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Atmospheric Chemistry and Physics Discussions

Atmospheric chemistry of carboxylic acids: microbial implication versus photochemistry

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Abstract

Clouds are multiphasic atmospheric systems in which the dissolved organic compounds, dominated by carboxylic acids, are subject to multiple chemical transformations in the aqueous phase. Among them, solar radiation, by generating hydroxyl radicals ($^{\bullet}$OH), is considered as the main catalyzer of the reactivity of organic species in clouds. We investigated to which extent the active biomass existing in cloud water represents an alternative route to the chemical reactivity of carboxylic acids. Pure cultures of seventeen bacterial strains (Arthrobacter, Bacillus, Clavibacter, Frigoribacterium, Pseudomonas, Sphingomonas and Rhodococcus), previously isolated from cloud water and representative of the viable community of clouds were first individually incubated in two artificial bulk cloud water solutions at 17 °C and 5 °C. These solutions mimicked the chemical composition of cloud water from "marine" and "continental" air masses, and contained the major carboxylic acids existing in the cloud water (i.e. acetate, formate, succinate and oxalate). The concentrations of these carboxylic compounds were monitored over time and biodegradation rates were determined. In average, they ranged from 2×10^{-19} for succinate to 1×10^{-18} mol cell^{-1} s^{-1} for formate at 17 °C and from 4×10^{-20} for succinate to 6×10^{-19} mol cell^{-1} s^{-1} for formate at 5 °C, with no significant difference between "marine" and "continental" media. In parallel, irradiation experiments were also conducted in these two artificial media to compare biodegradation and photodegradation of carboxylic compounds. To complete this comparison, the photodegradation rates of carboxylic acids by $^{\bullet}$OH radicals were calculated from literature data. Inferred estimations suggested a significant participation of microbes to the transformation of carboxylic acids in cloud water, particularly for acetate and succinate (up to 90%). Furthermore, a natural cloud water sample was incubated (including its indigenous microflora); the rates of biodegradation were determined and compared to the photodegradation rates involving $^{\bullet}$OH radicals. The biodegradation rates in "natural" and "artificial" cloud water were in the same order

of magnitude; this confirms the significant role of the active biomass in the aqueous reactivity of clouds.

1 Introduction

A huge variety of chemical compounds exists in the atmosphere as solid particles, gas, and dissolved into cloud droplets or ice crystals. This includes very diverse organic species (between 10^4 and 10^5 different molecules as estimated by Goldstein and Galbally, 2007), which have primary and secondary sources. The chemical transformations of these species can lead to the formation of new particles known as Secondary Organic Aerosols (SOA) (Chung and Seinfeld, 2002; Limbeck et al., 2003; Takekawa et al., 2003; Claeys et al., 2004; Davidson et al., 2005; Hallquist et al., 2009).

Clouds play a key role in the transformation of chemical species through reactions between the gaseous and the aqueous phase (Jacob et al., 1986; Möller et al., 1996; Laj et al., 1997; Fowler et al., 2009). In cloud droplets the organic matter represents a significant fraction of the soluble matter (Hadi et al., 1995; Saxena and Hildemann, 1996; Fuzzi et al., 2002); 36% of which are carboxylic acids (Marinoni et al., 2004) The carboxylic acids are produced in the gas-phase and dissolved into the aqueous phase (main source of mono-carboxylic acids such as acetic and formic acids); they can also result from the dissolution of the soluble part of organic particles (main source of dicarboxylic acids like oxalic, succinic, malonic and maleic acids ...); they also derive from the aqueous phase reactivity (Chebbi and Carlier, 1996; Sellegri et al., 2003; Goldstein and Galbally, 2007; Kroll and Seinfeld, 2008; Hallquist et al., 2009; Sun et al., 2010). The oxidation of organic matter due to the presence of free radicals such as $^{\bullet}$OH can be considered as an important source of carboxylic acids in the aqueous phase, but also as one of their main sinks (Karpel Vel Leitner and Doré, 1997; Herrmann, 2003; Warneck, 2003; Ervens et al., 2003a; Sun et al., 2010).

The aqueous phase of cloud also contains insoluble biological material such as bacteria, fungal spores, pollens, plant debris, etc. (Matthias-Maser et al., 2000; Bauer et al., 2002; Jaenicke, 2005; Burrows et al., 2009). Viable microorganisms have been recovered from rain (Casareto et al., 1996), cloud and fog samples (Fuzzi et al., 1997; Amato et al., 2005; Ahern et al., 2007; Amato, 2007c). The microbial strains isolated from the atmosphere were likely originating from vegetation, soil, aquatic environments (Amato, 2007c; Burrows et al., 2009), and most of these microorganisms were able to survive and develop under the specific conditions existing in cloud water (chemical composition, low temperature) (Sattler et al., 2001; Amato et al., 2007c). Possible C-sources for microorganisms in atmospheric waters are carboxylic acids, aldehydes and alcohols (Herlihy et al., 1987; Fuzzi et al., 1997; Ariya et al., 2002; Amato et al., 2005, 2007a; Côté et al., 2008; Deguillaume et al., 2008). Biological activity could therefore participate to the budget of the organic matter in cloud droplets.

Previous investigations of our group about a possible implication of microbes in cloud chemistry were reported in Amato et al. (2005, 2007a), in which the biodegradation ability of 60 microbial strains toward atmospheric organic compounds (formate, lactate (D and L), succinate, formaldehyde and methanol) were evaluated at 27 °C. Each strain consumed at least one of these compounds, and the highest efficiencies of biotransformation were observed toward acetate, formate, and formaldehyde. Using a similar approach we then measured the rates of biodegradation of the same compounds (except formaldehyde and methanol) at lower temperature (17 °C and 5 °C) (Vaïtilingom et al., 2010), and compared them to reaction rates involving the major free radicals: $^{\bullet}OH$ and $NO_3^{\bullet}$ (Herrmann, 2003; Ervens et al., 2003a). This comparison showed that microorganisms would dominate the reactivity of certain organic compounds in clouds during the night.

