simpleGAMMA v1.0 – A reduced model of secondary organic aerosol formation in the aqueous aerosol phase (aaSOA)

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Abstract

There is increasing evidence that the uptake and aqueous processing of water-soluble volatile organic compounds (VOCs) by wet aerosols or cloud droplets is an important source of secondary organic aerosol (SOA). We recently developed GAMMA (Gas-Aerosol Model for Mechanism Analysis), a zero-dimensional kinetic model that couples gas-phase and detailed aqueous-phase atmospheric chemistry for speciated prediction of SOA and organosulfate formation in cloudwater or aqueous aerosols. Results from GAMMA simulations of SOA formation in aerosol water (aaSOA) (McNeill et al. (2012), *Environ. Sci. Technol.* 46(15) 8075-8081) indicate that it is dominated by two pathways: isoprene epoxydiol (IEPOX) uptake followed by ring-opening chemistry (under low-NO_x conditions) and glyoxal uptake. This suggested that it is possible to model the majority of aaSOA mass using a highly simplified reaction scheme. We have therefore developed a reduced version of GAMMA, simpleGAMMA. Close agreement in predicted aaSOA mass is observed between simpleGAMMA and GAMMA under all conditions tested (between pH 1-4 and RH 40-80%) after 12 hours of simulation. simpleGAMMA is computationally efficient and suitable for coupling with larger-scale atmospheric chemistry models or analyzing ambient measurement data.

1   Introduction

Quantifying the sources of tropospheric aerosol material is important for accurate modeling of air quality and climate. In-situ processes leading to the formation of new organic aerosol material,

collectively known as secondary organic aerosol (SOA) formation, are poorly constrained in atmospheric chemistry models (Kanakidou et al., 2005; Hallquist et al., 2009; Hodzic et al., 2010). Disagreement between model results and observations of the quantity, degree of oxidation, and location of organic aerosols in the atmosphere has suggested an incomplete representation of SOA formation pathways in models (Heald et al., 2005; Jimenez et al., 2009). In the past decade, the uptake of water-soluble volatile organic compounds (VOCs) into cloud droplets or aerosol water, followed by aqueous-phase chemical processing, has received increased attention as a possibly important source of SOA (Blando and Turpin, 2000; Ervens et al., 2011). It is thought to be especially significant in the case of isoprene-derived SOA formation. This is because most of the gas-phase oxidation products of isoprene, are, like isoprene itself, highly volatile, however some, like glyoxal (GLYX), isoprene-derived epoxydiols (IEPOX) (Paulot et al., 2009; Surratt et al., 2010), and methacrylic acid epoxide (MAE) (Lin et al., 2013), are water-soluble. These species also undergo reactive processing in the aqueous phase of cloud droplets or aerosols, increasing their uptake from the gas-phase.

Despite mounting evidence that aqueous atmospheric chemistry is a significant source of SOA, aqueous aerosol and cloudwater SOA formation is not yet widely represented in 3D atmospheric chemistry and air quality models. This is due, in part, to the challenges of bridging scales between the detailed information generated by laboratory experiments, and simplified representations suitable for implementation in 3D models, which can afford to carry relatively few chemical tracers. Including cloudwater organic chemistry in large scale atmospheric chemistry models has improved agreement with observations (Carlton et al., 2008; Myriokefalitakis et al., 2011; Liu et al., 2012), but aqueous aerosol processes are just beginning to be represented (Pye et al., 2013; Knote et al., 2014; Lin et al., 2014).

Previously, we developed GAMMA (Gas-Aerosol Model for Mechanism Analysis), a zero-dimensional kinetic model that couples gas- and detailed aqueous aerosol-phase chemistry for speciated prediction of SOA and organosulfate formation in the aqueous aerosol phase under ambient or laboratory conditions (McNeill et al., 2012; Woo et al., 2013). GAMMA represents aaSOA formation in terms of aqueous uptake followed by aqueous-phase reaction (Schwartz, 1986). GAMMA includes IEPOX chemistry following Eddingsaas et al. (2010), and uses the effective Henry's Law constant, H*, constrained by aerosol chamber studies (Sumner et al., 2014)

to describe glyoxal uptake and dark reactions, as well as detailed photochemical organosulfate formation and brown carbon formation from glyoxal, methylglyoxal, and acetaldehyde (Woo et al., 2013). For more information regarding other specific mechanisms included in GAMMA, as well as rate constants for these reactions and other physical parameters, the reader is referred to McNeill et al. (2012) (including the Supporting Information) and Woo et al. (2013).

