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SEASONAL AND WATER COLUMN TRENDS OF THE RELATIVE ROLE OF NITRATE AND NITRITE AS •OH SOURCES IN SURFACE WATERS

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Summary – Based on literature data of sunlight spectrum, photolysis quantum yields, and absorption spectra, the relative role of nitrite and nitrate as •OH sources in surface waters was assessed, and its dependence on the season and the depth of the water column studied. In the majority of surface water samples (river, lake and seawater) nitrite is expected to play a more important role as •OH source compared to nitrate, in spite of the usually lower $[NO_2^-]$ values. Interestingly, under the hypothesis of a constant ratio of the concentrations of nitrate and nitrite (to be corrected later on for the actual concentration ratio in a given sample), the relative role of nitrite compared to nitrate would be minimum in summer, at noon, in the surface layer of natural waters. Any decrease in the sunlight intensity that can be experienced in the natural environment (different season than summer, water column absorption, time of the day other than the solar noon), with its associated influence on the sunlight spectrum, would increase the relative role of nitrite compared to nitrate.

INTRODUCTION

Photochemical processes are important pathways for the degradation of organic compounds, including organic pollutants, in surface waters, and in many cases they lead to faster transformation compared to biodegradation. Photoinduced degradation pathways include direct photolysis and reaction with photogenerated reactive species (excited triplet states, •OH, $•CO_3^-$, $•Cl_2^-$, $•NO_2$, $^1O_2$), formed upon irradiation by sunlight of water-dissolved photoactive compounds (DOM – Dissolved Organic Matter, NO_3^-, NO_2^-, Fe(III), metal oxides, inorganic ions reactive with •OH).[1-13]

Nitrate and nitrite, together with DOM, are important photochemical sources of •OH radicals in surface waters.[1,14] As far as their relative role is concerned, the lower concentration values of nitrite compared to nitrate that are usually observed in surface waters [15-18] are compensated by the higher photochemical activity and sunlight absorption of nitrite.[19-24] Actually, on an equimolar basis, the combination of higher photolysis quantum yield and higher molar absorbivity in the environmental UV range of nitrite compared to nitrate makes the former around two orders of magnitude more reactive under summertime irradiation conditions. Quite interestingly, the ratio of the concentration

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values of nitrate and nitrite in surface waters is often around one-two orders of magnitude, therefore compensating the difference in the respective photochemical activities.[21,23]

An interesting feature of the photochemistry of nitrate and nitrite is that their absorption spectra are quite different, nitrate showing a maximum in the UVB and nitrite in the UVA region. The sunlight spectrum at the ground varies according to the time of the day and the season. While the total irradiation intensity increases with increasing sun height up to the zenith, the spectral distribution of sunlight is not simply multiplied by a factor determined by the irradiation geometry. Actually, due to the higher atmospheric extinction in the UVB region, the relative weight of UVB to UVA irradiation intensity changes with the solar zenith angle. The UVB/UVA intensity ratio, although always lower than 1, is higher in summer and at midday, and lower in winter and at dawn and sunset.[25] This fact can deeply influence the relative role of nitrate and nitrite as $^\bullet$OH sources, which is expected to change during the time of the day and the different seasons of the year. To date, however, no data are available on the seasonal trend of $^\bullet$OH photogeneration by nitrate and nitrite. Another aspect to be considered is that UV light attenuation is not uniform in water bodies and that, generally speaking, the photons of lower wavelength could be more attenuated. Accordingly, the sunlight illumination spectrum varies with depth, which can have important consequences on the photochemistry of nitrate and nitrite. The expected effect is an increasing relative role of nitrite compared to nitrate with increasing depth of the water column,[23] but multi-wavelength calculations on this issue have not been carried out till now. The purpose of the present work is to cover the cited gaps by assessing the seasonal trend of the contributions of nitrate and nitrite to $^\bullet$OH photogeneration, based on the seasonal variations of the sunlight spectrum at the ground,[26] and to describe the variations of the relative role of nitrate and nitrite as $^\bullet$OH sources with increasing column depth in a water body.

METHODS

The intensity of radiation absorption by a given molecule A at the wavelength λ is given by the product of the molar absorbivity $\varepsilon_A(\lambda)$, the irradiation intensity $I(\lambda)$, the optical path length x and the concentration $[A]$, under the hypotheses that $[A]$ and x are sufficiently low that $I(\lambda)$ does not vary significantly within the solution:

$$I_{abs,A}(\lambda) = 2.3\, \varepsilon_A(\lambda)\, I(\lambda)\, x\, [A] \qquad\qquad (1)$$

The rate of photolysis of A is given by the product of the absorption intensity times the photolysis quantum yield of A at the wavelength λ ($\phi_A(\lambda)$), that is $Rate_{phot,A} = \phi_A(\lambda)\, I_{abs,A}(\lambda)$.

When the light source is polychromatic, which is the case of sunlight, there is the need to integrate the above-referred quantities over wavelength. Note that the sunlight irradiation intensity at the ground, $I_{sun}(\lambda)$, is usually reported in [Photons cm^{-2} s^{-1} nm^{-1}], thus integration will change the measure unit to [Photons cm^{-2} s^{-1}]. In the more general case the irradiation intensity will vary with the solution depth, thus it will also be necessary to integrate over the solution path length b (0 < x < b). If b is given in [cm], the resulting measure unit for the rate of photolysis would be [molecules cm^{-3} s^{-1}]. To have the more commons units for the reaction rates, that is [mol L^{-1} s^{-1}], it will be necessary to multiply the integral for 1000 **N**$^{-1}$, where **N** is the Avogadro number. The resulting rate of photolysis would thus be expressed as follows:

$$\text{Rate}_{\text{phot,A}} = \frac{2300\ [\text{A}]}{\mathbf{N}\ b} \cdot \int_0^b \int_\lambda \phi_A(\lambda) \cdot \varepsilon_A(\lambda) \cdot I_{\text{sun}}(\lambda, x)\ d\lambda\ dx \qquad (2)$$

Note, however, that the sunlight spectrum $I_{\text{sun}}(\lambda,x)$ would vary with x depending on the extinction spectrum of the water column under consideration, which is very variable from case to case.[22] At first, to attain the goal of comparing the rates of photolysis of nitrate and nitrite independently of the water column spectrum, the dependence on x will be neglected. The integration results will be relevant to the surface layer of natural waters only, before radiation extinction becomes significant. Moreover, as the concentration values of nitrate and nitrite undergo substantial variations according to the considered water body, it is better to compare the photolysis rates on an equimolecular basis, for the moment neglecting the actual concentration values. Accordingly, the ratio of the photolysis rates is the following:

$$\frac{\text{Rate}_{\text{phot,NO2}-}}{\text{Rate}_{\text{phot,NO3}-}} = \frac{\int_\lambda \phi_{\text{NO2}-}(\lambda) \cdot \varepsilon_{\text{NO2}-}(\lambda) \cdot I_{\text{sun}}(\lambda)\ d\lambda}{\int_\lambda \phi_{\text{NO3}-}(\lambda) \cdot \varepsilon_{\text{NO3}-}(\lambda) \cdot I_{\text{sun}}(\lambda)\ d\lambda} \qquad (3)$$

Note that $I_{\text{sun}}(\lambda)$ is referred to the surface layer of a water body, and the same will be true of all the derived quantities. The photolysis reactions of nitrate and nitrite both yield •OH in surface waters:

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet NO_2 + {}^\bullet OH \qquad (4)$$
$$NO_2^- + h\nu + H^+ \rightarrow {}^\bullet NO + {}^\bullet OH \qquad (5)$$
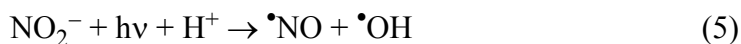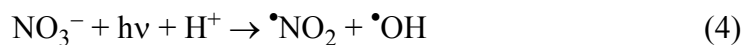
Accordingly, the ratio of the photolysis rates reported in equation (3) is also the relative contribution of nitrate and nitrite to •OH photogeneration, in the surface layer of the same water body and assuming a 1:1 molar ratio. The relative contribution of the two species in a real case would be given by equation (3), calculated assuming the relevant $I_{\text{sun}}(\lambda)$, times the actual ratio $[NO_3^-]/[NO_2^-]$ in the water body under consideration.

Figure 1 shows the spectral solar irradiance $I_{\text{sun}}(\lambda)$ in different months of the year, measured at 50°N latitude that can be considered representative of temperate locations.[26] Irradiance has been measured on the 15th of the given month at solar noon, whenever the weather conditions allowed it.[26] Problems with actual weather are the most likely reason why the reported irradiance is higher in August than in July. Figure 1 also reports the absorption spectra ($\varepsilon(\lambda)$) of nitrate and nitrite and the wavelength dependence of the quantum yield of nitrite photolysis ($\phi_{\text{NO2}-}(\lambda)$). The quantum yield of nitrate photolysis is $\phi_{\text{NO3}-} = 0.01$ in the whole relevant wavelength interval.[19,20] The data of Figure 1 allow the calculation of the product $\phi_A(\lambda)\ \varepsilon_A(\lambda)\ I_{\text{sun}}(\lambda)$, with $A = NO_3^-$ or NO_2^-, for all the months of the year. It will therefore be possible to obtain the seasonal trend of the ratio of nitrate and nitrite as •OH sources in surface waters.

A simple, approximate method to take into account the water column depth in the calculations, approximate because it neglects the phenomenon of multiple scattering by suspended particles and can therefore underestimate irradiation intensity in the deep water layers,[27] is to consider a surface water body having an extinction spectrum $A(\lambda)$ b, where $A(\lambda)$ is the measured absorbance of unfiltered water in a cuvette with an optical path length of 1 cm, and b is the water column depth in

cm. From the Lambert-Beer law, the following equation holds for the sunlight spectrum at the depth b:

$$I_{sun}(\lambda, b) = I_{sun}(\lambda) \cdot 10^{-A(\lambda) \cdot b} \qquad (6)$$

Equation (3) can therefore be modified to take into account the depth effect, substituting $I_{sun}(\lambda)$ (sunlight irradiation intensity at the ground, or at the depth b = 0 cm) with $I_{sun}(\lambda,b)$, that is the sunlight intensity at the depth b in the water body.

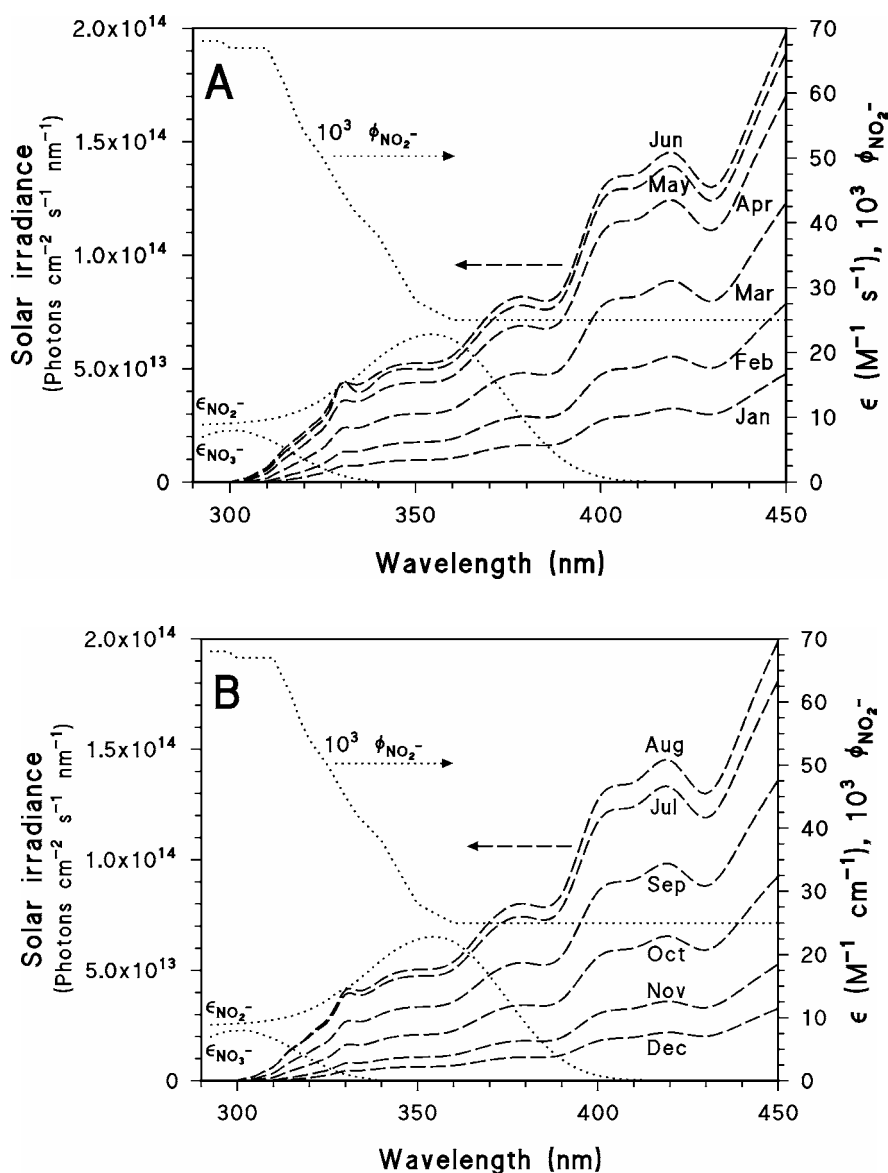FIGURE 1. Spectral solar irradiance $I_{sun}(\lambda)$ in the different months of the year, measured at 50°N latitude.[26] The absorption spectra of nitrate and nitrite are also reported, together with the photolysis quantum yield of nitrite as a function of wavelength (note that, for graphical reasons, $\phi_{NO2-}(\lambda)$ was multiplied by 10^3).[20] Also note the different scales in the Y axis.

