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ENHANCEMENT BY ANTHRAQUINONE-2-SULPHONATE OF THE PHOTONITRATION OF PHENOL BY NITRITE: IMPLICATIONS FOR THE PHOTOPRODUCTION OF NITROGEN DIOXIDE BY COLOURED DISSOLVED ORGANIC MATTER IN SURFACE WATERS

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Abstract

Anthraquinone-2-sulphonate (AQ2S) under UVA irradiation is able to oxidise nitrite to $\bullet\text{NO}_2$ and to induce the nitration of phenol. The process involves the very fast reactions of the excited triplet state $^3\text{AQ2S}^*$ and its 520-nm absorbing exciplex with water, at different time scales (ns and μs , respectively). Quinones are ubiquitous components of coloured dissolved organic matter (CDOM) in surface waters and AQ2S was adopted here as a proxy of CDOM. Using a recently developed model of surface-water photochemistry, we found that the oxidation of nitrite to $\bullet\text{NO}_2$ by $^3\text{CDOM}^*$ could be an important $\bullet\text{NO}_2$ source in water bodies with high $[\text{NO}_2^-]$ to $[\text{NO}_3^-]$ ratio, for elevated values of column depth and NPOC.

Keywords: aromatic photonitration; photosensitised processes; nitroaromatic compounds; nitrophenols; nitrogen dioxide.

Introduction

Nitrophenols are environmentally harmful nitroaromatic compounds, with a potential to act as uncoupling agents in oxidative phosphorylation (Shea et al., 1983) and to cause oxidative damage to DNA (Chiron et al., 2007a). Nitrophenols occur in surface waters because of several pathways: atmospheric deposition, hydrolysis of parathion and similar products (Agarwal et al., 1994), and

photonitration of the corresponding phenols (Chiron et al., 2007b). The latter may be environmental transformation intermediates of phenolic herbicides (Chiron et al., 2009). Exposure to nitrophenols can cause harmful effects to algae (Umamaheswari and Venkateswarlu, 2004) and aquatic organisms (Howe et al., 1994).

The photonitration of aromatic compounds is started by the production of $\bullet\text{NO}_2$ upon photolysis of nitrate and nitrite (Machado and Boule, 1995; Dzengel et al., 1999; Vione et al., 2002). Another potentially important source of $\bullet\text{NO}_2$ in the aqueous solution is the photooxidation of nitrite, in the presence of $\bullet\text{OH}$ or of irradiated metal oxides (Chiron et al., 2007b).

The excited triplet states of coloured dissolved organic matter ($^3\text{CDOM}^*$) are important reactive transients in surface waters (Halladja et al., 2007). The species $^3\text{CDOM}^*$ are often able to abstract electrons or hydrogen atoms from other dissolved molecules, as well as to transform ground-state O_2 into $^1\text{O}_2$. $^3\text{CDOM}^*$ is for instance involved to a very significant extent into the transformation of phenylurea herbicides (Canonica et al., 2006). The excited triplet states of quinones are representative of the coloured moieties of natural dissolved organic matter (Cory et al., 2005). They have often very high reduction potentials (Wardman, 1989) and could oxidise nitrite to $\bullet\text{NO}_2$ ($E^\circ_{\bullet\text{NO}_2/\text{NO}_2^-} \approx 1 \text{ V}$). However, no data are available on the process of $\bullet\text{NO}_2$ production by nitrite and $^3\text{CDOM}^*$, nor on the potential of such a reaction to induce aromatic nitration.

We chose anthraquinone-2-sulphonate (AQ2S) as model photoactive organic compound. The photochemistry and photophysics of AQ2S are rather well known (Loeff et al., 1983; Maurino et al., 2008). Interestingly, the excited triplet state of AQ2S ($^3\text{AQ2S}^*$) does not react with O_2 to yield $^1\text{O}_2$ (Maddigapu et al., 2010). With AQ2S it is thus possible to study the triplet-state reactivity, without the additional complication of the reactions of $^1\text{O}_2$.

The nitration of phenol was studied upon irradiation of AQ2S and nitrite, to get insight into the ability of the process to yield harmful nitroaromatic compounds. Moreover, the transformation of phenol into nitrophenols is a suitable probe reaction for the assessment of $\bullet\text{NO}_2$ generation (Chiron et al., 2007b). The potential importance of the production of $\bullet\text{NO}_2$ by triplet state reactivity under environmental conditions was assessed by means of a combination of experimental results and modelling of surface-water photochemistry.

Experimental

All reagents were of analytical grade and were used as received, without further purification. Water used was of Milli-Q quality.

Irradiation experiments. The aqueous solutions to be irradiated (5 mL total volume) were placed into cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height, lateral inlet with screw-cap closure). Irradiation with magnetic stirring took place under a 40 W Philips TL K05 UVA lamp. The incident photon flux in solution, actinometrically determined with the ferrioxalate method

(Kuhn et al., 2004) was $2.1 \cdot 10^{-5}$ Einstein $L^{-1} s^{-1}$ and corresponded to a UV irradiance (290-400 nm) of $28 W m^{-2}$, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. Figure 1 reports the emission spectrum of the adopted lamp, measured with an Ocean Optics SD 2000 CCD spectrophotometer and normalised to the actinometry results, taking into account the transmittance of the Pyrex glass window of the irradiation cells. The Figure also reports the absorption spectra of AQ2S and nitrite, taken with a Varian Cary 100 Scan UV-Vis spectrophotometer.

Analytical determinations. After irradiation the solutions were allowed to cool for 10-15 min under refrigeration, and then analysed by High Performance Liquid Chromatography coupled with UV-Vis detection (HPLC-UV). The adopted Merck-Hitachi instrument was equipped with AS2000A autosampler (100 μL sample volume), L-6200 and L-6000 pumps for high-pressure gradients, Merck LiChrocart RP-C18 column packed with LiChrospher 100 RP-18 (125 mm \times 4.6 mm \times 5 μm), and L-4200 UV-Vis detector (detection wavelength 210 nm). The isocratic elution was carried out with a 50:50 mixture of methanol: aqueous H_3PO_4 (pH 2.8). With an eluent flow rate of 1.0 $mL min^{-1}$ the retention times were (min): phenol (2.55), 4-nitrophenol (3.20), 2-nitrophenol (5.15). The column dead time was 0.90 min.

