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# Tryptophan and tryptophan-like substances in cloud water: Occurrence and photochemical fate

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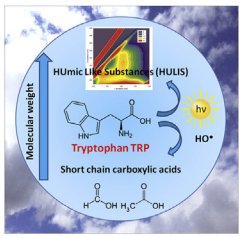
## HIGHLIGHTS

- Tryptophan and tryptophan-like substances were quantified in cloud water sampled at the puy de Dôme station.
- The fate of tryptophan was investigated in the cloud aqueous phase under sun-simulated conditions.
- The hydroxyl radical-mediated transformation of tryptophan in cloud water can be considered to be a source of carboxylic compounds.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This work investigates the occurrence and photochemical behaviour of tryptophan (TRP) in the cloud aqueous phase. The concentrations of tryptophan, TRYptophan LIke Substances (TRYLIS) and HUmic LIke Substances (HULIS) in real cloud water, collected between October 2013 and November 2014 at the top of the puy de Dôme station, were determined using the Excitation-Emission-Matrix (EEM) technique. The amount of free and complexed tryptophan (TRP) up to $10^{-7}$ M in cloud aqueous phase was quantified by HPLC-UV-fluorescence analysis, and its photoreactivity under sun-simulated conditions was investigated in synthetic water samples mimicking cloud aqueous phase compositions (oceanic and continental origins). TRP undergoes direct photolysis, and its degradation is enhanced in the presence of naturally occurring species able to photo-generate hydroxyl radicals (HO•). The polychromatic quantum yield of TRP ($\varphi^{TRP}_{290-340nm}$) is estimated to be $8.37 \times 10^{-4}$ between 290 and 340 nm, corresponding to the degradation rate ($R^{d}_{TRP}$) of $1.29 \times 10^{-11}$ M $s^{-1}$ under our irradiation conditions. The degradation is accelerated up to $3.65 \times 10^{-10}$ and $8.26 \times 10^{-10}$ M $s^{-1}$ in synthetic oceanic and continental cloud water samples doped with 100 μM hydrogen peroxide, respectively.

Hydroxyl radical-mediated transformation leads to the generation of different functionalized and oxidized products, as well as small carboxylic acids, such as formate and acetate. Moreover, fluorescent signals of irradiated solutions indicate the formation of HULIS.



## 1. Introduction

In the atmosphere, Primary Biological Aerosols (PBA) are

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ubiquitous and are comprised of either biological particles, including dead or live cells, or cell fragments (Deguillaume et al., 2008; Després et al., 2012; Zhu et al., 2015). They are able to nucleate cloud droplets and ice particles *via* physical processes (Möhler et al., 2007; Morris et al., 2014; Spracklen and Heald, 2014). PBA are mainly made up of organic substances and contribute to aerosol masses (organic carbon fraction, OC), and the organic fraction resulting from PBA components is made of biological compounds such as proteins and/or amino acids. These amino compounds were found to account for a significant fraction of fine particulate matter (Ge et al., 2011). For example, Zhang et al. (2002) showed that amino acids can represent between 1.6 and 14% of the $PM_{2.5}$ mass at Davis in California. Several sources can be responsible for the atmospheric amino acid content; over a continental area, the biological compounds are produced by plants, pollen, algae, fungi and bacteria spores (Mace et al., 2003a; Milne and Zika, 1993; Scheller, 2001; Zhang and Anastasio, 2003). Human activities can also lead to the input of amino acids into the atmosphere. Zhang and Anastasio (2003) identified livestock farming as the most important source of amino acids over the Californian region. These compounds are also present on anthropogenic coarse particles; soil and desert dust are also probably important sources of amino acids (Mace et al., 2003b). Moreover, marine emissions can also influence the atmospheric concentrations of amino acids (Matsumoto and Uematsu, 2005), as confirmed by Wedyan and Preston (2008) over the southern Atlantic Ocean. Finally, amino acids can be ejected into the atmosphere by volcanoes (Scalabrin et al., 2012) or by biomass burning (Chan et al., 2005; Mace et al., 2003a).

Amino acids can influence the microstructure of aerosol particles and consequently their water uptake, thus modifying cloud formation (Hock et al., 2008; McFiggans et al., 2006; Schwier et al., 2013). They can also act as ice-forming nuclei due to their hygroscopicity (Wedyan and Preston, 2008), leading to the formation of new particles in the atmosphere (De Haan et al., 2009).

