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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 #4

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My major concern about the atmospheric relevance of the experiments is the incubation of artificial and natural cloud water for 120 hours (5 days) (!) (all cases). This generates ideal conditions for inoculated solutions to develop into a microbial state that would never exist in the atmosphere. Conducting decomposition experiments in such a proliferating environment is interesting, but in my opinion the results should not be implied to be atmospherically relevant by any means. In the atmosphere normally no single cloud can last for 5 days. Clouds usually form and evaporate in several cycles until they precipitate. Individual cloud droplets which are the reaction media for such alleged microbial decomposition exist for a few minutes only before they evaporate then reform again at some time later in multiple cycles. While such a phase oscillation may not affect photochemical reactions which can resume after the cloud droplet forms again and again, I suppose it should be a devastating effect for the microorganism. I am not an expert on microbiology but I think that in the intermittent dry states the microorganisms may at best become dormant (viable and culturable but inactive) and they do not have time to recover in the short periods of hydration.

Another major shortcoming of the approach is that the two distinct mechanisms of degradation (microbial and photochemical) are treated separately throughout the entire manuscript. While I anticipate that the determination of degradation rates requires these distinct setups, I would have liked to see at least one combined experiment by letting the two mechanisms compete in model cloud water. In other terms, a microbial degradation experiment should have been 'spiked' with hydrogen-peroxide and got irradiated, in order to see how microorganisms perform under more stressed–and more realistic–conditions. I would expect that such an experiment would have not yielded a simple combination of the two separate mechanisms (as in the case of two competitive chemical reactions). I feel that the activities of the microorganisms would have been affected by the more aggressive medium.

Given the limitations above, I feel that the atmospheric implications of the paper are strongly exaggerated if not completely unfounded. Although the experimental setups and the results are well-documented and correct in themselves, for the reasons above they are absolutely unsuitable to imply that microbial decomposition may be as important as photochemical degradation in natural cloud water. Based on my limited knowledge on microbiology, I would even guess that it is likely not so: the atmosphere must be a harsh medium for living organisms to strive and reproduce.

Minor comments:

Page 4883 Line 7 In fact, the reactions of very few compounds are able to generate new particles.

Page 4883 Line 12 What are 'reactions between the gaseous and aqueous phase'?

Line 14 In fact, the cited papers state that a significant fraction of organic matter is

water-soluble; most cannot be identified individually, a single value (36 %) for carboxylic acids may be misleading

Page 4883 Line 16-25 This condensed overview does not make sense: the authors treat carboxylic acids either as being inherently present in organic particles (Line 18), or being produced in aqueous reactions (Line 20).

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