

We thank the referee for their constructive and positive comments on our manuscript. We respond to all comments in detail below. Our responses are in black, manuscript text is in italic with new/modified text is marked in blue. The line numbers cited here refer to those in the clean manuscript version.

**Referee comment:** - Throughout the manuscript I found terminology of VOC vs. NVOC somewhat confusing. It seems that you categorize compounds based on solubility ( $K_H$ ) but not with vapor pressures (no vapor pressures are given for treated compounds). For organic aerosol research, VOC is often used for compounds mostly in the gas phase, while NVOC for compounds mostly in the condensed phase. As you know, compounds which may exist both phases comparably are termed semi-volatile organic compounds (SVOC), so most compounds treated in this study appear better termed as SVOC. Some more clarifications with clear definition would help improve presentation quality.

**Author response:** We thank the referee for pointing out this inconsistency in our terminology. We agree that this was misleading as volatility is not the main criterion for the partitioning of species between the gas and aqueous phases, respectively. The categorization into VOC, NVOC and SVOC is mostly relevant for the partitioning of compounds between the gas and a condensed phase, such as present in aerosol. However, as the volatility does not (necessarily) correlate with water-solubility (e.g. alkanes and small aldehydes exhibit similar vapor pressures but vastly different Henry's law constants), these categories do not seem useful for the categorization of water-soluble compounds into the aqueous phase of cloud droplets.

Therefore, we categorize the various compounds now exclusively based on their solubility in water, i.e. on their Henry's law constant. We distinguish now four compound groups and we will add the following text at the end of the section 2.1.:

*We categorize four various compounds groups bases on their solubility in water and their Henry's law constant and we distinguish:*

*1) Low-solubility species with  $K_H < 10^3 \text{ M atm}^{-1}$ . Their dissolved fraction is  $< 1\%$  for the liquid water content (LWC) of  $0.68 \text{ g m}^{-3}$  in our model.*

*2) Intermediate solubility species with  $10^3 \text{ M atm}^{-1} < K_H < 10^6 \text{ M atm}^{-1}$  with dissolved fractions of  $\sim 1 - 58\%$  ( $\text{LWC} = 0.68 \text{ g m}^{-3}$ )*

*3) High-solubility species with  $K_H > 10^6 \text{ M atm}^{-1}$  for which the dissolved fraction exceeds  $95\%$  ( $\text{LWC} = 0.68 \text{ g m}^{-3}$ ).*

*4) Water-soluble CCN components which are dissolved in the aqueous phase upon dissolution of the condensation nucleus on which the cloud droplet grew. While these compounds have usually low volatility or are semivolatile, they also need to be water-soluble to be available for aqueous phase processes.*

We will modify the text accordingly:

The terms 'VOC' and 'NVOC' will be replaced by 'water-soluble organic gases' and 'CCN-derived compounds' or similar terms throughout the manuscript.

Specific changes include

- in the last paragraph of the introduction (l. 89):

Using a cloud multiphase box model, we explore the biological and chemical degradation of VOC and NVOC organic compounds over large parameter ranges of biodegradation activities, chemical rate constants and solubilities (Henry's law constants).

- Caption of Figure 1 : Schematic of the multiphase box model including chemical radical reactions in the gas and aqueous phases. Chemical reactions occur in both phases and in all droplets whereas biodegradation processes only occur in the aqueous phase in a small fraction of droplets, depending on the assumed bacteria cell concentration in clouds. (a) VOC water-soluble organic gases (b) NVOC CCN-derived compounds

- Caption of Figure 4: Comparison of the organic concentration in the bacteria-containing droplets  $[Org]_{bact}$  [mol L<sup>-1</sup>] for (a) NVOC CCN-derived compounds and (b) VOC water-soluble gases ( $K_H = 10^2, 10^5$  and  $10^9$  M atm<sup>-1</sup>), and the resulting  $fr_{bact}$  for these compounds (c, d). Results are shown for  $R_{bact} = 10^{-8}, 10^{-6}$  and  $10^{-4}$  s<sup>-1</sup>, and  $R_{chemgas} = 10^{-6}$  s<sup>-1</sup>,  $R_{chemaq} = 10^{-11}$  s<sup>-1</sup>.

- Caption of Figure 5: Schematic of the partitioning of VOC water-soluble organic gases between bacteria-containing, bacteria-free droplets and the gas phase: The inset figures show the temporal evolution of the organic concentration in the bacteria-containing droplets ( $[Org]_{bact}$ ) and bacteria free-droplets ( $[Org]_{non-bact}$ ) for VOC water-soluble organic gases with  $K_H = 10^5$  M atm<sup>-1</sup> and  $10^9$  M atm<sup>-1</sup>.

