Author response to comments by Referees R1 and R2

We thank both referees for their thoughtful comments on our manuscript. In the following, all referee comments are repeated in blue, author responses are in black. Original manuscript text is in *italic*, with new text in red and removed text marked. The line numbers refer to the revised manuscript version without track change. We also made numerous small edits in the manuscripts (correcting typos, grammar etc), which did not change the content. These changes are not explicitly listed here.

Comments by Referee 1 (R1):

General Comments:

R1 Comment 1: This work describes implementation of biodegradation loss rates for formic and acetic acids as in a detailed model of atmospheric gas and aqueous phase chemistry. There are few groups who can reliably do both chemical and biological modeling of clouds with skill. The novelty of this work, is that through explicit accounting of kinetic mass transfer limits during phase transfer processes between droplets, the authors find that biodegradation rates outpace chemical rates, which in contrary to conventional wisdom. The authors predict up to 20 ppt /h formic acid and 5 ppt /h acetic acid are biodegraded. The description of abiotic chemistry is much more complex than the microbiology. I think the authors seek to understand to what degree microbiology can compete with chemistry and are working to understand limits and boundaries. I am not an expert on microbiology. I think this is important work suitable for publication provided the following comments and questions can be addressed.

Author response: We appreciate the positive comments regarding the importance of our work as being important. We indeed show that biodegradation may represent significant losses that may exceed the chemical sinks under conditions when chemical losses are inefficient. Of course, the chemical budgets are determined by the combination of chemical losses and sources. To better clarify how biodegradation may affect the overall concentrations, we changed text (l. 7):

We predict that up to 20 ppt h^{-1} formic acid and 5 ppt h^{-1} acetic acid are biodegraded ~~, affecting the total change of acid concentrations by 20% and 3%, respectively.~~ This translates into a concentration change of 20% and 3% in addition to that caused by chemical losses..

In addition, we clarified it further at the end of section 3.1 (l. 124):

In other words, the formic acid loss by chemical processes of ∼300 ppt (pH = 5.5) is enhanced to 360 ppt due to biodegradation. Acetic acid is predicted to increase by ∼80 ppt h^{-1} due to chemical processes (at pH = 5.5); this net increase is reduced to 66 ppt h^{-1} in the presence of bacteria cells.

R1 Comment 2: My main concerns relate to how well the description of microbial biodegradation rates accurately reflect atmospheric processes. There is discussion on how abiotic chemical oxidation changes with temperature and pH, but not for biotic biodegradation.

Author response: We agree that we did not provide sufficient details on the pH and temperature dependence of the biodegradation processes. We provide more data in our responses to the referee comments 3 and 4 below.

R1 Comment 3: On Line 74, the kbact rate employed for biodegradation is taken to be empirical for 17°C (290K), while the simulations are at 286K. Do biodegradation rates change over this temperature range? Also, how representative is the chosen temperature representative of cloud conditions? If a temperature sensitivity was performed, would biodegradation rates be sufficiently well characterized so that we accurately understand the temperature dependence of the abiotic vs. biotic competition?

Author response: The referee is right that we used k_{bact} measured at 17°C (290.15K) while the temperature in

the simulations was 286 K. The model temperature was chosen such that it reflects an average temperature as typically observed at the Puy de Dome observatory (`https://www.meteoblue.com/en/weather/historyclimate/climatemodelled/puy-de-d%C3%B4me_france_3021215`.

For the exploratory simulations in the present study, we used the numbers in **bold** since *Pseudomonas sp.* is generally representative for the cloud microbiome. However, the more data in Table R1 show that the variation of biodegradation rates between other bacteria species differs at least as much as within the temperature interval between 5°C and 17°C. We are currently working on a follow-up study that takes into account the diversity of the microbiome represented by multiple bacteria species (Nuñez López et al., in preparation).

We added the following text to the manuscript:

In Section 2.1 (l. 78):
Unlike for chemical reactions, we did not account for the temperature dependent biodegradation rates. The reasoning for this assumption is explored in Section 4.2.

In Section 4.2:
We modified Figure 7 to include temperature

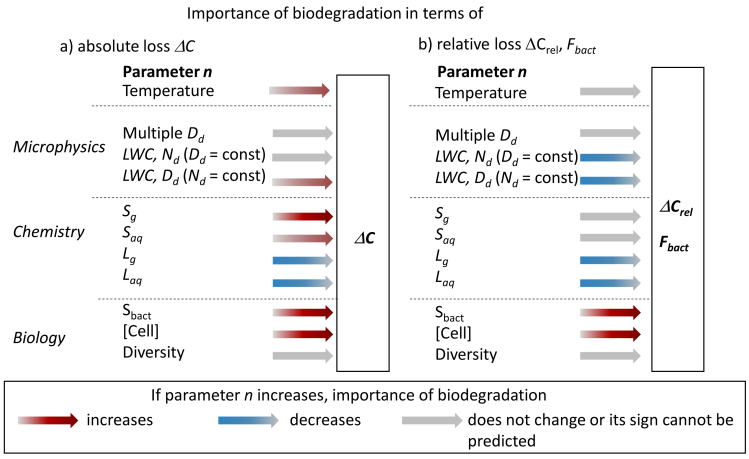

Figure R1: (Figure 7) Predicted change of absolute (ΔC) or relative (ΔC_{rel}, F_{bact}) importance of biodegradation as a function of temperature, cloud microphysical, chemical, and biological parameters. Red (blue) arrows indicate increased (decreased) importance with an increase of model parameter n; color intensity scales with expected strength of effect. Grey arrows denote either an insignificant change or an unpredictable sign of the change depending on n. These estimates are based on the assumption that one parameter at a time is varied.

and added (l. 378ff):
One simplified assumption regarding the biodegradation rates is the use of values derived in lab studies at 17°C. Similar to chemical rates, also biodegradation rates show a temperature dependence. Based on the measurements by Vaïtilingom et al. (2010) at 5°C and 17°C, we estimated activation energies E_a of 90 kJ mol^{-1} and 27 kJ mol^{1} for the biodegradation of formic and acetic acids, respectively (Section S2, Supplemental Information). To describe the temperature dependence of biological processes, often the Q_{10} factor is used that quantifies the change in a rate within a temperature interval of 10 K. The resulting Q_{10} factors are 3.9 and 1.5 for biodegradation of formic and acetic acids by *Pseudomonas sp.*, which are in general agreement for other biological processes that often show values between two and three. The overview of E_a and Q_{10} values in Section S1 suggests that differences between bacteria species may be larger than those due to temperature variation for a single species. However, these trends should be cautiously interpreted due to the very limited data base they are based on. It

should be also noted that the rates of biological processes often follow Arrhenius' law over limited temperature intervals only as they decrease beyond an optimum temperature (Schipper et al., 2014). Based on the current very limited data set it may be concluded that overall the temperature dependence of biodegradation rates may not have a large impact on ΔC. Given that the trend with temperature is similar for chemical reactions and biodegradation (both follow the Arrhenius law), ΔC_{rel} may be even less affected.