Simulations using GAMMA indicate that the IEPOX pathway dominates aaSOA formation, leading to up to ~0.9 μg m^{-3} of SOA mass under conditions typical of the rural SE USA (McNeill et al., 2012). Pye and coworkers predicted similar mean concentrations (0.6-1.0 μg m^{-3}) of IEPOX-derived SOA mass for the SE USA in Summer 2006, using CMAQ with a surface reactive uptake formulation of IEPOX aaSOA formation (Pye et al., 2013). In urban (high-NOx) environments, aaSOA is primarily formed via glyoxal uptake (McNeill et al., 2012).

This predominance of two aaSOA formation pathways involving relatively few species, compared to the total number of aqueous compounds tracked by GAMMA, suggests that it is possible to model the majority of aqueous aerosol phase SOA mass using a highly simplified reaction scheme, which is computationally efficient and suitable for coupling with larger-scale atmospheric chemistry models. GAMMA has therefore been used as a guide to develop a reduced mechanism for aaSOA formation, simpleGAMMA. simpleGAMMA reduces the total number of tracked aqueous species from 140 to 4 (glyoxal, IEPOX, 2-methyltetrol, and IEPOX organosulfate), with 2 species partitioning between the gas and aqueous aerosol phases (glyoxal and IEPOX), and a single aqueous-phase chemical process (reactive uptake of IEPOX), compared to 118 in GAMMA.

2   simpleGAMMA: Model Description

As in GAMMA, the time evolution of the aqueous aerosol phase concentration (C_i, in mol/L) of a given chemical species i is described in simpleGAMMA by the following differential equation (Schwartz, 1986):

$$\frac{dC_i}{dt} = \frac{k_{mt,i}}{\boldsymbol{R}T} P_i - \frac{k_{mt,i}}{H_i^* \boldsymbol{R}T} C_i + \sum_k r_{ik,aq} \tag{1}$$

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1 Here, P_i is the gas-phase partial pressure of species i, H^*_i is the effective Henry's Law constant, $\boldsymbol{R}$

2 is the universal gas constant, and T is temperature. The rates $r_{ik,aq}$ represent chemical reactions in

3 the aerosol phase that can act as sources or sinks for a given species. $k_{mt,i}$ is the gas-aerosol mass

4 transfer coefficient for species i, given by:

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6
$$k_{mt,i} = \frac{1}{\dfrac{R^2}{3D_{g,i}} + \dfrac{4R}{3\omega_i \alpha_i}}$$
(2)

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8 where R is the aerosol particle radius, $D_{g,i}$ is the gas-phase diffusion coefficient, ω_i is the thermal

9 velocity, and α_i is the accommodation coefficient. A suitable gas-phase chemical mechanism

10 should be employed, and the loss or gain of species to/from the aerosol phase should be accounted

11 for, following, for example:

12

13
$$\frac{dP_i}{dt} = -k_{mt,i} a_L P_i + \frac{k_{mt,i} a_L}{H^*_i} C_i + \sum_j r_{ij,gas} + E_i - D_i$$
(3)

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15 where a_L is the aerosol aqueous liquid volume fraction (cm^3 cm^{-3} of air), $r_{ij,gas}$ is the rate of gas

16 phase reaction j that species i participates in, and E_i and D_i are the emission and deposition rates of

17 species i, respectively.

18   Note that simpleGAMMA is a reduced version of the *aqueous-phase mechanism* of GAMMA

19 (McNeill et al., 2012). The gas-phase mechanism of GAMMA was not changed because it is

20 intended that simpleGAMMA take gas phase concentration fields as inputs from an external source,

21 i.e. from field measurements or from existing models of atmospheric chemistry, which have gas-

22 phase chemical mechanisms but lack representations of aqueous aerosol phase SOA formation. For

23 tests reported here, we ran simpleGAMMA with the full gas phase mechanism of GAMMA,

24 following Eqs. (1)–(3). A full description of the gas and aqueous phase mechanisms of GAMMA,

25 the simulation conditions, and results can be found in McNeill et al. (2012).

26   The processes leading to aaSOA formation in simpleGAMMA are a subset of those represented

27 in GAMMA, and they with the goal of minimizing the number of aqueous-phase tracers and species

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being exchanged between the gas and aerosol phases, while maximizing the aaSOA mass captured compared to that as predicted by GAMMA after 12 hours of simulated chemistry, assuming no initial aerosol-phase organic mass. The detailed comparison of GAMMA and simpleGAMMA output under a range of typical environmentally relevant conditions can be found in the following section. The aqueous phase species tracked in simpleGAMMA are: IEPOX, glyoxal, 2-methyltetrol, and IEPOX organosulfate. Mass transfer between the gas and aerosol phases only occurs for IEPOX and glyoxal. The effective Henry's Law constants (H*) and accommodation coefficients used to describe uptake for these species are given in Table 1. These H* values have been updated based on advances in literature since McNeill et al. (2012), and they represent our best understanding of the valid parameters for deliquesced aerosols. They are not valid for non-aqueous aerosols. The values, especially H* for IEPOX (Budisulistiorini et al., 2015), have significant uncertainty associated with them, largely because relatively few experimental studies of H* for uptake of these species to deliquesced aerosols are available in the literature (Kampf et al., 2013; Gaston et al., 2014; Nguyen et al., 2014).

We note that, subsequent to the publication of McNeill et al. (2012), the gas and aqueous phase chemistry of methacrylic acid epoxide (MAE) was introduced to the full version of GAMMA following Lin et al. (2013). The predicted contribution of this pathway to aaSOA was minor compared to IEPOX and glyoxal, consistent with the findings of Pye et al. (2013). Therefore, it is not included in simpleGAMMA.

Reversible hydration and oligomerization chemistry of glyoxal in the aqueous phase (Whipple, 1970) is captured using the effective Henry's Law constant, H* (Schwartz, 1986). Therefore, those processes are not represented explicitly in either GAMMA or simpleGAMMA, in order to avoid double counting. The aqueous processing of IEPOX to form 2-methyltetrols (tetrol) and and IEPOX organosulfate (IEPOXOS) is represented as one reactive process following a simplified version of the mechanism of Eddingsaas et al. (2010):

IEPOX (aq) $\rightarrow$ (1-β) tetrol + β IEPOXOS   (4)

Here, we apply a value for the branching ratio, β, of 0.4, which is an estimate based on the measurements of Eddingsaas and coworkers for the most concentrated bulk solution they studied. The rate constant for the reaction, k_1, is a function of proton activity and nucleophile concentrations,

1   again following Eddingsaas et al. (2010). We have modified the formula to include the possible

2   protonation of IEPOX (aq) by ammonium as observed by Nguyen et al. (2014).

3    $$k_1 = \left(\frac{[H_2O]}{55.1}\right) k_{H^+} a_{H^+} + k_{SO_4^{2-}}[SO_4^{2-}]a_{H^+} + k_{HSO_4^-}[HSO_4^-] + k_{NH_4^+}[NH_4^+] \qquad (5)$$

4   Here, a_{H^+} is the H$^+$ activity, $k_{H^+} = 5 \times 10^{-2} s^{-1}$, $k_{SO_4^{2-}} = 2 \times 10^{-4} M^{-1} s^{-1}$, and $k_{HSO_4^-} =$

5    $7.3 \times 10^{-4} M^{-1} s^{-1}$. The ammonium rate constant, $k_{NH_4^+}$, was calculated using GAMMA and the

6   results of the chamber study of Nguyen et al. (2014) to be $1.7 \times 10^{-5} M^{-1} s^{-1}$. The rate constant

7   term k_{H^+} from Eddingsaas et al (2010) has been scaled to account for variable water concentrations

8   within the seed aerosol at different pH and RH conditions, consistent with recent literature (Piletic

9   et al., 2013; Pye et al., 2013). The architecture of the simpleGAMMA program is similar to that of

10   GAMMA (McNeill et al., 2012). simpleGAMMA and GAMMA were originally written in

11   MATLAB (MathWorks, Inc.), utilizing the stiff initial value ordinary differential equation solver

12   `ode15s.m`, but simpleGAMMA is also available in Fortran. Required input parameters for

13   simpleGAMMA are: gas phase concentration fields for IEPOX and glyoxal, aerosol pH, aerosol

14   size distribution or volume-weighted average aerosol diameter, aerosol liquid water content, and

15   aerosol sulfate and bisulfate concentrations. The test simulations in this study were for the same

16   conditions as the high-NOx and low-NOx scenarios in McNeill et al. (2012), with one exception:

17   for the low-NOx simulation, the initial gas-phase mixing ratio of IEPOX is assumed to be 780 ppt,

18   instead of zero. This was the steady state value after three simulated day-night cycles in GAMMA,

19   in the absence of aerosol uptake. In all other simulations, the seed aerosols were assumed to be

20   initially composed solely of deliquesced ammonium sulfate, following the size distribution of

21   Whitby (1978), with aerosol loadings of 4.0 µg/m^3 (rural conditions, following Tanner et al. (2009))

22   or 20 µg/m^3 (urban conditions, following Jimenez et al. (2003)). Initial inorganic aerosol

23   composition was determined by E-AIM outputs for the defined initial pH and RH values.

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25   **3   Results**

26   *Low-NOx (Rural) Conditions*

27   Similar to what was observed in McNeill et al. (2012), under simulated rural (low-NOx)

28   environments, both GAMMA and simpleGAMMA predict that aaSOA is dominated by IEPOX

1   and its aerosol-phase reaction products. The evolution of aaSOA mass as predicted over 12 hours

2   of dawn-to-dusk simulation under low-NOx conditions using GAMMA and simpleGAMMA is

3   shown in Figure 1 (for aerosol pH = 1 and 45% RH). The pie charts compare the aaSOA

4   composition predicted by both models at 3, 6, 9, and 12 hours of simulation. Close agreement in

5   predicted aaSOA mass and its composition can be seen between the two models. Small differences

6   arise due to the fact that, although identical gas-phase mechanisms and initial conditions were used

7   in this model intercomparison, the gas-phase chemistry, especially gas-phase OH, is perturbed by

8   the differences in gas-aerosol mass transfer between the two models. Specifically, VOCs which

9   may partition into the particle phase in GAMMA but not simpleGAMMA are present in the gas

10 phase in higher concentrations in simpleGAMMA, creating an increased sink for OH**.**

11   Figure 2 shows the total aaSOA mass predicted by GAMMA and simpleGAMMA for 12 hours

12 of simulation under low-NOx conditions, with varying aerosol pH and RH. Like GAMMA,

13 simpleGAMMA predicts maximum aaSOA formation under low-NOx conditions when aerosol pH

14 is low and RH is low (but not so low as to cause aerosol efflorescence). This is because in-particle

15 processing of IEPOX is initiated by protonation, so conditions which maximize the in-particle

16 proton concentration yield the highest IEPOX processing. Close agreement (to within 30%) exists

17 between aaSOA mass predicted by GAMMA and by simpleGAMMA for pH 1, and within 0.02

18 $\mu g\ m^{-3}$ for aerosol pH $\geq$ 2.0. The highly efficient in-particle IEPOX chemistry at low pH leads to

19 larger discrepancies between the two models.

20 *High-NOx (Urban) Conditions*

21 aaSOA mass as predicted by GAMMA is dominated by "dark" uptake of glyoxal under high-NOx

22 conditions (McNeill et al., 2012). Gas-phase IEPOX formation is expected to be minor in this

23 regime (Paulot et al., 2009). A comparison of evolved aaSOA mass and composition under high-

24 NOx conditions as predicted by GAMMA and simpleGAMMA can be seen in Figure 3. Figure 4

25 shows total aaSOA mass predicted by the two models after 12 hours of simulation under high-NOx

26 conditions, with varying aerosol pH and RH. Close agreement (within 0.01 $\mu g\ m^{-3}$) in predicted

27 total aaSOA mass exists between simpleGAMMA and GAMMA for all relative humidity and pH

28 values tested. Like GAMMA, under high NO_x conditions simpleGAMMA predicts increasing

29 aaSOA formation with increasing RH (and therefore increasing aerosol liquid water content), and

30 no pH dependence, consistent with glyoxal dark uptake being the dominant aaSOA formation

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1   mechanism (Kroll et al., 2005; Galloway et al., 2009; Volkamer et al., 2009). The increased uptake

2   at higher RH amplifies small differences in gas phase chemistry between simpleGAMMA and

3   GAMMA, due to differing gas-phase OH sinks in the two models, as described above. GAMMA

4   predicts some contribution to aaSOA mass by photochemical production of succinic acid (vis.

5   Figure 3), which is not included in simpleGAMMA. However, since glyoxal is the dominant

6   precursor for succinic acid formation and the molecular weight of succinic acid (118 g/mol) is

7   comparable to the molecular weight of the two glyoxal molecules that comprise it (116 g/mol), the

8   predicted overall aaSOA mass is therefore very similar for the two models.

