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04 August 2022

UNIVERSITÀ DEGLI STUDI DI TORINO

QUANTIFICATION OF SINGLET OXYGEN AND HYDROXYL RADICALS UPON UV IRRADIATION OF SURFACE WATER

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Abstract

We measured the formation rate and the steady-state concentration of hydroxyl radicals and of singlet oxygen upon irradiation of lake water. There is controversy about the importance of singlet oxygen in the environmental photochemistry, but here we show that the steady-state concentration of $^1O_2$ under irradiation can be higher by about two orders of magnitude compared to the hydroxyl radical. The higher occurrence of singlet oxygen in surface waters is mainly due to a higher rate of formation, because the transformation rate constants of $^1O_2$ (collision with the solvent) and of $^\bullet OH$ (reaction with dissolved compounds) are comparable.

Keywords

Photochemistry; indirect photolysis; dissolved organic matter; phototransformation; furfuryl alcohol.

Introduction

Photochemical processes play an important role into the transformation of dissolved molecules in surface waters. They include direct photolysis processes and indirect phototransformation reactions induced by transient species, such as the triplet excited states of dissolved organic matter ($^3DOM^*$), the radicals $^\bullet OH$ and $CO_3^{-\bullet}$, singlet oxygen ($^1O_2$), and to a lesser extent a variety of other reactive species ($ROO^\bullet$, $^\bullet NO_2$, $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$) (Boule 1999). The cited reactions induce the transformation of dissolved compounds including man-made xenobiotics, limiting their persistence in the aquatic systems. However, such processes can also yield harmful secondary pollutants (Fenner et al. 2006; Lam and Mabury 2005; Vione et al. 2004).

Among the reactive species mentioned before, $^1O_2$ is generated in surface waters upon reaction between fundamental-state triplet oxygen and the triplet excited states of Dissolved Organic Matter ($^3DOM^*$) (Boule 1999). $^3DOM^*$ is produced upon radiation absorption by DOM, followed by Inter-System Crossing (ISC).

$$DOM + h\nu \rightarrow {}^1DOM^* \text{---} (ISC) \rightarrow {}^3DOM^* \qquad (1)$$
$${}^3DOM^* + O_2 \rightarrow DOM + {}^1O_2 \qquad (2)$$
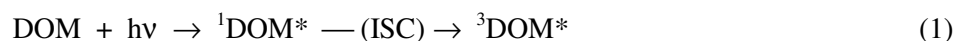
Singlet oxygen has perhaps the most controversial role among the reactive transients cited above, because it can be quickly inactivated in the aqueous solution upon collision with the solvent molecules (Hoigné 1990). The collisional deactivation can be considerably faster than the reaction between $^1O_2$ and most substrates, which would limit the importance of singlet oxygen in the photransformation processes (Boule 1999, and references therein). However, it has recently been shown that $^1O_2$ could play a significant role toward the photochemical transformation of the amino acids histidine, methionine, tryptophan and tyrosine in surface waters (Boreen et al. 2008). It could therefore be important in inducing the removal of easily oxidised substrates from water bodies.

The aim of the present paper was to gain further insight into the role of singlet oxygen in surface-water photochemistry. For this purpose we measured the formation rate and the steady-state concentration of $^1O_2$ and of $^{\bullet}OH$ upon irradiation of several lake water samples. We then compared the expected reactivity of $^1O_2$ and $^{\bullet}OH$ toward molecules of known reaction kinetics with the two transients. We could also find a statistically significant correlation of the formation rate of singlet oxygen with DOM-related quantities, such as the Non-Purgeable Organic Carbon (NPOC) and the photon flux absorbed by DOM ($P_a{}^{DOM}$).

Experimental

Surface water was sampled from the top layer (depth < 0.5 m) of freshwater lakes (Avigliana Grande, Avigliana Piccolo, Viverone, Meugliano, Soprano, Sottano, Laghetto, Blu), all located in NW Italy. The choice of the lakes was made to ensure a wide variety of conditions, in particular as far as the DOM content of water is concerned. Samples were transported to the laboratory under refrigeration, vacuum filtered upon arrival (0.45 μm pore diameter HA filters, Millipore), and stored under refrigeration.

