We thank both referees for their constructive comments on our manuscript. We respond to all of them in detail below. Referee comments are repeated in blue, responses are in black and modified text in the manuscript is in *italic* with added text in *green*. Page and line numbers refer to the revised manuscript without annotations.

Referee #1

1) Referee comment: The manuscript by Jaber et al. asks the important question of whether biological (enzymatic) oxidation of phenol and catechol in simulated cloud water is important in the atmosphere. Bacterial (enzymatic) degradation of organic matter in cloud water is an understudied area of atmospheric chemistry that deserves more attention. In the present study, the authors carried out microcosm studies on cloud water surrogates to study biodegradation rates of phenol and catechol by Rhodococcus enclensis, a bacteria strain found to be quite active at oxidizing phenols during a recent (2018) survey of microbes in real cloud water samples. The derived biodegradation rates, along with chemical kinetics data on abiotic degradation of these compounds were combined in a box model to assess the relative importance of chemical and microbial degradation processes in the fate of phenol and catechol in the atmosphere. The manuscript is well organized, concise, and well-written. Not only does the work show that phenol/catechol are consumed by Rhodococcus, but the authors use the derived degradation constants to compare it to abiotic loss processes in the atmosphere. This combination of laboratory and modeling work is a strength. The results conclude that microbial degradation has the potential to be as important as chemical loss processes of the compounds in cloud water, especially in the case of more reactive species such as catechol. This is an important finding that is a valuable contribution to the atmospheric community. I am supportive of publishing this work in ACP after the following questions are addressed.

Authors' response: We thank the referee for their constructive comments. We address all individual comments in detail below.

2) Referee comment: The only major questions I have for study have to do with the applicability of the chosen laboratory experimental conditions to atmospheric conditions. I see that a temperature of 17 degrees Celsius has been chosen as a working temperature for all experiments. I assume this has been chosen to be a typical cloud water temperature?

Authors' response: Yes, the referee is right. As explained in the "Material end Methods" section describing our microcosm mimicking cloud conditions at the puy de Dôme, we mention that (l. 90)

17°C is the average temperature in the summer at this location.

3) Referee comment: I note an absence of any information on solution pH, which is a significant environmental variable that controls both the chemistry (Fe speciation, ROS chemistry) and microbiology (viability of microbes, and enzyme turnover rates). I suggest the authors clarify under which pH conditions all experiments were carried out. Was a buffer used to control pH in these experiments or was solution pH adjusted in any way?

Authors' response: Our experiments were performed in Volvic® mineral water which pH is 7.0. Because of the presence of carbonates, which buffer the system and because no acid is formed as a product of the biotransformation or phototransformation of phenol and catechol, the pH is quite stable during the experiments. As explained in more detail (section 6) bacteria are able to control their intracellular pH

and are viable under cloud conditions. In addition, the Fe(EDDS) complex is stable at this pH as specified in the initial manuscript (Li et al., 2010), it is for this reason that we have chosen this iron form to perform our experiments. This information about pH was added in the text (l. 98):

Bacteria pellets were rinsed first with 5 mL of NaCl 0.8% and after with Volvic® mineral water (pH=7.0), previously sterilized by filtration under sterile conditions using a 0.22 µm PES filter.

4) Referee comment: Furthermore, it would be useful to discuss how the pH conditions used in their experiments compare to actual cloud water pH.

Authors' response: The mean pH in cloud water spans a range of ~3 to ~6, as it has been shown in many measurements at different locations (e.g., data compilation in Seinfeld and Pandis (2006)). In the current simulation, the pH was set to a constant value of 4. We note that the pH of the cloud water in the model does not directly affect any chemical reaction in focus here (i.e. radical reactions with phenolic compounds). Only in highly alkaline solutions (pH ~ 10), phenols will significantly dissociate, i.e. in a pH range that is not encountered in cloud water.

We added this information to the text (l. 193):

The pH value of cloud water is assumed to be constant (pH = 4).

5) Referee comment: A discussion of pH should also factor in when discussing the results shown in Figure 2 & 3. Does pH change during these experiments and could that explain trends in the phenol/catechol loss rates over time? Under what pH were the studies listed in Table S-2 carried out under?

Authors' response: Our experiments were performed in Volvic® mineral water which pH is 7.0. Because of the presence of carbonates which buffer the system and because no acid is formed as a product of the biotransformation of phenol and catechol, the pH is quite stable during the experiments. Incubations with *Pseudomonas aeruginosa* (Razika et al. 2010) and with *Pseudomonas putida* EKII (Hinteregger et al. 1992) were performed at pH=7. This information was added in the text:

l. 98: Bacteria pellets were rinsed first with 5 mL of NaCl 0.8% and after with Volvic® mineral water (pH=7.0), previously sterilized by filtration under sterile conditions using a 0.22 µm PES filter.

Supplement, S-1.1:

l. 2/3: To calculate the biodegradation rate of phenol and catechol by Pseudomonas putida EKII, based on experiments performed at pH=7.0, we used the following data from Hinteregger et al. (1992):

l. 12/13: To calculate the biodegradation rate of phenol and catechol by Pseusomonas aeriginosa, based on experiments performed at pH=7.0, we used the following data from Razika et al. (2010):

6) Referee comment: In the absence of the authors own data on pH effects, does the literature provide any insights into the effect of pH on phenol monooxygenases/hydroxylases and/or the activity of Pseudomonas and Rhodococcus strains?

Authors' response: Actually, the experiments are performed with bacteria and not purified enzymes. In that case, phenol monooxygenases/hydroxylases' activity takes place inside the cell and are not

impacted by the external pH. Bacteria are able to regulate their internal pH (which is usually ~6.5 -7) when exposed to external pHs within a very broad range, except at extreme conditions, e.g., pH < 2 or pH > 10. In that case only acidophilic or alcalinophilic bacteria can adapt to such extreme pH values. In our case, cloud water collected at the puy de Dôme have moderate pHs ranging from 3.8 to 7.6 (Deguillaume et al., 2014).

In our previous biodegradation experiments with 17 different cloud bacteria using artificial cloud water at pH =5.0 (continental) and pH= 6.5 (marine), respectively (Vaïtilingom et al., 2011), no influence of the pH was observed on the measured biodegradation rates. Also Razika et al., (2010) showed that biodegradation rates of phenol by *Pseudomonas aeruginosa* (used in this paper) were very similar when incubated at pH=5.8, 7.0 and 8.0, respectively.

We added the following text at the beginning of Section 3.1, l. 245-249:

The transformation rates described in this work were measured at pH=7.0 which is within the range of pHs encountered in real clouds as observed at the Puy de Dome (3.8 < pH < 7.6, Deguillaume et al, 2014). However, bacteria are able to control their intracellular pH under such conditions, and it has been shown that pH variation has a low impact on their biodegradation ability (Vaitilingom et al. 2011; Razika et al. 2010).

7) Referee comment: Under what pH is the modeling carried out under?

Authors' response: The pH in the model is set to a constant value of 4 which is representative of moderately polluted to polluted air masses, such as downwind of urban areas. As none of the reactions (OH, NO_3 + phenolic compounds) is directly dependent on the pH within the ranges typically found in clouds (~ 2 < pH < ~6), this value does not have a large impact on the model results.

We added this information to the text (l. 193):

The pH value of cloud water is assumed to be constant (pH = 4).

8) Referee comment: Although not done in this communication, future work should be focused on characterizing these rates as a function of T and pH.

Authors' response: We thank the referee for this suggestion. However, as explained above, the intracellular pH is regulated by the bacterial cells under cloud pH conditions. Therefore, we do not think that it is necessary to perform experiments (which are highly time consuming) at different pHs.

9) Referee comment: On line 354-355, the authors state, "...we caution that these results likely represent an upper estimate that might not correspond to the moderate pH values encountered in clouds." Please elaborate on this in light of the abovementioned questions. What do the authors mean by "moderate" and why wouldn't their experiments be applicable to the moderate pH values encountered in clouds? I feel that the lack of attention to pH is a major issue that needs to be addressed in the final manuscript.

Authors' response: As outlined above, the pH value does not have any significant impact on the chemical reactions of the aromatics in the model. The last sentence in Section 3.3. ("*However, we caution that these results likely represent an upper estimate that might not correspond to the moderate pH values as encountered in clouds.*") only refers to the sensitivity model study. In Section S-4 of the supplement, we discussed that the rate constants applied in the original model study by Hoffmann et al. (2018) and also

adopted in our study were determined in the original literature by Gurol and Nekouinaini (1984) at pH = 1.5. The rate constant shows a decreasing trend with increasing pH; however, the exact pH dependence is not known. Thus, we concluded that the predicted contribution by the ozone reaction is likely an overestimate. In order to make it clear, we modified the text as follows (l. 359-364):

However, we caution that these results of the model sensitivity study including the ozone and HO_2/O_2^- reactions likely represent an upper estimate. The rate constant used in the model was determined at pH = 1.5. In the original study, a decreasing trend with increasing pH was suggested; however, the exact pH dependence was not given. Thus, the prediction shown in Figure S-3 ~~that~~ might not correspond to the moderate pH values as encountered in clouds and thus might be an overestimate of the role of the ozone reaction.

10) Referee comment: Lastly, for the modeling work, simulations are performed on monodisperse cloud droplets with a diameter of 20 microns, with specific drop number concentration and liquid water content. Please indicate how these were chosen and whether they are representative of typical cloud water.

Authors' response: The drop diameter of 20 microm is a typical value that is often assumed in large scale models as being representative for clouds in clean or moderately polluted regions (cf, for example, the overview by Ervens (2015)). The cloud liquid water content is also typical for stratocumulus or cumulus clouds (~ 0.1 – 1 g m^{-3}, e.g. Pruppacher and Klett (2003)). In several recent studies, the dependence of the OH(aq) concentration on cloud drop sizes has been discussed, e.g. (Chakraborty et al., 2016; Ervens et al., 2014).

We show below a figure from additional model simulations using another monodisperse droplet size distribution (drop diameter 10 μm, Simulation I) and a polydisperse one with droplet sizes between 1 and 30 μm (Simulation III). Simulation II corresponds to the results shown in the manuscript.

Table R-1: Microphysical characteristics assumed in model sensitivity studies; Simulation II is the case presented in the manuscript

Simulation	Drop diameter [μm]	N_{dr} [cm^{-3}]	LWC [g m^{-3}]
I	10	550	0.29
II	20	220	0.92
III	1 – 30	293	0.3

It can be seen in Figure R-1 that smaller droplet sizes (Simulation I) tend to cause a higher importance for OH(aq)-initiated processes, in agreement with the conclusions by Ervens et al. (2014). In the latter study, it was discussed that smaller droplets (larger surface-to-volume ratio) allow more OH to be transported into the droplets and, thus, lead to higher rates of OH(aq) reactions. Simulation III represents a case in-between Simulation I and II in terms of the droplet interface and shows corresponding results in terms of the importance of microbial and chemical processes, respectively. Since these dependencies on drop surface and drop surface-to-volume ratio have been discussed in detail in previous publications (Ervens et al., 2014; McVay and Ervens, 2017) and are not focus of the current study, we refrained from adding these model sensitivity studies to the current manuscript.

We extended the following to the text (l. 380/381)

The relative importance of radical chemistry compared to biodegradation will also depend on the radical concentrations in both phases which, in turn, are a function of numerous factors such as air mass characteristics, pollution levels that affect OH concentrations and microphysical cloud properties (e.g., drop diameters, liquid water content) (Ervens et al., 2014).