Kinetic treatment of the data. The time evolution data of phenol were fitted with pseudo-first order equations of the form $C_t = C_o \exp(-k_d^{Ph} \cdot t)$, where C_t is the concentration of phenol at the time t, C_o its initial concentration, and k_d^{Ph} the pseudo-first order degradation rate constant. The initial transformation rate of phenol is $Rate_{Ph} = k_d^{Ph} C_o$. The time evolution of 2- and 4-nitrophenol was fitted with $C'_t = k_f^{NP} \cdot C_o \cdot (k_d^{NP} - k_d^{Ph})^{-1} \cdot [\exp(-k_d^{Ph} \cdot t) - \exp(-k_d^{NP} \cdot t)]$, where C'_t is the concentration of each nitrophenol at the time t and k_f^{NP} and k_d^{NP} are the pseudo-first order formation and transformation rate constants of each nitrophenol. C_o and k_d^{Ph} have the same meaning as before. The nitrophenol initial formation rate is $Rate_{NP} = k_f^{NP} C_o$. The reported errors on the rates were derived at the σ level from the fit of the experimental data (intra-series variability). The reproducibility of repeated runs (inter-series variability) was in the range of 10-15%.

Radiation absorption calculations. To calculate the photon flux absorbed by AQ2S (P_a^{AQ2S}) in the presence of nitrite, one should consider that nitrite and AQ2S compete for the lamp irradiance (see Figure 1). The absorbance of a species S does not vary if S is alone in solution or if it is in mixture with other radiation-absorbing compounds, but the photon flux absorbed by S is lower in the mixture. Interestingly, in a solution containing S and R as radiation-absorbing species, at a given wavelength λ the ratio of the respective absorbances would be equal to the ratio of the absorbed spectral photon flux densities: $A_S(\lambda) [A_R(\lambda)]^{-1} = p_{a,S}(\lambda) [p_{a,R}(\lambda)]^{-1}$ (Braslavsky, 2007). It is also $A_S(\lambda) [A_{tot}(\lambda)]^{-1} = p_{a,S}(\lambda) [p_{a,tot}(\lambda)]^{-1}$, where $A_{tot}(\lambda) = A_S(\lambda) + A_R(\lambda)$. Given these premises, the photon flux absorbed by AQ2S in the presence of nitrite (P_a^{AQ2S}) can be obtained as follows:

$$A_{tot}(\lambda) = b \cdot \{ \epsilon_{AQ2S}(\lambda) \cdot [AQ2S] + \epsilon_{NO_2^-}(\lambda) \cdot [NO_2^-] \} \quad (1)$$

$$P_{a,tot}(\lambda) = p^\circ(\lambda) \cdot [1 - 10^{-A_{tot}(\lambda)}] \quad (2)$$

$$P_{a,AQ2S}(\lambda) = P_{a,tot}(\lambda) \cdot \epsilon_{AQ2S}(\lambda) \cdot [AQ2S] \cdot \{\epsilon_{AQ2S}(\lambda) \cdot [AQ2S] + \epsilon_{NO_2^-}(\lambda) \cdot [NO_2^-]\}^{-1} \quad (3)$$

$$P_a^{AQ2S} = \int_{\lambda} P_{a,AQ2S}(\lambda) d\lambda \quad (4)$$

where $p^\circ(\lambda)$ is the lamp photon flux reaching the solution, ϵ_{AQ2S} and $\epsilon_{NO_2^-}$ the molar absorption coefficients of AQ2S and nitrite, respectively, and $b = 0.4$ cm the optical path length of the irradiated solution. P_a^{AQ2S} decreases with increasing nitrite concentration (see Figure A-SM in the Supplementary Material, hereafter SM). In the case of 0.1 mM AQ2S one gets the following linear trend: $P_a^{AQ2S} [Einstein L^{-1} s^{-1}] = (2.01 \pm 0.01) \cdot 10^{-6} - (1.62 \pm 0.04) \cdot 10^{-5} [NO_2^-]$.

Laser flash photolysis experiments. Laser flash photolysis (LFP) experiments were performed by using the third harmonic ($\lambda_{exc} = 355$ nm) of a Quanta Ray GCR 130-01 Nd:YAG laser system instrument, used in a right-angle geometry with respect to the monitoring light beam. The single pulses were ca. 9 ns in duration, with an energy of 65 mJ/pulse. Individual cuvette samples (3 mL volume) were used for a maximum of two consecutive laser shots. The transient absorbance at the pre-selected wavelength (λ_{det}) was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and a photomultiplier (1P28). A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitised by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitised signal.

The second-order rate constant with nitrite of $^3AQ2S^*$ and related exciplexes with water was determined from the regression lines of the absorbance logarithm decay against $[NO_2^-]$. All experiments were performed at ambient temperature (295 ± 2 K) in aerated solution. pH was adjusted at 8.0 with NaOH.

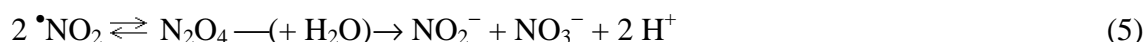
Three transient species were identified upon laser excitation of AQ2S as reported previously (Loeff et al., 1983; Maddigapu et al., 2010). The first one, monitored at 380 nm was identified with $^3AQ2S^*$. It quickly decays ($k_{decay}^{^3AQ2S^*} \sim 6.8 \cdot 10^7 s^{-1}$) leading to the formation of two exciplexes: B with a slow decay ($k_{decay}^B \sim 2.7 \cdot 10^4 s^{-1}$) and C ($k_{decay}^C \sim 2.8 \cdot 10^6 s^{-1}$), monitored at 520 and 600 nm respectively.

Results and Discussion

AQ2S-enhanced phenol photonitration

Figure 2 reports the time evolution of 2-nitrophenol (2NP, 2a) and 4-nitrophenol (4NP, 2b) upon UVA irradiation of 1 mM phenol, 1-4 mM NaNO₂ and 0.1 mM AQ2S. AQ2S considerably enhances the photonitration of phenol in the presence of nitrite, because no nitrophenols were detected in its absence. Figure 3 shows the corresponding initial formation rates of 2NP and 4NP, which are directly proportional to the concentration of nitrite. Negligible nitrophenol formation rates were observed without AQ2S. One gets the following linear dependence of Rate_{2NP} and Rate_{4NP} vs. [NO₂⁻]: $Rate_{2NP} = (2.54 \pm 0.08) \cdot 10^{-6} [NO_2^-]$; $Rate_{4NP} = (1.65 \pm 0.07) \cdot 10^{-6} [NO_2^-]$; $Rate_{NP} = Rate_{2NP} + Rate_{4NP} = (4.19 \pm 0.11) \cdot 10^{-6} [NO_2^-]$.