Phenol (purity grade >99%), furfuryl alcohol (FFA, 99%), $NaH_2PO_4 \cdot H_2O$ (>98%) and H_3PO_4 (85%) were purchased from Aldrich, CH_3CN (gradient grade) and benzene (>99.8%) from VWR Int., "Zero grade" (high purity) air from SIAD (Bergamo, Italy). All reagents were used as received without further purification.

Irradiation (up to 30 h) was carried out in magnetically stirred, cylindrical Pyrex glass cells (3.5 cm diameter, 2 cm height), containing 14 mL aqueous solution. The radiation source was a set of 5 Philips TL K05 UVA lamps, with emission maximum at 365 nm. The irradiance on top of the solutions was 57 W m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter and corresponding to a volumetric photon flux of 1.6×10^{-5} einstein L^{-1} s^{-1}. By comparison, the UV irradiance of sunlight at noon in a sunny summer day at mid latitude (15 July, 45°N) is around 30 W m^{-2} (Minero et al. 2007). Figure 1 reports the emission spectrum of the lamps ($p_o(\lambda)$), measured with an Ocean Optics SD2000 CCD spectrophotometer, and the absorption spectra of the lake water samples ($A_1(\lambda)$), measured with a Varian Cary 100 Scan UV-Vis spectrophotometer over an optical path length of 1 cm.
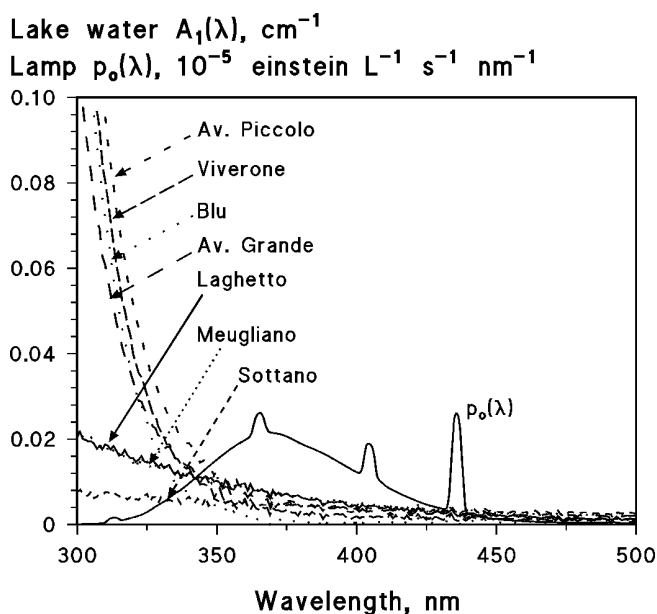
Figure 1. Emission spectrum of the adopted UVA lamps ($p°(\lambda)$). Absorption spectra of the lake water samples under study ($A_1(\lambda)$, measured over an optical path length of 1 cm).

After irradiation the solutions were analysed by High Performance Liquid Chromatography coupled with UV-Vis detection (HPLC-UV). The VWR-Hitachi HPLC-UV was equipped with an AS2000A autosampler, L-6200 and L-6000 pumps for high-pressure gradients, L-4200 UV-Vis detector, and a RP-C18 LichroCART column (VWR, length 125 mm, diameter 4 mm) packed with LiChrospher 100 RP-18 (5 μm particle diameter). Isocratic elution was carried out with a mixture of acetonitrile and aqueous H_3PO_4/NaH_2PO_4 (5 mM total phosphate, pH 2.8) at 1.0 mL min^{-1} flow rate. Phenol and benzene were eluted with 40% CH_3CN, furfuryl alcohol (FFA) with 10% CH_3CN. The detection wavelength in all the cases was 220 nm, and the retention times under the reported conditions were: 2.60 min for phenol, 8.40 for benzene, and 3.70 for FFA.