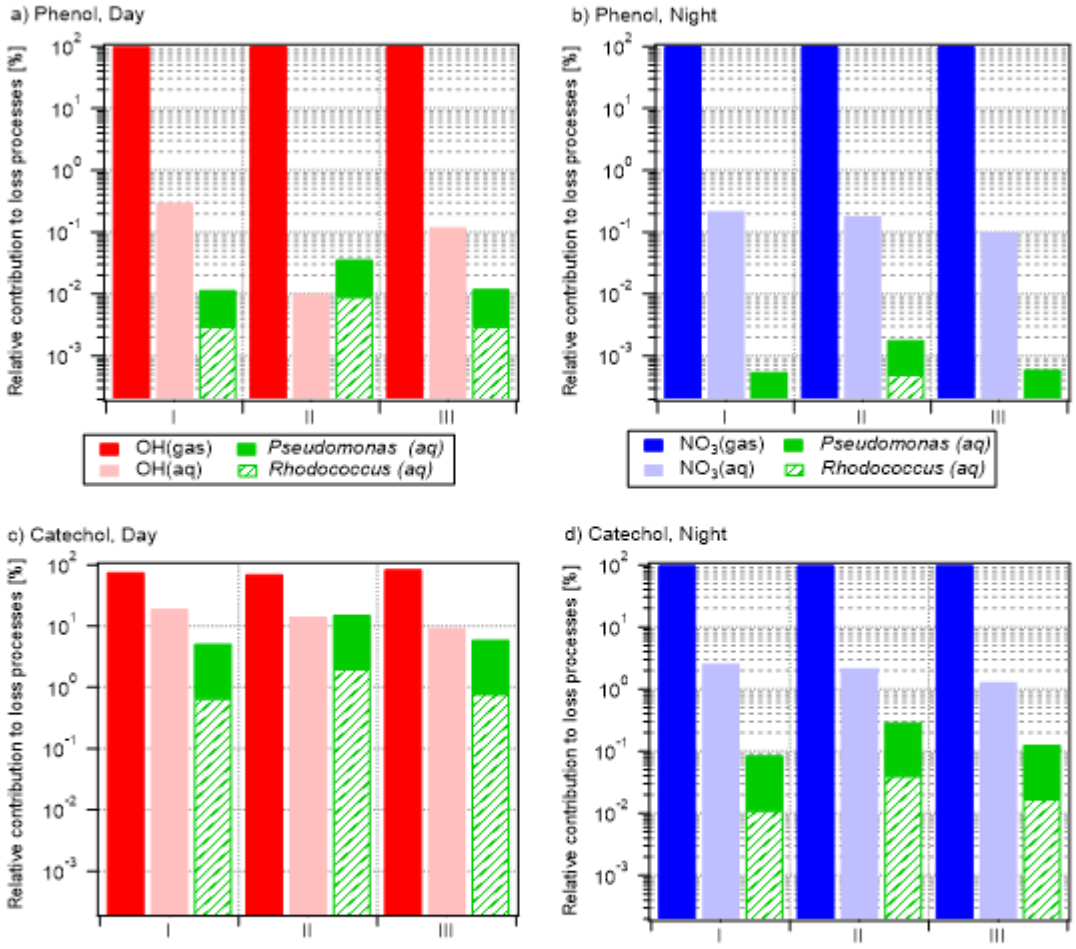

Figure R-1: Relative contributions to loss processes for phenol (a, b) and catechol (c, d) due to radical processes in the gas and aqueous phases and microbial activity by Pseudomonas and Rhodococcus in the aqueous phase for three model simulations (I– III, Table R-1)

Referee #2

This manuscript describes lab measurements of the ability of two bacteria species present in cloudwater to react with phenol and catechol molecules. The authors then run simple day and nighttime box model simulations to apportion the reactivity of these molecules to three bins: gas phase, aqueous phase chemical and aqueous phase biological reactivity. They find that bacterial transformation of catechol is an important loss process during the day, comprising 17% of the total losses in the daytime model. Daytime biotransformation of phenol, and nighttime biotransformation of either species, are minor loss

pathways. This work will be of interest to those interested in SOA formation and cloud processing, and is publishable after minor revision.

Authors' response: We thank the referee for their constructive comments and address all of them individually below.

Specific Comments

1) Referee comment: Table 2: How realistic is it to model bacterial degradation rates as the fastest measured in Figure 2? Some discussion on this point could strengthen the conclusions.

Authors' response: As explained in the initial text: *"A lag time of about 2.5 hours is observed, during which phenol is degraded extremely slowly. This is a well-known phenomenon under lab conditions corresponding to the induction period of the gene expression (Al-Khalid and El-Naas, 2012)."*

Given that the bacteria are present in the atmosphere for extended periods of time, it can be implied that this lag time is not of importance in cloud droplets. Therefore, we think that it is reasonable to use the rates of biodegradation, which correspond to the highest slopes in Figure 2 as it represents the real phase of biodegradation.

2) Referee comment: Line 283: The text states that at 10^9 cell concentrations catechol biodegradation "was too fast to be detected within the time resolution of the experiments (Figure 3)." However, the 10^8 data is identical to the 10^9 data, and should be included in this statement.

Authors' response: You are right; we have changed the text as follows (l. 285):

When the cell concentration was 10^8 or 10^9 cell mL^{-1}, the catechol biodegradation was too fast to be detected within the time resolution of the experiments (Figure 3).

We performed various experiments with reduced cell concentrations, from 10^7 cell mL^{-1} to 10^6 cell mL^{-1} (Figure 3).

3) Referee comment: Figure 3 is not very relevant to the aims of the paper and could be moved to the SI section.

Authors' response: We prefer to keep this figure in the main text for the following reasons:

1) To our knowledge, LC-MS has not been used in any previous studies to measure catechol biodegradation rates. Thus, the presented data are original.
2) These experiments are essential for the measurement of the biodegradation rates that are finally used in the model studies.

4) Referee comment: Figure S-3 is much more relevant to the aims of the paper, even though it doesn't necessarily strengthen the conclusions that biotransformation of catechol is significant during daytime. I urge the authors to move Figure S-3 into the manuscript, along with appropriate discussion.

Authors' response: We respectfully disagree with the suggestion to move Figure S-3 to the main text of the manuscript. Given the uncertainties in the rate constants for the HO_2/O_2^- and ozone reactions for

relevant cloud conditions (pH), it likely shows a biased picture on the importance of ozone reactions with phenolic compounds. As discussed in the supplement, the rate constant was determined at pH = 1.5 and shows a decreasing trend with increasing pH. Since this trend has not been quantified in the original literature, we want to caution to draw false conclusions based on Figure S-3. To make these concerns this clearer, we extended the last paragraph of Section 3.3 (l. 359-364):

However, we caution that these results of the model sensitivity study including the ozone and HO_2/O_2^- reactions likely represent an upper estimate of the role of the ozone reaction. The rate constant used in the model was determined at pH = 1.5. In the original study, a decreasing trend with increasing pH was suggested; however, the exact pH dependence was not given. Thus, the prediction shown in Figure S-3 ~~that~~ might not correspond to the moderate pH values as encountered in clouds and thus might be an overestimate of the role of the ozone reaction.

5) Referee comment: Line 315: The statement about catechol degradation rates "Values are only available for Ps. putida EKII" is confusing, given that values are listed for a second strain listed in Table 2 (from Razika 2010). Only by reading the supplemental information section can the reader ascertain that the Ps. aeriginosa catechol degradation rate listed in the table in the row marked "Razika 2010" was not measured by Razika, but is actually the phenol rate times the ratio 12 (measured for another Pseudomonas strain. This is unintentionally misleading. I suggest that the table entry be "ND" and the phenol rate x 12 be given in the table caption, or in some other way that makes it clear that it is not a measurement of Razika et al.

Authors' response: We agree with the referee that the wording was misleading. We extended the text and table as follows (l. 322-325):

As in the case of phenol, we also calculated catechol biodegradation rates with Pseudomonas strains based on literature data (Table 2). Values are only available for Pseudomonas putida EKII (Hinteregger et al., 1992) and show a biodegradation rate that is twelve times higher compared to that of phenol biodegradation. This confirms that catechol dioxygenases are much more active than phenol hydroxylases as observed for Rhodococcus enclensis. Similar to phenol, catechol biodegradation rates for Pseudomonas strains are somewhat higher than those for Rhodococcus, but within the same order of magnitude. The same ratio (~12) as for the Pseudomonas putida was applied to estimate the biodegradation rate of catechol by Pseudomonas aeruginosa, for which only the rate for phenol was experimentally determined by Razika et al. (2010).

***Table 2**: Biodegradation rates [mol cell^{-1} h^{-1}] of catechol and phenol of Rhodococcus and Pseudomonas strains normalized to the exact number of cells present in the incubations. The calculation of biodegradation rates for the Pseudomonas strains are detailed in S-1.*

Bacterial strain (experimental condition)	Biodegradation rate of phenol (10^{-16} mol cell^{-1} h^{-1})	Biodegradation rate of catechol (10^{-16} mol cell^{-1} h^{-1})	References
Rhodococcus enclensis PDD-23b-28 (dark)	1.8 ± 0.5	15.0 ± 0.5	This work
Rhodococcus enclensis PDD-23b-28 (light)	1.2 ± 0.5	ND[1)]	This work
Rhodococcus enclensis PDD-23b-28 (light+Fe(EDDS))	1.0 ± 0.3	ND[1)]	This work
Pseudomonas putida EKII (dark)	0.2	2.4	(Hinteregger et al., 1992)
Pseudomonas aeruginosa (dark)	5.9	70.7 [2)]	Phenol experiments (Razika et al., 2010)
Pseudomonas (average)	**Average: 3.0**	**Average: 36.6**	

[1)] *Not determined;* [2)] *This rate was estimated based on the value for phenol (Razika et al., 2010) and the ratio (~ 12) for phenol/catechol biodegradation rates as determined for Pseudomonas putida by Hinteregger et al. (1992) (cf also Section 1-1 in the supplement)*

6) Referee comment: Line 318: The claim that biodegradation rates of phenol or catechol are generally higher for Pseudomonas than for Rhodococcus has no statistical validity and cannot be made, especially in light of my previous comment. The variability between Pseudomonas strains is larger than the difference between the two species.

Authors' response: We agree with the referee. We have changed the text as follows (l. 322):

Similar to phenol, catechol biodegradation rates for *Pseudomonas* strains *are within the same order of magnitude as those for Rhodococcus.*

7) Referee comment: Figures 4cd and S-3cd: Some of the statements made in the text discussing Figure 4 appear to be quantitatively incorrect when looking at Figure S-3. For example, line 344 "The total microbial activity in the aqueous exceeds that of the chemical reactions (Figure 4c) and contributes up to 17% to the total loss of catechol in the multiphase system." According to Figure S-3c, this statement is likely true when reaction with dissolved OH is the only chemical reaction considered. The statement should be modified to reflect the information shown in both figures.

Authors' response: As pointed out above, the contributions of the HO_2/O_2^- and ozone reactions to the total chemical loss of phenol and catechol are highly uncertain. We modified the text as follows to (i) reflect that other oxidation reactions in addition to OH might take place but (ii) their contributions are very uncertain due to uncertainties in their rate constants.

We added (l. 349):

*During daytime, the loss by aqueous phase processes (chemical and microbial) is >30% for catechol (**Figure 4c**), with contributions by OH(aq), Pseudomonas and Rhodococcus of 14%, 10% and 7%, respectively, when OH as the only oxidant for the phenols in the aqueous phase is considered.*

8) Referee comment: Line 356: These sentences correspond with measurements in Figure 2, but do not correspond with the results shown in Figure 4, where the different processes are compared under the same conditions. It seems that with catechol (not phenol), photo- and biotransformations are of the same order or magnitude, and with phenol reactions with dissolved OH are significantly more important.

Authors' response: We agree with the referee that these sentences were misleading. We modified them as follows (l. 366-368):

Both experimental and modelling approaches show that, in the water phase of clouds suggest that phenol and catechol degradation by microbial and chemical OH(aq) processes may be within one order of magnitude. ~~phenol bio- and photo-transformations are within the same order of magnitude, while catechol biotransformation seems more efficient than OH(aq) chemistry under identical experimental and atmospheric conditions, respectively.~~ When the complete multiphase system is taken into account, phenol chemical transformation is largely dominant in the gas phase whereas the ~~might~~ more water-soluble catechol is more efficiently biodegraded in the aqueous phase.

9) Referee comment: Line 379: This conclusion needs more support. It is clear from this work that microbial processes must be included to give a complete representation of cloudwater chemistry. Whether this complete representation is necessary to improve air quality or climate predictions has not been established.

Authors' response: We agree with the referee that our statement was somewhat pretentious. However, we would like to point out that the implementation of microbial processes will not only help to complete the understanding of the chemical composition of cloud water but also of the atmospheric multiphase system. The fact that, for example, microbial processes may contribute ~10% to the total loss of catechol shows that for some pollutants these processes are an important multiphase sink.

We removed the last part of the sentence:

Thus, atmospheric models may be incomplete in describing the loss of some organic compounds and should be complemented by microbial processes in order to give a complete representation of the atmospheric multiphase system. ~~to eventually allow comprehensive air quality and climate predictions.~~

Technical corrections

10) Referee comment: Line 176: "turned" should be "tuned"

Authors' response: We corrected the typo.

11) Referee comment: Figure 2 caption should specify the Rhodococcus cell concentration.

Authors' response: Figure 2 caption was modified as follows:

Rhodococcus enclensis cell concentration was 10^9 cells mL^{-1}.

12) Referee comment: Figure S1: the figure legend does not match the description in the caption. Is the blue line the lamp spectrum or the absorption spectrum of phenol?