RESULTS AND DISCUSSION

Figure 2 reports the product $\varepsilon_{NO3-}(\lambda)$ $I_{sun}(\lambda)$ $\phi_{NO3-}(\lambda)$ for the various months of the year, based on the data of Figure 1 and considering that $\phi_{NO3-}(\lambda) = 0.01$, independent of wavelength in the useful $300 - 340$ nm range.[19] The result is relevant to the surface layer of water bodies, before radiation extinction becomes important. The maximum of $\varepsilon_{NO3-}(\lambda)$ $I_{sun}(\lambda)$ $\phi_{NO3-}(\lambda)$ vs. λ represents the wavelength where •OH photoproduction upon nitrate photolysis is most effective.
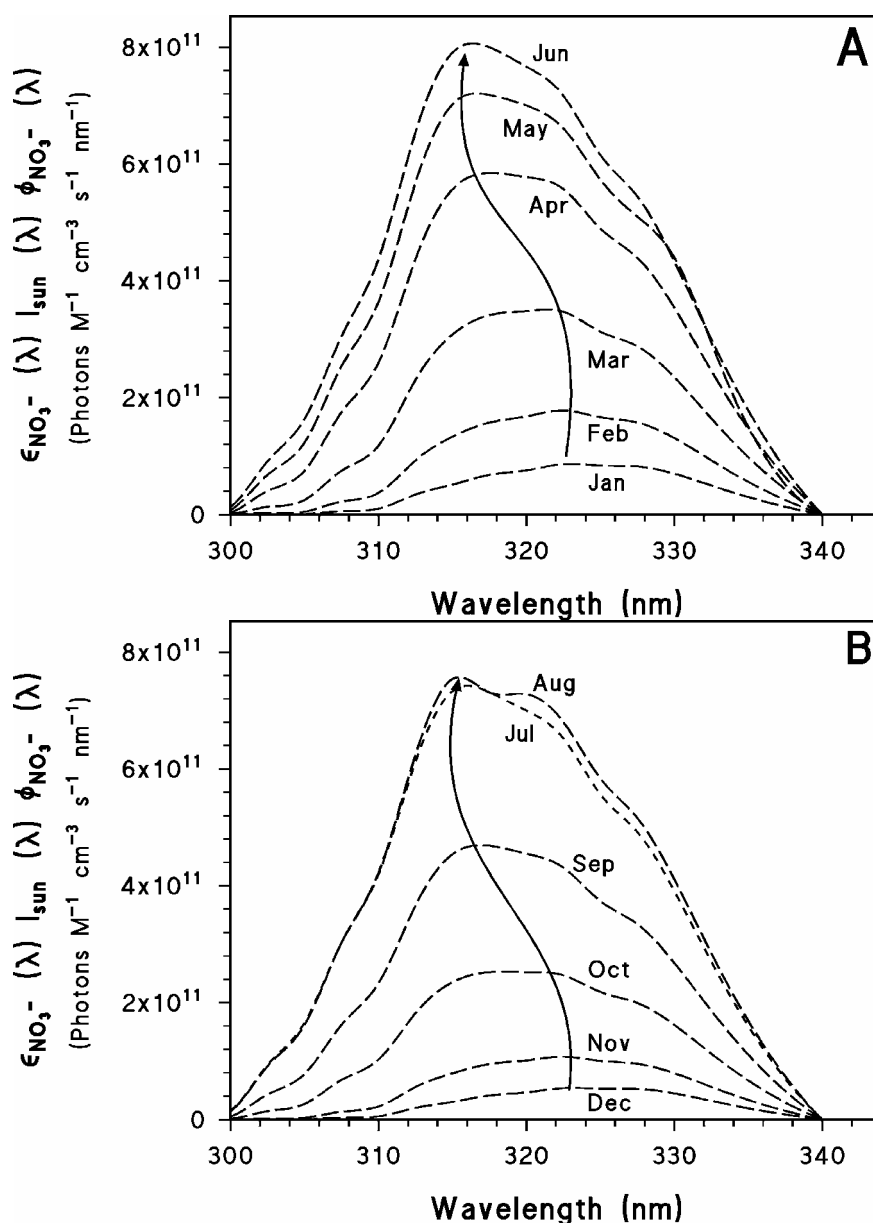

FIGURE 2. Wavelength dependence of the product of nitrate absorption spectrum ($\varepsilon_{NO3-}(\lambda)$, [$M^{-1}$ cm^{-1}]) times the sunlight intensity at the ground ($I_{sun}(\lambda)$, [Photons cm^{-2} nm^{-1} s^{-1}]) times the quantum yield of nitrate photolysis ($\phi_{NO3-}(\lambda) = 0.01$). Note the decrease of the function maximum in summer compared to winter, highlighted by the curved arrow.

