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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 toward the degradation of easily oxidisable molecules.

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 $^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$, $^{\bullet}NO_2$, 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 exceptions to the scavenging by DOM are the cases of $^1O_2$ and $^{\bullet}NO_2$, 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].

$$^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\bullet} \qquad [k_1 = 3.9\times10^8\ M^{-1}\ s^{-1}] \qquad (1)$$

$$^{\bullet}OH + HCO_3^- \rightarrow H_2O + CO_3^{-\bullet} \qquad [k_2 = 8.5\times10^6\ M^{-1}\ s^{-1}] \qquad (2)$$

$$^3DOM^* + CO_3^{2-} \rightarrow DOM^{-\bullet} + CO_3^{-\bullet} \qquad [k_3 \approx 1\times10^5\ M^{-1}\ s^{-1}] \qquad (3)$$

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.

$$DOM + CO_3^{-\bullet} \rightarrow DOM^{+\bullet} + CO_3^{2-} \qquad [k_4 = 10^2\ (mg\ C)^{-1}\ s^{-1}] \qquad (4)$$

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, 2) are concerned, it is essential to have an estimate of the formation rate of $^{\bullet}OH$ in the system ($R_{\bullet OH}^{tot}$) in order to derive the formation rate of the carbonate radical, $R_{CO3-\bullet}$, 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 = S d [22]. $S = 1.26\times10^{-3}$ 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 $R_{\bullet OH}^{tot}$ would be the absorption spectrum $A_1(\lambda)$ of the water over the optical path length b = 1 cm. However, in case the spectrum is not available it would be possible to approximately model it from the NPOC value, as [22]:

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

Equation (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. It is expressed in mol s^{-1} in the volume V = S d ($S = 1.26\times10^{-3}$ m^2; d = average depth of the water body).

$$R_{CO3-\bullet(\bullet OH)} = R_{\bullet OH}^{tot} \cdot \frac{8.5\cdot10^{6}\cdot[HCO_3^-] + 3.9\cdot10^{8}\cdot[CO_3^{2-}]}{5.0\cdot10^{4}\cdot \mathrm{NPOC} + 1.0\cdot10^{10}\cdot[NO_2^-] + 8.5\cdot10^{6}\cdot[HCO_3^-] + 3.9\cdot10^{8}\cdot[CO_3^{2-}]} \qquad (6)$$

The numerical values in equation (6) are the rate constants for the reaction between $^{\bullet}OH$ and carbonate, bicarbonate, DOM and nitrite [22]. Usually DOM is by far the main sink for $^{\bullet}OH$ in surface freshwaters [10]. Table 1 reports the values of the chemical composition and those of $R_{\bullet OH}^{tot}$ and $R_{CO3-\bullet(\bullet OH)}$ 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 equation (5). The absorption spectra of the relevant surface water samples are reported in Figure 1. The error bounds of the values in Table 1 are referred to those of $R_{\bullet OH}^{tot}$ as derived from the model reported in [22], modified according to the rules of error propagation.

2.2. Production of $CO_3^{-\bullet}$ 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 $[CO_3^{2-}] = 1\cdot 10^{-5}$ M [24] one gets that the volumetric rate of formation of $CO_3^{-\bullet}$ by irradiated DOM is $R_{CO3-\bullet(DOM)}\ V^{-1} = 1\cdot 10^{-14}$ 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 = S d = 1.26 L, and $R_{CO3-\bullet(DOM)} \approx 1.3\cdot 10^{-14}$ 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 equation (5) and the reported NPOC value. From these data one gets that the photon flux absorbed by DOM is $P_a^{DOM} = \int_{\lambda} q_{n,p}^0(\lambda)\cdot \left[1-10^{-A_1(\lambda)\cdot d}\right]\, d\lambda \approx 2.0\cdot 10^{-7}$ einstein s^{-1} in the first meter of Lake Greifensee, where d = 100 cm and $q^0_{n,p}(\lambda)$ 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 $R_{CO3-\bullet(DOM)} = 1.3\cdot 10^{-14}$ mol s^{-1} is proportional to the product of P_a^{DOM} times $[CO_3^{2-}]$, from which one gets equation (7):

$$R_{CO3-\bullet(DOM)} = 6.5\cdot 10^{-3}\cdot [CO_3^{2-}]\cdot P_a^{DOM} \qquad (7)$$

