 70%); 1.17 (RH = 80%); 1.25 (RH = 90%); 1.35 (RH = 95%); 1.60 (RH = 99%)	org.dat based on GADS (David Ridley)
Soot (black carbon), hydrophilic	0.020	0.035 (RH = 0%); 0.035 (RH = 50%); 0.035 (RH = 70%); 0.042 (RH = 80%); 0.049 (RH = 90%); 0.052 (RH = 95%); 0.066 (RH = 99%)	1.00 (RH = 0%); 1.00 (RH = 50%); 1.00 (RH = 70%); 1.20 (RH = 80%); 1.40 (RH = 90%); 1.49 (RH = 95%); 1.89 (RH = 99%)	soot.dat based on GADS (David Ridley)



**Figure S1.** Calculated  $\gamma_{GLYX}$  as a function of aerosol composition for SNA aerosols at varying relative humidity.



**Figure S2.** Calculated  $\gamma_{\text{GLYX}}$  and  $\gamma_{\text{MGLY}}$  for SNA aerosols displayed as a function of calculated aerosol pH and varying relative humidity

**Table S2.** Recommended parameterization of  $\gamma_{\text{GLYX}}$  as a function of RH and pH. For  $\text{pH} \leq \text{pH}_{\text{break}}$ ,  $\gamma_{\text{GLYX}} = \exp(a+b*\text{pH})$ . For  $\text{pH} > \text{pH}_{\text{break}}$ ,  $\gamma_{\text{GLYX}} = c+d*\text{pH}$ . Parameterization valid for  $-1.05 \leq \text{pH} \leq 4.64$ .

RH	$\text{pH}_{\text{break}}$	$a$	$b$	$c$	$d$
50%	2.30	*	*	$1.36(\pm 0.21) \times 10^{-3}$	$4.31(\pm 0.07) \times 10^{-3}$
70%	2.50	$-9.8 \pm 0.2$	$1.37 \pm 0.05$	$-1.53(\pm 0.11) \times 10^{-3}$	$7.02(\pm 0.34) \times 10^{-4}$
80%	2.63	$-12.2 \pm 0.3$	$1.58 \pm 0.13$	$-2.65(\pm 0.19) \times 10^{-4}$	$1.12(\pm 0.06) \times 10^{-4}$
90%	2.86	$-15.6 \pm 0.6$	$2.37 \pm 0.36$	$-2.81(\pm 0.20) \times 10^{-5}$	$1.06(\pm 0.06) \times 10^{-5}$
95%	3.13	$-14.8 \pm 1.0$	$1.84 \pm 0.51$	$-3.51(\pm 0.23) \times 10^{-5}$	$1.21(\pm 0.06) \times 10^{-5}$
99%	3.69	$-14.7 \pm 1.1$	$1.90 \pm 0.48$	$-8.34(\pm 0.41) \times 10^{-5}$	$2.39(\pm 0.09) \times 10^{-5}$

\* for 50% RH,  $\text{pH} \leq \text{pH}_{\text{break}}$ ,  $\gamma_{\text{GLYX}} = a+b*\text{pH}+c*\text{pH}^2$ , where  $a = 3.0(\pm 0.5) \times 10^{-3}$ ,  $b = -7.4(\pm 4.5) \times 10^{-4}$ , and  $c = 2.3(\pm 0.3) \times 10^{-3}$

**Table S3.** Recommended parameterization of  $\gamma_{\text{MGLY}}$  as a function of RH and pH. For  $\text{pH} \leq \text{pH}_{\text{break}}$ ,  $\gamma_{\text{MGLY}} = \exp(a+b*\text{pH})$  for  $\text{pH} > \text{pH}_{\text{break}}$ ,  $\gamma_{\text{MGLY}} = c+d*\text{pH}$ . Parameterization valid for  $-1.05 \leq \text{pH} \leq 4.64$ .

RH	$\text{pH}_{\text{break}}$	$a$	$b$	$c$	$d$
50%	2.30	$-25.7 \pm 0.2$	$1.49 \pm 0.13$	$-5.88(\pm 0.05) \times 10^{-10}$	$2.86(\pm 0.16) \times 10^{-10}$
70%	2.50	$-22.7 \pm 0.1$	$1.37 \pm 0.05$	$-1.95(\pm 0.13) \times 10^{-8}$	$8.60(\pm 0.41) \times 10^{-9}$
80%	2.63	$-22.0 \pm 0.2$	$1.58 \pm 0.13$	$-5.30(\pm 0.36) \times 10^{-8}$	$2.21(\pm 0.11) \times 10^{-8}$
90%	2.86	$-22.2 \pm 0.6$	$2.35 \pm 0.35$	$-5.71(\pm 0.40) \times 10^{-8}$	$2.15(\pm 0.11) \times 10^{-8}$
95%	3.13	$-21.3 \pm 1.0$	$2.04 \pm 0.50$	$-1.00(\pm 0.07) \times 10^{-7}$	$3.46(\pm 0.17) \times 10^{-8}$



99%	3.69	-19.9 ± 1.1	1.96 ± 0.48	-5.07(± 0.32)×10 <sup>-7</sup>	1.46(± 0.07)×10 <sup>-7</sup>
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## MATLAB routine for calculating reactive uptake coefficients

Example shown for glyoxal uptake to maritime clouds.

```
clear;

Da = 1e-9; %Gly aqueous diffusion constant, m2/s
kOH = 1.1e9; %Gly-OH bimolecular aqueous rate constant, 1/M/s
kB = 1.38e-23; %Boltzmann constant, m2*kg/s2/K
T = 298; % Temp, K
M = 58.04/6.023e23/1000; %% mass of one GLY molecule, kg
w = sqrt(8*kB*T/pi()/M); %m/s
alpha = 0.02;

%% Maritime CLOUD

H = 3.6e5; %Henry's constant for dilute conditions, M/atm
R = 10e-6; %radius, m
OHconc = [2e-12, 5.3e-12, 3.8e-14]; % Molar

for i = 1:3
    kI=kOH*OHconc(i); % calculate psuedo first order rate constant, 1/s
    q = R*sqrt(kI/Da);
    f = coth(q)-1/q;
    gMC(i) = (1/alpha+w/(4*H*82.06/1000*T*sqrt(Da*kI)))*1/f)^-1
end
```