Authors' response: We corrected the legend and it reads now:

Comparison of the actinic fluxes of the lamps used and the emission of the solar spectrum measured in-cloud at the puy de Dôme station. The ~~green~~ blue line represents the actinic flux of the lamp; the brown line corresponds to the actinic flux of the solar emission spectrum in cloud. The ~~red~~ pink line represents the molar absorption coefficient of the Fe-EDDS complex. The ~~blue~~ red line represents the molar absorption coefficient of phenol.

13) Referee comment: Line 360: "might" should be "slightly"?

Authors' response: We removed 'might'.

Biodegradation of phenol and catechol in cloud water: Comparison to chemical oxidation in the atmospheric multiphase system

Saly Jaber[1], Audrey Lallement[1], Martine Sancelme[1], Martin Leremboure[1], Gilles Mailhot[1], Barbara Ervens[1*] and Anne-Marie Delort[1*]

[1]Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France

Correspondence to: Anne-Marie Delort (a-marie.delort@uca.fr) and Barbara Ervens (barbara.ervens@uca.fr)

Abstract

The sinks of hydrocarbons in the atmosphere are usually described by oxidation reactions in the gas and aqueous (cloud) phases. Previous lab studies suggest that in addition to chemical processes, biodegradation by bacteria might also contribute to the loss of organics in clouds; however, due to the lack of comprehensive data sets on such biodegradation processes, they are not commonly included in atmospheric models. In the current study, we measured the biodegradation rates of phenol and catechol, which are known pollutants, by one of the most active strains selected during our previous screening in clouds (*Rhodococcus enclensis*). For catechol, biodegradation transformation is about ten times faster than for phenol. The experimentally derived biodegradation rates are included in a multiphase box model to compare the chemical loss rates of phenol and catechol in both the gas and aqueous phases to their biodegradation rate in the aqueous phase under atmospheric conditions. Model results show that the degradation rates in the aqueous phase by chemical and biological processes for both compounds are similar to each other. During daytime, biodegradation of catechol is even predicted to exceed the chemical activity in the aqueous phase and to represent a significant sink (17%) of total catechol in the atmospheric multiphase system. In general, our results suggest that atmospheric multiphase models may be incomplete for highly soluble organics as biodegradation may represent an unrecognized efficient loss of such organics in cloud water.

1. Introduction

Monocyclic aromatic compounds in the atmosphere are of great interest due to their influence on ozone formation (Hsieh et al., 1999) and their potential to form secondary organic aerosol (Ng et al., 2007). Their main sources include combustion processes of coal, oil and gasoline. Substituted monocyclic aromatics are semivolatile and partition between the atmospheric gas and particulate phases. Among those, phenol is of particular interest for air quality as it is considered one of the main pollutants listed by U.S Environmental Protection Agency (US EPA list) since it represents a risk for both humans and the environmental biota (TOXNET Toxicology Data Network, 2019). Measurements of gas phase mixing ratios of phenol in the atmosphere are sparse. The few available measurements show rather low values with 4 - 40 ppt at the continental site Great Dun Fell (Lüttke and Levsen, 1997), and 0.4 ppt, 2.6 ppt and 2.7 ppt at suburban, rural and urban locations (Delhomme et al., 2010), respectively. However, phenol's much higher water-solubility (K_H = 647 M atm^{-1}) as compared to benzene (K_H ~ 0.2 M atm^{-1}) leads to nanomolar levels in cloud water (5.5 – 7.7 nM at the puy de Dôme (France) (Lebedev et al., 2018), 30 – 95 nM at Great Dun Fell (Lüttke et al., 1997), and 37 nM in the Vosges Mountains (Levsen et al., 1993)). The further hydroxylated catechol is even less volatile and more water-soluble and, based on its Henry's law constant of $K_H = 8.3 \cdot 10^5$ M atm^{-1}, expected to be nearly fully dissolved (> 80%) in cloud water, which might explain the lack of its detection in the gas phase. Phenolic compounds have been shown to comprise 2 - 4% of the total organic particulate matter at several locations at the Northeastern US (Bahadur et al., 2010). In the same study, a strong correlation between seawater-derived organics and phenolic compounds was found, which suggests direct sources in addition to hydroxylation of the unsubstituted aromatics.

The oxidation of phenol by $^{\bullet}$OH radicals leads to catechol in the gas (Xu and Wang, 2013), the aqueous (Hoffmann et al., 2018) phases and at the gas/aqueous interface (Pillar et al., 2014); further $^{\bullet}$OH oxidation of catechol leads to ring-opening products. A recent multiphase model study suggests that the main aqueous phase loss processes of aromatics with two hydroxyl groups include not only $^{\bullet}$OH and $NO_3^{\bullet}$ reactions in clouds but also reactions with O_3 and $HO_2^{\bullet}$ (Hoffmann et al., 2018). The nitration of phenols represents the major atmospheric source of nitrophenols in the gas phase (Yuan et al., 2016) and aqueous phase (Harrison et al., 2005; Vione et al., 2003). Nitrophenols can be phytotoxic (Harrison et al., 2005) and also contribute to light-absorption of atmospheric particles ('brown carbon' (Xie et al., 2017)). They have been found in atmospheric particles (Chow et al., 2016) and in the aqueous phases of clouds, fog and lakes (Lebedev et al., 2018). In addition, phenols add to secondary organic aerosol formation in the aqueous phase by oligomerization reactions (Yu et al., 2014).

Not only chemical reactions, but also microbial processes in the aqueous phase of clouds act as sinks for organic compounds (Delort et al., 2010). Biodegradation rates for several bacteria strains and aliphatic mono- and dicarboxylic acids/carboxylates as well as for formaldehyde and methanol (Ariya et al., 2002; Fankhauser et al., 2019; Husárová et al., 2011; Vaïtilingom et al., 2010, 2011, 2013) have been measured

in laboratory experiments. Comparison of such rates to those of chemical radical ($^{\bullet}OH$ or $NO_3^{\bullet}$) reactions in the aqueous phase show comparable rates of chemical and microbial processes under atmospherically relevant conditions. Such a comparison has not been performed yet for phenolic compounds in the aqueous phase due to the lack of data on their biodegradation rates.

Our previous metagenomic and metatranscriptomic study, directly performed on cloud water samples collected at the puy de Dôme station in France, showed convincing evidence of the in-cloud expression of genes coding for enzymes involved in phenol biodegradation (Lallement et al., 2018b). We found transcripts for phenol monooxygenases and phenol hydroxylases responsible for the hydroxylation of phenol into catechol and transcripts for catechol 1,2-dioxygenases leading to the opening of the aromatic ring. These genes originated from the genera *Acinetobacter* and *Pseudomonas* belonging to Gamma-proteobacteria, a major class of bacteria in clouds (Lallement et al., 2018b). In the same study, a large screening of bacteria in parallel isolated from cloud water samples (*Pseudomonas* spp., *Rhodococcus* spp. and strains from the Moraxellaceae family) showed that 93% of the strains could biodegrade phenol. Altogether, these results indicate a high potential of cloud microorganisms to biotransform phenol and catechol in cloud water.

In the current study, we designed lab experiments in microcosms mimicking cloud water conditions in terms of light, bacteria and temperature. Under these conditions, we measured the biodegradation rates of phenol and catechol by *Rhodococcus enclensis* PDD-23b-28, isolated from cloud water and one of the most efficient strains able to degrade phenol during our previous screening (Lallement et al., 2018b). The derived biodegradation rates for *Rhodococcus*, together with literature data on phenol and catechol biodegradation by *Pseudomonas*, were implemented in a box model to compare chemical and microbial degradation rates in the atmospheric multiphase system.

2. Materials and Methods

2.1 Experiments in microcosms

The transformation rates of phenol and catechol were measured in microcosms mimicking cloud water conditions at the puy de Dôme station (1465 m). Solar light was fitted to that measured directly under cloudy conditions (*Figure S-1*); 17°C is the average temperature in the summer at this location. *Rhodococcus* bacterial strains belong to the most abundant bacteria in cloud waters and are very active phenol biodegraders (Lallement et al., 2018b; Vaïtilingom et al., 2012). Fe(EDDS) was used to mimic organic ligands of Fe(III), in particular siderophores (Vinatier et al., 2016). In addition, This complex is stable at the working pH of 6.0 (Li et al., 2010).

2.1.1. Cell preparation for further incubations

Rhodococcus enclensis PDD-23b-28 was grown in 25 mL of R2A medium for 48 h at 17°C, 130 rpm (Reasoner and Geldreich, 1985). Then cultures were centrifuged at 4000 rpm for 15 min at 4°C. Bacteria

pellets were rinsed first with 5 mL of NaCl 0.8% and after with Volvic® mineral water (pH = 7.0), previously sterilized by filtration under sterile conditions using a 0.22 µm PES filter. The bacterial cell concentration was estimated by optical density at 600 nm using a spectrophotometer UV3100 to obtain a concentration close to 10^9 cell mL^{-1}. Finally, the concentration of cells was precisely determined by counting the colonies on R2A Petri dishes.

2.1.2. Phenol transformation

Biotransformation: *Rhodococcus enclensis PDD-23b-28* cells were re-suspended in 5 mL of 0.1 mM phenol (Fluka > 99%) solution, prepared in Volvic® mineral water, and incubated at 17°C, 130 rpm agitation for 48 hours in the dark. 0.5 mL of this culture was incubated in 25 mL of the same medium and under the same conditions. In order to determine the concentration, the optical density for each strain was measured at 600 nm during the experiment. The strain concentration was ~10^9 cells mL^{-1}. The concentration ratio of bacterial cells to phenol was kept similar to that as measured in cloud water (Lallement et al., 2018b). We showed in the past that in repeated experiments identical cell / substrate ratios lead to the same biodegradation rates (Vaïtilingom et al., 2010).

A control experiment was performed by incubating phenol without bacteria; phenol concentration remained stable over time (0.1 mM of phenol was obtained at the end of the experiment). For phenol quantification over time in the incubation experiments, 600 µL samples were centrifuged at 12500 rpm for 3 min and the supernatants were kept frozen until HPLC analysis. Complementary experiments were also performed consisting of incubation of the cells and 0.1 mM phenol in the presence of light without Fe(EDDS).

Phototransformation: A 0.1 mM phenol solution (Fluka > 99%), prepared in Volvic® mineral water, was incubated at 17°C, 130 rpm agitation for 48 hours in photo-bioreactors designed by Vaïitilingom et al (2011). OH radicals were generated by photolysis adding 0.5 mM Fe(EDDS) complex solution. The Fe(EDDS) solution (iron complex with 1:1 stoichiometry) was prepared from iron(III) chloride hexahydrate ($FeCl_3$, $6H_2O$; Sigma-Aldrich) and (S,S)-ethylenediamine-N,N'-disuccinic acid trisodium salt (EDDS, 35% in water). A complementary experiment was also performed consisting of incubation of a 0.1 mM phenol solution in the presence of light without Fe(EDDS) complex.

The experimental conditions of the irradiation experiments (Sylvania Reptistar lamps; 15 W; 6500 K) are described by Wirgot et al (2017). They are mimicking the solar light measured under cloudy conditions at the puy de Dôme station (***Figure S-1***). The mechanism of the $^{\bullet}OH$ radical production under light irradiation is as follows (Brigante and Mailhot, 2015):

$$\text{Fe(III)-EDDS} \xrightarrow{h\nu} \text{[Fe(III)-EDDS]*} \longrightarrow \text{Fe(II)} + \text{EDDS}^{\bullet} \quad \text{(R-1)}$$

$$\text{EDDS}^{\bullet} + O_2 \longrightarrow O_2^{\bullet -} + \text{EDDS}_{ox} \quad \text{(R-2)}$$

$$HO_2 \rightleftharpoons O_2^- + H^+ \quad \text{(R-3)}$$

$$HO_2^{\bullet} + O_2^{\bullet-} \xrightarrow{H^+} H_2O_2 + O_2 + {}^{-}OH \quad \text{(R-4)}$$

$$HO_2^{\bullet} + HO^{\bullet}{}_2 \xrightarrow{H^+} H_2O_2 + O_2 \quad \text{(R-5)}$$

$$Fe(III) + O_2^{\bullet-} \longrightarrow Fe(II) + O_2 \quad \text{(R-6)}$$

$$Fe(III) + HO_2^{\bullet} \longrightarrow Fe(II) + O_2 + H^+ \quad \text{(R-7)}$$

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + {}^{\bullet}OH + {}^{-}OH \quad \text{(R-8)}$$

Using the specifications of the lamp, an overall rate constant of the photolysis of the Fe(III)-EDDS complex $j_{R\text{-}8} = 1.4 \cdot 10^{-3}$ s^{-1} was calculated (***Section S-2***).

$$\text{Fe(III)-EDDS} \xrightarrow{h\nu} {}^{\bullet}OH + \text{products} \quad \text{(R-9)}$$

Assuming steady-state conditions for $^{\bullet}$OH at the beginning of the experiments (i.e., equal $^{\bullet}$OH production and loss rates), an $^{\bullet}$OH concentration of $8.3 \cdot 10^{-13}$ M can be calculated. This concentration is at the upper limit of $^{\bullet}$OH concentrations as derived from various measurements and model studies (Arakaki et al., 2013; Lallement et al., 2018a).

