A Model Assessment of the Occurrence and Reactivity of the Nitrating/Nitrosating Agent Nitrogen Dioxide (\(^{•}\)NO\(_2\)) in Sunlit Natural Waters

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Abstract: Nitrogen dioxide (\(^{•}\)NO\(_2\)) is produced in sunlit natural surface waters by the direct photolysis of nitrate, together with \(^{•}\)OH, and upon the oxidation of nitrite by \(^{•}\)OH itself. \(^{•}\)NO\(_2\) is mainly scavenged by dissolved organic matter, and here, it is shown that \(^{•}\)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\(_2\)O\(_4\)) is also formed in the pathway of \(^{•}\)NO\(_2\) hydrolysis, but with a very low concentration, i.e., several orders of magnitude below \(^{•}\)NO\(_2\), and even below \(^{•}\)OH. Therefore, at most, N\(_2\)O\(_4\) would only be involved in the transformation (nitration/nitrosation) of electron-poor compounds, which would not react with \(^{•}\)NO\(_2\). Although it is known that nitrite oxidation by CO\(_3^{•−}\) in high-alkalinity surface waters gives a minor-to-negligible contribution to \(^{•}\)NO\(_2\) formation, it is shown here that NO\(_3^{−}\) oxidation by Br\(_2^{•−}\) can be a significant source of \(^{•}\)NO\(_2\) in saline waters (saltwater, brackish waters, seawater, and brines), which offsets the scavenging of \(^{•}\)OH by bromide. As an example, the anti-oxidant tripeptide glutathione undergoes nitrosation by \(^{•}\)NO\(_2\) preferentially in saltwater, thanks to the inhibition of the degradation of glutathione itself by \(^{•}\)OH, which is scavenged by bromide in saltwater. The enhancement of \(^{•}\)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 (\(^{•}\)OH) and carbonate (CO\(_3^{•−}\)) radicals, the excited triplet states of chromophoric dissolved organic matter (CDOM*, where CDOM is the chromophoric fraction of the dissolved organic matter, DOM), and singlet oxygen (\(^{1}\)O\(_2\)) [7]. PPRIs are produced upon sunlight absorption by photosensitisers, i.e., naturally occurring compounds such as nitrate and nitrite (\(^{•}\)OH sources), as well as CDOM (source of 3CDOM*, \(^{1}\)O\(_2\), and \(^{•}\)OH) [8–10]. Moreover, CO\(_3^{•−}\) is generated upon oxidation of HCO\(_3^{−}\)/CO\(_3^{2−}\) by \(^{•}\)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 •OH and CO₃²⁻, but it scavenges ³CDOM*/¹O₂ only to a very minor extent. Other important scavengers/quenchers are inorganic carbon, i.e., HCO₃⁻/CO₃²⁻ (for •OH), dissolved oxygen (for ³CDOM*), to yield ¹O₂, and collision with the water solvent (for ¹O₂) [6]. A schematic of the main processes involving photosensitizers, PPRIs’ production, their scavenging/quenching, and interaction with pollutants is provided in Figure 1.

In addition to •OH, CO₃²⁻, ³CDOM*, and ¹O₂, 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 (Br₂•⁻), which is mainly produced upon •OH scavenging by bromide in saltwater [15] and is an effective brominating agent, especially for phenols [16], as well as nitrogen dioxide (•NO₂). The latter is mostly generated by nitrate photolysis together with •OH, and by the oxidation of nitrite by •OH itself [8,17]. Other •NO₂ 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].

•NO₂ 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 nitrosodervatives from amines and amino acids [21,22]. •NO₂ 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)nitrination pathways of phenols and other aromatic compounds have found a plethora of nitrating agents (•NO₂, HNO₃, HOONO, H₂OONO⁺, and possibly also N₂O₄), 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)nitrination pathways, and the reactive species involved, may still be open to debate [24], in the case of natural surface waters, •NO₂ 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 •NO₂ (as well as its dimer, N₂O₄) 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].

