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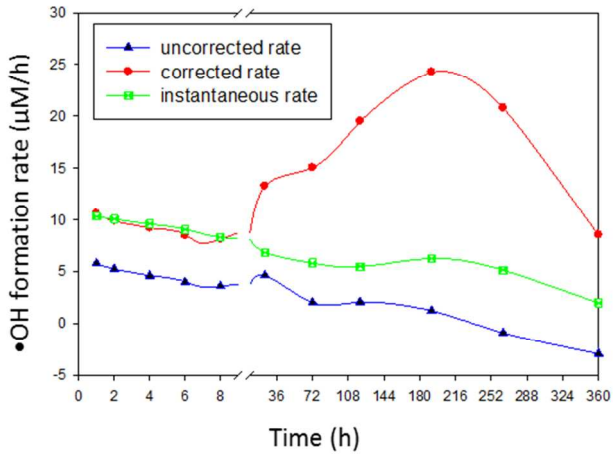
Title: Estimating OH radical photochemical formation rates in natural waters during long-term laboratory irradiation experiments (Sun et al.)

The hydroxyl (·OH) radical is known to be generated by photochemical reactions in natural waters. As the most oxidative reactant among the active oxygen species, it plays an important role in the transformation and oxidation of a variety of organic and inorganic compounds, including priority pollutants. Thus, estimation of its formation rate is significant for understanding these processes; however, its accurate estimation during long-term laboratory irradiations (days to weeks) has been problematic. This paper examines different approaches for accurately determining ·OH radical formation rates in natural waters using either short-term (hours) or long-term irradiations. It also discusses possible pathways of ·OH formation in long-term irradiations in relation to hydrogen peroxide and iron concentrations. The merit of this study is not only methodological improvement, but it also provides better understanding of phototransformation pathways of dissolved organic matter (DOM).



"Uncorrected rate, corrected rate and instantaneous rate of •OH photoproduction in Dismal Swamp water."

Estimating hydroxyl radical photochemical formation rates in natural waters during long-term laboratory irradiation experiments

Luni Sun; Hongmei Chen; Hussain A. Abdulla; Kenneth Mopper*

Abstract

In this study it was observed that, during long-term irradiations (> 2 days) of natural waters, the methods for measuring hydroxyl radical (•OH) formation rates based upon sequentially determined cumulative concentrations of photoproducts from probes significantly underestimate actual •OH formation rates. Performing a correction using the photodegradation rates of the probe products improves the •OH estimation for short term irradiations (< 2 days), but not long term irradiations. Only the 'instantaneous' formation rates, which were obtained by adding probes at each time point and irradiating the water sample (or sub-sample) for a short time (≤2 h), were found appropriate for accurately estimating •OH photochemical formation rates during long-term laboratory irradiation experiments. Our results also showed that in iron- and dissolved organic matter (DOM)-rich water samples, •OH appears to be mainly produced from the Fenton reaction initially, but subsequently from other sources possibly from DOM photoreactions. Pathways of •OH formation in long-term irradiations in relation to H_2O_2 and iron concentrations are discussed.

Introduction

The hydroxyl radical (•OH) is the most oxidative reactant among the reactive oxygen species, it plays an important role in the transformation and oxidation of a variety of organic and inorganic compounds[1, 2]. Photochemical reactions are the major sources of •OH radical in natural waters. The photo-formation of •OH depends on its major sources in sunlit waters, which include DOM photoreactions, the photo-Fenton reaction, and nitrate and nitrite photolyses[3]. Nitrate and nitrite photolyses are often found to be important sources[4], in rivers where their contributions are 1~89 % from nitrate and 2~70 % from nitrite, while in seawaters their contributions are 7~75 % from nitrate and 1~8 % from nitrite [3]. However, in iron-rich waters, the contribution of the photo-Fenton reaction (see below) can account for more than 70% the of total photochemical •OH production[5-7].

Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA

* Corresponding author. Email: kmopper@odu.edu. Tel: 757-683-4094 Fax: 757-683-5310

$Fe(II) + H_2O_2 \rightarrow Fe(III) + \bullet OH + OH^-$

where Fe(II) and Fe(III) include the hydrated and DOM-complexed iron species. In seawater and high DOM freshwaters, DOM photoreactions appear to be the main source for •OH[2,8-12]. Reactions involving hydroquinolic and phenolic moieties within humic substances appear to be responsible, at least in part, for •OH photoproduction in these waters[2, 8].

In natural waters, photochemical formation rates of •OH are determined indirectly using probes. The probe reactions can be split into two broad categories: 1) •OH addition to probes, with •OH either being added to the carbon atoms in probes such as 4-nitrophenol, nitrobenzene, benzene, benzoic acid, and terephthalate, or being added to the sulfoxide group in probes, e.g. dimethyl-sulfoxide; and 2) abstraction of a hydrogen atom on the probes such as methanol, formic acid, methane and butyl chloride[8, 13, 14]. Among these probes, benzene and benzoic acid have been commonly used. Typically, the probes are added initially to the samples and the cumulative concentrations of phenolic products are measured after irradiating for several minutes[15] or hours[3, 10, 16, 17]. These phenolic product compounds are non- or very weak absorbers of light in the solar irradiance spectrum and thus do not undergo direct photoreaction; however, in natural waters, their phototransformation/destruction may be promoted by the presence of DOM, possibly through electron or hydrogen atom transfer from reactive excited triplet states of DOM[18, 19], or reaction with reactive oxygen species, such as hydrogen peroxide[20], and singlet oxygen[21]. Thus, during long-term irradiations, this loss may lead to significant underestimation of the cumulative concentrations of phenolic products. This underestimation is likely minor when only initial •OH formation rates are taken into account[17], but it may be significant for time-course studies of •OH formation rates or its steady-state concentration, such as studies on the sources of •OH which usually require several hours to adequately measure the generation of •OH[3, 6, 16]. For example, in studies examining the photo-Fenton reaction in natural waters, the •OH formation rate, and H_2O_2 and Fe (II) concentrations were measured hourly under different experimental conditions[7]. Moreover, DOM photochemical transformation studies usually run for hours to days[22-24]. Since DOM is an important source and sink of •OH (as well as other reactive species), accurate estimation of •OH can improve our understanding of DOM transformation pathways. Therefore, it is necessary to establish the stability of both the •OH probe compound and the quantified product species with respect to direct and indirect photolysis in natural waters[25].

In this study, we estimated time-course •OH formation rates in DOM-rich water (Great Dismal Swamp) and estuarine water by two approaches: 1) correcting for product loss and 2) obtaining near-instantaneous formation rates. The corrected formation rates were obtained by adding the photodegradation rates of corresponding products to their formation rates, and the instantaneous rates

were obtained by adding probes at each time point and irradiating the sample for a short time (≤2h). Moreover, we discuss possible pathways of •OH formation in iron- and DOM-rich samples during long-term irradiations.

Experimental

Chemicals

Phenol (purity grade >99 %), sodium benzoate (99.5 %), benzene (HPLC grade), and desferrioxamine mesylate (DFOM) (92.5 %) were obtained from Sigma; salicylic acid (SA) (99%) was obtained from Fisher; H_2O_2 (35 % w/w) and methanol (HPLC grade) were obtained from Acros. Ultra-pure water (Milli-Q water, >18 $M\Omega cm^{-1}$) was used for solution preparation.

Sample description

Water samples were freshly obtained from the Great Dismal Swamp (near 36.7°S and 76.4°W, salinity 0 ppm, pH 3.7) and Elizabeth River estuary (near 36.9°S and 76.3°W, salinity 20 ppm, pH 7.5) in spring 2013. Samples were filtered within 24 hours of collection through a pre-cleaned 0.1 µm capsule filter (Polycap TC, Whatman). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were 54 ppm and 1.9 ppm for the Great Dismal Swamp sample, and 3 ppm and 0.9 ppm for the Elizabeth River estuarine sample.