The objective of the present study is to pursue our comparative approach between biodegradation and photodegradation processes occurring in cloud droplets. We developed a new experimental setup of biodegradation test in artificial cloud water media reflecting the chemical composition of natural cloud from “marine” and “continental” air-masses. These media are composed of the major inorganic ions and the main carboxylic acids detected in atmospheric water: acetate, formate, oxalate and succinate

(Löflund et al., 2002; Marinoni et al., 2004). The biodegradation rates of these carboxylic acids in artificial cloud solution were determined at 17 °C and 5 °C for 17 pure strains representative of the viable community existing in clouds. Then, the photodegradation rates in these media were evaluated in the presence of light and hydrogen peroxide (H_2O_2) as a source of hydroxyl radicals in order to allow comparison with biodegradation efficiencies. Finally, the biodegradation rates of carboxylic compounds in a natural unmodified cloud water sample, including its indigenous microflora, incubated under controlled conditions were measured and validated our experimental model.

2 Material and methods

2.1 Bacterial strains

Seventeen bacterial strains isolated from cloud water were selected; they are among the genera the most frequently recovered by culture from cloud water sampled at the puy de Dôme station (1465 m a.s.l.) between December 2003 and March 2009 (see Amato et al., 2007b). The strains used are: 2 *Pseudomonas* sp. strains PDD-6b-4 (DQ512766) and PDD-14b-10 (DQ512794), 3 *Pseudomonas syringae* strain PDD-13b-1 (DQ512737), PDD-12b-8 (DQ512783) and PDD-13b-2 (DQ512785), 1 *Pseudomonas viridiflava* strains PDD-14b-14 (DQ512797), 1 *Pseudomonas graminis* strain PDD-13b-3 (DQ512786), 3 *Sphingomonas* sp. strains PDD-3b-10 (DQ512744), PDD-14b-5 (DQ512789) and PDD-14b-6 (DQ512790), 2 *Frigoribacterium* sp. stains PDD-14b-13 (DQ512796) and PDD-30b-1 (HQ256816), 1 *Rhodococcus* sp. strain PDD-23b-5 (HQ256785), 1 *Arthrobacter rhombi* strain PDD-3b-7 (DQ512742), 1 *Bacillus pumilus* strain PDD-5b-1 (DQ512749) and 1 *Bacillus* sp. PDD-16b-1 (not available in GenBank), and 1 *Clavibacter michiganensis* strain PDD-25b-3 (HQ256805).

2.2 Biodegradation tests

Biodegradation experiments consisted in “marine” or “continental” artificial cloud water solutions inoculated with bacterial cells and incubated at 5 °C and 17 °C for 120 h under aerobic conditions. Incubation media consisted in “marine” and “continental” artificial cloud water solutions (see Table 1 for composition) made by diluting stock solutions in ultrapure water (resistivity $\geq 18.2\,\mathrm{M\Omega\,cm^{-1}}$). Stock solutions were prepared from the following products: acetic acid (Aldrich, ≥ 99.99%), formic acid (Fluka, ∼ 98%), oxalic acid (Fluka, ≥ 99%), succinic acid (Fluka, ≥ 99%), $MgCl_2{\cdot}6H_2O$ (Fluka, ≥ 99%), $CaCl_2{\cdot}2H_2O$ (Aldrich, 99%), K_2SO_4 (Fluka, ≥ 99%), NaCl (Aldrich, 99.5%), NO_3NH_4 (Fluka, ≥ 99.5%), NaOH (Merck, 99%) and H_2SO_4 (Acros Organics, ≥ 95%). The artificial cloud water solutions were sterilized by autoclave (20 min at 121 °C) and stored at 5 °C for less than 24 h. In the case of biodegradation experiments, in order to have a better stabilization of the chemical composition and pH after sterilization process, the cloud water solutions were prepared 10 times more concentrated than indicated in Table 1. In previous work (Vaïtilingom et al., 2010), we showed that, at constant ratio “cell concentration/degraded chemical compound concentration” and in the range of concentrations investigated, biodegradation rates are independent of the absolute cell and chemical concentrations.

Artificial cloud water solutions were inoculated with bacterial cells from pure cultures grown aerobically at 17 °C (200 rpm) in R2A broth (Reasoner and Geldreich, 1985). Cells were harvested by centrifugation (4000 × *g*, 15 min, 4 °C) after 18 h of growth (exponential phase), rinsed once in NaCl solution (8 g per liter) and twice in the incubation medium and finally resuspended in the incubation medium. The concentrations of cells in the test media were adjusted to 10^6 cells $\mathrm{mL^{-1}}$ (∼ 10 times higher than the average bacterial concentration found in clouds sampled at the pdD station, Amato et al., 2007b) based on the $OD_{575\,\mathrm{nm}}$ of the culture. Serial dilutions of the suspension were plated (0.1 mL) on R2A and incubated at 17 °C for Colony Forming Unit (CFU) counts. CFU counts were used to normalize the biodegradation rates and express them in mol

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cell^{-1} s^{-1}.

No chemical modification was observed during the time of incubation in the reference flask (cloud water solution without microorganisms). At defined time steps (every hour from 0 to 8 h and at times zero plus 24, 48, 72 and 120 h), samples were taken for analysis by ion chromatography: cells were pelleted (12 000 × g, 3 min) from 1 mL of the incubation medium, and the supernatants were kept frozen until analysis.

2.3 Photodegradation tests

For photodegradation experiments, artificial cloud water solutions were prepared as indicated in Table 1, supplemented with 20 µM of hydrogen peroxide H_2O_2 (Fluka, 30%), and exposed to controlled lights under agitation. The maximum concentration of H_2O_2 measured in natural cloud water sampled at the puy de Dôme were in the same range (∼ 19 µM) (Marinoni et al., 2011). H_2O_2 was added for generating hydroxyl radicals in the solutions by photolysis reaction ($\lambda < 380$ nm).

Two irradiation setups, characterized by different polychromatic light spectra were used:

The *Photochemical setup 1 (S1)*: Consisted in a light beam generated by a 1000 W Xenon lamp used on the top of a cylindrical reactor equipped by a Pyrex filter (thickness 3.3 mm, wavelength cut-off: 290 nm) containing 500 mL of magnetically stirred solution at 17 °C (by circulating temperature-regulated water through an outer jacket).

The *Photochemical setup 2 (S2)*: Consisted in a box equipped by 12 Philips Actinic BL 15 W fluorescent tubes emitting within the wavelength range 340–420 nm with a maximum emission at 365 nm and placed above the incubation flasks. The incubation flasks were cylindrical Pyrex crystallizer (100 mL) dishes covered with a Pyrex filter and incubated at 17 °C under agitation (110 r.p.m.).

The wavelength-dependent light fluxes reaching the solutions were measured by placing an optical fiber coupled to a spectrograph with a CCD detector (Ocean Optics SD 2000 CCD spectrophotometer) previously calibrated by using a DH-2000-CAL

Deuterium Tungsten Halogen reference lamp inside chemical reactor. Emission spectra of both photochemical setups and the UV-Vis spectra of nitrate and hydrogen peroxide in water solution are displayed in Fig. 1.

Effective degradation of hydrogen peroxide was verified in both setups by fluorimetry assay involving a Horse Radish Peroxydase in 4-Hydroxyphenylacetic acid solution (Lazrus et al., 1985). At defined time points, two aliquots of 1 mL of the solution incubated at 17 °C (no experiment of photochemistry was made at 5 °C due to technical limitations) were taken and kept frozen until ion chromatography analysis.

2.4 Natural cloud water sample collection and conditions of incubation

Cloud water was collected at the puy de Dôme station using a sterilized cloud water sampler (Kruisz et al., 1993). The sampling method was identical to those described in Amato et al. (2005). Briefly, 50 mL of cloud water were collected and kept cold until laboratory investigations that were started within a few hours after sampling. Half of the sample was sterilized by filtration (nylon filter 0.22 µm) and the other half was kept intact (included its endogenous microflora). Filtered and intact cloud samples were then incubated at 12 °C under agitation (200 r.p.m.) during 120 h. Every 24 h, 1 mL was taken out and frozen until ion chromatography analyses.

2.5 Analyses by ion chromatography

Artificial solutions and the natural cloud water samples were analyzed using ion chromatography Dionex DX320 for anions (column AS11, eluent KOH) and Dionex ICS1500 for cations (column CS16, eluent hydroxymethanesulfonate acid). Vials were previously rinsed three times with ultrapure water.

2.6 Calculations of bio- and photodegradation rates

The degradation rates of the compound C (k_c) have been determined by linear regression fits as follows:

- for biodegradation rates: $k_c = (k \times [C]_0)/N_{\text{cells}}$ $(\text{mol cell}^{-1}\,\text{s}^{-1})$ (1)
- for photodegradation rates: $k_c = k \times [C]_0$ $(\text{mol L}^{-1}\,\text{s}^{-1})$ (2)
- for estimated photodegradation rates resulting from the reactivity with free radicals and estimated from data from the literature:

$$k_c = k_{c,\text{radical}} \times [^\bullet\text{OH}] \times [C]_0 \qquad (\text{mol L}^{-1}\,\text{s}^{-1}) \qquad (3)$$

With $[C]_0$ the initial concentration of selected carboxylic acid C (mol L^{-1}), k the pseudo-first order decays (s^{-1}). N_{cells} the concentration of cells participating to the biodegradation and determined by CFU counts (cells L^{-1}), $[^\bullet\text{OH}]$ is the concentration of free radical $^\bullet$OH from literature and $k_{c,\text{radical}}$ $(\text{M}^{-1}\,\text{s}^{-1})$ is the reaction rate between the carboxylic acid C and $^\bullet$OH from the literature.

3 Results

3.1 Biodegradation in artificial cloud media

The artificial cloud water media used in these experiments contained the 4 major carboxylic compounds dominating the soluble organic composition of clouds (acetate, formate, succinate, and oxalate) and 8 major inorganic ions (see composition in Table 1). The inorganic composition differed by higher concentrated chloride and sodium in “marine” than in “continental” medium and inversely for nitrate, ammonium, and sulfate. The continental medium was more acidic (pH ∼ 5) than the marine one (pH ∼ 6.3). The organic compositions in “marine” and in “continental” media were similar to allow comparisons of the biotransformation rates measured and to detect possible effects of the concentration of inorganic ion and of the pH on the metabolic activity of microorganisms.

These media were incubated with a pure microbial culture at 5 °C and 17 °C. The colder temperature (5 °C) corresponds to the mean annual value measured at the puy de Dôme summit, while 17 °C is approximately the maximal temperature observed there when a cloud forms (see http://wwwobs.univ-bpclermont.fr/SO/mesures/pdd.php).

During the incubation period, only the degradation of organic species was observed and no extracellular accumulation of metabolite was detected. The measured rates of biotransformation of each compound by each microbial strain are reported in Table 2. The value "zero" was considered when no degradation was detected and was taken into account in the calculation of the average biodegradation rate presented further. Nine and eight strains out of seventeen were able to degrade carboxylic acids at 17 °C and 5 °C, respectively. Although some of the microorganisms used could have the enzymatic material necessary for transforming oxalate (Sahin, 2003), none was degrading it under our incubation conditions. Biodegradation rates of acetate ranged from 0 to 7×10^{-18} mol cell^{-1} s^{-1} (strain 14b10, "continental" medium) at 17 °C, and from 0 to 2×10^{-18} mol cell^{-1} s^{-1}(strains 14b10 and 23b5, continental) at 5 °C. For formate, they reached 1×10^{-17} mol cell^{-1} s^{-1} (strain 6b4, continental) at 17 °C, and 5×10^{-18} mol cell^{-1} s^{-1} (strain 12b8, marine) at 5 °C. For succinate, biodegradation rates ranged 0 to 1×10^{-18} mol cell^{-1} s^{-1} (strains 3b1 and 13b2, marine) at 17 °C, and from 0 to 3×10^{-19} mol cell^{-1} s^{-1} (strain 13b2, marine) at 5 °C.

Except in a few cases (*Pseudomonas* toward acetate at 5 °C), *Pseudomonas* strains and *Rhodococcus* were active towards all the tested compounds. On the contrary, *Bacillus*, *Arthrobacter*, *Clavibacter*, and *Frigoribacterium* strains were not able to degrade any of those under any of our experimental conditions. One of the three *Sphingomonas* strains tested was able to degrade formate and succinate at 17 °C, but none at 5 °C.

Regarding the influence of the chemical composition on the degradation rates, 5% of the measured biodegradation rates were higher in marine medium than in continental cloud water solution. However, no significant difference of the average rate of biodegradation of a given compound between these two artificial media was observed. Some strains degraded carboxylic acids more efficiently in the marine than in the continental medium, and inversely.

As expected, when detected, activities of biodegradation at 5 °C were lower than at 17 °C by factors ranging from 2.1 to 5.5 (considering the average biodegradation rates). No relationship between the chemical composition of the incubation medium and the temperature dependence of biodegradation activities was detected

3.2 Photodegradation in artificial cloud water media

To compare microbial and photochemical activities on carboxylic acid transformations, irradiation experiments were conducted in the artificial cloud solutions. Preliminary irradiation tests with no supplementation of H_2O_2 showed, as expected, that no direct photochemical degradation of carboxylic acids happened in both photochemical setups.

In the presence of H_2O_2, no intermediate organic photoproduct was detected by ion chromatography analyses. The photodegradation rates of carboxylic acids in "marine" and "continental" media measured at 17 °C in experimental setups S1 and S2 are given in Table 3.

Acetate and succinate were not degraded by photolysis in all experiments. In the experimental setup S1, there was no influence of the incubation medium ("marine" or "continental") on the photodegradation rates of formate and oxalate ($\sim 7 \times 10^{-10}\,\mathrm{M\,s^{-1}}$ and $\sim 3 \times 10^{-10}\,\mathrm{M\,s^{-1}}$ for formate and oxalate, respectively). In S2, the degradation rates of formate and oxalate were higher in continental than in marine medium by about one order of magnitude ($\sim 2 \times 10^{-10}\,\mathrm{M\,s^{-1}}$ and $\sim 2 \times 10^{-11}\,\mathrm{M\,s^{-1}}$ in continental and in marine medium, respectively, for both species). The difference of pH is thought not to influence the production of hydroxyl radical from photolysis of H_2O_2 and nitrates (Mack and Bolton, 1999). We can expect the difference of behaviour observed between continental and marine solutions to be due the relative contribution of nitrate and H_2O_2 to the total concentration of free radicals in S1 and S2 which is directly related to the respective light emission spectra. Nitrate concentration in continental medium was about 3 times higher than in marine medium (70 and 200 µM in marine and in continental medium, respectively). In the setup S1, light emission started at ~ 290 nm (Fig. 1), and the formation of hydroxyl radicals was mainly attributed to the photolysis of H_2O_2. Hence, there was no or very little influence of the concentration of nitrates on the concentration of total free radicals. In the setup S2, light emission started at 340 nm (Fig. 1), and the photolysis of H_2O_2 was lower than in S1. Consequently, the relative contribution of nitrates to the concentration of total free radicals was higher in S2 than in S1, explaining the differences observed between irradiations of "marine" and "continental" cloud solutions.

3.3 Microbial and photochemical contribution to carboxylic acid degradations

Biodegradation rates measured in artificial cloud media were compared with the photodegradation rates resulting from irradiation in S1 and S2. The aim was to evaluate the relative contribution of microbial activity and of photochemical reactivity on the fate of carboxylic acids. We also calculated the photodegradation rates in artificial cloud water for different photochemical scenarios; based on the reaction rates of carboxylic compounds with hydroxyl radical reactivity available in the literature, together with the hydroxyl radical concentration values in cloud water evaluated by cloud chemistry modelling studies. The reaction rate constants were taken from Ervens et al. (2003a) for formate, succinate and oxalate and from Chin and Wine (1994) for acetate. The simulated $^{\bullet}OH$ concentrations from several models are displayed in Table 4. For this calculation we chose to consider low and high extremes $^{\bullet}OH$ concentrations, i.e. 1×10^{-12} and 1×10^{-14} M.

The estimated degradation rates of carboxylic compounds in artificial cloud water by microorganisms and photochemical processes are given in Table 3. The values provided for microbial degradation correspond to the average of the biodegradation rates given in Table 2. Figure 2 shows, for marine and continental cloud media, the relative contribution of biodegradation and of photochemistry to the degradation of acetate, formate, succinate and oxalate. For photochemistry, we considered results from both setups S1 and S2 and the theoretical reactivity of $^{\bullet}$OH radicals at the highest and lowest concentrations extracted from the literature.

Considering the values of photodegradation rates obtained in S1 and S2, only microbial activity participated to the degradation of acetate and succinate, while oxalate was exclusively degraded by photochemical processes. For formate, microbial activity in the marine and continental medium contributes to 14% and 83% of its degradation in S1 and S2, respectively; in the continental medium, microbial contribution to the degradation of formate are equal to 16% and 48%, respectively.

At high $^{\bullet}$OH concentration (i.e. 1×10^{-12} M), in both artificial cloud water solutions, we estimated from literature data for photochemistry that microbial activity would contribute to less than 4% of the degradation of acetate and succinate, and would be negligible (<0.4%) for formate. However, at low OH concentration (i.e. 1×10^{-14} M), microbial degradation of acetate, formate, and succinate would reach 85%, 30%, and 70%, respectively, compared to photochemical activity. Oxalate in all cases would not be degraded by microbial activity.

3.4 Biodegradation in natural cloud water

In the biodegradation results presented above (Sect. 3.1), artificial cloud water media were incubated with 17 strains independently. In this experiment, natural cloud water was used without any chemical modification and in the presence of its own microflora. The cloud water sample was collected on 17 June 2008, during a North-Western flow air mass and the average temperature over the time of sampling was 11 °C. Its chemical composition is given in Table 5; nitrate, sulfate, and ammonium concentrations and pH value show that this cloud event was under continental influence. Carboxylic acids concentrations are usual for such cloud.

Half of the volume of the cloud water sample was sterilized by filtration (0.22 µm porosity) to be considered as the "reference sample" free of microorganisms. The other half was kept intact, so included indigenous microflora, and both subsamples were incubated at 12 °C, very close to the in situ temperature during sampling. During incubation, carboxylic acid concentrations remained constant in the reference sample. In intact cloud water, acetate, formate and succinate were degraded at rates given in Table 6. These rates were very similar to the average biodegradation rates measured in continental artificial cloud water and given in Table 3 (in $10^{-10}\,\mathrm{M\,s^{-1}}$: 1.2 and 0.7 for acetate; 0.9 and 1.4 for formate; 0.3 and 0.2 for succinate, respectively for natural and artificial cloud water), suggesting that the degradation observed in the intact natural cloud water sample was due to biological activity of its indigenous microorganisms (so named "microbial" in Table 6).

Biodegradation rates in natural cloud water were also compared with estimated photodegradation rates resulting from $^{\bullet}$OH reactivity (see Fig. 3) using literature data as previously. At high $^{\bullet}$OH concentration, microbial activity would contribute to up to 9%, 0%, and 2% of the degradation of acetate, formate and succinate, respectively; at low $^{\bullet}$OH concentration, microbial activity would contribute to up to 90%, 8%, and 63% of the degradation of these species.

4 Discussion and conclusion

This paper brings new answers to the emerging scientific question related to the relative contribution of microbial activity vs. photochemistry to atmospheric chemistry. Atmospheric chemistry in the liquid water phase is very complex, and detailed experiments can only be performed in bulk media with simplified situations that allow understanding the mechanisms taking place. One of the main results of this study is the high similarity between the biodegradation rates observed in "artificial" and in "natural" cloud water. To constitute our microcosms of cloud water, a panel of strains representative of the bacteria usually encountered in cloud water was chosen along with typical chemical compositions and cell numbers in natural clouds. Using this very simplified setup, we were able to reproduce the results obtained with a natural cloud sample whose composition is usually much more complex (more diverse organic and inorganic compounds, presence of HUmic Like Substances (HULIS), wider biodiversity ...).

In this work our strategy was to compare different conditions in order to explore different scenarios. We selected marine and continental air-mass types as chemical models for the artificial cloud water media, since they represent most of the clouds sampled at the puy de Dôme station. Among the 57 cloud events sampled between 2001 and 2010 at the puy de Dôme, based on their chemical composition and on their air mass origins, 71% were categorized as "marine" (mainly originating from West), 19% were "continental" (mainly originating from North), 8% were "anthropogenic" (mainly originating from North-east) and 2% were "Saharan" (mainly originating from South) (see for more details the database: http://wwwobs.univ-bpclermont.fr/SO/beam/data.php).

Our investigations on the biodegradation of carboxylic acids in artificial cloud water showed that the reactivity was different depending on the organic compound considered. For instance oxalate was only degraded by radical reactions, while acetate and succinate were better degraded by microorganisms in most cases. In addition, the activity of the investigated microbial strains was more constrained by temperature than by chemical composition ("marine" and "continental"), in the range of concentrations used. This suggests that microbial contribution to atmospheric chemistry would be more important in warm clouds than in high altitude clouds, and that the chemical composition of cloud water itself has very little influence. On the contrary, photodegradation processes are less sensitive to temperature and tend to be higher in "continental" cloud medium, mainly due to differences in nitrate concentration.

For photochemistry experiments, we need to determine the best conditions to reproduce the amount of solar radiation normally found in clouds. Moreover, is has to be decided which is the more realistic $^{\bullet}OH$ concentration to be used in radical chemistry calculations. Actual $^{\bullet}OH$ concentration data available in the literature arise from atmospheric chemistry modelling and not from in situ measurements. However, as shown in Table 4, the concentrations reported in the literature can differ by two orders of magnitude depending on the chemical scenario (marine, remote, or urban) and on the model of cloud chemistry model. So, what should we consider a relevant $^\bullet$OH concentration in cloud water? The discrepancy of the $^\bullet$OH concentration evaluation can be explained by considering how models are conceived. Since the 80's, numerical models were developed (Graedel et al., 1986; Jacob et al., 1989) that allow evaluating concentrations of hydroxyl radicals in the aqueous phase. These cloud chemistry models are based on up-to-date chemical mechanisms that contained explicit chemical processes in the aqueous phase such as the CAPRAM mechanism (Herrmann et al., 2005; Tilgner and Herrmann, 2010). They also considered complex microphysical processes that redistribute chemical species among the various phases of the cloud (Leriche et al., 2001; Wolke et al., 2005). Simulated $^\bullet$OH concentrations are dependant on the chemical scheme that is considered in the model and also on the cloud microphysical properties that control the mass transfer between the liquid and gas phases. In this work we have exemplified the consequence of considering the two extreme values ($[^\bullet\mathrm{OH}] = 1 \times 10^{-12}$ and 1×10^{-14} M, see Table 4). Results showed that at low $^\bullet$OH concentration, the microbial activity is of major relative importance, while it is not at high radical concentration. The day/night succession that was emphasized previously in Vaïtilingom et al. (2010) must then be taken into account. In addition to $^\bullet$OH, $NO_3^\bullet$ also participates to the oxidation processes in the atmosphere. Hydroxyl radicals are generated by photochemical pathways and are mostly present during the day, while in comparison, the role of nitrate radicals is prevalent during the night (Finlayson-Pitts and Pitts, 1997). This work and the one from Vaïtilingom et al. (2010) showed that microbial activity could be much more important than $NO_3^\bullet$ reactivity on the carboxylic acid degradation and that it could be considered as a relevant sink for organic compounds during the night. Hence, microorganisms can represent a significant actor of the reactivity of the atmosphere in its whole.

In conclusion, the hypothesis that biological activity would compete with radical reactivity in the chemistry of carboxylic compounds is the most likely scenario when considering night and day scenarios. To our opinion, future work should focus on the investigation of natural clouds of various chemical compositions, and include more parameters as descriptors of the processes going on in the reactivity of these environments, looking at both photo and biodegradation phenomena. In particular the evolution of microbial population and oxidants concentration such as H_2O_2 during the incubation period seem to be relevant parameters to consider. Finally, the biological activity data experimentally determined should be used to parameterize cloud chemistry models integrating both chemical and biological components.

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Table 1. Chemical composition of the artificial cloud water media used for photodegradation experiments, and range of values observed in natural cloud water collected at the puy de Dôme station. For technical reasons, the artificial cloud water media prepared for biodegradation experiments were similar but 10 times more concentrated than indicated here. Photodegradation experiments were carried out using the concentrations indicated in the table.

	Artificial cloud water media		Natural cloud water[a]	
	Marine	Continental	Min	Max
Compounds	Concentration (µM)			
Acetate	20	20	0.6	48.7
Formate	15	15	0.8	71.4
Succinate	1.5	1.5	0.1	4.1
Oxalate	3	3	0.1	17.4
Cl^-	320	250	0.5	1948.9
NO_3^-	70	200	3.4	766.8
SO_4^{2-}	35	50	1.9	369.5
Na^+	310	250	0.4	281.0
NH_4^+	70	200	6.3	1801.7
K^+	10	10	0.1	124.1
Mg^{2+}	10	10	0.2	45.6
Ca^{2+}	40	40	0.3	74.8
pH	6–6.5	4.7–5.2	3.9	7.6

[a] from the OPGC database on cloud chemical composition at the puy de Dôme station: http://wwwobs.univ-bpclermont.fr/SO/beam/data.php.

Table 2. Measured rates of biodegradation of carboxylic acids by pure strains at 5 and 17 °C.

		Marine			Continental		
		Rates of biodegradation (mol cell^{-1} s^{-1})					
		Acetate	Formate	Succinate	Acetate	Formate	Succinate
	17 °C						
3b-10	*Sphingomonas* sp.	0	0	0	0	0	0
14b-5	*Sphingomonas* sp.	0	2×10^{-19}	2×10^{-19}	0	2×10^{-19}	3×10^{-19}
14b-6	*Sphingomonas* sp.	0	0	0	0	0	0
6b-4	*Pseudomonas* sp.	7×10^{-19}	1×10^{-18}	1×10^{-19}	5×10^{-19}	1×10^{-17}	6×10^{-19}
14b-10	*Pseudomonas* sp.	2×10^{-18}	2×10^{-18}	2×10^{-19}	7×10^{-18}	7×10^{-18}	3×10^{-19}
3b-1	*Pseudomonas syringae*	1×10^{-18}	2×10^{-18}	1×10^{-18}	5×10^{-19}	1×10^{-18}	4×10^{-19}
12b-8	*Pseudomonas syringae*	6×10^{-19}	8×10^{-18}	4×10^{-20}	2×10^{-18}	2×10^{-18}	5×10^{-19}
13b-2	*Pseudomonas syringae*	1×10^{-18}	3×10^{-18}	1×10^{-18}	4×10^{-19}	2×10^{-18}	6×10^{-19}
13b-3	*Pseudomonas graminis*	4×10^{-19}	5×10^{-18}	5×10^{-19}	5×10^{-19}	4×10^{-18}	4×10^{-19}
14b-14	*Pseudomonas viridiflava*	9×10^{-19}	2×10^{-18}	6×10^{-19}	9×10^{-20}	7×10^{-19}	1×10^{-19}
16b-1	*Bacillus* sp.	0	0	0	0	0	0
5b-1	*Bacillus pumilus*	0	0	0	0	0	0
3b-7	*Arthrobacter rhombi*	0	0	0	0	0	0
14b-13	*Clavibacter michiganensis*	0	0	0	0	0	0
30b-1	*Frigoribacterium* sp.	0	0	0	0	0	0
14b-13	*Frigoribacterium* sp.	0	0	0	0	0	0
23b-5	*Rhodococcus* sp.	5×10^{-18}	8×10^{-19}	5×10^{-20}	4×10^{-18}	1×10^{-18}	7×10^{-20}
Microbial average rate		7×10^{-19}	1×10^{-18}	2×10^{-19}	8×10^{-19}	2×10^{-18}	2×10^{-19}
	5 °C						
3b-10	*Sphingomonas* sp.	0	0	0	0	0	0
14b-5	*Sphingomonas* sp.	0	0	0	0	0	0
14b-6	*Sphingomonas* sp.	0	0	0	0	0	0
6b-4	*Pseudomonas* sp.	5×10^{-19}	6×10^{-19}	3×10^{-20}	2×10^{-19}	2×10^{-18}	1×10^{-19}
14b-10	*Pseudomonas* sp.	7×10^{-19}	1×10^{-18}	9×10^{-21}	2×10^{-18}	3×10^{-18}	8×10^{-21}
3b-1	*Pseudomonas syringae*	0	4×10^{-19}	2×10^{-19}	0	2×10^{-19}	4×10^{-20}
12b-8	*Pseudomonas syringae*	2×10^{-19}	5×10^{-18}	3×10^{-20}	2×10^{-19}	9×10^{-19}	1×10^{-19}
13b-2	*Pseudomonas syringae*	0	1×10^{-18}	3×10^{-19}	0	6×10^{-19}	2×10^{-19}
13b-3	*Pseudomonas graminis*	1×10^{-19}	1×10^{-18}	1×10^{-19}	5×10^{-20}	7×10^{-19}	7×10^{-20}
14b-14	*Pseudomonas viridiflava*	0	6×10^{-19}	7×10^{-20}	0	9×10^{-20}	1×10^{-20}
16b-1	*Bacillus* sp.	0	0	0	0	0	0
5b-1	*Bacillus pumilus*	0	0	0	0	0	0
3b-7	*Arthrobacter rhombi*	0	0	0	0	0	0
25b-3	*Clavibacter michiganensis*	0	0	0	0	0	0
14b-13	*Frigoribacterium* sp.	0	0	0	0	0	0
30b-1	*Frigoribacterium* sp.	0	0	0	0	0	0
23b-5	*Rhodococcus* sp.	1×10^{-18}	4×10^{-19}	4×10^{-20}	2×10^{-18}	8×10^{-19}	4×10^{-20}
Microbial average rate		2×10^{-19}	6×10^{-19}	5×10^{-20}	2×10^{-19}	4×10^{-19}	4×10^{-20}

