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Modelling the occurrence and reactivity of the carbonate radical in surface freshwater

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Abstract

A model was developed to foresee the degradation kinetics of dissolved compounds for reaction with the carbonate radical in surface waters. It would contribute to the assessment of the environmental persistence of pollutants, therefore, allowing a better definition of the exposure of natural ecosystems and human communities to hazardous substances. The model is a function of the water chemical composition, the water column depth, and the second-order rate constant of the reaction between the relevant compound and the carbonate radical. A comparison between the reactivity of the carbonate and the hydroxyl radical shows that the latter would often play a more important role as reactive species, but the carbonate radical could prevail in carbonate-rich waters, giving the degradation of easily oxidisable molecules. *To cite this article: D. Vione et al., C. R. Chimie 12 (2009).*
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Keywords: Photochemistry; Pollutant fate; Lake water; Sensitised photolysis

1. Introduction

Photochemical reactions play an important role in the removal of biologically refractory pollutants from surface freshwater. They consist of the direct photolysis of sunlight-absorbing molecules and of a number of indirect photoreactions [1,2]. The latter can involve pollutants that do not absorb sunlight, and include the transformation processes photosensitised by dissolved organic matter (DOM), most likely through the excited triplet states (^{3}DOM*) [3,4], and the reaction with transient species such as $^\bullet$OH, $CO_3^{-\bullet}$, $^1O_2$, NO_2, and $Cl_2^{-\bullet}$ [5−9]. The cited transients can be produced upon irradiation by sunlight of photosensitisers such as DOM itself, nitrate, nitrite, and Fe(III). In some cases the interaction with inorganic anions such as bicarbonate, carbonate, chloride and nitrite is required. In many cases the transient species are consumed by natural scavengers, among which DOM is usually expected to play an important role [10]. Possible
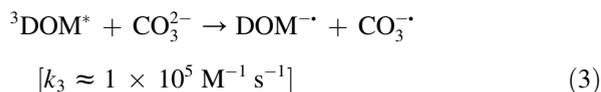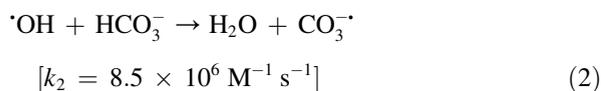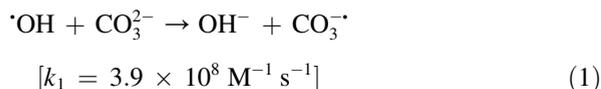
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exceptions to the scavenging by DOM are the cases of $^1O_2$ and NO_2, for which deactivation by collision with water molecules [11] and hydrolysis [12], respectively, might be major removal pathways.

Recent research has enabled the modelling of the steady-state concentration of $^{\bullet}OH$ in the surface layer of natural waters, as a function of the chemical composition of photoactive species. It is, therefore, possible to assess the lifetime of pollutants with known reaction rate constant with $^{\bullet}OH$, from the values of NPOC (non-purgeable organic carbon, which quantifies DOM), $[NO_3^-]$, $[NO_2^-]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ [13]. Such a result was mainly allowed by the quantification of the role of DOM as photochemical $^{\bullet}OH$ source. Interestingly the $^{\bullet}OH$ radical is involved not only into the degradation of organic pollutants but also in the production of other reactive transients such as $CO_3^{-\bullet}$ from carbonate and bicarbonate, and $^{\bullet}NO_2$ from nitrite [14,15].

This work is focused on the modelling of the occurrence and reactivity of the carbonate radical in surface freshwater. The radical $CO_3^{-\bullet}$ can be produced from $^{\bullet}OH$ and CO_3^{2-} or HCO_3^- [16], from CO_3^{2-} and $^3DOM^*$ [17], and possibly also from irradiated Fe(III) oxides and CO_3^{2-} [18]:

$$^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\bullet}$$

$$[k_1 = 3.9 \times 10^8 \, M^{-1} \, s^{-1}] \qquad (1)$$

$$^{\bullet}OH + HCO_3^- \rightarrow H_2O + CO_3^{-\bullet}$$

$$[k_2 = 8.5 \times 10^6 \, M^{-1} \, s^{-1}] \qquad (2)$$

$$^3DOM^* + CO_3^{2-} \rightarrow DOM^{-\bullet} + CO_3^{-\bullet}$$

$$[k_3 \approx 1 \times 10^5 \, M^{-1} \, s^{-1}] \qquad (3)$$

The radical $CO_3^{-\bullet}$ is less reactive than $^{\bullet}OH$ toward the degradation of organic compounds [16,19], but in surface freshwaters it is also scavenged by DOM to a lesser extent [17]. The consequence is that $CO_3^{-\bullet}$ can reach a higher steady-state concentration than the hydroxyl radical, which would compensate to a variable extent for the lower reactivity. It is generally believed that $CO_3^{-\bullet}$ can be an important sink for water-dissolved phenolates and sulphur-containing compounds [17].

2. The model for carbonate radicals in surface waters

The present model is based on the formation of $CO_3^{-\bullet}$ by $^{\bullet}OH$ and $^3DOM^*$ (reactions (1)–(3)), and on

its consumption by DOM itself (reaction (4)) and the pollutant(s) of interest.

$$DOM + CO_3^{-\bullet} \rightarrow DOM^{+\bullet} + CO_3^{2-}$$

$$[k_4 = 10^2 (mg \, C)^{-1} \, s^{-1}] \qquad (4)$$
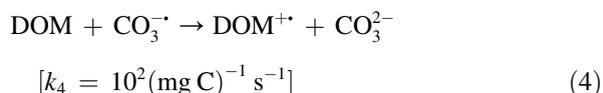
The main issue with reaction (4) is that there is some disagreement among the values of k_4 reported in the literature, either 40 [20] or 280 ± 90 [17] (mg C/L)$^{-1}$ s^{-1}. The value adopted in the present paper can be regarded as a reasonable estimate based on those figures. To apply the model, it is also necessary to know the second-order rate constant for the reaction of the pollutant with $CO_3^{-\bullet}$.

2.1. Production of $CO_3^{-\bullet}$ from $^{\bullet}OH$

As far as reactions (1) and (2) are concerned, it is essential to have an estimate of the formation rate of OH in the system ($R_{^{\bullet}OH}^{tot}$) in order to derive the formation rate of the carbonate radical, $R_{CO_3}-^{\bullet}$, from the concentration values of carbonate and bicarbonate. From the values of NPOC, $[NO_3^-]$ and $[NO_2^-]$ in the surface water layer, where most of the photochemical activity would occur [21], it is possible to derive the value of $R_{^{\bullet}OH}^{tot}$ (in mol s^{-1}) under 22 W m^{-2} sunlight UV irradiance in a water volume $V = Sd$ [22]. $S = 1.26 \times 10^{-3}$ m^2 is the surface of the photoreactor adopted in the irradiation experiments that have been the experimental basis of the $^{\bullet}OH$ model [22], and d is the water column depth best expressed as the average depth of the water body. All the calculations will be referred to the standard volume V (in litres), but it would be the same as referring them to the whole aquatic system. Another input datum for R_{OH}^{tot} would be the absorption spectrum $A_1(\lambda)$ of the water over the optical path length $b = 1$ cm. However, in case where the spectrum is not available it would be possible to approximately model it from the NPOC value, as [22]:

$$A_1(\lambda) = 0.45 \, NPOC \, e^{-0.015\lambda} \qquad (5)$$

Eq. (5) depends on NPOC because DOM is by far the main radiation absorber in surface waters in the very vast majority of the cases of environmental significance [23].

The formation rate of the carbonate radical, accounted for by $^{\bullet}OH$, is equal to $R_{^{\bullet}OH}^{tot}$ times the fraction of the hydroxyl radicals that react with carbonate and bicarbonate (Eq. 6). It is expressed in mol s^{-1} in the volume $V = Sd$ ($S = 1.26 \times 10^{-3}$ m^2; d = average depth of the water body):

$$R_{CO_3^-\cdot(\cdot OH)} = R_{\cdot OH}^{tot} \frac{8.5 \times 10^6 [HCO_3^-] + 3.9 \times 10^8 [CO_3^{2-}]}{5.0 \times 10^4 NPOC + 1.0 \times 10^{10} [NO_2^-] + 8.5 \times 10^6 [HCO_3^-] + 3.9 \times 10^8 [CO_3^{2-}]} \qquad (6)$$