Very interestingly, λ_{max} varies from 322-324 nm in winter to 316 nm in summer, when the irradiation intensity at the shorter wavelengths is much higher. Indeed the ratio of the solar irradiation intensity at the ground in June and in January is 10.1 at 320 nm and only 4.7 at 400 nm.[26]

Figure 3 reports the product $\varepsilon_{NO2-}(\lambda)\, I_{sun}(\lambda)\, \phi_{NO2-}(\lambda)$ for the various months of the year. Figures 2 and 3 show that the nitrite values are over an order of magnitude higher compared to nitrate. Moreover, the nitrite function has $\lambda_{max} = 340$ nm, with negligible variations between the various seasons. Actually, the June/January ratio at 340 nm is 5.6, not very different from that at 400 nm.[26]
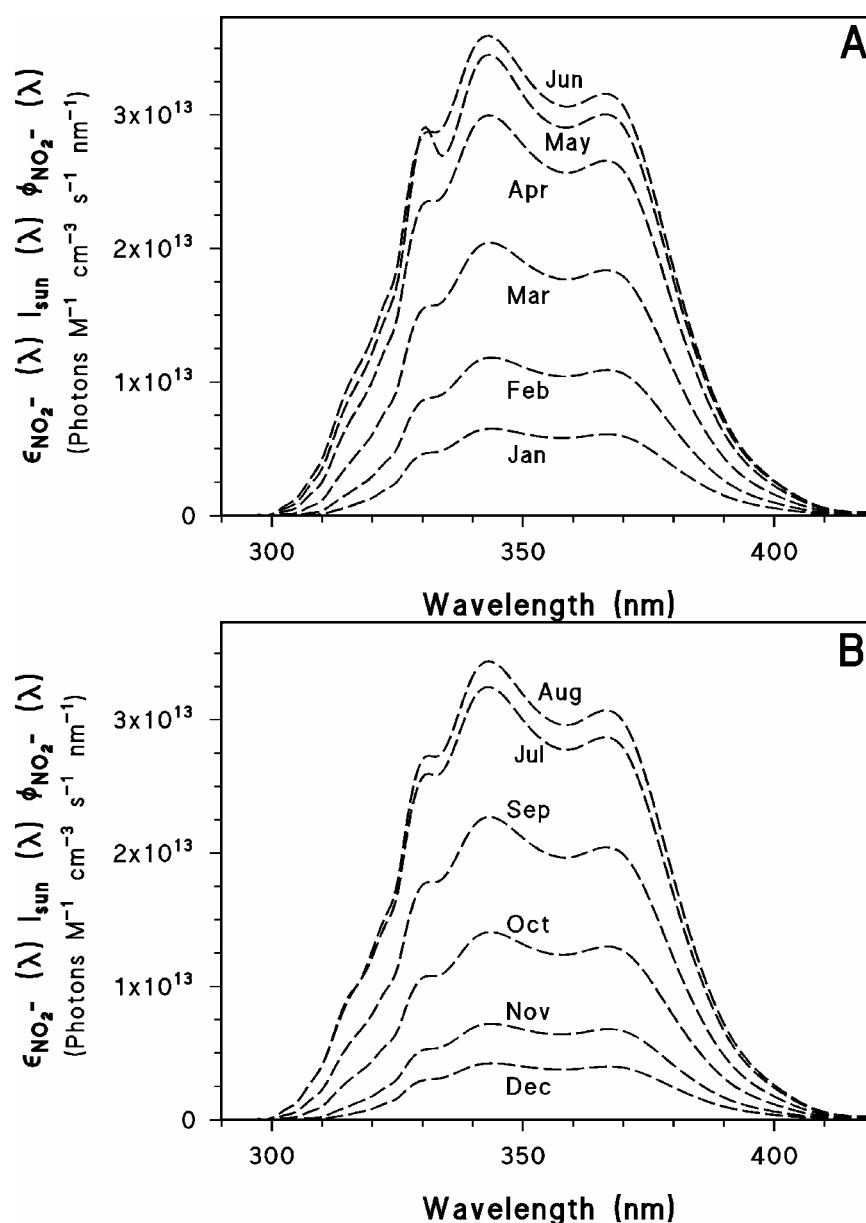

FIGURE 3. Wavelength dependence of the product of nitrite absorption spectrum ($\varepsilon_{NO2-}(\lambda)$, [$M^{-1}$ cm^{-1}]) times the sunlight intensity at the ground ($I_{sun}(\lambda)$, [Photons cm^{-2} nm^{-1} s^{-1}]) times the quantum yield of nitrite photolysis ($\phi_{NO2-}(\lambda)$, see Figure 1). The wavelength of the maximum is around 340 nm, almost independent of the season.