The time evolution of benzene and FFA (degradation) was fitted with pseudo-first order exponential functions of the form $C_t = C_0 \exp(-k\,t)$, where C_t is the concentration at the time t, C_0 the initial concentration, and k the pseudo-first order degradation rate constant. The initial degradation rate is $R = k\,C_0$. The time trend of phenol formation from benzene showed a monotonic increase. The time evolution of phenol was fitted with $P_t = C_0\,[1 - \exp(-k'\,t)]$, where P_t is the concentration of phenol at the time t, C_0 the initial concentration of benzene, and k' the pseudo-first order formation rate constant of phenol. The initial formation rate of phenol is $R' = k'\,C_0$. The variability of repeated runs was around 10-15%.

The quantification of DOM in the lake water samples was carried out as Non-Purgeable Organic Carbon (NPOC) with a Shimadzu TOC 5000 Analyser. The samples were acidified with $HClO_4$ and sparged with high-purity air for 20 minutes to drive out the inorganic carbon as CO_2. It followed the catalytic combustion for the measurement of total carbon, coupled with non-dispersive infra-red detection.

Results and discussion

Kinetic models for the quantification of $^{\bullet}OH$ and $^1O_2$

We assessed the formation and consumption of $^{\bullet}OH$ in the studied samples under the adopted irradiation conditions by adding benzene, and by monitoring the time evolution of phenol as the main reaction intermediate with the hydroxyl radical (95% yield; Deister et al. 1990). We have demonstrated in previous work that such a reaction is selective enough for a suitable quantification of $^{\bullet}OH$ upon irradiation of surface waters (Vione et al. in press). The following reactions were included in the model:

$$\text{Sources} + h\nu \rightarrow {}^{\bullet}OH \qquad\qquad [R_{\bullet OH}] \qquad\qquad (3)$$

$$^{\bullet}OH + \text{Benzene} \rightarrow \text{Products} \qquad [k_4] \qquad\qquad (4)$$

$$^{\bullet}OH + \text{Benzene} \rightarrow \text{Phenol} \qquad [k_5 = 0.95\, k_4] \qquad (5)$$

$$^{\bullet}OH + S_i \rightarrow \text{Products} \qquad\qquad [k_{Si}] \qquad\qquad (6)$$

$R_{\bullet OH}$ is the initial formation rate of $^{\bullet}OH$ produced by the different sources, $k_4 = 7.8 \times 10^9 \ M^{-1}\ s^{-1}$ (Deister et al. 1990), and S_i is a generic scavenger of $^{\bullet}OH$ naturally present in the sample (e.g. DOM constituents, carbonate, bicarbonate, or nitrite) (Boule 1999). From the irradiation experiments it is possible to determine the initial formation rate of phenol from benzene, R_P. The application of the steady-state approximation to $^{\bullet}OH$ yields the following expression for R_P, where $[\text{Benzene}]_0$ is the initial concentration of benzene:

$$R_P = 0.95\, R_{\bullet OH} \frac{k_4\, [\text{Benzene}]_0}{k_4\, [\text{Benzene}]_0 + \sum_i k_{Si}\, [S_i]} \qquad\qquad (7)$$

The fit of the experimental data (R_P vs. $[\text{Benzene}]_0$) with equation (7) yields $R_{\bullet OH}$ and $\Sigma_i\, k_{Si}\, [S_i]$ as fitting parameters, from which it is possible to derive $[^{\bullet}OH] = R_{\bullet OH}\, \{\Sigma_i\, k_{Si}\, [S_i]\}^{-1}$. The value of $[^{\bullet}OH]$ thus obtained represents the steady-state concentration of the hydroxyl radical in the irradiated natural sample, in the absence of benzene. Note that no formation of phenol from benzene was observed in lake water in the dark, without irradiation.