Photo-biotransformation: The protocols for biotransformation and photo-transformation of phenol in the presence of Fe(EDDS) as described above were combined.

2.1.3. Catechol transformation

Biotransformation: As for phenol, *Rhodococcus enclensis PDD-23b-28* cells were re-suspended in 5 mL of 0.1 mM catechol (Fluka > 99%) solution, prepared in Volvic® mineral water, and incubated at 17°C, 130 rpm agitation for 48 hours in the dark. Four experiments were carried out with different cell concentrations (10^9 cell mL^{-1}, 10^8 cell mL^{-1}, 10^7 cell mL^{-1} and 10^6 cell mL^{-1}). For catechol quantification over time in the incubation experiments, 600 µL samples were centrifuged at 12500 rpm for 3 min and the supernatants were kept frozen until LC-HRMS analysis.

2.2 Analytical methods

2.2.1. Phenol HPLC analysis

Before analysis, all samples were filtered on H-PTFE filter (pore size at 0.2 µm and diameter of 13 mm from Macherey-Nagel, Germany). Phenol detection was done on HPLC VWR Hitachi Chromaster apparatus fitted with a DAD detector and driven by Chromaster software. Isocratic mode was used with a reverse phase end-capped column (LiChrospher® RP-18, 150 mm x 4.6 mm, 5 µm, 100 Å). The mobile phase was composed of acetonitrile and filtered water (Durapore® membrane filters, 0.45 µm HVLP type, Ireland) in 25/75 ratio with a flow rate at 1.2 mL min^{-1}. Sample injection volume was 50 µL, spectra were recorded at 272 nm and the run time was 10 min.

2.2.2. Catechol LC-HRMS Analyses

LC-HRMS analyses of catechol were performed using an RSLCnano UltiMate™ 3000 (Thermo Scientific™) UHPLC equipped with an Q Exactive™ Plus Hybrid Quadrupole-Orbitrap™ Mass Spectrometer (Thermo Scientific™) ionization chamber. The same conditions were used for analyzing EDDS. Chromatographic separation of the analytes was performed on a Kinetex® EVO C18 (1.7 µm, 100 mm × 2.1 mm, Phenomenex) column with column temperature of 30°C. The mobile phases consisted of 0.1% formic acid and water (A) and 0.1% formic acid and acetonitrile (B). A three-step linear gradient of 95% A and 5% B in 7.5 min, 1% A and 99% B in 1 min, 95% A and 5% B for 2.5 min was used throughout the analysis. This device was associated with a Thermo Scientific™ Dionex™ UltiMate™ DAD 3000 detector (200-400 nm).

The Q-Exactive ion source was equipped with a electrospray ionization (ESI) and the Q-Orbitrap™. The Q-Exactive was operated in either full MS-SIM, the full MS scan range was set from m/z 80 to 1200. The mass resolution was set to 70000 fwhm, and the instrument was tuned for maximum ion throughput. AGC (automatic gain control) target or the number of ions to fill C-Trap was set to 10^6 with a maximum injection time (IT) of 50 ms. The C-Trap is used to store ions and then transfer them to the Orbitrap mass analyzer. Other Q-Exactive generic parameters were: gas (N_2) flow rate set at 10 a.u., sheath gas (N_2) flow rate set at 50 a.u., sweep gas flow rate set at 60 a.u., spray voltage at 3.2 kV in positive mode, and 3 kV in negative mode, capillary temperature at 320°C, and heater temperature at 400°C. Analysis and visualization of the data set were performed using Xcalibur™ 2.2 software from Thermo Scientific™.

2.2.3. Derivation of phenol and catechol degradation rates

The degradation rates of phenol and catechol were calculated after normalization based on the ratio of the concentration at time t (C) and the concentration at time t = 0 (C_0). The pseudo-first-order rate constants (k_{phenol} and $k_{catechol}$) were determined using ***Equation 1***:

$$\ln(C/C_0) = f(t) = - k_{phenol} \text{ (or } k_{catechol}) \, t \qquad \text{(Eq-1)}$$

2.3 Description of the multiphase box model

2.3.1. Chemical and biological processes

We use a multiphase box model to compare the loss reactions of phenol and catechol in the gas and aqueous phases by radicals ($^{\bullet}OH$, $NO_3^{\bullet}$) in both phases and bacteria only in the aqueous phase over a processing time of 15 min to simulate chemical and biological processing in a single cloud cycle. The pH value of cloud water is assumed to be constant (pH = 4). In addition to the data for *Rhodococcus* obtained in the current study, we also include literature data on the biodegradation of phenol and catechol by *Pseudonomas putida* and *Pseudonomas aeruginosa* (Section 3.2), which are usually more abundant in the atmosphere than *Rhodococcus*.

The processes considered in the gas and aqueous phases are summarized in ***Table S-1*** and ***Figure 1***. In both phases, the reaction of phenol with •OH is assumed to yield 50% catechol; other products of these reactions are not further tracked in the model. The reaction of phenol with NO_3• results in nitrophenols (Bolzacchini et al., 2001; Harrison et al., 2005); the loss of these products is not explicitly included in the model either as we solely focus on the comparison of the degradation rates. Recently, it was suggested that the reactions with ozone and HO_2•/O_2•- might represent major sinks (~50% and ~20%, respectively) of catechol in the aqueous phase (Hoffmann et al., 2018). However, the only available rate constant for the ozone reaction was derived at pH = 1.5 by Gurol and Nekouinaini (1984) who postulate that at higher pH (~5 - 6), the reaction with OH likely dominates the overall loss. Therefore, in our base case simulations, we limit the reactions of phenol and catechol to the reactions with •OH and NO_3• radicals. Sensitivity studies including the HO_2•/O_2•- and O_3 reactions are discussed in the supporting information (***Section S-4***).

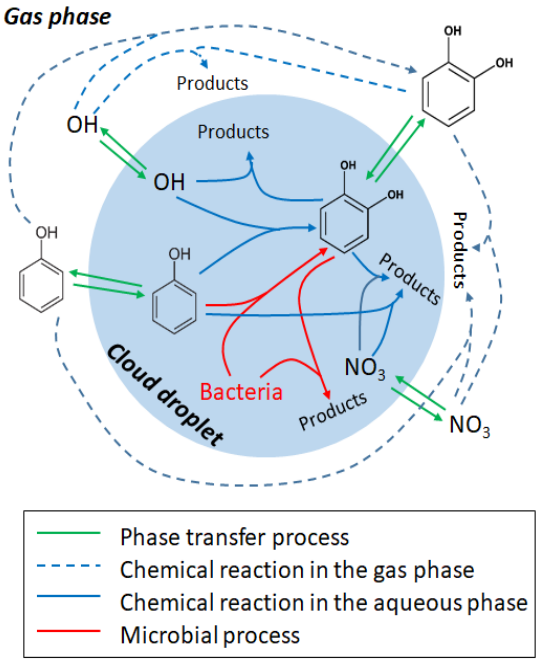

Figure 1: *Schematic of the multiphase system in the box model*

Microbial activity in the aqueous phase by *Rhodococcus* and *Pseudonomas* is usually expressed as rates [mol cell^{-1} h^{-1}] (Vaïtilingom et al., 2013). We converted these experimentally-derived rates into 'rate constants' [L cell^{-1} h^{-1}] in order to adjust them to the substrate and cell concentrations as assumed in the aqueous phase in the model (***Section S-3.2***), equivalent to the treatment of chemical processes. In order to account for the numerous additional loss processes of •OH(aq) and NO_3•(aq) in clouds, sinks for both radicals have been added: A general rate constant of OH with total water-soluble organic carbon (WSOC) ($k_{OH,WSOC}$ = 3.8·10^8 M^{-1} s^{-1}) lumps the main loss processes of OH in cloud water (Arakaki et al., 2013); assuming an average WSOC concentration of 5 mM results in a first-order loss process of k_{OH} = 2·10^6 s^{-1}. The main losses of NO_3•(aq) are likely reactions with halides (Herrmann et al., 2000);

as a proxy, we assume here a first-order loss process (k_{NO3} = 10^5 s^{-1}), reflecting the sum of the major $NO_3^{\bullet}$(aq) sinks. These lumped sink processes lead to aqueous phase radical concentrations of $[^{\bullet}OH(aq)]_{day}$~10^{-15} M and $[NO_3^{\bullet}(aq)]_{night}$ ~10^{-14} M, respectively, in agreement with predictions from previous model studies (Ervens et al., 2003). Kinetic phase transfer processes between the two phases are described for the radicals and aromatics based on the resistance model by Schwartz (1986); all phase transfer parameters (Henry's law constants K_H, mass accommodation coefficients α and gas phase diffusion coefficients D_g) are summarized in ***Table S-1***.

2.3.2. Initial concentrations

Initial concentrations of 4 ppt catechol and phenol are assumed in the gas phase that partition between both phases and are chemically consumed over the course of the simulation (15 min). These initial mixing ratios correspond to equivalent aerosol mass concentrations on the order of several 10s ng m^{-3}, in agreement with measurements of phenol compounds in aerosol samples (Bahadur et al., 2010; Delhomme et al., 2010) and nanomolar concentrations in cloud water (Lebedev et al., 2018). It should be noted that the assumption on the initial aromatic concentrations does not affect any conclusions of our model studies, as we compare the loss fluxes of all processes in a relative sense. Two simulations are performed for each set of conditions to simulate day or night time conditions, respectively, that only differ by the radical concentrations ($[^{\bullet}OH]_{day}$ = $5{\cdot}10^6$ cm^{-3}; $[NO_3^{\bullet}]_{night}$ = $5{\cdot}10^8$ cm^{-3}) that are constant throughout the simulations. Two types of bacteria are assumed (*Rhodococcus* and *Pseudomonas*). They have been found to contribute to 3.6% and 19.5% to the total number concentration of bacteria cells isolated from cloud waters and present in our lab collection. Using a typical cell concentration in cloud water of $6.8{\cdot}10^7$ cell L^{-1}(Amato et al., 2017), the assumed bacteria cell concentrations in the model are $2.7{\cdot}10^6$ cell L^{-1} and $1.3{\cdot}10^7$ cell L^{-1} for *Rhodococcus* and *Pseudomonas*, respectively. The simulations are performed for the conditions for monodisperse droplets with a diameter of 20 μm. The drop number concentration of 220 cm^{-3} results in a total liquid water content of 0.9 g m^{-3}. These parameters do not change over the course of the simulation.

3. Results

3.1 Incubations in microcosms

The transformation rates described in this work were measured at pH=7.0 which does not correspond to the whole range of pHs encountered in real clouds as observed at the Puy de Dome (3.8 < pH < 7.6, Deguillaume et al, 2014). However, bacteria are able to control their intracellular pH under such conditions, and it has been shown that pH variation has a low impact on their biodegradation ability (Vaitilingom et al. 2011; Razika et al. 2010).

3.1.1. Transformation of phenol

Abiotic degradation*:** In the presence of light and Fe(EDDS), phenol concentration decreases with time in the first two hours of the experiments and then remains rather stable (Figure 2***). In parallel, catechol, the first intermediate of phenol transformation is formed (***Figure S-2A***) and accumulates over time. Catechol concentration is quite low because it is further oxidized over time to yield CO_2. Phenol degradation slows down after two hours due to the lack of OH radical production resulting from the destruction of the EDDS ligand with time (***Figure S-2B***). Phenol is not directly photolyzed in the presence of light while it is oxidized in the presence of Fe(EDDS) complex (***Figure 2 and Figure S-2***).

Biotic degradation*:** In the dark, phenol is biotransformed by *Rhodococcus enclensis* cells (Figure 2***) and completely degraded after 5.5 hours. A lag time of about 2.5 hours is observed, during which phenol is degraded extremely slowly. This is a well-known phenomenon under lab conditions corresponding to the induction period of the gene expression (Al-Khalid and El-Naas, 2012). Catechol is slowly formed in parallel until t = 3.5 hours and is further biodegraded when bacteria have started to be more active (***Figure S-2A***).