The formation of nitrophenols in aqueous solution is initiated by the reaction of phenol with [•]NO₂, which is in competition with the hydrolysis of nitrogen dioxide (Machado and Boule, 1995; Dzengel et al., 1999):



In the presence of 1 mM phenol, practically all [•]NO₂ would react with phenol to give the nitrophenols (Chiron et al., 2007b). Under such circumstances, Rate_{NP} would be a measure of the generation rate of [•]NO₂ in the studied system. The quantum yield of nitrophenol generation by irradiated AQ2S is $\Phi_{NP}^{AQ2S} = Rate_{NP} (P_a^{AQ2S})^{-1}$, where P_a^{AQ2S} is the photon flux absorbed by AQ2S. As already reported, in the presence of competition for irradiance by nitrite it is $P_a^{AQ2S} = (2.01 \pm 0.01) \cdot 10^{-6} - (1.62 \pm 0.04) \cdot 10^{-5} [NO_2^-]$. Considering that $Rate_{NP} = (4.19 \pm 0.11) \cdot 10^{-6} [NO_2^-]$, one gets the following trend of Φ_{NP}^{AQ2S} vs. [NO₂⁻]:

$$\Phi_{NP}^{AQ2S} = \frac{(4.19 \pm 0.11) \cdot 10^{-6} [NO_2^-]}{(2.01 \pm 0.01) \cdot 10^{-6} - (1.62 \pm 0.04) \cdot 10^{-5} [NO_2^-]} \quad (6)$$

In the presence of 1 mM phenol, under the hypotheses that practically all [•]NO₂ reacts with phenol and that the nitrophenols (2NP and 4NP) are formed with unity yield by reaction of phenol with one [•]NO₂ molecule (Chiron et al., 2007b), Φ_{NP}^{AQ2S} would be a measure of the quantum yield of [•]NO₂ photoproduction by radiation-excited AQ2S: $\Phi_{NP}^{AQ2S} = \Phi_{\cdot NO_2}^{AQ2S}$ (otherwise it would be $\Phi_{NP}^{AQ2S} < \Phi_{\cdot NO_2}^{AQ2S}$). Interestingly, a sub-mM [NO₂⁻] would be sufficient to have $(1.62 \pm 0.04) \cdot 10^{-5} [NO_2^-] \ll (2.01 \pm 0.01) \cdot 10^{-6}$. In surface waters [NO₂⁻] has often sub-μM levels, thus equation (6) would be modified as follows:

$$\Phi_{\cdot NO_2}^{AQ2S} \approx (2.08 \pm 0.06) [NO_2^-] \quad (7)$$

Laser flash photolysis experiments

Figure 4 shows the trend of the pseudo-first order decay constant of $^3\text{AQ2S}^*$ vs. $[\text{NO}_2^-]$. The linear fit of the experimental data gives the second-order rate constant between $^3\text{AQ2S}^*$ and NO_2^- , $k_{^3\text{AQ2S}^*,\text{NO}_2^-} = (2.35 \pm 0.25) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($\mu \pm \sigma$). This value compares well with Loeff et al. (1983), who found $3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH ~ 6.0 .

At 520 nm the absorbance decay was fitted with a double-exponential plot, indicating the presence of two species: on the basis of literature data, the first was attributed to the exciplex B between $^3\text{AQ2S}^*$ and water (Maddigapu et al., 2010a), the second to the AQ2S radical anion ($\text{AQ2S}^{\bullet-}$) (Hulme et al., 1972). $\text{AQ2S}^{\bullet-}$ is formed by electron transfer between $^3\text{AQ2S}^*$ and NO_2^- :



Figure 5a shows the trend vs. $[\text{NO}_2^-]$ of the maximum absorbance reached by B and $\text{AQ2S}^{\bullet-}$ at 520 nm. The absorbance of B decreased from 0.081 in water to 0.020 with 5 mM NO_2^- . The absorbance of $\text{AQ2S}^{\bullet-}$ increased quickly and reached a plateau around 0.15 at 2 mM NO_2^- .

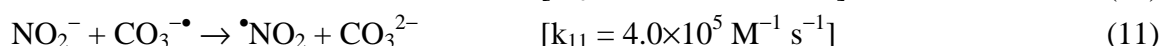
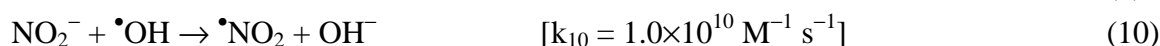
Figure 5b shows the pseudo-first order decay constants of B and $\text{AQ2S}^{\bullet-}$ as function of $[\text{NO}_2^-]$. In the case of B there is an evident quenching by NO_2^- and it is possible to calculate the second-order rate constant, $k_{B,\text{NO}_2^-} = (1.03 \pm 0.04) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This is interesting because B usually shows poor reactivity with dissolved species (Maddigapu et al., 2010). The pseudo-first order decay constant of $\text{AQ2S}^{\bullet-}$ ($k_{\text{AQ2S}^{\bullet-}}$) is close to $5.8 \cdot 10^5 \text{ s}^{-1}$. As expected, no reactivity was found with NO_2^- .

Finally, the reactivity between the second exciplex (C) and nitrite was investigated at 600 nm. The maximum absorbance of C decreased from 0.14 in water to 0.06 with 5 mM nitrite, but no reaction between C and NO_2^- could be detected. Nitrite inhibits the formation of C, rather than enhancing its decay, because reaction (8) consumes $^3\text{AQ2S}^*$ that is no longer able to yield C via reaction with water.

Note that $^3\text{AQ2S}^*$ reacts with nitrite faster than B, but it is also much more unstable: therefore, production of $\bullet\text{NO}_2$ by irradiated AQ2S involves $^3\text{AQ2S}^*$ in the ns scale and B in the μs one after photon absorption. Nitrite at mM levels is not able to totally quench $^3\text{AQ2S}^*$ (one needs some 3 mM NO_2^- to get $k_{\text{decay}}^{^3\text{AQ2S}^*}$ twice higher than in water, see Figure 4). Therefore, in the presence of sub-mM NO_2^- there would be limited quenching of $^3\text{AQ2S}^*$, which allows the formation of B and its further reaction with nitrite.