The transformation of furfuryl alcohol (FFA) is a suitable way to quantify the formation rate of $^1O_2$ (Halladja et al. 2007). In the kinetic model we considered the production of $^1O_2$ by the water constituents, the deactivation reaction (9) of $^1O_2$ upon collision with the solvent molecules, the reaction (10) between $^1O_2$ and FFA, and additional transformation processes of FFA because of reaction with $^{\bullet}OH$ (reaction 11), direct photolysis, and thermal degradation. The last two processes are taken into account together in reaction (12).

$$\text{Sources} + h\nu \rightarrow {}^1O_2 \qquad\qquad [R_{1O2}] \qquad\qquad (8)$$

$$^1O_2 \rightarrow O_2 \qquad\qquad\qquad\qquad [k_9] \qquad\qquad (9)$$

$$^1O_2 + \text{FFA} \rightarrow \text{Products} \qquad\quad [k_{10}] \qquad\qquad (10)$$

$$^{\bullet}OH + \text{FFA} \rightarrow \text{Products} \qquad\quad [k_{11}] \qquad\qquad (11)$$

FFA $\rightarrow$ Products $\qquad$ [k_{12}] $\qquad$ (12)

R_{1O2} is the rate of formation of singlet oxygen, and it is $k_9 = 2.5 \times 10^5$ s^{-1}, $k_{10} = 1.2 \times 10^8$ M^{-1} s^{-1} (Halladja et al. 2007, and references therein), and $k_{11} = 1.5 \times 10^{10}$ M^{-1} s^{-1} (Buxton et al. 1988). From the degradation rate obtained upon irradiation of FFA alone in Milli-Q quality water we also derived $k_{12} = 2.6 \times 10^{-7}$ s^{-1}, valid under the irradiation conditions we adopted.

The reaction between $^1O_2$ and naturally occurring dissolved molecules was neglected because literature data indicate that it is minor compared to reaction (9) (Hoigné 1990). Furthermore, we confirmed the literature results in the course of preliminary irradiation experiments. Also the possible reaction between FFA and the triplet excited states of Dissolved Organic Matter ($^3DOM^*$) was not considered on the basis of literature data (Halladja et al. 2007). Upon application of the steady-state approximation to $^\bullet OH$ and to $^1O_2$ we obtained the following equation to describe the initial degradation rate of FFA, R_{FFA}:

$$R_{FFA} = R_{1O2} \frac{k_{10} \, [FFA]_0}{k_9 + k_{10} \, [FFA]_0} + R_{\bullet OH} \frac{k_{11} \, [FFA]_0}{\sum_i k_{Si} \, [S_i] + k_{11} \, [FFA]_0} + k_{12} \, [FFA]_0 \qquad (13)$$

$[FFA]_0$ is the initial concentration of FFA. We obtained $R_{\bullet OH}$ and $\Sigma_i \, k_{Si} \, [S_i]$ by means of the experiments with benzene, and k_{12} by the irradiation experiments of FFA in pure water as described before. As a consequence, when using equation (13) to fit the experimental data (R_{FFA} vs. $[FFA]_0$), the only fitting variable was R_{1O2}. We obtained the steady-state concentration of singlet oxygen in the irradiated samples as $[^1O_2] = R_{1O2} \, (k_9)^{-1}$. Note that $[^1O_2]$ thus derived is referred to the irradiated natural sample, without FFA.

Results of lake water irradiation

A comparison of the reactivity of $^1O_2$ and $^\bullet OH$ is interesting because the hydroxyl radical can play a significant role toward the degradation of refractory compounds in surface waters (Boule 1999). Table 1 reports the data that we obtained for the lake water samples under study. The datum of the NPOC is the result of three independent measurements. The values that are referred to $^\bullet OH$ and to $^1O_2$ were obtained by fitting the experimental data with equations (7) and (13), respectively. Also see the previous section for the calculation of $[^\bullet OH]$ and of $[^1O_2]$. The Table shows that the initial formation rate of $^1O_2$ is two-three orders of magnitude higher compared to $R_{\bullet OH}$. Considering the steady-state concentration values, in most cases it is $[^1O_2] > [^\bullet OH]$ by about two orders of magnitude. The higher occurrence of $^1O_2$ compared to $^\bullet OH$ in the samples can mainly be ascribed to faster formation. Indeed the reaction rate constant of $^\bullet OH$ with the natural scavengers ($\Sigma_i \, k_{Si} \, [S_i]$) is in the $10^4 - 10^5$ s^{-1} range, and it is therefore not too far from k_9 for $^1O_2$.

