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Assessing the occurrence of the dibromide radical ($Br_2^{-\bullet}$) in natural waters: measures of triplet-sensitised formation, reactivity, and modelling

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Abstract

The triplet state of anthraquinone-2-sulphonate (AQ2S) is able to oxidise bromide to $Br^{\bullet}/Br_2^{-\bullet}$, with rate constant $(2\text{-}4)\cdot10^9$ M^{-1} s^{-1} that depends on the pH. Similar processes are expected to take place between bromide and the triplet states of naturally occurring chromophoric dissolved organic matter ($^3CDOM^*$). The brominating agent $Br_2^{-\bullet}$ could thus be formed in natural waters upon oxidation of bromide by both $^{\bullet}OH$ and $^3CDOM^*$. $Br_2^{-\bullet}$ would be consumed by disproportionation into bromide and bromine, as well as upon reaction with nitrite and most notably with dissolved organic matter (DOM). By using the laser flash photolysis technique, and phenol as model organic molecule, a second-order reaction rate constant of ~ $3\cdot10^2$ L (mg C)$^{-1}$ s^{-1} was measured between $Br_2^{-\bullet}$ and DOM. It was thus possible to model the formation and reactivity of $Br_2^{-\bullet}$ in natural waters, assessing the steady-state $[Br_2^{-\bullet}] \approx 10^{-13}$ - 10^{-12} M. It is concluded that bromide oxidation by $^3CDOM^*$ would be significant compared to oxidation by $^{\bullet}OH$. The $^3CDOM^*$-mediated process would prevail in DOM-rich and bromide-rich environments, the latter because elevated bromide would completely scavenge $^{\bullet}OH$. Under such conditions, $^{\bullet}OH$-assisted formation of $Br_2^{-\bullet}$ would be limited by the formation rate of the hydroxyl radical. In contrast, the formation rate of $^3CDOM^*$ is much higher compared to that of $^{\bullet}OH$ in most surface waters and would provide a large $^3CDOM^*$ reservoir for bromide to react with. A further issue is that nitrite oxidation by $Br_2^{-\bullet}$ could be an important source of the nitrating agent $^{\bullet}NO_2$ in bromide-rich, nitrite-rich and DOM-poor

environments. Such a process could possibly account for significant aromatic photonitration observed in irradiated seawater and in sunlit brackish lagoons.

Introduction

The bromide ion is an important saltwater component. It can also be present in surface waters that are affected by mixing with seawater (*e.g.* estuarine areas), in brackish or hyper-saline lakes and lagoons and, although more rarely, as a consequence of human activities (WHO, 1996; Leroy et al., 2006; Jiang et al., 2009). The ion Br^- is usually the main $^\bullet OH$ scavenger in seawater, where it prevails over dissolved organic matter (DOM) that is the main $^\bullet OH$ sink in most freshwaters (Brezonik and Fulkerson-Brekken, 1998; Nakatani et al., 2007). Bromide oxidation by $^\bullet OH$ produces the radical $Br^\bullet$, which in solution would mainly react with a further bromide ion to yield the dibromide radical, $Br_2^{-\bullet}$ (Neta et al., 1988; Jiao et al., 2001). Less important reactions of $Br^\bullet$, as far as environmental conditions are concerned, would take place with H_2O, OH^- and BrO^- (Neta et al., 1988).

The radical $Br_2^{-\bullet}$ is a moderately strong oxidant ($E_{Br_2^{-\bullet}/2Br^-} = 1.63\,V$) and a brominating agent (Neta et al., 1988; Nair et al., 2001), which is for instance able to transform phenol into bromophenols with very remarkable yield (Vione et al., 2008). The photochemical formation of bromoderivatives in the environment is potentially very important, because these compounds are usually persistent and toxic pollutants (Steen et al., 2009). Although bromide oxidation by $^\bullet OH$ is presently the main (known) source of $Br_2^{-\bullet}$ in natural waters, other processes such as the photocatalytic oxidation of bromide by, *e.g.*, Fe(III) oxides could play a secondary but significant role (Calza et al., 2005). Graetzel and Halmann (1990) observed $Br_2^{-\bullet}$ formation upon irradiation of Dead Sea water, the process being enhanced in the presence of triplet sensitizers such as the anthraquinones. The ability of reactive triplet states to oxidise bromide to $Br_2^{-\bullet}$ was recently confirmed by some of us in the case of 1-nitronaphthalene, showing that such a reaction could be a significant $Br_2^{-\bullet}$ source in atmospheric aerosols (Brigante et al., 2010). Because triplet states are supposed to play a substantial role in surface-water photochemistry (Canonica et al., 2006; Canonica, 2007; Halladja et al., 2009), triplet-sensitised bromide oxidation could be an important $Br_2^{-\bullet}$ source in environmental waters.

However, to the best of our knowledge, very scarce data exist in the literature on triplet-sensitised oxidation of bromide in the environment and its possible importance. The most likely explanation deals with the lack of quantitative data, and with the unavailability of a comparison between triplet states *vs.* $^\bullet OH$ as oxidants for bromide in environmental waters. Knowledge gaps of this kind are presently a very important limitation to the full acknowledgement of the importance of

surface-water photochemistry in the field of environmental science. To help addressing such problems, we have recently developed a photochemical model that foresees the steady-state concentration of reactive species in surface waters as a function of chemical composition and water depth (Albinet et al., 2010; Vione et al., 2010; Maddigapu et al., 2010a). The model was originally conceived to predict the photochemical persistence of pollutants in the aqueous environment, a field in which it has been validated (Maddigapu et al., 2011; Vione et al., 2011). However, the model can be easily extended to the general study of photochemical reactions, including the long-term effects of human disturbance and climate change on surface-water photochemistry (Minella et al., 2011).

The aim of the present paper is the quantitative assessment of: *(i)* the importance of triplet-sensitised bromide oxidation in environmental waters, and *(ii)* the environmental occurrence of $Br_2^{-\bullet}$ that depends on its formation-transformation budget. Our aim was achieved by combining laser flash photolysis measures and modelling, using anthraquinone-2-sulphonate (AQ2S) as a proxy for the triplet sensitizers that occur naturally in CDOM. Indeed, natural CDOM with its complex chemical composition is not suitable for flash photolysis measures, and AQ2S has often been used as model compound for ^{3}CDOM*-sensitised degradation reactions (Maddigapu et al., 2011; Vione et al., 2011; Sur et al., 2012). The main reasons for this choice are that *(i)* quinones as CDOM components are very important photoactive compounds in environmental waters (Cory and McKnight, 2005), and *(ii)* AQ2S is very suitable in the present context because it is easily studied by laser flash photolysis and its triplet state does not yield interfering transients such as $^{\bullet}OH$ or $^1O_2$ (Loeff et al., 1983; Maddigapu et al., 2010b), differently from *e.g.* 1-nitronaphthalene (Brigante et al., 2010; Sur et al., 2011). Furthermore, AQS photochemistry is very well known (Ma et al., 2000; Sheng et al., 2004) and a kinetic model has recently been proposed, which successfully describes the processes that follow radiation absorption and that account for the transformation of AQ2S itself and other molecules in solution (Bedini et al., 2012). In the present work, by combining experiments and modelling, we were able to show the potential importance of triplet-sensitised bromide oxidation to $Br_2^{-\bullet}$ in environmental waters.