Irradiations

All samples were placed into quartz tubes or flasks and kept oxygenated by periodic shaking in air. Irradiations were conducted using a solar simulator containing UVA340 bulbs (Q-Panel). The solar simulator is described elsewhere[26]. These lamps have a spectral output nearly identical to natural sunlight from ~295 to ~360 nm (http://www.solarsys.biz/0103.shtml). In a comparison of the light output from the solar simulator to natural sunlight, the solar simulator provided 127% of the photobleaching occurring under winter mid-day sunlight at 36.89°N latitude[27]. Consequently, the •OH production rates in this study are likely somewhat higher than in the environment. Dark controls were wrapped in foil and placed inside the solar simulator. All samples were irradiated at room temperature and at their natural concentrations and pH in order to approximately simulate surface conditions, and to avoid potential contamination.

Determination of •OH formation rate

Probe compounds (sodium benzoate or benzene) were added to aliquots of the water sample to final concentrations of 5.0 mM and 3.0 mM respectively. Complete dissolution of benzene was facilitated by

vigorous stirring at room temperature. These samples were used to determine the effect of long-term, continuous irradiation of the •OH probes. Other aliquots of the water sample were used for measuring instantaneous •OH formation rates and parameters including DOC, TDN, DFe and H_2O_2 production. The instantaneous •OH formation rates were determined by irradiating the latter aliquots without the probes present; subsamples were then removed at specific time points and irradiated for ≤2h with the •OH probes.

Benzoic acid reacts with •OH to form SA and other products, while benzene reacts to form phenol and other products. The fraction of SA (or phenol) formed relative to the other •OH photoproducts is constant[10] thereby enabling the use of SA (or phenol) production to determine the total •OH production, as described below. The SA and phenol photoproducts were measured using HPLC with fluorescence detection as described in detail elsewhere[10, 29]; the excitation/emission wavelengths were 300/400 nm [9] for SA and 260/310 nm for phenol[28], respectively. Cumulative SA and/or phenol concentrations were plotted vs. irradiation time. The observed photo-formation rates of SA and phenol (R_{ob}) were determined from the tangent slopes at each time point of the curve using Matlab. R_{ob} was used to evaluate the uncorrected •OH photo-production rate, R_{unc}, which was calculated by the following equation:

$$R_{unc} = \frac{R_{ob} \times F}{Y} \quad (1)$$

where Y is the yield of photoproduct formed per probe molecule oxidized by •OH. Since the reaction between probe and •OH forms more than one product[10, 29], this value is always less than 100 % (see Results and Discussion). F is a calibration factor, which is related to the fraction of the •OH flux that reacts with the probe and accounts for competing OH scavengers in natural waters, such as DOM. F is evaluated for each sample type by competition kinetics using a series of different probes concentrations as described in detail by Zhou and Mopper[30]. For our experiments, F was 1.11~1.26, depending on the probes and sample types.

Determination of photodegradation rates of •OH probe products

Photodegradation rates of SA and phenol were obtained by irradiating 40 µM SA and 180 µM phenol in the Dismal Swamp sample and measuring their concentrations over 24 h. The concentrations of SA and phenol chosen were close to the maximum cumulative concentrations formed in our irradiation experiments.

Determination of dissolved organic carbon (DOC)/total dissolved nitrogen (TDN), dissolved iron (DFe) and H_2O_2 production

DOC and TDN were measured for all samples using high temperature (720°C) catalytic combustion on a Shimadzu TOC-V-CPH carbon analyzer. DFe concentration and H_2O_2 production were measured for Dismal Swamp sample. DFe was measured using a Hitachi Z8100 polarized Zeeman flame atomic absorption spectrophotometer equipped with an iron hollow cathode lamp; and H_2O_2 production was measured by modified (p-hydroxyphenyl)-acetic acid dimerization method[31].

