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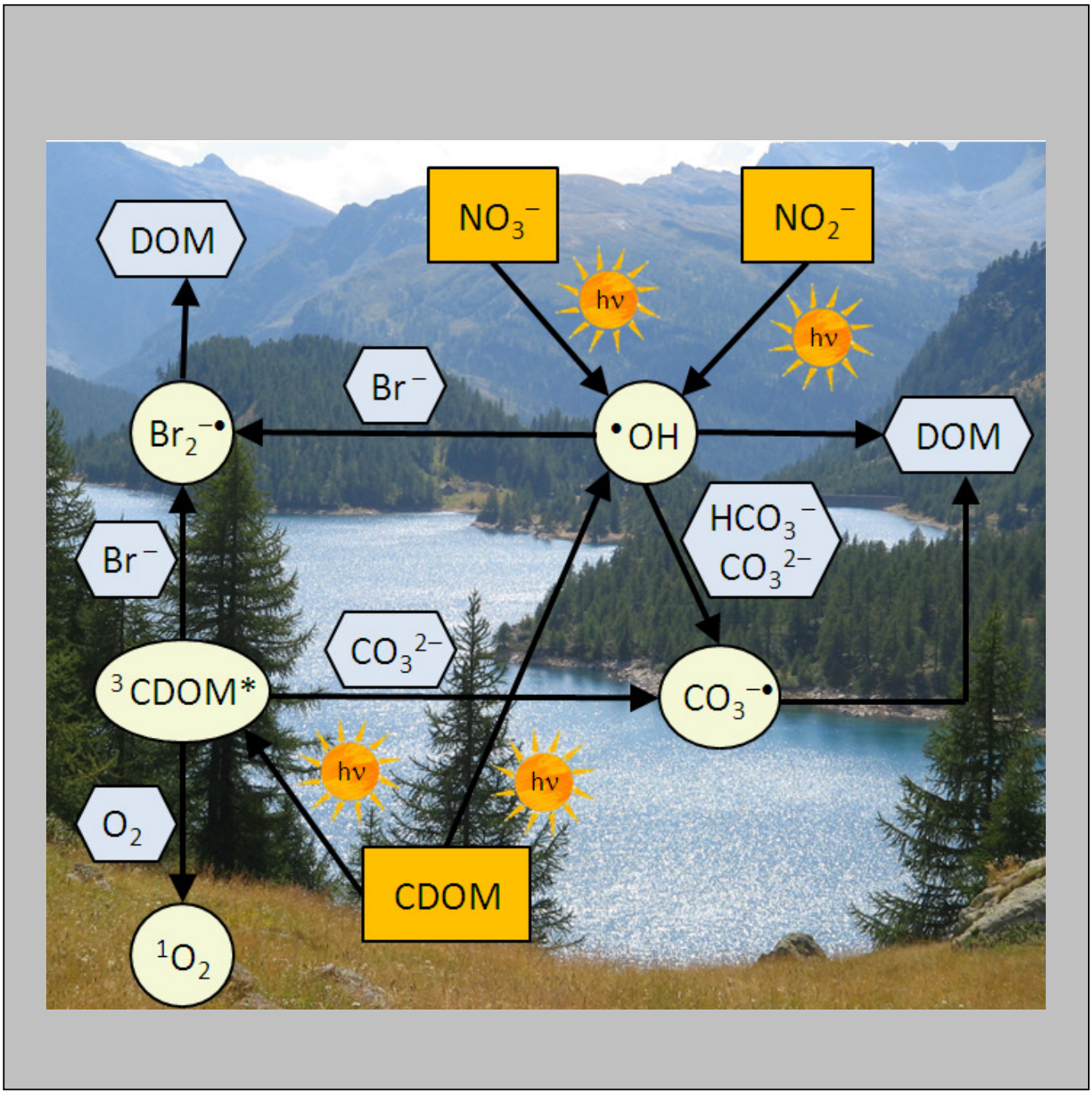
Davide Vione,*[a,b] Marco Minella,[a] Valter Maurino,[a] and Claudio Minero[a]



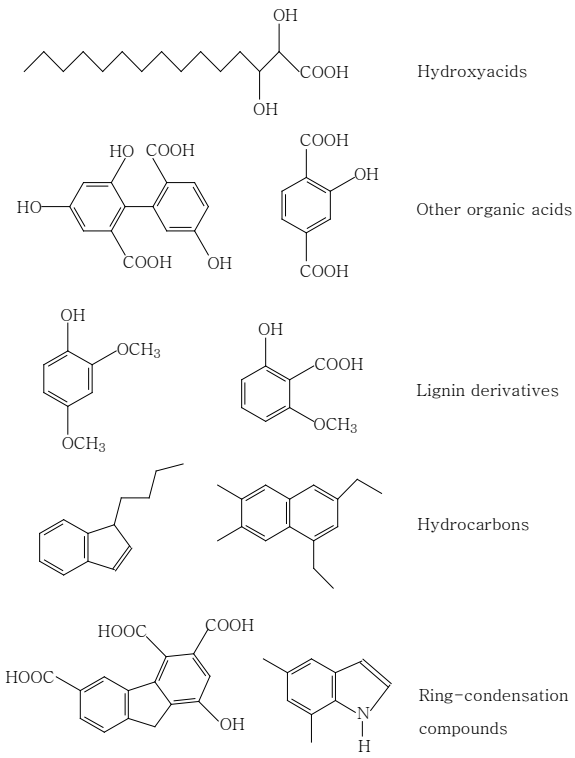
Abstract: This paper gives an overview of the main reactive transient species that are produced in surface waters by sunlight illumination of photoactive molecules (photosensitizers), such as nitrate, nitrite and chromophoric dissolved organic matter (CDOM). The main transients ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$ and CDOM triplet states) are involved in the indirect phototransformation of a very wide range of persistent organic pollutants in surface waters.

Introduction

Photochemical reactions play an important role in the transformation of naturally occurring compounds and of xenobiotics in both surface waters and the atmosphere.[1,2] They are also involved in the redox cycling and, as a consequence, the bioavailability of several inorganic nutrients, as well as in the photomineralization of organic matter with important implications for the carbon cycle.[3-5] In surface waters, the photochemical transformation of organic and inorganic solutes could take place by direct photolysis or indirect photoreactions. Direct photolysis takes place when radiation absorption by a molecule triggers its transformation. A key prerequisite for a molecule to undergo direct photolysis is its ability to absorb sunlight.[6,7] In the case of indirect photoreactions, sunlight is absorbed by compounds called photosensitizers and reactive transient species are produced as a consequence. Important photosensitizers in surface waters are the nitrate and nitrite anions and the chromophoric dissolved organic matter (CDOM), which is the fraction of dissolved organic matter (DOM) that is able to absorb sunlight.[8-11] Natural dissolved organic compounds are a very complex family of molecules, with extremely variable and still poorly understood structures. Some important recent advances have been made in the structural elucidation of humic substances, which are an important class of compounds within CDOM. Humic compounds have a supramolecular rather than a macromolecular structure, which includes diverse structural groups such as organic acids, lignin derivatives, hydrocarbons, condensed cycles and heterocycles. Some examples of possible functional groups that can be found in humic substances are reported in Scheme 1.[12,13]

Among the main transient species that can be produced by irradiation of the photosensitizers there are the radicals $^{\bullet}OH$ and $CO_3^{-\bullet}$, singlet oxygen ($^1O_2$) and the triplet states of CDOM (^{3}CDOM*).[14-17] The photogenerated reactive transients can undergo different fates in surface waters, including thermal deactivation or reaction with water components. The indirect photodegradation of pollutants is environmentally very important,[18-24] but usually only a minor fraction of the photogenerated transients takes part to such processes. In fact, in addition to thermal deactivation that can sometimes be very important, the main solutes that would scavenge the transients are DOM of mostly natural origin, inorganic carbon (especially bicarbonate and carbonate), bromide and (in the case of ^{3}CDOM*) dissolved oxygen.[25-27] Several components of surface waters can thus be involved in the formation and/or in the consumption of reactive transients, and important water chemistry parameters of photochemical significance are DOC (dissolved organic carbon, which is a measure of DOM), nitrate, nitrite, carbonate, bicarbonate, bromide and dissolved oxygen.[28-30]

As mentioned above, the photogenerated reactive species (*e.g.* $^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$ and ^{3}CDOM*) have a transient nature due to their high instability and chemical reactivity. They disappear rather quickly after formation, with typical lifetimes in the µs range. As a consequence, the transients rapidly reach steady-state concentrations in surface waters that are the result of the formation-transformation budget.[31-33]



Scheme 1. Examples of chemical functionalities that can be found in humic substances.

Assume P as a pollutant and X as a photogenerated transient with steady-state concentration [X], while $k_{X,P}$ is the second-order kinetic constant of the reaction between X and P. The kinetics of P transformation because of reaction with X depends on the pseudo-first order rate constant $k'_P = k_{X,P}$ [X], which defines the half-life time $\tau_P \approx 0.693\ (k'_P)^{-1}$.[34-36] Under steady irradiation conditions that are usual in the laboratory, [X] does not vary unless prolonged irradiation modifies the water sample, and k'_P is also constant. This issue is very convenient for lifetime calculations. However, in the natural environment the irradiance of sunlight is not constant and, even under stable fair-weather conditions, the day-night cycle is to be taken into account. By assuming for instance a fair-weather, mid-latitude 15 July as reference, one can have a sunlight UV irradiance (290-400 nm) of 30 W m^{-2} at the solar noon and of 22 W m^{-2} at

9 am or 3 pm solar time. The total UV energy reaching the ground over the whole 24-h day is $7.5 \cdot 10^5$ J m^{-2}, which would be delivered in just 7 h at a constant UV irradiance of 30 W m^{-2} (or in around 10 h at 22 W m^{-2}). Therefore, as a first approximation and neglecting weather-related issues, the transformation kinetics that is observed at a constant sunlight UV irradiance of 30 W m^{-2} is ~3.5 times faster than that taking place in the natural environment, on a mid-latitude and cloudless 15 July (and 2.5 times faster, if the constant UV irradiance is 22 W m^{-2}).[37] Note that several transients can be involved at the same time in the transformation of P, each with its own value of the second-order rate constant $k_{X,P}$. The overall first-order rate constant of P transformation by the transients is thus $k' = \alpha \sum_X k_{X,P}[X]$, where α is a correction factor that takes into account the relationship between steady irradiation and outdoor conditions.[38,39]

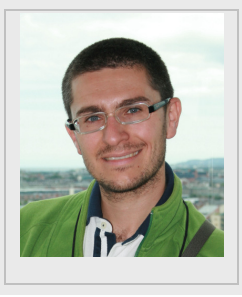
This review paper focuses on the main photogenerated transients that occur in surface waters ($^{\bullet}OH$, $^3CDOM^*$, $^1O_2$ and $CO_3^{-\bullet}$), as well as on some minor or less studied ones ($O_2^{-\bullet}$, $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $^{\bullet}NO_2$). The main sources and sinks will be considered, and particular attention will be given to the formation mechanisms and to the effect that several water parameters (most notably chemistry and depth) have on the steady-state concentrations [X]. The calculation of [X] makes use of a recently developed software tool (APEX: Aqueous Photochemistry of Environmentally-occurring Xenobiotics), which predicts pollutant degradation kinetics as a function of surface-water parameters.[40] APEX is freely available as Supplementary Information of Ref. 40 (.zip file). The software calculates the values of the steady-state concentration of each transient X under standard irradiation conditions (22 W m^{-2} UV irradiance of sunlight), and these values can be plotted as a function of water chemistry and depth.