Environmental significance

The photogeneration of $\bullet\text{NO}_2$ in surface waters can take place upon nitrate photolysis and nitrite photooxidation by $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$ (Mack and Bolton, 1999; Buxton et al., 1988; Neta et al., 1988), and probably also ${}^3\text{CDOM}^*$.



As far as reaction (12) is concerned, it is made the hypothesis that the quantum yield of $\bullet\text{NO}_2$ photoproduction by CDOM is described by equation (7). It is possible to model the photoproduction and the reactivity of $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$ and ${}^3\text{CDOM}^*$ in surface waters as a function of the water chemical composition and column depth d (Maddigapu et al., in press). The same models, which are described in the SM, can be adapted to the assessment of the formation rate of $\bullet\text{NO}_2$ via reactions (9-12). The corresponding equations are also reported in the SM.

In the case of nitrate photolysis (reaction (9)) it would be $R_{\bullet\text{OH}}^{\text{NO}_3^-} = R_{\bullet\text{NO}_2}^{\text{NO}_3^-}$. Interestingly, the formation rate of $\bullet\text{OH}/\bullet\text{NO}_2$ is influenced by the pH and the inorganic carbon content of the solution (Vione et al., 2009). About reaction (10), nitrite is usually a secondary $\bullet\text{OH}$ scavenger in surface waters compared to DOM or carbonate/bicarbonate. The same applies to NO_2^- and $\text{CO}_3^{\bullet-}$ in equation (11), the main $\text{CO}_3^{\bullet-}$ scavenger being DOM (Maddigapu et al., in press). Concerning reaction (12), it is $R_{\bullet\text{NO}_2}^{\text{CDOM}} = \Phi_{\bullet\text{NO}_2}^{\text{CDOM}} P_a^{\text{CDOM}}$, where $\Phi_{\bullet\text{NO}_2}^{\text{CDOM}}$ is given by equation (7) and P_a^{CDOM} is the sunlight photon flux absorbed by CDOM.

Assume $R_{\bullet\text{NO}_2}^{\text{NO}_3^-}$, $R_{\bullet\text{NO}_2}^{\text{NO}_2^-, \bullet\text{OH}}$, $R_{\bullet\text{NO}_2}^{\text{NO}_2^-, \text{CO}_3^{\bullet-}}$ and $R_{\bullet\text{NO}_2}^{\text{CDOM}}$ as the formation rates of $\bullet\text{NO}_2$ because of reactions (9), (10), (11) and (12), respectively. Model results yield negligible $R_{\bullet\text{NO}_2}^{\text{NO}_2^-, \text{CO}_3^{\bullet-}}$ under conditions that are significant for surface waters.

Figure 6a reports $R_{\bullet\text{NO}_2}^{\text{NO}_3^-}$, $R_{\bullet\text{NO}_2}^{\text{NO}_2^-, \bullet\text{OH}}$ and $R_{\bullet\text{NO}_2}^{\text{CDOM}}$, calculated according to the photochemical models described in SM, in a well-mixed water body containing 1 mM HCO_3^- , 10 μM CO_3^{2-} , 4 μM NO_3^- and 0.3 μM NO_2^- . The rates are plotted as a function of NPOC (Non-Purgeable Organic Carbon, which is a measure of the organic matter content) and of the water column depth d . As reported in the SM, the water absorption spectrum was modelled based on the NPOC value. The irradiation conditions correspond to sunlight with 22 W m^{-2} UV irradiance, which can be observed in a fair-weather 15 July at 45°N latitude, at 10 am or 2 pm (for the spectrum of sunlight see Figure B-SM). It can be seen that all the rates decrease with d ; this is reasonable considering that the photochemical reactions are most important in shallow water bodies. Both $R_{\bullet\text{NO}_2}^{\text{NO}_3^-}$ and $R_{\bullet\text{NO}_2}^{\text{NO}_2^-, \bullet\text{OH}}$ decrease with increasing NPOC: dissolved organic compounds absorb radiation, inhibiting the photolysis of nitrate, and consume $\bullet\text{OH}$ that is thus prevented to react with nitrite. On the contrary, $R_{\bullet\text{NO}_2}^{\text{CDOM}}$ increases with increasing NPOC. This is

reasonable considering the proportionality between $R_{\bullet NO_2}^{CDOM}$ and P_a^{CDOM} , the latter increasing with the organic matter content. Interestingly, if $d > 1$ m and $NPOC > 5$ mg C L⁻¹, reaction (12) between nitrite and ³CDOM* would become the main source of $\bullet NO_2$.

Figure 6b reports $R_{\bullet NO_2}^{tot} = R_{\bullet NO_2}^{NO_3^-} + R_{\bullet NO_2}^{NO_2^-, \bullet OH} + R_{\bullet NO_2}^{NO_2^-, CO_3^{\bullet-}} + R_{\bullet NO_2}^{CDOM}$ as a function of d and NPOC, for the same model water body assumed in Figure 6a. $R_{\bullet NO_2}^{tot}$ decreases with increasing NPOC and d . Moreover, the residual $R_{\bullet NO_2}^{tot}$ at elevated NPOC is mainly accounted for by $R_{\bullet NO_2}^{CDOM}$. It can be inferred that reaction (12) (nitrite + ³CDOM*) could play an important role as $\bullet NO_2$ source in water bodies with an elevated $[NO_2^-] [NO_3^-]^{-1}$ ratio (otherwise the photolysis of nitrate, reaction (9), could prevail as the source of $\bullet NO_2$), for elevated values of d and NPOC. The latter conditions are not the most favourable for $R_{\bullet NO_2}^{tot}$ to be elevated, but the contribution of ³CDOM* would prevent $R_{\bullet NO_2}^{tot}$ from being still lower. Also note that dissolved organic matter would be a minor sink of $\bullet NO_2$ at the NPOC values that can be found in most water bodies: hydrolysis (reaction (5)) would prevail in the vast majority of cases (Chiron et al., 2007b).

Conclusions

Here it is shown that UVA-irradiated AQ2S is able to oxidise nitrite to $\bullet NO_2$. Phenol nitration was adopted as $\bullet NO_2$ probe, giving a quantum yield $\Phi_{NO_2}^{AQ2S} = (2.08 \pm 0.06) [NO_2^-]$ for sub-mM nitrite under the hypothesis that nitrophenols (2NP and 4NP) are formed with unity yield from phenol and one $\bullet NO_2$ molecule. Both ³AQ2S* and its 520-nm absorbing exciplex with water are involved in the process, at different time scales (ns and μ s, respectively, after photon absorption).