Results and Discussions

Calibration of Y_{ph} value

Y is the yield of photoproduct formed per probe molecule oxidized by •OH. Most Y values of SA (Y_{SA}) from published radiolysis experiments are 17~18%[10, 14, 32] while the values of phenol (Y_{ph}) range from 66% to 95% [14, 33-35]; the high Y_{ph} of 95% was observed during nitrate photolysis[35]. Because of the wide range of published Y_{ph} values, we did not select a Y_{ph} value for our system from published data. Instead, we used the much less variable Y_{SA} value (17%[10]) to calibrate the Y_{ph} value by using H_2O_2 photolysis as a pure •OH source. Different concentrations of H_2O_2 were added to solutions containing sodium benzoate or benzene and irradiated for 1 h. Assuming the degradation of SA and phenol is negligible in this short period, at the same concentrations of H_2O_2, the •OH photoproduction rate R_{unc} should be the same for both probes, that is:

$$R_{unc=} \frac{R_{SA}\times F_{SA}}{Y_{SA}} = \frac{R_{ph}\times F_{ph}}{Y_{ph}} \quad (2)$$

but, since there are no other competing scavengers, $F_{SA}=F_{ph}=1$:

$$R_{unc=} \frac{R_{SA}}{Y_{SA}} = \frac{R_{ph}}{Y_{ph}} \quad (3)$$

Y_{ph} was then calculated as:

$$Y_{ph} = \frac{Y_{SA}\times R_{ph}}{R_{SA}} \quad (4)$$

In our experiments, Y_{ph} value was calculated as 69.3±2.2 %, which was then used for all calculations. This value is in agreement with most published values[21-24].

Corrections of •OH formation rates

Photodegradation was observed for both SA and phenol, and followed first order reaction kinetics. The photodegradation rate at each time point is k[SA or phenol]$_t$, where k is the slope of the plot of Ln (concentration) vs. the irradiation time; it is -0.0495 h^{-1} for SA and -0.0459 h^{-1} for phenol (Fig. 1).

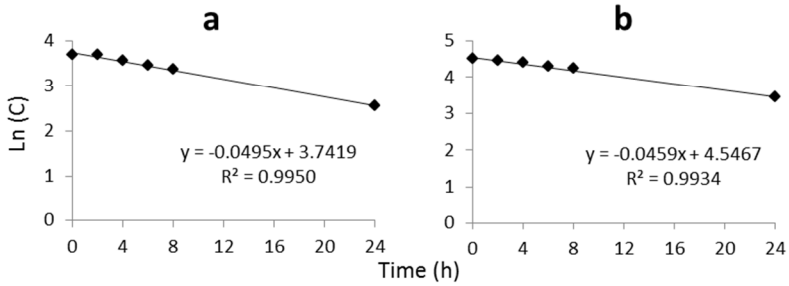


Fig. 1 SA (a) and phenol (b) photodegradation in the Dismal Swamp sample over a 24 h irradiation in a UV solar simulator. Subsamples for measuring SA and phenol degradation rates were taken at the same time as the •OH measurements.

The corrected photoformation rate of SA or phenol is the observed SA (or phenol) formation rate (R_{ob}) plus its degradation rate. Therefore, the •OH formation rate (R_{cor}) was corrected and calculated by the following equation:

$$R_{cor} = \frac{}{} = R_{unc} + \frac{}{} \quad (5)$$

Uncorrected •OH formation rate (R_{unc}), corrected formation rate (R_{cor}), and instantaneous formation rates (R_{ins}) at each time point during 15 d are shown in Fig. 2 and Fig. 3. R_{ins} was assumed to be the true •OH formation rate; i.e., the degradation of SA or phenol is negligible for a one hour irradiation (Fig. 1). The negative R_{unc} values at the longer irradiation times (Fig. 2 and Fig. 3) is probably due to the substantial photodegradation of the probe photoproducts upon long-term irradiation.