The first part of the review will deal with the absorption of radiation by mixtures of compounds (which is the typical case of surface waters), because this topic is essential to understand some of the effects that water chemistry has on photochemistry.

The present paper will not give an account of the techniques that can be used to detect and measure the photogenerated transients in illuminated natural waters, because this topic has already been addressed in a recent review.[41] The photochemical degradation processes of definite classes of pollutants are also outside the scope of this paper: interested readers can make reference to previously published reviews.[1,6,42-48]

Also note that reactions occurring at the gas-liquid interface will not be given much importance. The reason is that, differently from the atmosphere, surface waters have a very low surface-to-volume ratio that make interface reactions very little important for water chemistry. In contrast, the air-water interface of atmospheric droplets is a very efficient photoreactor as far as photolysis and $^{\bullet}OH$ chemistry are concerned.[49-51] Interface processes can be important for the generation of aerosol from the water surface,[52] but this topic is outside of the review scope.

Davide Vione *(b. 1974) got his PhD in Chemistry in 2001 from the University of Torino, where he is associate professor in the Department of Chemistry since 2011. His main research interests focus on the photochemical processes taking place in surface waters and atmospheric aerosols. In 2003 he received the young researcher award from the European Association of Chemistry and the Environment, and he has been a finalist of the EuCheMS European Young Chemist award in 2008.*



Marco Minella *(b. 1982) is researcher at the Department of Chemistry of the University of Torino. He got his PhD in Chemistry at the University of Torino in 2010, and his main research interests focus on the photochemistry of surface waters and the photochemical advanced oxidation processes for water treatment, with a particular interest in heterogeneous photocatalysis.*

Valter Maurino *(b. 1962) is associate professor at the Department of Chemistry of the University of Torino. His main research interests focus on heterogeneous photocatalysis, and particularly on the charge-transfer processes that take place at the interface between irradiated semiconductor oxides and the aqueous solution. In 2010-2012 he has been president of the Piedmont and Aosta Valley section of the Italian Chemical Society.*

Claudio Minero *(b. 1956) is full professor of environmental and analytical chemistry at the Department of Chemistry of the University of Torino. His main research interests deal with environmental photochemistry, with focus on both photochemical remediation techniques and the processes that occur in the natural environment. He has published over 200 ISI articles, with over 6800 citations.*

Radiation absorption in aqueous solution

In natural waters there are several photosensitizers that absorb sunlight and produce reactive transient species. The main photosensitizers are CDOM, nitrate and nitrite. CDOM is the main sunlight absorber in surface waters below 500 nm, a spectral interval that is most important from the point of view of photochemical reactions.[53-57] As a consequence, nitrate and nitrite compete with CDOM for sunlight irradiance and, at equal $[NO_3^-]$ or $[NO_2^-]$, their absorbed photon flux of sunlight is lower in high-CDOM waters than in low-CDOM ones.

The absorption spectrum of CDOM usually shows a featureless exponential decay with increasing wavelength λ.[58-61] It can be approximated by an equation of the kind $A_1(\lambda) = A_o$

exp(−S·λ), where $A_1(\lambda)$ is the absorbance referred to an optical path length of 1 cm, A_o is constant and S is the so-called spectral slope of CDOM. Usually S is in the range of 0.01-0.02 nm^{-1}, and it is inversely proportional to the molecular weight or aromaticity degree of CDOM itself.[62-64] Lower S means less pronounced decrease of the absorbance with increasing wavelength, with the result that compounds with higher molecular weight (often humic and fulvic substances)[65] absorb a larger fraction of sunlight (including the visible range) compared to smaller compounds. An important consequence of the exponentially decaying absorption spectrum of CDOM, which is a key absorber in natural waters, is the fact that sunlight attenuation decreases in the order UVB > UVA > visible. Because UVB radiation is the fraction of sunlight that is most efficiently absorbed by CDOM, it is also the one that penetrates less deeply in surface waters.[66-69]

In a Lambert-Beer approximation, the calculation of the photon flux absorbed by CDOM, nitrate and nitrite when present together in solution should take into account the fact that the absorbance is the same when a light-absorbing component is alone in solution, or when it is in mixture with other light-absorbing compounds. In contrast, the absorbed photon flux P_a is lower in the mixture because of competition for the photons among the different absorbing species.[70] Under conditions of polychromatic irradiation such as those occurring in the environment, the photon flux P_a can be calculated as the integral over wavelength of the absorbed photon flux densities $p_a(\lambda)$:

$$P_a = \int_\lambda p_a(\lambda)\, d\lambda \qquad (1)$$

Furthermore, at a given λ, the absorbance ratio of two species (or the ratio of the absorbance of a light-absorbing species to the total absorbance of the solution) is equal to the ratio of the respective $p_a(\lambda)$ values. Moreover, the total absorbed photon flux density of the solution ($p_a^{tot}(\lambda)$) can be calculated from the total absorbance $A_{tot}(\lambda)$.[71,72] Therefore, if b is the optical path length of sunlight in the water column, ε is the molar absorption coefficient of nitrate or nitrite and $p°(\lambda)$ is the incident photon flux density of sunlight, the following equations are operational:[70-72]

$$A_{CDOM}(\lambda) = A_1(\lambda) \cdot b \qquad (2)$$

$$A_{NO_3^-}(\lambda) = \varepsilon_{NO_3^-}(\lambda) \cdot b \cdot [NO_3^-] \qquad (3)$$

$$A_{NO_2^-}(\lambda) = \varepsilon_{NO_2^-}(\lambda) \cdot b \cdot [NO_2^-] \qquad (4)$$

$$p_a^{tot}(\lambda) = p°(\lambda)\, [1 - 10^{-Atot(\lambda)}] \qquad (5)$$

$$p_a^j(\lambda) = p_a^{tot}(\lambda)\, A_j(\lambda)\, [A_{tot}(\lambda)]^{-1} \qquad (6)$$

$$P_a^j = \int_\lambda p_a^j(\lambda)\, d\lambda \qquad (7)$$

where j = CDOM, NO_3^- or NO_2^-. Note that in most cases it is $A_{tot}(\lambda) \approx A_{CDOM}(\lambda)$.

The absorption of radiation by a photosensitizer can trigger the production of reactive transient species. The efficiency of production of the transient X per absorbed photon is measured by the quantum yield Φ_X. Depending on the transient and on the photosensitizer, Φ_X can be constant or wavelength-dependent. In the former case, the formation rate of X by the sensitizer j (R_X^j) is simply expressed as follows:[70-72]

$$R_X^j = \Phi_X^j\ P_a^j \qquad (8)$$

If the quantum yield depends on the wavelength ($\Phi_X^j(\lambda)$), the formation rate of X can be calculated as follows:[70-72]

$$R_X^j = \int_\lambda \Phi_X^j(\lambda) \cdot p_a^j(\lambda)\, d\lambda \qquad (9)$$

The formation and scavenging pathways of the main reactive transient species in surface waters will now be discussed.

Hydroxyl radicals (•OH)

The •OH radicals are the most reactive transients that can be generated in surface waters. Their very high second-order kinetic constants toward many persistent xenobiotics imply that the reaction rates involving •OH are often limited by mass-transfer (diffusion) phenomena. However, the elevated reactivity of •OH radicals means that they are effectively scavenged by several water constituents, including most notably DOM.[25,37,73,74] The consequence of the effective removal of •OH from surface-water environments is that the resulting steady-state concentration is very low (often in the range of 10^{-18}-10^{-16} M).[25,37,75,76] This is compensated for to a variable extent by the usually high second-order reaction rate constants with organic pollutants. Therefore, although •OH is undoubtedly the transient showing the highest reactivity with water pollutants, depending on environmental conditions and on the kind of substrate it may or may not play an important role in phototransformation.[20,38,77] Generally speaking, •OH tends to play an important role in the transformation of many emerging pollutants such as pharmaceuticals and personal care products [30,38,39] (although the easily oxidized acetaminophen is an important exception [77]), and it is strongly involved in the degradation of refractory compounds, including hydrocarbons such as toluene.[78]

Among the photochemical reactions that can produce •OH in surface waters, the photolysis of nitrate and nitrite has been studied in detail:[79-81]

$$NO_3^- + h\nu \leftrightarrows [{}^\bullet NO_2 + O^{-\bullet}]_{solvent\ cage} \rightarrow {}^\bullet NO_2 + O^{-\bullet} \qquad (10)$$

$$NO_2^- + h\nu \rightarrow {}^\bullet NO + O^{-\bullet} \qquad (11)$$

$$O^{-\bullet} + H^+ \leftrightarrows {}^\bullet OH \qquad (12)$$

In reactions (10,11), 'hν' represents a photon. The radical •OH has pK_a = 11.5,[82] thus the equilibrium reaction (12) is strongly shifted towards •OH at the typical pH values of surface waters. However, the production of •OH by nitrate shows a certain pH trend under typical environmental conditions, presumably because reaction (10) takes place in alternative to photoisomerization, which is a less important but non-negligible process:[83-86]

$$NO_3^- + h\nu \rightarrow ONOO^{-\bullet} \qquad (13)$$

$$ONOO^- + H^+ \leftrightarrows HOONO \qquad (14)$$

$$HOONO \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad (15)$$

Peroxynitrous acid (HOONO) has $pK_a \approx 7$ [87,88] and its conjugated base peroxynitrite ($ONOO^-$) does not evolve into •OH (it rather reacts with CO_2 and/or bicarbonate to produce $CO_3^{-\bullet}$ + $^\bullet NO_2$, as well as OH^-).[89,90] Therefore, the formation

yield of •OH upon reactions (13-15) decreases with increasing pH at values around neutrality.[91]

In the case of nitrite, the acid-base equilibrium $HNO_2 \leftrightarrows NO_2^- + H^+$ (pK_a = 3.3 [92]) could affect the photogeneration of •OH in acidic solutions (usually at pH < 5, which is however quite rare in surface waters),[93] because the photolysis of nitrous acid is more effective than that of nitrite ($\Phi_{\bullet OH}^{HNO_2}$ = 0.35, to be compared with $\Phi_{\bullet OH}^{NO_2^-}$ = 0.025-0.065 depending on the wavelength).[94] However, in most surface-water environments HNO_2 would not give a significant contribution to •OH photogeneration.

