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Formation and reactivity of the dichloride radical ($Cl_2^{-\bullet}$) in surface waters: A modelling approach

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Abstract

The occurrence of $Cl_2^{-\bullet}$ in natural waters would depend on the budget between triplet-sensitised photogeneration (which might have second-order rate constant of 10^7-10^9 M^{-1} s^{-1}) and scavenging by dissolved organic matter (DOM, with possible rate constant of 10-10^3 s^{-1}). The steady-state [$Cl_2^{-\bullet}$] in brackish to saline waters might be in the range of 10^{-13}-10^{-12} M in mid-latitude summertime, coherently with data of phenol photochlorination in seawater. Steady-state [$Cl_2^{-\bullet}$] would be enhanced by chloride (up to a plateau above 0.1 M Cl^-) and inhibited by DOM. The radical $Cl_2^{-\bullet}$ would also be a major oxidant of nitrite to the nitrating agent ${}^{\bullet}NO_2$ in brackish- and salt-water. This issue may explain the sustained formation of nitrophenols in phenol-spiked seawater and in natural brackish waters impacted by phenolic pollutants (Rhône delta, Southern France).

Keywords: Sensitised phototransformation; chlorination; reactive halogen species; environmental photochemistry; photoreactions in saltwater.

1. Introduction

The chlorine radical ($Cl^{\bullet}$) is a photogenerated transient. In the troposphere it is involved in the oxidation and chlorination of hydrocarbons (Arsene et al., 2007) and, together with the corresponding bromine species, it is thought to affect the ozone cycle in the polar regions (Monks, 2005; Thornton et al., 2010). The radical $Cl^\bullet$ is also formed in the aqueous environment, where it quickly reacts with Cl^- to produce $Cl_2^{-\bullet}$. In acidic solution the whole process can be triggered by $^\bullet OH$ that oxidises chloride (Jayson et al., 1973):

$$^\bullet OH + Cl^- \leftrightarrows ClOH^{-\bullet} \quad (1)$$
$$ClOH^{-\bullet} + H^+ \leftrightarrows ClOH_2^\bullet \quad (2)$$
$$ClOH_2^\bullet \rightarrow Cl^\bullet + H_2O \quad (3)$$
$$Cl^\bullet + Cl^- \rightarrow Cl_2^{-\bullet} \quad (4)$$

The described process yields $Cl^\bullet/Cl_2^{-\bullet}$ effectively at $pH \leq 5$, but under circumneutral conditions the equilibrium reactions (1-2) are shifted towards the reactants. Therefore, reactions (1-4) have limited significance in surface waters. At neutral pH, a possible source of $Cl^\bullet/Cl_2^{-\bullet}$ is chloride oxidation by irradiated Fe(III) (hydr)oxides, which can induce oxidation and chlorination of water-dissolved aromatic hydrocarbons (Calza et al., 2005; Chiron et al., 2006). Unfortunately, the environmental (photo)chemistry of Fe(III) species is too complex and still too little understood to allow a sound assessment of the importance of iron in the environmental formation of $Cl_2^{-\bullet}$.

The triplet states of chromophoric dissolved organic matter ($^3CDOM^*$) are important reactive species in surface waters. They are formed upon sunlight absorption by CDOM followed by inter-system crossing (ISC) (Richard et al., 2007; Canonica, 2007):

$$CDOM + h\nu \rightarrow {}^1CDOM^* \xrightarrow{ISC} {}^3CDOM^* \quad (5)$$

The transients $^3CDOM^*$ can degrade several organic pollutants, including sulphonylurea pesticides and sulphonamide antibiotics (Canonica et al., 2006). Moreover, they play a significant role in the oxidation of bromide to $Br^\bullet/Br_2^{-\bullet}$, of carbonate to $CO_3^{-\bullet}$, and of nitrite to $^\bullet NO_2$ (Canonica et al., 2005; Maddigapu et al., 2010a; De Laurentiis et al., 2012a). The ability of $^3CDOM^*$ to oxidise H_2O/OH^- to $^\bullet OH$ is still controversial, despite the demonstrated ability of single triplet sensitisers to do so (Sur et al., 2011; Chen et al., 2012), because H_2O_2-involving reactions are also operational in $^\bullet OH$ formation (Vermilyea and Voelker, 2010; Page et al., 2011). Considering that the oxidation of chloride to $Cl^\bullet/Cl_2^{-\bullet}$ is much easier compared to the transformation of H_2O/OH^- into $^\bullet OH$ (Wardman, 1989), $^3CDOM^*$ could produce $Cl_2^{-\bullet}$ in environmental waters.

The lack of selective probe molecules is the main limit to understand the environmental occurrence of $Cl_2^{-\bullet}$. The latter is involved in phenol chlorination (Vione et al., 2005) and it could produce chlorophenols in phenol-spiked seawater under irradiation (Calza et al., 2008 and 2012). However, the chlorination yield of the process is quite low and both *ortho* and *para* isomers can be formed (Khanra et al., 2008), making the reaction unsuitable for quantification purposes. In this paper, we study the triplet-sensitised oxidation of chloride and use a modelling approach to assess the possible occurrence of $Cl_2^{-\bullet}$ in surface waters. We chose anthraquinone-2-sulphonate (AQ2S) as CDOM proxy because its triplet state ($^3AQ2S^*$) is known to oxidise chloride to $Cl_2^{-\bullet}$ (Loeff et al., 1984). Moreover, the photochemical behaviour of AQ2S is very well understood and $^3AQ2S^*$ is easily studied by laser flash photolysis (Maddigapu et al., 2010b). Available literature data for the reactivity between $Cl_2^{-\bullet}$ and several organic compounds (Neta et al., 1988) were used jointly with triplet-sensitised formation kinetics to assess the steady-state $[Cl_2^{-\bullet}]$ in sunlit waters. Despite the unavoidable limitations of a pure modelling approach, this is the first attempt to assess the occurrence of $Cl_2^{-\bullet}$ in natural waters.

2. Materials and methods

All reagents were of analytical grade and were used as received, without further purification.

2.1. Laser flash photolysis (LFP) experiments

The laser apparatus is described in the Supplementary Material of this paper (hereafter SM; see also Maddigapu et al., 2010a/b, and De Laurentiis et al., 2012a). An appropriate volume of stock solutions (AQ2S and Cl^-) was mixed before each experiment to obtain the desired concentrations. To avoid sample photodegradation, a peristaltic pump was used to replace the solution inside the cuvette after each laser shot. The transient species of interest were investigated at pH 6.5 (natural pH) and 8.3 (adjusted with NaOH) at ambient temperature (295 K).

The second-order rate constant between excited AQ2S and Cl^- was calculated from the regression lines of the absorbance logarithm decay against $[Cl^-]$. The error bars were derived at the 3σ level from the scattering of the experimental data.

2.2. Photochemical modelling

We have developed a photochemical model predicting photodegradation kinetics of solutes in surface waters based on water chemistry, depth and photoreactivity parameters (direct photolysis quantum yields and reaction rate constants with $^\bullet OH$, $CO_3^{\bullet-}$, $^1O_2$ and $^3CDOM^*$). The model has been validated against the transformation of several organic pollutants in fresh and brackish water (Maddigapu et al., 2011; Vione et al., 2011; De Laurentiis et al., 2012b; Sur et al., 2012).

A detailed description of the model including the relevant equations is reported in the freely available supplementary material of several previous publications (see for instance Maddigapu et al., 2011; Minella et al., 2013). Moreover, a software application has been recently derived from the model (APEX: Aqueous Photochemistry of Environmentally-occurring Xenobiotics), which is available for free download at *http://chimica.campusnet.unito.it/do/didattica.pl/Quest?corso=7a3d* (including the User's Guide that contains a comprehensive account of model equations). In this work we have extensively used the *Savetable* function of APEX that reports, among others, the steady-state concentrations of $^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$ and $^3CDOM^*$ under a standard sunlight intensity of 22 W m^{-2} in the UV (290-400 nm). It corresponds for instance to fair-weather, mid-latitude 15 July at 9 am or 3 pm solar time. Also note that a fixed depth (d = 10 m) was used in the model. This means that the computed quantities are average values in a 10-m deep water column.

3. Results and Discussion

3.1. Reaction between AQ2S excited species and Cl^-

Three transient species were identified after LFP pulse excitation (355 nm) of 100 μM AQ2S: AQ2S triplet state ($^3AQ2S^*$, monitored at 380 nm) and the water adducts B (monitored at 520 nm) and C (600 nm), as previously reported (Maddigapu et al., 2010b). The pseudo-first order decay constants of $^3AQ2S^*$ ($k_{^3AQ2S^*}$) were $(4.1\pm0.5)\cdot10^6$ s^{-1} at circumneutral pH and $(5.5\pm0.3)\cdot10^6$ s^{-1} at basic pH (8.3). Figure 1 reports the decay of the 380-nm transient signal ($^3AQ2S^*$) at pH 8.3, in the absence and in the presence of chloride ions (20 mM). The $^3AQ2S^*$ decay gets faster with increasing $[Cl^-]$ and a linear trend is observed for $k_{^3AQ2S^*}$ *vs.* $[Cl^-]$ (Stern-Volmer plot, see insert in Figure 1). The relatively large errors for the higher values of $k_{^3AQ2S^*}$ are caused by the instrument being operated near the limit of its time resolution, thus relatively few data points were available for the fit. Data accuracy may suffer, too, as indicated by the small but noticeable deviation of the same values from a linear trend. Therefore, higher values of $[Cl^-]$ were not studied. The estimated second-order rate constants ($k_{^3AQ2S^*,Cl^-}$), obtained as the slopes of the regression lines of $k_{^3AQ2S^*}$ *vs.* $[Cl^-]$, are $(9.7\pm0.4)\cdot10^8$ M^{-1} s^{-1} and $(1.1\pm0.3)\cdot10^9$ M^{-1} s^{-1} at pH 6.5 and 8.3, respectively. These values are a bit lower than those between $^3AQ2S^*$ and Br^- (De Laurentiis et al., 2012a), which looks reasonable. The values found in this work are about twice higher than those reported in a previous study (Loeff et al., 1984), but in the cited paper a 2 mM initial concentration of AQ2S was used and in such conditions the system gets more complicated due to reaction between excited states and ground-state AQ2S (Bedini et al., 2012). For the first time to our knowledge we found that transient B reacts with Cl^-, with a second-order reaction rate constant (k_{B,Cl^-}) that varies with pH. At pH 8.3 it was k_{B,Cl^-} = (2.0±0.1)·10^6 M^{-1} s^{-1}, and k_{B,Cl^-} = (5.2±0.8)·10^7 M^{-1} s^{-1} at circumneutral pH. Note the much lower reactivity of B compared with ^{3}AQ2S*. The species C followed pseudo-first order decay kinetics with a rate constant of ~2.3×10^4 s^{-1}, which was not affected by either pH or chloride (tested up to 30 mM initial concentration).

The oxidation of Cl^- to $Cl^\bullet$ by ^{3}AQ2S* is expected to be followed by reaction between $Cl^\bullet$ and Cl^- to give $Cl_2^{-\bullet}$ (Loeff et al., 1984), which is the main process for $Cl^\bullet$ in aqueous solution (Neta et al., 1988).

3.2. Reaction between $Cl_2^{-\bullet}$ and organic compounds

After formation, the most likely fate of $Cl_2^{-\bullet}$ in natural waters is reaction with dissolved organic compounds. Known reaction rate constants vary widely, from 10^4-10^8 M^{-1} s^{-1} with aliphatics (the higher end is accounted for by unsaturated compounds) to 10^7-10^{10} M^{-1} s^{-1} for aromatics (Neta et al., 1988). In the latter case, a significant effect of ring substituents can be highlighted. A simplified Hammett-σ approach (Canonica and Tratnyek, 2003) can be used for compound classes for which enough kinetic data are available, such as phenols and benzoates (Neta et al., 1988). In the case of phenols, by plotting the logarithm of the second-order reaction rate constant with $Cl_2^{-\bullet}$ against the Hammett σ value of the ring substituent in *meta* or *para* position with respect to -OH, one gets a nice straight line (r^2 = 0.97, see Figure SM1 in the SM of this paper). Because the Hammett σ approach works well with electrophilic processes, the linear trend with phenols suggests that $Cl_2^{-\bullet}$ may react by one-electron abstraction. Indeed, phenol photochlorination involves oxidation of phenol to phenoxyl radical by $Cl_2^{-\bullet}$, followed by reaction between phenoxyl and $Cl_2^{-\bullet}$ to give chlorophenols (Vione et al., 2005). In the case of benzoates, the r^2 value of the linear trend is low (0.6). One could even assume that a linear trend is not followed at all by compounds with electron-withdrawing or weak electron-donating substituents ($\sigma \geq -0.2$, see Figure SM1 in the SM of this paper). In such a case, it is possible that the rate constant for electron abstraction becomes so low that other processes (*e.g.* ring addition) predominate.

By excluding the most as well as the least reactive compounds, one can assume that a reasonable rate constant range between $Cl_2^{-\bullet}$ and DOM is 10^6-10^8 M^{-1} s^{-1} (Neta et al., 1988). Outside this range one would find important compounds, such as unsaturated aliphatic alcohols (poorly reactive) and electron-rich phenols (highly reactive). However, their opposite contributions could cancel out when considering average DOM. By reasonably assuming 8 carbon atoms per molecule (~10^5 mg C $mole^{-1}$) for the tabulated compounds (Neta et al., 1988), the proposed range of 10^6-10^8 M^{-1} s^{-1} would correspond to $k_{Cl_2^{-\bullet},DOM}$ ~10-10^3 L (mg $C)^{-1}$ s^{-1}. This looks reasonable when comparing $Cl_2^{-\bullet}$ with transients species with higher or lower reactivity ($^\bullet$OH, $Br_2^{-\bullet}$ and $CO_3^{-\bullet}$, see Table SM1 in the SM of this paper).

3.3. Modelling the formation and reactivity of $Cl_2^{-\bullet}$ in natural waters

To model the occurrence of $Cl_2^{-\bullet}$ in surface waters, the following reactions where taken into account:

$$^3\text{CDOM}^* + \text{Cl}^- \xrightarrow{k_1} \text{CDOM}^{-\bullet} + \text{Cl}^\bullet \xrightarrow{+Cl^-} \text{CDOM}^{-\bullet} + \text{Cl}_2^{-\bullet} \quad (6)$$

$$\text{Cl}_2^{-\bullet} + \text{DOM} \xrightarrow{k_2} \text{Products} \quad (7)$$

Modelling obviously involved ^{3}CDOM* formation upon CDOM irradiation, carried out with APEX. The reactivity between excited AQ2S and chloride could be representative of that of ^{3}CDOM* and related species. A range of rate constant values $k_1 = 10^7$-10^9 M^{-1} s^{-1} is obtained when considering, in addition to ^{3}AQ2S*, also the reactivity of the water adduct B. This accounts for the fact that some CDOM triplet states may be significantly less reactive than ^{3}AQ2S*. As far as $Cl_2^{-\bullet}$ scavenging is concerned, it was assumed $k_2 = 10$-10^3 L (mg C)$^{-1}$ s^{-1} (see section 3.2). For modelling purposes and in analogy with the chemical composition of seawater, it was also assumed that $[Br^-] = 10^{-3}$ $[Cl^-]$ (Jiang et al., 2009). This allowed a reduction in the system variables, because bromide reacts with ^{3}CDOM* (in addition to scavenging $^\bullet OH$) to finally yield $Br_2^{-\bullet}$ in a process that is quite similar to that of chloride.

Figure 2A reports the modelled steady-state $[Cl_2^{-\bullet}]$ as a function of the second-order rate constants $k_1 = k_{^3CDOM^*,Cl^-}$ and $k_2 = k_{Cl_2^{-\bullet},DOM}$ (other conditions such as water chemistry are reported in the caption). One can see that $[Cl_2^{-\bullet}]$ increases with k_1 (formation rate constant from ^{3}CDOM*) and decreases with k_2 (scavenging rate constant by DOM). Less obviously, it is shown that k_2 has a more marked effect than k_1 on $[Cl_2^{-\bullet}]$. The most likely reason is that, at the chosen concentration of chloride (50 mM), the vast majority of ^{3}CDOM* would be consumed in reaction (6) even if k_1 is low (*e.g.* $2\cdot10^7$ M^{-1} s^{-1}). The process would thus prevail over competing ones, such as reaction between ^{3}CDOM* and O_2 to give $^1O_2$ (Canonica, 2007).

Figure 2B reports $[Cl_2^{-\bullet}]$ as a function of dissolved organic carbon (DOC, which controls both DOM and CDOM) and chloride concentration. Other conditions are reported in the caption, and intermediate values were chosen for k_1 and k_2 (10^8 M^{-1} s^{-1} and 100 L (mg C)$^{-1}$ s^{-1}, respectively). One can see that $[Cl_2^{-\bullet}]$ increases with chloride concentration up to a plateau, where practically all ^{3}CDOM* reacts with Cl^- in reaction (6). Furthermore, $[Cl_2^{-\bullet}]$ decreases with increasing DOC. This is not obvious, because DOC is involved in both $Cl_2^{-\bullet}$ generation (reaction (6) between ^{3}CDOM* and chloride) and $Cl_2^{-\bullet}$ scavenging (reaction (7) between $Cl_2^{-\bullet}$ and DOM). However, for water depth $d = 10$ m as used in the model, CDOM would absorb the vast majority of sunlight, especially in the UV region that triggers the highest photoreactivity. Almost total radiation absorption would already take place at low

DOC, thus ^{3}CDOM* formation rate would be poorly sensitive to DOC changes. Therefore, increasing DOC would produce a limited increase of $Cl_2^{-\bullet}$ formation rate. Because, on the contrary, the rate of $Cl_2^{-\bullet}$ scavenging by DOM would linearly increase with increasing DOC, the decrease of $[Cl_2^{-\bullet}]$ with DOC can be explained.

Figure 2 shows that $[Cl_2^{-\bullet}]$ in sunlit brackish surface waters would be in the range of 10^{-13}-10^{-12} M. Unfortunately, no direct measurements are available of $Cl_2^{-\bullet}$ in the natural environment to test our model predictions: indeed, filling the knowledge gap about $[Cl_2^{-\bullet}]$ is the main goal of the present paper. However, an indirect assessment of $[Cl_2^{-\bullet}]$ can be obtained from recent data of chlorophenol formation upon irradiation of seawater spiked with excess phenol (Calza et al., 2012). The relevant paper reports that around 6 μM chlorophenols are formed in 24 h from 1 mM phenol, upon seawater irradiation under simulated sunlight. Considering that such a chlorophenol concentration might derive from a formation/transformation budget, it places a lower limit for chlorophenol formation rate at about $7\cdot10^{-11}$ M s^{-1}. Considering *(i)* the reaction rate constant between phenol and $Cl_2^{-\bullet}$ ($2.5\cdot10^8$ M^{-1} s^{-1}; Neta et al., 1988), *(ii)* the fact that phenol chlorination yield by $Cl_2^{-\bullet}$ is around 1% (Khanra et al., 2008), and *(iii)* the fact that two $Cl_2^{-\bullet}$ radicals are involved in the chlorination process (the first to oxidise phenol to phenoxyl, the second to react with phenoxyl and yield chlorophenols; Vione et al., 2005), one obtains $3\cdot10^{-13}$ M as the lower limit for $[Cl_2^{-\bullet}]$ in the irradiated system. This is quite in the range predicted by our model, also noting that irradiated (coastal) seawater had DOC ≈ 10 mg C L^{-1} (Calza et al., 2012). A caveat is represented by the fact that the model we used is validated for salinity values up to estuarine water (0.2 M chloride) (Maddigapu et al., 2011; Sur et al., 2012), but not yet for seawater. However, 0.2 M Cl^- is not too far from the 0.7 M of seawater. Furthermore, 0.2 M Cl^- is right in the plateau region of chloride (see Figure 2), above which no enhancement of $[Cl_2^{-\bullet}]$ with increasing chloride is expected. Therefore, the only problem could be a ionic strength effect on the photoreactions, for which no full account is yet available.

3.4. Predicted role of $Cl_2^{-\bullet}$ in the formation of $^\bullet NO_2$ upon oxidation of nitrite

The radical $^\bullet NO_2$ plays an important environmental role and, in surface waters, it is involved in the nitration of aromatic compounds to yield potentially harmful and mutagenic nitroderivatives (Vione et al., 2004a,b). The radical $Cl_2^{-\bullet}$ can oxidise NO_2^- to $^\bullet NO_2$ (Neta et al., 1988), in a process that adds to the oxidation of nitrite by $^\bullet OH$, ^{3}CDOM* and $Br_2^{-\bullet}$. As far as the two latter transients are concerned, ^{3}CDOM* would play an important role in DOM-rich waters and $Br_2^{-\bullet}$ in DOM-poor and saline ones (Maddigapu et al., 2010a; De Laurentiis et al., 2012a). The radical $^\bullet NO_2$ can also be produced by nitrate photolysis, which plays a roughly comparable role as nitrite oxidation (Minero et al., 2007). To avoid additional complications, in this work we will focus on the oxidation of nitrite alone and we will compare the different pathways involved, including the reaction between nitrite and $Cl_2^{-\bullet}$ (Neta et al., 1988):

$$Cl_2^{-\bullet} + NO_2^{-} \rightarrow 2\ Cl^{-} + {}^{\bullet}NO_2 \qquad [k_8 = 2.5\cdot 10^8\ M^{-1}\ s^{-1}] \qquad (8)$$

The relative role of ${}^{\bullet}OH$, ${}^3CDOM^*$, $Br_2^{-\bullet}$ and $Cl_2^{-\bullet}$ in nitrite oxidation can be assessed with a modelling approach, based on known reaction rate constants (Buxton et al., 1988; Neta et al., 1988; Maddigapu et al., 2010a) and on the possibility to model the occurrence of all the relevant species in sunlit surface waters (Maddigapu et al., 2010a; De Laurentiis et al., 2012a, and this work). Hereafter, two different scenarios will be hypothesised: in the former, intermediate values for k_1 and k_2 are assumed (10^8 M^{-1} s^{-1} and 100 L (mg C)$^{-1}$ s^{-1}, respectively). In the latter scenario, the value of k_1 is decreased by ten times (10^7 M^{-1} s^{-1}).

Figure 3A,B reports the modelled fractions of nitrite oxidation / ${}^{\bullet}NO_2$ formation as a function of chloride concentration (A: $k_1 = 10^8$ M^{-1} s^{-1}; B: $k_1 = 10^7$ M^{-1} s^{-1}). The first issue is that, in both cases, $Cl_2^{-\bullet}$ would be the main oxidant for nitrite under conditions that are representative of brackish waters. Of course, the role of $Cl_2^{-\bullet}$ would be higher if k_1 is higher (Figure 3A). Also the relative role of $Br_2^{-\bullet}$ is expected to increase with increasing chloride, because of the assumption $[Br^-] = 10^{-3}$ $[Cl^-]$ that is reasonable for brackish waters. The importance of ${}^{\bullet}OH$ in ${}^{\bullet}NO_2$ formation decreases with $[Cl^-]$, both because of the enhancement of other processes and because of ${}^{\bullet}OH$ scavenging by bromide. In the case of ${}^3CDOM^*$, the decrease is due to scavenging by both bromide and chloride. Note that also the absolute formation rate of ${}^{\bullet}NO_2$ is expected to increase with increasing chloride, because in the absence of Cl^-/Br^- most ${}^3CDOM^*$ would react with O_2 and most ${}^{\bullet}OH$ with DOM, without yielding ${}^{\bullet}NO_2$. This issue might possibly account for the sustained production of nitrophenols upon irradiation of phenol-spiked seawater under simulated sunlight (Calza et al., 2008 and 2012).

Figure 3C,D reports the fractions of ${}^{\bullet}NO_2$ formation from nitrite as a function of DOC (C: $k_1 = 10^8$ M^{-1} s^{-1}; D: $k_1 = 10^7$ M^{-1} s^{-1}). Very interestingly, the fraction related to $Cl_2^{-\bullet}$ shows a maximum. The $Cl_2^{-\bullet}$ process is initially favoured by DOC, because both ${}^{\bullet}OH$ and $Br_2^{-\bullet}$ are strongly inhibited by organic matter (note that most $Br_2^{-\bullet}$ is produced upon bromide oxidation by ${}^{\bullet}OH$, and that both ${}^{\bullet}OH$ and $Br_2^{-\bullet}$ are effectively scavenged by DOM). At high DOC also the scavenging of $Cl_2^{-\bullet}$ by DOM becomes important, thereby inhibiting the $Cl_2^{-\bullet}$ process as well. At the same time, the relative role of ${}^3CDOM^*$ is understandably enhanced. The absolute formation rate of ${}^{\bullet}NO_2$ would decrease with increasing DOC, because DOM scavenges most of the relevant transients (${}^{\bullet}OH$, $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$).

Overall, Figure 3 suggests that $Cl_2^{-\bullet}$ would be a key player in the oxidation of nitrite to ${}^{\bullet}NO_2$ in brackish waters. Considering that $Cl_2^{-\bullet}$ is produced upon chloride oxidation by ${}^3CDOM^*$ and that the oxidation of nitrite by $Cl_2^{-\bullet}$ is expected to prevail over that by

^{3}CDOM*, the species $Cl^-/Cl_2^{-\bullet}$ would act as electron shuttles in the oxidation of nitrite driven by ^{3}CDOM*.

4. Conclusions

The radical $Cl_2^{-\bullet}$ is formed upon chloride oxidation by ^{3}CDOM* in sunlit surface waters, and it is scavenged by DOM. The combination of the two processes might produce steady-state $[Cl_2^{-\bullet}]$ in the range of 10^{-13}-10^{-12} M. This is consistent with experimental data of phenol chlorination in irradiated seawater (Calza et al., 2012). The very low chlorophenol yield from phenol upon reaction with $Cl_2^{-\bullet}$ might hamper the use of phenol itself as probe molecule. The identification of a more selective and sensitive probe molecule is, therefore, required to gather experimental data about the environmental occurrence of $Cl_2^{-\bullet}$. In the meanwhile, a modelling approach as that presented here is the only available option.

The radical $Cl_2^{-\bullet}$ would also play an important role in the oxidation of nitrite to the nitrating agent $^\bullet NO_2$, in particular in brackish or saline waters. This issue might not be disconnected from the fact that aromatic photonitration in the field has been first demonstrated in the brackish waters of the Rhône delta (Southern France) (Chiron et al., 2007).

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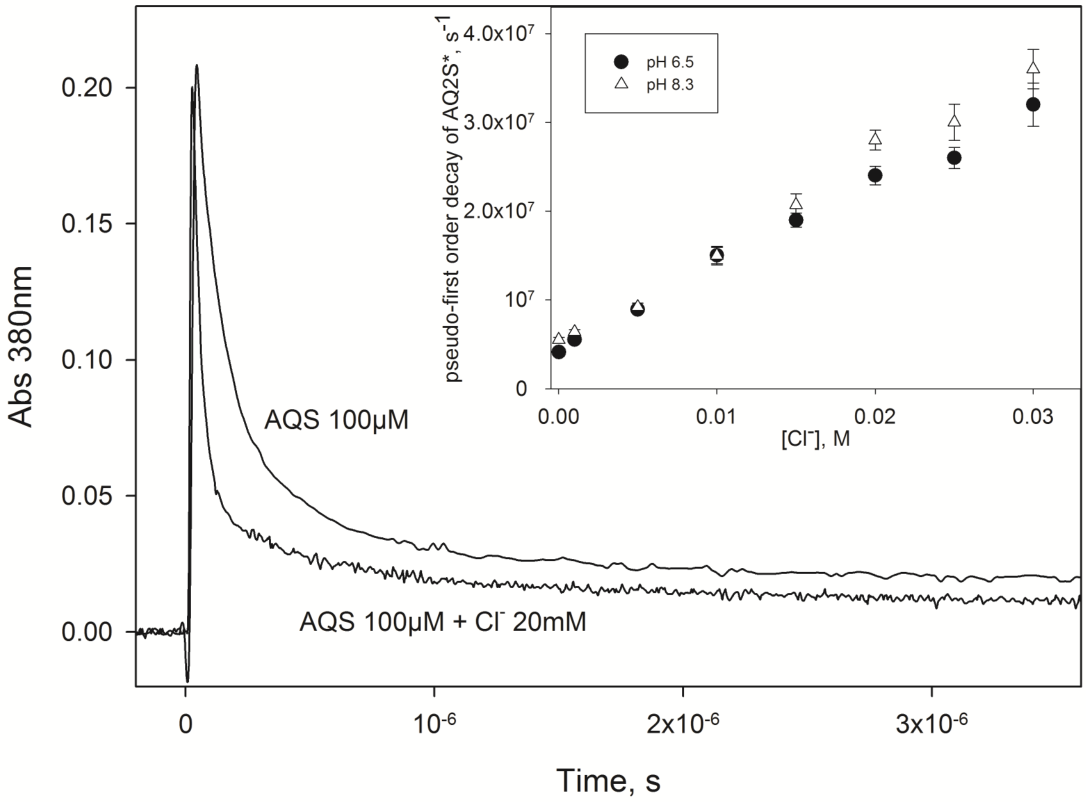

Figure 1. Time trend of the absorbance at 380 nm, following laser-pulse excitation (355 nm, 30 mJ) of 0.1 mM AQ2S in the absence and in the presence of 20 mM NaCl. Insert: Stern-Volmer plot of the pseudo-first order decay constant of ^{3}AQ2S* (absorbance at 380 nm) as a function of chloride concentration, at the natural pH and at pH 8.3.

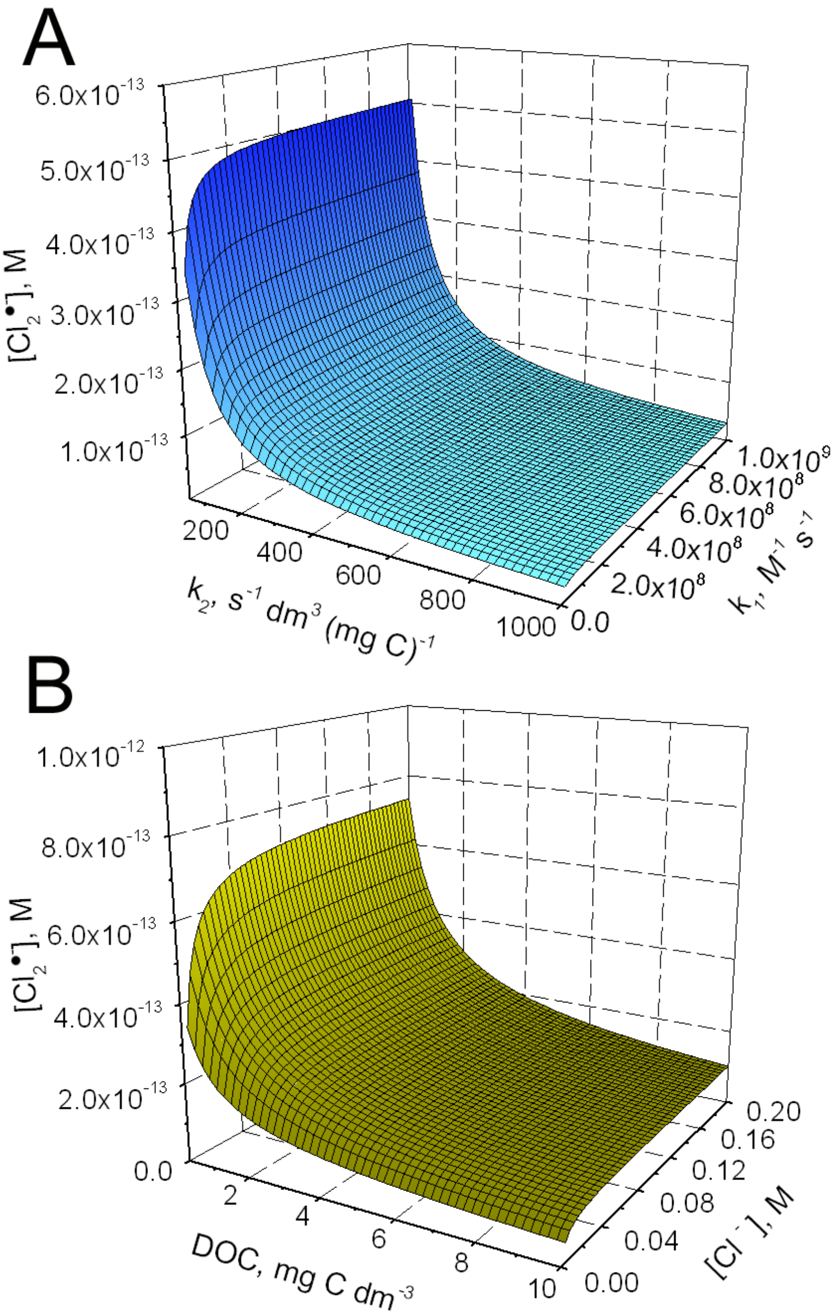

Figure 2. A) Steady-state [$Cl_2^{-•}$] as a function of the second-order rate constants k_1 and k_2. Other conditions: 2 mg C L^{-1} DOC, 50 mM chloride, 0.1 mM nitrate, 1 μM nitrite, 2 mM bicarbonate, 20 μM carbonate, 10 m water depth, 22 W m^{-2} sunlight UV irradiance.

B) Steady-state [$Cl_2^{-•}$] as a function of DOC and chloride concentration. Other conditions: $k_1 = 10^8$ M^{-1} s^{-1}, $k_2 = 10^2$ L (mg C)$^{-1}$ s^{-1}, 0.1 mM nitrate, 1 μM nitrite, 2 mM bicarbonate, 20 μM carbonate, 10 m water depth, 22 W m^{-2} sunlight UV irradiance.

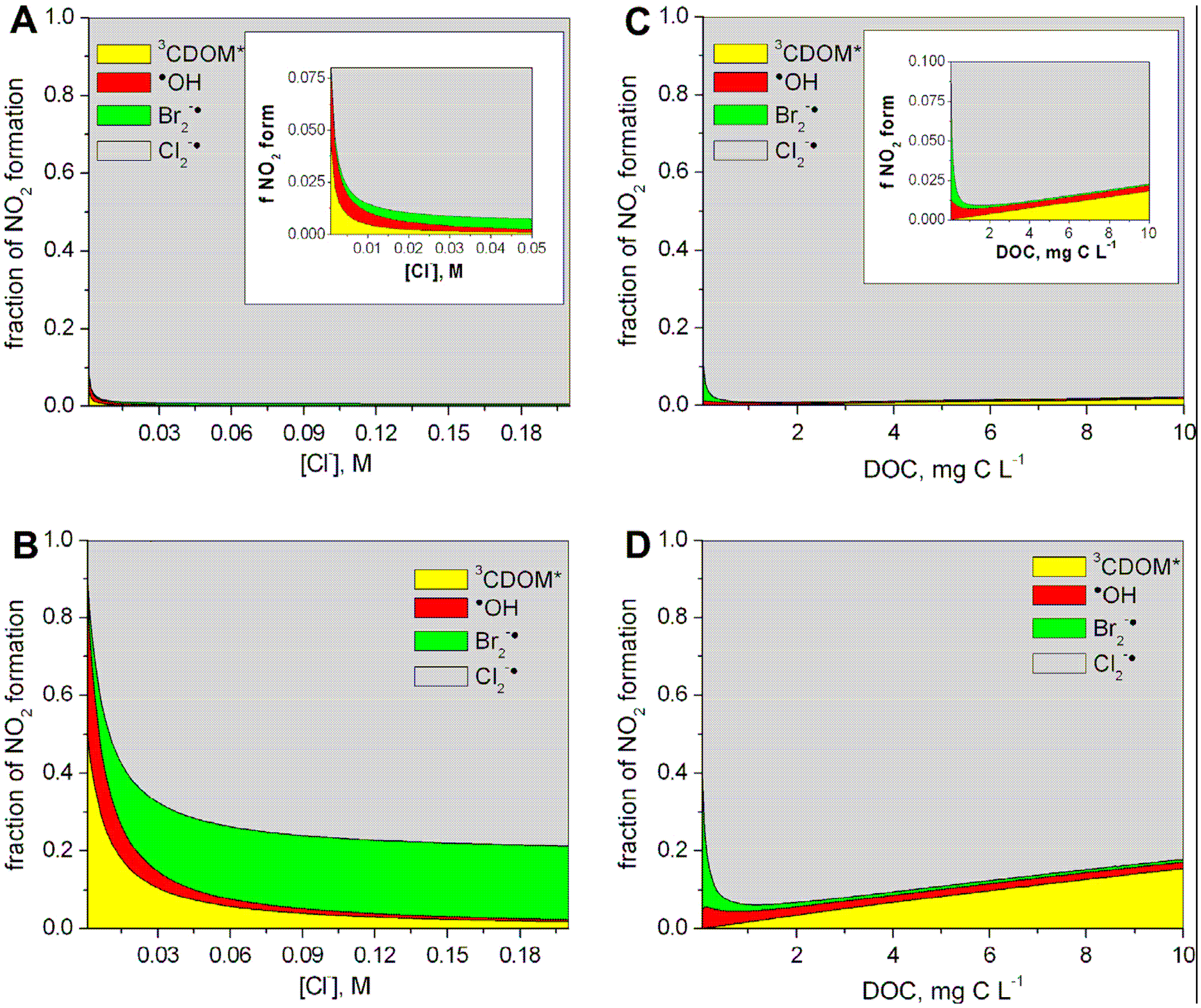

Figure 3. Fractions of $^{\bullet}NO_2$ formation accounted for by nitrite oxidation by $^{\bullet}OH$, $^3CDOM^*$, $Br_2^{-\bullet}$ and $Cl_2^{-\bullet}$. When not variable, model parameters were as follows: 2 mg C L^{-1} DOC, 50 mM chloride, 0.1 mM nitrate, 1 μM nitrite, 2 mM bicarbonate, 20 μM carbonate, 10 m water depth, 22 W m^{-2} sunlight UV irradiance.

A) Trend with chloride, $k_1 = 10^8$ M^{-1} s^{-1}.

B) Trend with chloride, $k_1 = 10^7$ M^{-1} s^{-1}.

C) Trend with DOC, $k_1 = 10^8$ M^{-1} s^{-1}.

D) Trend with DOC, $k_1 = 10^7$ M^{-1} s^{-1}.