9   *Computational performance*

10   The goal of simpleGAMMA is to faithfully represent aaSOA formation with a low number of

11   tracers, in order to simplify the implementation of aqueous aerosol SOA formation in 3-D models

12   (by coupling the gas-phase schemes of those models with simpleGAMMA). However,

13   simpleGAMMA is also computationally faster than GAMMA when run as a box model, as

14   described in this study, due to the reduced number of tracers and reactions in the aqueous phase

15   (recall that the gas phase mechanisms of GAMMA and simpleGAMMA were identical for

16   purposes of this study). In ten simulations with starting aerosol pH 1 and 65 % ambient RH,

17   computational run-time for simpleGAMMA under low-NOx conditions spanned between 10–12 s

18   for 12 h of simulation, compared to 33–42 s for GAMMA. These runs were performed on an Intel

19   Core i7-3520M CPU @2.90 GHz PC, using MATLAB R2014b with the solver `ode15s.m` Time

20   steps to completion between simpleGAMMA and GAMMA were comparable (~11,000 and

21   ~14,000 respectively) (indicating similar stiffness in the two models) but simpleGAMMA

22   necessarily utilized less memory cache due to the smaller number of aqueous-phase species and

23   reactions.

24   **4   Discussion and Outlook**

25   The agreement between GAMMA and simpleGAMMA indicate that this reduced framework can

26   be useful to represent aaSOA mass formation over a variety of relevant ambient conditions.

27   Coupling of simpleGAMMA with regional and global scale 3D atmospheric chemistry models

28   (Jathar et al., 2014) and its application to analysis of ambient measurement data (Budisulistiorini

29   et al., 2015) is currently underway.

While we have demonstrated good agreement between simpleGAMMA and GAMMA, the limitations of GAMMA also apply to simpleGAMMA; for example, neither model includes a treatment of oxidative aging of aaSOA at this time due to a lack of kinetic and mechanistic data. As a result, overprediction of total aaSOA mass is likely (Budisulistiorini et al., 2015). The only sources of aqueous-phase OH in GAMMA are HOOH photolysis or Henry's Law transfer of OH from the gas phase. Therefore we, like others (Waxman et al., 2013; Ervens et al., 2014), have observed OH-limited chemistry in the aqueous aerosol phase using GAMMA, and this informed the simpleGAMMA formulation. While transition metal ion chemistry, a possible source of OH (Herrmann et al., 2015), was not included in the first version of GAMMA (McNeill et al., 2012) due to the focus on ammonium sulfate aerosols in that study, these mechanisms may be active in ambient aerosols. Preliminary calculations in GAMMA show that including transition metal ion (Fe^{+3}, Cu^{+2}, Mn^{+3}) chemistry following CAPRAM 3.0 (Herrmann et al., 2005) does not perturb the predicted aaSOA yield or product distribution. Aqueous-phase diffusion is not accounted for in GAMMA or simpleGAMMA, that is, Henry's Law equilibration is assumed to occur instantaneously and no spatial concentration gradients within the particle are considered. This likely leads to an overestimate of OH chemistry when this very fast-reacting species is taken up from the gas phase. However, since we have found that aqueous phase photochemistry does not dominate aaSOA formation, inclusion of aqueous phase diffusion limitations in this calculation would not change our results or the formulation of simpleGAMMA. Aqueous phase diffusion may also be important for relatively large droplets such as those encountered in marine aerosols.

simpleGAMMA is not recommended for the treatment of aqueous SOA formation in cloudwater, which is dominated by aqueous phase photochemistry. The role of UV light in aaSOA formation by glyoxal is unresolved (Galloway et al., 2009, 2011; Volkamer et al., 2009; Kampf et al., 2013). A recent data analysis study using GAMMA (Sumner et al., 2014) suggested a possible role for photo-enhanced chemistry in aaSOA formation by glyoxal involving organic photosensitizers such as fulvic acid (Monge et al., 2012). This chemistry can be represented in simpleGAMMA by including irreversible glyoxal uptake with $\gamma \sim 10^{-3}$ during sunlit hours, consistent with Fu et al. (2008), who based their representation on the experiments of Liggio et al. (2005), and with Waxman et al. (2013). A reactive uptake formulation was also used to represent aaSOA formation by IEPOX by Pye et al. (2013). While reactive uptake may be the best alternative for representing unknown processes such as glyoxal surface photochemistry, potential issues with reactive uptake

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formulations stem from the fact that they generally represent two or more physical processes (e.g., reversible uptake of VOCs followed by aqueous phase reaction) as one irreversible reactive uptake step. Lin et al. (2014) and Knote et al. (2014) found that a surface reactive uptake formulation for glyoxal led to significantly higher predicted SOA mass than a reversible multiphase representation of the chemistry.