The referee comment inspired us to derive parameters to quantify the temperature dependence of the biodegradation rates for comparison to chemical processes - despite the very limited temperature-dependent data that are available.

We added all of the following into a new Section S1 in the supplemental information (including the tables and figures although they are not marked in red):

Section S1: Temperature dependence of biodegradation

Figure R2 shows k_{bact} *vs* T^{-1} [K^{-1}] (Table R1) compared to the corresponding trends for the OH reactions of formic acid/formate and acetic acid/acetate. This comparison suggests that the temperature dependencies for acetic acid are similar whereas the biodegradation of formic acid/formate seems more strongly T-dependent than the corresponding OH reactions.

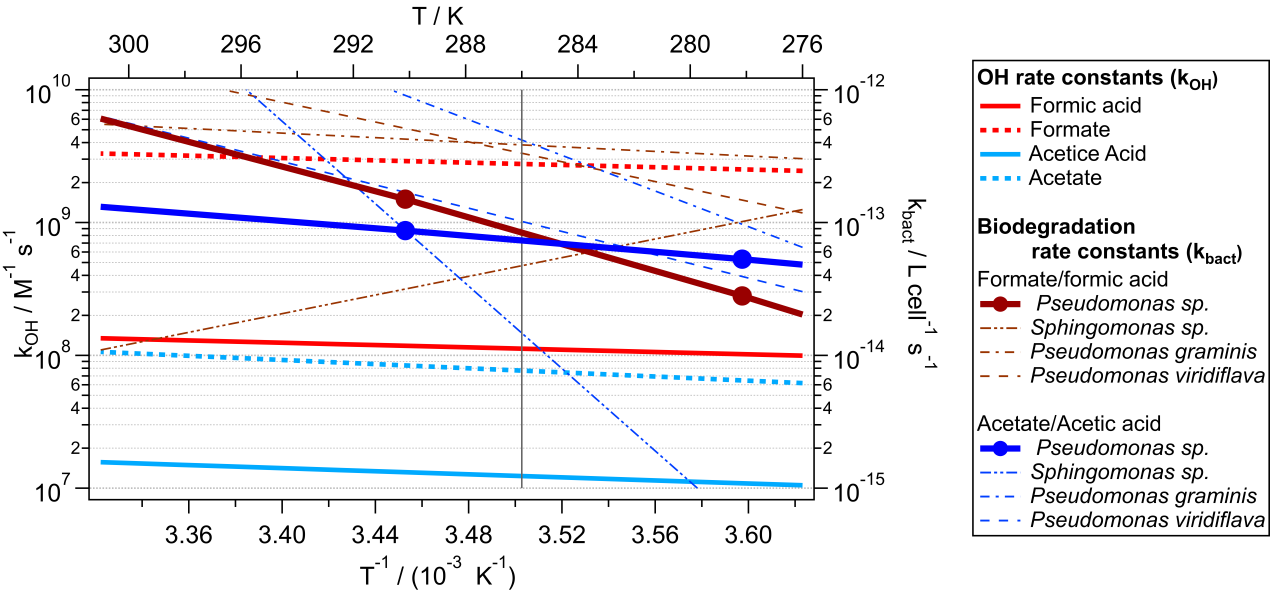

Figure R2: Temperature dependencies for chemical rate constants for the OH reactions (k_{OH}) and biodegradation (k_{bact}) of formic and acetic acids. The temperature dependencies for the OH reactions are taken from Chin and Wine (1994), while bacterial species data were derived by Khaled et al. (2021) based on the measurements by Vaïtilingom et al. (2010) at 278.15 K and 290.15 K. The vertical lines denotes the temperature at which the model simulation were performed.

Using the Arrhenius equation

$$k_2 = k_1 \cdot exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \quad (1)$$

we can derive the activation energies E_a of the biodegradation processes as 90 kJ mol^{-1} and 27 kJ mol^{-1} for

Table R1: k_{bact} values for formic and acetic acid, (Khaled et al., 2021) based on the measured biodegradation rates by (Vaïtilingom et al., 2010)

Species	k_{bact}(17°C)	k_{bact}(5°C)
	/10^{-13} L cell^{-1} s^{-1}	
Formic acid		
Sphingomonas sp.	0.3	1.0
P. graminis	4.3	3.2
Pseudomonas sp.	**1.5**	0.28
P. viridiflava	5.4	1.5
Acetic acid		
Sphingomonas sp.	1.1	0.0054
P. graminis	10	1.0
Pseudomonas sp.	**0.87**	0.53
P. viridiflava	1.8	0.4

Pseudomonas sp., but with large ranges of (-65 - +90 kJ mol^{-1} and 273 - 285 kJ mol^{-1}) for all species investigated by (Vaïtilingom et al., 2010). Using the E_a values, the biodegradation rates at our model temperature would have been $\sim$ 40% and $\sim$ 13% lower than the measurements at 17 °C.
However, given the uncertainties associated with the measured biodegradation rates and their derived temperature dependencies (based on the two data points only!), we do not put much confidence into the derived temperature dependencies. This uncertainty is even further supported by the large scatter of values and slopes for the temperature dependent values of the other bacteria species measured by Vaïtilingom et al. (2010) (Figure R2). Considering these large uncertainties, the use of the directly measured data at 17°C seems justified.
Activation energies for biodegradation processes are rarely measured directly. A study on biodegradation of aromatic compounds showed an average value of 65 kJ mol^{-1} (Knudsmark Sjøholm et al., 2021) which is within the range of the values determined (for quite different organic species).
The comparison of the E_a values for the OH reactions of the acids show similar trend but much lower values as compared to those for biodegradation with 8 kJ mol^{-1} and 9 kJ mol^{-1} for formic acid and formate and 11 kJ mol^{-1} and 15 kJ mol^{-1} for acetic acid and acetate (Chin and Wine, 1994).