AQ2S was adopted here as a proxy of CDOM, an important fraction of which is made up by quinones (Cory et al., 2005). Under the hypothesis that $\Phi_{NO_2}^{AQ2S}$ is representative of the behaviour of CDOM, the oxidation of nitrite to $\bullet NO_2$ by ³CDOM* would be an important $\bullet NO_2$ source in water bodies with high $[NO_2^-]$ to $[NO_3^-]$ ratio, for elevated values of column depth and NPOC.

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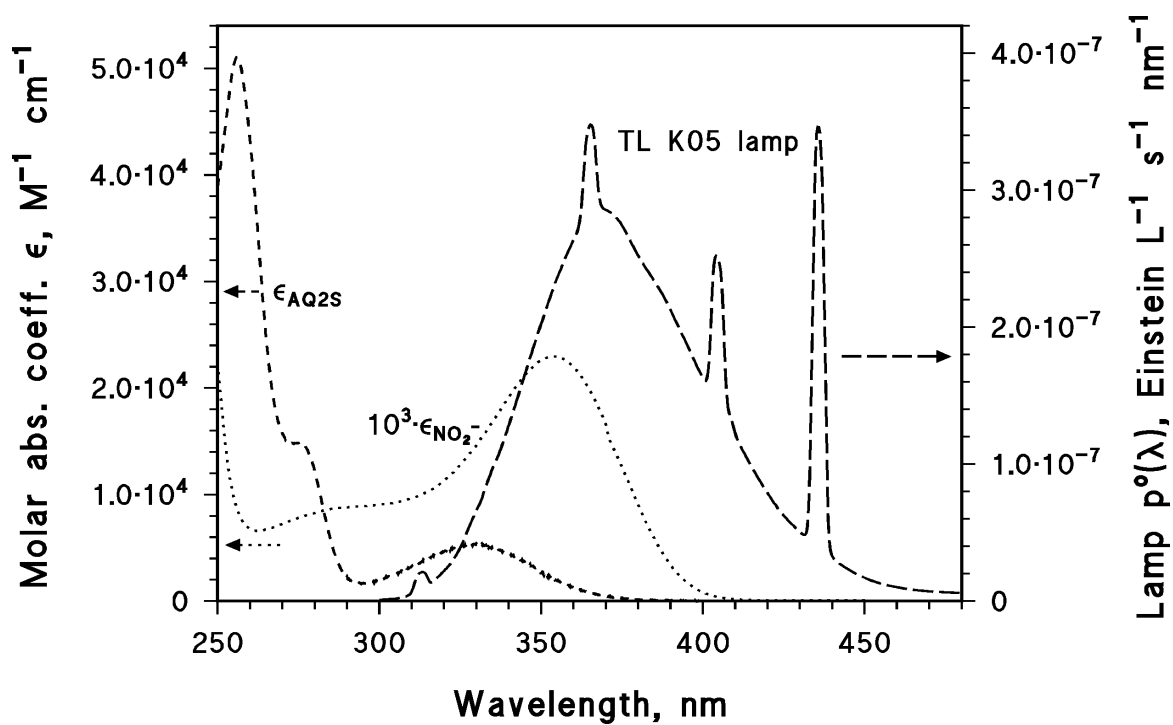


Figure 1. Molar absorption coefficients of AQ2S and nitrite (the latter multiplied by 10^3). Emission spectrum of the adopted UVA lamp.

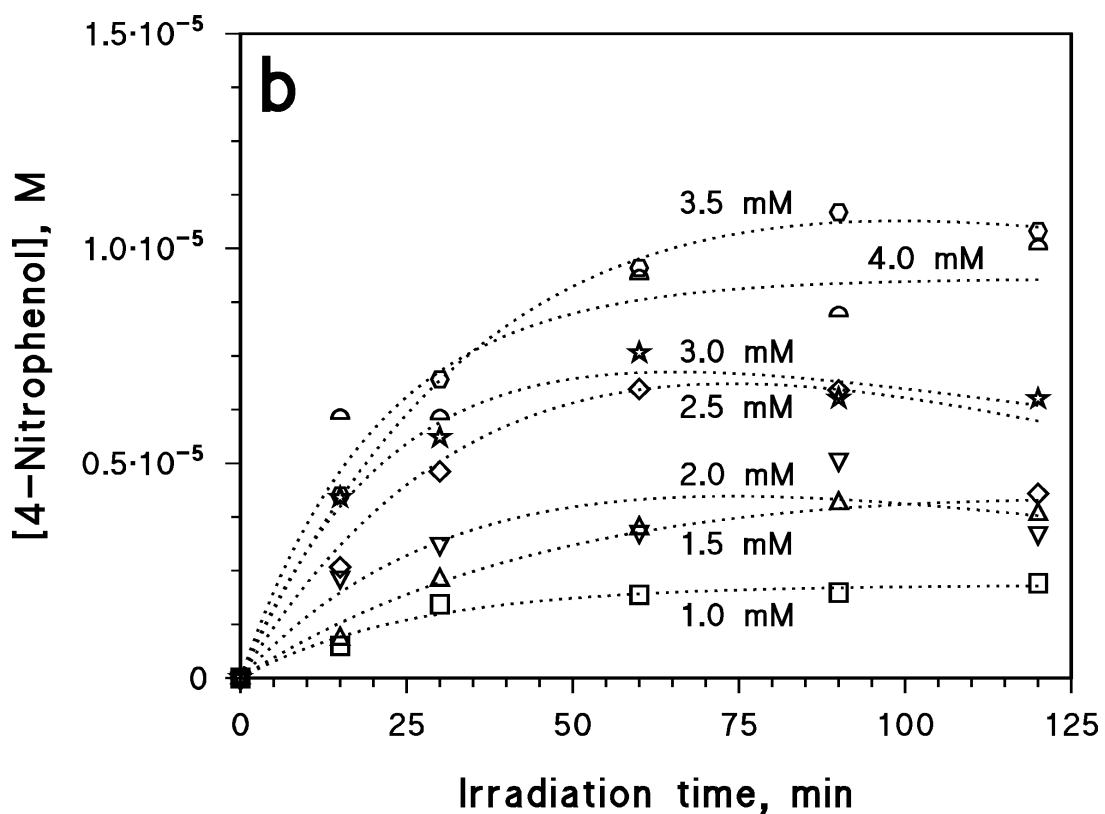
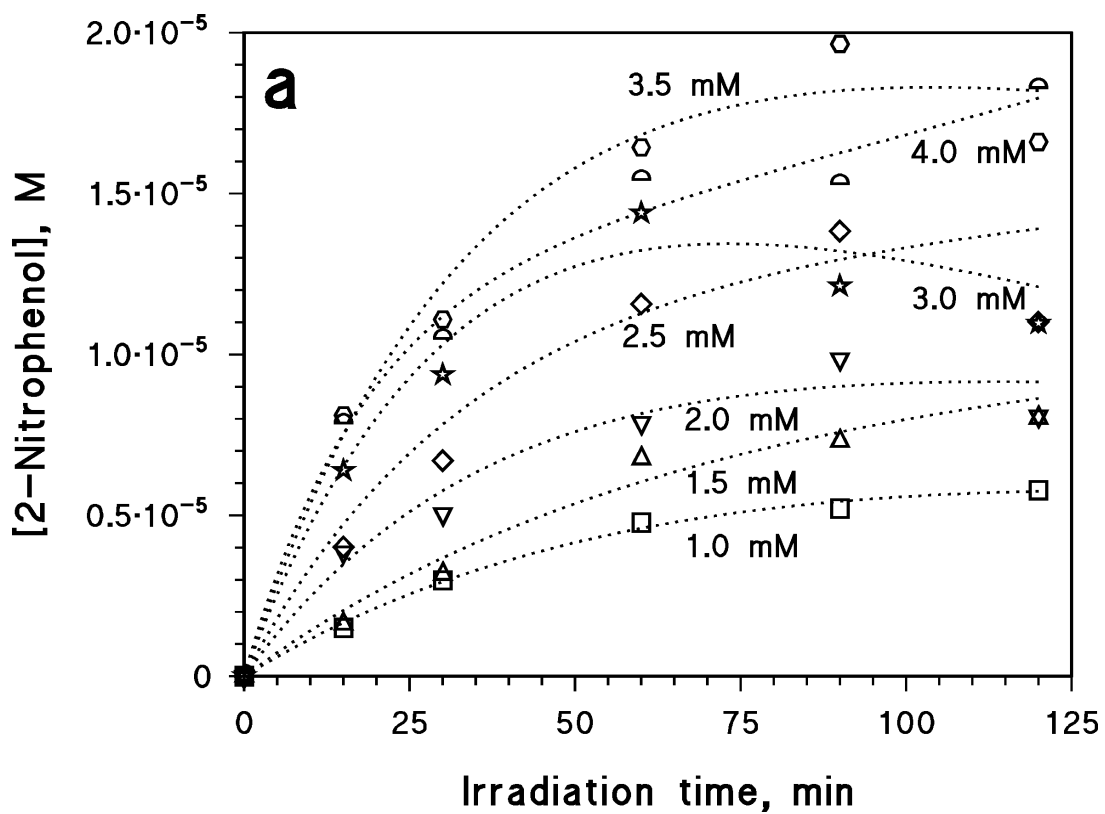


