



AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Assessing the occurrence of the dibromide radical ($\text{Br}_2\cdot^-$) in natural waters: Measures of triplet-sensitised formation, reactivity, and modelling**This is the author's manuscript***Original Citation:**Availability:*This version is available <http://hdl.handle.net/2318/118297> since 2016-10-06T10:41:36Z*Published version:*

DOI:10.1016/j.scitotenv.2012.09.037

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in

E. De Laurentiis, M. Minella, V. Maurino, C. Minero, G. Mailhot, M. Sarakha, M. Brigante, D. Vione. Assessing the Occurrence of the Dibromide Radical ($\text{Br}_2\cdot^*$) in Natural Waters: Measures of Triplet-Sensitized Formation, Reactivity, and Modelling. *Sci. Total Environ.* **2012**, 439, 299-306.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format:

E. De Laurentiis, M. Minella, V. Maurino, C. Minero, G. Mailhot, M. Sarakha, M. Brigante, D. Vione. Assessing the Occurrence of the Dibromide Radical ($\text{Br}_2\cdot^*$) in Natural Waters: Measures of Triplet-Sensitized Formation, Reactivity, and Modelling. *Sci. Total Environ.* **2012**, 439, 299-306.
DOI: 10.1016/j.scitotenv.2012.09.037 (<http://www.elsevier.com/locate/scitotenv>)

Assessing the occurrence of the dibromide radical ($\text{Br}_2\cdot^-$) in natural waters: measures of triplet-sensitised formation, reactivity, and modelling

Elisa De Laurentiis,^a Marco Minella,^a Valter Maurino,^a Claudio Minero,^a Gilles Mailhot,^{b,c}
Mohamed Sarakha,^{b,c} Marcello Brigante,^{b,c*} Davide Vione^{a,d*}

^a Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125 Torino, Italy.
<http://www.chimicadellambiente.unito.it>

^b Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP
10448, F-63000 Clermont-Ferrand, France.

^c CNRS, UMR 6296, ICCF, F-63171 Aubière, France.

^d Università degli Studi di Torino, Centro Interdipartimentale NatRisk, Via Leonardo da Vinci 44,
10095 Grugliasco (TO), Italy. <http://www.natrisk.org>

* Address correspondence to either author. E-mail: marcello.brigante@univ-bpclermont.fr (MB);
davide.vione@unito.it (DV).

Abstract

The triplet state of anthraquinone-2-sulphonate (AQ2S) is able to oxidise bromide to $\text{Br}\cdot/\text{Br}_2\cdot^-$, with rate constant $(2\text{-}4)\cdot10^9 \text{ M}^{-1} \text{ s}^{-1}$ 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 (${}^3\text{CDOM}^*$). The brominating agent $\text{Br}_2\cdot^-$ could thus be formed in natural waters upon oxidation of bromide by both $\cdot\text{OH}$ and ${}^3\text{CDOM}^*$. $\text{Br}_2\cdot^-$ 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 $\sim 3\cdot10^2 \text{ L (mg C)}^{-1} \text{ s}^{-1}$ was measured between $\text{Br}_2\cdot^-$ and DOM. It was thus possible to model the formation and reactivity of $\text{Br}_2\cdot^-$ in natural waters, assessing the steady-state $[\text{Br}_2\cdot^-] \approx 10^{-13} - 10^{-12} \text{ M}$. It is concluded that bromide oxidation by ${}^3\text{CDOM}^*$ would be significant compared to oxidation by $\cdot\text{OH}$. The ${}^3\text{CDOM}^*$ -mediated process would prevail in DOM-rich and bromide-rich environments, the latter because elevated bromide would completely scavenge $\cdot\text{OH}$. Under such conditions, $\cdot\text{OH}$ -assisted formation of $\text{Br}_2\cdot^-$ would be limited by the formation rate of the hydroxyl radical. In contrast, the formation rate of ${}^3\text{CDOM}^*$ is much higher compared to that of $\cdot\text{OH}$ in most surface waters and would provide a large ${}^3\text{CDOM}^*$ reservoir for bromide to react with. A further issue is that nitrite oxidation by $\text{Br}_2\cdot^-$ could be an important source of the nitrating agent $\cdot\text{NO}_2$ 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.

Keywords: Anthraquinone-2-sulphonate; photosensitised reactions; Dissolved organic matter; Bromide; Dibromide radical; Environmental photochemistry.

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 •OH scavenger in seawater, where it prevails over dissolved organic matter (DOM) that is the main •OH sink in most freshwaters (Brezonik and Fulkerson-Brekken, 1998; Nakatani et al., 2007). Bromide oxidation by •OH produces the radical Br[•], which in solution would mainly react with a further bromide ion to yield the dibromide radical, Br₂^{-•} (Neta et al., 1988; Jiao et al., 2001). Less important reactions of Br[•], as far as environmental conditions are concerned, would take place with H₂O, OH⁻ and BrO⁻ (Neta et al., 1988).

The radical Br₂^{-•} is a moderately strong oxidant ($E_{Br_2^{.-}/2Br^-} = 1.63\text{ V}$) 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 •OH is presently the main (known) source of Br₂^{-•} 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 Br₂^{-•} 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 Br₂^{-•} was recently confirmed by some of us in the case of 1-nitronaphthalene, showing that such a reaction could be a significant Br₂^{-•} 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 Br₂^{-•} 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.* •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 ${}^3\text{CDOM}^*$ -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 $\cdot\text{OH}$ or ${}^1\text{O}_2$ (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 $18 \text{ M}\Omega \text{ cm}$, $\text{DOC} < 0.1 \text{ mg L}^{-1}$). 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 $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ 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 $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ ($7 \cdot 10^{-4}$ 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 $\epsilon \sim 10^4$ 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 $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ 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 $\text{AQ2S} + \text{Br}^-$ were compared with literature data, and with the spectrum of Br_2^{\bullet} produced by photolysis of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{Br}^-$ (Hug, 1981). Figure 1 shows the UV-vis spectrum of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ 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).

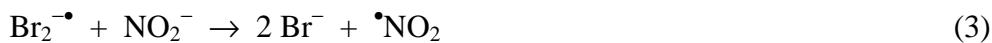
Laser irradiation of AQ2S at 355 nm produces the excited singlet state, which is efficiently transformed into the triplet ${}^3\text{AQ2S}^*$ by inter-system crossing (the quantum yield of triplet formation

is 0.18; Alegría et al., 1999). The transient ${}^3\text{AQ2S}^*$ is quite reactive and can oxidise a wide range of water-dissolved molecules and ions (Maddigapu et al., 2010b). The main ${}^3\text{AQ2S}^*$ 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, ${}^3\text{AQ2S}^*$ 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 (${}^3\text{AQ2S}^*$), 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. $[\text{Br}^-]$ 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 $i = \text{A}, \text{B}, \text{C}$) at the different pH values. All linear fits were statistically significant ($p < 0.05$ by Pearson correlation), with the exception of k_C vs. $[\text{Br}^-]$ at pH 6.0 and 7.7. At representative pH values for surface waters, triplet state A (${}^3\text{AQ2S}^*$) 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 ${}^3\text{AQ2S}^*$ 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^-} ($2\text{--}4 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$) will hereafter be assumed as representative of the reactivity between ${}^3\text{CDOM}^*$ and bromide.

Reaction kinetics between Br_2^{\bullet} and phenol

In surface waters, the most reasonable transformation pathways of Br_2^{\bullet} are disproportionation and reaction with DOM. Reaction (3) with nitrite is supposed to play a secondary role (Neta et al., 1988).



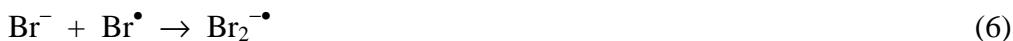
To get insight into the reactivity of Br_2^{\bullet} in the presence of DOM, the radical Br_2^{\bullet} was produced by photolysis of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and its decay monitored at 355 nm (see Figure 1). Phenol was adopted as model organic molecule, the choice being motivated by 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 $\text{Br}_2^{\bullet\bullet}$.

The first-order decay constant of $\text{Br}_2^{\bullet\bullet}$ ($k_{\text{Br}_2^{\bullet\bullet}}$) was measured in the presence of different phenol concentration values, to obtain the plot of $k_{\text{Br}_2^{\bullet\bullet}}$ 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 $\text{Br}_2^{\bullet\bullet}$ and phenol, $k_{\text{Br}_2^{\bullet\bullet}, \text{Phenol}} = (2.20 \pm 0.24) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Such a value compares reasonably well with literature data (Neta et al., 1988). The intercept $k_{\text{Br}_2^{\bullet\bullet}} = (7.6 \pm 0.6) \cdot 10^4 \text{ s}^{-1}$ represents the kinetics of additional $\text{Br}_2^{\bullet\bullet}$ transformation pathways (most notably disproportionation; Neta et al., 1988) under the adopted experimental conditions.

Modelling of $\text{Br}_2^{\bullet\bullet}$ formation and reactivity in natural waters

The formation of $\text{Br}_2^{\bullet\bullet}$ in natural waters would take place upon oxidation of bromide by $\bullet\text{OH}$ (reaction rate constant $1.1 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; Buxton et al., 1988) and by ${}^3\text{CDOM}^*$. 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 $k_{{}^3\text{CDOM}^*, \text{Br}^-} \approx 3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. By comparison, the reaction rate constant between bromide and the triplet state of 1-nitronaphthalene is $7.5 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Brigante et al., 2010), thus always in the $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ range. To summarise, the main formation processes of $\text{Br}_2^{\bullet\bullet}$ in natural waters would be the following:



Here it is assumed that all Br^\bullet reacts with bromide in reaction (6) to give $\text{Br}_2^{\bullet\bullet}$, which is quite reasonable (Neta et al., 1988). The main quenching processes of $\text{Br}_2^{\bullet\bullet}$ 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 $\text{Br}_2^{\bullet\bullet}$ and phenol is representative of $\text{Br}_2^{\bullet\bullet}$ reactivity with DOM, from which one gets $k_{2+2} = (2.20 \pm 0.24) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1} = (3.06 \pm 0.33) \cdot 10^2 \text{ L (mg C)}^{-1} \text{ s}^{-1}$. The rate of $\text{Br}_2^{\bullet\bullet}$ scavenging by DOM is $R_{2+2} = k_{2+2} \text{ DOC} [\text{Br}_2^{\bullet\bullet}]$, where DOC (dissolved organic carbon) is a measure of DOM. Disproportionation involving two $\text{Br}_2^{\bullet\bullet}$ radical ions has rate constant $k_1 \approx 2 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and reaction with nitrite has $k_3 = 2 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Neta et al., 1988). By applying the steady-state approximation to $\text{Br}_2^{\bullet\bullet}$ (and to Br^\bullet) one gets:

$$[\text{Br}_2^{\bullet\bullet}] = \frac{-(k_{2+2} \text{ DOC} + k_3 [\text{NO}_2^-]) + \sqrt{(k_{2+2} \text{ DOC} + k_3 [\text{NO}_2^-])^2 + 4k_1 R_{\text{Br}_2^{\bullet\bullet}}}}{2k_1} \quad (7)$$