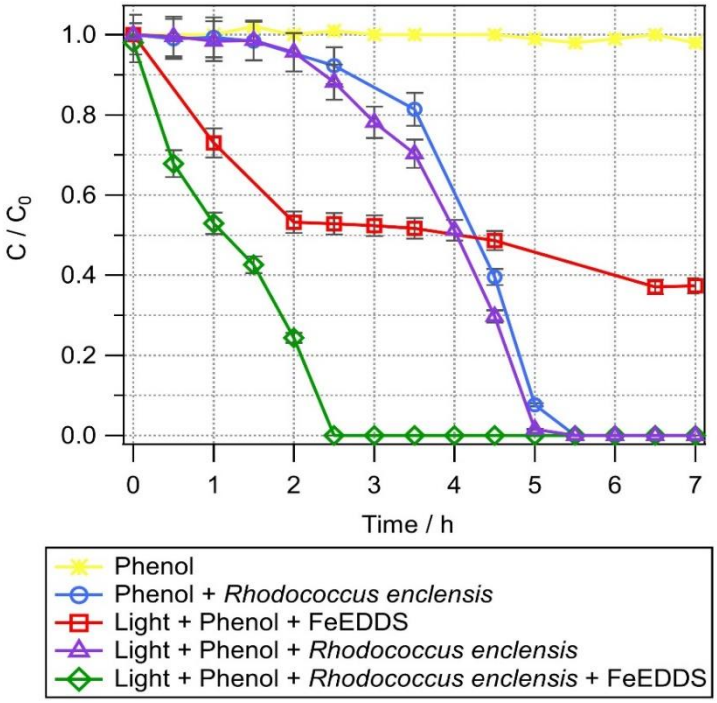

Figure 2: *Transformation of phenol with time under different conditions. Phenol+Light +Fe(EDDS) (red squares), Phenol+ R.enclensis +dark (blue circles), Phenol+R. enclensis +Light (purple triangles), Phenol+ R. enclensis +Light + Fe(EDDS) (green line). Rhodococcus enclensis cell concentration was 10^9 cells mL^{-1}.*

Abiotic and biotic combined transformation*:** When light (in the absence of Fe(EDDS)) is present no major change is observed for the biodegradation of phenol by *Rhodococcus enclensis* (Figure 2***); the

lag time is still observed. When light and Fe(EDDS) are present, the lag time is no longer observed and the degradation of phenol is completed within 2.5 hours instead of 5.5 hours when the bacteria are in the dark. The microbial activity compensates the limitation of radical processes due to the destruction of the Fe(EDDS) complex (after two hours). In parallel, the production of catechol is increased compared to biotic or abiotic conditions alone (Figure S-2A). Catechol accumulates over approximately three hours; after which it decreases. As observed previously, this decrease is likely a result of the bacterial activity.

Comparison of the rates of phenol transformation under the different conditions: If we consider the numerous uncertainties, the rates of transformation under abiotic, biotic and combined conditions are within the same order of magnitude, namely ~10^{-5} mol L^{-1} h^{-1} (***Table 1***). Biotic and combined conditions can be further compared in more detail by normalizing the transformation rates with the exact number of cells present in the different incubations (three biological replicates for each condition). Note that the number of cells varied from $4 \cdot 10^8$ to $8 \cdot 10^9$ cell mL^{-1}. After normalisation to the cell concentration used in the individual experiments, it is evident that the rates of phenol transformation are very close to each other and in the range of 10^{-16} mol $cell^{-1}$ h^{-1} (***Table 2***).

Table 1: *Transformation rates [10^{-5} mol L^{-1} h^{-1}] of catechol and phenol under abiotic and biotic conditions. The rates were measured from three biological or chemical replicates (independent experiments), respectively. They were derived based on the steepest slopes in Figure 2.*

Phenol Light + Fe(EDDS)	Phenol *Rhodococcus enclensis* (dark)	Phenol *Rhodococcus enclensis* + Light	Phenol *Rhodococcus enclensis* Light + Fe(EDDS)	Catechol *Rhodococcus enclensis* (dark)
3.1 ± 0.9	14 ± 6.4	4.7 ± 3.2	5.7 ± 0.5	15 ± 0.5

3.1.2. Biotransformation of catechol

As catechol is an intermediate of phenol transformation, we measured its biotransformation rate by *Rhodococcus enclensis* under dark conditions. When the cell concentration was 10^8 or 10^9 cell mL^{-1}, the catechol biodegradation was too fast to be detected within the time resolution of the experiments (Figure 3). We performed various experiments with reduced cell concentrations, from 10^7 cell mL^{-1} to 10^6 cell mL^{-1} (Figure 3). Finally, we used the results corresponding to 10^7 cell mL^{-1} to derive the initial rate of catechol biotransformation. It was estimated as $(15 \pm 0.5) \cdot 10^{-16}$ mol $cell^{-1}$ h^{-1}. This value is 8.5 times higher than the biodegradation rate of phenol and was used in the model (***Section 3.2***).

Straube (1987) showed that the activity of the catechol-1, 2-dioxygenase of *Rhodococcus* sp P1 was higher than that of its phenol hydroxylase. This trend is in agreement with our results as we know from the genome sequencing of our *Rhodococcus enclensis* strain that a catechol-1,2-dioxygenase is involved (and not a catechol-2,3-dioxygenase) (Lallement et al., 2017). As opposed to the results for phenol in Figure 2, it can be seen in Figure 3 that no lag time is observed for catechol biodegradation. This suggests

that the first step of oxidation of phenol to catechol by a phenol hydroxylase might be a limiting step as it needs to be induced, while the second step -corresponding to the opening of the ring cycle by a catechol-dioxygenase - is not induced and, thus, faster.

3.2 Comparison of biodegradation rates by *Rhodococcus* to literature data for *Pseudomonas* strains

As we previously have shown that *Pseudomonas* is one of the most dominant and active genus in cloud

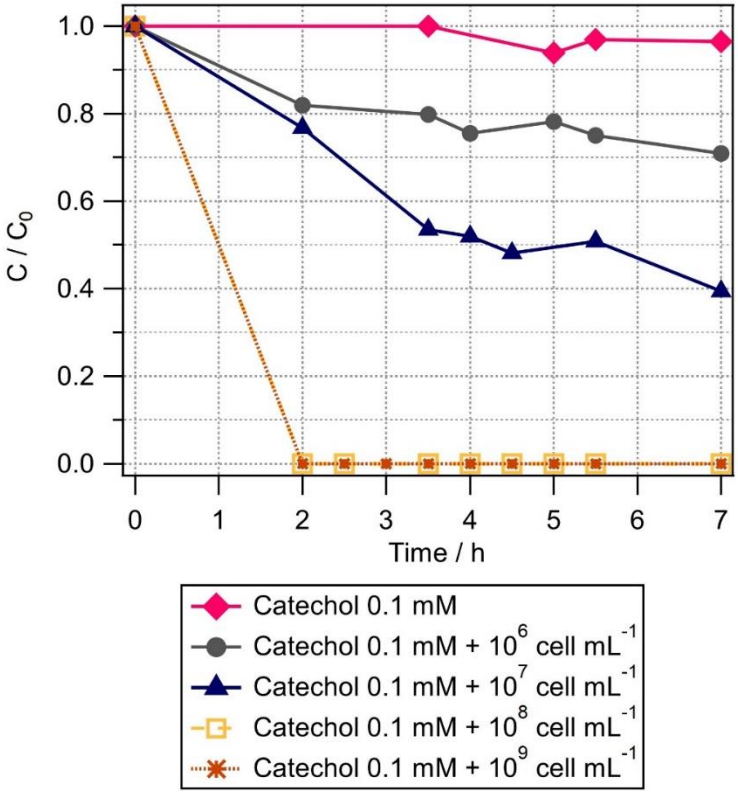

Figure 2: *Biotransformation of catechol with time by different concentrations of Rhodococcus enclensis: 10^9 cell mL^{-1} (brown stars), 10^8 cell mL^{-1} (brown squares), 10^7 cell mL^{-1} (blue triangles) , 10^6 cell mL^{-1} (black circles). C = phenol concentration at time t, C_0 = initial phenol concentration, C/C_0 was extrapolated from the ratio of the integrals of the catechol signal m/z = 110.03678 detected in mass spectra at time t = 0 and t, respectively. Initial catechol concentration was 0.1 mM.**Figure 3:** Transformation of phenol with time under different conditions. Phenol+Light +Fe(EDDS) (red*

waters (Amato et al., 2019) and that these strains are very active for phenol biodegradation (Lallement et al., 2018b and references therein), we compare in the following biodegradation rates of *Pseudomonas* from the literature (Table 2) to the data for *Rhodococcus* derived in the current study (Section 4). These rates differ for among *Pseudomonas* strains: for *Pseudomonas putida* EKII a value of $0.199 \cdot 10^{-16}$ mol cell^{-1} h^{-1} was found (Hinteregger et al., 1992), while it was $5.89 \cdot 10^{-16}$ mol cell^{-1} h^{-1} for *Pseudomonas aeruginosa* (Razika et al., 2010). Theses values are both on the same order of magnitude as the one measured here for *Rhodococcus enclensis PDD-23b-28.* Finally, we used an average value ($3.044 \cdot 10^{-16}$ mol cell^{-1} h^{-1}) for *Pseudomonas* strains to derive the rates used in the model (***Section S-3.2***).

***Table 2**: Biodegradation rates [mol cell^{-1} h^{-1}] of catechol and phenol of Rhodococcus and Pseudomonas strains normalized to the exact number of cells present in the incubations. The calculation of biodegradation rates for the Pseudomonas strains are detailed in S-1.*

Bacterial strain (experimental condition)	Biodegradation rate of phenol (10^{-16} mol cell^{-1} h^{-1})	Biodegradation rate of catechol (10^{-16} mol cell^{-1} h^{-1})	References
Rhodococcus enclensis PDD-23b-28 (dark)	1.8 ± 0.5	15.0 ± 0.5	This work
Rhodococcus enclensis PDD-23b-28 (light)	1.2 ± 0.5	ND[1)]	This work
Rhodococcus enclensis PDD-23b-28 (light+Fe(EDDS))	1.0 ± 0.3	ND[1)]	This work
Pseudomonas putida EKII (dark)	0.2	2.4	(Hinteregger et al., 1992)
Pseudomonas aeruginosa (dark)	5.9	70.7[2)]	Phenol experiments (Razika et al., 2010)
Pseudomonas (average)	**Average: 3.0**	**Average: 36.6**	

[1)] Not determined; [2)] This rate was estimated based on the value for phenol (Razika et al., 2010) and the ratio (~ 12) for phenol/catechol biodegradation rates as determined for Pseudomonas putida by Hinteregger et al. (1992) (cf also Section 1-1 in the supplement)

As in the case of phenol, we also calculated catechol biodegradation rates with *Pseudomonas strains* based on literature data (***Table 2***). Values are only available for *Pseudomonas putida* EKII (Hinteregger et al., 1992) and show a biodegradation rate that is twelve times higher compared to that of phenol biodegradation. This confirms that catechol dioxygenases are much more active than phenol hydroxylases as observed for *Rhodococcus enclensis*. Similar to phenol, catechol biodegradation rates for *Pseudomonas* are within the same order of magnitude as those for *Rhodococcus*. The same ratio (~12) as for the *Pseudomonas putida* was applied to estimate the biodegradation rate of catechol by *Pseudomonas aeruginosa*, for which only the rate for phenol was experimentally determined by Razika et al. (2010).

3.3 Model results

Model results are expressed as the relative contributions of each loss pathway in the gas and aqueous phases; they are summarized in ***Table S-4***. Both during day and night, the gas phase reactions of $^{\bullet}$OH and $NO_3^{\bullet}$ dominate the loss of phenol by > 99% (light red and blue bars in ***Figure 4a*** and ***b***, respectively). The contributions of *Pseudomonas* to the phenol loss are approximately a factor of three higher than those of *Rhodococcus,* in accordance with their higher cell concentration and comparable microbial activity (***Table S-3***). However, during daytime, the contribution of bacteria to the total loss in the aqueous phase is about one order of magnitude smaller than that of the chemical ($^{\bullet}$OH(aq)) reactions; during night-time, this difference is even larger and the $NO_3^{\bullet}$(aq) reactions dominate by far (factor > 100) the loss in the aqueous phase (***Figure 4b***).

While the microbial activity is the same during day and night time (i.e. there were no significant differences in experiments with and without light, respectively; ***Figure 2***), the night-time $NO_3^{\bullet}$(aq) concentration is about ten times higher (~10^{-14} M) than that of $^{\bullet}$OH(aq) (~10^{-15} M) during the day, and while the chemical rate constants also differ by a factor of four ($k_{OH,phenol}$ = $1.9 \cdot 10^9$ M^{-1} s^{-1}; $k_{NO3,Phenol}$ = $8.4 \cdot 10^9$ M^{-1} s^{-1}, Table S-1). These differences in radical concentrations and rate constants lead to much higher radical reaction rates during night than during the day and, thus, to a relatively lower importance of microbial activity during night time. Overall, the loss in the aqueous phase by both chemical and microbial processes contributes to ~ 0.1% to the total loss of phenol during night-time.