Comparison of •OH formation rates

Between 2h and 8 h, R_{unc} values were lower than R_{ins} values (Table 1). The differences averaged 29 % using benzoic acid and 16% using benzene as probes; thus R_{OH} significantly underestimated •OH formation. By performing corrections for probe product degradation, the agreement improved. The differences between R_{cor} and R_{ins} averaged 8 % using benzoic acid and 4% using benzene as probes. However, for longer irradiation periods (more than 8 h), neither R_{unc} nor R_{cor} agreed well with R_{ins}, as differences were >30 %. The reason for the large discrepancies might be that the added probes changed DOM photodegradation and OH production pathways, which only became significant after long-term irradiations containing the probe. Therefore, for long-term irradiations (*e.g.*, > ~1 day) R_{ins} should be used to determine the OH production rate. There were no significant differences in R_{ins} between two different probes (paired t test, P=0.1066) for up to 15 days of irradiation (Fig. 4).

Table 1. Uncorrected •OH formation rate (R_{unc}), corrected formation rate (R_{cor}), and instantaneous formation rates (R_{ins}) during 8 h (n=2)

Time (h)	•OH fomation rates (μM/h) by using					
	Benzoic acid			Benzene		
	R_{unc}	R_{cor}	R_{ins}	R_{unc}	R_{cor}	R_{ins}
1	10.5±0.1	11.0±0.1	10.8±0.1	10.3±0.5	10.6±0.5	10.7±0.1
2	9.0±0.1	9.9±0.1	10.1±0.4	9.3±0.4	9.9±0.5	10.0±0.4
4	6.5±0.3	8.3±0.3	9.6±0.4	8.0±0.1	9.0±0.1	9.6±0.5
6	5.6±0.2	7.8±0.2	9.0±0.3	7.2±0.1	8.6±0.1	9.0±0.3
8	5.2±0.4	8.0±0.4	8.3±0.5	6.6±0.6	8.1±0.6	8.3±0.5

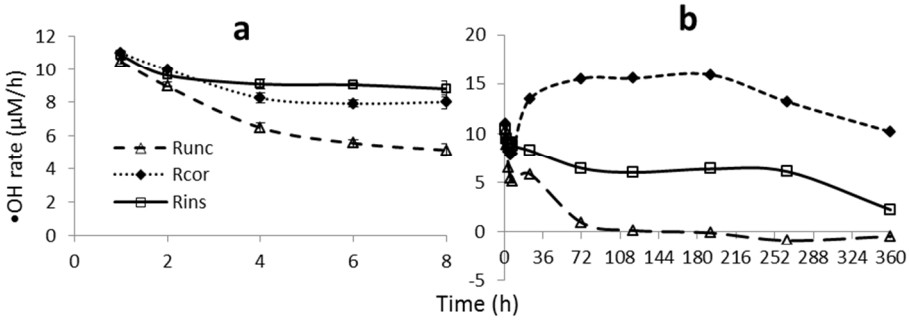


Fig. 2 R_{unc}, R_{cor} and R_{ins} using benzoic acid as probe for 8h (a) and 15 day (b) irradiations of Dismal Swamp water. Error bars are within the data points unless otherwise indicated.

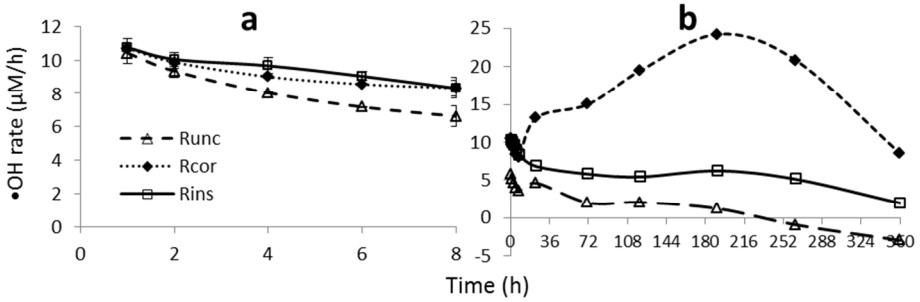


Fig. 3. R_{unc}, R_{cor} and R_{ins} using benzene as probe for 8 h (a) and 15 day (b) irradiations of Dismal Swamp water. Error bars are within the data points unless otherwise indicated.