where $R_{Br_2^-} = (k_4[\cdot OH] + k_5[{}^3CDOM^*])[Br^-]$ is the formation rate of Br_2^- . It is possible to assess the steady-state concentration values of $\cdot OH$ 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^- 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^- , $R_{Br_2^-}$, as a function of DOC, bromide, nitrite, and of the rate constant of reaction (5) between bromide and ${}^3CDOM^*$ ($k_3[{}^3CDOM^*, Br^-]$). The value of $k_3[{}^3CDOM^*, Br^-]$ was varied in a range ($(0.5\text{--}5.0)\cdot10^9 \text{ M}^{-1} \text{ s}^{-1}$) that includes the reaction rate constants of bromide with ${}^31\text{NN}^*$ (Brigante et al., 2010) and ${}^3\text{AQ2S}^*$ (this work). When not varying in the range shown on the relevant plots, water parameters were set as follows: 0.1 mM nitrate, $1 \mu\text{M}$ nitrite, 2 mM bicarbonate, $10 \mu\text{M}$ carbonate, $10 \mu\text{M}$ bromide, and 1 m depth. Furthermore, when not varying, $k_3[{}^3CDOM^*, Br^-]$ was set at $3\cdot10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Figure 3A shows that $R_{Br_2^-}$ would increase with increasing bromide, as expected, while the trend with DOC would depend on bromide concentration. At low bromide, $R_{Br_2^-}$ would slightly decrease with DOC, and it would increase with DOC at high bromide. Because bromide oxidation involves $\cdot OH$ and ${}^3CDOM^*$, and naturally-occurring organic matter is a source of ${}^3CDOM^*$ and mostly a scavenger of $\cdot OH$ (CDOM is also an $\cdot OH$ source, but scavenging of $\cdot OH$ usually prevails), a DOC-inhibited process is likely to involve $\cdot OH$. Conversely, a DOC-enhanced process would involve CDOM-derived transients (${}^3CDOM^*$ in the present case). Therefore, it is suggested that Br_2^- production by $\cdot OH$ (reaction (4)) prevails at low bromide, while Br_2^- production by ${}^3CDOM^*$ (reaction (5)) prevails at high bromide. The most likely explanation of this phenomenon is that elevated $[Br^-]$ would scavenge nearly all $\cdot OH$. Under such conditions, the formation rate of Br_2^- upon bromide oxidation by $\cdot OH$ would be $R_{Br_2^-}^{\cdot OH+Br^-} \approx R_{\cdot OH}$, where $R_{\cdot OH}$ is the formation rate of $\cdot OH$. Bromide would not scavenge all ${}^3CDOM^*$, because reaction (5) is not fast enough. Therefore, it would be $R_{{}^3CDOM^*} > R_{Br_2^-}^{\cdot OH+Br^-}$, where $R_{{}^3CDOM^*}$ is the formation rate of ${}^3CDOM^*$. However, because $R_{{}^3CDOM^*} \gg R_{\cdot OH} \approx R_{Br_2^-}^{\cdot OH+Br^-}$, it would be $R_{Br_2^-}^{\cdot OH+Br^-} > R_{Br_2^-}^{\cdot OH+Br^-}$. Interestingly, at intermediate $[Br^-]$ values the trend of $R_{Br_2^-}$ 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 $R_{Br_2^-}$ vs. DOC and nitrite. The fixed bromide concentration is here $10 \mu\text{M}$, which would be an “intermediate” value in Figure 3A. Note that nitrite enhances $R_{Br_2^-}$, very significantly at low DOC and almost unnoticeably at high DOC. At low DOC, nitrite is a very important $\cdot OH$ source and its increasing concentration enhances reaction (4), thereby increasing

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

Figure 3C reports $R_{Br_2^-}$ 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 $[Br_2^-]$ vs. DOC, bromide, nitrite and $k_{^3CDOM^*,Br^-}$. Apart from the rather obvious increase of $[Br_2^-]$ 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 $[Br_2^-]$. The very significant decrease of $[Br_2^-]$ with increasing DOC is accounted for by reaction (2+2') of Br_2^- with DOM. The increase of $[Br_2^-]$ with increasing nitrite suggests that the scavenging of Br_2^- by NO_2^- would be less important than the role of nitrite as $\cdot OH$ source, which enhances reaction (4). Model calculations suggest that $[Br_2^-]$ 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 $[Br_2^-]$ would be roughly proportional to the irradiance.

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

The rate of reaction (5) obviously has considerable impact on f_{DOM} , which increases with increasing $k_{^3CDOM^*,Br^-}$ (Figure 5C). In contrast, f_{DOM} decreases with increasing nitrite (Figure 5B) because the production of $\cdot OH$ 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^- .

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 $\bullet\text{NO}_2$ (rate constant $2 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$; 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 $\bullet\text{NO}_2$ source. In addition to (3), the following reactions would be other important $\bullet\text{NO}_2$ sources in natural waters (Mack and Bolton, 1999; Vione et al., 2001):



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

Figure 6 reports the fraction $f_{\text{NO}_2^-, \text{Br}}$ of $\bullet\text{NO}_2$ that would be produced by reaction (3) ($\text{Br}_2^{\bullet} + \text{NO}_2^-$), as a function of DOC, bromide and $k_{{}^3\text{CDOM}^*, \text{Br}^-}$. Understandably, $f_{\text{NO}_2^-, \text{Br}}$ increases with increasing bromide, which would enhance $[\text{Br}_2^{\bullet}]$. The decrease of $f_{\text{NO}_2^-, \text{Br}}$ 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 ${}^3\text{CDOM}^*$ (reaction 10) to be more important in the production of $\bullet\text{NO}_2$ (Maddigapu et al., 2010a), at the expense of reactions (3) and (9). There is also an expected increase of $f_{\text{NO}_2^-, \text{Br}}$ with $k_{{}^3\text{CDOM}^*, \text{Br}^-}$. Finally note that, under favourable circumstances (e.g. brackish waters having elevated $[\text{Br}^-]$ and low DOC) it would be $f_{\text{NO}_2^-, \text{Br}} > 0.5$. This means that reaction (3) would be the main $\bullet\text{NO}_2$ 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 $\bullet\text{NO}_2$ 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 $\bullet\text{OH}$ scavenging and to the inhibition of reaction (9). The replacement of reaction (9) with reaction (3) as $\bullet\text{NO}_2$ source would preserve significant $\bullet\text{NO}_2$ formation, also under conditions of strong $\bullet\text{OH}$ consumption. Considering that $\bullet\text{NO}_2$ 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 $\text{Br}_2^{\cdot\bullet}$ upon further reaction with bromide. The primary process (${}^3\text{AQ2S}^* + \text{Br}^-$) has a rate constant of about $(2\text{-}4)\cdot10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is higher than the rate constant for the reaction between bromide and the triplet state of 1-nitronaphthalene (${}^3\text{1NN}^*$). By use of AQ2S and 1NN as CDOM proxies, one could assume a rate constant of around $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction between ${}^3\text{CDOM}^*$ and bromide.