- Caption figure 9: Comparison of (a)  $fr_{bact}$ , (b)  $L_{bact}$  for volatile organics water-soluble organic gases for three the different model approaches: detailed model (red line), bulk approach (blue line) and low LWC model (green line) for different  $K_H$ ,  $R_{chemaq} = 10^{-7}$  s<sup>-1</sup>,  $R_{bact} = 10^{-6}$  s<sup>-1</sup> and  $R_{chemgas} = 10^{-6}$  s<sup>-1</sup>; (c)  $fr_{bact}$  and (d)  $L_{bact}$  for volatile organics water-soluble organic gases for the same approaches for different  $R_{bact}$ , one  $K_H = 10^5$  M atm<sup>-1</sup>, two  $R_{chemaq} = 10^{-7}$  s<sup>-1</sup>,  $R_{chemgas} = 10^{-6}$  s<sup>-1</sup>

As we changed the layout of figures 2,3,6,7,8 and 10 upon suggestion by referee 2, the revised figure captions are as follows:

- Caption of figure 2: Relative contribution of bacteria ( $fr_{bact}$ ) to the total loss rate of organics as a function of the full ranges of  $R_{chemaq}$  and  $K_H$ :  $R_{chemgas} = 10^{-6}$  s<sup>-1</sup> and a)  $R_{bact} = 10^8$  s<sup>-1</sup>, b)  $R_{bact} = 10^{-6}$  s<sup>-1</sup>, c)  $R_{bact} = 10^{-4}$  s<sup>-1</sup> and for  $R_{bact} = 10^{-6}$  s<sup>-1</sup> with d)  $R_{chemgas} = 10^{-5}$  s<sup>-1</sup> and e)  $R_{chemgas} = 10^{-4}$  s<sup>-1</sup>.

Relative contribution of bacteria to the total loss rate of organics ( $fr_{bact}$ , Eq-7) as a function of  $R_{chemaq}$  and  $K_H$ . All figure panels have the same scales on the ordinates and abscissas, respectively. The simulations were performed for constant values of  $R_{bact}$  and  $R_{chemgas}$ ; their values are indicated in the box at the bottom right.

- Caption figure 3: Relative contribution of bacteria to the total loss rate of organics ( $fr_{bact}$ ) for the full range of  $10^{-9} \leq R_{bact} [s^{-1}] \leq 10^{-6}$  and  $10^{-12} \leq R_{chemaq} [s^{-1}] \leq 10^{-5}$ . Relative contribution of bacteria to the total loss rate of CCN-derived organics ( $fr_{bact}$ , Eq-7) as a function of  $R_{bact} [s^{-1}]$  and  $R_{chemaq} [s^{-1}]$ .

- Caption of Figure 6: The total loss of VOC ( $L_t$ ) as a function of the full ranges of  $R_{chemaq}$  and  $K_H$ :  $R_{chemgas} = 10^{-6}$  s<sup>-1</sup> and a)  $R_{bact} = 10^8$  s<sup>-1</sup>, b)  $R_{bact} = 10^{-6}$  s<sup>-1</sup>, c)  $R_{bact} = 10^{-4}$  s<sup>-1</sup> and for  $R_{bact} = 10^{-6}$  s<sup>-1</sup> with d)  $R_{chemgas} = 10^{-5}$  s<sup>-1</sup> and e)  $R_{chemgas} = 10^{-4}$  s<sup>-1</sup>. The total loss of water-soluble organic gases ( $L_t$ , Eq-10) as a function of  $R_{chemaq}$  and  $K_H$ . All figure panels have the same scales on the ordinates and abscissas, respectively. The simulations were performed for constant values of  $R_{bact}$  and  $R_{chemgas}$ ; their values are indicated in the box at the bottom right.

- Caption of figure 7 : The loss of VOC by bacteria ( $L_{bact}$ ) as a function of the full ranges of  $R_{chemaq}$  and  $K_H$ :  $R_{chemgas} = 10^{-6}$  s<sup>-1</sup> and a)  $R_{bact} = 10^8$  s<sup>-1</sup>, b)  $R_{bact} = 10^{-6}$  s<sup>-1</sup>, c)  $R_{bact} = 10^{-4}$  s<sup>-1</sup> and for  $R_{bact} = 10^{-6}$  s<sup>-1</sup> with d)  $R_{chemgas} = 10^{-5}$  s<sup>-1</sup> and e)  $R_{chemgas} = 10^{-4}$  s<sup>-1</sup>. The loss of water-soluble organic gases by bacteria ( $L_{bact}$ , Eq-11)

as a function of  $R_{chemaq}$  and  $K_H$ . All figure panels have the same scales on the ordinates and abscissas, respectively. The simulations were performed for constant values of  $R_{bact}$  and  $R_{chemgas}$ ; their values are indicated in the box at the bottom right.