The temperature dependence for biological processes is often expressed by means of the Q_{10} factor according to

$$R_{cell}(T_2) = R_{cell}(T_1) \cdot Q_{10}^{(T_2-T_1)/10} \tag{2}$$

i.e., the Q_{10} factor quantifies the change in the rate constant in a temperature interval of 10 K

$$Q_{10} = \frac{k_2}{k_1} \tag{3}$$

Based on Equation 3, we derived Q_{10} values for the temperature interval 285 - 295 K (Table R2). They are in general agreement with those for cell generation rates ($\sim 2 \leq Q_{10} \leq \sim 3$).
By combining Equations 1 and 2, one can derive a simple relationship of Q_{10} and E_a, which is valid if T_1 and T_2 differ by 10 K (i.e. (T_2-T_1)/10 = 1):

$$Q_{10} = exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \tag{4}$$

Table R2: Q_{10} factors (12°C $\leq$ T $\leq$ 22°C) and activation energies derived from the biodegradation rates measured at 5°C and 17°C by Vaitilingom (2010). Q_{10} is temperature dependent and only valid for the indicated specific temperature interval.

	Formic acid		Acetic acid	
	Q_{10}	E_a /kJ mol^{-1}	Q_{10}	E_a /kJ mol^{-1}
Pseudomonas sp.	3.9	90	1.5	27
Sphingomonas sp.	0.4	-65	72	286
Pseudomonas graminis	1.3	16	6.4	124
Pseudomonas viridiflava	2.8	69	3.4	81

R1 Comment 4: How about for pH? It is difficult to understand how accurate the findings regarding pH dependence are, given the neglect of pH consideration for the biodegradation rates.

Author response: The biodegradation rates used in the current study were measured both at pH values relevant for marine (6 $\leq$ pH $\leq$ 6.5) and continental (4.7 $\leq$ pH $\leq$ 5.2) cloud water (Vaïtilingom et al., 2011).

Table R3: Average biodegradation rates [10^{-18} L cell^{-1} s^{-1}] for by different bacteria species of formic and acetic acid under marine (6 $\leq$ pH $\leq$ 6.5) and continental (4.7 $\leq$ pH $\leq$ 5.2) conditions; data taken from Table 2 by Vaïtilingom et al. (2010)

		Marine	Continental
Average rate (range)	Formic acid	1 (0.2 - 8)	2 (0.2 - 10)
	Acetic acid	0.7 (0.4 - 2)	0.8 (0.09 - 7)

The values do not show any consistent trend, even for strains within one bacteria species. Generally, the pH dependence of biodegradation is expected to be weak due to the capacity of cells to intracellular buffering. Thus, our assumption of neglecting pH dependence seems justified over the relevant pH range within the cloud. The pH dependence may become significant under more extreme pH conditions, its relevance within the context of our study is negligible.
We only added the following to the manuscript (l. 171):

The biodegradation rates themselves are assumed to be pH-independent due to intracellular buffering, in agreement with lab studies that showed only small variations in biodegradation rates for cloud relevant pH ranges (Liu et al., 2023; Vaïtilingom et al., 2011).

We feel that our model description makes it clear that the current study represents a continuation of our previous model study by Khaled et al. (2021) where it is explicitly stated:

"Experiments with 17 different cloud bacteria in artificial cloud water with pH = 5.0 and pH = 6.5 showed also nearly identical results so it can be concluded that biodegradation rates are largely independent of pH for values typical in cloud water (Vaïtilingom et al., 2010). Similar results were shown by (Razika et al., 2010) who demonstrated that biodegradation rates of phenol by Pseudomonas aeruginosa were very similar when incubated at pH = 5.8, 7.0 and 8.0. When exposed to very broad ranges of external pH values, bacteria can control their intracellular pH (∼6.5 – 7) by internal buffering (Delort et al., 2017). As biodegradation occurs inside the cell, it takes place at these (nearly) neutral conditions. The efficiency of buffering decreases at extreme conditions, e.g., pH < 2 or pH > 10 (Guan and Liu, 2020). However, such a pH range is not representative for cloud water where more moderate pH values (∼3–6) are typically found (Deguillaume et al., 2014). Therefore, we do not

consider a potential pH dependency of biodegradation rates in our model studies."

R1 Comment 5: I understand how Equation 7 is derived given constant values of LWC and bacteria. I am comfortable with the idea that an air parcel has a given amount of LWC that is distributed over the available activation particles. Is a similar approach for bacteria reasonable? Can the authors back up this assumption for bacteria?

Author response: We are not fully sure what the referee is asking. Below we address several aspects and hope that they answer the referee's question.

a) Generally, it can be assumed that bacteria act as efficient CCN due to their relatively large sizes and their sufficient hygroscopicity (Bauer et al., 2003). Thus, it seems reasonable to assume that the concentration of bacteria in an air volume inside clouds is the same as outside clouds. This assumption is supported by various measurements of bacteria concentrations in cloud water samples of $N_{cell,aq} \leq 2.4 \cdot 10^5$ cells L_{aq}^{-1} (Amato et al., 2007). that would correspond to cell concentrations in air volumes of $\leq$~0.01 - 0.1 cm^{-3} (for an average liquid water content of ~0.5 g m^{-3}), according to

$$N_{cell,air}[cm_{air}^{-3}] = N_{cell,air}[cells\, mL_{aq}^{-1}] \cdot LWC\,[g\, m_{air}^{-3}] \cdot 10^{-6} \quad (5)$$

whereas factor 10^{-6} accounts for conversion using water density (ρ_{H2O} ~1 g cm^{-3} and the volumes m^3 to cm^3. This concentration is in overall agreement with the average concentration of bacteria cells in air (~0.001 - 0.1 cm^{-3}) as shown in the review article by (Burrows et al., 2009). To the best of our knowledge, simultaneous measurements of bacteria cells outside and inside of a single cloud are not available to date to back up this estimate more accurately.

b) We realised that the equation 7 in our manuscript might have been somewhat misleading since it might have implied inverse relationship of N_{cell} with LWC. We did not mean to imply this. We rewrote the equation in the manuscript as follows

$$F_{NCell} = \frac{N_{cell}}{N_{tot}} = N_{cell} \frac{\frac{\pi\, D_d^3}{6}}{LWC} \cdot 100\% \quad (6)$$

which makes it clearer that the LWC is a function of N_{tot} (i.e. the sum of all droplet volumes $\pi/6 \cdot D_d^3$).

