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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric chemistry of carboxylic acids: microbial implication versus photochemistry" *by* M. Vaïtilingom et al.

Anonymous Referee #3

Received and published: 24 March 2011

General comments:

This manuscript describes biodegradation experiments of mono- and dicarboxylic acids with bacterial strains isolated from cloud water. The rates of degradation are compared to experimentally and theoretically derived photodegradation rates. The authors conclude that in low OH regimes, microbial degradation can compete with or even exceed photochemical degradation. This is surely an interesting result and within the scope of the journal. However, the manuscript needs major revisions according to the comments below to be suitable for publication in ACP.

Specific comments:

- The authors state that in their previous paper Vaitilingom 2010 they already measured

the biodegradation of formate and acetate. Why then measure again in this work? And how does the data presented here compare to the older data? Or is it the same? This is confusing and needs clarification.

- Throughout all the manuscript the term "reactivity“ is often used in a somewhat strange context. For example in the abstract the authors state that they “investigated to which extent the active biomass (. . .) represents an alternative route to the chemical reactivity of carboxylic acids.” Although I can vaguely guess what the authours intend to say (alternative way of degradation?), I suggest to phrase such sentences more accurately.

- The structure and content of section 3 has to be improved. In section 3.4 for example, the main result is that the biodegradation rates in the natural cloud water are very similar to the ones measured in the artificial cloud water. Most of the paragraph, however, consists of experimental descriptions. The authors might want to think about combining the results of biodegradation (both in natural and artificial cloud water) into one section and they should present them in a clearer way.

- Next, section 4 (Discussion and conclusion) has to be completely re-written. At present stage it is very poor. Instead of discussing the (sometimes surprising and striking) experimental results, it rather justifies how and why the study has been conducted in a very lengthy and confusing way. It is furthermore spiked with statements that are not justified neither by the experimental data nor by any reference. For example on p4895, l.21-22 “photodegradation processes are less sensitive to temperature”: The photodegradation experiments were done at one temperature only in this work. Or on p.4896, l.21-22 “this work (. . .) showed that microbial activity could be much more important than NO3 reactivity on the carboxylic acid degradation and that it could be considered as a relevant sink for organic compounds during night”: I cannot see in which part of the manuscript this has been shown or discussed.

- p.4882, l.1-2: “. . . dissolved organic compounds, dominated by carboxylic acids. . .“: I

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doubt this is true. Usually the carbon fraction of cloud water TOC that can be attributed to identified carboxylic acids is in the range of a few percent. Often even the water-soluble organic carbonyl compounds make up a larger fraction, irrespective of all the yet unidentified material.

- p.4882, l.3-4: Is solar radiation really a “catalyzer” of the reactivity”? I think I know what is meant here, but it should be phrased more accurately.

- p.4882, l. 10: “viable community of clouds” does not make sense

- p.4882, l.13-14: “major carboxylic acids existing in cloud water”: Among the DCAs, malonic and malic acid often show higher concentrations than succinic acid. Is there any reason why succinic acid was selected over the other two?

- p.4883, l.1-2: “aqueous reactivity”: see comment above

- p.4883, l.11-12: “through reactions between the gaseous and the aqueous phase”: Do you mean: . . .through reactions within the aqueous phase?

- p.4883, l.15: The value of 36% is certainly not universally true. Also, it seems rather high compared to the carbon fractions of carboxylic acids reported by others. In fact, Marinoni et al. 2004, seem to have calculated the fraction of total carboxylic acid mass to dissolved organic carbon, which is not correct. It has to be the carbon fraction, which will be much lower. Please include other/more references here.

- p.4883, l.20: “aqueous phase reactivity” see comment above

- p.4883, l.21: Are these really the best references for aqueous phase sources of carboxylic acids?

- p.4884, l.11: Do you mean: “influence the budget. . .”?

- p.4884, l.22: “reactivity of certain compounds” see comment above

- p.4884, l.26: How is the new setup different from the previous one? The authors

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should not expect the reader to be aware of the technical development of their laboratory setups.

- p.4884, l.29: see comment above, this is not generally true

- p.4885, l.9: Which model is meant here?

- p.4885, l.12: In their previous work, the authors studied 60 bacterial strains. Why only 17 in this work? Do they represent the most frequent ones? Or are they– as stated – among the most frequent ones? Then, what about the other frequent ones?

- p.4886: In line 6 it is stated "artificial cloud water solution (see Table 1 for composition)", in line 14 it is stated "the cloud water solutions were prepared 10 times more concentrated than indicated in Table 1". It is not fully clear to me to which (presumably different) solutions it is referred here.

- p.4886, l.24-26: Why not use the average bacterial concentration, rather than a 10 times more concentrated one?

- p.4886, l.26: What does OD575nm mean?

- p.4886, l.27-28: I am not sure whether ACP readers can be assumed to be familiar with CFU counts. I am not and I would appreciate some more (brief) explanations and maybe a reference here.

- p.4887, l.14: A brief explanation of how different light spectra influence the photodegradation would help here to understand why two different photochemical setups were used.

- p.4888, l.17: Why not every hour from 0 to 8 h, as done in the artificial biodegradation experiments?

- p.4888, l. 19-22: Please give more details of the method or at least a reference. What are the detection limits etc.?

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- p.4888-4889, section 2.6: As also stated by the other referees, it is not fully clear how the rates were determined. Please explain in more detail and include a Figure.

- p.4889, l.13-15: This has been mentioned in the Experimental section already.

- p.4889, l.16-22 and p.4890, l.1-5: This could be moved to the experimental section

- p.4891, l.14: “organic photoproduct” sounds odd to me. I guess “oxidation product” is meant here.

- p.4891, l.18: “Acetate and succinate were not degraded by photolysis in all experiments.” This is a surprising result to me. How can this be explained? The authors don’t even discuss it, which should definitely be done here.

- p.4891, l.24- p.4892, l.10: This might be better suited in a discussions section

- p.4893, l.4-5: This obviously is a result of the non-existent photodegradation of acetate and succinate in S1 and S2, but how realistic is this in real clouds?

- p.4893, l.18-28 and p.4894, l.1: This should all be moved to the experimental section, some information is also redundant.

- p.4904: What are global experimental uncertainties and how were they determined?

- p.4908: What does the asterisk after “Microbial activity” stand for?

- p.4908: How were the measurement uncertainties determined? Is the uncertainty the standard deviation of a mean value?

- p.4911: Fig. 3 is pretty much the same as the corresponding part of Fig. 2 because of the high similarity between the rates in artificial and natural cloud water. It might therefore be redundant.

Technical corrections:

- p.4882, l.1: multiphase atmospheric systems

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- p.4883, l.17: monocarboxylic
- p.4884, l.7: carbon sources
- p.4884, l.22: . . . dominate the degradation. . . (if this is what is meant here)
- p.4885, l.4: were studied
- p.4886, l.1 and l.4: consisted of
- p.4886, l.9: NH4NO3
- p.4887, l.24 and elsewhere: rpm
- p.4891, l.3: and vice versa
- p.4892, l.16: comma instead of semicolon
- p. 4910: Fig.2: Increase font in Figure
- p.4903: Table 1 caption: delete “similar but”

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