- ~~Caption of figure 8: Predicted loss of NVOC as a function of chemical ( $R_{chemaq}$ ) and microbial ( $R_{bact}$ ) activity in the aqueous phase, a) total loss ( $L_t$ ), b) loss by microbial processes ( $L_{bact}$ ). Predicted loss of CCN-derived species as a function of  $R_{chemaq}$  and  $R_{bact}$ , a) total loss ( $L_t$ ), b) loss by microbial processes ( $L_{bact}$ ).~~

- ~~Caption figure 10:  $L_{bact}$  for VOC for a specific combination of  $K_H$  and  $R_{chemaq}$  (a,b,c) and for NVOC (d) for a specific combination of  $R_{bact}$  and  $R_{chemaq}$  at 2 pH (3 and 6) for the acidic compounds.~~

a) – c)  $L_{bact}$  for water-soluble organic gases. The contour plots are identical to Figure 7 a, b and c. Symbols show combinations of  $R_{chemaq}$  and  $K_H$  for specific compounds (Table 1). For all simulations  $R_{chemgas} = 10^6 s^{-1}$ ; a)  $R_{bact} = 10^8 s^{-1}$  b)  $R_{bact} = 10^6 s^{-1}$  c)  $10^4 s^{-1}$

d)  $L_{bact}$  for CCN-derived organics (Table 1). The contour plot is identical to Figure 8 b) .Note that  $R_{chemaq}$  and  $R_{bact}$  for succinate (pH = 6) is nearly identical to the values for succinic acid (pH = 3) and were therefore omitted from the figure.

- ~~Header of Section 3.1.1:  $fr_{bact}$  for VOC :  $fr_{bact}$  for water-soluble organic gases~~

- ~~Header of section 3.1.2:  $fr_{bact}$  of NVOC and comparison to  $fr_{bact}$  of VOC :  $fr_{bact}$  of CCN-derived compounds and comparison to  $fr_{bact}$  of water-soluble organic gases.~~

- ~~Header of Section 3.2.1:  $L_t$  for VOC:  $L_t$  for water-soluble organic gases~~

- ~~Header of Section 3.2.2.:  $L_{bact}$  for VOC:  $L_{bact}$  for water-soluble organic gases~~

- ~~Header of Section 3.2.3:  $L_t$  and  $L_{bact}$  for NVOC:  $L_t$  and  $L_{bact}$  for CCN-derived compounds~~

**Referee comment:** - It was not clear to me how you treat phase transfer in your model. It is just simply stated that it is based on the resistance model (P3), but unclear how exactly you treat (Fuchs-Sutugin correction?) and what values you use for critical parameters such as gas diffusivity and mass accommodation coefficient.

**Author response:** Since also the other referee asked for more details on the model, we added three tables into the supplement with details of our aqueous phase chemical mechanism (Table S1), phase transfer parameters (Table S2) and initial mixing ratios and concentrations (Table S3). Please find all tables at the end of this response. In addition, we added the following set of equations for the description of the phase transfer to the supplement:

The mass transfer coefficient  $k_{mt} [s^{-1}]$  can be expressed as (Seinfeld and Pandis, 1998)

$$k_{mt} = \left[ \frac{r_d^2}{3D_g} + \frac{r_d}{3\alpha} \sqrt{\frac{2\pi M_g}{RT}} \right]^{-1} \quad (Eq-R1)$$

Whereas

$r_d$  = cloud droplet radius [cm]

$D_g$  = gas phase diffusion coefficient [cm s<sup>-1</sup>]

$\alpha$  = mass accommodation coefficient (dimensionless)

$M_g$  = molecular weight of gas [ $\text{g mol}^{-1}$ ]

$R$  = constant for ideal gases ( $8.314 \cdot 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$ )

$T$  = temperature [K]

The mass transfer coefficient is then applied to determine the sink and source terms of soluble species:

$$\frac{dc_g}{dt} = k_{mt} \cdot LWC \cdot \left[ \frac{c_{aq}}{LWC \cdot K_{H(eff)} \cdot R' \cdot T} - c_g \right] + (P_{gaschem} - L_{gaschem}) \quad (\text{Eq-R2})$$

$$\frac{dc_{aq}}{dt} = k_{mt} \cdot LWC \cdot \left[ c_g - \frac{c_{aq}}{LWC \cdot K_{H(eff)} \cdot R' \cdot T} \right] + (P_{aqchem} - L_{aqchem}) \quad (\text{Eq-R3})$$

whereas both the gas and the aqueous phase concentrations have units of  $\text{mol g(air)}^{-1}$ ;  $LWC$  is the liquid water content in  $\text{g/m}^3$ ,  $K_{H(eff)}$  is the effective Henry's law constant in  $\text{M atm}^{-1}$ ,  $R'$  is the ideal-gas constant ( $8.314 \cdot 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature [K] and  $P$  and  $L$  are the rates of the chemical production and loss reactions in the gas and aqueous phases, respectively.