![Figure 1. Schematic of the main processes involving photochemical production and scavenging/quenching of the main PPRIs (•OH, CO₃²⁻, ³CDOM*, and ¹O₂) in natural surface waters. DOM = dissolved organic matter; CDOM = chromophoric dissolved organic matter. Circles: photosensitizers and scavengers/quenchers; rectangles: PPRIs.](image-url)
2. Kinetic Model Development

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

\[
\text{NO}_3^- + \text{hv} + \text{H}^+ \rightarrow \cdot \text{OH} + \cdot \text{NO}_2 \left[ \frac{R_{\cdot \text{NO}_2}}{R_{\cdot \text{OH}}} \right]
\]  

\[
\text{NO}_2^- + \cdot \text{OH} \rightarrow \cdot \text{NO}_2 + \text{OH}^- \quad [k_2 = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}]
\]  

The quenching/scavenging processes of *NO₂ in an aqueous solution involve dimerization into dinitrogen tetroxide (N₂O₄), another potential nitrating agent, followed by the hydrolysis of the latter, as well as an *NO₂ reaction with the dissolved natural organic matter (DOM) [8]:

\[
2 \cdot \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \quad [k_3 = 4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}; k_{-3} = 6.9 \times 10^3 \text{ s}^{-1}]
\]  

\[
\cdot \text{NO}_2 + \text{DOM} \rightarrow \text{Products} \quad [k_4]
\]  

\[
\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NO}_2^- + 2 \text{H}^+ \quad [k_5 = 1 \times 10^3 \text{ s}^{-1}]
\]  

The value of \(k_3\) is still to be conclusively assessed. However, in the case of phenolic compounds, it is reported that \(k_4 \sim 10^4 \text{ M}^{-1} \text{ s}^{-1}\) [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 \(k_4 = 0.14 \text{ L mg}\text{C}^{-1} \text{ s}^{-1}\).

By assuming the formation rate of *NO₂ (R₅(NO₂)) as \(R_{\cdot \text{NO}_2} = \frac{R_{\cdot \text{OH}}}{k_4} + k_2 \times [\cdot \text{OH}] \times [\text{NO}_2^-]\), and applying the steady-state approximation to both *NO₂ and N₂O₄ (i.e., \(d[\text{NO}_2]/dt = 0\), and \(d[N_2O_4]/dt = 0\)), from reactions (1–5), one gets the following:

\[
\begin{align*}
\frac{[\cdot \text{NO}_2]}{[\text{N}_2\text{O}_4]} & = \left( \frac{k_{-3} + k_5}{k_3 \cdot \text{DOC}} \right) \frac{-k_4 \cdot \text{DOC} + \sqrt{k_4 \cdot \text{DOC}^2 + 8 k_3 k_5 R_{\cdot \text{NO}_2} (k_{-3} + k_5)}}{4 k_3 k_5} \\
\end{align*}
\]

Preliminary calculations showed that reaction (4) would strongly prevail over (3,5) as an *NO₂ sink. The rate difference between the two kinds of processes is so big that the conclusion would not change even if \(k_4 = 0.14 \text{ L mg}\text{C}^{-1} \text{ s}^{-1}\) turned out to be a generously high estimate for the reaction rate constant between *NO₂ and DOM. Therefore, when neglecting reactions (3,5) as *NO₂ sinks, one gets a considerable simplification for (6):

\[
\begin{align*}
\frac{[\cdot \text{NO}_2]}{[\text{N}_2\text{O}_4]} & = \frac{R_{\cdot \text{NO}_2}}{k_3 \cdot \text{DOC}} \quad (7)
\end{align*}
\]

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 [\*NO₂] and [N₂O₄] the most are the following:

1. DOC (dissolved organic carbon), when considering that DOM is the main *NO₂ scavenger [18], and that it also scavenges *OH [32], which plays a key role in the oxidation of NO₂ to *NO₂ [19];
2. Inorganic carbon (HCO₃⁻ and CO₃²⁻), because it enhances nitrate photolysis due to a solvent cage effect (see Figure 2) [33], but also acts as an *OH scavenger [32]. Interestingly, there is evidence that nitrite oxidation by CO₃²⁻ does not contribute to *NO₂ formation significantly [18];
3. Bromide (Br⁻), as a major *OH scavenger in saltwater and seawater [15,32].
The effect of different water components on [\textbullet NO_2] and [N_2O_4] was modeled by assessing the values of \( R_{\text{NO}_2} \) and [\textbullet OH], which are needed to calculate \( R_{\text{NO}_2} \), 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 ([\textbullet OH], CO_3^{2-}, \textbullet O_2, and \textbullet CDOM*) 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 \( R_{\text{NO}_2} = R_{\text{NO}_2}^{\text{OH}} + k_2 \times [\textbullet OH] \times [\text{NO}_2^-] \), as well as the steady-state \([\textbullet NO_2]\) and [N_2O_4], as per Equation (6) or Equation (7).

3. Results and Discussion
3.1. Effect of Water Parameters on \textbullet NO_2 Formation and Occurrence

First of all, the environmental occurrence of \textbullet NO_2 and N_2O_4 was assessed and compared with the other transient species (PPRs). The effect of the two main \textbullet NO_2/N_2O_4 sources (NO_3^- and NO_2^-) was modeled first, to check whether or not the steady-state \([\textbullet NO_2]\) 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 \textbullet NO_2, N_2O_4, \textbullet OH, and CO_3^{2-}. It is suggested that the concentration values of all these transient species increased with increasing nitrate and nitrite. At the same time, [\textbullet CDOM*] and [\textbullet O_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 \textbullet OH sources, and \textbullet OH plays an important role in the production of both \textbullet NO_2 from NO_2-, and CO_3^- from HCO_3^- / CO_3^{2-} [6]. Moreover, the production of \textbullet OH by NO_3^- is closely associated with the formation of \textbullet NO_2 (reaction (1)).

Increasing the [NO_2^-] leads to increasing [\textbullet OH] and, considering that \( R_{\text{NO}_2}^{\text{OH}} = k_2 \times [\textbullet OH] \times [\text{NO}_2^-] \), there is a higher-than-linear effect of [NO_2^-] on the formation rate of \textbullet NO_2 by NO_2^- itself. Moreover, because [N_2O_4] \propto [\textbullet 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 [\textbullet NO_2], and it is even lower than [\textbullet OH]. This means that, for N_2O_4 to be a competitive nitrating agent with \textbullet NO_2, it should react much faster than \textbullet NO_2 with organic compounds. This is highly unlikely, with the possible exception of very electron-poor aromatics, which would not react with \textbullet 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.
Additionally, the steady-state [CO$_3^{2-}$] follows the same trend as [•OH], because •OH is the main CO$_3^{2-}$ source through the oxidation of HCO$_3^{-}$/CO$_3^{2-}$ [11] (Figure 3d). Interestingly, there is evidence that NO$_2^-$ oxidation by CO$_3^{*−}$ does not contribute much to •NO$_2$ production [18].

As reported in Figure 4, nitrate photolysis (reaction (1)) would prevail as an •NO$_2$ source over nitrate oxidation by •OH (reaction (2)) in the vast majority of the conditions depicted in Figure 3. For nitrite oxidation to prevail, one needs [NO$_3^-$] < 10$^2$ [NO$_2^-$] [38]. Note that NO$_3^-$ and NO$_2^-$ play comparable roles as •OH sources when [NO$_3^-$]~10$^2$ [NO$_2^-$] [34].

**Figure 3.** Modeled steady-state concentrations of •NO$_2$ (a), N$_2$O$_4$ (b), •OH (c), and CO$_3^{*−}$ (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 mgC 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.