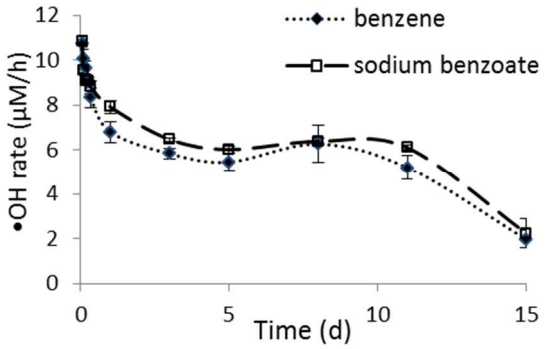


Fig.4. Comparison of R_{ins} between two probes for a 15 day irradiation of Dismal Swamp water. Error bars are within the data points unless otherwise indicated.

Measurements were also conducted in a low DOC (3 ppm) sample from the Elizabeth River (salinity of 20). Only benzene was used as the •OH probe because it has higher Y and, thus a somewhat better selectivity than benzoic acid[36]; and its corresponding photoproduct phenol has higher fluorescent intensity than SA. The photodegradation rate of phenol in the Elizabeth River sample was 0.00443 h^{-1}, which is only 1/10 of that for the Dismal Swamp water sample. •OH formation rates were also low in the Elizabeth River sample (< 40 nM/h). However, this is not only due to low DOM, but also due to competing natural •OH scavengers including CO_3^{2-} and Br^- in saline water[12, 37]. The t test showed no significant differences between R_{unc}, R_{cor} and R_{ins} during 6 h of irradiation (P>0.17) (Fig. 5. a): thus, use of a correction or instantaneous rate was not necessary. However, significant differences were observed for irradiations > ~24h (Fig. 5. b); thus the measurement of R_{ins} also appears to be necessary for long-term irradiations, even for this relatively low DOC sample.

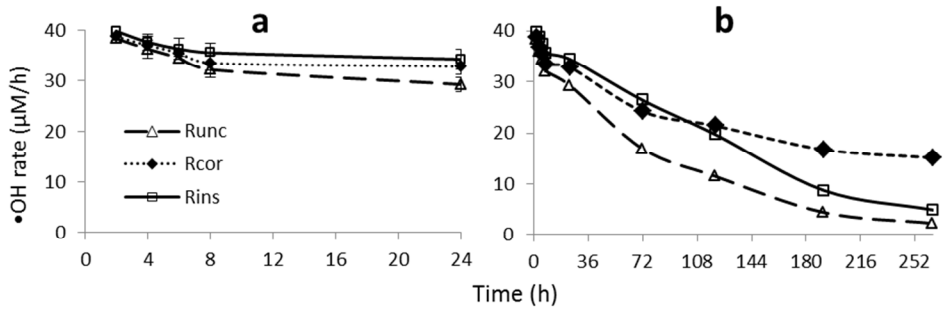


Fig. 5. R_{unc}, R_{cor} and R_{ins} for 24 h and 11 day irradiations of Elizabeth River water. Error bars are within the data points unless otherwise indicated.