In brief, we do not use the Fuchs and Sutugin correction as this applies for the transition regime of transport of gas molecules towards particles, i.e. when the mean free path length of molecules ( $\lambda$ ) is approximately equal to the particle diameter ( $D_p$ ), i.e. when the Knudsen number is  $\text{Kn} \sim 1$ . The transport of gas molecules towards droplets with typical diameters of  $10 \mu\text{m}$  or larger falls into the continuum regime. For this regime, the various processes that affect the transport of gas molecules into droplets were expressed in terms of 'resistances' by (Schwartz, 1986). These processes generally include gas phase diffusion, interfacial mass transport, aqueous phase diffusion and aqueous phase chemical reaction. In previous sensitivity studies, we have shown that aqueous phase diffusion is usually sufficiently fast compared to the interfacial mass transfer chemical reaction in cloud droplets so its term can be neglected (Ervens et al., 2003b, 2014).

We add the following text at the beginning of Section 2.1:

*We use a multiphase box model with detailed gas and aqueous phase chemistry (75 species, 44 gas phase reactions, 31 aqueous reactions). The chemical aqueous phase mechanism with rate constants is listed in **Table S1**. The chemical gas phase mechanism is based on the NCAR Master mechanism (Aumont et al., 2000; Madronich and Calvert, 1989). The two phases are coupled by 26 phase transfer processes which is described kinetically based on the resistance model by Schwartz (1986). The parameters describing the phase transfer of the soluble species are presented in **Table S2**. In addition, the initial mixing ratios of gas phase species are included in **Table S3**.*

*The equations for the mass transfer coefficient  $k_{mt}$  and the differential equations for the aqueous and gas phase concentrations were added to the supplement (**Eq-R1-R3**; Section 'Description of phase transfer') (Seinfeld and Pandis, 1998).*

**Referee Comment:** - I wonder what is cell viability and how long bacteria would survive in cloud droplets. Would this be something should be discussed and considered in the model with some sensitivity studies?

**Author response:** We thank the referee for pointing to the uncertainties associated with the biological activity of bacteria in clouds vs lab studies. We did not perform any sensitivity studies on the viability and survival time of bacteria cells in cloud water due to the large uncertainties associated with their estimates. Viable cells have been isolated from aerosol samples (Bovallius et al., 1978; Lighthart, 1997). Given that

living bacteria cells have been found in the atmosphere at many different places around the world, not only in clouds but also in particles, it seems reasonable to assume that cells survive for several hours or days (Fahlgren et al., 2010; Lighthart and Shaffer, 1994). Metabolic activity in cloud water was confirmed by assaying ATP (Adenosine 5'triphosphate) in cloud water samples (Amato et al., 2007b). ATP is considered as a key molecule of the energetic cell metabolism. We also would like to refer to a discussion on uncertainties in determining viable, cultivable and living cell fractions in our previous publication (Ervens and Amato, 2020). We will add some information on this topic throughout the manuscript; see our response to the next comment.

**Referee Comment:** Cloud droplets contain oxidants (e.g., OH, H<sub>2</sub>O<sub>2</sub>, etc.), so I wonder if they experience oxidative stress and eventually degraded? In other words, would  $k_{\text{bact}}$  be time-dependent?

**Author response:** The referee is correct that high oxidant concentrations in the atmosphere and in particular in cloud water lead to stressful conditions for the bacteria cells, in addition to other factors such as UV exposure, low pH and temperature (Sattler et al., 2001). In addition, other effects such as substrate limitation may impact  $k_{\text{bact}}$ . Thus, given these different aspects, we respond to this referee comment in three parts:

a) Previous experiments in our research group have shown that cloud microorganisms can resist the oxidative stress due to the presence of reactive oxygen species, such as OH. The ADP/ATP ratio was monitored during such experiments which showed that even after exposure to oxidants over several hours, biodegradation rates were not significantly affected (Vařtilingom et al., 2013). Based on these experiments, we can conclude that the presence of oxidants at typical levels as found in cloud water probably does not significantly affect  $k_{\text{bact}}$  during the cloud cycles.