**Figure 4.** Comparison between the contributions to •NO$_2$ generation by nitrate photolysis ($R_{\text{NO}_2^{\text{OH}}}=R_{\text{NO}_2}^{\text{NO}_3}k_{\text{NO}_2}\times[\text{NO}_3^-]\times[\text{OH}])$, and by nitrite oxidation by •OH ($R_{\text{NO}_2^{\text{OH}}}^{\text{NO}_2}=k_2\times[\text{OH}]\times[\text{NO}_2^-]$). 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 •NO$_2$ formation is depicted in Figure 5, where conditions were chosen so that nitrate and nitrite contributed equally to •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 •NO$_2$, presumably because their role as •OH scavengers in the solution bulk prevails over the solvent cage effect that enhances nitrate photolysis by inhibiting the geminate recombination of O$^\cdot$ and •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 [•NO$_2$] and [N$_2$O$_4$]. 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 •OH scavenger is expected to inhibit •NO$_2$ formation by quenching reaction (2), that is, the nitrite route to •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 •NO$_2$ by nitrate, and that of •OH by nitrate and nitrite, are both inhibited by CDOM. Last but not least, reaction with DOM is the main scavenging process for •NO$_2$. For all of these reasons, the overall DOM effect to decrease [•NO$_2$] is very important, as shown in Figure 6a.

Figure 6b,c additionally shows the decreasing formation rates of •NO$_2$ from nitrate and nitrite with increasing DOC, mostly due to competition for irradiance by CDOM (both cases), and •OH scavenging by DOM (•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 •OH scavenger. However, there is also the possibility that ³CDOM$^*$ oxidizes NO$_2^-$ to •NO$_2$, and such a process is expected to contribute to •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), •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 [•NO$_2$] is strongly negative.

The bromide anion plays a minor role as an •OH scavenger in most freshwaters, but its importance increases considerably with increasing salinity, until it becomes the main •OH scavenger in seawater, where [Br$^-$]=0.8 mM [6,15]. Indeed, the second-order reaction rate constant between Br$^-$ and •OH is 1.1 × 10$^{10}$ M$^{-1}$ s$^{-1}$, while the reaction rate constant between •OH and DOM is in the (2–5) × 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 •OH at a comparable level as 0.8 mM Br$^-$. 

Figure 4. Comparison between the contributions to •NO$_2$ formation by quenching reaction (2), that is, the nitrite route to •NO$_2$, presumably because their role as •OH scavengers in the solution bulk prevails over the solvent cage effect that enhances nitrate photolysis by inhibiting the geminate recombination of O$^\cdot$ and •NO$_2$ (see Figure 2 for such a solvent cage effect).
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 mgC L$^{-1}$ has a far more important effect on [•NO$_2$] than an increase in [Br$^-$] by an order of magnitude.

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$^-_3$] = 10$^{-2}$ [NO$_3^-$], 1 mgC 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 3CDOM*. The second-order rate constant of the latter process was assumed to be 10$^9$ M$^{-1}$ s$^{-1}$.

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 $\text{Br}^-$ and $^*\text{OH}$ yields $\text{Br}_2^-$, and then $\text{Br}_2^-$ upon further reaction with $\text{Br}^-$ [15]. $\text{Br}_2^-$ is able to oxidize $\text{NO}_2^-$ to $^*\text{NO}_2$ (reaction rate constant of $2 \times 10^7 \ \text{M}^{-1} \ \text{s}^{-1}$) [39], thereby contributing to $^*\text{NO}_2$ generation. The radical $\text{Br}_2^-$ can dimerize to form $\text{Br}_2^-$ and $\text{Br}_2$, with a rate constant of $1.8 \times 10^3 \ \text{M}^{-1} \ \text{s}^{-1}$ [39], but the main quenching reaction of $\text{Br}_2^-$ in natural waters is scavenging by DOM, with an estimated rate constant of $3 \times 10^2 \ \text{L} \ \text{mg}_C^{-1} \ \text{s}^{-1}$ [40]. A schematic of the mentioned processes involving $\text{Br}_2^-$ is provided in Figure 8. As shown in Figure 7, when taking into account the oxidation of $^*\text{NO}_2$ by $\text{Br}_2^-$ (see the curve highlighted as “$\text{Br}_2^-$” in the plot), $[^*\text{NO}_2]$ would significantly increase over the levels obtained by neglecting the $\text{Br}_2^-$ reactions. Indeed, when considering the whole process, $\text{Br}^-$ does not appear to inhibit $^*\text{NO}_2$ occurrence to a significant extent. On the one side, these results show that $^*\text{NO}_2$ is more sensitive to the DOC than to $\text{Br}^-$. However, $\text{Br}^-$ is able to enhance the formation of $^*\text{NO}_2$ through $\text{Br}_2^-$, presumably because $\text{Br}^-$ acts as an effective electron shuttle between $^*\text{OH}$ and $\text{NO}_2^-$ (see Figure 8). Indeed, the reaction rate constant between $\text{Br}_2^-$ and DOM is a couple of orders of magnitude lower than the rate constant between $^*\text{OH}$ and DOM [6,40].

