Atmos. Chem. Phys. Discuss., 11, C3716–C3723, 2011
www.atmos-chem-phys-discuss.net/11/C3716/2011/

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.

Overall comments:

"The objective of this manuscript is to investigate the relative competition of carboxylic acid degradation via chemical/radical oxidation versus microbial processes. A motivating factor for this work is to compare/contrast microbial decomposition vs. NO3 reactions, to investigate which is the predominant nighttime decomposition route."

Actually we are comparing biodegradation rates towards OH radical reactivity, the major oxidants during daytime condition. The comparison of biodegradation vs. NO3 reactions for carboxylic acids was investigated previously in Vaitilingom et al., AEM,

2010. This showed a more efficient degradation by microorganisms of carboxylic acids in comparison to their oxidation by the NO3 radicals.

“However, it is curious that results (e.g., plots) of time series comparisons of degradation rates are not presented.”

In this work, we determined biodegradation rates per cell (mol cell-1 s-1) or biodegradation rates (M s-1) and not rate constants (M-1 s-1). For this, we used 272 plots to determine biodegradation rates (17 strains, 2 different temperatures, 2 media, 4 carboxylic acids). For photochemical rates, we used 48 plots (2 media, 2 photo-reactors, 4 carboxylic acids and measurements are performed in triplicates). For the real cloud experiments, we plotted 8 figures (4 carboxylic acids, filtered and non-filtered). In total, it represents 328 figures. This is why we didn’t show them in the manuscript. For quality control, we added in the supplementary material (SM) two examples of these plots and the way we determine the initial biodegradation rates.

“Overall this manuscript would benefit from a more clear and thorough presentation of quality assurance/control experiments. Results from those control experiments should be shown as well.”

Details about the control experiments we performed during our experimental work have been included in the revised version. For example, we added information about the potential chemical modification during freezing process etc. For photodegradation studies, we performed triplicates and for biodegradation we performed one experience. Indeed, one incubation with one strain at a certain temperature in one medium needs one month to be completed. So it is a really heavy work. The biodegradation rate variability for a specific strain is much lower than the one between two different strains (as shown in Table 2). For this reason, we preferred to test a great number of strains instead of repeating the same experiment for one specific strain. Our discussion is based on average values of the whole microbial population and how the medium influence the biological activity. On the contrary, photochemical experiments which are much easier to handle are performed in triplicates that allows calculating uncertainties (see Table 3).

Detailed comments on the text:

"Abstract: Typically reaction rate constants are given with uncertainty bounds e.g., _____+/- _____."

We decided to fully rewrite the abstract that needs to be shortened. For biodegradation rates, this reflects the great biodiversity of cloud population and in that case, giving uncertainty bounds is not relevant. For the average calculated biodegradation rates, we considered strains that did not degrade the organic compounds.

"Introduction: (Page 4833): Lines 15-20. There is a lot of experimental work that demonstrates carboxylic acids form in the aqueous phase (Tan et al., Atmos. Environ. 2010; and references therein). It is extremely likely that this is the predominant source of atmospheric observations, not particle into liquid partitioning of particulate species as suggested by the authors. It is curious that a large body literature related to similar experimental investigations is missing from this work."

We agree with the reviewer about the major contribution of carboxylic acids from the aqueous phase reactivity. We modified the text accordingly and we added the references from Ervens et al., J. Geophys. Res., 2004; Carlton et al., Atmos. Environ., 2007 and Tan et al., Atmos; Environ., 2010.

"(Page 4884) Line 7: should this sentence read "and high UV" (in addition to chemical composition and temperature)"

We added in the revised manuscript "UV exposure" in this sentence.

"(Page 4885) Some biological organisms secrete compounds (e.g., catalase) to prevent oxidation reactions. Do the microorganisms listed in this section (and used during the experiments) also secrete similar anti-oxidants?"

The reviewer is right. All the aerobic microorganisms are able to produce anti-oxidants (see response to reviewer 4 for more details). For incubation of microorganisms in artificial cloud media, neither H2O2 nor OH radicals are present.

"(Page 4886) "OD575nm" My assumption is that this means optical depth at 575nm. This should be defined somewhere in the text."

We agree with the reviewer. OD575nm is the optical depth at 575nm. We have changed the text accordingly.

"(Page 4887) Were control experiments with just solution and lamp (no H2O2) performed? Results should be presented."

Yes, a control experiment was performed under irradiation without H2O2. No degradation was observed for all the organic compounds except for oxalate but this degradation was less than 5% over the whole incubation time. This was not indicated in the manuscript because it is negligible. This is added at the end of section 2.3.

"(Page 4888) Can the authors verify that no chemical reaction occurred during the freezing process? For example, were any recovery experiments done to estimate potential losses during freezing? Those recoveries should be presented."

During the freezing process, no reaction or fate of carboxylic compounds were observed. We think that these experiments should not be shown in the manuscript. However, we indicate in the text that there is no bias during the freezing process.

"(Page 4888) The authors' calculations of degradation rates would be more compelling if times series data was provided."