Experimental

Materials
Anthraquinone-2-sulphonic acid, sodium salt (AQ2S), phenol, NaBr, HClO$_4$ and NaOH were purchased from Sigma-Aldrich (purity grade 97-99%) and were used as received, without further purification. The water used to prepare the solutions was purified with a Millipore water system (Millipore αQ, resistivity 18 MΩ cm, DOC < 0.1 mg L^{-1}). All stock solutions were stored in the dark at 4° C. Before each experiment, solutions were prepared by diluting appropriate volumes of stock solutions in a 50 mL volumetric flask. The Co(NH$_3$)$_5$Br^{2+} complex was prepared as previously described (Booth, 1939) and stored in the dark.

Laser Flash Photolysis

For 355 nm excitation, experiments were carried out using the third harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser system instrument, used in a right-angle geometry with respect to the monitoring light beam. The single pulses were *ca.* 9 ns in duration, with energy of ~ 60 mJ/pulse. Individual cuvette samples (3 mL volume) were used for a maximum of four consecutive laser shots. The transient absorbance at the pre-selected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and photomultiplier (1P28). A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitised by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitised signal.

Solutions were prepared in Milli-Q water and an appropriate volume of reactants was mixed in a flask before each experimental series, in order to obtain desired concentration of both compounds. The second-order rate constants for the quenching of AQ2S excited species by bromide were determined from the plots of the first-order decay constants against bromide concentration. All experiments were performed at ambient temperature (295 ± 2 K) in aerated solution. Excitation of $Co(NH_3)_5Br^{2+}$ ($7 \cdot 10^{-4}$ M) at 355 nm in the presence of Br^- (5 mM) leads to the formation of $Br_2^{-\bullet}$ (Edincott et al., 1965 and 1975) as shown by the presence of a long-lived transient species that absorbs from 300 to 420 nm (maximum at 355 nm with $\varepsilon \sim 10^4$ M^{-1} cm^{-1}; Hug, 1981). To derive the second-order rate constant for the quenching of $Br_2^{-\bullet}$ by phenol, plots were made of the first-order decay constant of $Br_2^{-\bullet}$ (monitored at 355 nm) against phenol concentration. All first-order decay constants were determined from regression lines of logarithmic decays of the relevant absorbance values.

The UV-Vis absorption spectrum of $Co(NH_3)_5Br^{2+}$ was taken with a Varian CARY 300 spectrophotometer, adopting quartz cuvettes with $b = 1$ cm.

Results and discussion

Reaction kinetics between excited AQ2S and bromide

The generation of $Br_2^{-\bullet}$ was achieved by laser excitation of AQ2S in the presence of bromide. To verify the actual formation of $Br_2^{-\bullet}$, spectra of transient species produced by laser-pulse irradiation of $AQ2S + Br^-$ were compared with literature data, and with the spectrum of $Br_2^{-\bullet}$ produced by photolysis of $Co(NH_3)_5Br^{2+} + Br^-$ (Hug, 1981). Figure 1 shows the UV-vis spectrum of $Co(NH_3)_5Br^{2+}$ and the transient absorption spectrum obtained after excitation at 355 nm. The obtained spectrum has a maximum around 355 nm and can be attributed to $Br_2^{-\bullet}$, in agreement with literature data (Hug, 1981).

Laser irradiation of AQ2S at 355 nm produces the excited singlet state, which is efficiently transformed into the triplet $^3AQ2S^*$ by inter-system crossing (the quantum yield of triplet formation

is 0.18; Alegría et al., 1999). The transient ^{3}AQ2S* is quite reactive and can oxidise a wide range of water-dissolved molecules and ions (Maddigapu et al., 2010b). The main ^{3}AQ2S* transformation pathway is reaction with water to yield two transient water adducts, which are termed in the literature as B and C (Loeff et al., 1983; Phillips et al., 1986). In this context, ^{3}AQ2S* is indicated as A. The species B is an adduct where the water molecule is attached to a carbonyl group, while in the case of C (usually more reactive than B) the water molecule interacts with one of the two aromatic rings (Bedini et al., 2012).

The reactivity of A (^{3}AQ2S*), B and C with bromide was studied by laser flash photolysis, by measuring the pseudo-first order decay constants of the three transient species (k_A, k_B and k_C) in the presence of variable concentration values of Br$^-$. The values of k_A, k_B and k_C were determined by fitting the decay traces at the relevant absorption maxima (380, 520 and 600 nm, respectively) with first-order kinetic equations. Experiments were carried out at pH 3.7, 6.0 (natural pH of AQ2S solutions) and 7.7. The plots of {k_A, k_B, k_C} $vs.$ [Br$^-$] are reported in Figure SM1 (hereafter, SM = Supplementary Material). When statistically significant, the slope of the fit line to the relevant experimental data represents the second-order reaction rate constant between each transient and bromide. Table 1 reports the relevant rate constants ($k_{i,Br-}$, with i = A, B, C) at the different pH values. All linear fits were statistically significant (p < 0.05 by Pearson correlation), with the exception of k_C $vs.$ [Br$^-$] at pH 6.0 and 7.7. At representative pH values for surface waters, triplet state A (^{3}AQ2S*) would be by far the most reactive transient. The rate constants of B ($k_{B,Br-}$) are almost three orders of magnitude lower than $k_{A,Br-}$, and $k_{C,Br-}$ values are insignificant. Considering that ^{3}AQ2S* is the AQ2S transient that is most representative of CDOM triplet states (Maddigapu et al., 2010a, 2010b and 2011), rate constant values of the order of $k_{A,Br-}$ (2÷4·10^9 M^{-1} s^{-1}) will hereafter be assumed as representative of the reactivity between ^{3}CDOM* and bromide.

Reaction kinetics between Br$_2^{-•}$ and phenol

In surface waters, the most reasonable transformation pathways of Br$_2^{-•}$ are disproportionation and reaction with DOM. Reaction (3) with nitrite is supposed to play a secondary role (Neta et al., 1988).

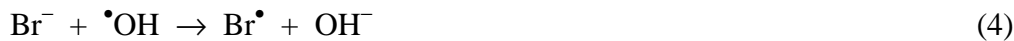$$2\,Br_2^{-•} \rightarrow Br_3^- + Br^- \tag{1}$$
$$Br_2^{-•} + DOM \rightarrow 2\,Br^- + DOM^{+•} \tag{2}$$
$$Br_2^{-•} + DOM \rightarrow Br^- + DOM\text{-}Br^• \tag{2'}$$
$$Br_2^{-•} + NO_2^- \rightarrow 2\,Br^- + {}^•NO_2 \tag{3}$$

To get insight into the reactivity of Br$_2^{-•}$ in the presence of DOM, the radical Br$_2^{-•}$ was produced by photolysis of Co(NH$_3$)$_5$Br^{2+} and its decay monitored at 355 nm (see Figure 1). Phenol was adopted as model organic molecule, the choice being motivated by the widespread occurrence of lignin-derived phenols in DOM (Benner and Kaiser, 2011). Moreover, phenol-like antioxidants occurring in humic and fulvic acids are able to inhibit the triplet-sensitised oxidative degradation of pollutants

(Canonica and Laubscher, 2008; Wenk and Canonica, 2012). Phenol has the additional advantage of not to absorb radiation at 355 nm, differently from whole humic substances that yield triplet states that would interfere with the detection of $Br_2^{-\bullet}$.

The first-order decay constant of $Br_2^{-\bullet}$ ($k_{Br_2^{-\bullet}}$) was measured in the presence of different phenol concentration values, to obtain the plot of $k_{Br_2^{-\bullet}}$ *vs.* [Phenol] reported in Figure 2. The statistically significant linear fit to the experimental data (p < 0.001) yielded, as the line slope, the second-order reaction rate constant between $Br_2^{-\bullet}$ and phenol, $k_{Br_2^{-\bullet},Phenol} = (2.20\pm0.24)\cdot10^7$ M^{-1} s^{-1}. Such a value compares reasonably well with literature data (Neta et al., 1988). The intercept $k_{Br_2^{-\bullet}} = (7.6\pm0.6)\cdot10^4$ s^{-1} represents the kinetics of additional $Br_2^{-\bullet}$ transformation pathways (most notably disproportionation; Neta et al., 1988) under the adopted experimental conditions.

Modelling of $Br_2^{-\bullet}$ formation and reactivity in natural waters

The formation of $Br_2^{-\bullet}$ in natural waters would take place upon oxidation of bromide by $^\bullet$OH (reaction rate constant $1.1\cdot10^{10}$ M^{-1} s^{-1}; Buxton et al., 1988) and by ^{3}CDOM*. As far as the latter process is concerned, by adopting AQ2S as CDOM proxy and based on the data of Table 1, one derives a second-order rate constant $k_{^3CDOM*,Br^-} \approx \cdot3\cdot10^9$ M^{-1} s^{-1}. By comparison, the reaction rate constant between bromide and the triplet state of 1-nitronaphthalene is $7.5\cdot10^8$ M^{-1} s^{-1} (Brigante et al., 2010), thus always in the $\sim10^9$ M^{-1} s^{-1} range. To summarise, the main formation processes of $Br_2^{-\bullet}$ in natural waters would be the following:

$$Br^- + {}^\bullet OH \rightarrow Br^\bullet + OH^- \tag{4}$$
$$Br^- + {}^3CDOM* \rightarrow Br^\bullet + CDOM^{-\bullet} \tag{5}$$
$$Br^- + Br^\bullet \rightarrow Br_2^{-\bullet} \tag{6}$$

Here it is assumed that all $Br^\bullet$ reacts with bromide in reaction (6) to give $Br_2^{-\bullet}$, which is quite reasonable (Neta et al., 1988). The main quenching processes of $Br_2^{-\bullet}$ would be disproportionation and reaction with DOM and nitrite (reactions (1)-(3); Neta et al., 1988; Fu et al., 2009). We assume that the reaction rate constant between $Br_2^{-\bullet}$ and phenol is representative of $Br_2^{-\bullet}$ reactivity with DOM, from which one gets $k_{2+2'} = (2.20\pm0.24)\cdot10^7$ M^{-1} s^{-1} = $(3.06\pm0.33)\cdot10^2$ L (mg C)$^{-1}$ s^{-1}. The rate of $Br_2^{-\bullet}$ scavenging by DOM is $R_{2+2'} = k_{2+2'}$ DOC [$Br_2^{-\bullet}$], where DOC (dissolved organic carbon) is a measure of DOM. Disproportionation involving two $Br_2^{-\bullet}$ radical ions has rate constant $k_1 \approx 2\cdot10^9$ M^{-1} s^{-1}, and reaction with nitrite has $k_3 = 2\cdot10^7$ M^{-1} s^{-1} (Neta et al., 1988). By applying the steady-state approximation to $Br_2^{-\bullet}$ (and to $Br^\bullet$) one gets:

$$[Br_2^{-\bullet}] = \frac{-(k_{2+2'} DOC + k_3 [NO_2^-]) + \sqrt{(k_{2+2'} DOC + k_3 [NO_2^-])^2 + 4k_1 R_{Br_2^{-\bullet}}}}{2k_1} \tag{7}$$

where $R_{Br_2^{-\bullet}} = (k_4[^\bullet OH] + k_5[^3CDOM^*])\,[Br^-]$ is the formation rate of $Br_2^{-\bullet}$. It is possible to assess the steady-state concentration values of $^\bullet OH$ and $^3CDOM^*$, based on water chemical composition and column depth, by means of a model that has been validated for the prediction of the photochemical degradation kinetics of organic pollutants (Maddigapu et al., 2011; Vione et al., 2011). The relevant model approach is here described as SM. The photochemically relevant water parameters are nitrate, nitrite, DOC, carbonate, bicarbonate, bromide, and depth. It is possible to use the model, coupled with equation (7), to assess the formation rate and steady-state concentration of $Br_2^{-\bullet}$ under a variety of environmentally significant conditions. Note that here the model adopts a sunlight UV irradiance of 22 W m^{-2}, which can for instance be observed in a summer sunny day (15 July) at 45°N latitude, at 10 am or 2 pm (Frank and Klöpffer, 1988).