Possible •OH formation pathways in Dismal Swamp water

R_{ins} values were positive through 15 days of continuous irradiation, and ranged from ~10.5 µM/h on day 1 to ~2 µM/h on day 15 (Fig. 4). After day 1, the rate decreased until a plateau at ~6 µM/h was reached (from ~day 3 to day 12), after which it dropped to ~2 µM/h on day 15. During the irradiation, DFe decreased from nearly 20 µM to 3 µM (Fig. 6a), and photochemically-induced flocculation was observed after day 4. The photoproduction of H_2O_2 varied widely over the irradiation (Fig. 6c.d). H_2O_2 showed strong initial production, but fell to zero between day 2 and day 4, and then was produced again after day 4 upon the onset of flocculation. We hypothesize that the photo-Fenton reaction was the main source of the •OH initially, on the basis of high DFe and high H_2O_2 photoproduction from DOM during the first day. Nitrate photolysis was likely a negligible source of •OH as the maximum •OH production from nitrate was only ~2.1 x 10^{-3} µM /h, based on a dissolved nitrogen concentration and assuming all dissolved nitrogen was nitrate and assuming an •OH photo-production rate from nitrate of ~1.1 x 10^{-3} µM •OH/h per µM nitrate[12, 37]. To test for the effect of iron (i.e., the photo-Fenton reaction), an aliquot of Dismal Swamp sample was irradiated with 100 µM DFOM, which effectively binds all DFe into a photochemically unreactive complex[6]. The DFOM addition reduced the •OH formation rate by about 90% during an 8 h irradiation, thus confirming the initial importance of Fenton chemistry in •OH photoproduction in the Dismal Swamp sample. Between day 4 to day 7, $H_2O_2$was again being photoproduced (Fig. 6c, d), but a sharp decrease in DFe was also observed during this period, which is likely decreased the importance of Fenton chemistry relative to OH photoproduction from other sources, in particular DOM photoreactions[23]. The reasons for the reappearance of H_2O_2 after day 4 are not known, but may be related to major photochemically-induced changes in DOM composition and structure[38] and to the initialization of DOM photoflocculation after day 4 [23, 39]. This is supported by the inverse relation (R^2=0.97) between the DOC-normalized OH production rate and the DOC-normalized DFe concentration, particularly after day 4 (Fig. 6b). To our knowledge, this behavior of H_2O_2 photoproduction has not been previously observed and, thus, warrants further study. After day 10, as most DOM had been degraded or mineralized, •OH formation decreased again.

It needs to be pointed out that, in addition to trapping the free •OH, these probes (as well as most other commonly used •OH probes) also react with other highly reactive hydroxylating species [8, 40-42]: *e.g.*, excited quinones triplets photochemically produce a species capable of hydroxylation, even though these species exhibit reactivities about one an order of magnitude lower than the free •OH[40]. As quinone structures were observed in the Dismal Swamp DOM by FTIR (unpublished data), it is likely that these hydroxylating species contributed to the formation of hydroxylated compounds from the added probes. Moreover, during the photo-Fenton reaction, the highly reactive and oxidizing ferryl ion, Fe(IV), can be formed, although at relatively low rates[34, 43]. This species is capable not only of abstraction of a hydrogen

atom, even from methane[44], but also of aromatic and benzylic hydroxylation, *e.g.* conversion of benzene to phenol[45, 46]. Although the ferryl ion is less oxidizing than the hydroxyl radical[47] , we cannot reject its possible minor contribution to probe product formation in our iron rich system. Thus, in this study, all reported •OH production rates include both free •OH and any highly reactive species capable of hydroxylation the probe molecules. However, even if part of the probe product signal is due these other reactive species, they (in addition to •OH) may have played role in the transformation of DOM, as DOC decreased about 75 % after 15 days irradiation, in agreement with Helms et al.[39]. Details of phototransformation pathways of DOM will be further discussed in a future study.