The ratio N_{cell}/N_{tot} has been shown to vary over large ranges. We added after the equation (l. 145):

F_{NCell} can largely vary, depending on conditions and on the aerosol size range that is considered. It may be as high as several percent if N_{tot} is assumed to constitute only supermicron particles in dust storms (Hu et al., 2020) or in the upper troposphere (DeLeon-Rodriguez et al., 2013). If the full particle size range is taken into account ($D_{particle} > 10$ nm), the fraction can be calculated as being < 0.001%, e.g. for conditions as being typical at the Puy de Dôme station ($N_{tot,average}$ ~2000 cm^{-3} for $D > 10$ nm, and 0.01 cm $^{-}3 \leq N_{cell} \leq 0.1^{-3}$, Baray et al. (2020)). In a coniferous forest, the fraction of bioaerosol particles (including bacteria and other microbes) to total particles has been found to be in the range of 0.1 - 0.5 % for supermicron particles (Petersson Sjögren et al., 2023).

Accordingly, Figure 3c shows that F_{NCell} spans several orders of magnitude from ~ 10^{-4}% to ~0.3%.

Specific comments:

R1 Comment 6: Line 10: instead of (high effective Henry's law coefficient), which is subjective - it would be better to list both the FA and AA Heff values.

Author response: Thanks for this suggestion. We have now explicitly included the values for the effective Henry's law constants in the abstract as follows (l. 11):

~~*high effective Henry's law constant)*~~

($K_H^{eff}(HCOOH)$ = 2·10^5 M atm^{-1} vs $K_H^{eff}(CH_3COOH)$ = 3·10^4 M atm^{-1})

R1 Comment 7: Line 11: "...from bacteria-free and subsequent uptake into bacteria-containing droplets ...." This is awkwardly written and hard to understand.

Author response: We have rephrased the sentence for clarity and readability (l. 9).

~~*This trend is explained by the higher solubility of formic acid (high effective Henry's law constant) that results in less evaporation from bacteria-free and subsequent uptake into bacteria-containing droplets.*~~

This trend can be explained by the fact that formic acid is partitioning more efficiently into the aqueous phase due to its higher Henry's law constant ($K_H^{eff}(HCOOH) = 2{\cdot}10^5$ $M\ atm^{-1}$ vs $K_H^{eff}(CH_3COOH) = 3{\cdot}10^4$ $M\ atm^{-1}$ at $pH = 5$). Therefore, under such conditions, formic acid evaporates less efficiently from bacteria-free droplets resulting in less formic acid in the gas phase for dissolution bacteria-containing droplets to replenish biodegraded acid.

R1 Comment 8: Line 50: The authors state "Species concentrations in the atmosphere are much lower than in the denser soil; however, the atmospheric volume is much larger as compared to the biotic terrestrial and aquatic environments. Therefore, it seems reasonable to infer a potential role of biodegradation as a competitive sink to other atmospheric loss processes". Is that right? It is not the volume of atmospheric water, not the total atmosphere, that is available for biodegradation?

Author response: The referee made us aware that our text was not very clear since we mixed two different aspects. Biodegradation kinetics can be compared in two ways to answer different research questions:

1. If one wants to address the question *"What fraction of a specific organic compound is (bio)degraded in the atmosphere as compared to other environments (e.g. ocean, soil)?"*, one needs to consider the total multiphase systems in the respective environmental compartments and not only the aqueous phases. The total absolute loss rate is then determined by the number of bacteria cells (i.e. concentration × volume). Significant microbial activity takes place in the aerobic parts of aquatic environments. While cloud droplets are always saturated with oxygen, such conditions are only met in the upper layers of soil and surface waters, where also nutrient concentrations might be highest.
   Given that bacteria need water to sustain their metabolic activity, these losses may occur in the full volume of aquatic environments (ocean, lakes), but only in a small of fraction of soil or the atmosphere which comprise multiphase phases.

2. In the atmosphere, the aqueous phase is not limited to clouds; there is indeed evidence of microbial activity in aqueous particles outside of clouds exhibiting different functional profiles (Péguilhan et al., 2023). For a comparison of the efficiency of biodegradation in- *vs* outside clouds, one should scale the rates with the volumes of the aqueous phases. Due to the lack of systematic data for out-of-cloud conditions, to date our model cannot be applied for such a comparison.

3. One may compare the biodegradation in the aqueous phases of other water-containing environments (e.g., surface waters or the aqueous phase of soil) to explore the question *"What is the extent to which kinetic data for biodegradation processes measured for aquatic environments (e.g. sea water) can applied to biodegradation in the atmosphere?"*. Indeed, for such a comparison, one should only take into account the aqueous volume fraction of the atmosphere. Such a comparison gives potentially information whether the specific conditions (e.g., chemical and biological composition) in the different aqueous phases affect the biodegradation kinetics. Such a comparison will be provided in a future study (Ervens et al., *in preparation*).

We clarified the text as follows (l. 48ff):

Biodegradation is a well-known efficient aerobic loss process of organics in soil where bacteria cell concentrations

are on the order of 10^9 cell cm^{-3} (Adeleke et al., 2017). Cell concentrations in the atmosphere are much lower ($\sim$0.01 cm^{-3}) than in the denser soil that typically has an aerobic layer of $\sim$10 cm. ~~however, t~~ Therefore the atmospheric volume is much larger as compared to the aerobic terrestrial and aquatic environments which may result in comparable rates (cell concentration $\times$ volume) if one compares losses in different environments (atmosphere vs soil vs surface waters). ~~Therefore, it seems reasonable to infer a potential role of biodegradation as a competitive sink to other atmospheric loss processes.~~
A first comparison of biodegradation rates to those of chemical processes in clouds was performed~~First estimates~~ based on atmospherically relevant cell concentrations and lab-derived biodegradation rates of organic acids This comparison suggests that biodegradation might be similarly efficient as OH or NO_3 reactions in cloud water (Vaïtilingom et al., 2013; Jaber et al., 2021).

R1 Comment 9: The Figure 2 caption should include an explanation of the isopleths.
Author response: We have included the isopleths in the caption for clarity.
Figure 2. Predicted concentration differences (ΔC; Equation 5) derived from 900 model simulations, through all combinations of 30 pH and 30 Dd values, depicted using isopleths. a) formic acid, and b) acetic acid. The red lines denote conditions that are discussed in detail in Sections 3.2 and 3.3. The numbers on the contour lines indicate ΔC in ppt h^{-1}.