The dependence of equation (7) from 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 $CO_3^{-\bullet}$ in a water system would be $R_{CO3-\bullet}^{tot} = R_{CO3-\bullet(\bullet OH)} + R_{CO3-\bullet(DOM)}$. It can be observed that $R_{CO3-\bullet(\bullet OH)} \gg R_{CO3-\bullet(DOM)}$ in all the cases (Table 1). It is also $R_{CO3-\bullet}^{tot} < R_{\bullet OH}^{tot}$, and the ratio $R_{\bullet OH}^{tot}\ (R_{CO3-\bullet}^{tot})^{-1}$ varies in the range from 6 to 175. However, once $CO_3^{-\bullet}$ is formed it is scavenged by DOM to a lesser extent compared with $^\bullet$OH, and the reactivity of $CO_3^{-\bullet}$could therefore be significant.

Also note that the formation rate of $CO_3^{-\bullet}$ 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 $CO_3^{-\bullet}$ will require further studies, and for the moment that possible source will not be considered.

3. Modelling the reactivity of $CO_3^{-\bullet}$ in surface waters

The carbonate radical reaches a steady-state concentration in surface waters [17], which implies that the rate of formation $R_{CO3-\bullet}^{tot}$ is equal to that of consumption of $CO_3^{-\bullet}$, 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 $k_{P,CO3-\bullet}$ with $CO_3^{-\bullet}$ (in M^{-1} s^{-1}). The scavenging rate constant for $CO_3^{-\bullet}$ in the system would be $\Sigma_i\ k_{Si}\ [S_i] = k_4\ NPOC + k_{P,CO3-\bullet}\ [P]_0$. In many cases $k_{P,CO3-\bullet}\ [P]_0 \ll k_4\ NPOC$, 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 ($R'_{P,CO3-\bullet}$, in M s^{-1}) will be (note that V = S d, and that $R_{CO3-\bullet}^{tot}$ should be divided by V to have it in M s^{-1}):

$$R'_{P,CO3-\bullet} = -\frac{d[P]}{dt} = \frac{R_{CO3-\bullet}^{tot} \cdot V^{-1} \cdot k_{P,CO3-\bullet} \cdot [P]}{k_4 \cdot NPOC + k_{P,CO3-\bullet} \cdot [P]} \qquad (8)$$

Among the natural scavengers, low-molecular weight carboxylic acids (LMWA) are expected to play an important role [26]. The most common 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 equation (8) between $[P]_0$ and ½ $[P]_0$, and between 0 and $t_{½}$ yields the following result for the half-life time of P (in seconds if V is in litres):

$$t_{1/2}^{P,CO3-\bullet} = \frac{[P]_0 \cdot V}{2 \cdot R_{CO3-\bullet}^{tot}} + 0.693 \cdot \frac{k_4 \cdot NPOC \cdot V}{R_{CO3-\bullet}^{tot} \cdot k_{P,CO3-\bullet}} \qquad (9)$$

Indeed if $k_{P,CO3-\bullet}\ [P]_0 \ll k_4\ NPOC$, the value of $t_{½}^{P,CO3-\bullet}$ would be independent of $[P]_0$. The result of equation (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 $t_{½}^{P,CO3-\bullet}$ in summer sunny day equivalents (SSD) by dividing its value in seconds by 10 h = $3.6\cdot10^4$ s.

$$\left(t_{1/2}^{P,CO3-\bullet}\right)_{SSD} = 2.8\cdot 10^{-5}\cdot\left(\frac{[P]_0\cdot V}{2\cdot R_{CO3-\bullet}^{tot}} + 0.693\cdot\frac{k_4\cdot NPOC\cdot V}{R_{CO3-\bullet}^{tot}\cdot k_{P,CO3-\bullet}}\right) \qquad (10)$$

The reported model was applied to 5 substrates (diuron, atrazine, aniline, phenolate, 4-hydroxybenzoate), for which the reaction rate constants with the carbonate radical are known and reported in Table 2. The Table 2 also reports the rate constants for the reaction with $^{\bullet}OH$, and it is interesting to observe that the ratio $k_{P,\bullet OH}$ $(k_{P,CO3-\bullet})^{-1}$ varies from 800 for the least reactive compound (atrazine) to 28 for the most reactive one (aniline).