Yes, this section has been improved. The section 2.6 was totally rewritten for more clarity and we added an example of calculation in the Supplementary Material. The explanations are now the following:

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 [mol cell-1 s-1] (1)

- for photodegradation rates : vc = k . [C]0 [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 [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.

“(Page 4889) [OH] was not measured, rather taken from the literature? This is confusing. Why not estimate [OH] from [H2O2] decomposition or explicitly estimate from the polychromatic photon flux? Can the authors justify and define application of a steady state concentration to their experiments?”

OH concentrations were taken from the literature in order to consider “representative” values from the level of OH radicals in the atmospheric aqueous phase. Actually no measurement is available and only cloud chemistry models can estimate OH concentrations in the cloud medium. These models, even they remain theoretical, consider explicit multiphase chemistry combined with microphysical processes. Therefore, OH concentrations that are considered for our calculation are more “atmospherically relevant”. For more consistency, we calculated, with the M2C2 model (Model of Multiphase Cloud Chemistry), the photolysis of H2O2 considering the polychromatic photon flux of both setups. This model allows calculating the photolysis rates of various chemical compounds both in the gas and aqueous phases (see Deguillaume et al., 2004 for more details). The experimental photon flux was fitted and we obtained a simulated value for the photolysis rate for H2O2 of 2.8 10-5 s-1 for the S1 setup and a photolysis rate of 5 10-6 s-1 for the S2 setup. These values are rather coherent with values obtained with our M2C2 model simulating the H2O2 degradation at noon during summertime with a photolysis rate equal to 4.8 10-6 s-1.

“(Page 4889) Do photodegradation rates resulting from reactivity with free radicals mean oxidation rates? Photodegredation implies a photolytic reaction (i.e., ___ + hv !)”

No, in this study, we only considered indirect photo-degradation of carboxylic acids through production of OH by H2O2 photolysis. OH radical then oxidized the organic compounds. In this work, photo-degradation refers to the oxidation of organics by OH resulting from a photolytic reaction (H2O2 + hv).

“(Page 4889) Equation 3. Why is [Co] used and not the instantaneous value of [C]?”

To be coherent with the calculation of the biodegradation rates, we consider the highest photo-degradation rates with the highest organic compound concentrations. For this theoretical calculation, we also consider extreme constant OH concentrations.

“(Page 4890) line 7: “no extracellular accumulation of metabolite was detected”. Can the authors elaborate on this method? What metabolic products were searched for? Could any of the chemical products identified be a metabolite? What are the detection limits of metabolites? Overall, there should be more description of the biological methods."

When talking about "accumulation of metabolites", we meant metabolites that could be detected by ionic chromatography (essentially carboxylic acids). We changed the text accordingly.

"(Page 4895) Lines 6-10: These are methods and should be in the appropriate section."

We think that this does not correspond to material and method section. These sentences describe the occurrence of air masses sampled at the puy de Dôme station.

"Comments on Tables and Figures:"

"Table 1. Why is the [Na] concentration outside the observed range? Can the authors comment on what possible effects might be and how laboratory results might be different than what would actually happen in the environment?"

Table 1 was modified in the final version. The maximal measured concentration of sodium is equal to 681 μM and not 281 μM. This was an error.

"Table 2. What does the footnote "global experimental uncertainties are evaluated from 30-35% mean?"

The global experimental uncertainty is the result from two additive errors: 1) the one from the analysis with the ionic chromatography (less than 10%); 2) the one from the biological variability that was calculated from five replicates on 2 strains (between 20 and 25%).

"Table 3. The table is confusing. Are the authors presenting rates or rate constants? If they are measured rates from their experiments, the data would be better as a figure with all of the time series data."

In Table 3, we present biodegradation and photo-degradation rates and not rate constants. For more clarity, the calculation for values in Table 3 is now explained in the footnote. In addition, we modified in the whole manuscript whether we are talking about “biodegradation per cell” (mol cell-1 s-1) or “biodegradation rates” (M s-1) that are comparable to photo-degradation rates in a defined situation.

“Table 4. These are maxima for what conditions (e.g., summer equinox at noon)?”

Yes, these values correspond to extreme concentrations simulated by cloud chemistry model at noon during summertime conditions. We decided to consider the most extreme simulated values for OH concentrations to evaluate the role of biodegradation in the most unfavourable conditions.

“Figure 1. Do the other species exhibit absorbance in this spectrum (e.g., oxalate, formate)? If not, this should be explicitly stated.”

As stated above, there is not direct photolysis of organic compounds in the aqueous phase in this spectrum.

“Figure 2. What is the time scale? The authors seem to make the assumption of peudo steady for OH concentrations in the aqueous phase? Can they defend and justify this assumption?”

No, OH values are simulated by models that consider aqueous phase reactivity and transfers between the various phases of the cloud. Therefore, maximal OH concentrations that are considered depend on various sources that are time dependant. This calculation remains theoretical but, as indicated above, no measurement of OH concentration in the aqueous phase is available during the incubation period.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper