



# First evaluation of the effect of microorganisms on steady state hydroxyl radical concentrations in atmospheric waters

A. Lallement<sup>a</sup>, V. Vinatier<sup>a</sup>, M. Brigante<sup>a</sup>, L. Deguillaume<sup>b</sup>, A.M. Delort<sup>a, \*\*</sup>, G. Mailhot<sup>a, \*</sup>

<sup>a</sup> Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, 63000, Clermont-Ferrand, France

<sup>b</sup> Université Clermont Auvergne, CNRS, Laboratoire de Météorologie Physique, 63000, Clermont-Ferrand, France

## HIGHLIGHTS

- New method is proposed for the determination of hydroxyl radical concentration present in atmospheric natural waters.
- It allows to evaluate steady state OH radical concentrations at very low concentrations ( $10^{-17}$  M) and is biocompatible.
- Steady state concentration of hydroxyl radicals are determined in 5 different samples of cloud and rain waters.
- Mean value in cloud water of  $7.2 \pm 5.0 \times 10^{-16}$  M are more than four times higher than in rain water  $1.6 \pm 1.5 \times 10^{-16}$  M.
- The evaluated values are much lower than most of the values estimated by cloud chemistry models.

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## ABSTRACT

Clouds are complex multiphase media where efficient chemical reactions take place and where microorganisms have been found to be metabolically active. Hydroxyl radical is the main oxidant in cloud water, and more generally in the atmosphere, during the day and drives the cloud oxidative capacity. However, only one measurement of the steady state hydroxyl radical concentrations in cloud water has been reported so far. Cloud chemistry models are used to estimate the hydroxyl radical concentrations with values ranging from  $10^{-12}$  to  $10^{-15}$  M that are surely overestimated due to a lack of knowledge about the speciation of the organic matter acting as a sink for hydroxyl radicals. The aim of this work is to quantify the concentration of hydroxyl radicals at steady state in rain and cloud waters and to measure the impact of native microflora on this concentration. First, the non-toxicity of terephthalic acid as probe is controlled before the analysis in real atmospheric water samples. Higher concentrations of hydroxyl radicals are found in cloud waters than in rain waters, with a mean value " $1.6 \pm 1.5 \times 10^{-16}$  M and " $7.2 \pm 5.0 \times 10^{-16}$  M for rain and cloud waters respectively and no real impact of microorganisms was observed. This method allows the measurement of steady state hydroxyl radical levels at very low concentrations (down to  $10^{-17}$  M) and it is biocompatible, fast and easy to handle. It is a useful tool, complementary to other methods, to give a better overview of atmospheric water oxidant capacity.

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## 1. Introduction

Clouds are multiphase systems where many chemical reactions occur, particularly in droplets (Faust, 1994; Herrmann et al., 2015; Lelieveld and Crutzen, 1991). Very efficient photochemical processes take place inside droplets and chemical reactions within clouds can be faster than the equivalent reactions in the gas phase.

The aqueous phase chemistry leads to oxidation processes that can be driven by reactions with radicals. Among the radicals, hydroxyl radical is the most efficient oxidant in the atmosphere (Lelieveld et al., 2004). Several works were carried out on hydroxyl radical chemistry in cloud to define OH sources and reactivity (Blough and Zepp, 1995; Chameides and Davis, 1982; Jacob, 1986; Mauldin et al., 1997). Main sources of hydroxyl radical are i) hydrogen peroxide, nitrite and nitrate photolysis (Yu and Barker, 2003; Zafriou and Bonneau, 1987; Zellner et al., 1990; Zepp et al., 1987), ii) iron via ligand-to-metal charge-transfer reactions or photo-Fenton chemistry (Deguillaume et al., 2004, 2005; Faust and Hoigné, 1990; Faust and Zepp, 1993; Nakatani et al., 2007; Weschler et al., 1986),

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [A-marie.Delort@uca.fr](mailto:A-marie.Delort@uca.fr) (A.M. Delort), [gilles.mailhot@uca.fr](mailto:gilles.mailhot@uca.fr) (G. Mailhot).

iii) the reaction of ozone towards the superoxide radicals and iv) the mass transfer of  $\text{OH}$  from the gas phase to the aqueous phase (Arakaki and Faust, 1998; Faust and Allen, 1993). In terms of  $\text{OH}$  sinks, the main way is the reactivity with dissolved organic matter (Arakaki et al., 2013). However, due to the complexity of this environmental matrix, the organic composition is poorly characterized (Herckes et al., 2013); for example, only 21% of the organic matter in cloud waters sampled at the puy de Dôme station is characterized (Bianco et al., 2016). Furthermore, microorganisms are also present and metabolically active in cloud water. They can survive in spite of numerous stress factors like osmotic shocks, temperature changes and freeze-thaw cycles (Amato et al., 2007a; Joly et al., 2015). In order to survive, they use organic matter as a source of carbon such as short chain aldehydes and carboxylic acids (Amato et al., 2007b; Ariya et al., 2002; Vaitilingom et al., 2011) but they also have an effect on the oxygenated compounds. As aerobic cells, they are able to consume or either neutralize Reactive Oxygen Species (ROS) like hydroxyl radical, singlet oxygen and hydrogen peroxide. Cloud microorganisms, present in cloud water, have the capacity to degrade hydrogen peroxide and can contribute to the degradation of organic compounds during the day and even more during the night (Vaitilingom et al., 2010, 2013).

Up to now, the hydroxyl radical concentrations have been estimated using cloud chemistry models. These models consider multiphase chemistry and the mass transfer from the gas to the aqueous phase. Simulated concentrations range from  $10^{-12}$  to  $10^{-15}$  M (Deguillaume et al., 2004, 2005, Herrmann et al., 2000, 2010; Mouchel-Vallon et al., 2017; Tilgner and Herrmann, 2010; Tilgner et al., 2013) depending on the chemical scenarios and on the complexity of the chemical mechanisms. For example, the amounts of organic matter and iron are key parameters that drive the level of  $\text{OH}$ . Moreover, formation rates of hydroxyl radical in irradiated rain or cloud waters are measured in the laboratory (Faust and Allen, 1993; Nakatani et al., 2007) and are used to evaluate cloud chemistry models (Bianco et al., 2015); they express the maximum of  $\text{OH}$  concentration formed without taking into account the different scavengers present in cloud water. The steady state hydroxyl radical concentrations have been estimated in different surface waters (Arakaki et al., 1999; Brezonik and Fulkerson-Brekken, 1998; Haag and Hoigné, 1985; al Housari et al., 2010; Mill et al., 1980; Qian et al., 2001; Russi et al., 1982; Zepp et al., 1987; Zhou and Mopper, 1990) but, to our knowledge, the study of Anastasio and McGregor (2001) is the only one on cloud water. In their experiments, they used benzene and benzoic acid as chemical probes at concentrations ranging from 50 to 1500  $\mu\text{M}$  and analyzed reaction products by HPLC. Because the most concentrated species in cloud water are in the  $\mu\text{M}$  range, addition of a probe in high concentration can impact the biological activity which is controlled by the environment (Metallo and Vander Heiden, 2013; Shingler, 2003; Tropel and van der Meer, 2004). Toxicity issues could also arise. Existing methods must then be adapted to study the impact of microorganisms. Moreover to take biological variability into account several experiments must be performed in parallel with strictly identical conditions.

The main goal of our study is to evaluate the stationary concentration of  $\text{OH}$  radicals in atmospheric waters and the potential impact of microorganisms on this concentration. For that purpose we had to develop a specific method which main characteristics are i) to take into account the native microorganisms, and their viability, ii) the use of small volume of sample (300  $\mu\text{L}$ /well) for one measurement so 6 mL for a complete analysis, and iii) the direct and fast measurement by fluorescence, without chromatography techniques.

## 2. Experimental section

### 2.1. Chemicals

Terephthalic acid (TA) (Sigma Aldrich) and 2-hydroxyterephthalic acid (TAOH) (Atlantic Research Chemical), with a purity of 98 and 97% respectively, are used without additional purification. Acetic acid and  $\text{H}_2\text{SO}_4$  are from Acros Organic. Formic acid, oxalic acid, succinic acid,  $\text{K}_2\text{SO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NO}_3\text{NH}_4$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , ferrozine and hydrogen peroxide (30% in water, not stabilized) are from Fluka.  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaCl}$ , horse radish peroxidase, Tris-EDTA buffer solution, dimethylsulfoxide (DMSO),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and ethylenediamine- $\text{N,N}'$ -disuccinic acid (EDDS) are from Sigma Aldrich.  $\text{NaOH}$  is from Merck and 4-hydroxyphenylacetic acid is from Alfa Aesar®.

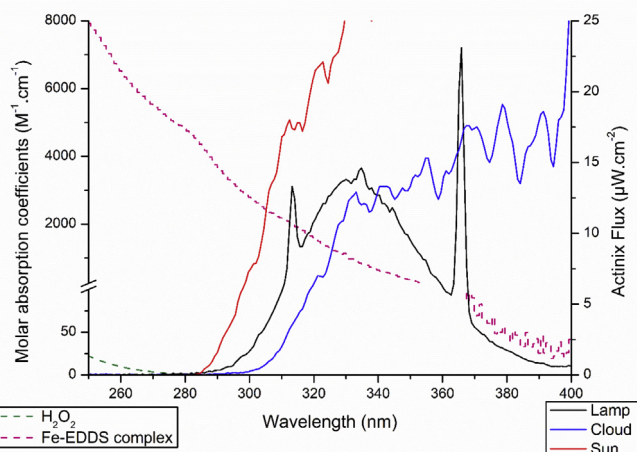
### 2.2. Irradiation setup

Lamps used for the irradiation setup are tropical terrarium bulb call Reptile UVB (13 W) from Exo Terra®. The polychromatic emission spectrum of the irradiation system reaching the solution is recorded using an optical fiber with a charge coupled device (CCD) spectrophotometer (Ocean Optics USD, 2000 + UV-vis) which is calibrated using a DH-2000-CAL Deuterium Tungsten Halogen reference lamp. The total irradiance in the UV region of solar spectrum (290 and 400 nm) reaching the solution is then estimated to be  $915 \mu\text{W cm}^{-2}$ .

In Fig. 1, the lamp emission is compared with the solar spectrum measured at the puy de Dôme station under cloudy or clear sky conditions.

### 2.3. Sampling and analysis of natural atmospheric waters (cloud and rain)

Rain samples were collected in September 17th, October 28th and December 2nd, 2015 and on February 17th and September



**Fig. 1.** Comparison of actinic fluxes of the lamp used in the present work together with the ones measured under natural conditions during cloudy and sunny situations at the puy de Dôme station (Solar emission in cloudy condition was measured in October 16th, 2013 and in sunny condition in September 23th, 2013). Black line represents the lamp actinic flux, blue line is the actinic flux measured under cloudy condition and red line is the actinic flux measured under sunny condition. Dotted lines represent molar absorption coefficient ( $\text{M}^{-1} \text{cm}^{-1}$ ) for Fe-EDDS complex (pink) and for  $\text{H}_2\text{O}_2$  (green). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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