Global experimental uncertainties are evaluated from 30 to 35%.

Table 3. Estimated rates of photo and biodegradation in artificial cloud water at 17 °C.

	17 °C	Rates in artificial cloud water ($M\,s^{-1}$)			
Medium/compounds		Acetate	Formate	Succinate	Oxalate
Marine	S1	0	$7.1(\pm2.2)\times10^{-10}$	0	$2.7(\pm1.2)\times10^{-10}$
	S2	0	$2.4(\pm0.1)\times10^{-11}$	0	$2.2(\pm0.4)\times10^{-11}$
	Microbial*	5.3×10^{-11}	1.1×10^{-11}	1.9×10^{-11}	0
Continental	S1	0	$7.4(\pm2.5)\times10^{-10}$	0	$3.4(\pm0.9)\times10^{-10}$
	S2	0	$1.5(\pm0.8)\times10^{-10}$	0	$1.9(\pm0.9)\times10^{-10}$
	Microbial*	6.7×10^{-11}	1.4×10^{-10}	1.5×10^{-11}	0
Marine and continental	$^{\bullet}OH$ (1×10^{-12} M)	1.2×10^{-9}[a]	3.2×10^{-8}[b]	6.6×10^{-10}[b]	3.2×10^{-10}[b]
	$^{\bullet}OH$ (1×10^{-14} M)	1.2×10^{-11}[a]	3.2×10^{-10}[b]	6.6×10^{-12}[b]	3.2×10^{-12}[b]

Photodegration rates (± absolute uncertainties for 3 replicates)

* Cellular concentration is equal to 8×10^{7} cells L^{-1} (mean value observed in natural cloud water sampled at the puy de Dôme station, Amato et al., 2007b)

[a] Chin and Wine, 1994; [b] Ervens et al., 2003a.

Table 4. Maximal aqueous $^\bullet$OH concentrations simulated by various multiphase cloud chemistry models. These models consider different explicit chemical mechanism and simulate clouds with different microphysical properties (monodisperse to polydisperse).

Chemical mechanisms	Cloud simulation	Chemical scenario	Simulated $^\bullet$OH concentration (max) (M)	References
Aqueous: Chemistry of some inorganic and organic compounds	Permanent Monodisperse	Polluted cloud	2×10^{-13}	Graedel et al. (1986)
Gas phase: Lurmann et al. (1986) *Aqueous* : Chemistry of some inorganic and organic compounds	Permanent Polydisperse	Polluted cloud	1.6×10^{-14}	Jacob et al. (1989)
Gas phase: RACM *Aqueous*: CAPRAM 3.0 Chemistry of inorganic and organic compounds (up to 5 carbon atoms)	Permanent Monodisperse	Remote Urban Marine	2×10^{-13} 1×10^{-13} 4.5×10^{-13}	Ervens et al. (2003b)
	Permanent Polydisperse	Remote	1.4×10^{-13}	Herrmann et al. (2005)
	Non-permanent Polydisperse	Remote Urban	5×10^{-14} 1×10^{-14}	Tilgner and Herrmann (2010)
Gas: Madronich and Calvert (1990) *Aqueous*: Chemistry of inorganic and organic compounds (up to 2 carbon atoms)	Permanent Monodisperse	Polluted cloud	2×10^{-14}	Leriche et al. (2001)
	Permanent Monodisperse	Remote Urban	1.7×10^{-12} 1×10^{-12}	Deguillaume et al. (2004)
	Non-permanent Polydisperse	Polluted cloud	7×10^{-14}	Leriche et al. (2007)
	Permanent Monodisperse	Remote	3.5×10^{-13}	Deguillaume et al. (2010)

Table 5. Ionic composition and pH of the natural cloud water sampled at the puy de Dôme station.

Compounds	Concentrations (µM)
Acetate	24.3
Formate	48.1
Succinate	4.7
Oxalate	9.8
Cl^-	60.4
NO_3^-	192.1
SO_4^{2-}	78.2
Na^+	46.4
NH_4^+	287.6
K^+	11.7
Mg^{2+}	31.3
Ca^{2+}	45.9
pH	5.1

Table 6. Comparison between biodegradation rates in the natural cloud water at 12 °C measured in this work and theoretical degradation rates for extreme $^{\bullet}$OH concentrations.

12 °C	Degradation rates ($M\,s^{-1}$) Acetate	 Formate	 Succinate	 Oxalate
Microbial activity* (Natural cloud water)	$1.2(\pm 0.4) \times 10^{-10}$	$9.1(\pm 1.9) \times 10^{-11}$	$3.3(\pm 0.9) \times 10^{-11}$	0
$^{\bullet}$OH (1×10^{-12} M)	1.3×10^{-9} [a]	9.8×10^{-8} [b]	1.9×10^{-9} [b]	8.0×10^{-10} [b]
$^{\bullet}$OH (1×10^{-14} M)	1.3×10^{-11} [a]	9.8×10^{-10} [b]	1.9×10^{-11} [b]	8.0×10^{-12} [b]

Biodegration rates (±measurement uncertainties).

* No variation of concentrations over time was detected in filter-sterilized natural cloud water taken as reference sample.

