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A Model Assessment of the Occurrence and Reactivity of the Nitrating/Nitrosating Agent Nitrogen Dioxide ($^\bullet NO_2$) in Sunlit Natural Waters

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Abstract: Nitrogen dioxide ($^\bullet NO_2$) is produced in sunlit natural surface waters by the direct photolysis of nitrate, together with $^\bullet OH$, and upon the oxidation of nitrite by $^\bullet OH$ itself. $^\bullet NO_2$ is mainly scavenged by dissolved organic matter, and here, it is shown that $^\bullet NO_2$ levels in sunlit surface waters are enhanced by high concentrations of nitrate and nitrite, and depressed by high values of the dissolved organic carbon. The dimer of nitrogen dioxide (N_2O_4) is also formed in the pathway of $^\bullet NO_2$ hydrolysis, but with a very low concentration, i.e., several orders of magnitude below $^\bullet NO_2$, and even below $^\bullet OH$. Therefore, at most, N_2O_4 would only be involved in the transformation (nitration/nitrosation) of electron-poor compounds, which would not react with $^\bullet NO_2$. Although it is known that nitrite oxidation by $CO_3^{\bullet -}$ in high-alkalinity surface waters gives a minor-to-negligible contribution to $^\bullet NO_2$ formation, it is shown here that NO_2^- oxidation by $Br_2^{\bullet -}$ can be a significant source of $^\bullet NO_2$ in saline waters (saltwater, brackish waters, seawater, and brines), which offsets the scavenging of $^\bullet OH$ by bromide. As an example, the anti-oxidant tripeptide glutathione undergoes nitrosation by $^\bullet NO_2$ preferentially in saltwater, thanks to the inhibition of the degradation of glutathione itself by $^\bullet OH$, which is scavenged by bromide in saltwater. The enhancement of $^\bullet NO_2$ reactions in saltwater could explain the literature findings, that several phenolic nitroderivatives are formed in shallow (i.e., thoroughly sunlit) and brackish lagoons in the Rhône river delta (S. France), and that the laboratory irradiation of phenol-spiked seawater yields nitrophenols in a significant amount.

Keywords: environmental chemistry; photochemistry; indirect photolysis; photonitration; reactive nitrogen species

1. Introduction

Photochemical reactions are important processes in sunlit natural surface waters. They play a significant role in the transformation of biorecalcitrant pollutants, and of some natural compounds, and often result in decontamination. However, sometimes photochemistry yields secondary contaminants, which may be more harmful than the parent molecules [1,2]. Phototransformation by direct photolysis is operational for those compounds, which absorb sunlight, and get degraded as a consequence, because they have a non-nil quantum yield of direct photolysis [3,4]. Conversely, indirect photochemistry is the transformation of dissolved compounds upon reaction with the so-called photochemically produced reactive intermediates (PPRIs), independent of sunlight absorption by the molecules that get transformed [5,6]. The main PPRIs in natural surface waters are the hydroxyl ($^\bullet OH$) and carbonate ($CO_3^{\bullet -}$) radicals, the excited triplet states of chromophoric dissolved organic matter ($^3CDOM^*$, where CDOM is the chromophoric fraction of the dissolved organic matter, DOM), and singlet oxygen ($^1O_2$) [7]. PPRIs are produced upon sunlight absorption by photosensitisers, i.e., naturally occurring compounds such as nitrate and nitrite ($^\bullet OH$ sources), as well as CDOM (source of $^3CDOM^*$, $^1O_2$, and $^\bullet OH$) [8–10]. Moreover, $CO_3^{\bullet -}$ is generated upon oxidation of HCO_3^-/CO_3^{2-} by $^\bullet OH$, and of CO_3^{2-} by $^3CDOM^*$ [11,12]. After

being produced, PPRIs can be quickly quenched/scavenged by DOM, either chromophoric or not. In particular, DOM scavenges $^{\bullet}OH$ and $CO_3^{\bullet-}$, but it scavenges $^3CDOM^*/^1O_2$ only to a very minor extent. Other important scavengers/quenchers are inorganic carbon, i.e., HCO_3^-/CO_3^{2-} (for $^{\bullet}OH$), dissolved oxygen (for $^3CDOM^*$, to yield $^1O_2$), and collision with the water solvent (for $^1O_2$) [6]. A schematic of the main processes involving photosensitizers, PPRIs' production, their scavenging/quenching, and interaction with pollutants is provided in Figure 1.
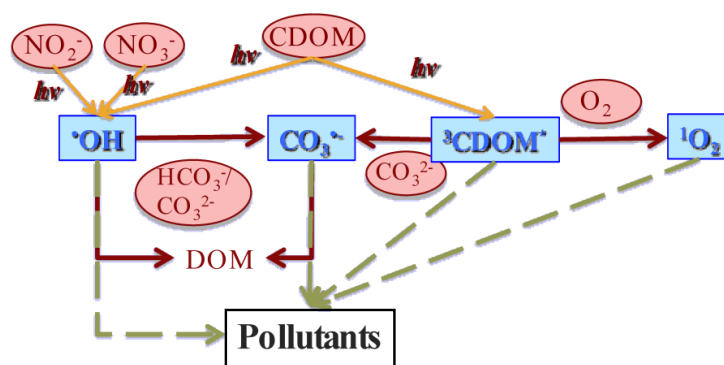

Figure 1. Schematic of the main processes involving photochemical production and scavenging/quenching of the main PPRIs ($^{\bullet}OH$, $CO_3^{\bullet-}$, $^3CDOM^*$, and $^1O_2$) in natural surface waters. DOM = dissolved organic matter; CDOM = chromophoric dissolved organic matter. Circles: photosensitizers and scavengers/quenchers; rectangles: PPRIs.
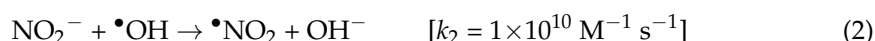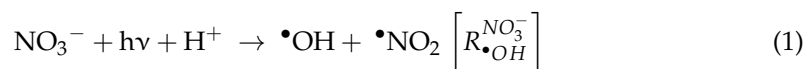
In addition to $^{\bullet}OH$, $CO_3^{\bullet-}$, $^3CDOM^*$, and $^1O_2$, there are other PPRIs that are either lesser known at the moment, e.g., longer-lived species such as superoxide and organic peroxyl radicals [13,14], or have the potential to produce harmful secondary contaminants to a higher extent compared to the PPRIs depicted in Figure 1. Examples are the dibromine (or dibromide) radical ($Br_2^{\bullet-}$), which is mainly produced upon $^{\bullet}OH$ scavenging by bromide in saltwater [15] and is an effective brominating agent, especially for phenols [16], as well as nitrogen dioxide ($^{\bullet}NO_2$). The latter is mostly generated by nitrate photolysis together with $^{\bullet}OH$, and by the oxidation of nitrite by $^{\bullet}OH$ itself [8,17]. Other $^{\bullet}NO_2$ formation processes, the environmental importance of which is still to be conclusively elucidated, consist in the oxidation of nitrite by either $^3CDOM^*$ [18], or irradiated Fe(III) oxides [19].

$^{\bullet}NO_2$ is a nitrating/nitrosating agent, which is involved in the production of toxic nitroderivatives from aromatic compounds [20], as well as of toxic and, possibly, mutagenic/carcinogenic nitrosoderivatives from amines and amino acids [21,22]. $^{\bullet}NO_2$ is not the only possible nitrating agent in an aqueous solution, but it is probably the most likely one to be involved in photonitration processes in circumneutral conditions. Actually, studies on the (photo)nitration pathways of phenols and other aromatic compounds have found a plethora of nitrating agents ($^{\bullet}NO_2$, HNO_2, $HOONO$, H_2OONO^+, and possibly also N_2O_4), but most of them tend to be operational at an acidic pH only [20,23]. Indeed, although in (often acidic) atmospheric waters the actual (photo)nitration pathways, and the reactive species involved, may still be open to debate [24], in the case of natural surface waters, $^{\bullet}NO_2$ is more likely to play a substantial role [25].

In this work, a model approach based on (photo)reaction kinetics and a steady-state approximation is applied to assess the conditions that would most favor the occurrence of $^{\bullet}NO_2$ (as well as its dimer, N_2O_4) in sunlit natural surface waters. Model findings help explain why, so far, literature reports about environmental photonitration processes in natural surface waters have focused on shallow and brackish lagoons, near the sea [26–28].

2. Kinetic Model Development

Nitrogen dioxide is produced in natural surface waters upon the photolysis of nitrate, and upon the oxidation of nitrite by $^\bullet OH$ [29]:

$$NO_3^- + h\nu + H^+ \rightarrow \, ^\bullet OH + \, ^\bullet NO_2 \quad \left[R_{^\bullet OH}^{NO_3^-} \right] \tag{1}$$

$$NO_2^- + \, ^\bullet OH \rightarrow \, ^\bullet NO_2 + OH^- \qquad [k_2 = 1 \times 10^{10} \, M^{-1} \, s^{-1}] \tag{2}$$

The quenching/scavenging processes of $^\bullet NO_2$ in an aqueous solution involve dimerization into dinitrogen tetroxide (N_2O_4), another potential nitrating agent, followed by the hydrolysis of the latter, as well as an $^\bullet NO_2$ reaction with the dissolved natural organic matter (DOM) [8]:

$$2 \, ^\bullet NO_2 \leftrightarrows N_2O_4 \qquad [k_3 = 4.5 \times 10^8 \, M^{-1} \, s^{-1}; k_{-3} = 6.9 \times 10^3 \, s^{-1}] \tag{3}$$

$$^\bullet NO_2 + DOM \rightarrow Products \qquad [k_4] \tag{4}$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2 \, H^+ \qquad [k_5 = 1 \times 10^3 \, s^{-1}] \tag{5}$$
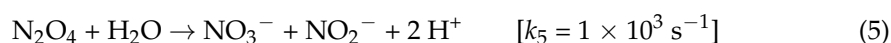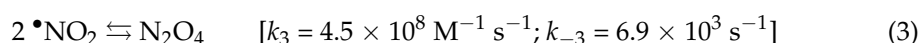
The value of k_4 is still to be conclusively assessed. However, in the case of phenolic compounds, it is reported that $k_4 \sim 10^4 \, M^{-1} \, s^{-1}$ [30]. Moreover, it is well known that phenolic moieties are ubiquitous in DOM. When considering the dissolved organic carbon (DOC) contents of phenols [31], one may assume $k_4 = 0.14 \, L \, mg_C^{-1} \, s^{-1}$.

By assuming the formation rate of $^\bullet NO_2$ ($R_{^\bullet NO_2}$), as $R_{^\bullet NO_2} = R_{^\bullet OH}^{NO_3^-} + k_2 \times [^\bullet OH] \times [NO_2^-]$, and applying the steady-state approximation to both $^\bullet NO_2$ and N_2O_4 (i.e., $d[NO_2]/dt = 0$, and $d[N_2O_4]/dt = 0$), from reactions (1–5), one gets the following:

$$\begin{cases} [^\bullet NO_2] = (k_{-3} + k_5) \dfrac{-k_4 \, DOC + \sqrt{(k_4 \, DOC)^2 + 8 \, k_3 k_5 R_{^\bullet NO_2} (k_{-3} + k_5)^{-1}}}{4 k_3 k_5} \\ [N_2O_4] = \dfrac{k_3 \, [^\bullet NO_2]^2}{k_{-3} + k_5} \end{cases} \tag{6}$$

Preliminary calculations showed that reaction (4) would strongly prevail over (3,5) as an $^\bullet NO_2$ sink. The rate difference between the two kinds of processes is so big that the conclusion would not change even if $k_4 = 0.14 \, L \, mg_C^{-1} \, s^{-1}$ turned out to be a generously high estimate for the reaction rate constant between $^\bullet NO_2$ and DOM. Therefore, when neglecting reactions (3,5) as $^\bullet NO_2$ sinks, one gets a considerable simplification for (6):

$$\begin{cases} [^\bullet NO_2] = \dfrac{R_{^\bullet NO_2}}{k_4 \, DOC} \\ [N_2O_4] = \dfrac{k_3 \, [^\bullet NO_2]^2}{k_{-3} + k_5} \end{cases} \tag{7}$$

Again, the same preliminary calculations suggested that (7) approximates (6) to better than 4‰, in a wide variety of conditions that are significant for surface waters. Based on the above reactions, it appears that the main water components that are expected to impact $[^\bullet NO_2]$ and $[N_2O_4]$ the most are the following:

1. DOC (dissolved organic carbon), when considering that DOM is the main $^\bullet NO_2$ scavenger [18], and that it also scavenges $^\bullet OH$ [32], which plays a key role in the oxidation of NO_2^- to $^\bullet NO_2$ [19];
2. Inorganic carbon (HCO_3^- and CO_3^{2-}), because it enhances nitrate photolysis due to a solvent cage effect (see Figure 2) [33], but also acts as an $^\bullet OH$ scavenger [32]. Interestingly, there is evidence that nitrite oxidation by $CO_3^{\bullet -}$ does not contribute to $^\bullet NO_2$ formation significantly [18];
3. Bromide (Br^-), as a major $^\bullet OH$ scavenger in saltwater and seawater [15,32].
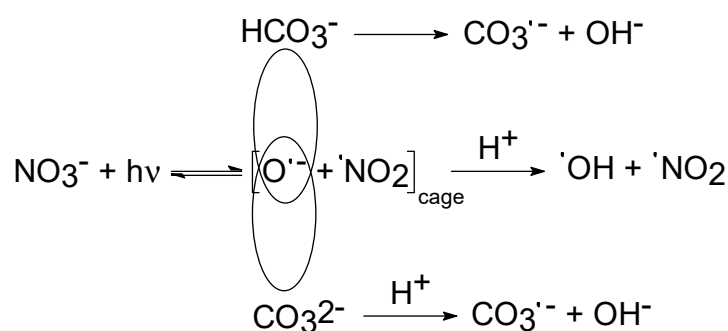
Figure 2. Schematic of the solvent-cage enhancement of nitrate photolysis by HCO_3^- and CO_3^{2-}, which inhibits geminate recombination between the photo-fragments $O^{\bullet-}$ ($^{\bullet}OH$ precursor) and $^{\bullet}NO_2$.

The effect of different water components on $[^{\bullet}NO_2]$ and $[N_2O_4]$ was modeled by assessing the values of $R_{\bullet OH}^{NO_3^-}$ and $[^{\bullet}OH]$, which are needed to calculate $R_{\bullet NO_2}$, by means of the APEX software (Apex Srl; Modena, Italy). APEX (Aqueous Photochemistry of Environmentally occurring Xenobiotics) computes steady-state concentrations of reactive transient species ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$, and $^3CDOM^*$) as a function of water chemistry, depth, and seasonal sunlight irradiance [34–36]. In this case, typical irradiance conditions for APEX were assumed: 22 W m^{-2} UV irradiance, i.e., 290–400 nm, which corresponds to fair weather 15 July at 45° N latitude, at 9 a.m. or 3 p.m., solar time. By doing so, it was possible to compute $R_{\bullet NO_2} = R_{\bullet OH}^{NO_3^-} + k_2 \times [^{\bullet}OH] \times [NO_2^-]$, as well as the steady-state $[^{\bullet}NO_2]$ and $[N_2O_4]$, as per Equation (6) or Equation (7).

3. Results and Discussion

3.1. Effect of Water Parameters on $^{\bullet}NO_2$ Formation and Occurrence

First of all, the environmental occurrence of $^{\bullet}NO_2$ and N_2O_4 was assessed and compared with the other transient species (PPRIs). The effect of the two main $^{\bullet}NO_2/N_2O_4$ sources (NO_3^- and NO_2^-) was modeled first, to check whether or not the steady-state $[^{\bullet}NO_2]$ and $[N_2O_4]$ were linearly dependent on $[NO_3^-]$ and $[NO_2^-]$. The steady-state concentrations of the reactive transient species were thus calculated as a function of the concentration values of nitrate and nitrite, letting all the other parameters (DOC, HCO_3^-, CO_3^{2-}, and water depth) constant. Calculation results are shown in Figure 3 for $^{\bullet}NO_2$, N_2O_4, $^{\bullet}OH$, and $CO_3^{\bullet-}$. It is suggested that the concentration values of all these transient species increased with increasing nitrate and nitrite. At the same time, $[^3CDOM^*]$ and $[^1O_2]$ were constant at around 10^{-16} M in all conditions. These results are easily explained by the fact that nitrate and nitrite are both $^{\bullet}OH$ sources, and $^{\bullet}OH$ plays an important role in the production of both $^{\bullet}NO_2$ from NO_2^-, and $CO_3^{-\bullet}$ from HCO_3^-/CO_3^{2-} [6]. Moreover, the production of $^{\bullet}OH$ by NO_3^- is closely associated with the formation of $^{\bullet}NO_2$ (reaction (1)).

Increasing the $[NO_2^-]$ leads to increasing $[^{\bullet}OH]$ and, considering that $R_{\bullet NO_2}^{NO_2^-} = k_2 \times [^{\bullet}OH] \times [NO_2^-]$, there is a higher-than-linear effect of $[NO_2^-]$ on the formation rate of $^{\bullet}NO_2$ by NO_2^- itself. Moreover, because $[N_2O_4] \propto [^{\bullet}NO_2]^2$ (Equation (7)), one explains the faster-than-linear increase of $[N_2O_4]$ with the increasing nitrite, reported in Figure 3b.

An interesting issue is that $[N_2O_4]$ is 6–7 orders of magnitude or more lower than $[^{\bullet}NO_2]$, and it is even lower than $[^{\bullet}OH]$. This means that, for N_2O_4 to be a competitive nitrating agent with $^{\bullet}NO_2$, it should react much faster than $^{\bullet}NO_2$ with organic compounds. This is highly unlikely, with the possible exception of very electron-poor aromatics, which would not react with $^{\bullet}NO_2$ to a significant extent. Therefore, the reported finding, that the nitration of some pyridine derivatives involves N_2O_4 as a nitrating agent [37], looks more like an exception rather than a typical event.
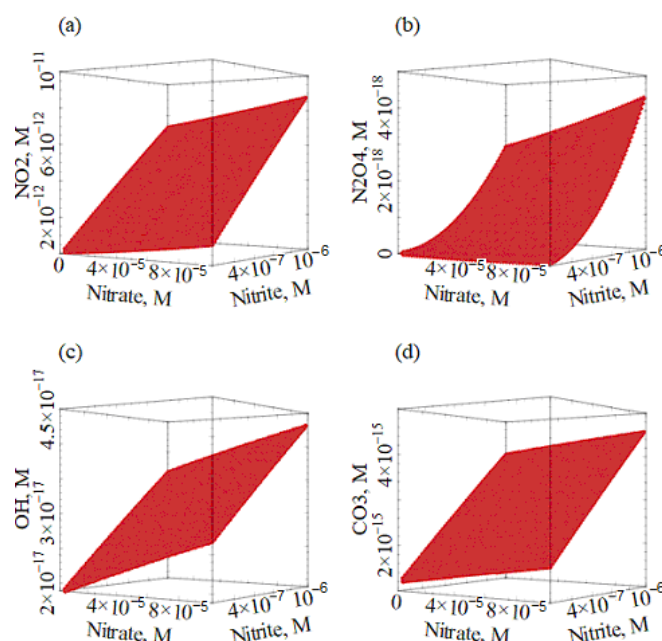
Figure 3. Modeled steady-state concentrations of $^\bullet NO_2$ (**a**), N_2O_4 (**b**), $^\bullet OH$ (**c**), and $CO_3^{\bullet-}$ (**d**) as a function of nitrate and nitrite concentrations. Other conditions: 5 m water depth, 1 mM HCO_3^-, 10 µM CO_3^{2-}, 1 mg$_C$ L^{-1} DOC, and 22 W m^{-2} sunlight UV irradiance, which is equivalent to fair weather, 45° N latitude 15 July, at 9 a.m. or 3 p.m.

Additionally, the steady-state $[CO_3^{\bullet-}]$ follows the same trend as $[^\bullet OH]$, because $^\bullet OH$ is the main $CO_3^{\bullet-}$ source through the oxidation of HCO_3^-/CO_3^{2-} [11] (Figure 3d). Interestingly, there is evidence that NO_2^- oxidation by $CO_3^{\bullet-}$ does not contribute much to $^\bullet NO_2$ production [18].

As reported in Figure 4, nitrate photolysis (reaction (1)) would prevail as an $^\bullet NO_2$ source over nitrate oxidation by $^\bullet OH$ (reaction (2)) in the vast majority of the conditions depicted in Figure 3. For nitrite oxidation to prevail, one needs $[NO_3^-] < 10\ [NO_2^-]$. In contrast, in natural waters, it is often found that $[NO_3^-] \sim 10^2\ [NO_2^-]$ [38]. Note that NO_3^- and NO_2^- play comparable roles as $^\bullet OH$ sources when $[NO_3^-] \sim 10^2\ [NO_2^-]$ [34].
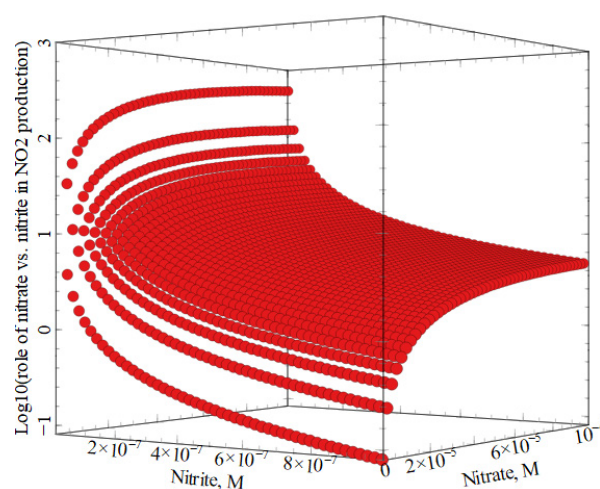

Figure 4. Comparison between the contributions to $^\bullet NO_2$ generation by nitrate photolysis ($R_{\bullet NO_2}^{NO_3^-} = R_{\bullet OH}^{NO_3^-}$), and by nitrite oxidation by $^\bullet OH$ ($R_{\bullet NO_2}^{NO_2^-} = k_2 \times [^\bullet OH] \times [NO_2^-]$). Nitrate and nitrite concentrations and other conditions are the same as for Figure 3. The nitrate process prevails when the logarithm is positive (most cases), whereas the nitrite process prevails when the logarithm is negative.

The possible role of HCO_3^- and CO_3^{2-} in $^\bullet NO_2$ formation is depicted in Figure 5, where conditions were chosen so that nitrate and nitrite contributed equally to $^\bullet NO_2$ generation (11 μM NO_3^-, 0.85 μM NO_2^-). It appears that inorganic carbon species would play a limited and slightly negative role towards the occurrence of $^\bullet NO_2$, presumably because their role as $^\bullet OH$ scavengers in the solution bulk prevails over the solvent cage effect that enhances nitrate photolysis by inhibiting the geminate recombination of $O^{\bullet-}$ and $^\bullet NO_2$ (see Figure 2 for such a solvent cage effect).
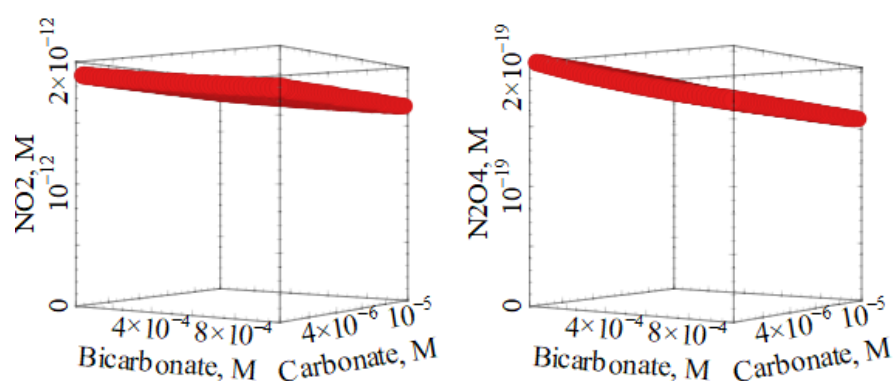

Figure 5. Effects of the concentration values of carbonate and bicarbonate on the steady-state concentrations of [$^\bullet NO_2$] and [N_2O_4]. Other conditions: 5 m water depth, 11 μM NO_3^-, 0.85 μM NO_2^-, 1 mg$_C$ L^{-1} DOC, and 22 W m^{-2} sunlight UV irradiance, which is equivalent to fair weather, 45°N latitude 15 July, at 9 a.m. or 3 p.m.

DOM as an $^\bullet OH$ scavenger is expected to inhibit $^\bullet NO_2$ formation by quenching reaction (2), that is, the nitrite route to $^\bullet NO_2$. Moreover, the chromophoric moieties within DOM (i.e., CDOM) compete with radiation absorption by both nitrate and nitrite, thereby inhibiting their photolysis [34]. As a consequence, the photogeneration of $^\bullet NO_2$ by nitrate, and that of $^\bullet OH$ by nitrate and nitrite, are both inhibited by CDOM. Last but not least, reaction with DOM is the main scavenging process for $^\bullet NO_2$. For all of these reasons, the overall DOM effect to decrease [$^\bullet NO_2$] is very important, as shown in Figure 6a.

Figure 6b,c additionally shows the decreasing formation rates of $^\bullet NO_2$ from nitrate and nitrite with increasing DOC, mostly due to competition for irradiance by CDOM (both cases), and $^\bullet OH$ scavenging by DOM ($^\bullet NO_2$ formation from NO_2^-).

The results shown in Figure 6a were obtained under the hypothesis that (C)DOM mostly operates as an irradiance competitor and $^\bullet OH$ scavenger. However, there is also the possibility that $^3CDOM^*$ oxidizes NO_2^- to $^\bullet NO_2$, and such a process is expected to contribute to $^\bullet NO_2$ production to a higher extent when the DOC is higher. There is evidence that a rate constant around 10^9 M^{-1} s^{-1} would be an upper limit for the reaction kinetics between $^3CDOM^*$ and NO_2^- [18]. That would be an upper limit, as well, for the ability of $^3CDOM^*$ to offset the inhibition effects by (C)DOM, shown in Figure 6a. As reported in Figure 6d (compare with Figure 6a), [$^\bullet NO_2$] would undergo almost negligible variations, even when considering such an upper-limit $^3CDOM^*$ contribution. Therefore, the overall role of (C)DOM towards the occurrence of [$^\bullet NO_2$] is strongly negative.

The bromide anion plays a minor role as an $^\bullet OH$ scavenger in most freshwaters, but its importance increases considerably with increasing salinity, until it becomes the main $^\bullet OH$ scavenger in seawater, where [Br^-]~0.8 mM [6,15]. Indeed, the second-order reaction rate constant between Br^- and $^\bullet OH$ is 1.1×10^{10} M^{-1} s^{-1}, while the reaction rate constant between $^\bullet OH$ and DOM is in the $(2–5) \times 10^4$ L mg$_C^{-1}$ s^{-1} range [6,15]. This means that one would need DOC = 160–400 mg$_C$ L^{-1}, which is hardly reasonable for a water matrix, to scavenge $^\bullet OH$ at a comparable level as 0.8 mM Br^-.
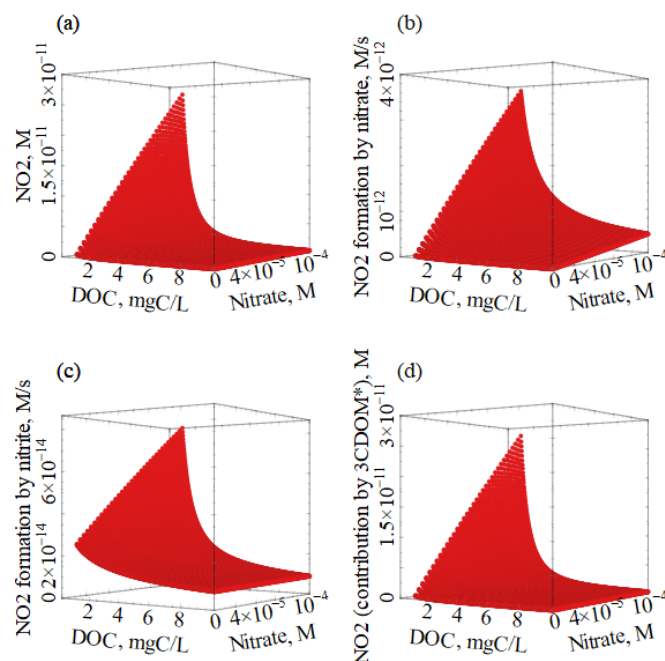
Figure 6. (**a**) Steady-state [•NO_2], assumed to be generated by nitrate photolysis and nitrite oxidation by •OH, as a function of DOC and nitrate concentration. Other conditions: 5 m water depth, [NO_2^-] = 10^{-2} [NO_3^-], 1 mg$_C$ L^{-1} DOC, and 22 W m^{-2} sunlight UV irradiance (equivalent to fair weather, 45° N latitude 15 July, at 9 a.m. or 3 p.m.). In the same conditions: (**b**) •NO_2 formation rate by nitrate photolysis; (**c**) •NO_2 formation rate upon •OH oxidation of nitrite, and (**d**) steady-state [•NO_2], assumed to be generated by nitrate photolysis, nitrite oxidation by •OH, and nitrite oxidation by ^{3}CDOM*. The second-order rate constant of the latter process was assumed to be 10^9 M^{-1} s^{-1}.

It is shown in Figure 7 that despite the important role of Br$^-$ as an •OH scavenger in saltwater and seawater, increasing [Br$^-$] decreases [•NO_2] only to a rather limited extent, because Br$^-$ is only able to inhibit the nitrite pathway to •NO_2 (reaction (2)). Indeed, differently from (C)DOM, Br$^-$ is not able to inhibit nitrate or nitrite photolysis, or to directly scavenge •NO_2. Figure 7 also shows that doubling the DOC from 1 to 2 mg$_C$ L^{-1} has a far more important effect on [•NO_2] than an increase in [Br$^-$] by an order of magnitude.
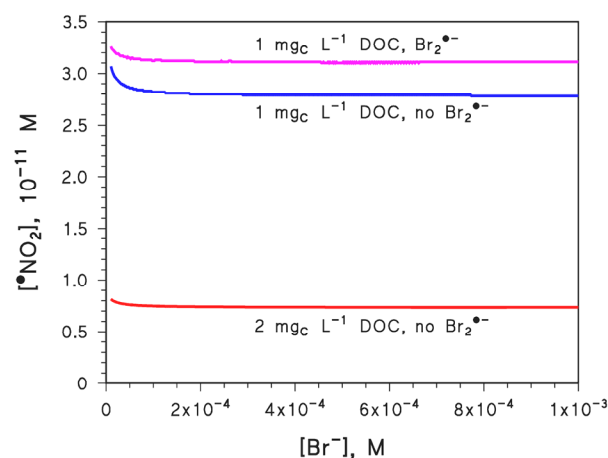
Figure 7. Steady-state [•NO_2] as a function of bromide concentration (in typical seawater, it is [Br$^-$] = 0.8 mM). The three curves differ on the value of the DOC and on whether or not the oxidation of nitrite by $Br_2^{•-}$ was taken into account as an •NO_2 source. Other conditions: 5 m water depth, 0.1 mM NO_3^-, 1 μM NO_2^-, 1 mM HCO_3^-, 10 μM CO_3^{2-}, and 22 W m^{-2} sunlight UV irradiance, which is equivalent to fair weather, 45°N latitude 15 July, at either 9 a.m. or 3 p.m.

The reaction between Br^- and $^\bullet OH$ yields $Br^\bullet$, and then $Br_2^{\bullet-}$ upon further reaction with Br^- [15]. $Br_2^{\bullet-}$ is able to oxidize NO_2^- to $^\bullet NO_2$ (reaction rate constant of 2×10^7 M^{-1} s^{-1}) [39], thereby contributing to $^\bullet NO_2$ generation. The radical $Br_2^{\bullet-}$ can dimerize to form Br^- and Br_2, with a rate constant of 1.8×10^9 M^{-1} s^{-1} [39], but the main quenching reaction of $Br_2^{\bullet-}$ in natural waters is scavenging by DOM, with an estimated rate constant of 3×10^2 L mg_C^{-1} s^{-1} [40]. A schematic of the mentioned processes involving $Br_2^{\bullet-}$ is provided in Figure 8. As shown in Figure 7, when taking into account the oxidation of NO_2^- by $Br_2^{\bullet-}$ (see the curve highlighted as "$Br_2^{\bullet-}$" in the plot), $[^\bullet NO_2]$ would significantly increase over the levels obtained by neglecting the $Br_2^{\bullet-}$ reactions. Indeed, when considering the whole process, Br^- does not appear to inhibit $^\bullet NO_2$ occurrence to a significant extent. On the one side, these results show that $^\bullet NO_2$ is more sensitive to the DOC than to Br^-. However, Br^- is able to enhance the formation of $^\bullet NO_2$ through $Br_2^{\bullet-}$, presumably because Br^- acts as an effective electron shuttle between $^\bullet OH$ and NO_2^- (see Figure 8). Indeed, the reaction rate constant between $Br_2^{\bullet-}$ and DOM is a couple of orders of magnitude lower than the rate constant between $^\bullet OH$ and DOM [6,40].
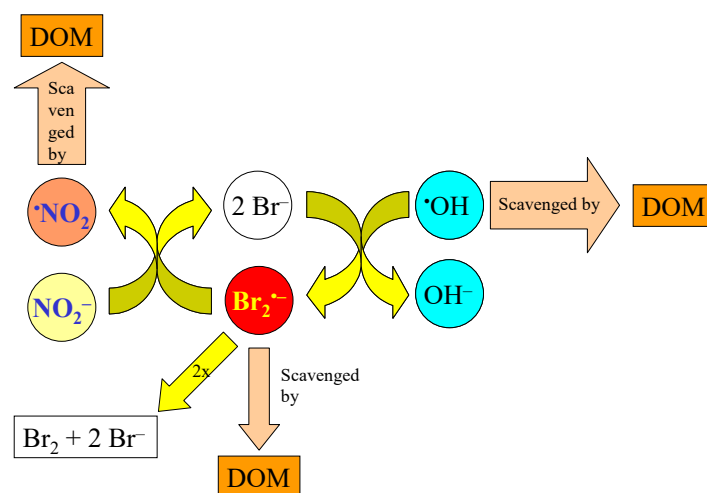

Figure 8. Schematic of the main processes involving $Br_2^{\bullet-}$ in sunlit saltwater. The thickness of the scavenging arrows is intended to suggest that $^\bullet OH$ reacts with DOM much faster compared to $Br_2^{\bullet-}$. Therefore, when Br^- outcompetes DOM as an $^\bullet OH$ scavenger, the couple $Br^-/Br_2^{\bullet-}$ acts as a very effective electron shuttle between $^\bullet OH$ and NO_2^-.

3.2. Role of $^\bullet NO_2$ in the Transformation/Nitrosation of Glutathione (GSH)

GSH is a tripeptide that plays an important role as an antioxidant in living organisms [41,42]. GSH does not undergo direct photolysis because it does not absorb sunlight [43], but it is photochemically degraded by $^\bullet OH$ in sunlit natural waters (second-order reaction rate constant of 3.5×10^9 M^{-1} s^{-1}) and by $^3CDOM^*$ (8×10^7 M^{-1} s^{-1}). In saltwater, some role is also played by $Br_2^{\bullet-}$ (2×10^8 M^{-1} s^{-1}) [44]. $^\bullet NO_2$ reacts with GSH by transforming it into nitroso-GSH, with a second-order reaction rate constant in the order of 10^7 M^{-1} s^{-1} [45].

In the case of freshwaters, it is suggested in Figure 9a that $^\bullet NO_2$ would play a minor role in the photochemical transformation of GSH, which is dominated by $^\bullet OH$ and by $^3CDOM^*$. In this circumstance, the relative role of $^\bullet OH$ decreases and that of $^3CDOM^*$ increases with increasing DOC, because $^\bullet OH$ is scavenged by organic matter, the chromophoric fraction of which is, vice versa, the source of $^3CDOM^*$.

The scenario gets very different in saltwater (Figure 9b), where $^\bullet OH$ is effectively scavenged by bromide, and where the $^\bullet OH$ role in GSH degradation is strongly decreased as a consequence. At the same time, the contribution of NO_2^- oxidation by $Br_2^{\bullet-}$ enhances the role of $^\bullet NO_2$ in the transformation of GSH. In seawater conditions (0.8 mM Br^-), $^\bullet NO_2$ and $^3CDOM^*$ would be the main reactive species for GSH transformation, with their

relative role depending on the DOC, which enhances ^{3}CDOM* and inhibits $^\bullet$NO$_2$, and on nitrate and nitrite concentration values.
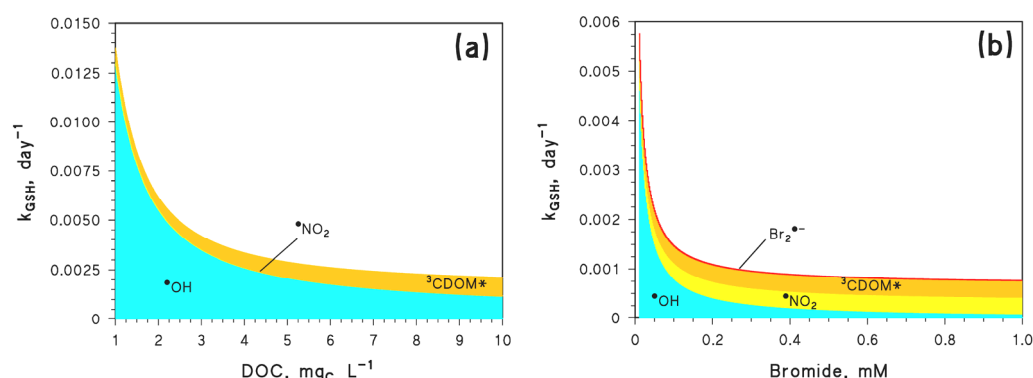

Figure 9. Pseudo-first order rate constants of the GSH's indirect phototransformation, as a function of (**a**) the DOC, and (**b**) the bromide concentration. Other conditions (when the given parameter is not set to vary on the X-axis): 5 m water depth, 0.1 mM NO$_3$$^-$, 1 µM NO$_2$$^-$, 1 mM HCO$_3$$^-$, 10 µM CO$_3$$^{2-}$, 1 mg$_C$ L^{-1} DOC, negligible Br$^-$, and 22 W m^{-2} sunlight UV irradiance (equivalent to fair weather, 45°N latitude 15 July, at 9 a.m. or 3 p.m.). The color code depicts the relative importance of the different phototransformation processes.

4. Conclusions

The nitrating and nitrosating agent $^\bullet$NO$_2$ is produced in sunlit natural waters upon nitrate photolysis and upon nitrite oxidation by $^\bullet$OH. The nitrate process would usually prevail in typical conditions found in natural waters, except when [NO$_2$$^-$] > 0.1 [NO$_3$$^-$]. Obviously, elevated concentration values of nitrate and nitrite are very favorable to the occurrence of $^\bullet$NO$_2$. Inorganic carbon has a limited effect on the steady-state [$^\bullet$NO$_2$], because small positive and negative effects offset each other, while elevated DOC is highly detrimental to the occurrence of $^\bullet$NO$_2$. Indeed, organic matter competes with nitrate and nitrite for sunlight irradiance and, therefore, for $^\bullet$OH photoproduction. Moreover, DOM scavenges $^\bullet$OH that is needed for NO$_2$$^-$ oxidation, and it also directly scavenges $^\bullet$NO$_2$.

It is suggested here that bromide occurring in saltwater and seawater would favor the degradation processes induced by $^\bullet$NO$_2$ (e.g., glutathione nitrosation) by decreasing the role of $^\bullet$OH and by enhancing that of $^\bullet$NO$_2$: indeed, in the presence of bromide, a further source of $^\bullet$NO$_2$ is operational, which is represented by NO$_2$$^-$ oxidation by Br$_2$$^{\bullet-}$. In these conditions, the couple Br$^-$/Br$_2$$^{\bullet-}$ acts as an effective electron shuttle between $^\bullet$OH and NO$_2$$^-$. This latter issue might explain why the photonitration of several phenolic compounds has been observed in the brackish waters of the Rhône delta lagoons (Southern France) [26–28]. In these environments, the concentration of nitrate (around 50 µM [26]) is not particularly high, despite there being important impact by agricultural activities, partly because of the elevated denitrification ability of paddy fields, and partly perhaps because of the assimilation of inorganic nitrogen by algae during the summer season [38]. By comparison, these levels are just double when compared to some mountain lakes (over 2000 m asl, NW Italy, 30 km as the crow flies off the city of Torino [46]), where nitrate occurs because of atmospheric depositions, but microorganisms are not much able to consume it. They are also comparable to the nitrate levels occurring in presently oligotrophic Lago Maggiore (NW Italy [47]). In the Rhône delta lagoons, bromide would play a role in inhibiting the degradation of the parent phenols by $^\bullet$OH, and it would allow $^\bullet$NO$_2$ to significantly contribute to the production of the nitrophenols. When also considering the ability of DOM to scavenge $^\bullet$NO$_2$, the mentioned photonitration processes are more likely to take place in lagoon water (DOC = 4–5 mg$_C$ L^{-1}) compared to the flooded rice fields (DOC around 12 mg$_C$ L^{-1}) [26]. Similarly, bromide could also play a role in the photonitration of phenol in seawater [48].

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