The numerical values in Eq. (6) are the rate constants for the reaction between OH and carbonate, bicarbonate, DOM and nitrite [22]. Usually DOM is by far the main sink for $\cdot OH$ in surface freshwaters [10]. Table 1 reports the values of the chemical composition and those of $R_{\cdot OH}^{tot}$ and $R_{CO_3^-\cdot(\cdot OH)}$ for the case of four lakes and one river. The chemical composition is referred to the surface water layer because the photochemical reactions mostly occur within the first meter of the water column [21,22]. The water absorption spectrum was not available for the river, and it was simulated according to Eq. (5). The absorption spectra of the relevant surface water samples are reported in Fig. 1. The error bounds of the values in Table 1 are referred to those of $R_{\cdot OH}^{tot}$ as derived from the model reported in Ref. [22] ($\mu \pm \alpha$), modified according to the rules of error propagation.

2.2. Production of $CO_3^-\cdot$ from $^3DOM^*$

Canonica et al. [17] have quantified the generation rate of the carbonate radical from irradiated DOM and CO_3^{2-} in the surface layer (1 m) of Lake Greifensee (Switzerland, 47°N). In the presence of NPOC = 3.5 mg C L^{-1} and $[CO_3^{2-}] = 1 \times 10^{-5}$ M [24] one gets that the volumetric rate of formation of $CO_3^-\cdot$ by irradiated DOM is $R_{CO_3^-\cdot(DOM)} V^{-1} = 1 \times 10^{-14}$ M s^{-1} under noon summertime irradiation conditions [17]. With $S = 1.26 \times 10^{-3}$ m^2 and $d = 100$ cm one gets $V = Sd = 1.26$ L, and $R_{CO_3^-\cdot(DOM)} \approx 1.3 \times 10^{-14}$ mol s^{-1} as a consequence. Under noon summertime irradiation the UV irradiance of sunlight would be around 30 W m^{-2} [25], namely 1.4 times more intense than our model conditions. It is possible to model the absorption spectrum of the Greifensee water by means of Eq. (5) and the reported NPOC value. From these data one gets that the photon flux absorbed by DOM is $P_a^{DOM} = \int_\lambda q_{n,p}^0(\lambda)[1-10^{-A_1(\lambda)d}]d\lambda \approx 2.0 \times 10^{-7}$ einsteins^{-1} in the first meter of Lake Greifensee, where $d = 100$ cm and $q_{n,p}(\lambda)^0$ is the incident photon flux of sunlight, in einstein s^{-1} over the surface $S = 1.26 \times 10^{-3}$ m^2 [22]. It is reasonable to hypothesise that $R_{CO_3^-\cdot(DOM)} = 1.3 \times 10^{-14}$ mol s^{-1} is proportional to the product of P_a^{DOM} times $[CO_3^{2-}]$, from which one gets:

$$R_{CO_3-\cdot(DOM)} = 6.5 \times 10^{-3} [CO_3^{2-}] P_a^{DOM} \qquad (7)$$

The dependence of Eq. (7) on the irradiation intensity is taken into account in P_a^{DOM}, which is also reported in Table 1 for the samples under consideration. The total formation rate of $CO_3^-\cdot$ in a water system would be $R_{CO_3^-\cdot}^{tot} = R_{CO_3^-\cdot(\cdot OH)} + R_{CO_3^-\cdot(DOM)}$. It can be observed that $R_{CO_3^-\cdot(\cdot OH)} \gg R_{CO_3^-\cdot(DOM)}$ in all the cases (Table 1). It is also $R_{CO_3^-\cdot}^{tot} < R_{\cdot OH}^{tot}$, and the ratio $R_{\cdot OH}^{tot} (R_{CO_3^-\cdot}^{tot})^{-1}$ varies in the range from 6 to 175. However, once $CO_3^-\cdot$ is formed it is scavenged by DOM to a lesser extent compared with $\cdot OH$, and the reactivity of $CO_3^-\cdot$ could therefore be significant.

Also note that the formation rate of $CO_3^-\cdot$ in the systems under consideration might be higher in the case that the Fe(III) species were a significant source of the carbonate radical upon photo-oxidation of CO_3^{2-} [18]. However, the exact quantification of the Fe(III) contribution to $CO_3^-\cdot$ will require further studies, and for the moment that possible source will not be considered.