Figure 3 shows the modelled initial formation rate of $Br_2^{-\bullet}$, $R_{Br_2^{-\bullet}}$, as a function of DOC, bromide, nitrite, and of the rate constant of reaction (5) between bromide and $^3CDOM^*$ ($k_{^3CDOM^*,Br^-}$). The value of $k_{^3CDOM^*,Br^-}$ was varied in a range $((0.5\text{-}5.0)\cdot10^9$ M^{-1} s$^{-1})$ that includes the reaction rate constants of bromide with $^31NN^*$ (Brigante et al., 2010) and $^3AQ2S^*$ (this work). When not varying in the range shown on the relevant plots, water parameters were set as follows: 0.1 mM nitrate, 1 µM nitrite, 2 mM bicarbonate, 10 µM carbonate, 10 µM bromide, and 1 m depth. Furthermore, when not varying, $k_{^3CDOM^*,Br^-}$ was set at $3\cdot10^9$ M^{-1} s^{-1}.

Figure 3A shows that $R_{Br_2^{-\bullet}}$ would increase with increasing bromide, as expected, while the trend with DOC would depend on bromide concentration. At low bromide, $R_{Br_2^{-\bullet}}$ would slightly decrease with DOC, and it would increase with DOC at high bromide. Because bromide oxidation involves $^\bullet OH$ and $^3CDOM^*$, and naturally-occurring organic matter is a source of $^3CDOM^*$ and mostly a scavenger of $^\bullet OH$ (CDOM is also an $^\bullet OH$ source, but scavenging of $^\bullet OH$ usually prevails), a DOC-inhibited process is likely to involve $^\bullet OH$. Conversely, a DOC-enhanced process would involve CDOM-derived transients ($^3CDOM^*$ in the present case). Therefore, it is suggested that $Br_2^{-\bullet}$ production by $^\bullet OH$ (reaction (4)) prevails at low bromide, while $Br_2^{-\bullet}$ production by $^3CDOM^*$ (reaction (5)) prevails at high bromide. The most likely explanation of this phenomenon is that elevated $[Br^-]$ would scavenge nearly all $^\bullet OH$. Under such conditions, the formation rate of $Br_2^{-\bullet}$ upon bromide oxidation by $^\bullet OH$ would be $R_{Br_2^{-\bullet}}^{\bullet OH+Br^-} \approx R_{\bullet OH}$, where $R_{\bullet OH}$ is the formation rate of $^\bullet OH$. Bromide would not scavenge all $^3CDOM^*$, because reaction (5) is not fast enough. Therefore, it would be $R_{^3CDOM^*} > R_{Br_2^{-\bullet}}^{^3CDOM^*+Br^-}$, where $R_{^3CDOM^*}$ is the formation rate of $^3CDOM^*$. However, because $R_{^3CDOM^*} \gg R_{\bullet OH} \approx R_{Br_2^{-\bullet}}^{\bullet OH+Br^-}$, it would be $R_{Br_2^{-\bullet}}^{^3CDOM^*+Br^-} > R_{Br_2^{-\bullet}}^{\bullet OH+Br^-}$. Interestingly, at intermediate $[Br^-]$ values the trend of $R_{Br_2^{-\bullet}}$ vs. DOC has a minimum, which can be seen (although with difficulty) on the 3A plot. This issue will be clarified below.

Figure 3B reports the trends of $R_{Br_2^{-\bullet}}$ vs. DOC and nitrite. The fixed bromide concentration is here 10 µM, which would be an "intermediate" value in Figure 3A. Note that nitrite enhances $R_{Br_2^{-\bullet}}$, very significantly at low DOC and almost unnoticeably at high DOC. At low DOC, nitrite is a very important $^\bullet OH$ source and its increasing concentration enhances reaction (4), thereby increasing

$R_{Br_2^{-\bullet}}$. At high DOC, CDOM would be the main producer of $Br_2^{-\bullet}$ *via* reactions (5,6) that depend on $^3CDOM^*$. One should also observe that, under high-DOC conditions, CDOM would be the main $^\bullet OH$ source, more important than nitrite. Furthermore, the role of $^\bullet OH$ in bromide oxidation to $Br_2^{-\bullet}$ (reactions 4,6) would be decreased by DOM upon $^\bullet OH$ scavenging. All these issues account for the low effect of $[NO_2^-]$ on $R_{Br_2^{-\bullet}}$ at high DOC. The already-described minimum of $R_{Br_2^{-\bullet}}$ *vs.* DOC, which is very evident in Figure 3B, represents the DOC level where reactions (4) and (5) have comparable importance. At lower DOC, reaction (4) prevails and organic matter inhibits the formation of $Br_2^{-\bullet}$ through $^\bullet OH$ scavenging. At higher DOC, reaction (5) prevails and DOC is expected to enhance $Br_2^{-\bullet}$ formation via $^3CDOM^*$.

Figure 3C reports $R_{Br_2^{-\bullet}}$ *vs.* DOC and $k_{^3CDOM^*,Br^-}$. Intuitively, the importance of reaction (5) would increase with increasing its rate constant $k_{^3CDOM^*,Br^-}$.

Figure 4 reports the trends of the steady-state $[Br_2^{-\bullet}]$ *vs.* DOC, bromide, nitrite and $k_{^3CDOM^*,Br^-}$. Apart from the rather obvious increase of $[Br_2^{-\bullet}]$ with increasing bromide and $k_{^3CDOM^*,Br^-}$, the latter most notably at high DOC where reactions (5,6) are more important, one can easily see that DOC is by far the main factor that influences $[Br_2^{-\bullet}]$. The very significant decrease of $[Br_2^{-\bullet}]$ with increasing DOC is accounted for by reaction (2+2') of $Br_2^{-\bullet}$ with DOM. The increase of $[Br_2^{-\bullet}]$ with increasing nitrite suggests that the scavenging of $Br_2^{-\bullet}$ by NO_2^- would be less important than the role of nitrite as $^\bullet OH$ source, which enhances reaction (4). Model calculations suggest that $[Br_2^{-\bullet}]$ would be in the 10^{-13} - 10^{-12} M range under most environmental conditions, if sunlight UV irradiance is 22 W m^{-2}. Note that $[Br_2^{-\bullet}]$ would be roughly proportional to the irradiance.

Figure 5 reports the fraction $\mathbf{f_{DOM}}$ of $Br_2^{-\bullet}$ that would be produced by reaction (5), which involves bromide and $^3CDOM^*$. This process is in competition with reaction (4) that involves bromide + $^\bullet OH$. Of course, both reactions have to be followed by (6) to yield $Br_2^{-\bullet}$. The value of $\mathbf{f_{DOM}}$ increases with increasing bromide and DOC (Figure 5A). DOM is an $^\bullet OH$ scavenger that would inhibit the competitive reaction (4), while at elevated bromide it would be $R_{Br_2^{-\bullet}}^{^3CDOM^*+Br^-} > R_{Br_2^{-\bullet}}^{^\bullet OH+Br^-}$ as explained before. Moreover, reaction (5) is in competition with other deactivation processes for $^3CDOM^*$ (internal conversion and reaction with O_2 to yield $^1O_2$), thus at higher bromide there would be a higher fraction of $^3CDOM^*$ that is involved in the formation of $Br^\bullet/Br_2^{-\bullet}$. Interestingly, at high DOC one expects very low $[Br_2^{-\bullet}]$ due to scavenging of $Br_2^{-\bullet}$ by DOM, but at the same time the oxidation of bromide by $^3CDOM^*$ would be the main $Br_2^{-\bullet}$ source. Therefore, under high-DOC conditions, irradiated CDOM would be the main $Br_2^{-\bullet}$ source and DOM its main sink.

The rate of reaction (5) obviously has considerable impact on $\mathbf{f_{DOM}}$, which increases with increasing $k_{^3CDOM^*,Br^-}$ (Figure 5C). In contrast, $\mathbf{f_{DOM}}$ decreases with increasing nitrite (Figure 5B) because the production of $^\bullet OH$ upon NO_2^- photolysis would increase the relative importance of reaction (4). Quite interestingly, depending on environmental conditions, reaction (5) could be unimportant or could be the main pathway involved in the generation of $Br_2^{-\bullet}$.

Assessment of the Br$_2^{-\bullet}$-induced formation of nitrogen dioxide

One of the possible processes of Br$_2^{-\bullet}$ scavenging is reaction (3) with nitrite to yield $^\bullet$NO$_2$ (rate constant $2 \cdot 10^7$ M^{-1} s^{-1}; Neta et al., 1988). While being a secondary sink for Br$_2^{-\bullet}$ (the main one is reaction 2+2' with DOM), such a process might be a significant $^\bullet$NO$_2$ source. In addition to (3), the following reactions would be other important $^\bullet$NO$_2$ sources in natural waters (Mack and Bolton, 1999; Vione et al., 2001):

$$NO_3^- + h\nu \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad (8)$$
$$NO_2^- + {}^\bullet OH \rightarrow {}^\bullet NO_2 + OH^- \qquad (9)$$
$$NO_2^- + {}^3CDOM^* \rightarrow {}^\bullet NO_2 + CDOM^{-\bullet} \qquad (10)$$

Reaction (8) has quantum yield 0.01 (Warneck and Wurzinger, 1988), reaction (9) has rate constant $1.0 \cdot 10^{10}$ M^{-1} s^{-1} (Buxton et al., 1988), and reaction (10) has rate constant $2.3 \cdot 10^9$ M^{-1} s^{-1} (Maddigapu et al., 2010a). By adopting the model approach described above, it is possible to quantify and compare the four relevant processes involved in $^\bullet$NO$_2$ generation, and to obtain the relative role of reaction (3) as $^\bullet$NO$_2$ source.

Figure 6 reports the fraction $f_{NO_2^-,Br}$ of $^\bullet$NO$_2$ that would be produced by reaction (3) (Br$_2^{-\bullet}$ + NO$_2^-$), as a function of DOC, bromide and $k_{{}^3CDOM^*,Br^-}$. Understandably, $f_{NO_2^-,Br}$ increases with increasing bromide, which would enhance [Br$_2^{-\bullet}$]. The decrease of $f_{NO_2^-,Br}$ with DOC is most likely accounted for by reactions (2, 2') of Br$_2^{-\bullet}$ scavenging by DOM. Moreover, at high DOC one expects nitrite oxidation by ^{3}CDOM* (reaction 10) to be more important in the production of $^\bullet$NO$_2$ (Maddigapu et al., 2010a), at the expense of reactions (3) and (9). There is also an expected increase of $f_{NO_2^-,Br}$ with $k_{{}^3CDOM^*,Br^-}$. Finally note that, under favourable circumstances (*e.g.* brackish waters having elevated [Br$^-$] and low DOC) it would be $f_{NO_2^-,Br} > 0.5$. This means that reaction (3) would be the main $^\bullet$NO$_2$ source under such conditions.

Although our model has worked very successfully in describing the photochemistry of estuarine waters (Maddigapu et al., 2011; Sur et al., 2012), presently it does not take salinity into account. Therefore, great care should be taken when extrapolating model results to seawater. However, under seawater-like circumstances (around 1 mM bromide; Jiang et al., 2009) one would expect reaction (3) to be the main $^\bullet$NO$_2$ formation process if nitrite is present in sufficient amount (around 1 μM). The occurrence of bromide, in addition to enhancing reaction (3), would also lead to considerable $^\bullet$OH scavenging and to the inhibition of reaction (9). The replacement of reaction (9) with reaction (3) as $^\bullet$NO$_2$ source would preserve significant $^\bullet$NO$_2$ formation, also under conditions of strong $^\bullet$OH consumption. Considering that $^\bullet$NO$_2$ is able to nitrate phenols under photochemical conditions (Dzengel et al., 1999) *via* the intermediacy of the phenoxy radical (Bedini et al., 2012), our model results could account for the significant detection of phenol nitroderivatives upon irradiation of seawater (Calza et al., 2008) and for important aromatic photonitration processes in the brackish lagoons of the Rhône delta (S. France) (Chiron et al., 2009).

Conclusions

The excited triplet state of AQ2S is able to oxidise bromide to the radical $Br^\bullet$, finally leading to the formation of $Br_2^{-\bullet}$ upon further reaction with bromide. The primary process ($^3AQ2S^* + Br^-$) has a rate constant of about $(2\text{-}4)\cdot10^9$ M^{-1} s^{-1}, which is higher than the rate constant for the reaction between bromide and the triplet state of 1-nitronaphthalene (^{3}1NN*). By use of AQ2S and 1NN as CDOM proxies, one could assume a rate constant of around 10^9 M^{-1} s^{-1} for the reaction between ^{3}CDOM* and bromide.

By using phenol as model molecule for DOM, we assessed a reaction rate constant between DOM and $Br_2^{-\bullet}$ of about $3\cdot10^2$ L (mg C)$^{-1}$ s^{-1}. This value, which is a couple of orders of magnitude lower than the rate constant between DOM and $^\bullet OH$ (Brezonik and Fulkerson-Brekken, 1998), is comparable to the proposed rate constant between DOM and $CO_3^{-\bullet}$ (Canonica et al., 2005). This finding looks reasonable, because the radicals $Br_2^{-\bullet}$ and $CO_3^{-\bullet}$ have similar reduction potential (around 1.6-1.8 V; Wardman, 1989).

With the above data it is possible to model the formation and reactivity of $Br_2^{-\bullet}$, obtaining its formation rate and steady-state concentration as a function of water parameters. The steady-state [$Br_2^{-\bullet}$] would be around 10^{-13} - 10^{-12} M under most conditions that are relevant to environmental waters, under 22 W m^{-2} sunlight UV irradiance. Furthermore, the oxidation of bromide by ^{3}CDOM* would be a competitive process, as $Br_2^{-\bullet}$ source, compared to oxidation by $^\bullet OH$. In particular, the ^{3}CDOM*-mediated process would prevail in DOM-rich and bromide-rich environments. Because DOM is involved at the same time in both $^\bullet OH$ scavenging and ^{3}CDOM* formation, the formation rate of $Br_2^{-\bullet}$ would reach a minimum as a function of DOC. Such a minimum would be located below 2 mg C L^{-1} DOC, and its exact position would depend on the actual environmental conditions. We also found that high-DOC conditions are expected to produce low [$Br_2^{-\bullet}$], because of $Br_2^{-\bullet}$ scavenging by DOM. Under such circumstances, irradiated CDOM would be the main $Br_2^{-\bullet}$ source and DOM its main sink.

Oxidation of nitrite by $Br_2^{-\bullet}$ could play a potentially important role as $^\bullet NO_2$ source in natural waters, in particular in bromide-rich, nitrite-rich and DOM-poor environments. Alternative $^\bullet NO_2$ formation pathways are nitrate photolysis and the oxidation of nitrite by $^\bullet OH$ and ^{3}CDOM*. The latter process is expected to prevail in DOM-rich waters (Maddigapu et al., 2010a). Our model, validated for fresh- and brackish-water environments (Maddigapu et al., 2011; Vione et al., 2011; Sur et al., 2012), would not allow a straightforward application to seawater. Anyway, it is not excluded that nitrite oxidation to $^\bullet NO_2$ by $Br_2^{-\bullet}$ could account for the significant nitration of phenol that has been observed upon irradiation of seawater (Calza et al., 2008). Under conditions of full model validation, the cited reaction could also account for the effective aromatic photonitration observed in the brackish lagoon water of the Rhône delta (S. France) (Chiron et al., 2009).

Additional studies should assess the actual formation of $Br_2^{-\bullet}$ in irradiated natural waters. They could make use of the bromination reaction of phenol with $Br_2^{-\bullet}$, which has a practically

quantitative yield (Vione et al., 2008). Moreover, surface-water CDOM could be characterised on the basis of its ability to absorb sunlight (absorption spectrum and spectral slope), and its different components could be identified from their fluorescence spectra (excitation-emission matrices) (Loiselle et al., 2012; De Laurentiis et al., 2012).

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Table 1. Reaction rate constants of bromide with the triplet state of AQ2S (A), and with two transient water adducts (B, C) derived from A.

|	pH 3.7	pH 6.0	pH 7.7
k_{A,Br^-}, $M^{-1}\,s^{-1}$	$(2.68\pm0.27)\cdot10^9$	$(3.98\pm0.34)\cdot10^9$	$(3.46\pm0.20)\cdot10^9$
k_{B,Br^-}, $M^{-1}\,s^{-1}$	$(2.40\pm0.26)\cdot10^6$	$(6.30\pm0.71)\cdot10^6$	$(4.34\pm1.15)\cdot10^6$
k_{C,Br^-}, $M^{-1}\,s^{-1}$	$(3.87\pm0.86)\cdot10^8$	$< 1\cdot10^7$	$< 3\cdot10^7$
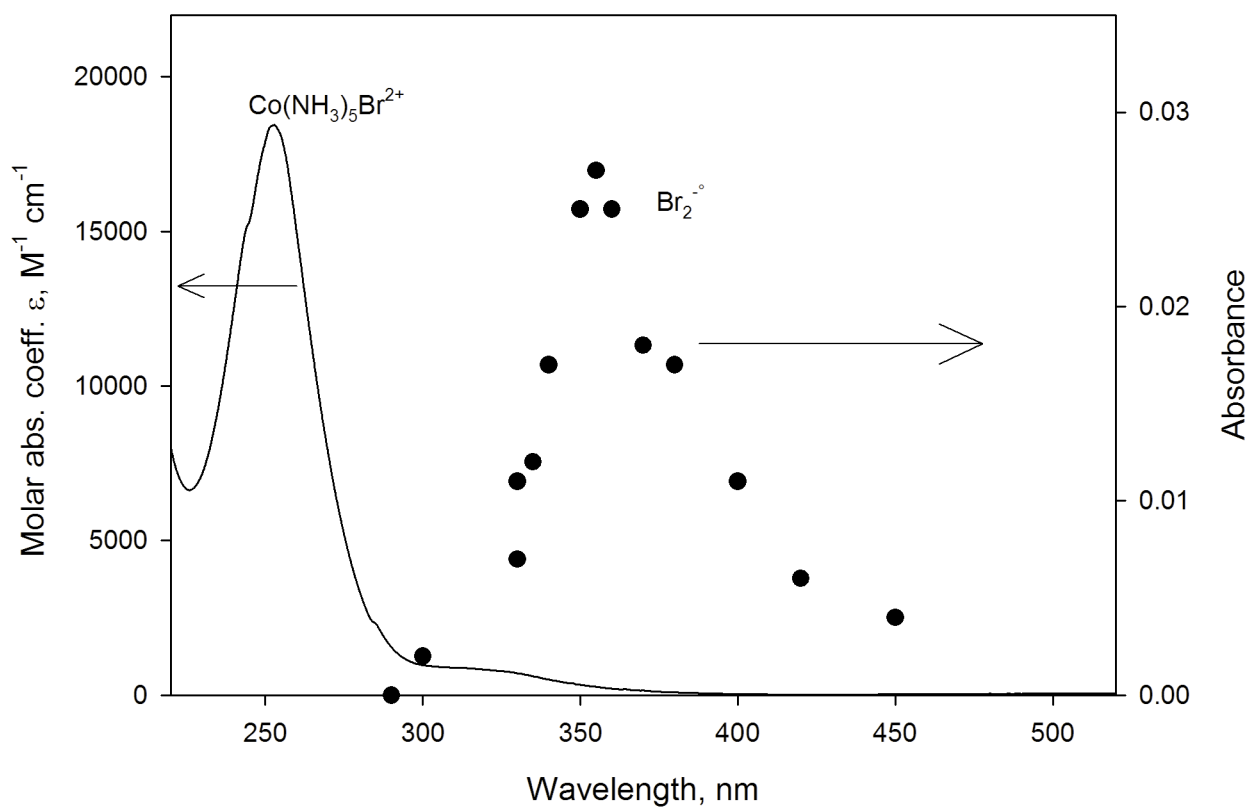
Figure 1. Molar absorption coefficient of $Co(NH_3)_5Br^{2+}$ in aqueous solution (left-axis) and absorbance of $Br_2^{-\bullet}$ (right-axis), produced upon laser flash photolysis (355 nm, 60 mJ/pulse) of 0.7 mM $Co(NH_3)_5Br^{2+}$ in the presence of 5 mM Br^-. The pH was 6.0 at ambient temperature.
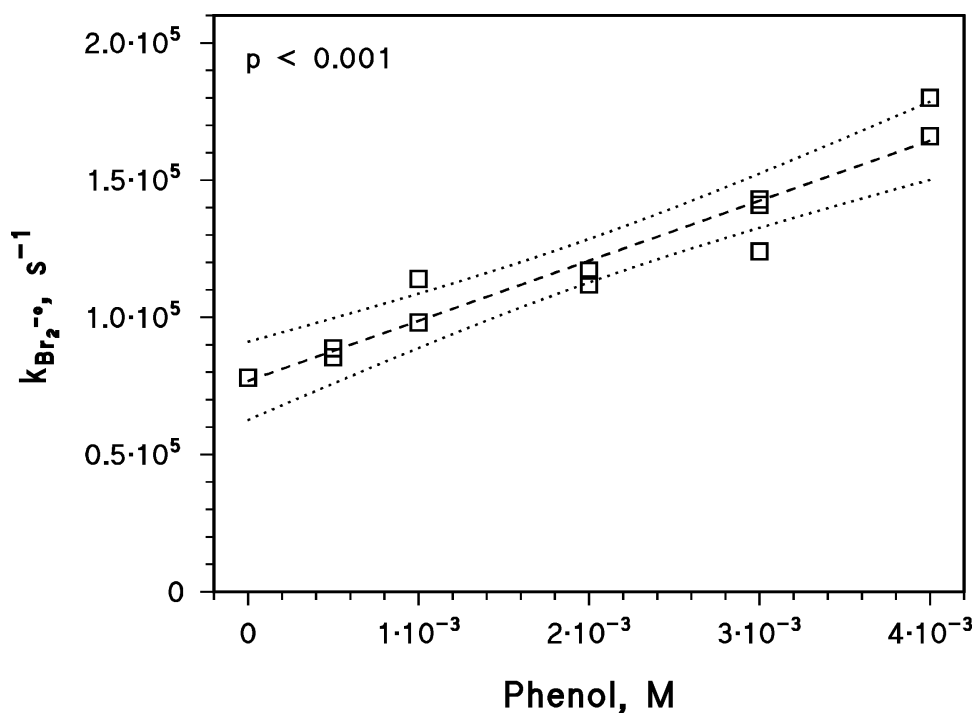
Figure 2. Trend of the pseudo-first order degradation rate constant of the radical $Br_2^{-\bullet}$, as a function of phenol concentration. The fit line is dashed, the 95% confidence bands are dotted. The line slope represents the second-order reaction rate constant between $Br_2^{-\bullet}$ and phenol. Laser flash experiments were performed at 355 nm and 60 mJ/pulse, at ambient temperature.
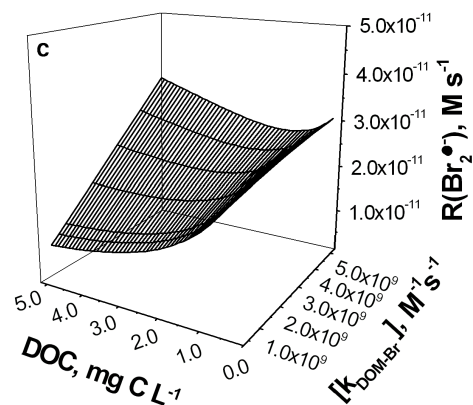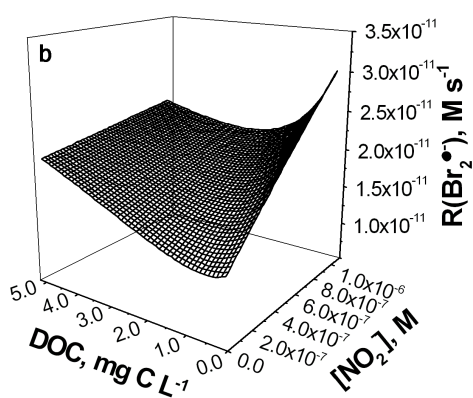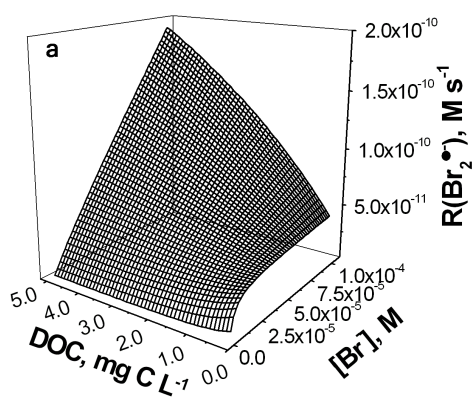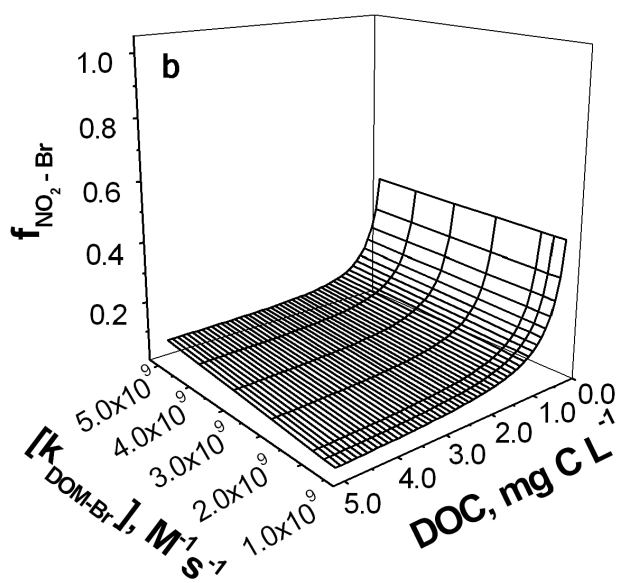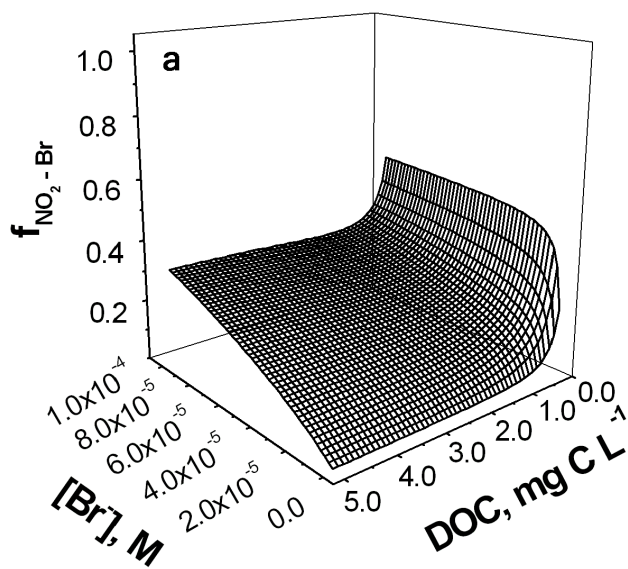
Figure 3. Modelled trends of $Br_2^{-\bullet}$ initial formation rate as a function of: a) DOC and bromide; b) DOC and nitrite; c) DOC and the reaction rate constant between Br^- and $^3CDOM*$. Solar UV irradiance: 22 W m^{-2}. Other photochemically important parameters are reported in the text.
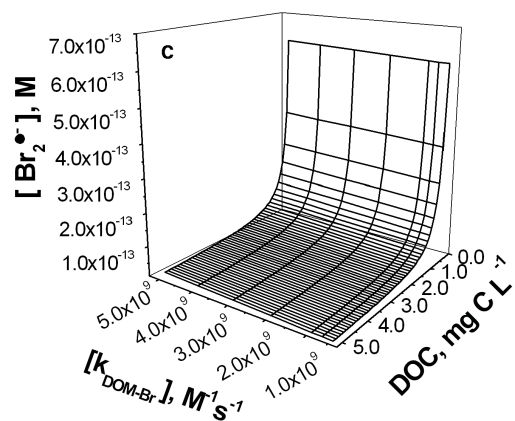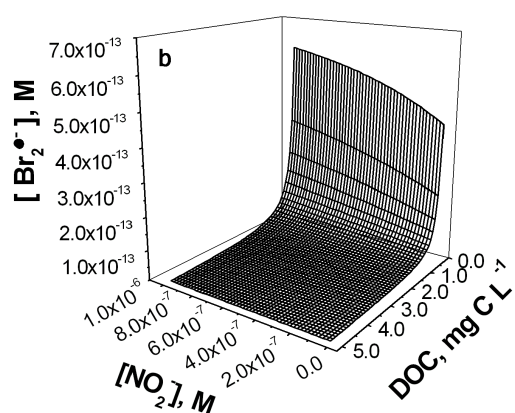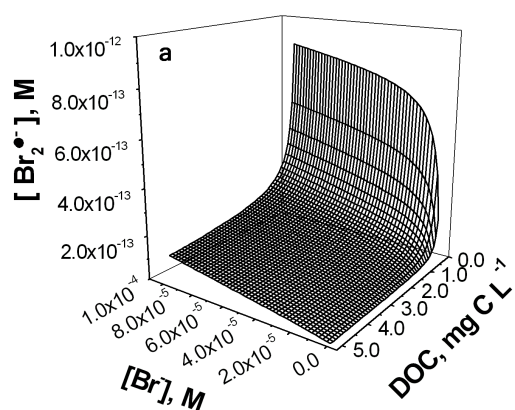
Figure 4. Modelled trends of $Br_2^{-\bullet}$ steady-state concentration as a function of: a) DOC and bromide; b) DOC and nitrite; c) DOC and the reaction rate constant between Br^- and $^3CDOM^*$. Solar UV irradiance: 22 W m^{-2}. Other photochemically important parameters are reported in the text.
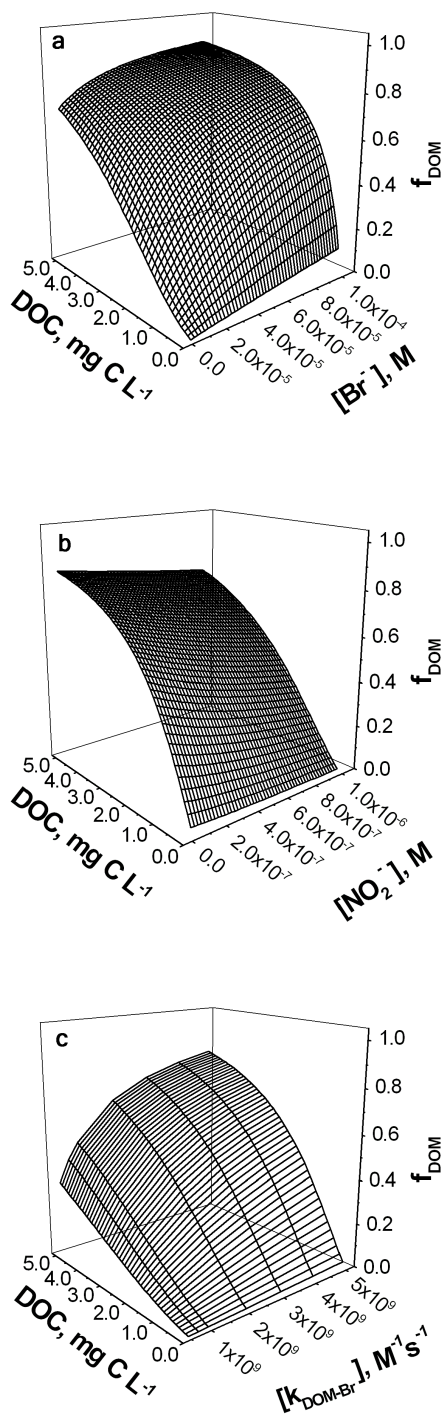
Figure 5. Modelled trends of the fraction of $Br_2^{-\bullet}$ that is generated upon bromide oxidation by $^3CDOM^*$, as a function of: a) DOC and bromide; b) DOC and nitrite; c) DOC and the reaction rate constant between Br^- and $^3CDOM^*$. Solar UV irradiance: 22 W m^{-2}. Other photochemically important parameters are reported in the text.

Figure 6. Modelled trends of the fraction of $^{\bullet}NO_2$ that is generated upon nitrite oxidation by $Br_2^{-\bullet}$, as a function of: a) DOC and bromide; b) DOC and the reaction rate constant between Br^- and $^3CDOM^*$. Solar UV irradiance: 22 W m^{-2}. Other photochemically important parameters are reported in the text.