Figure 2. Time evolution of 2NP (**2a**) and of 4NP (**2b**) upon UVA irradiation of 0.1 mM AQ2S in aerated solution at pH 8.0, in the presence of 1 mM phenol and variable concentration values of nitrite (reported near each curve).

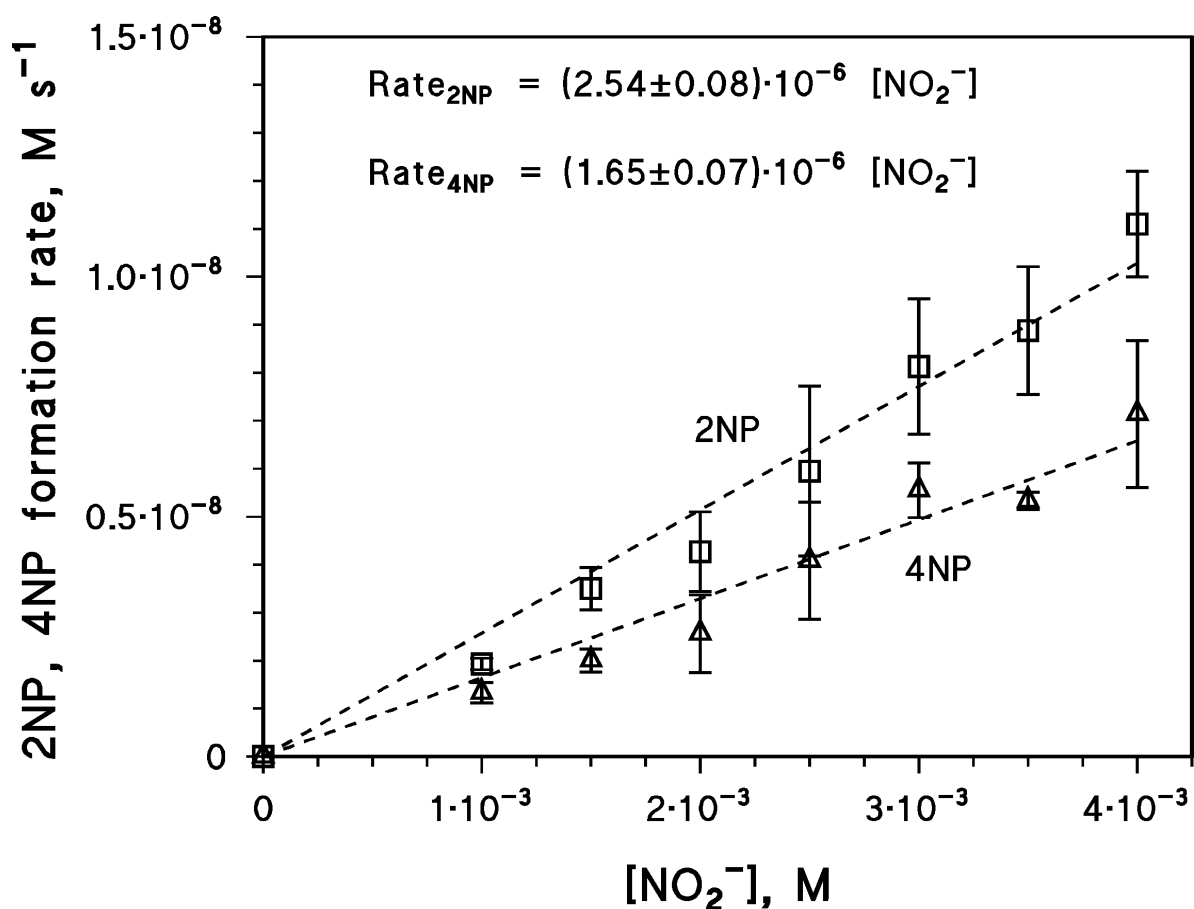


Figure 3. Initial formation rates of 2NP and 4NP upon UVA irradiation of 0.1 mM AQ2S with 1 mM phenol, as a function of nitrite concentration. Error bars derived at σ level from the fitting of the experimental data.