Figure 4 reports the values of $\int\{\phi_A(\lambda)\ \epsilon_A(\lambda)\ I_{sun}(\lambda)\}\ d\lambda$, for A = NO_3^- and NO_2^-, and their ratio (indicated as NO_2^-/NO_3^-) calculated according to equation (3), for the different months of the year. Note that the ratio varies from around 120 in summer to over 220 in winter, indicating that the relative importance of nitrite compared to nitrate as •OH source in the water surface layer would be higher by a factor of 2 in winter. Figure 4 also helps appreciating the seasonal trend of the formation rate of •OH by both nitrate and nitrite, which is around one order of magnitude lower in winter. This is obviously an important difference, but it should be considered that the steady-state [•OH] in natural waters under comparable irradiation conditions can vary by over one order of magnitude depending on water composition.[1,14,22] Accordingly, the seasonal variability would be of the same order of magnitude as the variability associated to the chemical composition of different water bodies.
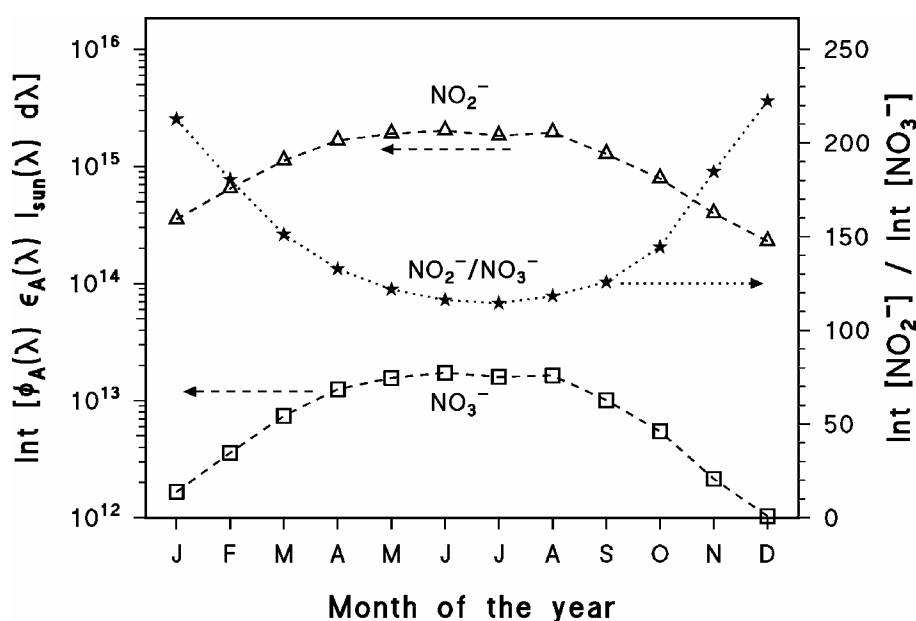

FIGURE 4. Values of $Int[\phi_A(\lambda)\ \epsilon_A(\lambda)\ I_{sun}(\lambda)\ d\lambda] = \int\{\phi_A(\lambda)\ \epsilon_A(\lambda)\ I_{sun}(\lambda)\}\ d\lambda$ for both nitrate and nitrite, for the different months of the year. Note the logarithmic scale in the left Y-axis. The ratio of the photolysis rates of nitrite and nitrate, NO_2^-/NO_3^-, calculated according to equation (3) is also reported on the graph, with a different scale (linear, right Y-axis).

The data reported in Figure 4 are referred to equimolar values of nitrite and nitrate. Generally speaking, NO_2^- and NO_3^- have different concentration values in surface waters, with $[NO_3^-] > [NO_2^-]$ as a common scenario. It is therefore interesting to see the relative contributions of nitrate and nitrite to •OH photogeneration in real water samples (surface layer). Note that, in an actual sample where the concentration values of nitrate and nitrite are generally much below 0.01 M and saturation of absorption by these species is not expected, the formation rate of •OH upon photolysis of nitrate (or nitrite) would be directly proportional to $[NO_3^-]$ (or $[NO_2^-]$). Accordingly, the ratio of the •OH formation rates by nitrite and nitrate can be expressed as follows:

$$\frac{\text{Rate}_{\bullet\text{OH}}\left(\text{NO}_2^-\right)}{\text{Rate}_{\bullet\text{OH}}\left(\text{NO}_3^-\right)} = \frac{\left[\text{NO}_2^-\right]}{\left[\text{NO}_3^-\right]} \cdot \frac{\int_\lambda \phi_{\text{NO2-}}(\lambda) \cdot \varepsilon_{\text{NO2-}}(\lambda) \cdot I_{\text{sun}}(\lambda) \ d\lambda}{\int_\lambda \phi_{\text{NO3-}}(\lambda) \cdot \varepsilon_{\text{NO3-}}(\lambda) \cdot I_{\text{sun}}(\lambda) \ d\lambda} \tag{7}$$