R1 Comment 10: Does Fig 3 present the initial aqueous phase concentrations or are calculations for a give cloud processing time presented?
Author response: We have clarified that the figure presents results after a specific cloud processing time.
Figure 3. Dependence of a) ΔC of formic acid ($pH = 4.6$) and acetic acid ($pH = 5.6$) on the droplet diameter D_d, b) aqueous phase concentrations of formic acid ($pH = 4.6$) and acetic acid ($pH = 5.6$) (left scale) and the OH radical (right scale) as a function of D_d, and c) the percentage of bacteria-containing droplets F_{NCell} for $LWC = 0.42$ g m^{-3}, $N_{Cell} = 0.1$ cm^{-3} as a function of D_d. All values were derived from simulations after one hour simulation time.

Editorial:
R1 Comment 11: Line 21: grammar "...are ubiquitous main components of the global ..." Ubiquitous main reads a little awkwardly and should be rephrased.
Author response: We agree with the suggestion and have modified the sentence as follows (l. 23):
Formic and acetic acids, which are the smallest organic acids, are commonly found as major contributors to the global organic acid budget.

R1 Comment 12: Line 50: "... as a competitive sink to other atmospheric..." This reads a little awkwardly. I think the authors mean to say "competitive sink relative to ..." However, as described above, I am not sure they make this point
Author response: This sentence was deleted as part of our revision. Please see our response to comment 8.

R1 Comment 13: Line 92: I think "a" is missing between "to" and "second"
Author response: Corrected. The sentence reads now:
The results are compared to a second set of simulations...

R1 Comment 14: Line 99: I think "were" should be 'is' The paper is written in the present tense and biodegradation is singular.
Author response: The referee is right that subjunctive was not the right form here.
Thus, it quantifies the extent to which the total acid concentration is overestimated if biodegradation ~~were~~ is not

included.

R1 Comment 15: Fig. 3 caption, should delta D be delta C?
Author response: Thanks for spotting the typo. We corrected it.

Comments by Referee 2 (R2):

R2 Comment 1: The authors present a modeling study of the impact of bacterial metabolism of acetic and formic acids in cloud water and its impact on the atmospheric chemistry of these species. The topic is important, since the chemistry of formic acid in the upper atmosphere is not well understood and it has been suspected for some time that cloud chemistry and possibly biology play critical roles.
Author response: We thank the referee for their positive and constructive comments. We split the single paragraph provided by R2 into multiple sections (Comments 2 - 5) and respond to each of them separately. We addressed all of them in a new section in the revised manuscript that is provided after our responses.

R2 Comment 2: The premise of this study is similar to that of Fankhauser et al. (2019) who did a similar simulation in the GAMMA model, considering more organic species in both cloud droplets and aqueous aerosols in equilibrium with the gas phase. Although the fundamental chemistry and physics (and biology) in the models is similar, the authors emphasize that the important difference (other than the simulated droplet life cycle) is that the current study simulates an ensemble of droplets rather than focusing on a single droplet in equilibrium with the gas phase.
Author response: The referee is correct that there are similarities of our model study compared to previous model studies, including the one by Fankhauser et al. (2019) but also that by Pailler et al. (2023). All three model studies explored the potential importance of biodegradation in the atmospheric multiphase system. How-

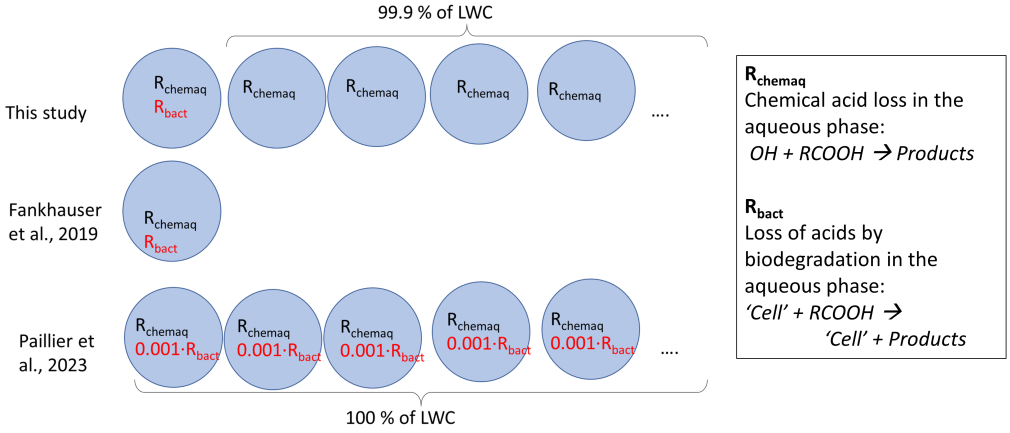

Figure R3: Schematic of the three model approaches that have been used to assess the role of biodegradation in the atmospheric multiphase system

ever, there are distinct differences between the three model approaches that allow for a different set of research questions to be answered. For illustration, we depict schematically the three approaches in Figure R3.
In brief: The model in our study used a population of droplets with only a few droplets (0.1%) containing bacteria. Fankhauser et al. (2019) only considered such bacteria-containing droplets and neglected the major part of the cloud liquid water content. Pailler et al. (2023) used a similar model set-up as ours but considered bacterial activity in all droplets with a rate scaled down by a factor of ∼1000. Table R4 lists a series of questions that can be addressed (or not) by the different model approaches. In response to the referee's comments, we

describe below the relevance of the various questions.

One *commonality* (I in Table R4) of all three models is the fact that they include a full multiphase chemistry mechanism (i.e. gas and aqueous phase chemistry). (All three mechanisms participated in a recent multiphase chemistry model intercomparison by Barth et al. (2021) and have been shown to differ in predictions of chemical concentrations.) These mechanisms were complemented by additional processes to account for biodegradation of organic species, in competition to chemical losses. All three model studies performed *sensitivity simulations with and without bacteria cells* (II) to assess the differences in formic and acetic acid concentrations for the two cases.

Table R4: Comparison of model features between our model study [1] and the ones by Fankhauser et al. (2019) [2] and Pailler et al. (2023) [3]

	Does the model ...	[1]	[2]	[3]
I.	...include a full multiphase chemistry mechanism ?	✓	✓	✓
II.	...allow for a comparison of acid concentrations in the absence and presence of bacteria cells?	✓	✓	✓
III.	...consider acid processing by chemical and biological processes in a realistic water volume to account for the total organic acid budget?	✓	✗	✓
IV.	...point to uptake limitation due to the very high biodegradation rates by individual bacteria cells?	✓	✓	✗
V.	...consider realistic distribution of bacteria cells in a few droplets only?	✓	✓	✗
VI.	...simulate biodegradation of organics with $K_{H,eff} \geq 10^5$ M atm^{-1}?	✓	✗	✗
VII.	...reveal the need of considering multiple drop classes to correctly account for the role of biodegradation in the atmosphere?	✓	✗	✗

R2 Comment 3: The authors posit that droplet-gas-droplet partitioning between droplets in the ensemble towards the droplets containing bacteria enhances the impact of bacteria on the organic acid budget despite the low total number of droplets containing bacteria in the ensemble. This is logical but most likely overstated in this study.

Author response:

This addresses ***Question III*** **in Table R4**: The sequence of events of (1) efficient net formation of acid in bacteria-free droplets, (2) acid evaporation, (3) uptake into bacteria-containing droplets, (4) biodegradation of acid that was formed in different droplets, is an important feature that has not been shown before. In the absence of bacteria, all droplets would produce formic and acetic acids at pH = 3 (cf Figure 6a in our paper). By no means, we think this sequence is logical and overstated. We identify specific conditions under which such sequence occurs, i.e. at pH = 3 for both formic and acetic acid and at pH = 5.6 for acetic acid only (cf the yellow arrows in Figure 6 of our manuscript). We explain these patterns by the differences in reactivities in the gas and aqueous phases. To the best of our knowledge, such an analysis has not been performed before for specific biodegradable compounds (or in fact, for any compounds, that show very different formation loss rates in an inhomogeneously composed droplet population). While our previous model study by Khaled et al. (2021) pointed to similar patterns, that study was purely based on 'hypothetical compounds' for which no chemical aqueous phase sources were considered.

In the present study, we show that the efficiency of biodegradation in decreasing the total organic acid budget despite the fact that the acid was formed in bacteria-free droplets. The model by Fankhauser et al. (2019) only

considers a very small liquid water volume (i.e. ∼1/1000 of a real cloud) and therefore does not account for all organic acid sources within the multiphase system. Therefore, we identify one of the major differences to the model by Fankhauser et al. (2019) that only our model and that by Pailler et al. (2023) can account for the full organic acid budget (i.e. gas + aqueous phase).

Therefore we think that the 'droplet-gas-droplet partitioning' under some conditions is a novel finding and neglecting it leads to an underestimate of the amount of biodegraded acid in the atmospheric multiphase system.

R2 Comment 4: The droplets in Fankhauser et al. were in equilibrium with the gas phase, and formic acid levels in the gas phase were not depleted by microbial activity on the timescale of the simulation (see, e.g. Figure S3 of that paper)- that is, the destruction of formic acid in the droplets was not limited by partitioning from the gas phase and any hypothetical partitioning to the gas phase from other cloud droplets would not have impacted this.

Author response:

We are somewhat confused about the referee's terminology of 'thermodynamic equilibrium'. We agree that the drop volumes do not change in either of the models (ours and theirs); therefore, water vapor is in thermodynamic equilibrium with the gas phase (droplets neither grow nor shrink). However, we understand that Fankhauser et al. (2019) used the same kinetic approach to describe the phase transfer of other chemical compounds as we did, i.e. considering a mass transfer coefficient (their equation 3 and our equation 3 are the same) to account for potential deviations from thermodynamic equilibrium due to kinetic limitations.

To address accordingly our **Question IV in Table R4**:

There may have been a misunderstanding of our definition of 'limitation' in this context. We mean by 'limitation' the lack of a sufficiently high phase transfer rate from the gas phase into bacteria-containing droplets to replenish biodegraded acids.

In fact, we think that the phase transfer limitation is a *commonality* between our and Fankhauser et al. (2019)'s model whereas this aspect was not fully represented by Pailler et al. (2023).

To demonstrate how we come to this conclusion, the following calculation are now included in the supplemental information as

Section S2 'Derivation of the factor *q* based on the model studies by Fankhauser et al. (2019) and Pailler et al. (2023)' .

The study by Fankhauser et al. (2019) provides predicted aqueous and gas phase concentrations in the absence and presence of bacteria cells. Pailler et al. (2023) reports aqueous phase concentrations and total concentrations (gas + aqueous). Based on their figures, we are able to derive (approximate) q values to explore the extent to which uptake limitations occurred. The q value is defined as the ratio of predicted aqueous and gas phase concentrations divided by teh Henry's law constant (Equation 14)

Figure 2 by Fankhauser et al. (2019) shows aqueous phase concentrations of ∼0.3·10^{-5} M and ∼0 in the absence and presence of bacteria cells, respectively. For both simulations, their Figure S3 shows a gas phase concentration of ∼2·10^{p} molec cm^{-3}. In the absence of bacteria cells, their concentration ratio is, thus,

$$\frac{c_{aq}[M]}{p_g[atm]} = \frac{0.3 \cdot 10^{-5} M}{2 \cdot 10^{9} molec\,cm^{-3} / 2.5 \cdot 10^{19} molec\,cm^{-3}\,atm^{-1}} \sim 37800\,Matm^{-1} \tag{7}$$

This concentration ratio corresponds to

$$q = \frac{C_{aq}}{p_g\,K_{H,eff}} = \frac{37800\,Matm^{-1}}{36500\,Matm^{-1}} \sim 1 \tag{8}$$

indicating thermodynamic equilibrium between the gas and aqueous phases in absence of bacteria and biodegradation.

In the presence of bacteria cells, the aqueous phase concentration was basically completely depleted (∼0, Fankhauser et al. (2019)'s Figure 2B) implying a q value much lower than unity by several orders of magnitude, and also lower than our value of q ∼0.8 predicted for bacteria-containing droplets (our Figure 5c). We cannot reconcile the reasons for this difference by several orders of magnitude. However, the significantly lower q based on the results by Fankhauser et al. (2019) suggests that there was no thermodynamic equilibrium between the gas and aqueous phases in their model and that despite a relatively high gas phase concentration, the phase transfer was not sufficiently fast to replenish the formic acid concentration in the aqueous phase. Therefore, we conclude that the biodegradation of formic acid in Fankhauser's model was significantly limited due to the relatively inefficient uptake of formic acid from the gas phase (and chemical production within the droplet) as compared to the efficient loss by biodegradation.
Since Fankhauser et al. (2019) do not report gas phase concentrations of acetic acid, we cannot perform the corresponding analysis for this acid. However, given that the aqueous phase concentration was only ∼10% lower in the presence of bacteria may imply that the biodegradation did not lead to such strong subsaturation of acetic acid in the droplets, in agreement with our results ($q(aceticacid) \sim 1$ at $pH = 4.5$, Figure 5b).