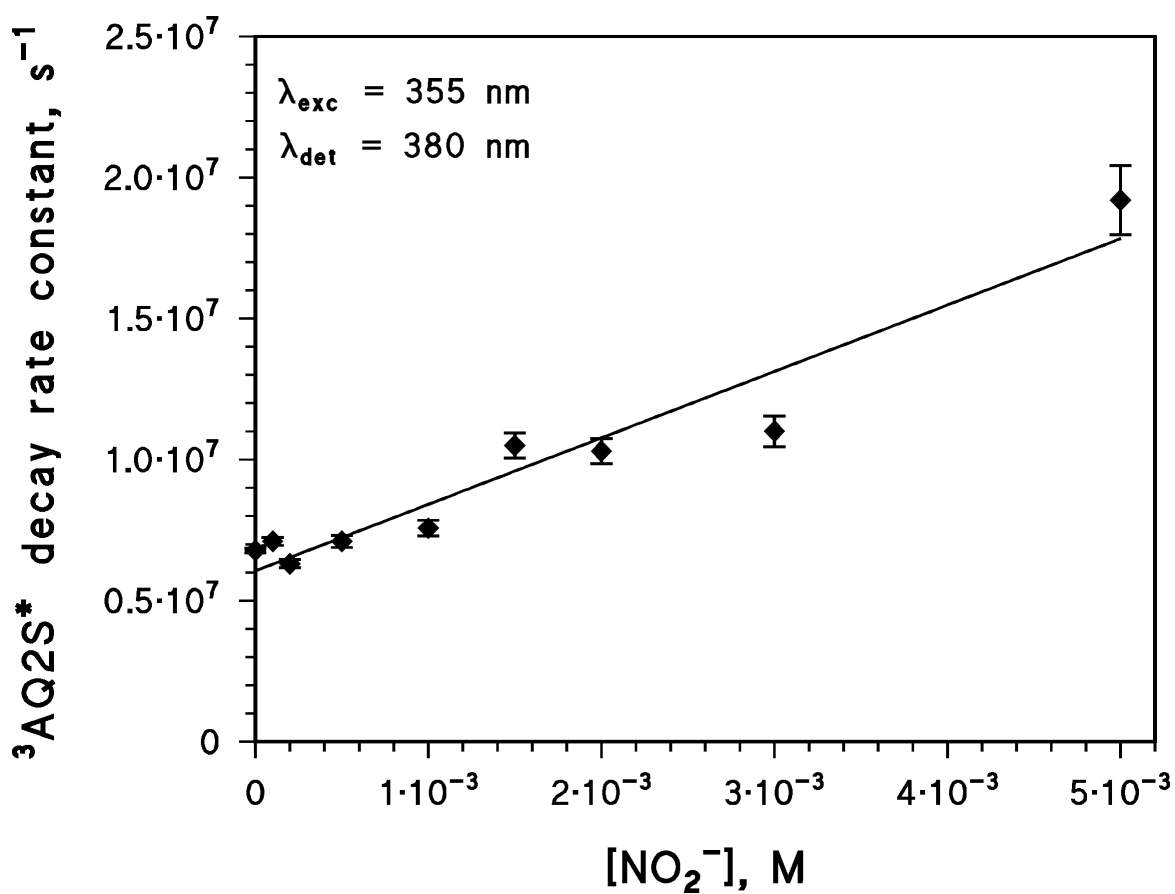


Figure 4. Pseudo-first order decay constant (s^{-1}) of ${}^3\text{AQ2S}^*$, followed at 380 nm after laser pulse excitation (65mJ, 355nm) of AQ2S in the presence of different nitrite concentrations. The experiments were carried out in aerated solution at $295 \pm 2 \text{ K}$ and pH 8.0. Error bars derived at 3σ level from the monoexponential fitting of the experimental data.