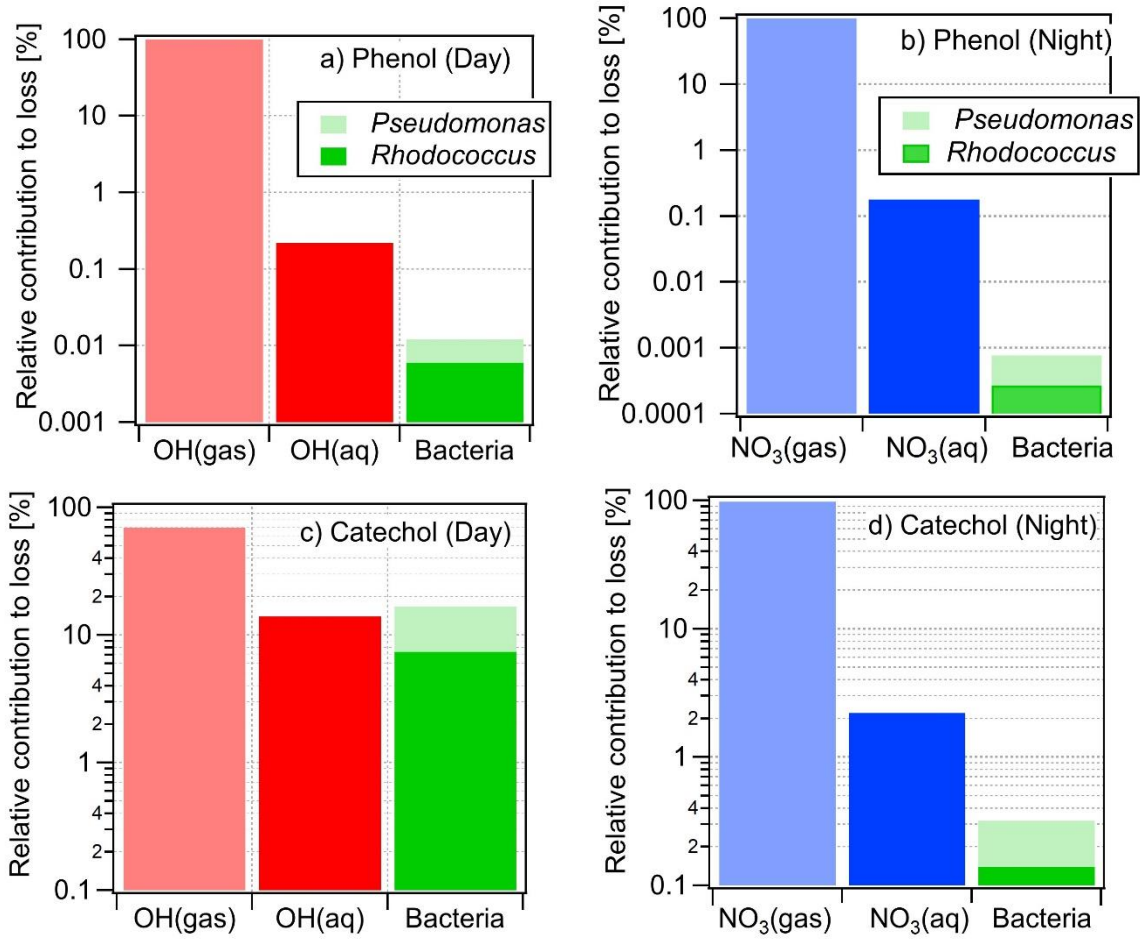

Figure 4 *: Relative contributions of multiphase processes to total loss of phenol (a, b) and catechol (c, d) during day (a, c) and night (b, d) time. Loss by bacteria processes only occur in the aqueous phase. Note that the ordinate is shown as a logarithmic scale which might falsely lead to the impression of larger contributions of Rhodococcus compared to Pseudomonas.*

The catechol fraction dissolved in the aqueous phase is much greater (≥ 85%) as its Henry's law constant is about 1000 times larger than that of phenol (***Table S-1***) of which only ~2% partition to the aqueous phase. Its enhanced solubility leads to a more important role of aqueous phase processes. During daytime, the loss by aqueous phase processes (chemical and microbial) is >30% for catechol (***Figure 4c***), with contributions by $^{\bullet}$OH(aq), *Pseudomonas* and *Rhodococcus* of 14%, 10% and 7%, respectively, when OH as the only oxidant for the phenols in the aqueous phase is considered. Thus, for this case, the

total microbial activity in the aqueous exceeds that of the chemical reactions (***Figure 4c***) and contributes to up to 17% to the total loss of catechol in the multiphase system. The relative higher gas phase rate constants and $NO_3^{\bullet}$ concentrations as compared to the corresponding values for $^{\bullet}OH$ during daytime, is reflected in the much higher contributions by the gas phase reactions to catechol loss during night (> 97%) than during daytime (***Figure 4d***).

The model results in ***Figure 4*** imply that the only chemical loss reactions of phenol and catechol are the reactions with the $^{\bullet}OH$ and $NO_3^{\bullet}$ radicals. In agreement with findings from a recent multiphase modeling study that discussed possible contributions of aqueous phase reactions with additional oxidants (O_3 and $HO_2^{\bullet}/O_2^{\bullet-}$) (Hoffmann et al., 2018), we show that including these reactions might add significant sinks for catechol (***Section S-4***). However, we caution that these results of the model sensitivity study including the ozone and HO_2/O_2^- reactions likely represent an upper estimate The rate constant used in the model was determined at pH = 1.5. In the original study, a decreasing trend with increasing pH was suggested; however, the exact pH dependence was not given. Thus, the prediction shown in Figure S-3 might not correspond to the moderate pH values as encountered in clouds and thus might be an overestimate of the role of the ozone reaction. .

4. Atmospheric implications

Both experimental and modelling approaches show that, in the water phase of clouds, suggest that phenol and catechol degradation by microbial and chemical OH(aq) processes may be within one order of magnitude. When the complete multiphase system is taken into account, phenol chemical transformation is largely dominant in the gas phase whereas the more water-soluble catechol is efficiently biodegraded in the aqueous phase.

Our estimates are only based on a limited number of cloud microorganisms (*Pseudomonas* and *Rhodococcus*). These microorganisms represent strains which are very efficient and previous works showed that these genera are active in clouds (Amato et al., 2017; Lallement et al., 2018b). However, they only comprise a fraction of the total microfora, i.e. about 22% of all prokaryotes in clouds. Even if other bacterial genera are less metabolically active, their combined metabolic activity might contribute substantially to the total biodegradation of phenols (and likely other water-soluble organics) in clouds. In addition, other microorganisms could be active as well, such as fungi and yeasts. The relative importance of radical chemistry compared to biodegradation will also depend on the radical concentrations in both phases which, in turn, are a function of numerous factors such as air mass characteristics, pollution levels that affect OH concentrations and microphysical cloud properties (e.g., drop diameters, liquid water content) (Ervens et al., 2014). In general, the importance of aqueous phase processes increases with increasing solubility (Henry's law constants). Our recent cloud FT-ICR-MS analyses of cloud water samples have shown that about 50% of ~2100 identified compounds were utilized by cloud microorganisms (Bianco et al., 2019). Thus, microbial processes in cloud water may

represent efficient sinks for numerous organics and might even result in products different from those of chemical reactions (Husárová et al., 2011). Thus, atmospheric models may be incomplete in describing the loss of some organic compounds and should be complemented by microbial processes in order to give a complete representation of the atmospheric multiphase system. While it has been recognized for a long time that microbial remediation in the environment is a common process (Kumar et al., 2011; Watanabe, 2001), we suggest that the atmosphere represents an additional medium for such processes.

5. Summary and conclusions

The newly derived biodegradation data for *Rhodococcus* with phenol and catechol were implemented in a multiphase box model, together with additional literature data for *Pseudomonas* degradation of the two aromatics and their chemical radical processes in the gas and aqueous phases. Model results reveal for the chosen model conditions ($[^{\bullet}OH]_{gas}$ = $5 \cdot 10^{6}$ cm^{-3}; $[NO_3^{\bullet}]_{gas}$ = $5 \cdot 10^{8}$ cm^{-3}; $[^{\bullet}OH]_{aq} \sim 10^{-15}$ M; $[NO_3^{\bullet}]_{aq} \sim 10^{-14}$ M; [Bacteria cell] =$1.7 \cdot 10^{7}$ cell mL^{-1}), the chemical and microbial activities in the aqueous phase are comparable. However, for catechol the loss processes in the aqueous phase are relatively more important (~30% of total loss) than for phenol (0.1% of total loss) due to its much greater water solubility ($K_{H,Phenol}$ = 647 M atm^{-1}; $K_{H,catechol}$ = $8.3 \cdot 10^{5}$ M atm^{-1}). It can be concluded that under some atmospheric conditions, the loss of highly soluble organics may be underestimated by chemical reactions only as the biodegradation of these organics by bacteria (and possibly other microorganisms) could represent additional sinks resulting in different products. Our model approach is highly simplified and limited in terms of biological, chemical and cloud microphysical conditions. More comprehensive experimental and model studies are needed to explore parameters spaces for relevant cloud water constituents (highly water-soluble, relatively low chemical reactivity) in order to better quantify the role of bacteria and other microorganisms in clouds as active entities that take part in the conversion of organics in the atmospheric multiphase system.

Data availability: All experimental and additional model data can be obtained from the authors upon request.

Author contributions: AMD and GM designed the experiments in microcosms. SJ, AL, MS and ML performed the experiments. BE performed the model simulations. BE and AMD wrote the manuscript.

Competing interests: The authors declare that they have no conflict of interest.

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Supporting information

Biodegradation of phenol and catechol in cloud water: Comparison to chemical oxidation in the atmospheric multiphase system

Saly Jaber[1], Audrey Lallement[1], Martine Sancelme[1], Martin Leremboure[1], Gilles Mailhot[1], Barbara Ervens[1*] and Anne-Marie Delort[1*]

[1]Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France

Correspondence to: Anne-Marie Delort (a-marie.delort@uca.fr) and Barbara Ervens (barbara.ervens@uca.fr)

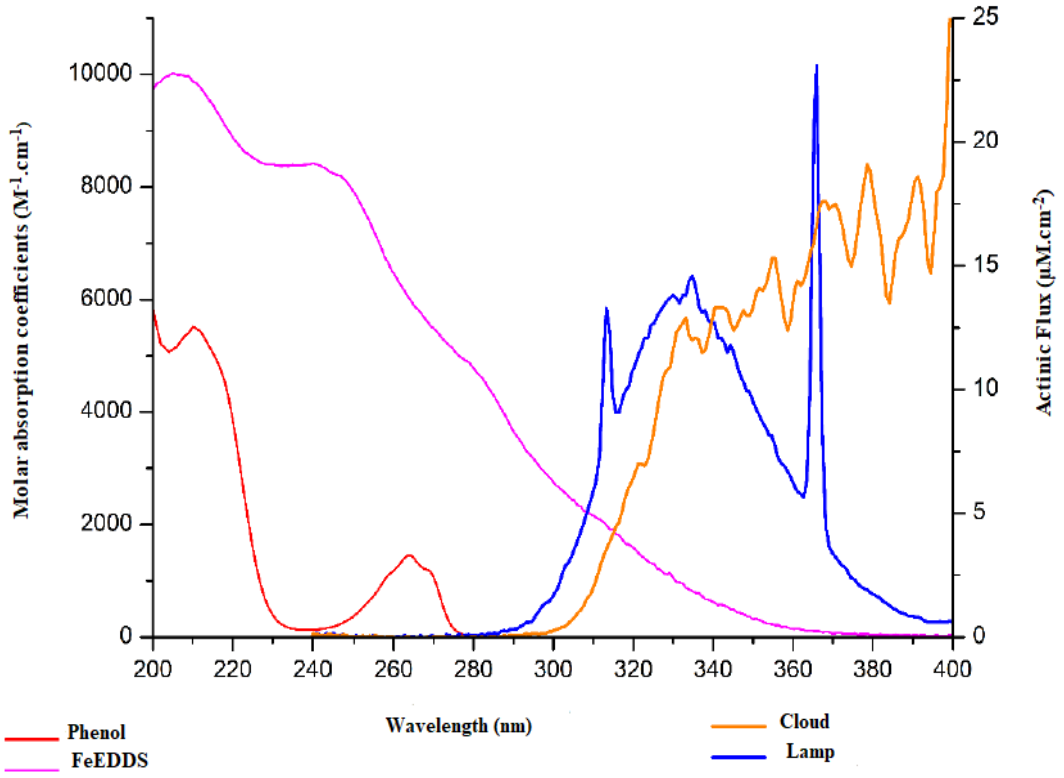

Figure S- 1 : *Comparison of the actinic fluxes of the lamps used and the emission of the solar spectrum measured in-cloud at the puy de Dôme station. The blue line represents the actinic flux of the lamp; the brown line corresponds to the actinic flux of the solar emission spectrum in cloud. The pink line represents the molar absorption coefficient of the Fe-EDDS complex. The red line represents the molar absorption coefficient of phenol.*

