

Interactive comment on “Atmospheric chemistry of carboxylic acids: microbial implication versus photochemistry” by M. Väitingom et al.

Anonymous Referee #1

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Overall comments: The objective of this manuscript is to investigate the relative competition of carboxylic acid degradation via chemical/radical oxidation versus microbial processes. A motivating factor for this work is to compare/contrast microbial decomposition vs. NO₃ reactions, to investigate which is the predominant nighttime decomposition route. However, it is curious that results (e.g., plots) of time series comparisons of degradation rates are not presented. Determination of which process dominates loss is dependent on the time scale. Overall this manuscript would benefit from a more clear and thorough presentation of quality assurance/control experiments. Results from those control experiments should be shown as well. Should this manuscript be majorly revised to address the specific comments below, it could perhaps be suitable for publication in Atmospheric Chemistry and Physics.

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Detailed comments: Abstract: Typically reaction rate constants are given with uncertainty bounds e.g., _____+/- ____.

Introduction: (Page 4833):Lines 15-20. There is a lot of experimental work that demonstrates carboxylic acids form in the aqueous phase (Tan et al., Atmos. Environ. 2010; and references therein). It is extremely likely that this is the predominant source of atmospheric observations, not particle into liquid partitioning of particulate species as suggested by the authors. It is curious that a large body literature related to similar experimental investigations is missing from this work.

(Page 4884) Line 7: should this sentence read “and high UV” (in addition to chemical composition and temperature)

(Page 4885) Some biological organisms secrete compounds (e.g., catalase) to prevent oxidation reactions. Do the microorganisms listed in this section (and used during the experiments) also secrete similar anti-oxidants?

(Page 4886) “OD575nm” My assumption is that this means optical depth at 575nm. This should be defined somewhere in the text.

(Page 4887) Were control experiments with just solution and lamp (no H₂O₂) performed? Results should be presented.

(Page 4888) Can the authors verify that no chemical reaction occurred during the freezing process? For example, were any recovery experiments done to estimate potential losses during freezing? Those recoveries should be presented.

(Page 4888) The authors’ calculations of degradation rates would be more compelling if times series data was provided.

(Page 4889) [OH] was not measured, rather taken from the literature? This is confusing. Why not estimate [OH] from [H₂O₂] decomposition or explicitly estimate from the polychromatic photon flux? Can the authors justify and define application of a steady state concentration to their experiments?

Interactive
Comment

(Page 4889) Does photodegradation rates resulting from reactivity with free radicals mean oxidation rates? Photodegradation implies a photolytic reaction (i.e., ___ + $h\nu$ →)

(Page 4889) Equation 3. Why is [Co] used and not the instantaneous value of [C]?

(Page 4890) line 7: “no extracellular accumulation of metabolite was detected”. Can the authors elaborate on this method? What metabolic products were searched for? Could any of the chemical products identified be a metabolite? What are the detection limits of metabolites? Overall, there should be more description of the biological methods.

(Page 4895) Lines 6-10: These are methods and should be in the appropriate section.

Table 1. Why is the [Na] concentration outside the observed range? Can the authors comment on what possible effects might be and how laboratory results might be different than what would actually happen in the environment?

Table 2: What does the footnote “global experimental uncertainties are evaluated from 30-35% mean?”

Table 3: The table is confusing. Are the authors presenting rates or rate constants? If they are measured rates from their experiments, the data would be better as a figure with all of the time series data.

Table 4: These are maxima for what conditions (e.g., summer equinox at noon)?

Figure 1. Do the other species exhibit absorbance in this spectrum (e.g., oxalate, formate)? If not, this should be explicitly stated.

Figure 2. What is the time scale? The authors seem to make the assumption of pseudo steady for OH concentrations in the aqueous phase? Can they defend and justify this assumption?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4881, 2011.

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