Atmos. Chem. Phys. Discuss., 11, C3724–C3732, 2011
www.atmos-chem-phys-discuss.net/11/C3724/2011/

Atmospheric Chemistry and Physics Discussions

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

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Received and published: 21 May 2011

"The scientific objectives of this work are relevant and the experiments generally well conducted. Based on the results presented, the conclusions seem sound and the overall message of the paper is clear. However, the quality of the presentation is not sufficient for publication. Some information is missing on the photodegradation experiments to demonstrate the validity of the results. The presentation of previous works and of the literature is not satisfactory either: important literature is missing while some citations are irrelevant or out-of-place. The structure of the paper also needs to be improved for clarity. All these improvements need to be made before publication."

We thank the referee for her/his interest in our work and for her/his valuable remarks. We have followed the general comments to improve the quality of the manuscript. The

literature has been corrected; additional information has been given and the structure of the paper has been changed. All the modifications are listed in the next section.

"Detailed comments:"

"1) Presentation of the literature"

"The literature cited, in particular in the introduction, is surprising as many important papers are not cited while others are irrelevant or out-of-place."

We agree with all the reviewer comments. The introduction has been strongly modified and now takes into account all the referee comments about the literature.

"The first part of the introduction and related literature (li. 7-10) discusses secondary organic aerosols, the relevance of which to the present paper is dubious. If the argument here is that the cloud processing of organic compounds can produce SOA, just say it like this and give specific references supporting this. For instance, Blando & Turpin, Atmos. Environ., 34, 1623, 2000, and more recent papers from the same group."

Yes, we agree with your comment. We discussed the potential role of micrrorganisms in the formation of SOA during the cloud processing in the last section (perspectives). We cited to illustrate this idea the two papers from (Blando and Turpin, Atmos. Environ., 34, 1623, 2000) and (Lim et al., ACP, 10, 10521, 2010).

"In the literature of the role of cloud chemistry (li. 11-13 of the introduction), some groundbreaking literature is missing, such as Lelieveld and Crutzen, Nature, 343, 227, 1990; Lelieveld and Crutzen, J. Atmos. Chem., 12, 229, 1991; Herrmann et al., Chemosphere, 38, 1223, 1999; Monod and Carlier, Atmos. Environ., 33, 4431, 1999."

We have added the above articles in the revised manuscript.

"The references supporting the fact that carboxylic acids dominate the organic compounds in cloud droplets need to be reinforced (the text gives only one, Marinoni et al., 2004). This is a surprising statement, in particular in the abstract, and needs to be double checked."

This sentence about the dominant fraction of carboxylic acids among organic compounds is not fully justified. After checking, the percentage of 36% was wrong. Actually, the corrected carboxylic acids fraction at the puy de Dôme station represent between 5 and 10% of the dissolved organic content (DOC) (Charbouillot et al., submitted paper, 2011). This is confirmed by other field measurements (Saxena and Hildemann, 1996; Hadi et al., 1995).

"Quoting review articles focusing on aerosols, not cloud droplets (Goldstein and Galbally, 2007; Hallquist et al., 2009) to support the fact that organic acids are aqueous phase products (li. 20-21) is completely out-of-place. On the other hand, many more studies have identified organic acids in aqueous-phase reactions in laboratory, which should be cited there."

Yes, this is true. We deleted these two reviews that were out-of-place. We have cited different relevant articles to illustrate the fact that organic compounds are produced in the aqueous phase by reactivity (Ervens et al., J. Geophys. Res., 2004; Carlton et al., Atmos. Environ., 2007; Tan et al., Atmos. Environ., 2010).

"2) Previous works and experimental information:"

"Some results from previous works, which are used as the basis and/or justification for the present work, are insufficiently presented. For instance, in the statement li. 26-27 of p. 4883 "the aqueous phase of clouds also contain insoluble biological material: : :" it is not clear if it has been proven that biological material was present in all the droplets of a cloud, or in only some of them (for instance in 1 out of 10 or 1 out of 1000 droplets)."

The presence of biological material has been shown experimentally in bulk samples collected from natural clouds. No information is actually available about the distribution in droplets. The study from Matthias-Maser and Jaenicke (1995) indicates that bioaerosols can represent up to 25% of the total number of insoluble aerosols in clouds. In clouds, bacteria range from 4.0 103 to 2.4 105 cells. mL-1 and fungi and yeasts from 8.9 102 to 2.5 104 cells. mL-1 (Delort et al., Atmos. Res., 2010). Two sentences have been added in the text.

"Also, has this material been found in cloud water from many different regions? Most of the references quoted seem to refer to the puy de Dôme station. This information is directly relevant to estimate the importance of the processes studied here in the real atmosphere."

Few studies have been done at various sites concerning biological measurements in natural clouds: the Rax Mountain in Austria by Bauer et al., 2002; the Sonnblick mountain in Austria by Satller et al., 2001; the Hebridean mountain in Scotland by Ahern et al., 2007 and at the puy de Dôme mountain in France by Amato et al., 2005 and 2007c. All these studies are cited in the manuscript and reinforce the statement that viable microorganisms are present in clouds. Moreover, the puy de Dôme station is a unique site to sample air masses from various origins (marine, continental, polluted).

"Another point that needs clarification is that, since similar experiments have already been made by the same group (Vaitilingom et al., 2010), what is exactly the new information targeted by the present study? If previous works already showed that biodegradation can compete with chemical degradation, why this new study?"

We agree with the reviewer, the objectives and complementarities of each individual work need to be clearly defined. Consequently, we have rewritten the two last paragraphs of the introduction as follows:

To test this hypothesis, in previous work, our strategy was first to screen the ability of a large number of microbial strains (60) isolated from clouds to degrade organic compounds (formate, acetate, lactate (D & L), succinate, formaldehyde and methanol) under optimal conditions (27°C) (Amato et al., (2005; 2007a)). We have shown that enzymes responsible for these transformations were present in these microorganisms. To go further, we studied the response of one single strain (Pseudomonas graminis) under more realistic atmospheric conditions (Vaïtilingom et al., 2010). We used a microcosm mimicking cloud chemical composition typical from continental influence at two different temperatures representative of warm clouds (5°C and 17°C). Biodegradation rates of formate, succinate and acetate were measured and compared to radical chemistry. For this, the reactions of the followed organic compounds with the two major free radicals OH and NO3 were considered. We calculated theoretical photodegradation rates from radical concentrations simulated by cloud chemistry models (Ervens et al., 2003b; Herrmann, 2003). This comparison showed that microorganisms would dominate the degradation of certain organic compounds in clouds during the night.

The objective of this work was to generalize our conclusions previously obtained on a single strain. For this, we selected 17 strains representative of the viable community existing in clouds and worked on two distinct artificial cloud media that reproduce marine and continental cloud chemical composition. Biodegradation rates of acetate, formate, oxalate and succinate were measured for all the strains on both media at 5°C and 17°C. The goal was to investigate the effect of environmental parameters on the biodegradation efficiency of microorganisms. Biodegradation rates in a natural cloud water sampled at the puy de Dôme station (France) with its own endogenous microflora and chemical composition was also investigated. The objective was to compare artificial microcosm and natural clouds. In addition, photodegradation experiments with hydrogen peroxide (H2O2) as a source of hydroxyl radicals were performed under the same microcosm conditions to compare directly photochemistry to biodegradation processes. This is the first report of such comparison using experimental data. In the discussion, theoretical calculations based on various scenarios of the OH reactivity were presented.

“Some important information on the photodegradation experiments are missing. This information might be provided in the previous papers from the same group, but the

present manuscript needs to give enough information to support the results and conclusions. For instance, there is no information on how the rate constants of photodegradation are measured (section 2.6). A vague reference to a “linear regression” is made in section 2.6 but a linear regression of what? This probably refers to the first-order decay of the organic compounds, but no detail is given. Also, the title “Calculation of the degradation rates” is confusing. The whole point of this work was to measure these rates experimentally, not to calculate them, wasn’t it? In addition to the information on the determination of the rates (in fact, rate constants), a figure illustrating the principle of the measurement should be provided. For instance, a figure showing the decay of the organic concentration. This would at the same time clearly show how these measurements were performed and justify that the decays were first order and that Equations (1)-(3) can indeed apply.”

In this study, we measured biodegradation rates (mol.cell-1.s-1) and photodegradation rates in M.s-1 and not rate constants (M-1 s-1). Two figures were added in the SM for more clarity. Section 2.6 was rewritten as follows:

To calculate the bio- and photodegradation rates, time evolution of each carboxylic acids concentration was plotted (Figure S1 for illustration). Then the pseudo-first order decay “k” (s-1) is determined by the linear regression of:

ln([C]/[C]0) = f(t) = -k . t (see Figure S2 in the SM).

