Atmos. Chem. Phys. Discuss., 11, C3746–C3753, 2011
www.atmos-chem-phys-discuss.net/11/C3746/2011/

Atmospheric Chemistry and Physics Discussions

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

M. Vaïtilingom et al.

mickael.vaitilingom@univ-bpclermont.fr

Received and published: 21 May 2011

We would like to thank the reviewer for her/his helpful comments and corrections.

"General comment:"

"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

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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."

Reviewer 4 doubts about the atmospheric relevance of our study while the other reviewers did consider our work as relevant.

This remark is quite surprising because the idea that microbial activity could play a

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role in the liquid phase transformation of some organic compounds is not new. Already many papers have been published showing that the scientific community is now admitting this new concept (Ariya et al., 2002; Ariya and Amyot, 2004; Amato et al., 2005; 2007b; Deguillaume et al., 2008; Cote et al., 2008; Hallquist et al., 2009; Vaitilingom et al., 2010; Delort et al., 2010; Womack et al., 2010). Most of these papers have been published in reviews on atmospheric sciences. Experiments such as those presented in this paper have to be made to check this hypothesis and go further. We agree that a lot of work is still needed, more laboratory experiments have to be performed and modelling will be necessary in the future to really evaluate the relative contribution of biology vs. photochemistry in cloud chemistry. Consequently we propose to modify the conclusion of the paper and to insist on the explorative aspect of this work and showing that microorganisms have only, at the moment, a potential role in atmospheric chemistry.

Specific comments:

The experiments of incubation are long in order to get precise values of the initial biodegradation rates, and only these values are used to make our calculations (see the Electronic Supplementary Material); this is the classical way in biochemistry to determine rates; only this part of the curve is linear and can be used. These values have been measured during the first 8 hours for the artificial clouds at 5°C and 6 hours at 17°C. Note also that the same kinetics and experimental times are used for photochemistry, clearly demonstrating that there are in the same range of order.

Reviewer 4 is not an expert in microbiology and therefore makes some statements which are not scientifically sound. Cycles of evaporation do not imply “devastating effects” on microorganisms. It is now well established that living microorganisms are present in clouds (Ahern et al., 2007; Amato et al., 2005, 2007a, c; Bauer et al., 2002; Fuzzi et al., 1997; Sattler et al., 2001) and can be cultured in laboratories conditions; we have now a collection of 500 strains in our group. These microorganisms are active in clouds as shown by ATP (Adenine Tri Phosphate) measurements (Amato et al.,

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2007c) and CTC (5-Cyano-2,3-ditotyl tetrazolium chloride) staining (Hill et al., 2007). These two techniques describe the metabolic activity and the energetic state of the cells. This implies the uptake of nutrients from the liquid phase by cells and suggests that they can develop within cloud water. For microbiologists "viable but non cultivable" microorganisms means "metabolically active" but not "dormant" microorganisms. Also, as biocatalysts, they can induce chemical transformations even in the absence of growt (This is the basis of biotechnologies using isolated enzymes for organic synthesis for instance). May be the best proof of the efficient survival of microorganisms in clouds is given by the experiment performed with the real cloud water in this work. In this experiment, all the microorganisms present in cloud water have experienced cycles of evaporation, UV exposure etc... in the atmosphere and we showed that they are perfectly active. We found the same efficiency of transformation with this endogenous microflora than with pure strains isolated and grown in the laboratory. Microorganisms are very resistant organisms compared to mammalian cells for instance; they have been found in extreme environments (very low pH, very high temperatures...). It is well known that they can be freeze dried for their conservation in microbiological laboratory, and they can live again afterwards. In addition, I don't believe they are completely dry in the atmosphere, because of their highly hydrophilic surface (presence of sugars, proteins...). So, we think that they are always surrounded by a film of water.

We agree that a more realistic experiment could be designed by adding H2O2 to the microbial incubations under irradiation. However, our strategy was to go step by step. Our present goal was to measure the activity of a great number of cells (17 strains) under various scenarios; we wanted to measure "pure" biodegradation rates. We also wanted to check that the incubations in artificial clouds were consistent with the results obtained with real cloud water. The experiments of biodegradation presented here represent about two years of experiments; one incubation with one condition needs about 1 month, so everything could not be tested at the same time. Next step is to perform photo-biodegradation experiments with H2O2 and light. For that purpose we have constructed special photo-bioreactors which are not commercial. We have shown

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in a preliminary experiment with Pseudomonas graminis and artificial cloud water that this bacterium is not affected by this treatment. The photodegradation, biodegradation and photo-biodegradation rates are in the same range of order. We can send the results to the reviewer if he is interested. More, we obtained very good results with real cloud waters, these results will be sent for publication as another article. We can also provide to the reviewer these results if he wants to. Actually microbiologists have studied oxidative stress in microorganisms for a long time (see the reviews from Imlay, 2008 ; Ziegelhoffer and Donohue, 2009) and it is not surprising that they can resist to such conditions in clouds thanks to their enzymes (catalases, SOD...) and antioxidant pigments for instance.

To conclude, microorganisms are not in such a "harsh medium"; they are fully equipped to survive to such conditions including evaporation cycles, UV and H2O2 exposure and they can be active to transform organic compounds. The only main limitation is temperature, even if microorganisms have been shown to be active in very cold conditions (Sattler et al., 2001). Their activities are slowed down under 0°C, so as indicated in the paper, microbial activity will be limited to "warm clouds".

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“Minor comments:”

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

Yes, we agree and have corrected the sentence.

“Page 4883 Line 12: What are reactions between the gaseous and aqueous phase’?”

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Yes, the sentence was unclear. We have modified it.

“Page 4883: 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.”

We agree with the referee and we have deleted the sentence describing this single value for the puy de Dôme measurements.

“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).”

The sentence was rewritten to make it more understandable.

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