We add to the introduction (1.48, 52):

*The atmosphere is a stressful environment for microorganisms (low temperature, UV exposure, acidic pH, quick hydration/drying cycles and the presence of oxidants such as OH, H<sub>2</sub>O<sub>2</sub>) which might limit the survival time of cells in the atmosphere. Marker compounds such as adenosine 5'-triphosphate (ATP) (Amato et al., 2007c), rRNA 50 (Krumins et al., 2014) or mRNA (Amato et al., 2019) have been used to demonstrate metabolic activity in the atmosphere. The ADP/ATP ratio was monitored during such experiments which showed that even after exposure to oxidants over several hours, biodegradation rates were not significantly affected (Vařtilingom et al., 2013).*

b) Recent experiments of airborne bacteria suggested that metabolic rates are a function of substrate availability (Krumins et al., 2014). Cloud water can be considered an oligotrophic medium. As the biodegradation experiments by (Husárová et al., 2011; Vařtilingom et al., 2010, 2013) were performed in real or artificial cloud water with realistic solute concentrations, it is assumed that biodegradation occurs at the same rates in clouds. In the case of the CCN-derived water-soluble substrates that are not replenished within a cloud cycle, such substrate limitation might occur. However, as we do not have any data on the change of biodegradation rates as a function of substrate limitation, we do not perform any additional sensitivity studies. Our conclusions would not change, namely that the amount of CCN-derived organics that can be consumed by biodegradation is constrained by the fraction of cloud droplets that contain bacteria cells. Soluble gases are continuously replenished in the cloud water due to uptake processes from the gas phase (cf our discussion of Figure 5 in Section 3.1.2). If the availability of substrates with intermediate water-solubility decreases,  $k_{\text{bact}}$  may decrease as well. However, as a response, the substrate concentration might increase due to a relatively more efficient replenishment from the gas phase, which may, in turn, lead to an increase in  $k_{\text{bact}}$  again. Currently, no data is available on the absolute changes in  $k_{\text{bact}}$  at different levels of substrate availability and/or on the time scales during which  $k_{\text{bact}}$  might adjust to such conditions. Therefore, we do not think sensitivity studies on would be useful at this point due to the lack of parameter

constraints. We will add some discussion of such potential feedbacks in Section 4, highlighting the need of future experiments.

We add in the introduction (line 66):

*The biodegradation rate likely depends on the availability of the substrate in the aqueous phase. In the case of soluble substrates, it can be expected that uptake of soluble substrates from the gas phase leads to a continuous replenishment of the organics.*

We add in Section 5 (l. 591):

*Recent experiments of airborne bacteria suggested that metabolic rates are a function of substrate availability in oligotrophic media such as cloud droplets (Krumins et al., 2014). In the case of CCN-derived organics or those that are inefficiently replenished by uptake from the gas phase, substrate limitation might result in lower metabolic rates. Currently, no data is available on the absolute changes in  $k_{bact}$  at different levels of substrate availability and/or on the time scales during which  $k_{bact}$  might adjust to such conditions.*

c) The initial biodegradation rates of acetic and formic acid in lab experiments were observed to be very small if detectable at all (Herlihy et al., 1987). Only after incubation of several hours or days, biodegradation was observed. However, such incubation periods are likely due to the adjustment of the bacteria cells to the ambient conditions in the lab experiments. As bacteria cells are continuously exposed to water, solutes, substrates etc in the atmosphere, such incubation periods are unlikely to occur in clouds. Indeed, experiments in our lab performed in real cloud water did not exhibit such lag periods (e.g. (Amato et al., 2007a; Vařtilingom et al., 2010, 2013) which supports this hypothesis. While we touched briefly on this topic in Section 4, we will extend this discussion in the revised manuscript adding the latter references.

While some text on the incubation effects was already included in Section 4.3, the following references will be added there (line 535):

*While the latter was regarded as being inefficient due to long incubation time as observed in lab experiments, more recent experiments suggest that such incubation times are likely not occurring in the atmosphere where bacteria cells are continuously exposed to water and substrates (Amato et al., 2007a; Vařtilingom et al., 2010, 2013).*

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**Table S1.** Aqueous phase chemical mechanism : aqueous phase irreversible reactions with rate constants  $k$  and temperature dependencies ( $E_a/R$ ) where available and aqueous phase equilibria (Ervens et al., 2003, 2008) .

