Atmos. Chem. Phys. Discuss., 11, C3754–C3758, 2011
www.atmos-chem-phys-discuss.net/11/C3754/2011/

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

"Thank you for submitting your manuscript 'Atmospheric chemistry of carboxylic acids: microbial implication versus photochemistry' to Atmospheric Chemistry Discussions After the discussion stage has been closed, I would like to give you my summary of the major concerns raised by the reviewers to be considered for further proceeding of your manuscript : Prior to submission of a revised manuscript for possible publication, please decide whether the relevance, and accuracy of your results warrant publication in ACP. If so, of course, please, go through all individual reviewer comments and address them point-by-point as well."

We thank the editor for her summary of the major concerns raised by the reviewers. We decided to go through all reviewer comments and we addressed them our responses

point-by-point.

"1) Atmospheric relevance"

"Reviewer 4 doubts the atmospheric relevance of your study since the lifetime of cloud droplets is on the order of minutes, and not hours as assumed in your experiments. While cloud droplet residuals (hygroscopic aerosols), certainly still contain some water, the aqueous phase on such particles is definitely very different in terms of ionic strength, pH etc as in relatively dilute cloud droplets. While your results are definitely interesting in terms of kinetics, product and loss studies, I agree with the reviewer that they might not be atmospherically relevant (and thus warrant publication in ACP), unless you can show their validity under more realistic atmospheric conditions."

See response to referee 4 where we demonstrated that microbes are viable and metabolically active in real clouds.

"Are the results independent of time? I.e. do you derive the same rates (rate constants) also for shorter time scales (minutes)?"

We measured rates and not rate constants. In biology, initial rates can be compared because they are exactly performed under the same experimental conditions.

"How realistic is the oxidant-free environment in your experiments solutions for microorganisms in real cloud droplets? Are microorganisms impacted by the presence of OH, H2O2, pH etc?"

See response to referee 4.

"What is the effect of additional products, such as antioxidants (e.g., catalase – cf Reviewer 1) for feedbacks on photodegradation rates?"

In this study, we did not perform combined photo and biodegradation experiments. 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 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. 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.

"Are the microorganism concentrations and number distributions similar to those in clouds?"

Yes, microorganism concentrations are in the same range than in real cloud liquid phase (bulk) (see footnote in Table 5 and the "material and method" section).

"2) Context of the role of carboxylic acids"

"All reviewers agree that the abstract and introduction contains vague if not even wrong statements about the atmospheric abundance and chemical (production and loss) pathways. The fraction of carboxylic acids to total organic aerosol mass usually does not exceed a few %. Also in cloud water, their mass contribution to the solute mass is i) strongly dependent on location (ii) usually no more than a few %. Note that common analytical techniques cannot resolve the total organic mass but only a small fraction of it."

All these points are now considered in the paper.

"3) Methodology, and derivation of results"

"a) Since readers of ACP are not necessarily familiar with microorganisms, you need to add more information on these biological systems and the analytical methods applied."

We added more information about biological analysis and we explained acronyms.

"b) Even though you have performed similar experiments in a previous study, it is desirable to give more detail on the methodology of the experiments In order to be more confident of your experimental method; results of quality assurance experiments should be presented."

This is now taken into account all along the new manuscript (see response to referee 1). See for example the new "Electronic Supplementary Material" where the way we determined biodegradation rates is presented.

"c) How applicable are Equations 1-3 to derive meaningful results? do the rates change over time? These could be illustrated by a figure."

In this work, we have considered initial biodegradation and photodegradation rates (see response to referee 1).

"assuming an OH concentration from model studies in the literature definitely introduces a huge uncertainty in the interpretation of results. [OH] should be calculated based on the light intensity and H2O2 concentration. In addition, it is likely that OH reacts over the course of the experiment. Instead of assuming a constant concentration, I suggest to set up a box model to simulate the experimental conditions."

This work has been separately to this work with the M2C2 model as indicated in response to referee 1. This shows that photodegradation of H2O2 is effective in both systems and our modelling results confirm the experimental results about H2O2 photodegradation. To our opinion, the objective of the present paper is not to simulate these laboratory experiments that need too much work and a total revision of the manuscript. Moreover, a paper will be submitted soon where intercomparisons between the model and experimental results are presented.

"It would be more useful to present data in terms of rate constants (k) that are independent of time and [OH] and not as reaction rates in order to facilitate a more general comparison."

We determined in this study biodegradation and photodegradation rates and not rate constants that are independent of time and [OH]. Determining rate constants at various temperatures, for various strains, in various media (different chemical compositions, pH) cannot be performed within less than a few years time. This work is currently under progress for a few selected strains.

“4) Structure of manuscript”

“I agree with the reviewers that several sections of the paper are hard to read: The abstract should only state your main findings: Under what conditions is microbial degradation of carboxylic more, as important as, or less important than photochemistry? Details on methodology do not need to appear there. Make sure that ‘Methods’ and ‘Discussion’ are clearly separated and only refer to the results of the experiments presented here. E.g., information on T dependence of photo vs. microbial degradation are not a direct conclusion form the present study. If relevant, you can add an extra section ‘Atmospheric implications’ that may include a discussion of your results in the context of atmospheric conditions, OH scenarios etc.”

All your comments are now taken into account in the new manuscript.

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