



Light absorption and the photoformation of hydroxyl radical and singlet oxygen in fog waters



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HIGHLIGHTS

- Dissolved organic carbon (DOC) and light absorption are well correlated.
- DOC mass absorption coefficients (MAC) are large and extend into visible region.
- NO_2^- and NO_3^- photolysis are main sources of $\bullet\text{OH}$; organics are main sinks.
- Compared to $\bullet\text{OH}$, $^1\text{O}_2^*$ levels are 100 times higher but reactivity is lower.
- Compared to past fog, current samples have less DOC and $\bullet\text{OH}$ but similar MAC, $^1\text{O}_2^*$.

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ABSTRACT

The atmospheric aqueous-phase is a rich medium for chemical transformations of organic compounds, in part via photooxidants generated within the drops. Here we measure light absorption, photoformation rates and steady-state concentrations of two photooxidants – hydroxyl radical ($\bullet\text{OH}$) and singlet molecular oxygen ($^1\text{O}_2^*$) – in 8 illuminated fog waters from Davis, California and Baton Rouge, Louisiana. Mass absorption coefficients for dissolved organic compounds (MAC_{DOC}) in the samples are large, with typical values of 10,000–15,000 $\text{cm}^2 \text{g}^{-1}$ at 300 nm, and absorption extends to wavelengths as long as 450–600 nm. While nitrite and nitrate together account for an average of only 1% of light absorption, they account for an average of 70% of $\bullet\text{OH}$ photoproduction. Mean $\bullet\text{OH}$ photoproduction rates in fogs at the two locations are very similar, with an overall mean of $1.2 (\pm 0.7) \mu\text{M h}^{-1}$ under Davis winter sunlight. The mean ($\pm 1\sigma$) lifetime of $\bullet\text{OH}$ is $1.6 (\pm 0.6) \mu\text{s}$, likely controlled by dissolved organic compounds. Including calculated gas-to-drop partitioning of $\bullet\text{OH}$, the average aqueous concentration of $\bullet\text{OH}$ is approximately $2 \times 10^{-15} \text{ M}$ (midday during Davis winter), with aqueous reactions providing approximately one-third of the hydroxyl radical source. At this concentration, calculated lifetimes of aqueous organics are on the order of 10 h for compounds with $\bullet\text{OH}$ rate constants of $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ or higher (e.g., substituted phenols such as syringol (6.4 h) and guaiacol (8.4 h)), and on the order of 100 h for compounds with rate constants near $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (e.g., isoprene oxidation products such as glyoxal (152 h), glyoxylic acid (58 h), and pyruvic acid (239 h)). Steady-state concentrations of $^1\text{O}_2^*$ are approximately 100 times higher than those of $\bullet\text{OH}$, in the range of $(0.1\text{--}3.0) \times 10^{-13} \text{ M}$. Since $^1\text{O}_2^*$ is a more selective oxidant than $\bullet\text{OH}$, it will only react appreciably with electron-rich species such as dimethyl furan (lifetime of 2.0 h) and substituted polycyclic aromatic hydrocarbons (e.g., 9,10-dimethylbenz[a]anthracene with a lifetime of 0.7 h). Comparing our current Davis samples with Davis fogs collected in the late 1990s shows a decrease in dissolved organic carbon content, similar mass absorption coefficients, lower $\bullet\text{OH}$ concentrations, but very similar $^1\text{O}_2^*$ concentrations.

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1. Introduction

Photochemical reactions in fog and cloud drops, and aqueous airborne particles, play important roles in the cycling of organic carbon and nitrogen (Graedel and Weschler, 1981; Munger et al.,

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1983; Blando and Turpin, 2000; Gelencsér and Varga, 2005; Hastings et al., 2005; Dall'Osto et al., 2009). For example, aqueous reactions can be significant sources of sulfate, nitrate, and secondary organics, and can be a sink for toxic species such as pesticides and polycyclic aromatic hydrocarbons (Jacob, 1986; Glotfelty et al., 1987; Leuener et al., 1988; Zabik and Seiber, 1993; Chen et al., 2006; Shunthirasingham et al., 2011).

Many of these drop and particle aqueous reactions are driven by photochemically generated oxidants, i.e., photooxidants. The best studied aqueous atmospheric photooxidant is hydroxyl radical ($\bullet\text{OH}$), although there are only roughly a dozen papers on this topic. This small body of literature includes measurements of $\bullet\text{OH}$ photofragmentation rates, lifetimes, and/or steady-state concentrations in fog and cloud waters (Faust and Allen, 1993; Matthijsen et al., 1995; Arakaki and Faust, 1998; Monod and Carlier, 1999; Anastasio and McGregor, 2001; Tilgner and Herrmann, 2010; Bianco et al., 2015), rain waters (Albinet et al., 2010), dew (Arakaki et al., 1999), and particles (Anastasio and Jordan, 2004; Anastasio and Newberg, 2007; Zhou et al., 2008; Arakaki et al., 2013). Based on these measurements, and on separate modeling studies, the main sources of $\bullet\text{OH}$ in atmospheric drops and particles include the photo-Fenton reaction, and photolysis of nitrite, nitrate, and hydrogen peroxide (Jacob et al., 1989; Pandis and Seinfeld, 1989; Zepp et al., 1992; Arakaki and Faust, 1998; Herrmann et al., 2000, 2010). Transport of $\bullet\text{OH}$ from the gas phase is also significant, accounting for approximately half of the $\bullet\text{OH}$ source in aqueous drops and particles (Arakaki et al., 2013).