By using phenol as model molecule for DOM, we assessed a reaction rate constant between DOM and $\text{Br}_2^{\cdot\bullet}$ of about $3\cdot10^2 \text{ L (mg C)}^{-1} \text{ s}^{-1}$. This value, which is a couple of orders of magnitude lower than the rate constant between DOM and $\cdot\text{OH}$ (Brezonik and Fulkerson-Brekken, 1998), is comparable to the proposed rate constant between DOM and $\text{CO}_3^{\cdot\bullet}$ (Canonica et al., 2005). This finding looks reasonable, because the radicals $\text{Br}_2^{\cdot\bullet}$ and $\text{CO}_3^{\cdot\bullet}$ 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 $\text{Br}_2^{\cdot\bullet}$, obtaining its formation rate and steady-state concentration as a function of water parameters. The steady-state $[\text{Br}_2^{\cdot\bullet}]$ would be around $10^{-13} - 10^{-12} \text{ M}$ under most conditions that are relevant to environmental waters, under 22 W m^{-2} sunlight UV irradiance. Furthermore, the oxidation of bromide by ${}^3\text{CDOM}^*$ would be a competitive process, as $\text{Br}_2^{\cdot\bullet}$ source, compared to oxidation by $\cdot\text{OH}$. In particular, the ${}^3\text{CDOM}^*$ -mediated process would prevail in DOM-rich and bromide-rich environments. Because DOM is involved at the same time in both $\cdot\text{OH}$ scavenging and ${}^3\text{CDOM}^*$ formation, the formation rate of $\text{Br}_2^{\cdot\bullet}$ 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 $[\text{Br}_2^{\cdot\bullet}]$, because of $\text{Br}_2^{\cdot\bullet}$ scavenging by DOM. Under such circumstances, irradiated CDOM would be the main $\text{Br}_2^{\cdot\bullet}$ source and DOM its main sink.

Oxidation of nitrite by $\text{Br}_2^{\cdot\bullet}$ could play a potentially important role as $\cdot\text{NO}_2$ source in natural waters, in particular in bromide-rich, nitrite-rich and DOM-poor environments. Alternative $\cdot\text{NO}_2$ formation pathways are nitrate photolysis and the oxidation of nitrite by $\cdot\text{OH}$ and ${}^3\text{CDOM}^*$. 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 $\cdot\text{NO}_2$ by $\text{Br}_2^{\cdot\bullet}$ 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 $\text{Br}_2^{\cdot\bullet}$ in irradiated natural waters. They could make use of the bromination reaction of phenol with $\text{Br}_2^{\cdot\bullet}$, 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).

Acknowledgements

DV, VM and CM acknowledge support by PNRA – Progetto Antartide. DV also acknowledges support by MIUR-PRIN 2009 (Project 20092C7KRC-ARCTICA). EDL, GM, MB and DV acknowledge financial support by Progetto Galileo (Università Italo-Francese and EGIDE). The PhD grant of EDL was financially supported by Progetto Lagrange – Fondazione CRT (Torino, Italy). MB, MS and GM acknowledge additional financial support obtained through the “Fédération des Recherches en Environnement” from the CPER (council of «Région Auvergne», FEDER European funding, French ministry of higher Education and Research)

References

- Albinet A, Minero C, Vione D. UVA irradiation induces direct phototransformation of 2,4-dinitrophenol in surface water samples. *Chemosphere* 2010;80:759-63.
- Alegría AE, Ferrer A, Santiago G, Sepúlveda E, Flores W. Photochemistry of water-soluble quinones. Production of hydroxyl radical, singlet oxygen and the superoxide ion. *J Photochem Photobiol A* 1999;127:57-65.
- Bedini A, Maurino V, Minero C, Vione D. Theoretical and experimental evidence of the photonitration pathway of phenol and 4-chlorophenol: A mechanistic study of environmental significance. *Photochem Photobiol Sci* 2012;11:418-24.
- Bedini A, De Laurentiis E, Sur B, Maurino V, Minero C, Brigante M, Mailhot G, Vione D. Phototransformation of anthraquinone-2-sulphonate in aqueous solution. *Photochem Photobiol Sci* 2012;11:1445-53.
- Benner R, Kaiser K. Biological and photochemical transformations of amino acids and lignin phenols in riverine dissolved organic matter. *Biogeochemistry* 2011;102:209-22.
- Booth HS (Ed.). Inorganic Synthesis, Vol. VIII. McGraw-Hill, New York, 1939.
- Brezonik PL, Fulkerson-Brekken J. Nitrate-induced photolysis in natural waters: Controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents. *Environ Sci Technol* 1998;32: 3004-10.
- Brigante M, Charbouillet T, Vione D, Mailhot G. Photochemistry of 1-nitronaphthalene: A potential source of singlet oxygen and radical species in atmospheric waters. *J Phys Chem A* 2010;114: 2830-6.

- Buxton GV, Greenstock CL, Helman WP, Ross AB. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\text{O}^-$) in aqueous solution. *J Phys Chem Ref Data* 1988;17:513-886.
- Calza P, Maurino V, Minero C, Pelizzetti E, Sega M, Vincenti M. Photoinduced halophenol formation in the presence of iron(III) species or cadmium sulfide. *J Photochem Photobiol A: Chem* 2005;170:61-7.
- Calza P, Massolino C, Pelizzetti E, Minero C. Solar driven production of toxic halogenated and nitroaromatic compounds in natural seawater. *Sci Total Environ* 2008;398:196-202.
- Canonica S, Kohn T, Mac M, Real FJ, Wirz J, Von Gunten U. Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ Sci Technol* 2005;39:9182-8.
- Canonica S, Hellrung B, Muller P, Wirz J. Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones. *Environ Sci Technol* 2006;40: 6636-41.
- Canonica S. Oxidation of aquatic organic contaminants induced by excited triplet states. *Chimia* 2007;61:641-4.
- Canonica S, Laubscher HU. Inhibitory effect of dissolved organic matter on triplet-induced oxidation of aquatic contaminants. *Photochem Photobiol Sci* 2008;7:547-51.
- Chiron S, Comoretto L, Rinaldi E, Maurino V, Minero C, Vione D. Pesticide by-products in the Rhone delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative. *Chemosphere* 2009;74:599-604.
- Cory RM, McKnight DM. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environ Sci Technol* 2005;39:8142-9.
- De Laurentiis E, Minella M, Maurino V, Minero C, Brigante M, Mailhot G, Vione D. Photochemical production of organic matter triplet states in water samples from mountain lakes, located below or above the tree line. *Chemosphere* 2012;88:1208-13.
- Dzengel J, Theurich J, Bahnemann DW. Formation of nitroaromatic compounds in advanced oxidation processes: Photolysis versus photocatalysis. *Environ Sci Technol*. 1999;33:294-300.
- Edincott FJ, Ferraudi JG, Barber RJ. Charge transfer spectroscopy, redox energetic and photoredox behaviour of transition metal ammine complexes. A critical comparison of observations with mechanisms and models. *J Phys Chem*, 1975;79:630-43.
- Edincott FJ, Hoffman MZ. Photoreduction of Cobalt (III) complexes at 2537 Å. *J Am Chem Soc*. 1965;87:3348-57.
- Frank R, Klöpffer W. Spectral solar photon irradiance in Central Europe and the adjacent North Sea. *Chemosphere* 1988;17:985-94.
- Fu HY, Lin MZ, Muroya Y, Hata K, Katsumura Y, Yokoya A, Shikazono N, Hatano Y. Free radical scavenging reactions and antioxidant activities of silybin: Mechanistic aspects and pulse radiolytic studies. *Free Rad Res* 2009;43:887-97.
- Graetzel M, Halmann M. Photosensitized oxidation of bromide in Dead Sea water. *Mar Chem* 1990;29: 169-82.

- Halladja S, Ter Halle A, Pilichowski JF, Boulkamh A, Richard C. Fulvic acid-mediated phototransformation of mecoprop. A pH-dependent reaction. *Photochem Photobiol Sci* 2009;8:1066-71.
- Hug GL. Optical spectra of non-metallic inorganic transient species in aqueous solution NSRDS-NBS 69, US. Government Printing Office: Washington DC 1981.
- Jiang XL, Lim LW, Takeuchi T. Determination of trace inorganic anions in seawater samples by ion chromatography using silica columns modified with cetyltrimethylammonium ion. *Anal Bioanal Chem* 2009;393:387-91.
- Jiao XD, Metelski PD, Espenson JH. Equilibrium and kinetics studies of reactions of manganese acetate, cobalt acetate, and bromide salts in acetic acid solutions. *Inorg Chem* 2001;40: 3228-33.
- Leroy SAG, Marret F, Giralt S, Bulatov SA. Natural and anthropogenic rapid changes in the Kara-Bogaz Gol over the last two centuries reconstructed from palynological analyses and a comparison to instrumental records. *Quatern Int* 2006;150:52-70.
- Loeff I, Treinin A, Linschitz H. Photochemistry of 9,10-anthraquinone-2-sulfonate in solution. 1. Intermediates and mechanism. *J Phys Chem* 1983;87:2536-44.
- Loiselle S, Vione D, Minero C, Maurino V, Tognazzi A, Dattilo AM, Rossi C, Bracchini L. Chemical and optical phototransformation of dissolved organic matter. *Wat Res* 2012;46:3197-207.
- Ma JH, Lin WZ, Wang WF, Han ZH, Yao SD, Lin NY. Triplet state mechanism for electron transfer oxidation of DNA. *J Photochem Photobiol B* 2000;57:76-81.
- Mack J, Bolton JR. Photochemistry of nitrite and nitrate in aqueous solution: a review. *J Photochem Photobiol A* 1999;128:1-13.
- Maddigapu PR, Minero C, Maurino V, Vione D, Brigante M, Mailhot G. Enhancement by anthraquinone-2-sulphonate of the photonitration of phenol by nitrite: Implication for the photoproduction of nitrogen dioxide by coloured dissolved organic matter in surface waters. *Chemosphere* 2010a;81:1401-6.
- Maddigapu PR, Bedini A, Minero C, Maurino V, Vione D, Brigante M, Mailhot G, Sarakha M. The pH-dependent photochemistry of anthraquinone-2-sulfonate. *Photochem Photobiol Sci* 2010b;9:323-30.
- Maddigapu PR, Minella M, Vione D, Maurino V, Minero C. Modeling phototransformation reactions in surface water: 2,4-Dichloro-6-nitrophenol as a case study. *Environ Sci Technol* 2011;45:209-14.
- Minella M, Rogora M, Vione D, Maurino V, Minero C. A model approach to assess the long-term trends of indirect photochemistry in lake water. The case of Lake Maggiore (NW Italy). *Sci Total Environ* 2011;409:3463-71.
- Nair V, Panicker SB, Augustine A, George TG, Thomas S, Vairamani M. An efficient bromination of alkenes using cerium(IV) ammonium nitrate (CAN) and potassium bromide. *Tetrahedron* 2001;57:7417-22.

- Nakatani N, Hashimoto N, Shindo H, Yamamoto M, Kikkawa M, Sakugawa H. Determination of photoformation rates and scavenging rate constants of hydroxyl radicals in natural waters using an automatic light irradiation and injection system. *Anal Chim Acta* 2007;581:260-7.
- Neta P, Huie RE, Ross AB. Rate constants for reactions of inorganic radicals in aqueous solution. *J Phys Chem Ref Data* 1988;17:1027-284.
- Phillips D, Moore JN, Hester RE. Time-resolved resonance Raman spectroscopy applied to anthraquinone photochemistry. *J Chem Soc Faraday Trans 2* 1986;82:2093-104.
- Sheng ZY, Pan Y, Yan LQ, Hei XM, Guo ZY, Dai JH, Song QH, Yu SQ. Steady-state and laser flash photolysis studies on the oxidative splitting of cyclobutane thymine dimer by triplet 9,10-anthraquinone-2-sulfonate. *J Photochem Photobiol A* 2004;161:99-104.
- Steen PO, Grandbois M, McNeill K, Arnold WA. Photochemical formation of halogenated dioxins from hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and chlorinated derivatives (OH-PBCDEs). *Environ Sci Technol* 2009;43:4405-11.
- Sur B, Rolle M, Minero C, Maurino V, Vione D, Brigante M, Mailhot G. Formation of hydroxyl radicals by irradiated 1-nitronaphthalene (1NN): oxidation of hydroxyl ions and water by the 1NN triplet state. *Photochem Photobiol Sci* 2011;10:1817-24.
- Sur B, De Laurentiis E, Minella M, Maurino V, Minero C, Vione D. Photochemical transformation of anionic 2-nitro-4-chlorophenol in surface waters: Laboratory and model assessment of the degradation kinetics, and comparison with field data. *Sci Total Environ* 2012;426:296-303.
- Vione D, Maurino V, Minero C, Pelizzetti E. Phenol photonitration upon UV irradiation of nitrite in aqueous solution II: effects of pH and TiO₂. *Chemosphere* 2001;45:903-10.
- Vione D, Maurino V, Man SC, Khanra S, Arsene C, Olariu RI, Minero C. Formation of organobrominated compounds in the presence of bromide under simulated atmospheric aerosol conditions. *ChemSusChem* 2008;1:197-204.
- Vione D, Khanra S, Das R, Minero C, Maurino V, Brigante M, Mailhot G. Effect of dissolved organic compounds on the photodegradation of the herbicide MCPA in aqueous solution. *Wat Res* 2010;44:6053-62.
- Vione D, Maddigapu PR, De Laurentiis E, Minella M, Pazzi M, Maurino V, Minero C, Kouras S, Richard C. Modelling the photochemical fate of ibuprofen in surface waters. *Wat Res* 2011;45:6725-36.
- Wardman P. Reduction potentials of one-electron couples involving free radicals in aqueous solution. *J Phys Chem Ref Data* 1989;18:1637-755.
- Warneck P, Wurzinger C. Product quantum yields for the 305-nm photodecomposition of nitrate in aqueous solution. *J Phys Chem* 1988;92:6278-83.
- Wenk J, Canonica S. Phenolic antioxidants inhibit the triplet-induced transformation of anilines and sulfonamide antibiotics in aqueous solution. *Environ Sci Technol* 2012;46:5455-62.
- WHO. Guidelines for drinking water quality. Volume 2. Health criteria and other supporting information. World Health Organization, Geneva, 1996.

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
$k_{A,\text{Br}-}, \text{M}^{-1} \text{s}^{-1}$	$(2.68 \pm 0.27) \cdot 10^9$	$(3.98 \pm 0.34) \cdot 10^9$	$(3.46 \pm 0.20) \cdot 10^9$
$k_{B,\text{Br}-}, \text{M}^{-1} \text{s}^{-1}$	$(2.40 \pm 0.26) \cdot 10^6$	$(6.30 \pm 0.71) \cdot 10^6$	$(4.34 \pm 1.15) \cdot 10^6$
$k_{C,\text{Br}-}, \text{M}^{-1} \text{s}^{-1}$	$(3.87 \pm 0.86) \cdot 10^8$	$< 1 \cdot 10^7$	$< 3 \cdot 10^7$

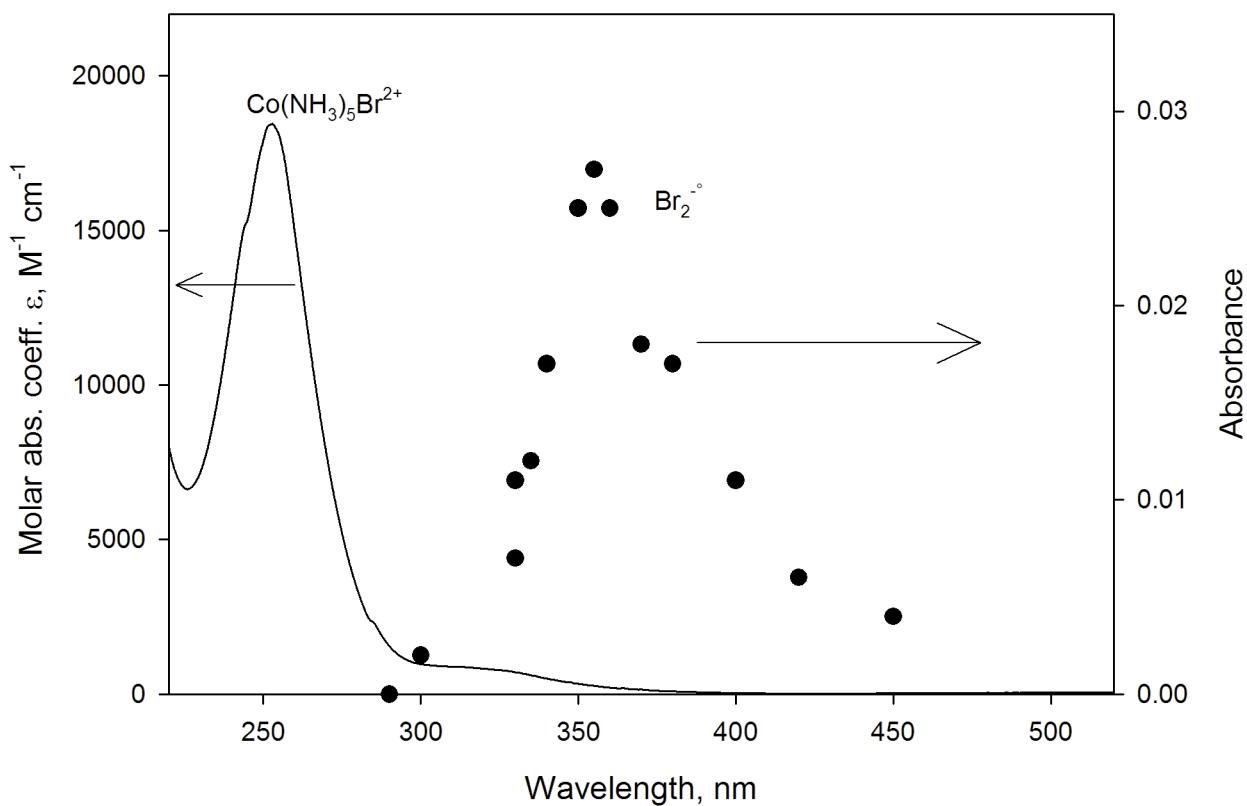


Figure 1. Molar absorption coefficient of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in aqueous solution (left-axis) and absorbance of $\text{Br}_2\cdot$ (right-axis), produced upon laser flash photolysis (355 nm, 60 mJ/pulse) of 0.7 mM $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in the presence of 5 mM Br^- . The pH was 6.0 at ambient temperature.

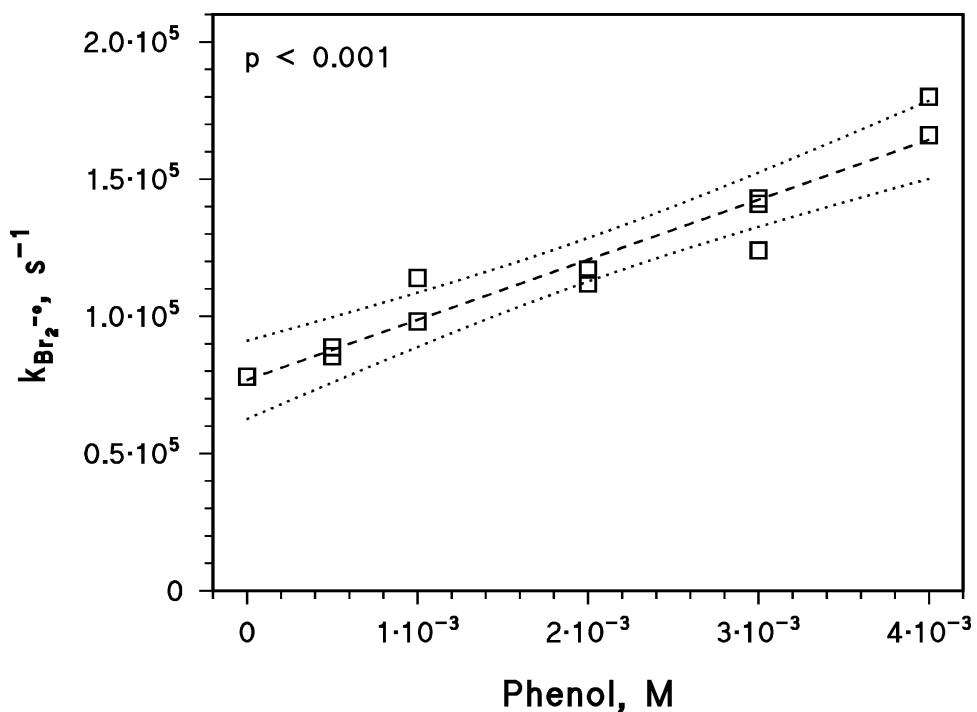


Figure 2. Trend of the pseudo-first order degradation rate constant of the radical $Br_2^{-\bullet}$, as a function of phenol concentration. The fit line is dashed, the 95% confidence bands are dotted. The line slope represents the second-order reaction rate constant between $Br_2^{-\bullet}$ and phenol. Laser flash experiments were performed at 355 nm and 60 mJ/pulse, at ambient temperature.

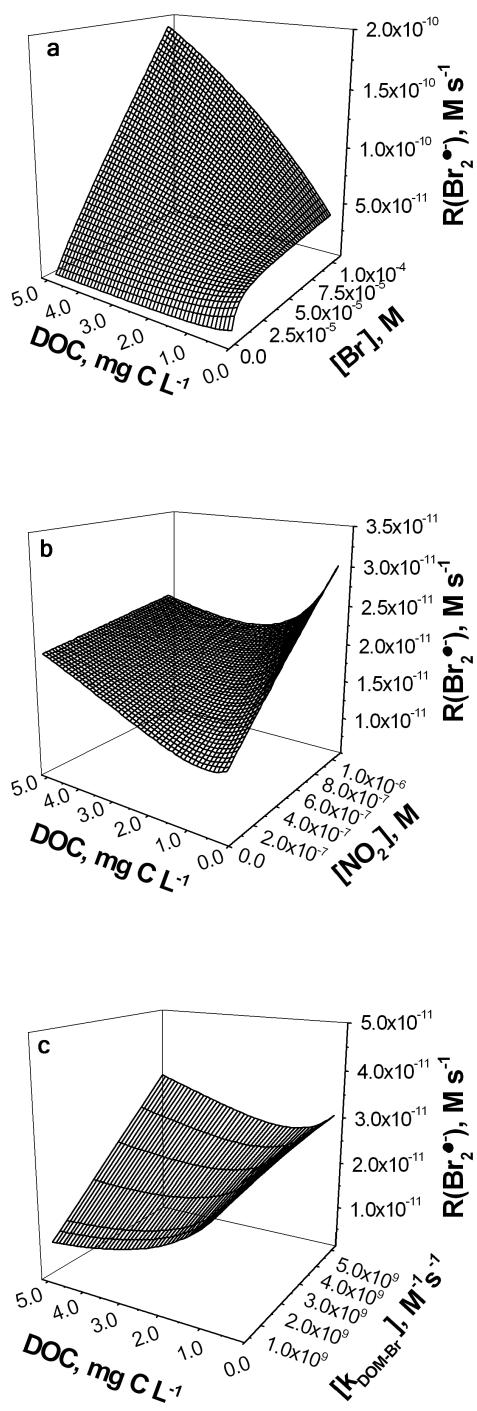


Figure 3. Modelled trends of Br_2^\bullet initial formation rate as a function of: a) DOC and bromide; b) DOC and nitrite; c) DOC and the reaction rate constant between Br^- and ${}^3\text{CDOM}^*$. Solar UV irradiance: 22 W m^{-2} . Other photochemically important parameters are reported in the text.

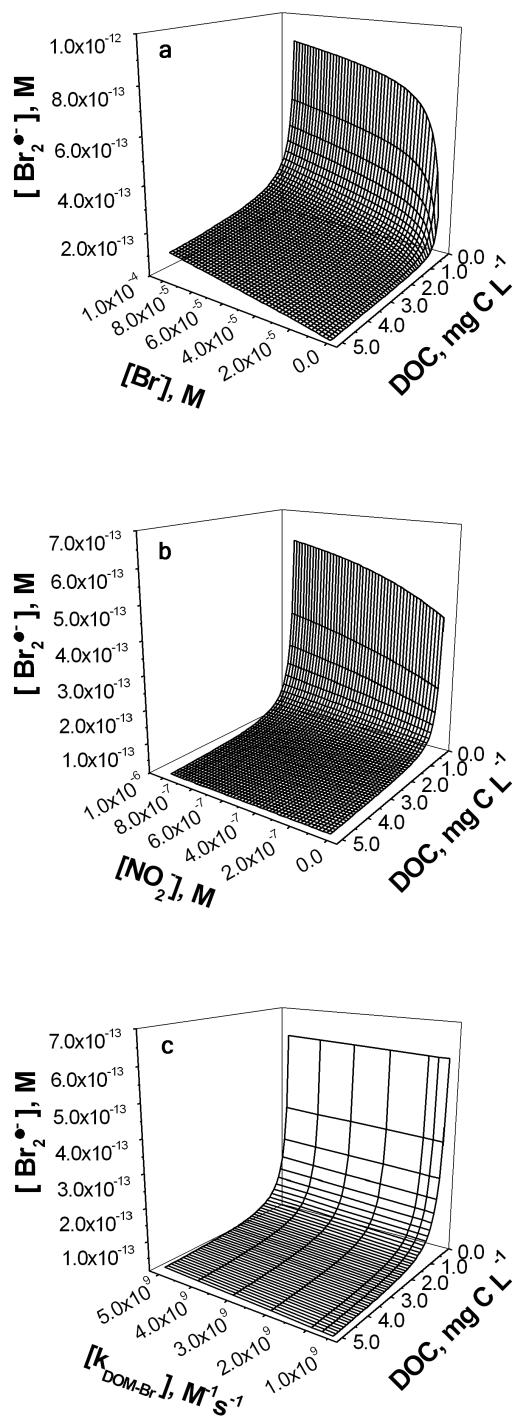


Figure 4. Modelled trends of $\text{Br}_2\cdot$ steady-state concentration as a function of: a) DOC and bromide; b) DOC and nitrite; c) DOC and the reaction rate constant between Br^- and ${}^3\text{CDOM}^*$. Solar UV irradiance: 22 W m^{-2} . Other photochemically important parameters are reported in the text.

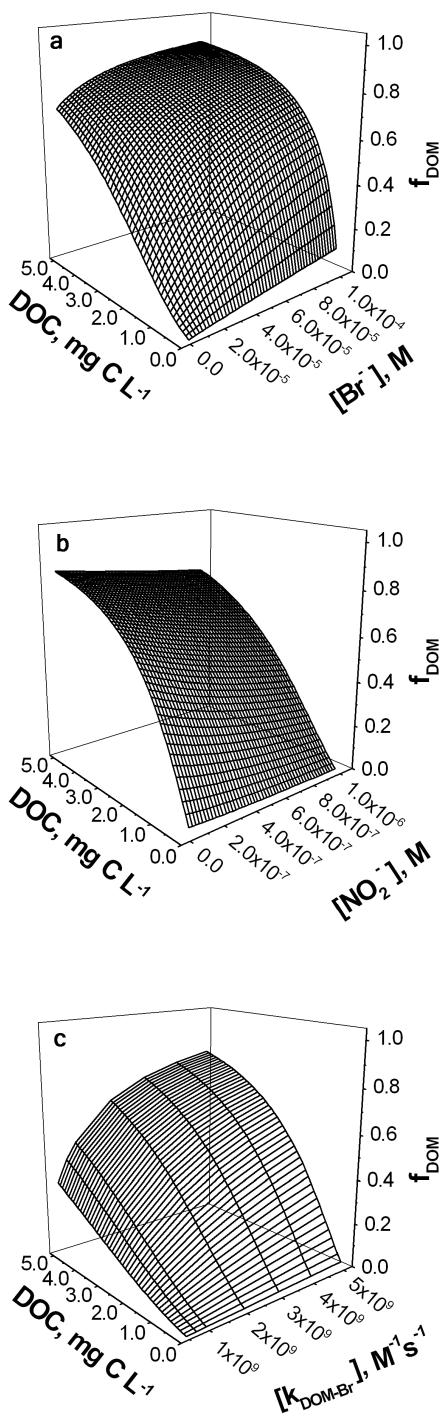


Figure 5. Modelled trends of the fraction of Br_2^{\bullet} that is generated upon bromide oxidation by ${}^3\text{CDOM}^*$, as a function of: a) DOC and bromide; b) DOC and nitrite; c) DOC and the reaction rate constant between Br^- and ${}^3\text{CDOM}^*$. Solar UV irradiance: 22 W m^{-2} . Other photochemically important parameters are reported in the text.

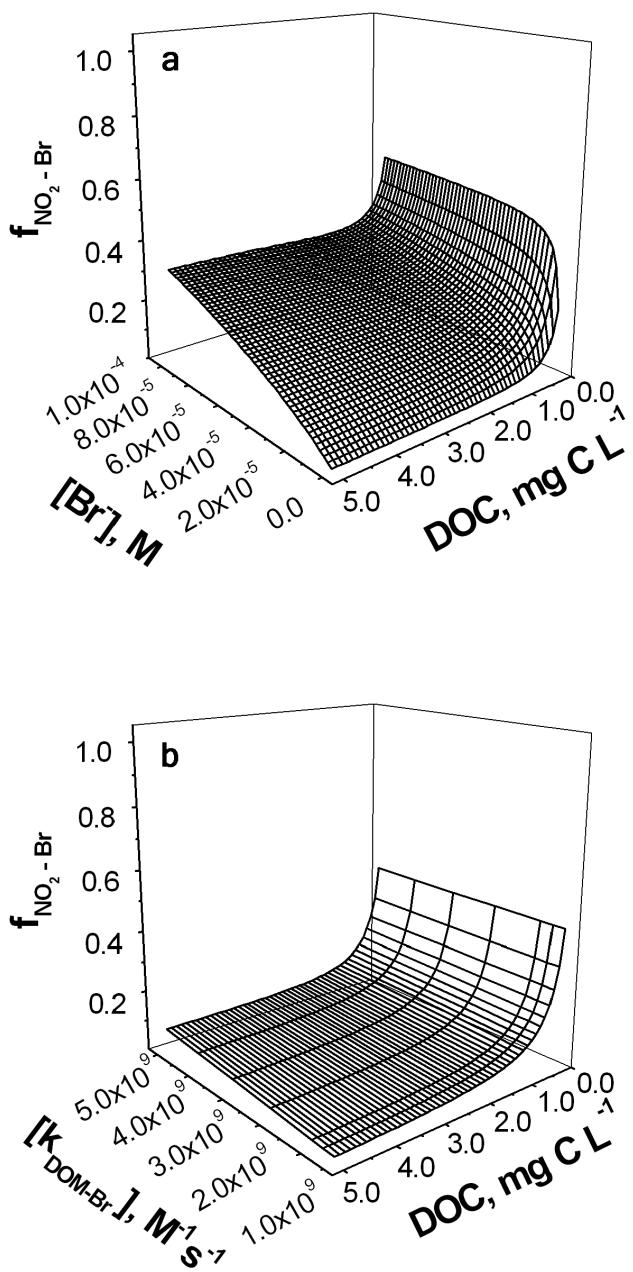


Figure 6. Modelled trends of the fraction of $\bullet\text{NO}_2$ that is generated upon nitrite oxidation by Br_2^{\bullet} , as a function of: a) DOC and bromide; b) DOC and the reaction rate constant between Br^- and ${}^3\text{CDOM}^*$. Solar UV irradiance: 22 W m^{-2} . Other photochemically important parameters are reported in the text.