3. Modelling the reactivity of $CO_3^-\cdot$ in surface waters

The carbonate radical reaches a steady-state concentration in surface waters [17], which implies that the rate of formation $R_{CO_3^-\cdot}^{tot}$ is equal to that of consumption of $CO_3^-\cdot$, by DOM as the expected main scavenger (reaction (4)) and by the pollutant(s) that can be present in the system. Be P a pollutant molecule at molar concentration $[P]_0$, with rate constant $k_{P,CO_3^-\cdot}$ with $CO_3^-\cdot$ (in M^{-1} s^{-1}). The scavenging rate constant for $CO_3^-\cdot$ in the system would be $\Sigma_i k_{Si} [S_i] = k_4 NPOC + k_{P,CO_3^-\cdot} [P]_0$. In many cases $k_{P,CO_3^-\cdot} [P]_0 \ll k_4 NPOC$, and the value of $\Sigma_i k_{Si} [S_i]$ would be independent of $[P]_0$. In the most general case the degradation rate of P due to the carbonate radical ($R'_{P,CO_3^-\cdot}$, in M s^{-1}) will be (note that $V = Sd$, and that $R_{CO_3^-\cdot}^{tot}$ should be divided by V to have it in M s^{-1}):

$$R'_{P,CO_3^-\cdot} = -\frac{d[P]}{dt} = \frac{R_{CO_3^-\cdot}^{tot} \cdot V^{-1} k_{P,CO_3^-\cdot} [P]}{k_4 NPOC + k_{P,CO_3^-\cdot} [P]} \qquad (8)$$

Among the natural scavengers, low-molecular weight carboxylic acids (LMWAs) are expected to play an important role [26]. The most common

Table 1

Parameters of photochemical significance in the surface water systems under consideration. Note that d is the average depth, and $V = Sd$ is the volume of the water column with surface $S = 1.26 \times 10^{-3}$ m^2. The data in the lower section of the table were calculated based on those of the upper one. The four lakes (Avigliana Piccolo, Candia, Avigliana Grande and Rouen) are all located in NW Italy [22], the Blue Earth River is in Minnesota [10]. In the latter case the concentration of nitrite, not reported, was not considered. Standard sunlight UV irradiance was 22 W m^{-2}. SSD means summer sunny days equivalent to 15 July at 45°N latitude. The conditions in which $CO_3^{-\bullet}$ prevails over $^\bullet OH$ as reactive species are highlighted in bold italic, the reverse case is reported in normal font.