The data of $(t_{½}^{P,CO3-\bullet})_{SSD}$ for the five substrates, relevant to the different water bodies are reported in Table 1, with $[P]_0 = 1\cdot 10^{-9}$ 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 $4\cdot 10^4$ 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:

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

Table 1 reports the $^{\bullet}OH$ scavenging rate constant $(\Sigma_i\ k_{Si}\ [S_i])_{\bullet OH}$ for the surface water bodies under consideration [22], and the values of $(t_{½}^{P,\bullet OH})_{SSD}$ calculated with equation (11) and $[P]_0 = 1\cdot 10^{-9}$ 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 $(t_{½}^{P,CO3-\bullet})_{SSD}$ and $(t_{½}^{P,\bullet OH})_{SSD}$ 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 $t_{½}$ 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, it is required 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, which would be 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 significant 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 for 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 $^3DOM^*$.

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 $R_{CO3-\bullet}\ V^{-1}$ [17].

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Table 1. Parameters of photochemical significance in the surface water systems under consideration. Note that d is the average depth, and V = S d is the volume of the water column with surface $S = 1.26\times10^{-3}$ 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})		$3.2\cdot10^{-7}$	$2.5\cdot10^{-7}$	$3.2\cdot10^{-7}$	$2.2\cdot10^{-7}$	$2.6\cdot10^{-7}$
$R_{\bullet OH}^{tot}$ (mol s^{-1})		$(4.1\pm0.5)\cdot10^{-11}$	$(2.4\pm0.2)\cdot10^{-11}$	$(8.4\pm0.4)\cdot10^{-11}$	$(3.5\pm0.3)\cdot10^{-11}$	$(1.5\pm0.1)\cdot10^{-10}$
$R_{CO3-\bullet(\bullet OH)}$ (mol s^{-1})		$(5.8\pm0.7)\cdot10^{-13}$	$(1.0\pm0.1)\cdot10^{-12}$	$(1.3\pm0.1)\cdot10^{-11}$	$(2.0\pm0.2)\cdot10^{-13}$	$(2.1\pm0.2)\cdot10^{-11}$
$R_{CO3-\bullet(DOM)}$ (mol s^{-1})		$2.3\cdot10^{-15}$	$1.0\cdot10^{-14}$	$1.0\cdot10^{-13}$	$3.4\cdot10^{-18}$	$6.2\cdot10^{-14}$
$R_{CO3-\bullet}^{tot}$ (mol s^{-1})		$(5.8\pm0.7)\cdot10^{-13}$	$(1.0\pm0.1)\cdot10^{-12}$	$(1.3\pm0.1)\cdot10^{-11}$	$(2.0\pm0.2)\cdot10^{-13}$	$(2.1\pm0.2)\cdot10^{-11}$
$(\Sigma_i k_{Si} [S_i])_{\bullet OH}$ (s^{-1})		$2.7\cdot10^5$	$2.8\cdot10^5$	$3.2\cdot10^5$	$3.5\cdot10^4$	$2.4\cdot10^5$
Diuron	**$(t_{½}^{P,CO3-\bullet})_{SSD}$**	$(2.1\pm0.3)\cdot10^4$	$(9.7\pm1.0)\cdot10^3$	$(2.3\pm0.1)\cdot10^3$	$(1.9\pm0.2)\cdot10^3$	$(1.9\pm0.2)\cdot10^2$
	$(t_{½}^{P,\bullet OH})_{SSD}$	$(2.5\pm0.3)\cdot10^2$	$(3.4\pm0.3)\cdot10^2$	$(3.6\pm0.2)\cdot10^2$	9.7 ± 1.0	25 ± 2
Atrazine	**$(t_{½}^{P,CO3-\bullet})_{SSD}$**	$(4.1\pm0.5)\cdot10^4$	$(1.9\pm0.2)\cdot10^4$	$(4.6\pm0.2)\cdot10^3$	$(3.8\pm0.4)\cdot10^3$	$(3.9\pm0.4)\cdot10^2$
	$(t_{½}^{P,\bullet OH})_{SSD}$	$(4.1\pm0.5)\cdot10^2$	$(5.6\pm0.5)\cdot10^2$	$(6.1\pm0.3)\cdot10^2$	16 ± 2	41 ± 4
Aniline	**$(t_{½}^{P,CO3-\bullet})_{SSD}$**	$(3.3\pm0.4)\cdot10^2$	$(1.6\pm0.2)\cdot10^2$	***37 ± 2***	31 ± 3	***3.1 ± 0.3***
	$(t_{½}^{P,\bullet OH})_{SSD}$	89 ± 11	$(1.2\pm0.1)\cdot10^2$	***$(1.3\pm0.1)\cdot10^2$***	3.5 ± 0.3	***8.9 ± 0.9***
Phenolate	**$(t_{½}^{P,CO3-\bullet})_{SSD}$**	$(6.6\pm0.8)\cdot10^2$	$(3.1\pm0.3)\cdot10^2$	***73 ± 3***	61 ± 6	***6.2 ± 0.6***
	$(t_{½}^{P,\bullet OH})_{SSD}$	$(1.3\pm0.2)\cdot10^2$	$(1.7\pm0.2)\cdot10^2$	***$(1.9\pm0.1)\cdot10^2$***	5.1 ± 0.5	***13 ± 1***
4-Hydroxy benzoate	**$(t_{½}^{P,CO3-\bullet})_{SSD}$**	$(1.7\pm0.2)\cdot10^3$	$(7.8\pm0.8)\cdot10^2$	***$(1.8\pm0.1)\cdot10^2$***	$(1.5\pm0.2)\cdot10^2$	16 ± 2
	$(t_{½}^{P,\bullet OH})_{SSD}$	$(1.5\pm0.2)\cdot10^2$	$(2.0\pm0.2)\cdot10^2$	***$(2.1\pm0.1)\cdot10^2$***	5.7 ± 0.6	15 ± 1

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 Reference [17]. In the latter case the half-life time (in SSD) was calculated as: $t_{½} = 0.693\ (2.6\cdot 10^4\ k_{P,CO3-\bullet}\ [CO_3^{-\bullet}])^{-1}$. The conversion factor compensates for the different irradiation intensity. For our model it was adopted equation (10). The value of $[CO_3^{-\bullet}]$ was derived from the literature estimate of $R_{CO3-\bullet}^{tot}\ V^{-1}$ [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 $t_{½}$ 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**	**Reference [17]**
NPOC (mg C L^{-1})		3.5	3.5
NO_3^- (M)		$1\cdot10^{-4}$	$1\cdot10^{-4}$
HCO_3^- (M)		$2\cdot10^{-3}$	$2\cdot10^{-3}$
CO_3^{2-} (M)		$1\cdot10^{-5}$	$1\cdot10^{-5}$
d (m)		1	1
V (L)		1.26	
P_a^{DOM} (einstein s^{-1})		$1.5\cdot10^{-7}$	
$R_{\bullet OH}^{tot}$ (mol s^{-1})		$2.7\cdot10^{-11}$ $(1.6\cdot10^{-11})$	
$R_{CO3-\bullet(\bullet OH)}$ (mol s^{-1})		$3.3\cdot10^{-12}$	
$R_{CO3-\bullet(DOM)}$ (mol s^{-1})		$1.0\cdot10^{-14}$	
$R_{CO3-\bullet}^{tot}$ (mol s^{-1})		$2.8\cdot10^{-12}$ $(1.7\cdot10^{-12})$	
$R_{CO3-\bullet}^{tot}\ V^{-1}$ (M s^{-1})			$2\cdot10^{-12}$
$(\Sigma_i\ k_{Si}\ [S_i])_{\bullet OH}$ (s^{-1})		$2\cdot10^{5}$	
$[CO_3^{-\bullet}]$, M			$6\cdot10^{-15}$
Diuron, $(t_{½}^{P,CO3-\bullet})_{SSD}$	$k_{P,CO3-\bullet} = 8\cdot10^6\ M^{-1}\ s^{-1}$ [17] $k_{P,\bullet OH} = 5\cdot10^9\ M^{-1}\ s^{-1}$ [30]	300 (500)	560
Atrazine, $(t_{½}^{P,CO3-\bullet})_{SSD}$	$k_{P,CO3-\bullet} = 4\cdot10^6\ M^{-1}\ s^{-1}$ [17] $k_{P,\bullet OH} = 3\cdot10^9\ M^{-1}\ s^{-1}$ [31]	600 (980)	1100
Aniline, $(t_{½}^{P,CO3-\bullet})_{SSD}$	$k_{P,CO3-\bullet} = 5\cdot10^8\ M^{-1}\ s^{-1}$ [17] $k_{P,\bullet OH} = 1.4\cdot10^{10}\ M^{-1}\ s^{-1}$ [16]	4.8 (8.0)	8
Phenolate, $(t_{½}^{P,CO3-\bullet})_{SSD}$	$k_{P,CO3-\bullet} = 2.5\cdot10^8\ M^{-1}\ s^{-1}$ [17] $k_{P,\bullet OH} = 9.6\cdot10^9\ M^{-1}\ s^{-1}$ [16]	9.7 (16)	18
4-Hydroxybenzoate, $(t_{½}^{P,CO3-\bullet})_{SSD}$	$k_{P,CO3-\bullet} = 1\cdot10^8\ M^{-1}\ s^{-1}$ [17] $k_{P,\bullet OH} = 8.5\cdot10^9\ M^{-1}\ s^{-1}$ [16]	25 (41)	42

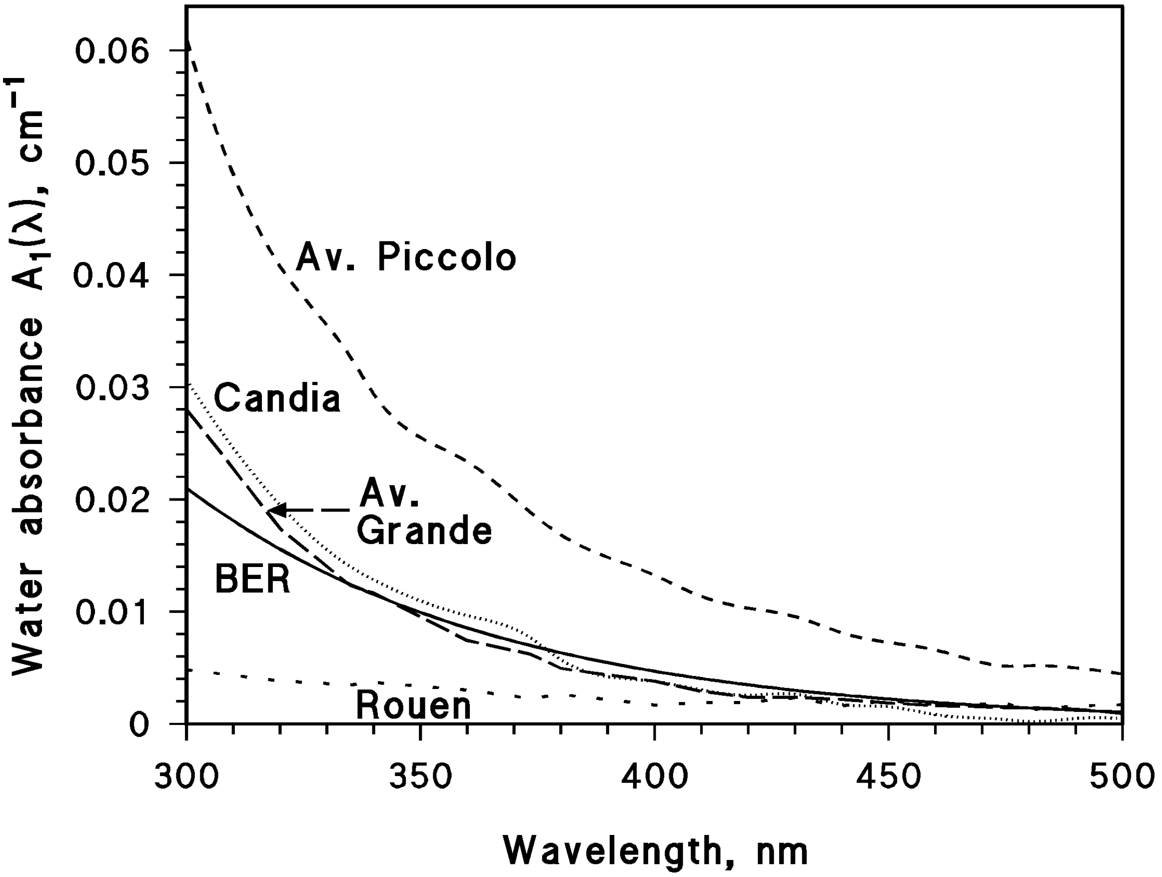

Figure 1. Absorption spectra of the surface water samples, the data of which are reported in Table 1. In the case of the Blue Earth River (BER) the spectrum (not available) was simulated according to equation (5).