Reactions	Reactants	Products	$k$ [ $M^{-1} s^{-1}$ ]	$E_a/R$ [K]
Aqueous phase irreversible reactions				
R <sub>1</sub>	SO <sub>2</sub> + O <sub>3</sub>	S(VI) + O <sub>2</sub>	2.4×10 <sup>4</sup>	
R <sub>2</sub>	HSO <sub>3</sub> <sup>-</sup> + O <sub>3</sub>	S(VI) + O <sub>2</sub>	3.7×10 <sup>5</sup>	5530
R <sub>3</sub>	SO <sub>3</sub> <sup>2-</sup> + O <sub>3</sub>	S(VI) + O <sub>2</sub>	1.5×10 <sup>9</sup>	5280
R <sub>4</sub>	H <sub>2</sub> O <sub>2</sub> + HSO <sub>3</sub>	S(VI) + H <sub>2</sub> O	7.2×10 <sup>7</sup>	14000
R <sub>5</sub>	HO <sub>2</sub> + HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	8.3×10 <sup>5</sup>	2720
R <sub>6</sub>	O <sub>2</sub> <sup>-</sup> + HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	9.7×10 <sup>7</sup>	1060
R <sub>7</sub>	OH + CH <sub>2</sub> O	HO <sub>2</sub> + HCOOH	1×10 <sup>9</sup>	1020
R <sub>8</sub>	OH + CH <sub>3</sub> OOH	CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	2.4×10 <sup>7</sup>	1680
R <sub>9</sub>	OH + CH <sub>3</sub> OOH	HO <sub>2</sub> + HCOOH	6×10 <sup>6</sup>	1680
R <sub>10</sub>	O <sub>3</sub> + O <sub>2</sub> <sup>-</sup> (+ H <sup>+</sup> )	OH + 2 O <sub>2</sub>	1.5×10 <sup>9</sup>	2200
R <sub>11</sub>	OH + CHOCHO	HO <sub>2</sub> + CHOCOOH	1.1×10 <sup>9</sup>	1516
R <sub>12</sub>	OH + CHOCOOH	HO <sub>2</sub> + H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	3.6×10 <sup>8</sup>	1000
R <sub>13</sub>	OH + CHOCOO <sup>-</sup>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	2.9×10 <sup>9</sup>	4300
R <sub>14</sub>	OH + CH <sub>3</sub> COCHO	HO <sub>2</sub> + 0.92 CH <sub>3</sub> COCOOH + 0.08 CHOCOOH	1.1×10 <sup>9</sup>	1600
R <sub>15</sub>	OH + CH <sub>2</sub> (OH)CHO	HO <sub>2</sub> + COOHCH <sub>2</sub> OH	1.2×10 <sup>9</sup>	
R <sub>16</sub>	OH + COOHCH <sub>2</sub> OH	HO <sub>2</sub> + CHOCOOH	1.2×10 <sup>9</sup>	
R <sub>17</sub>	OH + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	O <sub>2</sub> <sup>-</sup> + 2 CO <sub>2</sub> + OH <sup>-</sup>	1.6×10 <sup>8</sup>	4300
R <sub>18</sub>	OH + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	HO <sub>2</sub> + 2 CO <sub>2</sub> + OH <sup>-</sup>	1.9×10 <sup>8</sup>	2800
R <sub>19</sub>	OH + HOCCOOH	HO <sub>2</sub> + 2 CO <sub>2</sub> + H <sub>2</sub> O	1.4×10 <sup>6</sup>	
R <sub>20</sub>	OH + CH <sub>3</sub> C(O)COOH	HO <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> COO <sup>-</sup>	7×10 <sup>8</sup>	
R <sub>21</sub>	OH + CH <sub>3</sub> COCOOH	HO <sub>2</sub> + H <sub>2</sub> O + CH <sub>3</sub> COOH	1.2×10 <sup>8</sup>	
R <sub>22</sub>	OH + HCOO <sup>-</sup>	HO <sub>2</sub> + CO <sub>2</sub> + H <sub>2</sub> O	3.2×10 <sup>9</sup>	1000