|		Av. Piccolo	Candia	Av. Grande	Rouen	Blue Earth River
NPOC (mg C L^{-1})		5.1	5.4	5.0	0.63	4.2
NO_3^- (M)		1.9×10^{-5}	1.6×10^{-6}	9.6×10^{-6}	1.9×10^{-5}	6.3×10^{-4}
NO_2^- (M)		1.2×10^{-6}	1.5×10^{-7}	1.4×10^{-6}	3.7×10^{-7}	
HCO_3^- (M)		4.0×10^{-4}	1.1×10^{-3}	3.6×10^{-3}	2.4×10^{-5}	2.2×10^{-3}
CO_3^{2-} (M)		1.1×10^{-6}	6.1×10^{-6}	4.8×10^{-5}	2.4×10^{-9}	3.7×10^{-5}
d (m)		7.7	5.9	19.5	2.0	3
V (L)		9.7	7.4	24.6	2.5	4
P_a^{DOM} (einstein s^{-1})		3.2×10^{-7}	2.5×10^{-7}	3.2×10^{-7}	2.2×10^{-7}	2.6×10^{-7}
$R_{^\bullet OH}^{tot}$ (mol s^{-1})		$(4.1 \pm 0.5) \times 10^{-11}$	$(2.4 \pm 0.2) \times 10^{-11}$	$(8.4 \pm 0.4) \times 10^{-11}$	$(3.5 \pm 0.3) \times 10^{-11}$	$(1.5 \pm 0.1) \times 10^{-10}$
$R_{CO_3^{-\bullet}\,(^\bullet OH)}$ (mol s^{-1})		$(5.8 \pm 0.7) \times 10^{-13}$	$(1.0 \pm 0.1) \times 10^{-12}$	$(1.3 \pm 0.1) \times 10^{-11}$	$(2.0 \pm 0.2) \times 10^{-13}$	$(2.1 \pm 0.2) \times 10^{-11}$
$R_{CO_3^{-\bullet}\,(DOM)}$ (mol s^{-1})		2.3×10^{-15}	1.0×10^{-14}	1.0×10^{-13}	3.4×10^{-18}	6.2×10^{-14}
$R_{CO_3^{-\bullet}}^{tot}$ (mol s^{-1})		$(5.8 \pm 0.7) \times 10^{-13}$	$(1.0 \pm 0.1) \times 10^{-12}$	$(1.3 \pm 0.1) \times 10^{-11}$	$(2.0 \pm 0.2) \times 10^{-13}$	$(2.1 \pm 0.2) \times 10^{-11}$
$(\Sigma_i k_{Si} [S_i])_{^\bullet OH}$ (s^{-1})		2.7×10^{5}	2.8×10^{5}	3.2×10^{5}	3.5×10^{4}	2.4×10^{5}
Diuron	$(t_{1/2}^{P,CO_3^{-\bullet}})_{SSD}$	$(2.1 \pm 0.3) \times 10^{4}$	$(9.7 \pm 1.0) \times 10^{3}$	$(2.3 \pm 0.1) \times 10^{3}$	$(1.9 \pm 0.2) \cdot 10^{3}$	$(1.9 \pm 0.2) \cdot 10^{2}$
	$(t_{1/2}^{P,^\bullet OH})_{SSD}$	$(2.5 \pm 0.3) \times 10^{2}$	$(3.4 \pm 0.3) \times 10^{2}$	$(3.6 \pm 0.2) \times 10^{2}$	9.7 ± 1.0	25 ± 2
Atrazine	$(t_{1/2}^{P,CO_3^{-\bullet}})_{SSD}$	$(4.1 \pm 0.5) \times 10^{4}$	$(1.9 \pm 0.2) \times 10^{4}$	$(4.6 \pm 0.2) \times 10^{3}$	$(3.8 \pm 0.4) \times 10^{3}$	$(3.9 \pm 0.4) \times 10^{2}$
	$(t_{1/2}^{P,^\bullet OH})_{SSD}$	$(4.1 \pm 0.5) \times 10^{2}$	$(5.6 \pm 0.5) \times 10^{2}$	$(6.1 \pm 0.3) \times 10^{2}$	16 ± 2	41 ± 4
Aniline	$(t_{1/2}^{P,CO_3^{-\bullet}})_{SSD}$	$(3.3 \pm 0.4) \times 10^{2}$	$(1.6 \pm 0.2) \times 10^{2}$	*37 ± 2*	31 ± 3	*3.1 ± 0.3*
	$(t_{1/2}^{P,^\bullet OH})_{SSD}$	89 ± 11	$(1.2 \pm 0.1) \times 10^{2}$	*(1.3 ± 0.1) × 10^2*	3.5 ± 0.3	*8.9 ± 0.9*
Phenolate	$(t_{1/2}^{P,CO_3^{-\bullet}})_{SSD}$	$(6.6 \pm 0.8) \times 10^{2}$	$(3.1 \pm 0.3) \times 10^{2}$	*73 ± 3*	61 ± 6	*6.2 ± 0.6*
	$(t_{1/2}^{P,^\bullet OH})_{SSD}$	$(1.3 \pm 0.2) \times 10^{2}$	$(1.7 \pm 0.2) \times 10^{2}$	*(1.9 ± 0.1) × 10^2*	5.1 ± 0.5	*13 ± 1*
4-Hydroxybenzoate	$(t_{1/2}^{P,CO_3^{-\bullet}})_{SSD}$	$(1.7 \pm 0.2) \times 10^{3}$	$(7.8 \pm 0.8) \times 10^{2}$	*(1.8 ± 0.1) × 10^2*	$(1.5 \pm 0.2) \times 10^{2}$	16 ± 2
	$(t_{1/2}^{P,^\bullet OH})_{SSD}$	$(1.5 \pm 0.2) \times 10^{2}$	$(2.0 \pm 0.2) \times 10^{2}$	*(2.1 ± 0.1) × 10^2*	5.7 ± 0.6	15 ± 1
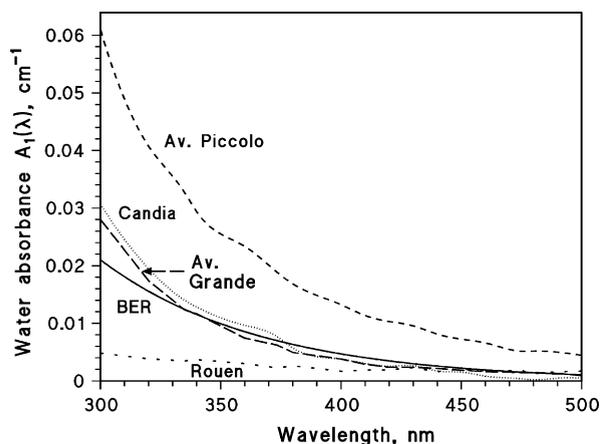
Fig. 1. Absorption spectra of the surface water samples, the data of which are reported in Table 1. In the case of the Blue Earth River (BER) the spectrum (not available) was simulated according to Eq. (5).