An extensive survey of nitrate and nitrite concentration values in surface waters of different origin in temperate regions is reported in the literature,[21] and it is therefore possible to apply equation (7) given the $[\text{NO}_2^-]/[\text{NO}_3^-]$ ratio and the sampling month. The application of equation (7) to a total of 28 samples is reported in Figure 5, where the different values of the ratio $\text{Rate}_{\bullet\text{OH}}(\text{NO}_2^-)/\text{Rate}_{\bullet\text{OH}}(\text{NO}_3^-)$ have been grouped according to their order of magnitude. Quite interestingly, nitrite prevails over nitrate as $^\bullet$OH source in the vast majority of cases. Moreover, while nitrate would prevail over nitrite as $^\bullet$OH source by at most one order of magnitude, there are samples where the prevalence of nitrite can well exceed two orders of magnitude. These data are in reasonable agreement with the results obtained upon irradiation of lakewater samples under simulated summertime irradiation conditions.[23]
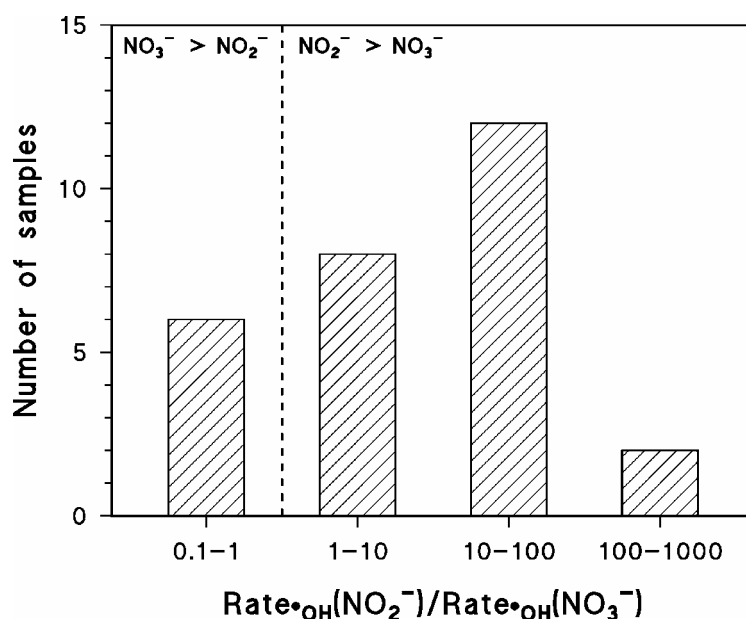

FIGURE 5. Ratio of the contributions of nitrite and nitrate to $^\bullet$OH photogeneration in surface water samples (from the reported concentration data [21]), calculated according to equation (7). The $[\text{NO}_2^-]/[\text{NO}_3^-]$ ratio and the month of the sampling, influencing the sunlight spectrum and intensity, were taken into account for each sample.

Water column effects

The data presented so far are referred to the surface layer of natural waters, in which radiation extinction by the water column is not operational. However, photochemical reactions in actual cases take place within a certain column depth, where the effects of radiation extinction are very significant. It is therefore important to assess the relative role of nitrite and nitrate as $^\bullet$OH sources

also in a whole water column. In this case it is necessary to refer the photochemical parameters to a definite water column of given extinction spectrum, which causes a loss of generality. Accordingly, the relative role of nitrite and nitrate has to be assessed case by case. For calculation purposes the spectrum of water sampled in the Lake Piccolo of Avigliana (TO, NW Italy) on 2 October 2005 [23] was used in the present case. The spectrum (1 cm path length) was taken of unfiltered water to preserve similarity with actual conditions, and is reported in Figures 6,7 (dashed curve). Under the hypothesis that the water spectrum undergoes limited changes with depth it is possible to apply equation (6) to correct the October sunlight spectrum at the surface and obtain the irradiation spectrum that would reach a given depth b. The resulting sunlight spectra are reported in Figures 6,7 as a function of depth (dotted curves).

Figure 6 also reports the wavelength trend of $\phi_{NO2-}(\lambda)\ \varepsilon_{NO2-}(\lambda)\ I_{sun}(\lambda,b)$ in logarithmic scale, for different values of the column depth b (solid curves). Interestingly, the wavelength for which nitrite photolysis would be most effective undergoes a substantial variation with depth, from 340 nm at the surface till 375 nm at 1 m. Figure 7 reports the corresponding data for nitrate ($\phi_{NO3-}(\lambda)\ \varepsilon_{NO3-}(\lambda)\ I_{sun}(\lambda,b)$), also in logarithmic scale, for different values of b. In this case the wavelength of most efficient photolysis by nitrate would vary from 320 nm at the surface to about 330 nm at 1 m depth.