Pailler et al. (2023) report that net phase transfer rates in their simulations are zero in the presence and absence of bacteria, indicating thermodynamic equilibrium. This claim can be corroborated by an estimate of the corresponding q value based on their Figures 3 and 6 (very approximate since the exact data were not given in table form): E.g. for day conditions during summer in the presence of bacteria cells: $c_{aq}(HCOOH)$ 20 μM, $c_{total}(HCOOH)$ ∼3.6e9 molec cm^{-3} results in

$$\frac{c_{aq}[M]}{p_g[atm]} = \frac{20 \cdot 10^{-6} M}{(4.3 \cdot 10^9 - 3.6 \cdot 10^9) molec\, cm^{-3} / 2.5 \cdot 10^{19} molec\, cm^{-3}\, atm^{-1}} = 7 \cdot 10^5 Matm^{-1} \quad (9)$$

leading to

$$q = \frac{7 \cdot 10^5 Matm^{-1}}{5.2 \cdot 10^5\, Matm^{-1}} \sim 1 \quad (10)$$

whereas the denominator is the effective Henry's law constant for pH = 5.5. using the K_H and K_a as applied in the CLEPS mechanism that is used by Pailler et al. (2023). This result shows that in their model, the aqueous phase concentration was not limited by uptake and the acids were in thermodynamic equilibrium.

This comparison above allows to address our **Question V in Table R4**:
Our findings show that the consideration of a realistic distribution of bacteria cells in a few droplets only is essential to correctly predict the aqueous phase concentrations in droplets where biodegradation occurs.
The extremely efficient biodegradation rate 'per cell' can be much faster than the acid replenishment from the gas phase. This competition between uptake and loss by biodegradation cannot be correctly represented in a model assuming 'some biodegradation' in all droplets (i.e. implying a scaled-down biodegradation rate).
The model approach by Pailler et al. (2023) led to an overestimate of the role biodegraded acid due to the omission of uptake limitations, whereas it was properly accounted for in the present and Fankhauser et al. (2019)'s model studies.

Fankhauser et al. (2019) and Pailler et al. (2023) perform model studies at a single pH value only (4.5 and 5.5, respectively). Therefore, they do not describe biodegradation of compounds that are predicted to partition to $>$ 50% into the aqueous phase under equilibrium conditions at typical cloud LWCs (cf Figure 5a in our manuscript). To address our **Question VI in Table R4**: Our model study is the only one among the three approaches that systematically explores the sensitivity of biodegradation (as quantified by our parameters ΔC and ΔC_{rel}) on the solubility ($K_{H(eff)}$ of the substrates.
Our finding that biodegradation of species with $K_{H(eff)} \geq 10^5$ is likely unimportant in the atmosphere, gives important guidance for future research, e.g. for lab experiments dedicated to the

investigation of biodegradation rates..

Finally, while all three models were box models, our model approach is the only one that clearly points to potenital challenges associated with the implementation of biodegradation in larger scale models: To address our **Question VII in Table R4**: A common assumption in larger (regional, global) models is the distribution of the liquid water content into a monodisperse cloud droplet distribution where all droplets have the same chemical composition. Our model study reveals that this assumption may be too simple to account for biodegradation since (at least) two different drop classes have to be considered. Only that way, one can correctly account for the redistribution of acids due to the efficient chemical net production in the one class and uptake-limited biodegradation in the other(s). Since both Pailler et al. (2023) and Fankhauser et al. (2019) only considered a single drop class (though with very different number concentrations), they could not have come to this conclusion. **Our model study shows that biodegradation cannot be implemented in larger scale models in the same way as chemical reactions that occur in all cloud droplets. We highlight the need of the development of adequate parameterizations to account for biodegradation in total cloud water volumes.**

R2 Comment 5: The authors need to add some more nuance to their discussion of Fankhauser et al.
Author response: We hope that our discussion above makes the differences clear between our model versus the models by Fankhauser et al. (2019) and Pailler et al. (2023). Our extended discussion further clarifies that our model approach allows for unique conclusions that have not been and could not have been derived in these previous studies.

Further changes in the manuscript in response to R2:
We re-organized Section 4.1 in the paper and split it into two sub-sections:
4.1.1 Estimates based on the comparison of measured chemical and biodegradation rates
where we removed
~~*When acids are chemically formed in bacteria-free-droplets, evaporate and then taken up into bacteria-containing droplets (Figure 6), contributions by biodegradation can exceed by far the fraction of the aqueous volume where it occurs. This may ultimately result in biodegradation rates being comparable to chemical loss rates in the total aqueous phase (Table S6). Considering bacteria-containing droplets as isolated systems is only appropriate for non-volatile organics, including (di)carboxylic and amino acids, that are not replenished by phase transfer into bacteria-containing droplets.*~~

4.1.2 Implementation of organic acid biodegradation into multiphase chemistry models
~~*Even fewer*~~ *The few studies that implemented biodegradation of organic acids into multiphase chemistry model*~~*s studies, applying*~~ *applied different assumptions:*

1. *The model approach by Khaled et al. (2021) is similar to the current model. The only difference is that they focused on the comparison of loss processes of generic organics over wide ranges of chemical and biodegradation rates and solubility but without any chemical sources.*

2. *Fankhauser et al. (2019) considered only bacteria-containing droplets, i.e. a total LWC that is several orders of magnitudes smaller than in real clouds ($N_{d1} = 0$). Thus, the reactor volume for aqueous phase chemical reactions is small.*

3. *Pailler et al. (2023)* ~~*and Jaber et al. (2020)*~~ *used a multiphase box model with similar LWC and drop sizes as in the current model. They assumed that biodegradation occurs in all droplets, in analogy to chemical reactions. They used the same lab data for biodegradation rates by Vaïtilingom et al. (2010) as in the current study. However, their model approach implied that the biodegradation rate in each droplet*

is smaller by a factor 1 / F_{NCell} as compared to our approach, where no biodegradation occurs in > 99% of the droplets. ~~*In addition, Pailler et al. (2023) describe biodegradation rates as a non-linear function of acid concentrations to account for potential substrate-limitation at low concentrations. In our model study, this relationship is considered to be linear for simplicity (k_{bact} [Acid]$_{aq}$).*~~

The commonalities and differences between these approaches are summarized in Table R5. All three models included a (I) multiphase chemistry mechanism and explored the potential importance of biodegradation in the atmosphere by (II) sensitivity studies in the absence and presence of bacteria cells, respectively. However, there are distinct differences between the three model approaches that allow for addressing different aspects of the importance of biodegradation. They are briefly discussed in the following.