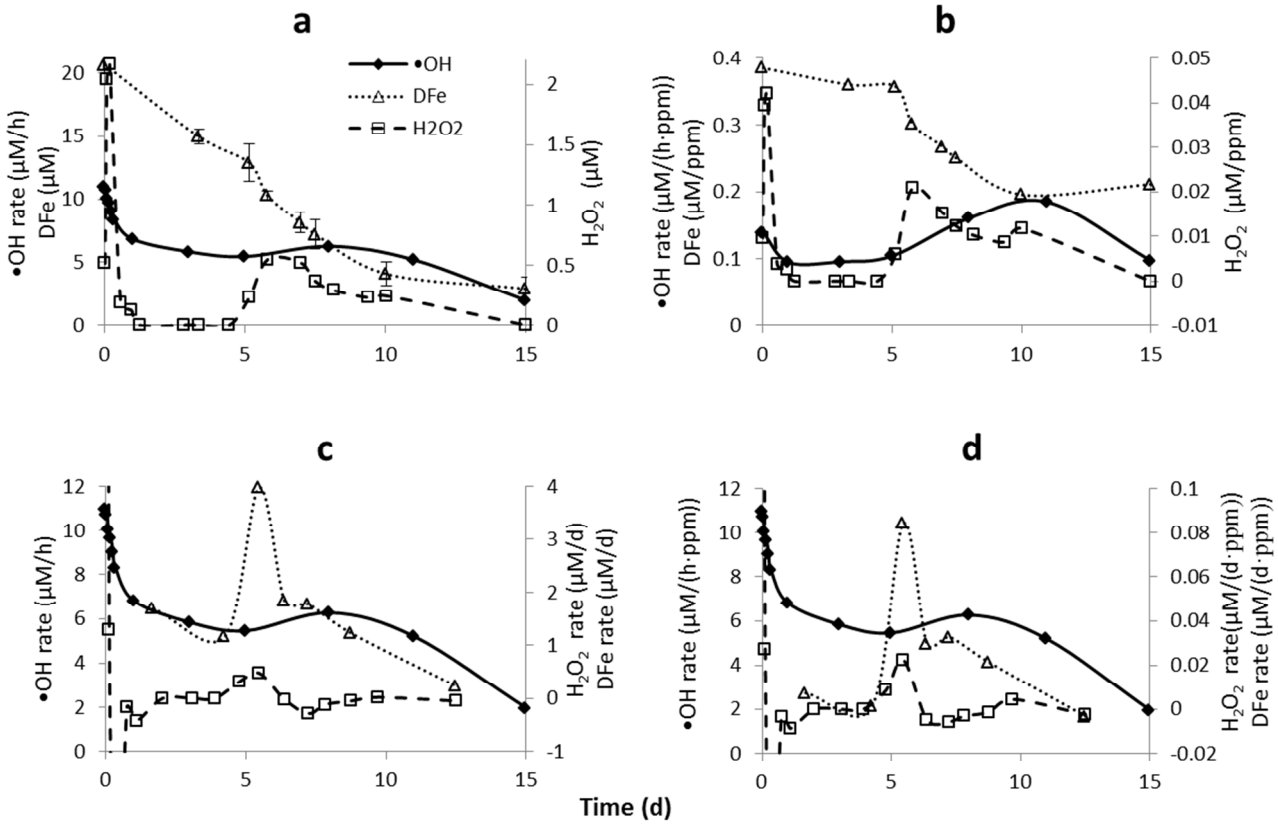


Fig.6. (a) •OH formation rate, DFe and H_2O_2 concentration; (b) •OH formation rate, DFe and H_2O_2 concentration normalized to DOC; (c) •OH formation rate, DFe loss rate and H_2O_2 formation rate; (d) •OH formation rate, DFe loss rate, and H_2O_2 formation rate normalized to DOC during irradiation. •OH (◆), H_2O_2 (□), and DFe (△). Equivalent time points for iron and H_2O_2 were calibrated based on measured DOC in photodegraded subsamples relative to the original sample (DOC as %).

Conclusions

In both DOM-rich and poor natural waters examined in this study, the methods for measuring •OH formation rates by obtaining sequential cumulative concentrations of photoproducts from probes substantially underestimated the actual •OH formation rate during long-term irradiations. Therefore, it is recommended that instantaneous formation rates be used to estimate •OH photochemical formation rates during long-term irradiation experiments, regardless of the probe used. For short-term irradiations of natural waters, it is recommended that photodegradation rates of corresponding probe photoproducts be determined in order to correct the OH production rate. Our results also showed that, in the iron- and DOM-rich sample, •OH is likely produced mainly from the Fenton and photo-Fenton reactions initially, but after that, •OH appears to be produced mainly by other pathways, in particular DOM photoreactions, the mechanisms of which need to be further studied.

Acknowledgments

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