LMWA is formate, which can reach μM levels in surface waters [27] and is for instance the main $^{\bullet}$OH scavenger among LMWA in cloud water [28]. Given the reaction rate constants of formate with $^{\bullet}$OH (3.2×10^9 M^{-1} s^{-1} [16]) and CO$_3^{\bullet}$ (1.5×10^5 M^{-1} s^{-1} [19]), in the presence of 1 mg C L^{-1} NPOC one can expect that 1 μM formate would account for about 5−10% of the $^{\bullet}$OH scavenging by DOM, and for less than 0.5% of the scavenging of CO$_3^{\bullet}$. The integration of Eq. (8) between $[P]_0$ and 1/2 $[P]_0$, and between 0 and $t_{1/2}$ yields the following result for the half-life time of P (in seconds if V is in litres):

$$t_{1/2}^{P,\mathrm{CO_3^-}} = \frac{[P]_0 V}{2 R_{\mathrm{CO_3^-}}^{\mathrm{tot}}} + 0.693 \frac{k_4 \, \mathrm{NPOC} \, V}{R_{\mathrm{CO_3^-}}^{\mathrm{tot}} \cdot k_{P,\mathrm{CO_3^-}}} \quad (9)$$

Indeed if $k_{P,\mathrm{CO_{3-}}}$. $[P]_0 \ll k_4$ NPOC, the value of $t_{1/2}^{P,\mathrm{CO_{3-}}}$ would be independent of $[P]_0$. The result of Eq. (9) is valid for continuous irradiation under 22 W m^{-2} sunlight UV irradiance. However, the intensity of sunlight is not constant. It has been observed that the energy emitted by constant irradiation for 10 h at 22 W m^{-2} UV irradiance is equivalent to that reaching the ground on a summer sunny day (15 July) at 45°N latitude [29]. It is, therefore, possible to obtain $t_{1/2}^{P,\mathrm{CO_3^-}}$ in summer sunny day (SSD) equivalents by dividing its value in seconds by 10 h = 3.6×10^4 s.

$$(t_{1/2}^{P,\mathrm{CO_3^-}})_{\mathrm{SSD}} = 2.8 \times 10^{-5} \left(\frac{[P]_0 V}{2 R_{\mathrm{CO_3^-}}^{\mathrm{tot}}} \right.$$
$$\left. + 0.693 \frac{k_4 \, \mathrm{NPOC} \, V}{R_{\mathrm{CO_3^-}}^{\mathrm{tot}} \cdot k_{P,\mathrm{CO_3^-}}} \right) \quad (10)$$

The reported model was applied to five substrates (diuron, atrazine, aniline, phenolate, 4-hydroxybenzoate), for which the reaction rate constants with the carbonate radical are known and reported in Table 2. Table 2 also reports the rate constants for the reaction with $^{\bullet}$OH, and it is interesting to observe that the ratio $k_{P,^{\bullet}\mathrm{OH}}$ $(k_{P,\mathrm{CO_3}}-^{\bullet})^{-1}$ varies from 800 for the least reactive compound (atrazine) to 28 for the most reactive one (aniline).

The data of $(t_{1/2}^{P,\mathrm{CO_3^-}})_{\mathrm{SSD}}$ for the five substrates, relevant to the different water bodies, are reported in Table 1, with $[P]_0 = 1 \times 10^{-9}$ M for each substrate. The half-life times (in summer sunny day equivalents) due to reaction with the carbonate radical would vary from 3 days for aniline in the Blue Earth River, to 4×10^4 days for atrazine in Lake Avigliana Piccolo.