The higher steady-state concentration of $^1O_2$ would be compensated to a variable extent by its lower reactivity compared to $^\bullet OH$. Let $k_{P,\bullet OH}$ be the reaction rate constant of a generic compound P with $^\bullet OH$, and $k_{P,1O2}$ the corresponding rate constant with $^1O_2$. Note that it is $k_{P,\bullet OH} > k_{P,1O2}$ for practically all compounds, thus the key issue is the ratio of the two constants. The half-life time $t\frac{1}{2}(P,X)$ of a compound P for reaction with the transient species X under a pseudo-first order kinetics is:

$$t_{\frac{1}{2}}(P,X) = \frac{\ln 2}{k_{P,X}[X]} = \frac{0.693}{k_{P,X}[X]} \qquad (14)$$

where [X] is a steady-state concentration ($[^\bullet OH]$ or $[^1O_2]$ in our case). Because for many samples it is $[^1O_2] \sim 10^2 [^\bullet OH]$, $^1O_2$ is very likely to be more important than $^\bullet OH$ toward the degradation of compounds, for which $k_{P,\bullet OH}(k_{P,1O2})^{-1} < 10^2$. The comparison of $t\frac{1}{2}(P,^\bullet OH)$ and $t\frac{1}{2}(P,^1O_2)$ for a certain compound P requires the knowledge of both $k_{P,\bullet OH}$ and $k_{P,1O2}$. Such values are reported in Table 2 for tyrosine (Tyr), histidine (His), 4-chlorophenol (4CP), and 4-chlorophenolate (4CP$^-$) (Buxton et al. 1988; Czaplicka 2006; Boreen et al. 2008). Table 1 reports the half-life times $t\frac{1}{2}(P,X)$ of the compounds under consideration, calculated for the different lake water samples under study by means of equation (14), with P = Tyr, His, 4CP or 4CP$^-$, and X = $^\bullet OH$ or $^1O_2$. The values of $t\frac{1}{2}(P,X)$ are referred to steady irradiation under the adopted device. In general Tyr and 4CP would undergo faster reaction with $^\bullet OH$, while His and 4CP$^-$ would mainly react with $^1O_2$. There are some exceptions because in the samples from the lakes Blu and Sottano the reactions of $^\bullet OH$ are particularly favoured (it is $[^1O_2]/[^\bullet OH] = 50\text{-}70$), and the same happens with $^1O_2$ for Viverone ($[^1O_2]/[^\bullet OH] = 1400$).

Table 1. Parameters of photochemical significance concerning the lake water samples under investigation. Lake acronyms: AvG = Avigliana Grande (sampling site 45°04'13"N, 7°23'00"E), AvP = Avigliana Piccolo (45°03'13"N, 7°23'51"E), Blu = Lago Blu (45°03'39"N, 7°11'18"E), Viv = Viverone (45°24'27"N, 8°01'57"E), Meu = Meugliano (45°28'38"N, 7°47'23"E), Sop = Soprano (45°02'15"N, 7°10'28"E), Sot = Sottano (45°02'17"N, 7°10'53"E), Lag = Laghetto (45°02'18"N, 7°11'16"E). The reported steady-state concentrations are referred to steady irradiation under the adopted device. The half-life times that some compounds would show in the samples because of reaction with $^{\bullet}OH$ and with $^1O_2$ are also reported (see Table 2 for rate constants and abbreviations). To simplify Table reading, the cases in which singlet oxygen would be a more important reactive species than $^{\bullet}OH$ are highlighted by grey shadowing. The opposite cases are on white background. The photochemically significant quantities have an incertitude of 10-15%.