Section S-1 Calculation of the biodegradation rates for the *Pseudomonas* strains

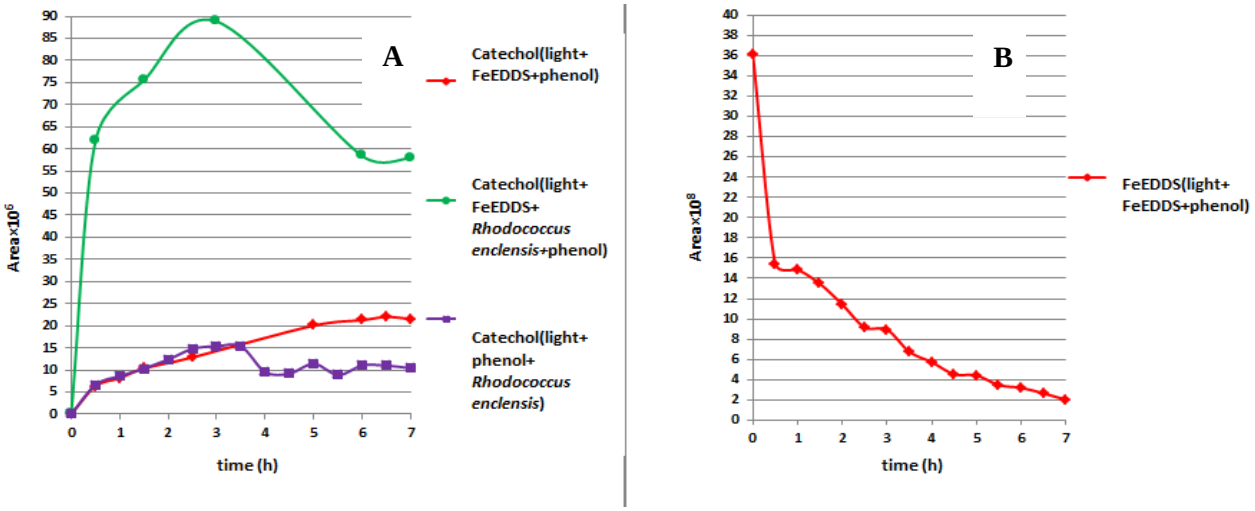

Figure S- 2 : *A) time dependence of the integral of catechol signal (m/z= 110.03678) detected in mass spectra of incubations with Fe(EDDS)+light and Phenol (red), Fe(EDDS)+ light, Phenol and R. enclensis (green), light + Phenol and* R. enclensis *without Fe(EDDS)(violet). B) Time dependence of the integral of Fe(EDDS) signal (m/z = 346.0086) detected in the mass spectrum, recorded during the incubation with Fe(EDDS)+ light and Phenol.*

S-1.1 Pseudomonas putida EKII

To calculate the biodegradation rate of phenol and catechol by *Pseudomonas putida* EKII, based on experiments performed at pH = 7.0, we used the following data from Hinteregger et al. (1992):

Phenol: Biodegradation of 654 μmol L^{-1} h^{-1}, number of cells: 3.3 ·10^9 cell L^{-1}

Biodegradation rate of phenol: 1.98·10^{-17} mol $cell^{-1}$ h^{-1}

Catechol: Biodegradation rate of catechol is twelve times higher than of phenol (ratio = 2.4μmol min^{-1} mg^{-1} / 0.2 μmol min^{-1} mg^{-1}, expressed per mg of cells)

Biodegradation of catechol: 1.98·10^{-17} ·12 = 23.78 ·10^{-17} mol $cell^{-1}$ h^{-1}

S-1.2 Pseudomonas aeruginosa

To calculate the biodegradation rate of phenol and catechol by *Pseusomonas aeriginosa*, based on experiments performed at pH=7.0, we used the following data from Razika et al. (2010):

Phenol: Biodegradation of 10 mg L^{-1} during 96 hours, number concentration of cells: 4.7. 10^9 cell L^{-1}

Biodegradation rate of phenol: 23.49·10^{-17} mol $cell^{-1}$ h^{-1}

Biodegradation of 50 mg L^{-1} during 120 hours, number concentration of cells: 4.7·10^9 cell L^{-1}

Biodegradation rate of phenol: 94.31·10^{-17} mol $cell^{-1}$ h^{-1}

Biodegradation rate of phenol (average value) taken into account: 58.9·10^{-17} mol $cell^{-1}$ h^{-1}

Catechol: No information is available in Razika et al (2010), so we multiplied the biodegradation rates of phenol with a factor of twelve as it is within the same order of magnitude of what we found in our study (Factor ~ 10)

Biodegradation rate of catechol (average value): 58.9·10^{-17} mol $cell^{-1}$ h^{-1}·12= 706.8 10^{-17} mol $cell^{-1}$.

Section S-2: Calculation of photolysis rate j(Fe(EDDS)) and resulting OH concentration in the experiments

$$j = \int_{250}^{400} I_{0,\lambda} \cdot \varepsilon_\lambda \cdot \phi_\lambda \cdot d\lambda \; \frac{photons}{cm^2\ s\ nm} \frac{cm^3}{molec\ cm} \frac{nm}{} \qquad [s^{-1}]$$

$I_{0,\lambda}$ = spectral actinic flux [photons cm^{-2} s^{-1} nm^{-1}]

ε_λ = extinction coefficient [cm^3 $molec^{-1}$ cm^{-1}]

ϕ_λ = Quantum yield [dimension less]

Experimental data

Irradiance E(λ) [μW cm^{-2}] ; convert into SI units E'[W/m^2] = E·10^{-6} W/μW ·10^4 cm^2/m^2 = E·0.01

Convert irradiance E(λ) [μW cm^{-2}] to actinic flux I [photons cm^{-2} s^{-1}]:

Actinic flux $I' = \frac{E\prime\,\lambda}{h \cdot c} \left[\frac{W\ m}{m^2} \frac{s}{J\ s\ m}\right] = \frac{E\,\lambda}{h \cdot c} \left[\frac{kg\ m^2}{s^3 m^2} \frac{m}{} \frac{s^2}{kg\ m^2 s} \frac{s}{m}\right] = \frac{photons}{m^2\ s}$

Spectral actinic flux $I_\lambda = \frac{I'}{\lambda} \cdot\ 10^{-4} = \frac{E(\lambda)}{h \cdot c} \left[\frac{W}{m^2} \frac{s}{J\ s\ m}\right] = \frac{E\,\lambda}{h \cdot c} \left[\frac{kg\ m^2}{s^3 m^2} \frac{m}{} \frac{s^2}{kg\ m^2 s} \frac{s}{m}\right] = \frac{photons}{cm^2\ s\ nm}$

h = 6.62606×10^{-34} J s

c = 3·10^8 m/s

ε' molar absorption coefficient (L mol^{-1} cm^{-1}) = extinction coefficient

ε_λ = ε' $\frac{L}{mol\ cm} \cdot \frac{1000\ cm^3}{L} \cdot \frac{mol}{6.022e23\ molec} = \varepsilon' \cdot 1000/N_A$ [cm^3 $molec^{-1}$ cm^{-1}]

Quantum yield: ϕ_λ = 0.025 (at 290 < λ < 400 nm)

$$j = \int_{250}^{400} I_\lambda \cdot \varepsilon_\lambda \cdot \phi_\lambda \cdot d\lambda \; \frac{photons}{cm^2\ s\ nm} \frac{cm^3}{molec\ cm} \frac{nm}{} = \mathbf{0.001388\ s^{-1}}$$

Calculation of steady-state References: •OH(aq) concentration

<u>OH formation:</u>

[Fe-EDDS] + hν → •OH + products j = 1.388e-3 s^{-1} $[Fe(EDDS)]_0$ = 0.5 mM

$$-\frac{d[Fe(EDDS)]}{dt} = \frac{d[OH]}{dt} = j\,[Fe(EDDS)]$$

<u>•OH loss</u>

•OH + Phenol → Products k = 8.41e9 M^{-1} s^{-1} $[Phenol]_0$ = 0.1 mM

$$\frac{d[OH]}{dt} = -\,k\,[OH][Phenol]$$

→ Steady-state OH concentration at the beginning of experiment

k [•OH] [Phenol] = j [Fe(EDDS)]

$$[OH] = \frac{j\,[Fe(EDDS)]}{k\,[Phenol]} = \frac{1.388e-3\ s^{-1}\ 5e-4\ M}{8.41e9\ M^{-1}s^{-1}\ \ 1e-4\ M} = 8.3e-13\ M$$

Section S-3: Input data to the multiphase box model

S-3.1: Multiphase processes

Table S-1: *Chemical and microbial processes in the multiphase model*

Gas Phase		
	Chemical rate constant [cm^3 s^{-1}]	**Reference**
$^{\bullet}OH$ + Phenol → 0.5 Catechol + 0.5 Prod [a)]	$2.81 \cdot 10^{-11}$	(Berndt and Böge, 2001)
$NO_3^{\bullet}$ + Phenol → Products	$5.8 \cdot 10^{-12}$	(Bolzacchini et al., 2001)
$^{\bullet}OH$ + Catechol → Products	$1.1 \cdot 10^{-10}$	(Olariu et al., 2000)
$NO_3^{\bullet}$ + Catechol → Products	$9.8 \cdot 10^{-11}$	(Olariu et al., 2004)
Aqueous phase		
	Chemical rate constant [M^{-1} s^{-1}]	
$^{\bullet}OH$ + Phenol → 0.5 Catechol + 0.5 Prod [b)]	$8.41 \cdot 10^{9}$	(Raghavan and Steenken, 1980)
$NO_3^{\bullet}$ + Phenol → Products	$1.9 \cdot 10^{9}$	(Umschlag et al., 2002)
$^{\bullet}OH$ + Catechol → Products	$4.7 \cdot 10^{9}$	(Hoffmann et al., 2018)
$NO_3^{\bullet}$ + Catechol → Products	$1.9 \cdot 10^{9}$	(Hoffmann et al., 2018)
$^{\bullet}OH$ + WSOC → Products	$2 \cdot 10^{6}$ s^{-1}	Based on (Arakaki et al., 2013), assuming [WSOC] = 5 mM
NO_3 → Products	10^{5} s^{-1}	Based on (Exner et al., 1992; Zellner and Herrmann, 1994); assuming 1 mM Cl^-, 0.01 mM Br^-
The following three reactions are only considered in sensitivity simulations, Figure S-4		
O_3 + Phenol → Products	1300	(Hoigné and Bader, 1983)
O_3 + Catechol → Products	$3.1 \cdot 10^{5}$	(Gurol and Nekouinaini, 1984)
$HO_2^{\bullet}/O_2^{\bullet-}$ + Catechol → Products	$7.8 \cdot 10^{4}$	Rate constant for HO_2/O_2^- ratio at pH = 4 ($pK_a(HO_2^{\bullet})$ = 4.8) calculated based on k_{HO2}, k_{O2}- by (Bielski et al., 1985)

	Microbial rate constant [L $cell^{-1}$ s^{-1}]	
Rhodococcus + Phenol → Catechol	$1.8 \cdot 10^{-13}$	[d)]
Rhodococcus + Catechol → Products	$1.5 \cdot 10^{-12}$	[d)]
Pseudomonas + Phenol → Catechol	$1 \cdot 10^{-13}$	[d)]
Pseudomonas + Catechol → Prod	$1.2 \cdot 10^{-12}$	[d)]

Phase transfer processes				
	K_H [M atm^{-1}]	**Reference**	**α [c)]**	**D_g [cm^2 s^{-1}][c)]**
$^{\bullet}OH(aq) \leftrightarrow {}^{\bullet}OH(gas)$	25	(Kläning et al., 1985)	0.05	0.15
$NO_3^{\bullet}(aq) \leftrightarrow NO_3^{\bullet}(gas)$	0.6	(Rudich et al., 1996)	0.1	0.1
Phenol(aq) ↔ Phenol(gas)	647	(Feigenbrugel et al., 2004)	0.027	0.09
Catechol(aq) ↔ Catechol(gas)	$8.31 \cdot 10^{5}$	(Sander, 2015)	0.1	0.08