We previously predicted using GAMMA that glyoxal is the main contributor to aqueous aerosol-phase "brown carbon" formation by carbonyl-containing VOC precursors (Woo et al., 2013). Following that work, it is straightforward to track the formation of light-absorbing glyoxal derivatives in simpleGAMMA, with concentration-dependent aerosol light absorption calculated in post-processing. However, we note that fast photobleaching of aerosol brown carbon formed via this pathway has been demonstrated, limiting its potential impact on atmospheric chemistry and climate (Sareen et al., 2013; Woo et al., 2013; Lee et al., 2014).

Code Availability

For more information and to access the simpleGAMMA program, please visit mcneill-lab.org/gamma or contact V. Faye McNeill, vfm2103@columbia.edu. simpleGAMMA was originally written in MATLAB (MathWorks, Inc.) and is also available in Fortran.

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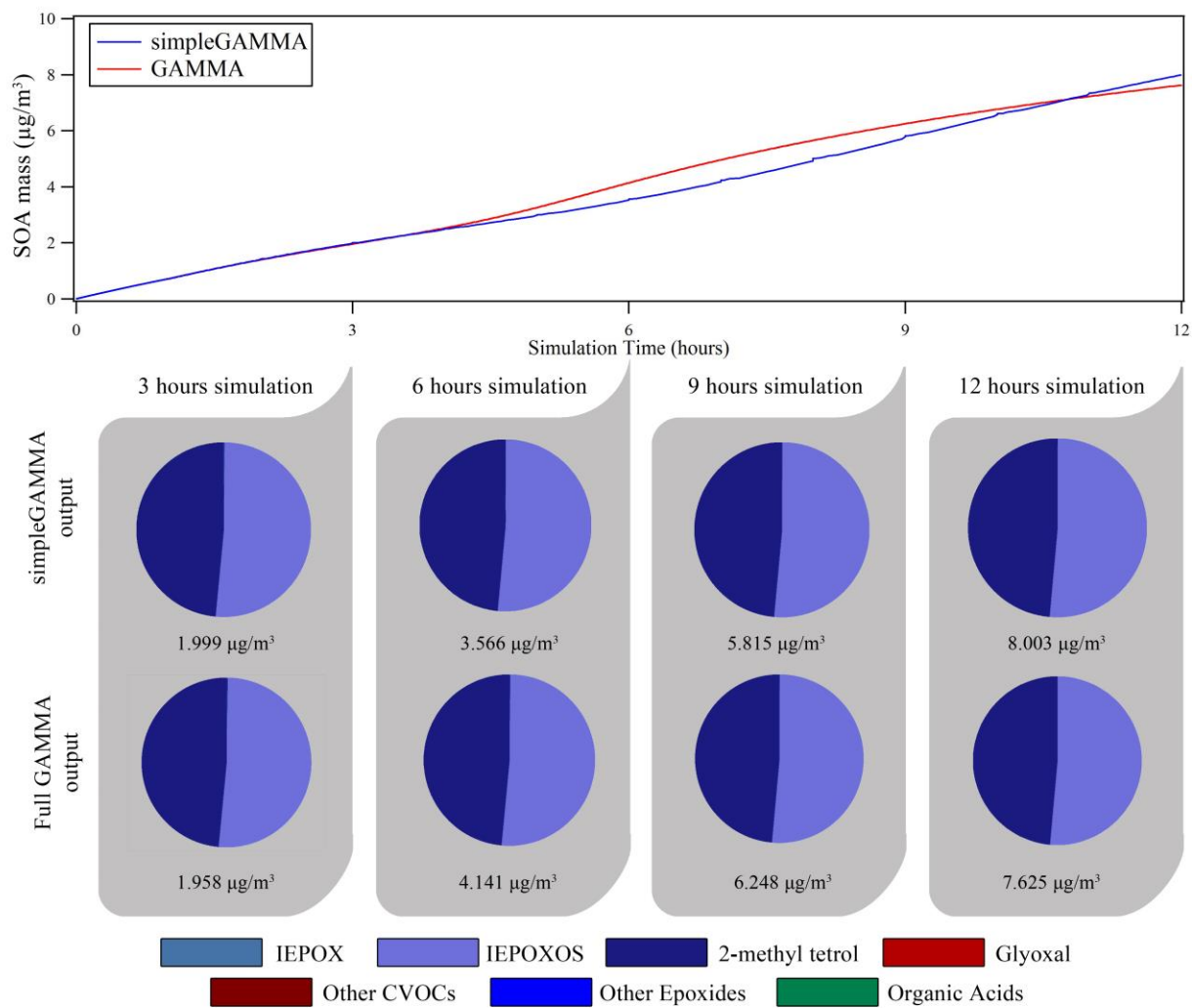
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Table 1. Gas-aerosol mass transfer parameters in simpleGAMMA