The results for the carbonate radical are compared with those of a corresponding model for $^{\bullet}$OH, for which the half-life time of P in SSD equivalents is given by:

$$(t_{1/2}^{P,^{\bullet}\mathrm{OH}})_{\mathrm{SSD}} = 2.8 \times 10^{-5} \left(\frac{[P]_0 V}{2 R_{^{\bullet}\mathrm{OH}}^{\mathrm{tot}}} + 0.693 \frac{(\Sigma_i k_{\mathrm{Si}} [S_i])_{^{\bullet}\mathrm{OH}} V}{R_{^{\bullet}\mathrm{OH}}^{\mathrm{tot}} k_{P,^{\bullet}\mathrm{OH}}} \right) \quad (11)$$

Table 1 reports the $^{\bullet}$OH scavenging rate constant $(\Sigma_i k_{\mathrm{Si}} [S_i])_{^{\bullet}\mathrm{OH}}$ for the surface water bodies under consideration [22], and the values of $(t_{1/2}^{P,^{\bullet}\mathrm{OH}})_{\mathrm{SSD}}$ calculated with Eq. (11) and $[P]_0 = 1 \times 10^{-9}$ M. Also, in this case, a wide variability is estimated (from 3 to 600 days), albeit lower than for the case of CO$_3^{\bullet}$. The comparison between $(t_{1/2}^{P,\mathrm{CO_3^-}})_{\mathrm{SSD}}$ and $(t_{1/2}^{P,^{\bullet}\mathrm{OH}})_{\mathrm{SSD}}$ for the same substrate and the same aquatic system indicates that the hydroxyl radical would be more important as reactive species for degradation in 20 cases out of 25. In the other cases the carbonate radical would account for a higher reactivity and, what is most important, they are all cases in which photochemistry is expected to be a significant removal pathway. Actually, a half-life time in the 10^3–10^4 day range means that the relevant pathway(s) would play a negligible role in the degradation of the substrate, other routes being more important. Indeed, out of the 11 cases in which at least one of the two $t_{1/2}$ values (relative to CO$_3^{\bullet}$ and/or $^{\bullet}$OH) is lower than 100 days, therefore, pointing to a significant radical reactivity, in 5 of these the carbonate radical is a more important reactive species than $^{\bullet}$OH.

Very interestingly, for CO$_3^{\bullet}$ to prevail over $^{\bullet}$OH as reactive species, the combination of a water body rich of carbonate/bicarbonate (as Lake Avigliana Grande and the Blue Earth River in the present case) and an easily oxidisable substrate is required, which would be

Table 2
Comparison between our model, applied to the first meter of the Lake Greifensee (Switzerland), and the data derived from Ref. [17]. In the column of our model it was adopted 22 W m^{-2} sunlight UV irradiance, and 30 W m^{-2} in that of Ref. [17]. In the latter case the half-life time (in SSD) was calculated as: $t_{1/2} = 0.693 \, (2.6 \times 10^4 \, k_{P,CO_3}-^\bullet \, [CO_3^{-\bullet}])^{-1}$. The conversion factor compensates for the different irradiation intensities. For our model it was adopted eq.(10). The value of $[CO_3^{-\bullet}]$ was derived from the literature estimate of $R_{CO_3}-^{\bullet tot} \, V^{-1}$ [17], and from the rate of scavenging of the carbonate radical by DOM (reaction (4)). Only the entries required by each model have been inserted as data in the table. The main difference between our model and the approach of Ref. [17] is that in the latter case the contribution of nitrate only to $^\bullet$OH photoproduction has been taken into account [17,24]. By doing the same with our model one obtains the $t_{1/2}$ data reported in brackets. The table also reports the reaction rate constants of five organic compounds with the radicals $CO_3^{-\bullet}$ and $^\bullet$OH, together with the corresponding literature references.