[a)] Catechol yield likely represents an upper estimate for the total of all dihydroxybenzene compounds [b)] Initial formation of the phenoxy radical and the subsequent reaction with O_2 are lumped here, leading to 0.5 catechol into one step since the second reaction is diffusion controlled; [c)] These values were taken from CAPRAM (Ervens et al., 2003; Hoffmann et al., 2018) [d)] See calculation of values in Section S-3.2

S-3.2 Calculation of microbial rate constants from experimentally derived rates

Experimentally-derived rates R of microbial activity towards phenol and catechol are summarized in Table 2 of the main part of the manuscript, together with the bacteria type (*Rhodococcus*, *Pseudomonas putida*, *Pseudomonas aeruginosa*) and aqueous phase concentrations of substrate (phenol, catechol) and bacteria cells. Strictly, the measured rates might be only valid for the same substrate-to-cell ratio as the substrate availability determines the cell activity. Since these concentrations differ greatly, we derive the first-order rate constant k' [h^{-1}]

$$k' = R\,[Cell] / [Substrate] \quad \text{(S-1)}$$

Ambient cell concentrations in cloud water are on the order of $10^6 – 10^8$ cell L^{-1}. We assume a total cell concentration of $6.8 \cdot 10^7$ cell L^{-1} of which 3.6% are *Rhodococcus* ($C_{Rh,cloud} = 2.7 \cdot 10^6$ cell L^{-1}) and 19.5% *Pseudomonas* ($C_{Ps,cloud} = 1.3 \cdot 10^7$ cell L^{-1}). Phenol concentrations in cloud water are in the range of 5.5 - 7.7 nM (Lebedev et al., 2018). Using the lower value of this range yields phenol-to-cell ratios in cloud water of $2 \cdot 10^{-15}$ mol $cell^{-1}$ and $4.2 \cdot 10^{-16}$ mol $cell^{-1}$ for *Rhodococcus* and *Pseudomonas*, respectively, which is within two orders of magnitude of the ratios as used in the experiments. Corresponding cloud water measurements for catechol are not available.

In the multiphase model, we describe the microbial processes analogous to chemical reactions, i.e. with a formal second-order rate constant in units of L $cell^{-1}$ s^{-1} using the constant cell concentrations in the aqueous phase.

$$k_{2nd}\,[L\ cell^{-1}\ s^{-1}] = k' \ / \ [Cell]_{cloud} \ / 3600\ s\ h^{-1} \quad \text{(S-2)}$$

The resulting k_{2nd} are then used in the model studies for the assumed (constant) cell concentrations in cloud water

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Table S-2: *Summary of literature data on microbial activity towards phenol and catechol by Rhodococcus and Pseudomonas. For the estimates of unknown rates, refer to Section 3.2 (Comparison to literature data) in the main part of the manuscript*

Substrate	**Bacteria type**	**R** / **mol cell^{-1} h^{-1}**	**[Substrate]** / **M**	**[Cell]$_{experiment}$** / **(cell L^{-1})**	**Ref**	**[Substrate]/ [Cell]** / **mol cell^{-1}**	**k'** / **h^{-1}**	**[Cell]$_{cloud}$**	**k$_{2nd}$** / **L cell^{-1} s^{-1}**
Phenol	*Rhodococcus*	$1.76\cdot10^{-16}$	10^{-4}	10^{9}	a	10^{-13}	$1.76\cdot10^{-3}$	$2.7\cdot10^{6}$	$1.8\cdot10^{-13}$
Catechol	*Rhodococcus*	$1.5\cdot10^{-15}$	10^{-4}	10^{9}	b	10^{-13}	$1.5\cdot10^{-2}$	$2.7\cdot10^{6}$	$1.5\cdot10^{-12}$
Phenol	*Pseudomonas putida*	$1.99\cdot10^{-17}$	$6.54\cdot10^{-4}$	$3.3\cdot10^{9}$	c	$2\cdot10^{-13}$	$1\cdot10^{-4}$		
Catechol	*Pseudomonas putida*	$2.39\cdot10^{-16}$			c		$2.4\cdot10^{-3}$		
Phenol	*Pseudomonas*	$2.35\cdot10^{-16}$	$1.06\cdot10^{-4}$	$4.7\cdot10^{9}$	d	$2.3\cdot10^{-14}$	$1\cdot10^{-2}$		
	aeruginosa	$9.43\cdot10^{-16}$	$5.31\cdot10^{-4}$	$4.7\cdot10^{9}$		$1.1\cdot10^{-13}$	$8.3\cdot10^{-3}$		
Catechol	*Pseudomonas aeruginosa*				e		0.11		
Phenol	*Pseudomonas (Average)*						$5\cdot10^{-3}$	$1.3\cdot10^{7}$	$1\cdot10^{-13}$
Catechol	*Pseudomonas (Average)*							$1.3\cdot10^{7}$	$1.2\cdot10^{-12}$

[a)] (Lallement et al., 2018), [b)] This study, [c)] (Hinteregger et al., 1992) [d)] (Razika et al., 2010), [e)] Scaled up from data for phenol by reference [d)] using the same ratio of activities to phenol and catechol (12) as for the average value for *Pseudomonas putida*

Section S-4: Model sensitivity study including the aqueous phase reactions of phenol with ozone and of catechol with ozone and $HO_2^\bullet/O_2^{\bullet-}$

In a recent model study by (Hoffmann et al., 2018), it was suggested that catechol (and other dihydroxybenzenes) are efficiently oxidized not only by $^\bullet$OH but also by ozone and the hydroperoxy ($HO_2^\bullet/O_2^{\bullet-}$) radical. Also the reaction of phenol with ozone was included in this model study. In that latter model study, a rate constant of k(O_3 + Catechol) = $5.2 \cdot 10^5$ M^{-1} s^{-1} was estimated. This rate constant is similar to an experimentally-derived value of k(O_3 + Catechol) = $3.1 \cdot 10^5$ M^{-1} s^{-1} (Gurol and Nekouinaini, 1984). This latter study was performed at very acidic conditions (pH = 1.5) and a strong pH dependence of the rate constant was pointed out leading to a decreasing rate constant with increasing pH and resulting in the predominance of the $^\bullet$OH reaction at atmospherically-relevant pH values (~5).

Since the exact pH dependence is not available, we show in the following model results from a sensitivity studies including the $HO_2^\bullet$ and O_3 reactions in order to provide an upper estimate of their role in the multiphase system. Initial concentrations of 0.1 ppt $HO_2^\bullet$ and 40 ppb ozone in the gas phase are assumed and held constant throughout the simulation. In agreement with the model results by Hoffmann et al. (2018), we find large contributions of the ozone reactions in the aqueous phase to the total loss. The relative contributions of the ozone (57 – 68%) and $HO_2^\bullet/O_2^{\bullet-}$ (16 – 19%) reactions with catechol predicted here are also similar as predicted in the previous model study.

S-4.2 Model results

All model results [relative contribution to total loss [%]) are summarized in Table S-3. The upper part of the table contains results for the base simulations as shown in Figure 4 (microbial aqueous phase processes and $^\bullet$OH and $NO_3^\bullet$ reactions in gas and aqueous phases); the bottom part of the table includes results for the sensitivity simulations that also include $HO_2^\bullet$(aq) and O_3(aq) reactions (Figure S-3).

Table S-3: *Model results of base case and sensitivity simulations: Relative contributions to total loss of phenol and catechol, respectively*

		$^\bullet$OH(g)	$NO_3^\bullet$(g)	$^\bullet$OH(aq)	$NO_3^\bullet$(aq)	O_3(aq)	$HO_2^\bullet$(aq)	*Rhodo-coccus*	*Pseudo-monas*
Base case									
Day	Phenol	99.8	0	0.22	0	-	-	0.01	0.006
	Catechol	69.3	0	14	0	-	-	9.3	7.4
Night	Phenol	0	99.8	0	0.18	-	-	0.0005	0.00027
	Catechol	0	97.5	0	2.2	-	-	0.18	0.14
Sensitivity simulation including aqueous phase reactions of O_3 (phenol, catechol) and HO_2/O_2^- (catechol)									
Day	Phenol	99.7	0	0.22	0	0.02	0	0.01	0.0056
	Catechol	6.1	0	1.2	0	58.9	33	0.81	0.65
Night	Phenol	0	99.8	0	0.18	0.0007	0	0.0005	0.00027
	Catechol	0	86.4	0	2	11.4	0	0.16	0.13

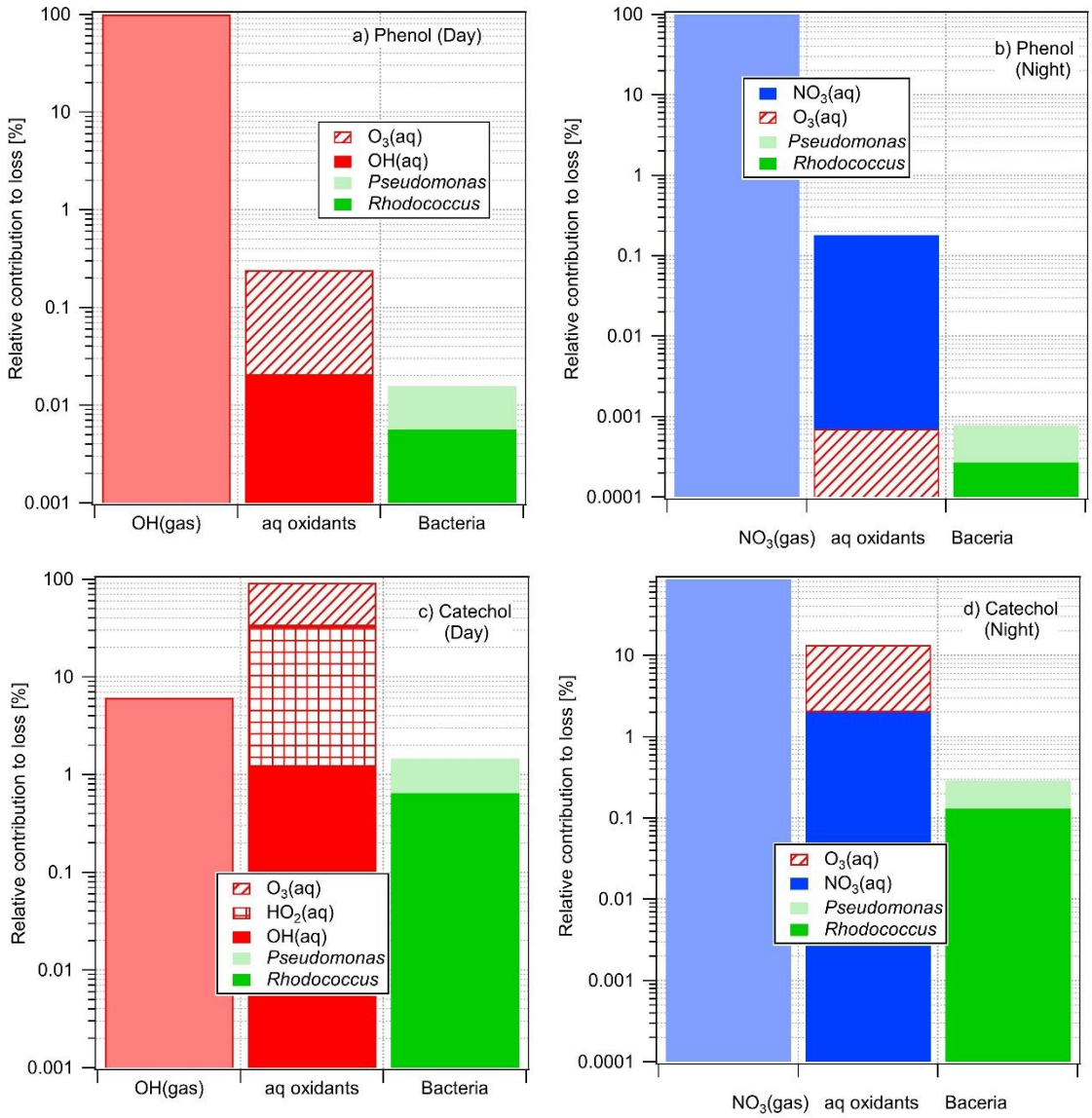

***Figure S- 3** : Relative contributions to total loss of phenol (a, b) and catechol (c, d) in the multiphase system including $HO_2^{\bullet}$ and O_3 reactions in the aqueous phase (Table S-3).*

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