3

Species	Effective Henry's Law constant, H* (M/atm)	Accomodation Coefficient, α	References
IEPOX	3×10^7	0.02	(McNeill et al., 2012; Nguyen et al., 2014)
GLYX	2.7×10^7	0.023	(Herrmann et al., 2005; Sumner et al., 2014)

4

1

3 **Figure 1**. Comparison of simpleGAMMA and GAMMA under low-NOx conditions, pH 1, RH
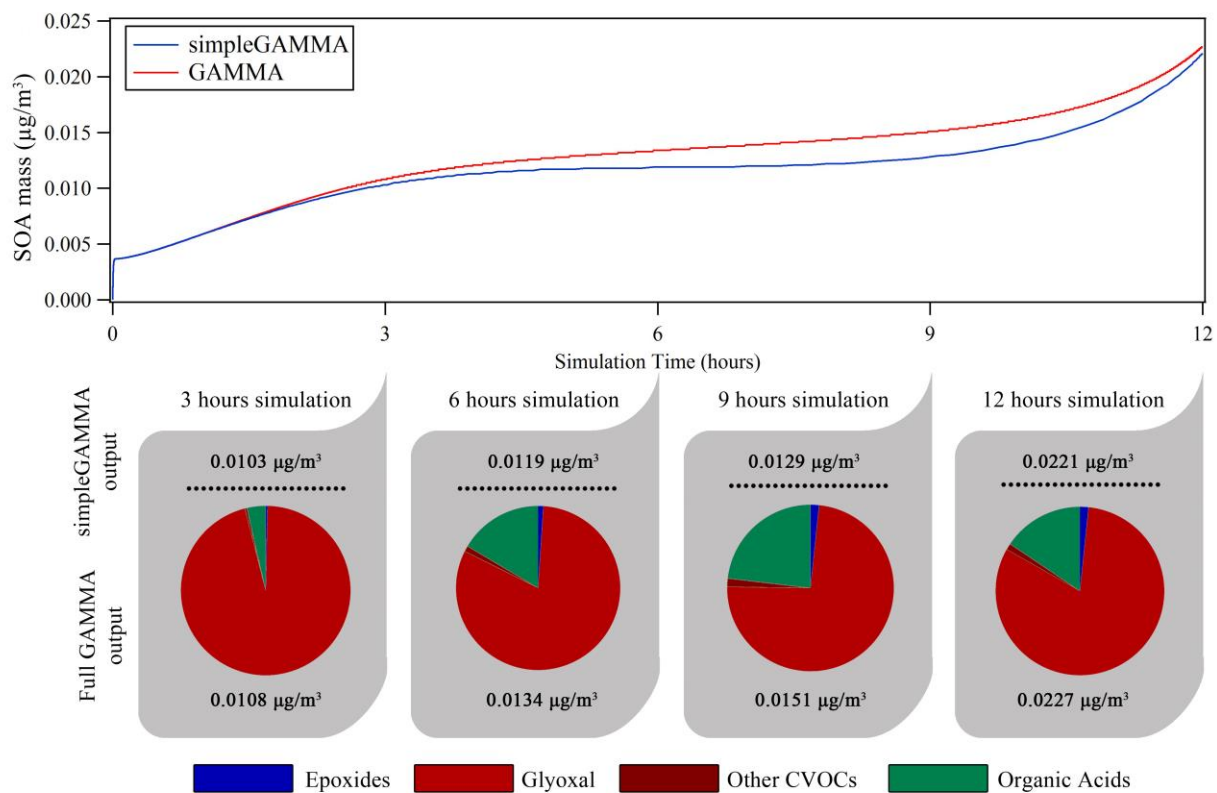
4 45%

5

1
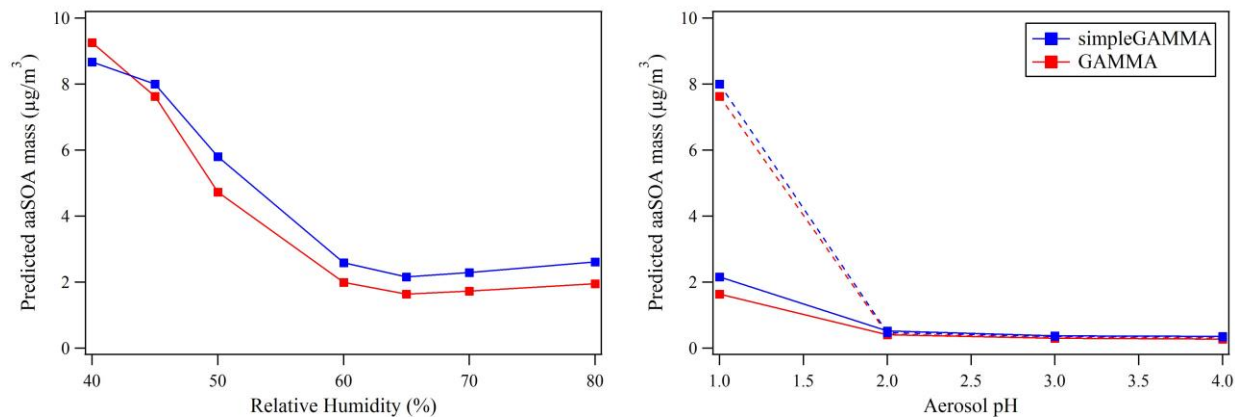
2

3   **Figure 2.** Comparison of predicted aaSOA after 12 hours of simulated time with respect to RH at

4   pH 1 (left) and with respect to pH at 45% and 65% RH (right, dotted and solid lines respectively),
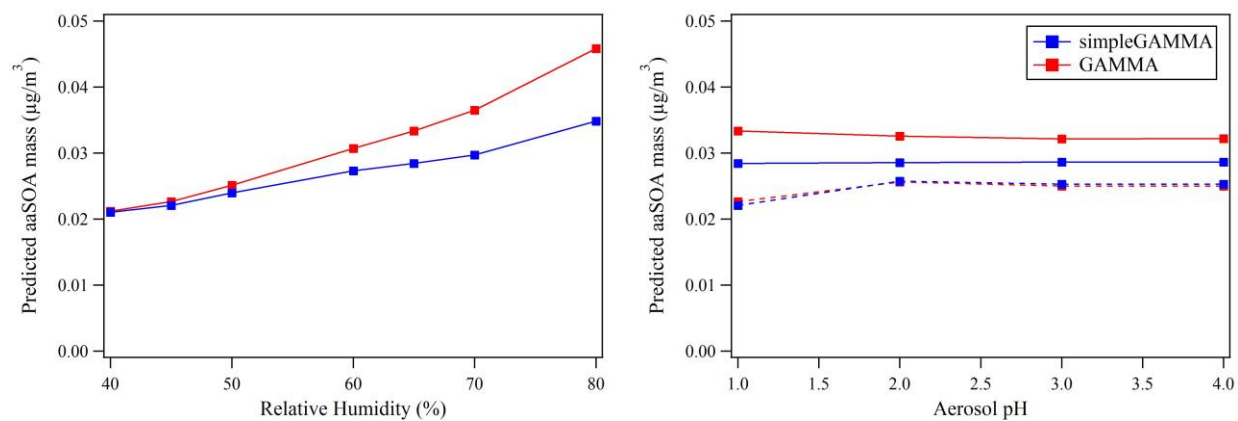
5   low-NOX conditions.

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3 **Figure 3.** Comparison of high-NOx simpleGAMMA and the full high-NOx GAMMA, pH1, RH45.

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2

3   **Figure 4.** Comparison of predicted aaSOA after 12 hours of simulated time with respect to RH at

4   pH 1 (left) and with respect to pH at 45% and 65% RH(right, dotted and solid lines respectively),

5   high-NOx conditions.

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