[a] Chin and Wine, 1994; [b] Ervens et al., 2003a.

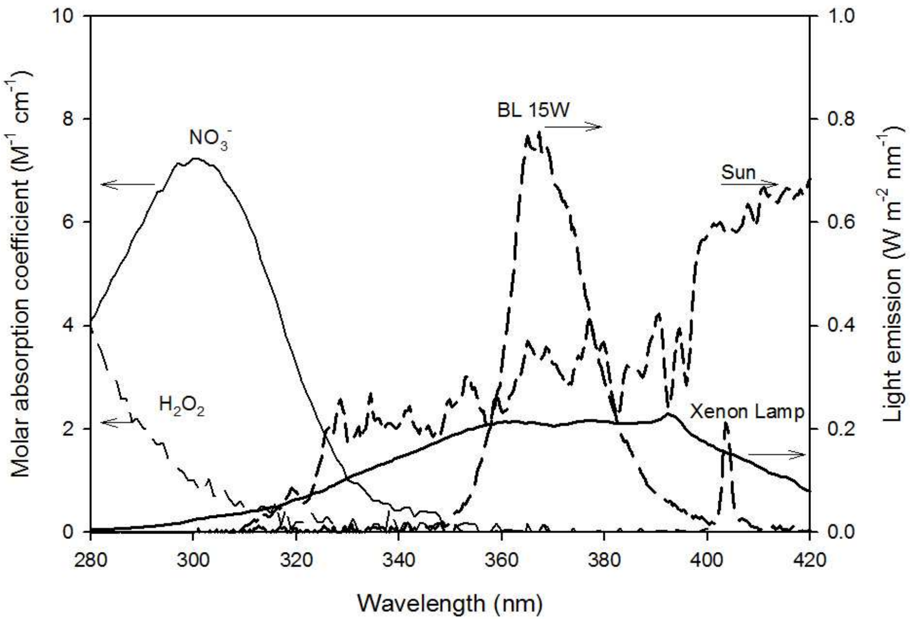

Fig. 1. Emission spectra of the 1000 W xenon lamp (S1), of the Philips Actinic BL 15 W lamps (S2), of the sun at Earth's surface and molar absorption coefficients of nitrate and H_2O_2 aqueous solutions.

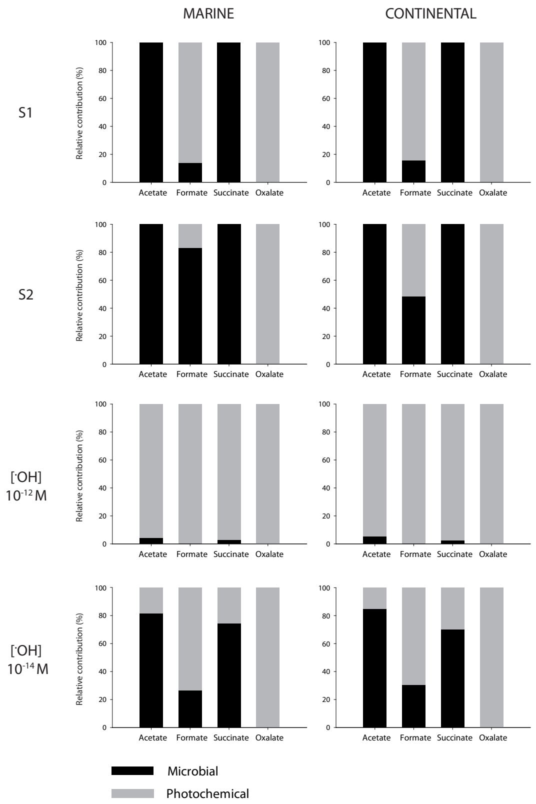

Fig. 2. Microbial and photochemical relative contributions to the degradation of carboxylic compound in "marine" (left side) and "continental" (right side) artificial cloud water. S1 and S2 correspond to the 2 irradiation setups. [$^\bullet$OH] 10^{-12} M and [$^\bullet$OH] 10^{-14} M are calculations based on data in the literature: simulated standard $^\bullet$OH concentrations in cloud water (10^{-12} and 10^{-14} M, respectively) and reaction rates with the respective acids (see Tables 3 and 4 for the references).

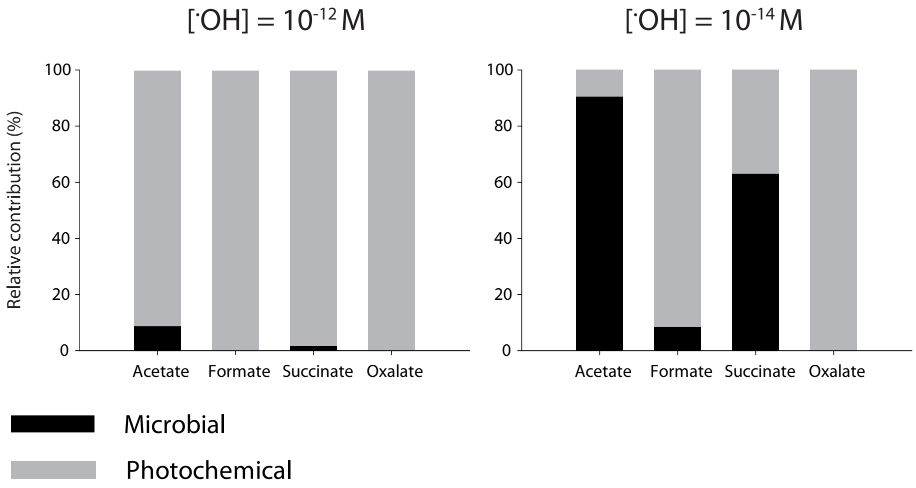

Fig. 3. Relative contribution of microbial activity (measured) and of photochemical reactivity (estimated from literature) to the degradation of carboxylic acids in natural cloud water at 12 °C. These calculations are based on the rates of degradation measured in unfiltered natural cloud water, taking filtered subsample as an abiotic reference.