Nitrite usually has much lower concentration values than nitrate in natural waters,[95,96] but it absorbs sunlight much more effectively and has a higher quantum yield of •OH generation (to be compared with $\Phi_{\bullet OH}^{NO_3^-} \approx 0.01$ in reactions 10,12, to which some contribution by reactions 13-15 should be added at pH < 7).[97,98] In very shallow and clear water bodies, during mid-latitude summer around noon, nitrate and nitrite would be comparable •OH sources if $[NO_3^-] \approx 10^2 [NO_2^-]$.[99] Nitrite mainly absorbs sunlight in the UVA region (absorption maximum around 355 nm), while nitrate mostly absorbs in the UVB (absorption maximum around 305 nm, see Figure 1). Because UVA radiation penetrates more deeply than UVB in the water columns and the UVB/UVA ratio is maximum in summer at noon, any change from the scenario of clear and shallow water in midday summer would favor the photochemistry of nitrite compared to nitrate.[99]

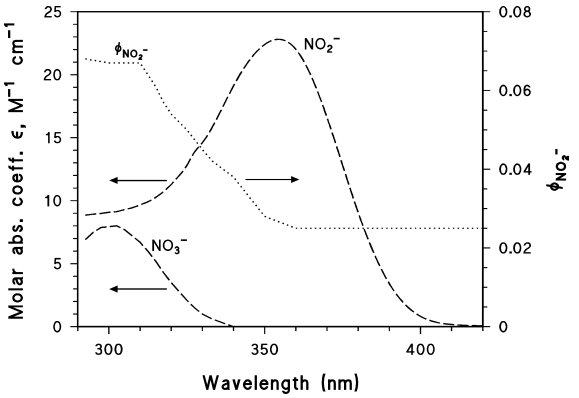


Figure 1. Left Y axis: absorption spectra (molar absorption coefficients) of nitrate and nitrite. Right Y axis: wavelength trend of the quantum yield of •OH photogeneration upon nitrite photolysis.

Overall, given the typical $[NO_3^-]/[NO_2^-]$ ratios that are observed in surface waters, nitrite is often a more important source of •OH compared to nitrate.[99,100] It is important to point out that nitrite can be a very significant •OH source even at sub-μM concentration levels, where detection by typical ion chromatography methods is extremely difficult, and even the more sensitive spectrophotometric determinations (Griess reaction and its variants)[101,102] can prove inadequate. Therefore, the typical analytical techniques that are routinely used to assess the nitrogen balance in surface waters may be unsuitable for photochemistry applications. More sensitive methods are often needed to assess the photochemistry of nitrite.[103-105]

Much interest has recently been devoted to the photochemical generation of •OH by CDOM, as there is indication that CDOM itself would be the main source of •OH in many (and possibly most) surface-water environments.[57,77,106-108] Given the high structural complexity of CDOM, the understanding of the processes involved in •OH generation is much more difficult (and much less clear at present) compared to the cases of nitrate and nitrite. The quantum yields of •OH photoproduction have been experimentally determined to be in the range of 10^{-5}-10^{-4} by irradiation of surface-water CDOM or of CDOM isolates (*e.g.* humic substances extracted from humic-rich waters or from wastewater).[15,26,37,75,100,109-111] Although these $\Phi_{\bullet OH}$ values are considerably lower than those of nitrate and nitrite, they can be high enough to make CDOM the main source of •OH, because of its much higher ability to absorb sunlight compared to nitrate and nitrite.[99,106]

An important issue connected with the photogeneration of •OH by CDOM is represented by the fact that the overall process is found to consist of at least two main pathways (or possibly groups of pathways), one involving and the other not involving H_2O_2.[112] These pathways can be differentiated by adding catalase to speed up the decomposition of H_2O_2, which could be present in the initial sample or (more likely) could be generated photochemically. The prevailing formation route of •OH varies depending on the CDOM sample, but overall it appears that the two pathways have, on average, roughly comparable importance, with a possible prevalence of the H_2O_2-independent one.[112] The H_2O_2-dependent formation route is probably connected with Fenton or Fenton-like reactions,[109,113-116] while the possible involvement of H_2O_2 photolysis is more controversial.[117] As far as the latter issue is concerned, the concentration of hydrogen peroxide that can be measured at any moment in a surface-water sample is largely insufficient to account for a significant fraction of •OH photoproduction,[100,118] unless H_2O_2 is also continuously and efficiently regenerated by photochemical processes.

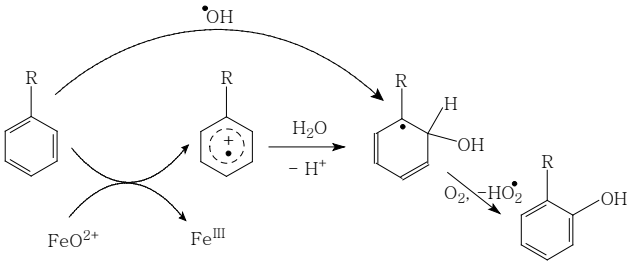
Besides Fe(III) hydroxocomplexes (*e.g.* $Fe(OH)_2^+$ or $Fe(OH)^{2+}$) that do not occur significantly at the typical pH values of surface waters, photo-Fenton reactions could involve complexes between Fe(III) and organic compounds.[113-116] Sunlight absorption is enabled by the ligand-to-metal charge transfer that characterizes bonds in such complexes. A possible reaction scheme could be the following, where L is an organic ligand undergoing two-electron oxidation to L_{ox}, and A is an electron acceptor:[119]

$$Fe^{III}\text{-}L + h\nu \rightarrow Fe^{II} + L^{+\bullet} \quad (16)$$
$$L^{+\bullet} + A \rightarrow L_{ox} + A^{-\bullet} \quad (17)$$
$$A^{-\bullet} + O_2 \rightarrow A + O_2^{-\bullet} \quad (18)$$
$$2\ O_2^{-\bullet} + 2\ H^+ \rightarrow H_2O_2 + O_2 \quad (19)$$
$$Fe^{II} + H_2O_2 \rightarrow Fe^{III}OH + {}^\bullet OH \quad (20)$$

A major issue is the fact that the Fenton reaction (20) is never as straightforward as shown, especially under ~neutral pH conditions.[120] Actually, the process proceeds through intermediate transients that could either evolve into •OH, or produce high-valence and oxidizing Fe species (such as the ferryl ion, FeO^{2+}, or similar ferryl hydroxyl/hydro species).[121,122] The •OH yield of the Fenton reaction is maximum under acidic conditions (pH 2-3), but even in this case it is hardly quantitative: recent evidence suggests that, at pH 2, a 60% fraction of reaction (20) proceeds as shown, while the remainder would yield ferryl species.[123] Under the pH conditions of surface waters, the •OH yield is expected to be much lower than 60%.[120] The limited inhibition of the

degradation of phenolic compounds that is observed by adding •OH scavengers in Fenton or photo-Fenton processes suggests an important role of ferryl species as active oxidants at circumneutral pH.[124]

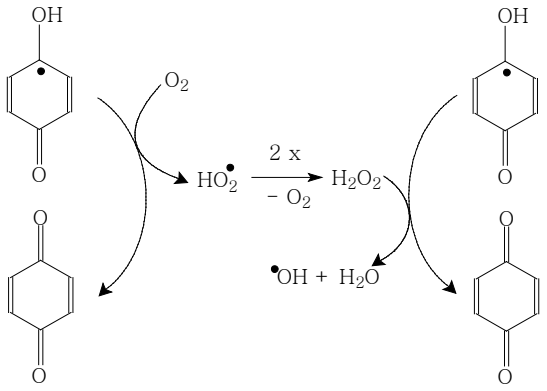
From this point of view, ferryl and related oxidants could be potentially interfering agents in the determination of •OH by means of probe molecules such as benzene or terephthalic acid,[112,125,126] because a one-electron oxidation (as carried out by ferryl on aromatic compounds) followed by reaction with water could simulate the •OH attack (see Scheme 2).[127] However, ferryl proved to be much less reactive than •OH towards electron-rich aromatic compounds such as azo dyes and anilines.[123] Therefore, its potential for interference in the case of the electron-poor •OH probes that are typically used for surface-water samples should be limited, unless the ratio of the steady-state concentrations [Ferryl] [•OH]$^{-1}$ is very high. Furthermore, the pH trend of the •OH yields in the Fenton and photo-Fenton reactions partially explains (together with the HNO_2/NO_2^- equilibrium) the considerable enhancement of •OH photogeneration in acidified surface waters.[128,129]



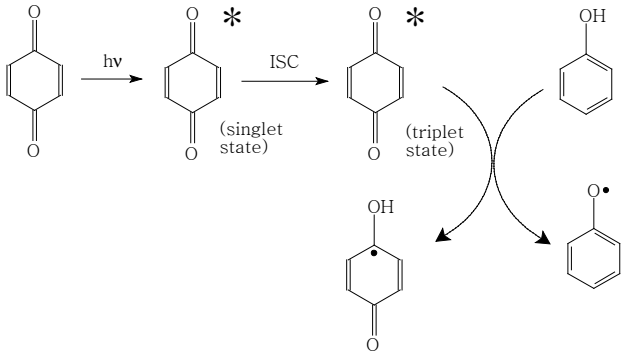
Scheme 2. Simulation of the •OH attack by one-electron oxidation, carried out by ferryl (FeO^{2+}), followed by hydration in aqueous solution.

Fenton-like reactions can also take place in the presence of semiquinone radicals, as shown in Scheme 3. Reduction of Fe^{III} to Fe^{II} by semiquinones is also possible and it could contribute to the process, but it is not strictly necessary.[130,131]

The formation of semiquinone radicals would take place from CDOM quinones, upon photochemical reactions in the presence of electron-rich compounds (*e.g.* phenols, see Scheme 4),[132,133] or upon dark reduction under anoxic conditions.[134,135] The dark reduction of quinones to semiquinones in anoxic systems (in which Fe^{II} can also be present), followed by the formation of •OH when the solution is aerated (see Scheme 3) is potentially important whenever anoxic waters are brought in contact with oxygen. In such systems, an •OH spike is observed soon after aeration and it is characterized by very elevated [•OH] levels, which could be important in the transformation of dissolved compounds.[134,135]



Scheme 3. Fenton-like process induced by semiquinone radicals in the presence of oxygen.



Scheme 4. Formation of semiquinones from irradiated quinones in the presence of phenols as reducing agents. The asterisk denotes a photochemically excited state, ISC means inter-system crossing.

As far as the H_2O_2-independent formation of •OH by irradiated CDOM is concerned, the detailed pathways are still to be elucidated. For instance, while some excited triplet states are able to oxidize water and/or OH^- to •OH,[136,137] this is not a general feature of triplet-state reactivity.[112,132,138] Furthermore, the environmental importance of the water oxidation pathway is still to be demonstrated. A very interesting feature of the H_2O_2-independent route to •OH is that the photogeneration of hydroxyl radicals is most efficient when taking place from the low-molecular-weight (LMW) fractions of CDOM.[139] A possible explanation of this phenomenon is that the high molecular weight (HMW) CDOM fractions are made up by assemblages of smaller molecules, where charge-transfer interactions between electron donors and acceptors (*e.g.* phenols and benzophenones) can take place. Such interactions would enhance the deactivation of the excited states by internal conversion, thereby decreasing the yields of both photochemical and photophysical processes.[140] The enhancement of internal conversion may explain why fluorescence quantum yields are also lower for the HMW fractions of CDOM.[139,140]

As indicated above, the •OH radicals are effectively scavenged by natural water components and most notably by DOM. The latter accounts on average for ~90% of •OH scavenging in surface freshwaters.[37,76] The reaction rate constant(s) between •OH and DOM are obviously lumped values that reflect the contribution of thousands of compounds, and variability between samples may be very high. Anyway, average values in the order of $10^4 – 10^5$ L (mg C)$^{-1}$ s^{-1} (where

mg C means milligrams of carbon), corresponding to approximately 10^8 – 10^9 L (mol C)$^{-1}$ s^{-1} are often reported.[15,37,76,141-143] Interestingly, at least in wastewater organic matter, it has been shown that the LMW fractions are those showing the highest reactivity toward $^{\bullet}$OH.[142] However, this result has been attributed to the occurrence of soluble microbial products in LMW wastewater DOM, and the relevance of such results for typical surface-water DOM is still to be assessed. The reaction between $^{\bullet}$OH and many small organic molecules has very low to nil activation energy,[78] resulting in second-order reaction rate constants that are near the diffusion limit for aqueous solutions (~10^{10} M^{-1} s^{-1} [144]). In the case of DOM the activation energy is in the order of 10-20 kJ mol^{-1},[145] which suggests that the reaction rate constants would also be lower. This issue could make additional evidence that reactivity with $^{\bullet}$OH tends to decrease with increasing molecular weight, or it may reflect the occurrence in DOM of aliphatic moieties that are less reactive than the aromatic ones.[144]

Among the other $^{\bullet}$OH scavengers in surface waters, bromide needs to be mentioned first because it is the main one in seawater (where it approaches a concentration value of 1 mM), and it plays an important role in brackish waters as well.[146] Other important scavengers are carbonate and bicarbonate, which yield $CO_3^{-\bullet}$ upon reaction with $^{\bullet}$OH.[144] In contrast, nitrite usually accounts for no more than 1% of $^{\bullet}$OH consumption.[99] However, reaction between $^{\bullet}$OH and nitrite is important as a source of $^{\bullet}NO_2$ in freshwater (*vide infra*).

$$Br^- + {}^{\bullet}OH \rightarrow Br^{\bullet} + OH^- \quad [k_{21} = 1.1\cdot10^{10}\ M^{-1}\ s^{-1}] \quad (21)$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{-\bullet} + H_2O \quad [k_{22} = 8.5\cdot10^{6}\ M^{-1}\ s^{-1}] \quad (22)$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{-\bullet} + OH^- \quad [k_{23} = 3.9\cdot10^{8}\ M^{-1}\ s^{-1}] \quad (23)$$

$$NO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_2 + OH^- \quad [k_{24} = 1.0\cdot10^{10}\ M^{-1}\ s^{-1}] \quad (24)$$

The budget between formation and scavenging produces a relatively low steady-state concentration of $^{\bullet}$OH. Generally speaking, the values of [$^{\bullet}$OH] are enhanced in the presence of elevated concentrations of nitrate or nitrite and decreased by high DOC, bromide, carbonate and bicarbonate.[25,37,99,109,146] The roles of nitrate, nitrite ($^{\bullet}$OH sources), bromide and inorganic carbon ($^{\bullet}$OH scavengers) towards [$^{\bullet}$OH] are rather straightforward. On the other hand, DOC measures both DOM ($^{\bullet}$OH scavenger) and CDOM ($^{\bullet}$OH source) and its effect needs some further comment. In most surface waters the importance of DOM as $^{\bullet}$OH scavenger is higher than that of CDOM as $^{\bullet}$OH source, thus [$^{\bullet}$OH] usually anticorrelates with DOC.[25,147] Exceptions may be represented by the (presumably rare) cases in which inorganic carbon is an important $^{\bullet}$OH scavenger and nitrate and/or nitrite are very minor sources.[148] The evolution of this scenario is modeled in Figure 2, where the steady-state [$^{\bullet}$OH] is plotted as a function of nitrite and DOC.

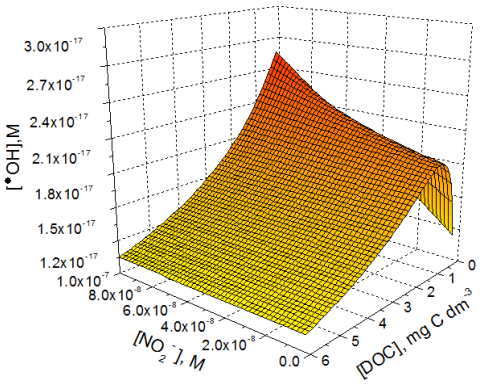


Figure 2. Steady-state [$^{\bullet}$OH] as a function of nitrite and DOC. Other water conditions: 1 µM nitrate, 3 mM bicarbonate, 3 µM carbonate, 5 m depth. The ratio [HCO_3^-]/[CO_3^{2-}] = 10^3 implies that pH ~ 7. Sunlight UV irradiance: 22 W m^{-2}, as can be found for instance on 15 July at mid-latitude, at 9 am or 3 pm solar time. The simulation was carried out with the APEX software. The modeled steady-state [$^{\bullet}$OH] is an average value over the 5-m water column.

At low nitrite, [$^{\bullet}$OH] has a maximum for DOC around or below 1 mg C L^{-1}. The initial increase of [$^{\bullet}$OH] with increasing DOC is accounted for by the fact that CDOM strongly prevails as $^{\bullet}$OH source (nitrate and nitrite are very low), while the relatively elevated concentration of inorganic carbon limits the (however important) role of DOM as scavenger. About the decrease of [$^{\bullet}$OH] with increasing DOC after the maximum, one should consider that over a 5 m water column it is easy for CDOM to almost totally absorb the incident sunlight. Under these conditions of absorption saturation, a further increase of DOC would not lead to an important increment of the photon flux absorbed by CDOM, and the corresponding formation rate of $^{\bullet}$OH would be almost unchanged. In contrast, the rate of $^{\bullet}$OH scavenging is directly proportional to the DOC value and it does not reach saturation. Therefore, as DOC increases, almost constant $^{\bullet}$OH formation combined with increasing scavenging leads to a decreasing [$^{\bullet}$OH].

At high nitrite, the role of DOM as $^{\bullet}$OH scavenger is always more important than the role of CDOM as $^{\bullet}$OH source. As a consequence (and as it is expected in the majority of environmental cases), [$^{\bullet}$OH] monotonically decreases with increasing DOC. An additional issue is the competition for sunlight irradiance between CDOM, nitrate and nitrite, which would decrease the photon flux absorbed by nitrate and nitrite (and, as a consequence, the associated rates of $^{\bullet}$OH formation) in high-DOC waters. This phenomenon would only be partially offset by the generation of $^{\bullet}$OH by irradiated CDOM, because the quantum yield of $^{\bullet}$OH formation by CDOM is lower compared to nitrate and nitrite.

CDOM triplet states (^{3}CDOM*)

The formation of ^{3}CDOM* in surface waters is triggered by the absorption of sunlight by CDOM chromophores. Radiation absorption excites the chromophore-containing molecules to the singlet states, which under favorable conditions can evolve to triplet states by inter-system crossing (ISC, reaction 25).[17,149]

$$\text{CDOM} + h\nu \rightarrow {}^1\text{CDOM}^* \xrightarrow{ISC} {}^3\text{CDOM}^* \qquad (25)$$

The formation quantum yields of ^{3}CDOM* from irradiated CDOM are in the range of 10^{-3} – 10^{-2}, which averages the behavior of compounds with very different photoreactivity.[15,150] Among the CDOM chromophores that are most likely to be involved in reaction (25) there are aromatic carbonyls and quinones. Such compounds yield excited triplet states that may have sufficiently high redox potentials to allow significant chemical reactivity.[132,151-153] Generally speaking, the ^{3}CDOM* states can react with dissolved compounds by energy, electron or hydrogen transfer. In the latter two cases, the triplet states generally behave as oxidants. In oxygenated surface waters, a very important reaction of ^{3}CDOM* is the transfer of energy to ground-state molecular oxygen to produce singlet oxygen, $^1O_2$. Such a reaction is able to control the lifetime of most excited triplet states in these environments.[154]

$$^3\text{CDOM}^* + O_2 \rightarrow \text{CDOM} + {}^1O_2 \qquad (26)$$

The lifetime of ^{3}CDOM* in aerated aqueous solutions is in the µs range, and it is around an order of magnitude higher (20-80 µs) in the absence of oxygen.[27,155] These lifetimes are too short to enable significant scavenging of ^{3}CDOM* by DOM, at least for DOC < 20 mg C L^{-1} as it has been recently found.[156] Figure 3 reports the modeled steady-state [^{3}CDOM*] as a function of water depth and DOC. The increase of [^{3}CDOM*] with increasing DOC is due to the fact that the ^{3}CDOM* states are formed by irradiated CDOM, but they are not efficiently scavenged by DOM.[154] The decrease of [^{3}CDOM*] with increasing depth is due to the poor illumination of the bottom layers of the water column. Because the reported [^{3}CDOM*] is the average value over the whole water column, it results from the contribution of both the higher concentrations near the well-illuminated surface layer and the lower values in the darker bottom. This depth issue is valid for all photochemical processes, which are favored in shallow waters.[157]

The triplet states ^{3}CDOM* are important transient species in surface waters. They play a role in the degradation of several pollutants, such as most notably phenols, phenylurea herbicides and sulfonamide antibiotics.[149,152,154,155,158,159]

Although the scavenging by DOM of the ^{3}CDOM* states is of limited importance, DOM is still able to inhibit the transformation processes of organic compounds induced by ^{3}CDOM*.[160,161] The reason is to be found in the reactions that follow the transfer of electrons or of hydrogen atoms from the substrate to the triplet state. Such reactions lead to the oxidation of the substrate S (yielding $S^{+\bullet}$ in the case of electron transfer) and to the reduction of ^{3}CDOM* (*e.g.* to $CDOM^{-\bullet}$). The key issue is that DOM contains antioxidant moieties (*e.g.* phenolic compounds) that may reduce $S^{+\bullet}$ back to the initial substrate S, thereby inhibiting its transformation (see Scheme 5).[162]

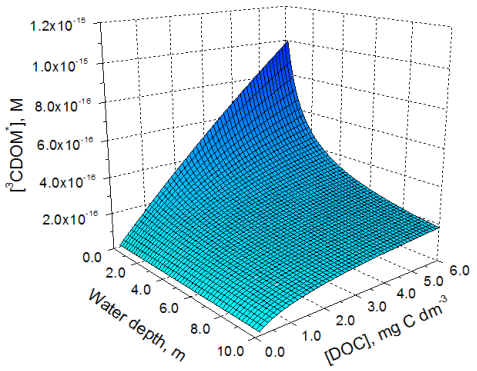
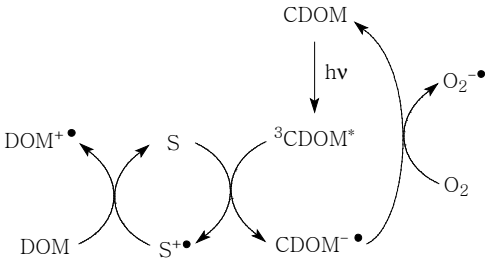


Figure 3. Steady-state [^{3}CDOM*] as a function of DOC and water depth, in aerated solution. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 1 µM carbonate. Sunlight UV irradiance: 22 W m^{-2}. The simulation was carried out with the APEX software. The modeled steady-state [^{3}CDOM*] is an average value over the water column of given depth.

Scheme 5 suggests that the ability of organic matter to sensitize the degradation of S depends both on the efficiency with which its chromophores induce the generation of reactive triplet states, and on the abundance and reactivity of its antioxidant sites. The outcome depends on the nature of both the organic matter and the substrate: for instance, 2,4,6-trimethylphenol (TMP) that is frequently used as ^{3}CDOM* probe [15,150,163] does not undergo significant back-reduction after its initial oxidation by the CDOM triplet states,[162] and a similar issue holds for 4-methylphenol.[160,162] The most likely reason is that the oxidation of TMP and 4-methylphenol yields rather stable phenoxy radicals, which are not easily reduced to the starting compounds by antioxidant moieties including less electron-rich phenolic compounds.[164] The cationic species formed in such processes and shown in Scheme 5 are most likely to react with water and/or dissolved oxygen to give oxidized/hydroxylated compounds. Unlike inorganic cations,[165] the organic ones are very little likely to produce radical species (e.g. $^{\bullet}$OH upon activation of water).



Scheme 5. Inhibition pathways by DOM of the ^{3}CDOM*-induced transformation of a generic substrate S.

As already mentioned, the lifetime of ^{3}CDOM* is longer in deoxygenated solution than in the presence of O_2, in which case reaction (26) is also operational. At equal formation rates, this means that [^{3}CDOM*] would be higher in the absence of oxygen. While this issue might lead to an enhancement of triplet-sensitized degradation processes in anoxic systems,[166] one should also consider the possibility that null cycles like the following one may inhibit the transformation of a generic substrate S, following a recombination/deactivation process mediated by the substrate itself:[132]

$$^3CDOM^* + S \rightarrow CDOM^{-\bullet} + S^{+\bullet} \quad (27)$$

$$CDOM^{-\bullet} + S^{+\bullet} \rightarrow CDOM + S \quad (28)$$

In aerated solution, the back reaction (28) would be inhibited by the scavenging of $CDOM^{-\bullet}$ by oxygen, with formation of the superoxide radical anion (reaction 29). In anoxic systems, on the contrary, the back reactivity to CDOM and S could be important.[132]

$$CDOM^{-\bullet} + O_2 \rightarrow CDOM + O_2^{-\bullet} \quad (29)$$

While it has been found that larger CDOM fractions and even suspended particles can yield reactive triplet states,[167] the formation of such transients is most effective upon irradiation of the smaller CDOM fractions.[168,169] Possibly, as already assumed, the HMW moieties of CDOM undergo fast internal conversion to their ground states and this deactivation process inhibits both fluorescence emission and photoreactivity.[140]

Finally, by use of electron-rich phenols (including TMP) as probe molecules, it has been found that irradiated CDOM produces both short- and long-lived oxidants. The short-lived oxidants are identified with ^{3}CDOM*, while the long-lived ones could be less reactive radicals that may be formed in the subsequent photoinduced processes, including peroxy radicals of the general form $ROO^{\bullet}$.[170]

Singlet oxygen ($^1O_2$)

Singlet oxygen is produced in aerated surface waters by reaction (26), which involves ^{3}CDOM* and O_2.[111] The measured formation quantum yields of $^1O_2$ from irradiated CDOM in aerated solution are in the range of 10^{-3} – 10^{-2},[15,76,111,171-173] namely very similar to those of ^{3}CDOM*. This is additional evidence that reaction (26) is a major deactivation process for ^{3}CDOM* in the presence of oxygen.

The deactivation of $^1O_2$ mainly takes place upon collision with water molecules, with a first-order rate constant of $2.5 \cdot 10^5$ s^{-1}.[174] In surface waters, such a deactivation kinetics is usually much faster than the reactions between $^1O_2$ and dissolved organic substrates, thus DOM is expected to play a negligible role as a scavenger of $^1O_2$ in the solution bulk.[119,175] Singlet oxygen shows a very variable reactivity towards organic compounds. While it is often poorly reactive, $^1O_2$ would play an important role in the transformation of chlorophenolates,[6,20,44] including some phenolic pesticides,[176] and of some easily oxidized aminoacids (histidine, methionine, tyrosine and tryptophan).[6,44,177,178]

Figure 4 reports the modeled steady-state [$^1O_2$] as a function of DOC and water depth. As already seen for ^{3}CDOM*, [$^1O_2$] increases with increasing DOC because $^1O_2$ is produced by irradiated CDOM, while it is not scavenged significantly by DOM. As a consequence, reactions induced by $^1O_2$ are favored in high-DOC waters.[20] The decrease of [$^1O_2$] with increasing depth is accounted for by the poor illumination of the water-column bottom layers in deep water bodies, which causes photochemical reactions to slow down and the column-averaged concentration of photoinduced transients to decrease.

A remarkable issue in the case of singlet oxygen is that its reactivity is not confined to the bulk aqueous phase. Indeed, $^1O_2$ has a microheterogeneous distribution within DOM and it reaches very high steady-state concentrations in the hydrophobic sites of DOM, sometimes much higher than in the bulk aqueous solution.[179,180] This means that hydrophobic sites could be very efficient microreactors as far as $^1O_2$ chemistry is concerned, and that they could induce effective transformation of hydrophobic pollutants that are most likely to be partitioned in such environments.[181]

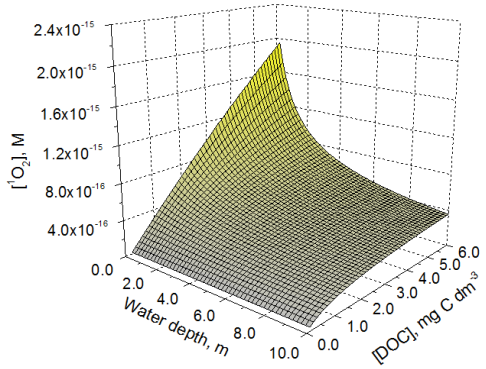


Figure 4. Steady-state [$^1O_2$] as a function of DOC and water depth, in aerated solution. Other water conditions: 0.1 mM nitrate, 1 μM nitrite, 1 mM bicarbonate, 1 μM carbonate. Sunlight UV irradiance: 22 W m^{-2}. The simulation was carried out with the APEX software. The modeled steady-state [$^1O_2$] is an average value over the water column of given depth.

The $^1O_2$ that is produced in hydrophobic sites would be confined there and it is very little likely to escape significantly into the solution bulk to induce transformation reactions. As a consequence, the degradation of hydrophilic $^1O_2$ probes (such as furfuryl alcohol) that only react in the water bulk may be significantly slower than the degradation of hydrophobic $^1O_2$ probes, which are mainly partitioned in hydrophobic cores.[179,180] Another issue is that the hydrophobic cores would be more abundant in HMW DOM fractions and in particles, where the hydrophilic surface that is exposed to the aqueous solution is less important in terms of relative volume (note that, for a generic particle, the surface-to-volume ratio decreases with increasing size). Interestingly, when using hydrophilic probes, one finds higher CDOM photoactivity towards $^1O_2$ generation in the LMW fractions compared to the HMW ones, and limited to negligible contribution to probe degradation by suspended organic particles.[168,169,173,182,183] This is further evidence of the fact that $^1O_2$ produced in hydrophobic cores is poorly able (or totally unable) to escape into the water bulk and react there.

The elevated steady-state concentrations of $^1O_2$ in hydrophobic sites could be assigned either to fast formation or to slow deactivation. The main problem with the former hypothesis is that HMW fractions and particles (where hydrophobic sites should be more abundant) do not seem to differ abruptly from the LMW ones in terms of radiation absorption.[169] Furthermore, the more efficient internal conversion of the excited states in the larger fractions would not be favorable to the generation of $^1O_2$. Coherently, correlation has been found between CDOM fluorescence and its ability to sensitize the degradation of hydrophilic $^1O_2$ probes.[184] Moreover, there is no evidence that ^{3}CDOM* ($^1O_2$ precursor, see reaction 26) is produced more efficiently by HMW fractions or particles, while there is evidence of the contrary.[168,169,185,186] As far as the hypothesis of slower $^1O_2$ deactivation in hydrophobic sites is concerned, a major difference between such sites and the bulk aqueous phase is the absence or

presence of water. Because collision with H_2O is the main deactivation pathway of $^1O_2$ in the solution bulk, the relatively low concentration of water in the hydrophobic sites might be consistent with a slower deactivation kinetics.[169] However, in these sites the H_2O environment of the solution would be replaced by organic functional groups, with which $^1O_2$ could react. Very little is presently known about the reaction kinetics of $^1O_2$ in hydrophobic sites, including the reaction rate constants with the prevailing functional groups, which is key to the assessment of the validity of the hypothesis that hydrophobic sites protect $^1O_2$ from deactivation.

Carbonate radical anions ($CO_3^{-\bullet}$)

The carbonate radical anions in surface waters are mainly produced by reaction of $^\bullet$OH with carbonate and bicarbonate (reactions 22,23) and upon oxidation of carbonate by ^{3}CDOM* (reaction 30).[14,144,187]

$$^3\text{CDOM}^* + CO_3^{2-} \rightarrow \text{CDOM}^{-\bullet} + CO_3^{-\bullet} \qquad (30)$$

The reaction between ^{3}CDOM* and carbonate is usually a minor source of $CO_3^{-\bullet}$ compared to those involving $^\bullet$OH. Under favorable conditions (high-DOC waters), reaction (30) can account for about 10% of $CO_3^{-\bullet}$ generation, but in many cases its importance is lower.[187,188] The radical $CO_3^{-\bullet}$ can also be formed upon oxidation of carbonate by irradiated Fe(III) oxides, but the environmental importance of this process is still uncertain.[189] Considering that carbonate and bicarbonate are key players in the production of $CO_3^{-\bullet}$, that carbonate is more reactive than bicarbonate towards $^\bullet$OH, and that only carbonate reacts with ^{3}CDOM*, it is quite evident that pH is an important factor in the formation of $CO_3^{-\bullet}$ in surface waters.

Figure 5 shows the formation rate of $CO_3^{-\bullet}$ that results from the oxidation of carbonate and bicarbonate by $^\bullet$OH, as a function of pH. Under the hypothesis of constant [$^\bullet$OH], the reported rate is relative to that calculated at pH 7 that has been posed equal to 1. The plot also reports the pH trends of the molar fractions of dissolved CO_2, HCO_3^- and CO_3^{2-} (pKa_1 = 6.3, pKa_2 = 10.3).[92]

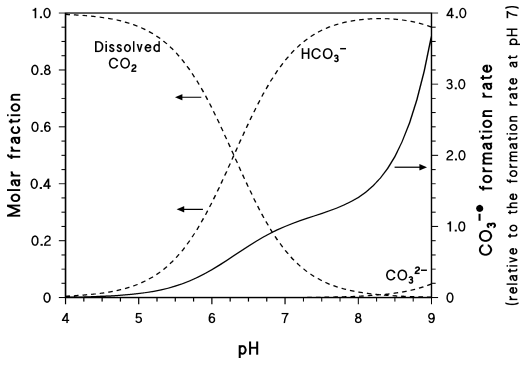


Figure 5. Formation rate of $CO_3^{-\bullet}$ upon oxidation of carbonate and bicarbonate by $^\bullet$OH, as a function of pH. The graph also reports the molar fractions of carbonic acid, bicarbonate and carbonate at the different pH values. The formation rate of $CO_3^{-\bullet}$ is normalized to the value at pH 7, arbitrarily posed equal to 1.

It can be seen that the formation rate of $CO_3^{-\bullet}$ increases with increasing pH, but the trend is little marked in the 7-8 pH interval. Under such conditions, bicarbonate is both the main inorganic carbon species and the main source of $CO_3^{-\bullet}$ upon reaction with $^\bullet$OH. At pH < 7, the formation of $CO_3^{-\bullet}$ decreases because of the decreasing molar fraction of bicarbonate, while dissolved CO_2 is practically unreactive with $^\bullet$OH.[144] At pH > 8, the $CO_3^{-\bullet}$ formation increases because of the increasing molar fraction of carbonate. The pH trend of the reaction (30) involving CDOM triplet states could be even more marked compared to the $^\bullet$OH processes, because carbonate is the only inorganic carbon species that reacts with ^{3}CDOM* to produce $CO_3^{-\bullet}$.[187]

The majority of $CO_3^{-\bullet}$ formation is caused by oxidation of inorganic carbon by $^\bullet$OH. Because DOM is the main $^\bullet$OH scavenger in surface waters and inorganic carbon plays a less important role, it can be inferred that only a fraction of $^\bullet$OH reacts with inorganic carbon to produce $CO_3^{-\bullet}$. Therefore, the formation rate of $CO_3^{-\bullet}$ is lower than the rate of $^\bullet$OH formation in most surface-water environments. DOM is also the main scavenger of $CO_3^{-\bullet}$ in surface waters.[14,187,188] In this context, it is important to point out that $CO_3^{-\bullet}$ is less reactive than $^\bullet$OH toward both organic and inorganic compounds,[144,190] including most notably DOM that is the main scavenger of both $CO_3^{-\bullet}$ and $^\bullet$OH. In fact, while the reaction rate constant between $^\bullet$OH and DOM is in the order of $10^4 - 10^5$ L (mg C)$^{-1}$ s^{-1},[15,37,76,141-143] the corresponding rate constant in the case of $CO_3^{-\bullet}$ is only around 10^2 L (mg C)$^{-1}$ s^{-1}.[187,191] The consequence is that the steady-state [$CO_3^{-\bullet}$] in surface waters is often higher than the steady-state [$^\bullet$OH],[14,187,188] provided that enough inorganic carbon is present (and that pH is high enough) for $CO_3^{-\bullet}$ formation to occur to a sufficient extent.

Figure 6 reports the modeled steady-state [$CO_3^{-\bullet}$], as a function of DOC and of carbonate concentration. Note that increasing carbonate at constant bicarbonate is roughly equivalent to increasing the pH and, in analogy with the trend reported in Figure 5 for the $CO_3^{-\bullet}$ formation rate, the steady-state [$CO_3^{-\bullet}$] increases with increasing carbonate. The steep decrease of [$CO_3^{-\bullet}$] with increasing DOC can be accounted for by the fact that DOM has a double negative effect on the carbonate radical: *(i)* on the one side, DOM inhibits the formation of $CO_3^{-\bullet}$ by scavenging $^\bullet$OH, which is involved in the main generation pathway of $CO_3^{-\bullet}$; *(ii)* on the other side, DOM directly scavenges the carbonate radical.

Indeed, the increase of DOC decreases [$CO_3^{-\bullet}$] to a higher extent compared to [$^\bullet$OH]. Therefore, the [$CO_3^{-\bullet}$] [$^\bullet$OH]$^{-1}$ ratio decreases with increasing DOC, as shown in Figure 7. The usually higher steady-state concentration of $CO_3^{-\bullet}$ in surface waters, compared to $^\bullet$OH, is compensated for to a variable extent by the lower reactivity of $CO_3^{-\bullet}$. Indeed, for many compounds that are difficult to be oxidized, $CO_3^{-\bullet}$ plays a negligible role in transformation compared to $^\bullet$OH.[91] On the other hand, $CO_3^{-\bullet}$ plays a very important role in the transformation of some easily oxidized molecules (*e.g.* aromatic amines and phenols, sulfur-containing compounds) in surface-water environments, including the antipyretic drug acetaminophen.[192-194,77]

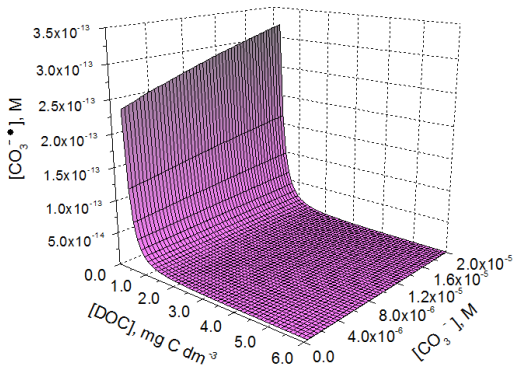


Figure 6. Steady-state [$CO_3^{-\bullet}$] as a function of DOC and carbonate. Other water conditions: 0.1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 5 m depth. Sunlight UV irradiance: 22 W m^{-2}. The simulation was carried out with the APEX software. The modeled steady-state [$CO_3^{-\bullet}$] is an average value over the 5-m water column.

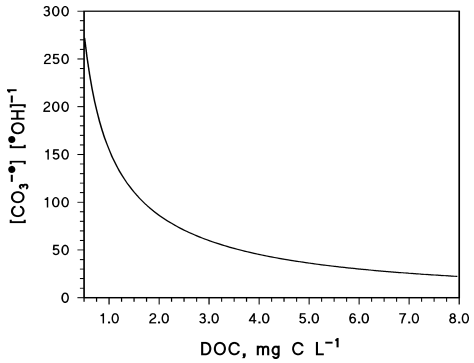


Figure 7. Ratio of the steady-state concentrations of $CO_3^{-\bullet}$ and $^{\bullet}OH$ ([$CO_3^{-\bullet}$] [$^{\bullet}OH$]$^{-1}$) as a function of DOC. Other water conditions: 1 mM nitrate, 1 µM nitrite, 1 mM bicarbonate, 1 µM carbonate, 5 m depth. Sunlight UV irradiance: 22 W m^{-2}. The simulation was carried out with the APEX software.

Other photoinduced transient species ($O_2^{-\bullet}$, $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $^{\bullet}NO_2$)

The ***superoxide radical anion*** ($O_2^{-\bullet}$) can be formed by photoinduced processes, upon reduction of O_2 by organic radicals (see *e.g.* reaction 29) or upon reaction between H_2O_2 and $^{\bullet}OH$:[132,144,195,196]

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad [k_{31} = 2.7{\cdot}10^7\ M^{-1}\ s^{-1}] \quad (31)$$
$$HO_2^{\bullet} \leftrightarrows O_2^{-\bullet} + H^+ \quad [pKa_{32} = 4.8] \quad (32)$$

Superoxide has also important non-photochemical (bacterial) sources.[197,198] An important process involving $HO_2^{\bullet}/O_2^{-\bullet}$ in natural waters is the dismutation to H_2O_2 and O_2, which is catalyzed by metals such as Fe and most notably Cu.[199,200] Superoxide can also react with organic compounds.[201,202] It is a very weak oxidant and the corresponding reaction rate constants are very low, with the partial exception of the oxidation of ascorbic acid (around 10^5-10^6 M^{-1} s^{-1}, depending on pH) [203] and of Mn(II) (around 10^6-10^7 M^{-1} s^{-1}, depending on the type of water).[204] In contrast, $O_2^{-\bullet}$ reacts quite efficiently as a reductant and the reaction rate constants for the reduction of some quinones to the corresponding semiquinone radicals are in the range of 10^7-10^9 M^{-1} s^{-1}.[203] Recent evidence suggests that reaction with organic and inorganic compounds could be an important sink for $O_2^{-\bullet}$.[205,206] Differently from dismutation, $O_2^{-\bullet}$ redox processes often involve the consumption or the release of H^+ with some ability to alter locally the pH of natural waters. The extent of pH change might be comparable to that induced by enhanced dissolution of atmospheric CO_2, and $O_2^{-\bullet}$ redox chemistry may act as a local confounding factor in the assessment of the long-term acidification of natural waters.[207]

The ***dichloride radical anion*** ($Cl_2^{-\bullet}$) is formed upon reaction between a chloride ion and a $Cl^{\bullet}$ radical, and it is the typical form in which $Cl^{\bullet}$ occurs in natural waters.[208] The formation of $Cl^{\bullet}$ takes place upon one-electron oxidation of chloride. The reaction (33) between chloride and $^{\bullet}OH$ is quite fast (the direct process has a second-order rate constant of $4.3{\cdot}10^9$ M^{-1} s^{-1}),[144] but it yields $Cl^{\bullet}$ (and $Cl_2^{-\bullet}$ upon reaction with a further chloride ion) only in acidic conditions, typically at pH < 5. Under ~neutral to slightly basic conditions, which are of higher significance for surface waters, the process yields back the reactants.[209]

$$^{\bullet}OH + Cl^- \leftrightarrows ClOH^{-\bullet} \quad (33)$$
$$ClOH^{-\bullet} + H^+ \leftrightarrows Cl^{\bullet} + H_2O \quad (34)$$
$$Cl^{\bullet} + Cl^- \leftrightarrows Cl_2^{-\bullet} \quad (35)$$

The photoinduced oxidation of chloride to $Cl^{\bullet}$ can also take place without the active role of $^{\bullet}OH$ as oxidant, in the presence of irradiated Fe(III) (hydr)oxides such as hematite and goethite, which act as photocatalysts. The corresponding reduction process yields $O_2^{-\bullet}$ from O_2 or Fe(II) from Fe(III).[127,210] Unfortunately, the Fe(III) speciation in natural waters is much more complex than it could be studied in the laboratory. It involves complexes with organic ligands as well as oligomeric or polymeric Fe(III) species with variable chemical and photochemical reactivity, which is still far from being satisfactorily elucidated.[211,212] As a consequence, the environmental importance of the photo-oxidation of chloride to $Cl^{\bullet}$ by irradiated Fe(III) species is difficult to assess and model. The oxidation of chloride could also involve ^{3}CDOM*, a process that would be understandably favored in high-DOC waters. However, elevated DOC would not enhance the steady-state [$Cl_2^{-\bullet}$], because DOM is the main scavenger of the dichloride radical anion. With k' ~ 10^7 M^{-1} s^{-1} as the reaction rate constant between ^{3}CDOM* and Cl^-, k" ~ 10^3 L (mg C)$^{-1}$ s^{-1} as the reaction rate constant between $Cl_2^{-\bullet}$ and DOM, and assuming that [$Cl_2^{-\bullet}$] = k' [^{3}CDOM*] [Cl^-] (k" DOC)$^{-1}$, the steady-state [$Cl_2^{-\bullet}$] could reach concentration values of 10^{-15}-10^{-14} M in chloride-rich environments.[213] Therefore, $Cl_2^{-\bullet}$ could be an important reactive transient in brackish to saline waters. The radical $Cl_2^{-\bullet}$ is both an oxidizing and a chlorinating agent,[127,210,214,215] but the chlorination yields are quite low (~1%) even with phenolic substrates that are activated to radical halogenation.[214] This means that, on the one hand, $Cl_2^{-\bullet}$ may have limited ability to generate toxic and potentially persistent organochlorinated compounds. On the other hand, the prevalently oxidizing nature of $Cl_2^{-\bullet}$ means that it is difficult to find a probe molecule or probe reaction to measure it in illuminated natural waters, where many other potentially competing oxidants (*e.g.* $^{\bullet}OH$, $CO_3^{-\bullet}$, ^{3}CDOM*, $^1O_2$) are also present.

The ***dibromide radical anion*** ($Br_2^{-\bullet}$) is formed in surface waters by reaction between Br^- and $Br^{\bullet}$, and $Br^{\bullet}$ is generated by one-electron oxidation of bromide:[144,216]

$$^{\bullet}OH + Br^- \rightarrow OH^- + Br^{\bullet} \quad [k_{36} = 1.1{\cdot}10^{10}\ M^{-1}\ s^{-1}] \quad (36)$$

$^3CDOM^* + Br^- \rightarrow CDOM^{-\bullet} + Br^\bullet$ (37)

$Br^\bullet + Br^- \leftrightarrows Br_2^{-\bullet}$ (38)

The reaction (36) between $^\bullet OH$ and bromide is the main scavenging process for $^\bullet OH$ in seawater, and it is also important in brackish-water environments.[146] The rate constant of the one-electron oxidation of Br^- by $^3CDOM^*$ (reaction 37) could be in the range of 10^8-10^9 M^{-1} s^{-1}, and the DOC values of surface waters would play an important role in channeling bromide oxidation through reaction (36) or (37). Indeed, reaction (36) would prevail in low-DOC and reaction (37) in high-DOC conditions.[217] Oxidation of Br^- to $Br^\bullet$ can also take place in the presence of irradiated Fe(III) (hydr)oxides,[210] but the environmental importance of such a process is difficult to assess for the same reasons already specified for $Cl_2^{-\bullet}$.

DOM is the main scavenger of $Br_2^{-\bullet}$ in surface waters, for which reason the steady-state $[Br_2^{-\bullet}]$ decreases with increasing DOC, despite the involvement of $^3CDOM^*$ in reaction (36).[217] With a second-order reaction rate constant of ~10^2 L (mg C)$^{-1}$ s^{-1} between $Br_2^{-\bullet}$ and DOM, the steady-state $[Br_2^{-\bullet}]$ could reach 10^{-13} M levels in brackish waters.[217] The radical $Br_2^{-\bullet}$ is an effective brominating agent, showing almost quantitative bromination yields in the case of phenol. Therefore, it could potentially form aromatic bromoderivatives as secondary pollutants, with proven toxicity in aqueous environments.[218]

Nitrogen dioxide ($^\bullet NO_2$) is formed upon nitrate photolysis (reaction 10) and nitrite oxidation. The latter can take place upon reaction with $^\bullet OH$ (reaction 24), $CO_3^{-\bullet}$, $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $^3CDOM^*$:[144,190,219]

$NO_2^- + CO_3^{-\bullet} \rightarrow {}^\bullet NO_2 + CO_3^{2-}$ [$k_{39} = 4{\cdot}10^5$ M^{-1} s^{-1}] (39)

$NO_2^- + Cl_2^{-\bullet} \rightarrow {}^\bullet NO_2 + 2\ Cl^-$ [$k_{40} = 2.5{\cdot}10^8$ M^{-1} s^{-1}] (40)

$NO_2^- + Br_2^{-\bullet} \rightarrow {}^\bullet NO_2 + 2\ Br^-$ [$k_{41} = 2{\cdot}10^7$ M^{-1} s^{-1}] (41)

$NO_2^- + {}^3CDOM^* \rightarrow {}^\bullet NO_2 + CDOM^{-\bullet}$ [k_{42}~10^9 $M^{-1}s^{-1}$] (42)

The relative role of nitrate photolysis and nitrite oxidation as sources of $^\bullet NO_2$ depends on several factors, such as the $[NO_3^-]$ $[NO_2^-]^{-1}$ ratio and the steady-state concentrations of the transients involved in the oxidation of nitrite. The photolysis of nitrate (reaction 10) would be inhibited in high-DOC waters because of competition for sunlight irradiance between nitrate and CDOM. However, organic compounds that do not absorb sunlight could enhance the photogeneration of $^\bullet NO_2$ by reacting with $^\bullet O^-$ when still in the solvent cage. The latter process would increase the quantum yield of $^\bullet NO_2$ photogeneration, by inhibiting the cage recombination of $^\bullet NO_2$ and $^\bullet O^-$ to nitrate.[98,219,220] As far as nitrite is concerned, elevated DOM would inhibit reactions (24) and (39-41) by scavenging all of the involved transients ($^\bullet OH$, $CO_3^{-\bullet}$, $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$). In contrast, reaction (42) that involves $^3CDOM^*$ would be favored in high-DOC waters.[219] Generally speaking, nitrate photolysis and nitrite photooxidation could play overall comparable roles as sources of $^\bullet NO_2$ in environmental waters, with either process prevailing under particular conditions.[99,221]

By use of the APEX software and with additional calculations on the output data, it is possible to model the expected importance of the different reactions that are involved in the oxidation of nitrite.[219] Sample results are shown in Figure 8, where the relative role of $^\bullet OH$, $CO_3^{-\bullet}$, $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $^3CDOM^*$ toward nitrite oxidation is reported as a function of DOC, for 10^{-4} M Cl^- (8a, as for freshwaters) and for 10^{-2} M Cl^- (8b, as for brackish waters). In both cases the ratio $[Cl^-]$ $[Br^-]^{-1}$ was fixed at 10^3, as is found in brackish water and saltwater.[146]

First of all, it can be seen that $Br_2^{-\bullet}$ plays a minor to very minor role in nitrite oxidation, even at the highest concentration values of bromide. The radical $CO_3^{-\bullet}$ has some importance only at very low DOC, due to the very fast decrease of $[CO_3^{-\bullet}]$ with increasing DOC (see Figure 6). Such a decreasing importance of $CO_3^{-\bullet}$ as a source of $^\bullet NO_2$ accounts for the maximum shown by the $^\bullet OH$ contribution in Figure 8a: the role of $^\bullet OH$ initially increases at the expense of that of $CO_3^{-\bullet}$, and then decreases because of the growing importance of $^3CDOM^*$ at higher DOC. Obviously, the importance of $Cl_2^{-\bullet}$ in nitrite oxidation is higher in the brackish-water scenario (Figure 8b). The involvement of $^3CDOM^*$ in the generation of $Cl_2^{-\bullet}$ accounts for the slight initial increase of the $Cl_2^{-\bullet}$ role with increasing DOC, at the expense of $^\bullet OH$ and $CO_3^{-\bullet}$. However, the growing importance of $^3CDOM^*$ with increasing DOC accounts for the decrease of the $Cl_2^{-\bullet}$ role above 1 mg C L^{-1} DOC.

The main sink of $^\bullet NO_2$ in aqueous solution is the dismutation to nitrate and nitrite (reactions 43,44), which would prevail over competitive processes (reaction with DOM, I^-, Fe^{2+}) under most environmental conditions.[99,190,221,222]

$2\ {}^\bullet NO_2 \leftrightarrows N_2O_4$ [$k_{43}=2.5{\cdot}10^8$ $M^{-1}s^{-1}$; $k_{-43}=6.9{\cdot}10^3$ s^{-1}] (43)

$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2\ H^+$ [$k_{44} = 1{\cdot}10^3$ s^{-1}] (44)

With reactions (43,44) as sinks and the sources considered above, the steady-state $[^\bullet NO_2]$ in environmental waters could be in the range of 10^{-11}-10^{-9} M.[221] Nitrogen dioxide is a nitrating agent, which is particularly effective in the case of electron-rich aromatic compounds such as phenols (HPhOH). In this case, nitration takes place *via* the intermediate formation of a phenoxy radical ($HPhO^\bullet$) and it involves two $^\bullet NO_2$ radicals:[223]

$HPhOH + {}^\bullet NO_2 \rightarrow HPhO^\bullet + HNO_2$ (45)

$HPhO^\bullet + {}^\bullet NO_2 \rightarrow O_2N\text{-}PhOH$ (46)

Typical rate constant values for reaction (45) are around 10^2 – 10^4 M^{-1} s^{-1}.[224,225] The resulting nitrophenols (O_2N-PhOH) are toxic and potentially mutagenic secondary pollutants.[226-229] Photonitration reactions induced by nitrate photolysis and nitrite photooxidation have been observed in shallow lagoons receiving drainage water from paddy fields, in the presence of chlorophenols and methylchlorophenols that are transformation intermediates of the phenoxy-acid herbicides used in flooded rice farming.[224,225,230]

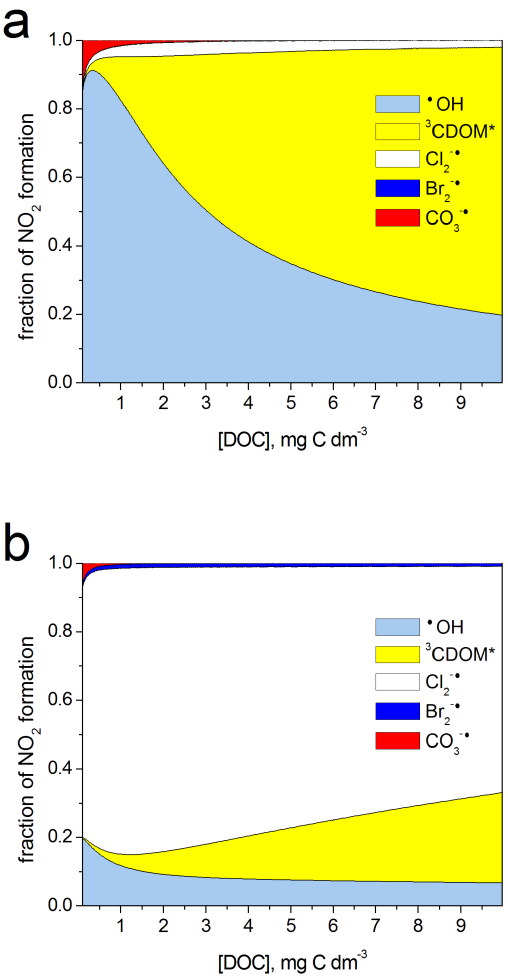


Figure 8. Relative roles played by $^{\bullet}OH$, $CO_3^{-\bullet}$, $Br_2^{-\bullet}$, $Cl_2^{-\bullet}$ and $^3CDOM^*$ in the oxidation of nitrite to $^{\bullet}NO_2$, in the presence of 10^{-4} M Cl^- and 10^{-7} M Br^- (**8a**) and of 10^{-2} M Cl^- and 10^{-5} M Br^- (**8b**). Other water conditions for both cases: 0.1 mM nitrate, 1 μM nitrite, 3 mM bicarbonate, 3 μM carbonate, 5 m depth. Sunlight UV irradiance was 22 W m^{-2}. The steady-state concentrations of $^{\bullet}OH$, $CO_3^{-\bullet}$ and $^3CDOM^*$ were modeled with the APEX software, those of $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ by means of additional calculations. In particular, 10^7 M^{-1} s^{-1} was used as the reaction rate constant between $^3CDOM^*$ and Cl^-, $5{\cdot}10^8$ M^{-1} s^{-1} as the reaction rate constant between $^3CDOM^*$ and Br^-, 10^9 M^{-1} s^{-1} as the reaction rate constant between $^3CDOM^*$ and NO_2^-, 10^3 L (mg C)$^{-1}$ s^{-1} as the reaction rate constant between $Cl_2^{-\bullet}$ and DOM, and $3{\cdot}10^2$ L (mg C)$^{-1}$ s^{-1} as the reaction rate constant between $Br_2^{-\bullet}$ and DOM.

Summary and Outlook

The main reactive transients that are involved in the indirect phototransformation of organic pollutants in surface waters are $^{\bullet}OH$, $^3CDOM^*$, $^1O_2$ and $CO_3^{-\bullet}$. Their relative role depends both on the specific reactivity of each pollutant (second-order reaction rate constants) and on the environmental conditions. In particular, the processes that involve $^{\bullet}OH$ and $CO_3^{-\bullet}$ are enhanced in the presence of elevated concentration values of nitrate and nitrite, and they are inhibited with increasing DOC (with some minor exceptions in the case of $^{\bullet}OH$). In contrast, high-DOC waters that are rich in both DOM and CDOM are favorable to the reactions that involve $^3CDOM^*$ (with a *caveat* concerning the antioxidants sites of DOM) and $^1O_2$. Obviously, all photochemical processes are favored in shallow water bodies where the water column is better illuminated by sunlight, compared to deeper water environments. All the above-cited transient species are involved in the transformation of water-dissolved pollutants in the solution bulk. Moreover, $^1O_2$ could also induce transformation of poorly soluble compounds. This happens because of the high steady-state concentrations that $^1O_2$ reaches in the hydrophobic cores of natural organic matter, where non-polar pollutants would undergo preferential partitioning.

CDOM is a key photosensitizer in surface waters, because it is the only source of $^3CDOM^*$ and $^1O_2$ and a very important one for $^{\bullet}OH$. CDOM is a minor source of $CO_3^{-\bullet}$ upon direct oxidation of CO_3^{2-} by $^3CDOM^*$, but it plays an important role in the production of the carbonate radical anion though $^{\bullet}OH$ generation. The production of $^{\bullet}OH$ by irradiated CDOM is still a matter of debate. It involves at least two family of processes, a H_2O_2-dependent and a H_2O_2-independent one. The pathways involving H_2O_2 probably proceed through Fenton or photo-Fenton reactions, which would also yield additional oxidants (most notably ferryl) under circumneutral conditions. The H_2O_2-independent pathways are much less clear, because there is only very preliminary evidence that they might involve the direct oxidation of water and/or OH^-.

Additional photogenerated transient species are $O_2^{-\bullet}$, $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $^{\bullet}NO_2$. The role of $O_2^{-\bullet}$ in the transformation of organic compounds is still unclear, as it is a very weak oxidant but it could be an effective reductant for some quinones. However, it is thought to play a key role in the redox cycling of metals such as Fe, Cu and Mn. The radical $Cl_2^{-\bullet}$ is mainly an oxidant, and a chlorinating agent only to a minor extent. In contrast, $Br_2^{-\bullet}$ is an effective brominating agent and $^{\bullet}NO_2$ a nitrating one. Both species could be involved in the photochemical formation of secondary pollutants in surface waters (bromo- and nitroderivatives, respectively), a possibility that for $^{\bullet}NO_2$ has been demonstrated in the field.

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