![Figure 8. Schematic of the main processes involving $\text{Br}_2^-$ in sunlit saltwater. The thickness of the scavenging arrows is intended to suggest that $^*\text{OH}$ reacts with DOM much faster compared to $\text{Br}_2^-$.
](image)

Therefore, when $\text{Br}^-$ outcompetes DOM as an $^*\text{OH}$ scavenger, the couple $\text{Br}^-/\text{Br}_2^-$ acts as a very effective electron shuttle between $^*\text{OH}$ and $\text{NO}_2^-$.  

### 3.2. Role of $^*\text{NO}_2$ 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 $^*\text{OH}$ in sunlit natural waters (second-order reaction rate constant of $3.5 \times 10^9 \ \text{M}^{-1} \ \text{s}^{-1}$) and by $^3\text{CDOM}^*$ ($8 \times 10^9 \ \text{M}^{-1} \ \text{s}^{-1}$). In saltwater, some role is also played by $\text{Br}_2^-$ (2 $\times$ $10^8 \ \text{M}^{-1} \ \text{s}^{-1}$) [44]. $^*\text{NO}_2$ reacts with GSH by transforming it into nitroso-GSH, with a second-order reaction rate constant in the order of $10^7 \ \text{M}^{-1} \ \text{s}^{-1}$ [45].

In the case of freshwaters, it is suggested in Figure 9a that $^*\text{NO}_2$ would play a minor role in the photochemical transformation of GSH, which is dominated by $^*\text{OH}$ and by $^3\text{CDOM}^*$. In this circumstance, the relative role of $^*\text{OH}$ decreases and that of $^3\text{CDOM}^*$ increases with increasing DOC, because $^*\text{OH}$ is scavenged by organic matter, the chromophoric fraction of which is, vice versa, the source of $^3\text{CDOM}^*$.

The scenario gets very different in saltwater (Figure 9b), where $^*\text{OH}$ is effectively scavenged by bromide, and where the $^*\text{OH}$ role in GSH degradation is strongly decreased as a consequence. At the same time, the contribution of $\text{NO}_2^-$ oxidation by $\text{Br}_2^-$ enhances the role of $^*\text{NO}_2$ in the transformation of GSH. In seawater conditions (0.8 mM $\text{Br}^-$), $^*\text{NO}_2$ and $^3\text{CDOM}^*$ would be the main reactive species for GSH transformation, with their
relative role depending on the DOC, which enhances $^3$CDOM$^*$ and inhibits $^*\text{NO}_2$, and on nitrate and nitrite concentration values.

![Figure 9](image)

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

It is suggested here that bromide occurring in saltwater and seawater would favor the degradation processes induced by $^*\text{NO}_2$ (e.g., glutathione nitrosation) by decreasing the role of $^*\text{OH}$ and by enhancing that of $^*\text{NO}_2$: indeed, in the presence of bromide, a further source of $^*\text{NO}_2$ is operational, which is represented by NO$_2^-$ oxidation by Br$_2[^*]$.

In these conditions, the couple Br$^-$/Br$_2[^*]$ acts as an effective electron shuttle between $^*\text{OH}$ 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 $^*\text{OH}$, and it would allow $^*\text{NO}_2$ to significantly contribute to the production of the nitrophenols. When also considering the ability of DOM to scavenge $^*\text{NO}_2$, 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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