R <sub>23</sub>	OH + HCOOH	HO <sub>2</sub> + CO <sub>2</sub> + H <sub>2</sub> O	1.3×10 <sup>8</sup>	1000
R <sub>24</sub>	OH + CH <sub>3</sub> COO <sup>-</sup>	HO <sub>2</sub> + OH <sup>-</sup> + 0.15 CH <sub>2</sub> O + 0.85 CHOCOOH	1×10 <sup>8</sup>	1800
R <sub>25</sub>	OH + CH <sub>3</sub> COOH	HO <sub>2</sub> + H <sub>2</sub> O + 0.15 CH <sub>2</sub> O + 0.85 CHOCOOH	1.5×10 <sup>7</sup>	1330
R <sub>26</sub>	CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	CH <sub>2</sub> O + CH <sub>3</sub> OH + HO <sub>2</sub>	1.7×10 <sup>8</sup>	2200
R <sub>27</sub>	H <sub>2</sub> O <sub>2</sub> + OH	HO <sub>2</sub> + H <sub>2</sub> O	3×10 <sup>7</sup>	1680
R <sub>28</sub>	OH + CH <sub>3</sub> CHO	HO <sub>2</sub> + H <sub>2</sub> O + CH <sub>3</sub> COOH	3.6×10 <sup>9</sup>	580
R <sub>29</sub>	O <sub>2</sub> <sup>-</sup> + CH <sub>3</sub> (CO)OO	CH <sub>3</sub> COOH	1×10 <sup>9</sup>	
R <sub>30</sub>	CH <sub>3</sub> C(O)OO + CH <sub>3</sub> C(O)OO	2 CH <sub>3</sub> O <sub>2</sub> + 2 CO <sub>2</sub>	1.5×10 <sup>8</sup>	
R <sub>31</sub>	OH + HO-CH <sub>2</sub> -CHO	HO <sub>2</sub> + CH <sub>2</sub> (OH)COOH	5×10 <sup>8</sup>	
R <sub>32</sub>	OH + WSOC	WSOC + HO <sub>2</sub>	3.8×10 <sup>8</sup>	
Aqueous phase equilibria				
E	Reactants	products	K <sub>a</sub> [M]	
E <sub>1</sub>	H <sub>2</sub> O	OH <sup>-</sup> +H <sup>+</sup>	1.0×10 <sup>-14</sup>	
E <sub>2</sub>	HO <sub>2</sub>	O <sub>2</sub> <sup>-</sup> + H <sup>+</sup>	1.60×10 <sup>-5</sup>	
E <sub>3</sub>	CHOCOOH	CHOCOO <sup>-</sup> +H <sup>+</sup>	6.60×10 <sup>-4</sup>	
E <sub>4</sub>	HCOOH	HCOO <sup>-</sup> + H <sup>+</sup>	1.77×10 <sup>-4</sup>	
E <sub>5</sub>	CH <sub>3</sub> COCOOH	CH <sub>3</sub> COCOO <sup>-</sup> + H <sup>+</sup>	4.07×10 <sup>-3</sup>	
E <sub>6</sub>	CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup> + H <sup>+</sup>	1.77×10 <sup>-5</sup>	
E <sub>7</sub>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> +H <sup>+</sup>	6.40×10 <sup>-2</sup>	
E <sub>8</sub>	HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> +H <sup>+</sup>	5.25×10 <sup>-5</sup>	
E <sub>9</sub>	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	22	
E <sub>10</sub>	HOCH <sub>2</sub> CH <sub>2</sub> OH	HOCH <sub>2</sub> CH <sub>2</sub> O <sup>-</sup> + H <sup>+</sup>	1.54×10 <sup>-4</sup>	
E <sub>11</sub>	SO <sub>2</sub> + H <sub>2</sub> O	HSO <sub>3</sub> <sup>-</sup> +H <sup>+</sup>	0.013	
E <sub>12</sub>	HSO <sub>3</sub> <sup>-</sup>	SO <sub>3</sub> <sup>2-</sup> +H <sup>+</sup>	6.60×10 <sup>-8</sup>	
E <sub>13</sub>	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	1000	
E <sub>14</sub>	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	0.102	
E <sub>15</sub>	CO <sub>2</sub> (aq)+H <sub>2</sub> O	HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	7.70×10 <sup>-7</sup>	
E <sub>16</sub>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup>	4.84×10 <sup>-11</sup>	
E <sub>17</sub>	NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup> + OH <sup>-</sup>	1.76×10 <sup>-5</sup>	
E <sub>18</sub>	H <sub>2</sub> O	H <sup>+</sup> + OH <sup>-</sup>	1×10 <sup>-14</sup>	

**Table S2.** Phase transfer parameters of soluble species to calculate the mass transfer coefficient (Eq-S1) and Henry's law constants K<sub>H</sub>. (M<sub>g</sub>: molecular weight, α: mass accommodation coefficient (*dimensio less*), D<sub>g</sub>: gas phase diffusion coefficient)

Species	M <sub>g</sub> [g mol <sup>-1</sup> ]	α <sup>[1]</sup>	D <sub>g</sub> [cm s <sup>-1</sup> ] <sup>[1]</sup>	K <sub>H</sub> [M atm <sup>-1</sup> ]
O <sub>3</sub>	48	0.05	0.148	1.14×10 <sup>-2</sup> <sup>[1]</sup>
H <sub>2</sub> O <sub>2</sub>	34	0.1	0.11	1.02×10 <sup>5</sup> <sup>[1]</sup>
HO	17	0.05	0.153	25 <sup>[1]</sup>
HO <sub>2</sub>	33	0.01	0.104	9×10 <sup>3</sup> <sup>[1]</sup>
HCHO	30	0.02	0.164	4.99×10 <sup>3</sup> <sup>[1]</sup>
CH <sub>3</sub> O <sub>2</sub>	47	0.0038	0.135	310 <sup>[1]</sup>
CH <sub>3</sub> OOH	48	0.0038	0.135	310
HNO <sub>3</sub>	63	0.054	0.132	2.1×10 <sup>5</sup> <sup>[1]</sup>
N <sub>2</sub> O <sub>5</sub>	108	0.0037	0.110	1.4 <sup>[1]</sup>
Hydroxyaldehyde	60	0.03	0.195	4.1×10 <sup>4</sup> <sup>[3]</sup>
Glyoxal	58	0.023	0.115	4.19×10 <sup>5</sup> <sup>[1]</sup>