	AvG	AvP	Blu	Viv	Meu	Sop	Sot	Lag
NPOC, mg C L^{-1}	3.95±0.05	3.83±0.05	0.60±0.03	6.50±0.08	7.00±0.06	0.99±0.02	0.78±0.02	2.06±0.02
R$_{\bullet OH}$, M s^{-1}	2.4×10^{-11}	1.3×10^{-11}	5.4×10^{-12}	4.7×10^{-12}	4.0×10^{-11}	1.2×10^{-11}	3.2×10^{-12}	7.9×10^{-12}
Σ$_i$ k$_{Si}$ [S$_i$], s^{-1}	6.4×10^4	5.7×10^4	7.5×10^4	2.5×10^5	4.1×10^5	1.6×10^5	2.6×10^4	9.9×10^4
[$^{\bullet}$OH], M	3.8×10^{-16}	2.3×10^{-16}	7.2×10^{-17}	1.9×10^{-17}	9.8×10^{-17}	7.5×10^{-17}	1.2×10^{-16}	8.0×10^{-17}
R$_{1O2}$, M s^{-1}	1.4×10^{-8}	1.8×10^{-8}	1.2×10^{-9}	6.8×10^{-9}	5.9×10^{-9}	2.9×10^{-9}	1.5×10^{-9}	4.2×10^{-9}
[^{1}O$_2$], M	5.7×10^{-14}	7.2×10^{-14}	4.8×10^{-15}	2.7×10^{-14}	2.4×10^{-14}	1.2×10^{-14}	5.8×10^{-15}	1.7×10^{-14}
t½(Tyr, $^{\bullet}$OH), h	39	64	210	780	150	200	120	190
t½(Tyr, ^{1}O$_2$), h	380	300	4500	790	890	1800	3700	1300
t½(His, $^{\bullet}$OH), h	100	170	530	2000	390	510	320	480
t½(His, ^{1}O$_2$), h	50	41	610	110	120	240	500	170
t½(4CP, $^{\bullet}$OH), h	67	110	350	1300	260	340	210	320
t½(4CP, ^{1}O$_2$), h	560	450	6700	1200	1300	2700	5500	1900
t½(4CP$^-$, $^{\bullet}$OH), h	120	200	650	2500	480	630	390	590
t½(4CP$^-$, ^{1}O$_2$), h	18	14	210	38	42	84	170	60

Table 2. Reaction rate constants with $^\bullet OH$ ($k_{P,\bullet OH}$) and with $^1O_2$ ($k_{P,1O2}$) of a number of organic compounds. The abbreviations adopted in the text and the literature references are also reported.

Compound	Abbr.	$k_{P,\bullet OH}$, $M^{-1}s^{-1}$	Reference	$k_{P,1O2}$, $M^{-1}s^{-1}$	Reference	$k_{P,\bullet OH}/k_{P,1O2}$
Tyrosine	Tyr	1.3×10^{10}	Buxton et al. 1988	9.0×10^6	Boreen et al. 2008	1400
Histidine	His	5.0×10^9	Buxton et al. 1988	6.6×10^7	Boreen et al. 2008	76
4-Chlorophenol	4CP	7.6×10^9	Buxton et al. 1988	6.0×10^6	Czaplicka 2006	1300
4-Chlorophenolate	4CP$^-$	4.1×10^9	Czaplicka 2006	1.9×10^8	Czaplicka 2006	22

Among other compounds for which $k_{P,\bullet OH}$ and $k_{P,1O2}$ are both available (Boreen et al. 2008; Buxton et al. 1988; Czaplicka 2006), methionine ($k_{P,\bullet OH}$ / $k_{P,1O2}$ = 380) and 2-chlorophenol ($k_{P,\bullet OH}$ / $k_{P,1O2}$ = 1300) would mainly react with $^\bullet OH$; tryptophan ($k_{P,\bullet OH}$ / $k_{P,1O2}$ = 72) and 2-chlorophenolate ($k_{P,\bullet OH}$ / $k_{P,1O2}$ = 100) would react faster with $^1O_2$. For photodegradable aminoacids it has been reported that the role of $^1O_2$ in photochemical degradation is significant in all the cases, and the order of importance is histidine (His) > tyrosine (Tyr) > methionine (Met) > tryptophan (Trp) (Boreen et al. 2008). By comparison of our data with those of Boreen et al., it is possible to infer that $^1O_2$ would be the main reactive species for His in surface waters. Tyr and Met would react faster with $^\bullet OH$, and the relevant reaction could be the main removal pathway for the two compounds. Trp reacts with $^1O_2$ faster than with $^\bullet OH$, but in surface waters it would mainly undergo direct reaction with $^3DOM*$ (Boreen et al. 2008).