While the most important sink for $\bullet\text{OH}$ is dissolved organic matter (DOM), only six studies have quantified the $\bullet\text{OH}$ sink in drops and particles (Arakaki et al., 1999; Anastasio and McGregor, 2001; Anastasio and Newberg, 2007; Arakaki and Faust, 1998; Zhou et al., 2008; Arakaki et al., 2013). As described by Arakaki et al. (2013), models typically underpredict the $\bullet\text{OH}$ sink because they use a “bottom up” approach based on concentrations and rate constants for individual organic species (Herrmann et al., 2010). The difficulty with this approach is identifying all of the significant organic molecules and their concentrations. Arakaki et al. (2013) recently suggested an alternative, “top down” approach after discovering that the $\bullet\text{OH}$ reactivity of bulk DOM is similar for different atmospheric waters and even surface waters. However, more data are needed to examine the robustness of the relationship in a wider range of atmospheric drops and particles.

Another significant aqueous photooxidant is singlet molecular oxygen ($^1\text{O}_2^*$), which reacts with electron-rich organics such as phenols, furans, polycyclic aromatic hydrocarbons (PAHs), amino acids, and reduced sulfur species. $^1\text{O}_2^*$ has been studied extensively in surface waters, where the primary source of $^1\text{O}_2^*$ is energy transfer from photoexcited DOM to ground-state molecular oxygen, and the primary sink is water (Zepp et al., 1977; Haag and Gassman, 1984; Haag and Hoigné, 1986; Tratnyek and Hoigné, 1994; Wilkinson et al., 1995). While these surface water observations are applicable to atmospheric waters, only three studies have measured $^1\text{O}_2^*$ concentrations in rain or cloud/fog drops. $^1\text{O}_2^*$ concentrations are generally much lower than $\bullet\text{OH}$ in rain waters (Albinet et al., 2010) but much higher than $\bullet\text{OH}$ in fog and cloud waters, where $^1\text{O}_2^*$ can be a significant sink for some electron-rich organics (Anastasio and McGregor, 2001; Faust and Allen, 1992). Given the paucity of data in atmospheric samples, assessing the significance of singlet oxygen in drops and particles requires more measurements.

In this study we characterize two photooxidants, hydroxyl radical ($\bullet\text{OH}$) and singlet molecular oxygen ($^1\text{O}_2^*$), in bulk fog waters from two locations: Davis, California and Baton Rouge, Louisiana, which experience dense seasonal fogs with regional differences in composition. The first four goals of our research are

to: (i) measure light absorption by the fogs, (ii) characterize the rates of formation, lifetimes, and steady-state concentrations of $\bullet\text{OH}$ and $^1\text{O}_2^*$, (iii) compare composition and photooxidant measurements in fogs from both locations and (iv) estimate the importance of these oxidants as sinks for water-soluble organic species. In addition, while a recent paper evaluated changes in fog composition in California over the past two decades (Herckes et al., 2015), there are no such comparisons for oxidants. Thus our final goal is to compare our current results with previous composition and photooxidant measurements made on Davis fog waters collected in the late 1990s (Anastasio and McGregor, 2001; Zhang and Anastasio, 2001).

2. Experimental methods

2.1. Materials

All chemicals were used as received. Benzene (99.9%, HPLC grade), furfuryl alcohol (98%), and phenol (99%+, ACS reagent) were from Sigma-Aldrich and deuterium oxide (D-enrichment $\geq 99.9\%$) was from Acros Organics. All chemical solutions and fog collection blanks were prepared using purified water (Milli-Q water) from a Milli-Q Plus system (Millipore; ≥ 18.2 M Ω cm) with an upstream Barnstead activated carbon cartridge.

2.2. Fog sample collection

Fog samples were collected in Davis, California, USA (38.5539° N, 121.7381° W, 16 m above sea level) and Baton Rouge, LA, USA (30.4500° N, 91.1400° W, 17 m ASL). In both locations, the fog collectors were set up in open fields adjacent to agricultural areas. 12 bulk samples (8 fog samples and 4 field blanks) were collected using stainless steel Caltech Active Strand Cloudwater Collectors (CASSCs) with pre-cleaned HDPE (Davis) or PFA (Baton Rouge) bottles. In Davis, samples were filtered using 0.45 μm membrane filters within a few hours of collection, flash frozen with liquid nitrogen, and stored at -20 °C until analysis. Samples from Baton Rouge were refrigerated (4 °C) immediately upon collection, transported frozen to Davis, then thawed, filtered and flash frozen. Field blanks were collected after fog collection episodes. In Davis, the fog collector was first cleaned using ethanol and Milli-Q water; field blanks were Milli-Q water sprayed into the collector and collected in HDPE bottles. In Baton Rouge, the fog sampler was cleaned using ultrapure (UP) water before each fog collection event (Heath et al., 2015). For field blanks, the collector was first cleaned by spraying with UP water and dried. It was then sprayed with more UP water, which was collected in PFA bottles as blanks. All blanks were processed (collection, filtration and storage) in the same manner as the fog samples.

2.3. Sample illumination and chemical analysis

Samples were illuminated in bulk with a 1000 W Xenon arc lamp filtered with an AM 1.0 air mass filter (AM1D-3L, Scientech) and 295-nm long-pass filter (20CGA-295, Thorlabs) to mimic tropospheric solar light (Figure S1). Air-saturated fog samples were illuminated in closed, 1-cm quartz cuvettes (Spectrocell) at 25 °C with constant stirring. Concentrations of probe compounds (see below) during illumination were determined using high performance liquid chromatography (HPLC) (Shimadzu LC-10AT pump, ThermoScientific BetaBasic-18 C₁₈ column (250 × 33 mm, 5 μm bead), and Shimadzu-10AT UV-Vis detector). Details of HPLC parameters are provided in Sections 2.6 and 2.7. The daily photon flux was measured using 2-nitrobenzaldehyde (2NB) as a chemical actinometer (Galbavy et al., 2010).

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