With [C]0 (mol L-1) the initial concentrations of selected carboxylic acid C. In biodegradation experiments, the pseudo-first order decays was determined over the 6 and the 8 first hours of incubation at 17°C and 5°C, respectively. In photo-degradation experiments, the pseudo-first order decays was determined over the 4 and the 8 first hours of irradiation in the photochemical setups S1 and S2, respectively; at this incubation time, H2O2 was available since it was totally consumed after 6h in S1 and 48h in S2. The measured degradation rates of the compound C (vc) have been determined as follows:

- for biodegradation rates per cell: vc = (k . [C]0) / Ncells in [mol cell-1 s-1] (1)

- for photodegradation rates : vc = k . [C]0 in [M s-1] (2)

With Ncells (cells L-1) the concentration of cells participating to the biodegradation. The estimated photodegradation rates resulting from the reactivity with free radicals from data of the literature:

vc = K . [OH] . [C]0 in [M s-1] (3)

With [C]0 the initial concentrations of selected carboxylic acid C (mol L-1), [OH] is the concentration of free radical OH from literature and K (M-1 s-1) is the degradation rate constant of the carboxylic acid C by OH.

“The other reviewer and external comments have addressed the question of the concentrations of H2O2 and OH in these experiments. Showing the decay of organics would indicate if H2O2 was in excess and OH concentration was constant during these experiments. If neither the concentrations of organics or of OH were constant, I do not understand how the rate constants were measured, therefore it is important to clearly explain these measurements.”

As explained above, we measured photodegradation rates and not rate constants. The measurements of photodegradation rates in S1 and S2 systems were determined respectively during the 4 first hours and 8 first hours of incubation. During these incubation times, H2O2 was available to produce OH radicals as it was totally consumed after 6h in S1 and 48h in S2.

“For the results, Tables 2 and 3 must absolutely be presented in a similar manner (i.e “marine” vs “continental” in row or in column in both tables) so that the rates in these tables can be compared directly. Although the text is not clear about the typical concentration of cells in cloud droplets, section 2.2 suggests that it is of the order of 108 cell L-1 (and this is an information that should be given more clearly). Thus, multiplying all the rate constants in Table 2 by this figure gives directly rate constants to compare with those in Table 3. This is a simple and clear way to present the results, that could

be used in the abstract and conclusion.”

We agree with the reviewer. Table 3 is now presented in similar manner than Table 2. The point about the typical number of bacteria in cloud water used for the calculation in Table 3 is now clearly explained. The footnotes of Table 3 were strongly improved.

“3) Structure/presentation of the paper”

“The abstract needs to be shorten and more synthetic, i.e. focus on the main results. Right now, the abstract is difficult to read because too much detail is given on the experimental conditions and the rate constants obtained, and the main conclusion is lost. Also, it would be more informative (and clearer) in the abstract to give a range of values for the rate constants of biodegradation in mol s-1 (thus assuming an average concentration of cell) to compare directly with the photodegradation constants. Chemical sources and sinks for compounds are usually given in as rates (s-1) or rate constants (mol s-1), and the results in this paper should be presented in a way that can be directly compared to these.”

We agree that the abstract is too complex and confusing. It has been completely rewritten and shortened. The average values for biodegradation rates from Table 3 will be indicated in the abstract to be more informative. These values are directly comparable to photodegradation rates.

“The structure of the manuscript towards the end is quite confusing and needs to be shorten and clarified. Right after section 3.2 “photodegradation”, it would be more logical to present current section 3.4, which also presents experiments, and keep current section 3.3 for the discussion, since it only presents a discussion of the concentration of OH given by different models. Having section 3.3 as a first part of the discussion (section 4) would also allow regrouping some information, which is right now redundant between both, in particular the paragraph from li. 23 p. 4895 to li. 25 p. 4896, also discussing the concentration of OH reported by different models.

- once the discussion on the relevant concentrations of OH is made and the rate constants for bio- and photodegradation compared, the last part of the discussion should focus on the main results and conclusions of the paper. Describing the strategy of the work in detail (li.3 p. 4895 and following) or lengthy discussions of various cloud events are out of place here. In general, the conclusion should be much more synthetic, i.e. shorten and the main points made more clearly. Once all these changes made, the manuscript should be considerably easier to follow."

We totally agree with the reviewer comments. We modified the structure of the results and discussion for more clarity. The discussion on OH concentrations estimated by models is now in the discussion part. A new Table 4 describing our theoretical calculations (at 5°C and 17°C) that are compared with the experimental biodegradation rates is added in the revised manuscript. The Figure 2 is also modified and now only present experimental comparisons of photochemical rates (S1 and S2) and biodegradation rates at 17°C. A new Figure 3 is now introduced in the paper that presents relative contributions (at 5°C and 17°C) of photochemical and biological degradations of carboxylic acids based on Table 4.

"Small comment: - li 4 of abstract: "catalyzer" should be catalyst"

Done.

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