Table R5: *Comparison of model features between our model study [1] and the ones by Fankhauser et al. (2019) [2] and Pailler et al. (2023) [3]*

		[1]	[2]	[3]
I.	Full multiphase chemistry mechanism	✓	✓	✓
II.	Comparison of acid concentrations in the absence and presence of bacteria cells	✓	✓	✓
III.	Chemical and biological processing of acids in a realistic water volume to account for the total organic acid budget	✓	✗	✓
IV.	Uptake limitation due to the very high biodegradation rates by individual bacteria cells	✓	✓	✗
V.	Realistic distribution of bacteria cells in a few droplets only	✓	✓	✗
VI.	Sensitivity studies of biodegradation of organics with $K_{H,eff} \geq 10^5$ M atm^{-1}	✓	✗	✗
VII.	Concluding on the need of considering multiple drop classes to correctly account for the role of biodegradation in the atmosphere?	✓	✗	✗

***Realistic cloud liquid water content (III)**: We show in Figure 6 that at pH = 3, the bacteria-free droplets act as efficient reactors of formic and acetic acid production. In the absence of bacteria, all droplets would produce these acids at pH = 3 and, thus, increase the total acid concentration in the atmosphere. This acid production is not fully represented in the model by Fankhauser et al. (2019) because of the limited 'reactor size' comprised of the very small aqueous phase volume that did not comprehensively represent the full organic acid budget. Thus, in their study, the importance of biodegradation may have been generally underestimated because of an incomplete multiphase system.*

*When acids are chemically formed in bacteria-free-droplets, evaporate and then taken up into bacteria-containing droplets (**??**), contributions by biodegradation can exceed by far the fraction of the aqueous volume where it occurs. This may ultimately result in biodegradation rates being comparable to chemical loss rates in the total aqueous phase (Table S6). Considering bacteria-containing droplets as isolated systems is only appropriate for non-volatile organics, including (di)carboxylic and amino acids, that are not replenished by phase transfer into bacteria-containing droplets. For such compounds, the upper limit of F_{bact} is indeed constrained by the aqueous phase volume that contains bacteria. This limit may be as high as 0.3% depending on LWC, N_d and D_d (**??**c).*

***Uptake limitation (IV)**: As discussed in Section 3.4 and shown in Figure 6, the loss by biodegradation in the bacteria-containing droplets is very efficient; neither chemical reactions in the aqueous phase nor the uptake from the gas phase are sufficient to compensate for this rapid acid consumption, resulting in $q \leq 1$ (Figure 5c). Even though Fankhauser et al. (2019) did not explicitly discuss it in their study, similar trends can be deduced from their results since the formic acid concentration in the aqueous phase is basically zero in the presence of bacteria cells whereas in the absence of cells the aqueous phase concentration corresponds to its equilibrium value*

(Section S2, Supplemental Information). Pailler et al. (2023) did not observe that uptake limitation affected the the formic acid aqueous phase concentration. In their model, biodegradation occurred in all droplets but at moderate rates which could be always compensated for by acid sources (either uptake or chemical production in the aqueous phase). Even in the presence of bacteria cells, formic acid was apparently (approximately) in thermodynamic equilibrium which may explain their findings that the net phase transfer was negligible. Thus, their predictions of biodegraded formic acid might represent overestimates since the acid concentration available for biodegradation may have been to high. Although they implemented expression to account for non-linear decrease of biodegradation at low low substrate (acid) concentrations, such conditions may not have been even reached. In our model study, the biodegradation rate depends linearly on the substrate concentration ($k_{bact} \times [Acid]_{aq}$) and was, thus, significantly suppressed under uptake-limited conditions.

***Biodegradation of species with $K_{H(eff)} \geq\sim 10^5$ M atm^{-1} (VI)**: Uptake limitations are most prominent for species that are predicted to partition to a significant fraction to the aqueous phase, such as formic acid at $pH \geq 5$ ($K_{H,eff} \geq 10^5$ M atm^{-1}). Our model study is the first one to systematically explore the sensitivity of biodegradation (as quantified by ΔC and ΔC_{rel}) on the solubility ($K_{H(eff)}$ of specific substrates. The finding that biodegradation of species with $K_{H(eff)} \geq 10^5$ is likely unimportant in the atmosphere, gives important guidance for future research, e.g., for lab experiments dedicated to the investigation of biodegradation rates of additional compounds.*

***Consideration of multiple drop classes with/out bacteria (V and VII)**: We conclude that it is essential in models to distinguish the small number concentration of bacteria-containing droplets from those without cells to properly account for uptake limitations. The implementation of biodegradation in models of larger (regional, global) scales may, thus, not be straightforward since such models usually do not distinguish drop classes but rather assume homogenous monodisperse drop populations.*

We modified the conclusion section as follows (l. 461):

We compared our results to previous estimates of the importance of biodegradation as a loss process in the atmospheric aqueous phase ($F_{bact,aq}$) and in the complete atmospheric multiphase system (F_{bact}) based on the simplistic comparison of chemical vs biodegradation rates. ~~The comparison reveals~~ The analysis of our model results revealed that the assumption of an averaged biodegradation rate in the full aqueous volume is only appropriate for volatile compounds with low or moderate solubility and aqueous phase reactivity. A detailed comparison of our model results to those of the previous model studies by Pailler et al. (2023) and Fankhauser et al. (2019) highlighted important differences between the three model approaches. Based on this, we conclude that the role of biodegradation of ~~more highly soluble~~ compounds with $K_{H(eff)} \geq\sim 10^5$ M atm^{-1} will be overestimated by a bulk approach, in which biodegradation is assumed to occur in the full aqueous volume, since ~~diffusion~~uptake-limited phase transfer processes between bacteria-containing and bacteria-free droplets cannot be properly described. For the same reasons, bulk models overestimate the biodegradation of non-volatile species that in the real atmosphere only takes in the small subset of bacteria=-containing droplets. ~~Due to the separate droplet classes ,~~ For such species the upper limit of biodegradable mass of non-volatile species (e.g. dicarboxylic acids) is constrained by the number fraction of bacteria-containing droplets. Our conclusions based on the comparison of the three model approaches show the need of the developments of parameterizations to describe biodegradation in larger scale models since such models usually do not distinguish individual drop classes with different chemical composition (e.g. with and without bacteria cells).

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