Lake Greifensee ([17], [25])			Present model	Ref. [17]
NPOC (mg C L^{-1})			3.5	3.5
NO_3^- (M)			1×10^{-4}	1×10^{-4}
HCO_3^- (M)			2×10^{-3}	2×10^{-3}
CO_3^{2-} (M)			1×10^{-5}	1×10^{-5}
d (m)			1	1
V (L)			1.26	
P_a^{DOM} (einstein s^{-1})			1.5×10^{-7}	
$R_{^\bullet OH}^{tot}$ (mol s^{-1})			2.7×10^{-11} (1.6×10^{-11})	
$R_{CO_3}-^\bullet(^\bullet OH)$ (mol s^{-1})			3.3×10^{-12}	
$R_{CO_3}-^\bullet(DOM)$ (mol s^{-1})			1.0×10^{-14}	
$R_{CO_3}-^{\bullet tot}$ (mol s^{-1})			2.8×10^{-12} (1.7×10^{-12})	
$R_{CO_3}-^{\bullet tot} \, V^{-1}$ (M s^{-1})				2×10^{-12}
$(\Sigma_i k_{Si} [S_i]) \cdot_{OH}$ (s^{-1})			2×10^5	
$[CO_3^{-\bullet}]$, M				6×10^{-15}
Diuron, $(t_{1/2}^{P,CO_3-^\bullet})_{SSD}$	$k_{P,CO_3}-^\bullet = 8 \times 10^6$ M^{-1} s^{-1} [17]	$k_{P,^\bullet OH} = 5 \times 10^9$ M^{-1} s^{-1} [30]	300 (500)	560
Atrazine, $(t_{1/2}^{P,CO_3-^\bullet})_{SSD}$	$k_{P,CO_3}-^\bullet = 4 \times 10^6$ M^{-1} s^{-1} [17]	$k_{P,^\bullet OH} = 3 \times 10^9$ M^{-1} s^{-1} [31]	600 (980)	1100
Aniline, $(t_{1/2}^{P,CO_3-^\bullet})_{SSD}$	$k_{P,CO_3}-^\bullet = 5 \times 10^8$ M^{-1} s^{-1} [19]	$k_{P,^\bullet OH} = 1.4 \times 10^{10}$ M^{-1} s^{-1} [16]	4.8 (8.0)	8
Phenolate, $(t_{1/2}^{P,CO_3-^\bullet})_{SSD}$	$k_{P,CO_3}-^\bullet = 2.5 \times 10^8$ M^{-1} s^{-1} [19]	$k_{P,^\bullet OH} = 9.6 \cdot 10^9$ M^{-1} s^{-1} [16]	9.7 (16)	18
4-Hydroxybenzoate, $(t_{1/2}^{P,CO_3-^\bullet})_{SSD}$	$k_{P,CO_3}-^\bullet = 1 \times 10^8$ M^{-1} s^{-1} [19]	$k_{P,^\bullet OH} = 8.5 \times 10^9$ M^{-1} s^{-1} [16]	25 (41)	42

significantly reactive toward both $CO_3^{-\bullet}$ and $^\bullet$OH (e.g. atrazine, phenolate, 4-hydroxybenzoate).

4. Conclusions

The model that was developed for the reactivity of the carbonate radical toward target compounds in surface waters shows that the chemistry of $CO_3^{-\bullet}$, compared to that of $^\bullet$OH, can be in some cases in which the radical reactions would be expected to play a significant role. For $CO_3^{-\bullet}$ to play an important role one needs a carbonate-rich water and a reactive substrate. The application of the model to the reactivity of both $^\bullet$OH and $CO_3^{-\bullet}$ would be of great help in the assessment of the exposure of aquatic ecosystems and human communities to water-dissolved pollutants. Note that the actual lifetimes in water bodies could be significantly lower because of the presence of additional transformation pathways, including reaction with ^{3}DOM*.

Table 2 reports a comparison between our model and the approach adopted in Ref. [17] to account for the production of $CO_3^{-\bullet}$ in the first meter of Lake Greifensee (Switzerland). The main difference between our model and the calculations of Ref. [17] is that, in the latter case, nitrate was considered to be the only source of $^\bullet$OH. According to our model nitrate would account for 60% of the $^\bullet$OH generation in that system, the remainder being attributable to DOM. If one considers nitrate as the sole source of $^\bullet$OH in our model also, the results (in brackets, Table 2) for the calculated half-life times of diuron, atrazine, aniline, phenolate and 4-hydroxybenzoate are in very reasonable agreement with those derived from the literature data of $R_{CO_3}-^\bullet \, V^{-1}$ [17].

Acknowledgements

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