These compounds belong to the Water-Soluble Organic Compounds (WSOC) and consequently dissolve into the atmospheric aqueous phase. Several studies have reported concentrations of amino acids in the condensed phase of aerosols (Barbaro et al., 2015; Mandalakis et al., 2011; Mochizuki et al., 2015; Zhang and Anastasio, 2003) as well as in rainwater and fog (Zhang and Anastasio, 2001). For example, the total amino acids have been evaluated to account for 13% of the Dissolved Organic Carbon (DOC) in fog waters and approximately 10% of the WSOC in $PM_{2.5}$ (Zhang and Anastasio, 2003). Amino acids should also be present in cloud water and could contribute to the dissolved organic content of cloud water that is currently still not well characterized (Herckes et al., 2013; Herrmann et al., 2015).

In atmospheric water and aerosols, amino acids have been classified into the following different categories: DFAA (Dissolved Free Amino Acids), which indicates the free amino acids, and DCAA (Dissolved Combined Amino Acids), which indicates peptides, proteins and free amino acids that are also constituents of humic and fulvic acids (Kuznetsova et al., 2005). Another classification distinguishes between FAC (Free Amino Compounds), which are comprised of amino acids and alkyl amines, and CAC (Combined Amino Compounds) if they are free or combined in proteins, peptides or HULIS substances (Zhang and Anastasio, 2003).

Amino acids, and more particularly TRP, present in atmospheric water can directly absorb sun radiation or react with oxidants leading to the formation of inorganic and organic products (Creed, 1984; McGregor and Anastasio, 2001; Milne and Zika, 1993; Suzuki et al., 1985; Zhang and Anastasio, 2003). Their reactivity can therefore modify the chemical composition of dissolved organic matter changing the chemical properties of water droplets and thus of aerosol particles.

Currently, scarce data are present in the literature on the occurrence and fate of amino acids or amino compounds in atmospheric water. To our knowledge, only Muller et al. (2008) have previously reported the presence of TRYptophan LIke Substances (TRYLIS) in rainwater. In our work, we quantified the TRP concentration and detected the presence of TRYLIS and HUmic-LIke-Substances (HULIS) in cloud water samples collected at the puy de Dôme mountain station (France). To assess the possible impact on the aqueous organic chemical composition, TRP solutions are irradiated under sun-simulated conditions and transformation products are characterized. Oxidation processes occur and lead to the formation of carboxylic acids, as well as HULIS, which are followed during our experiments.

## 2. Materials and methods

### 2.1. Sampling method

A total of 23 cloud samples were collected during two field campaigns in October and November 2013 and in March and April 2014 at the top of puy de Dôme mountain (1465 m a.s.l.) in France that belongs to the GAW (Global Atmosphere Watch) stations network. Cloud samples are spread among the following three classes: marine, highly marine and continental following the statistical analysis from Deguillaume et al. (2014).

The cloud droplet sampling was carried out by a one stage cloud droplet impactor. The sampling times ranged from 120 to 180 min depending on the Liquid Water Content (LWC), which was in the range of 0.1–0.2 g $cm^{-3}$.

### 2.2. Chemical analysis

In order to characterize the main physicochemical properties of the sampled solution, the following physico-chemical measurements are performed immediately after cloud sampling and filtration: conductivity, redox potential, pH, UV–visible spectrum, and Excitation Emission Matrix (EEM) are carried out in less than one hour, while ion chromatography, quantification of the nitrite concentration and determination of the Total Organic Carbon (TOC) were performed on frozen samples. Analyses on frozen samples (kept at 255 K) are carried out in less than 48 h after sampling. The results of the physico-chemical analysis are reported in Bianco et al. (2015).

### 2.3. Irradiation experiments

One hundred millilitre aliquots of TRP solutions are irradiated in a photoreactor placed in a cylindrical stainless steel container. Six fluorescent lamps (Philips TL D15W/05), whose emission spectrum ranges from 290 to 500 nm, are separately placed along three different axes, while the photoreactor, a Pyrex tube with a 2.6 cm internal diameter, is placed in the centre of the setup. All of the experiments are carried out at 278 ± 2 K. An aliquot of the solution (3 mL) is withdrawn from the reactor and used for analysis at fixed times. In Fig. 1, the emission spectrum of the lamp recorded using fibre optics coupled with a CCD spectrophotometer (Ocean Optics USD 2000+UV–VIS) is reported. The energy has been normalized to the actinometry results using paranitroanisole (PNA)/pyridine actinometer (Dulin and Mill, 1982). Over the UV region (wavelength range 290–400 nm), a total flux of 15.8 W $m^{-2}$ is measured. The adopted intensity was close to the intensity measured between 290 and 400 nm at the top of puy de Dôme mountain during a late-autumn cloudy day at 11:00a.m. (see Fig. 1). Moreover, the absorption spectrum of TRP in water at a pH of 6.0 is reported in Fig. 1, showing an overlap with the emission spectrum of the irradiation