Methylglyoxal	72	0.1	0.115	$3.2 \times 10^4$ <sup>[3]</sup>
HCOOH	74	0.012	0.153	$1.77 \times 10^{-4}$ <sup>[1]</sup>
Acetic acid	46	0.1	0.1	$4 \times 10^3$ <sup>[4]</sup>
Glyoxylic acid	60	0.019	0.124	$9 \times 10^3$ <sup>[2]</sup>
Glycolic acid	76	0.1	0.1	$9 \times 10^3$ <sup>[2]</sup>
Pyruvate	88	0.1	0.1	$3.11 \times 10^5$ <sup>[3]</sup>
Oxalate	90	0.1	0.1	$9 \times 10^3$ <sup>[3]</sup>
Hydroxyketone	88	0.1	0.1	100 <sup>[3]</sup>
CH <sub>3</sub> O <sub>3</sub>	75	0.1	0.1	669 <sup>[3]</sup>
Aldehyde	44	0.1	0.1	11.4 <sup>[3]</sup>
SO <sub>2</sub>	64	0.035	0.128	1.23 <sup>[3]</sup>
CO <sub>2</sub>	44	$2 \cdot e^{-4}$	0.155	$3.11 \times 10^{-2}$ <sup>[1]</sup>
Glycolaldehyde	58	0.1	0.1	$4.1 \times 10^4$ <sup>[3]</sup>
C <sub>2</sub> H <sub>5</sub> OOH	62	0.1	0.1	310 <sup>[1]</sup>
Organic compound that reacts with OH and is consumed by bacteria	150	0.1	0.1	$10^2 - 10^9$

[1]: (Ervens et al., 2003a), [2]: (Ip et al., 2009), [3]: (Sander, 2015), [4]: (Johnson et al., 1996)

**Table S3.** Initial gas phase mixing ratios of gas phase species and the concentration of species only in the aqueous phase; all other compounds considered in the mechanism were not initialized

Species formula	Species name	Mixing ratio [ppb]
<b>Gases with phase transfer into the aqueous phase</b>		
O <sub>3</sub>	ozone	39
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide	1.202
OH	hydroxyl radical	$3.05 \times 10^{-11}$
HO <sub>2</sub>	hydroperoxyl radical	$9.07 \times 10^{-3}$
HCHO	formaldehyde	2.519
CH <sub>3</sub> O <sub>2</sub>	methylperoxy radical	$1.38 \times 10^{-3}$
CH <sub>3</sub> OOH	methyl hydrogen peroxide	0.211
HNO <sub>3</sub>	nitric acid	0.397
N <sub>2</sub> O <sub>5</sub>	dinitrogen pentoxide	$4.806 \times 10^{-4}$
CH <sub>2</sub> (OH)CHO	hydroxy acetaldehyde	0.437
CHOCHO	glyoxal	0.218
CH <sub>3</sub> COCHO	methyl glyoxal	0.190
HCOOH	formic acid	$2.239 \times 10^{-3}$
HAc	Acetic acid	0.198
CH <sub>3</sub> CO(OO)	acetylperoxy radical	$5.5 \times 10^{-5}$
SO <sub>2</sub>	sulfur dioxide	0.150
CH <sub>3</sub> CHO	acetaldehyde	0.409
CO <sub>2</sub>	carbon dioxide	$3.96 \times 10^5$
CH <sub>2</sub> (OH)CHO	glycolaldehyde	0.4273
CH <sub>3</sub> CH <sub>2</sub> (OOH)	ethyl hydrogen peroxide	$2.423 \times 10^{-3}$
Organic compound		1
<b>compounds without phase transfer into the gas phase</b>		
NO	nitric oxide	0.0429
NO <sub>2</sub>	nitrogen dioxide	0.179
NO <sub>3</sub>	nitrate radical	$3.5 \times 10^{-4}$

HNO <sub>4</sub>	Peroxynitric acid	8.83×10 <sup>-3</sup>
CO	carbon monoxide	140.3
C <sub>5</sub> H <sub>8</sub>	isoprene	1.031
MACR	methacrolein	0.282
MVK	methyl vinyl ketone	0.113
C <sub>2</sub> H <sub>6</sub>	ethane	0.846
C <sub>2</sub> H <sub>4</sub>	ethene	0.469
C <sub>3</sub> H <sub>6</sub>	propene	0.118
H <sub>2</sub>	hydrogen	550
CH <sub>3</sub> CO(OOH)	peracetic acid	0.240
C <sub>4</sub> H <sub>10</sub>	butane	0.142
CH <sub>3</sub> CH <sub>2</sub> (OO)	ethylperoxy radical	7.144×10 <sup>-6</sup>
PO <sub>2</sub>	Other peroxy radicals (C <sub>2</sub> , C <sub>3</sub> )	1.414×10 <sup>-4</sup>
POOH	Hydroperoxides of PO <sub>2</sub>	2.076×10 <sup>-3</sup>
PAN	peroxy acetyl nitrate	0.586
Isop-OO		4.181×10 <sup>-3</sup>