Note that in the actual water bodies the absolute lifetimes would be quite higher than those reported in Table 1, because the irradiation intensity is low at the bottom of the water column. However, because irradiated DOM would be the main source both of $^\bullet OH$ (on average) and of $^1O_2$ (Hoigné 1990; Minero et al. 2007), the relative role of the two transient species could not change much with depth. The ratio $t\frac{1}{2}(P,^\bullet OH)$ $[t\frac{1}{2}(P,^1O_2)]^{-1}$ would therefore be similar in the irradiated samples and in the real water bodies.

Finally, considering that the irradiation of DOM would be the main source of $^1O_2$ via the reaction (2) between $^3DOM*$ and O_2, it is reasonable to look for a linear correlation between R_{1O2} (in M s^{-1}) and NPOC (in mg C L^{-1}), which measures the amount of DOM. By linear least-square regression we found that $R_{1O2} = [(2.2\pm0.7)\times10^{-9}]$ NPOC (the error bounds represent $\mu\pm\sigma$). It is also interesting to test the correlation between R_{1O2} and the photon flux absorbed by DOM, P_a^{DOM}. Because DOM is by far the main radiation absorber in surface waters above 300 nm (Del Vecchio and Blough 2002), the calculation of P_a^{DOM} (in einstein L^{-1} s^{-1}) can be based on the sample absorption spectrum $A_1(\lambda)$ and the lamp emission spectrum $p°(\lambda)$ (see Figure 1). It would be (Braslavsky 2007): $P_a^{DOM} = \int_\lambda p°(\lambda)\,(1-10^{-A1(\lambda)b})\,d\lambda$, with b = 1.6 cm as the optical path length. The linear least-square regression of R_{1O2} vs. P_a^{DOM} yielded $R_{1O2} = [(1.1\pm0.3)\times10^{-2}]\,P_a^{DOM}$.

Conclusions

We measured the formation of $^\bullet OH$ and $^1O_2$ upon irradiation of lake water samples, using as probe reactions the transformation of benzene into phenol and the degradation of FFA, respectively. The data show that the steady-state concentrations are $[^1O_2] \gg [^\bullet OH]$, with a ratio $[^1O_2]\,[^\bullet OH]^{-1}$ ranging from about 50 to around 1400. The higher occurrence of $^1O_2$ would mainly be accounted for by its higher formation rate compared to the hydroxyl radical ($R_{1O2} \gg R_{\bullet OH}$), because the transformation rate constants of the two species ($\Sigma_i\,k_{Si}\,[S_i]$ and k_9) are not much different. By comparison, also the carbonate radical $CO_3^{-\bullet}$ is a transient species that reaches a much higher steady-state concentration than $^\bullet OH$ in surface waters. However, $CO_3^{-\bullet}$ is mainly produced in surface waters by the minority of hydroxyl radicals that react with carbonate or bicarbonate. As a consequence, the formation rate of $CO_3^{-\bullet}$ is just a fraction of that of $^\bullet OH$. The apparent contradiction ($R_{CO3-\bullet} < R_{\bullet OH}$ and $[CO_3^{-\bullet}] \gg [^\bullet OH]$ at the same time) is explained by the fact that $CO_3^{-\bullet}$ is scavenged by DOM to a much lesser extent than $^\bullet OH$ (Canonica et al. 2005). In contrast, $^1O_2$ is more concentrated than $^\bullet OH$ because of faster formation and not because of slower transformation.

The higher occurrence of $^1O_2$ would be compensated to a variable extent by the higher reactivity of $^\bullet OH$ toward the solutes, and the outcome would depend very much on the substrate. We show that $^1O_2$ is very likely to be more important than $^\bullet OH$ toward the degradation of compounds, for which $k_{P,\bullet OH}\,(k_{P,1O2})^{-1} \le 100$. However, note that the values of $k_{P,\bullet OH}$ are available for many more compounds than $k_{P,1O2}$. In many cases the unavailability of $k_{P,1O2}$ would imply that it is very low. In contrast, the availability of $k_{P,1O2}$ might indicate a higher than average reactivity with $^1O_2$. For randomly chosen compounds, the reaction with $^\bullet OH$ could be more important in the majority of the cases.

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