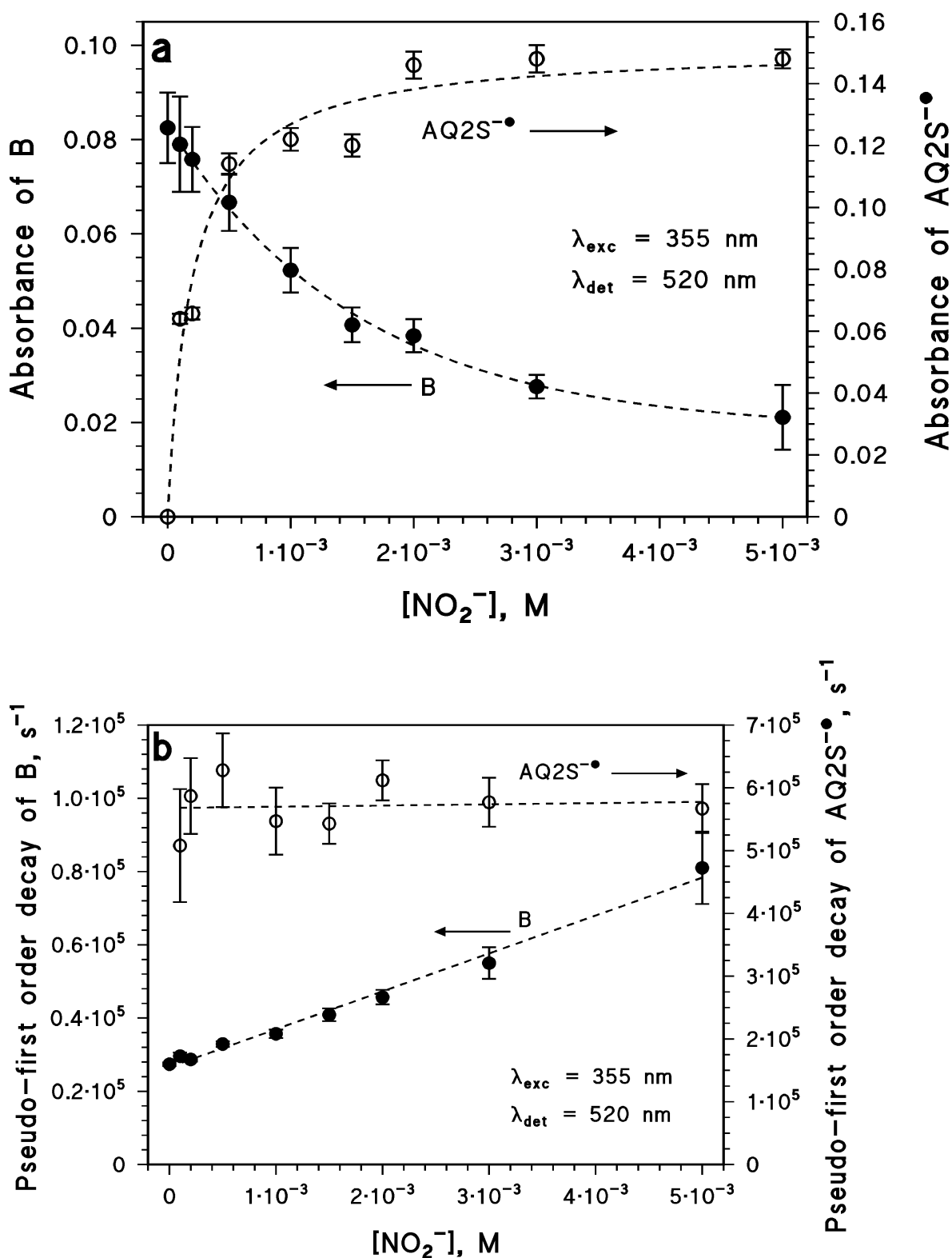


Figure 5. a) Absorbance at 520 nm of B and AQ2S^{\bullet} with different $[\text{NO}_2^-]$.

b) Pseudo-first order decay constants (s^{-1}) of B and AQ2S^{\bullet} as function of $[\text{NO}_2^-]$. The experiments were carried out in aerated solution at $295 \pm 2 \text{ K}$ and pH 8.0 and were followed at 520 nm. Error bars derived at 3σ level from the fitting of the experimental data.

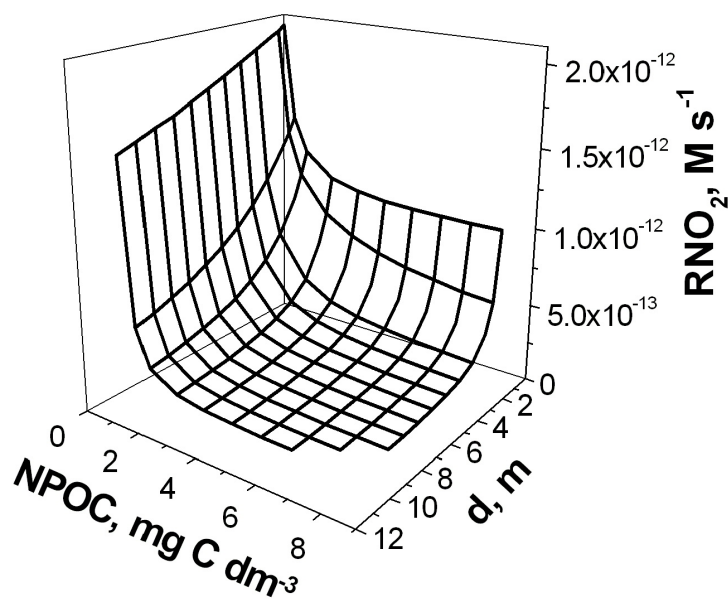
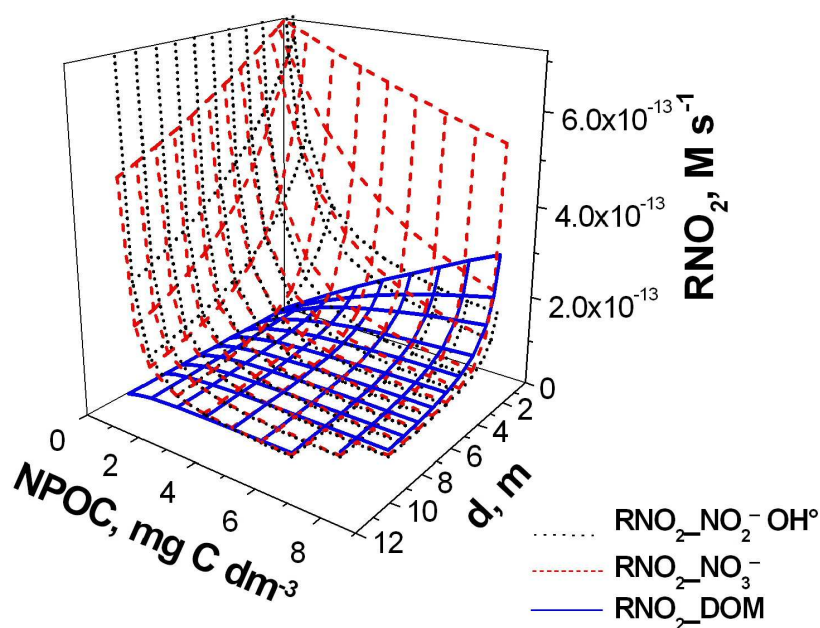


Figure 6. a) Modelled formation rate of $\bullet\text{NO}_2$ upon nitrate photolysis ($R_{\text{NO}_2\text{NO}_3^-}$), nitrite oxidation by $\bullet\text{OH}$ ($R_{\text{NO}_2\text{NO}_2^- \bullet\text{OH}}$) and nitrite oxidation by ${}^3\text{CDOM}^*$ ($R_{\text{NO}_2\text{DOM}}$), as a function of the column depth d and of the dissolved organic carbon (DOC) content, measured as NPOC, of a hypothetical water body. The water-body photochemistry was modelled as described in the SM. Irradiation conditions on top of the water surface correspond to a 22 W m^{-2} sunlight UV irradiance (see Figure B-SM).

b) Total formation rate of $\bullet\text{NO}_2$ ($R_{\text{NO}_2}^{\text{tot}} = R_{\text{NO}_2\text{NO}_3^-} + R_{\text{NO}_2\text{NO}_2^- \bullet\text{OH}} + R_{\text{NO}_2\text{DOM}}$), as a function of d and NPOC.