From equations (3) and (6) one obtains that the rate of •OH photoproduction by nitrite or nitrate at the depth b is proportional to $\int_{\lambda} \phi_A(\lambda)\ \varepsilon_A(\lambda)\ I_{sun}(\lambda,b)\ d\lambda$, with A = NO_2^- or NO_3^-. Such an integral quantity referred to Lake Piccolo and October sunlight irradiation is reported in Figure 8 for both nitrite and nitrate, for b values up to 1 m. There is an obvious decrease with depth for both nitrite and nitrate, due to absorption by the water column. The relative role of equimolar values of nitrite and nitrate as •OH sources can be calculated by equation (8) as the ratio of the respective integrals $\int_{\lambda} \phi_A(\lambda)\ \varepsilon_A(\lambda)\ I_{sun}(\lambda,b)\ d\lambda$. Equation (8) is derived from equation (3) by substituting $I_{sun}(\lambda)$ with $I_{sun}(\lambda,b)$ (see equation 6).

$$\frac{Rate_{phot,NO2-}}{Rate_{phot,NO3-}}(b) = \frac{\int_{\lambda} \phi_{NO2-}(\lambda)\cdot\varepsilon_{NO2-}(\lambda)\cdot I_{sun}(\lambda)\cdot 10^{-A(\lambda)b}\ d\lambda}{\int_{\lambda} \phi_{NO3-}(\lambda)\cdot\varepsilon_{NO3-}(\lambda)\cdot I_{sun}(\lambda)\cdot 10^{-A(\lambda)b}\ d\lambda} \qquad (8)$$

The nitrite/nitrate ratio is reported as NO_2^- / NO_3^- in Figure 8. It varies from 140 at b = 0 cm to 4150 at 1 m depth, indicating that the importance of nitrite compared to nitrate as •OH source would increase with the depth of the water column. This is reasonable because nitrate absorbs radiation at lower wavelengths, where water extinction is higher (see the spectrum of the lakewater sample in Figures 6,7). Note that most natural waters show a similar spectral profile in the UV-Vis region.[22,23]

It is also possible to calculate the average relative role of nitrite and nitrate in the water column, by integrating $\int_{\lambda} \phi_A(\lambda)\ \varepsilon_A(\lambda)\ I_{sun}(\lambda,b)\ d\lambda$ over the optical path length (column depth) b. In this way it is possible to take into account the higher contribution to •OH generation of the surface water layers, where sunlight intensity is higher, but also the higher residual absorption of nitrite around 1 m depth, resulting into much higher contribution to •OH photoproduction compared to nitrate.

The average of the relative role of nitrite and nitrate over the first metre of the water column is expressed by equation (9). Interestingly the result is 240, nearer to the value of 140 at the surface than to over 4000 at 1 m depth, because the water upper layer weights more than the deeper ones in the average due to its higher photochemical activity.
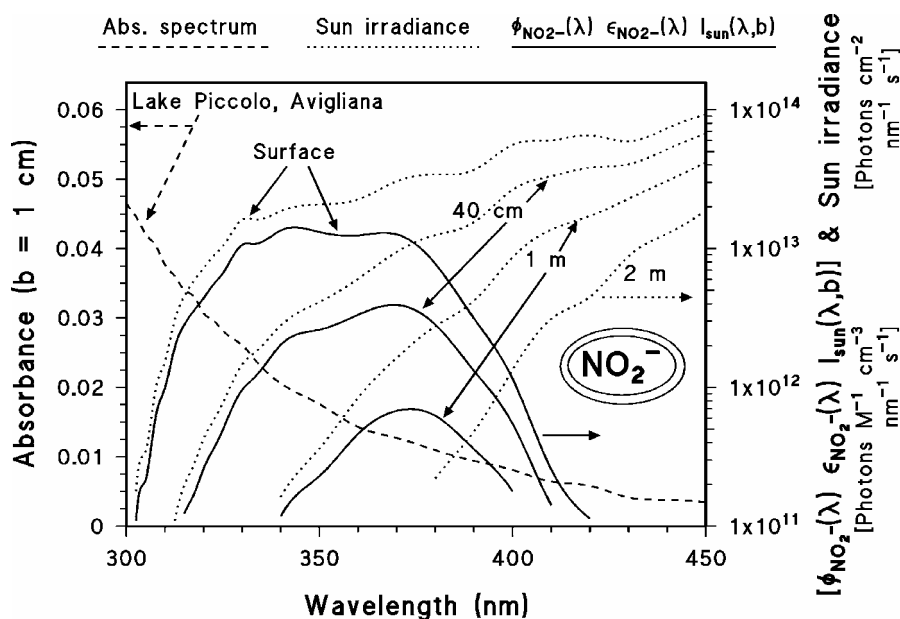
FIGURE 6. Dashed curve: absorption spectrum of unfiltered water from Lake Piccolo in Avigliana.[23] Dotted curves: October sunlight spectra at the ground and at different column depths, as expected in the Lake Piccolo water column based on equation (6). Solid curves: wavelength trend of the product $\phi_{NO2-}(\lambda)\ \varepsilon_{NO2-}(\lambda)\ I_{sun}(\lambda,b)$ at each depth b. The curve at 2 m depth is too low to be reported. Note the logarithmic scale on the right Y-axis.
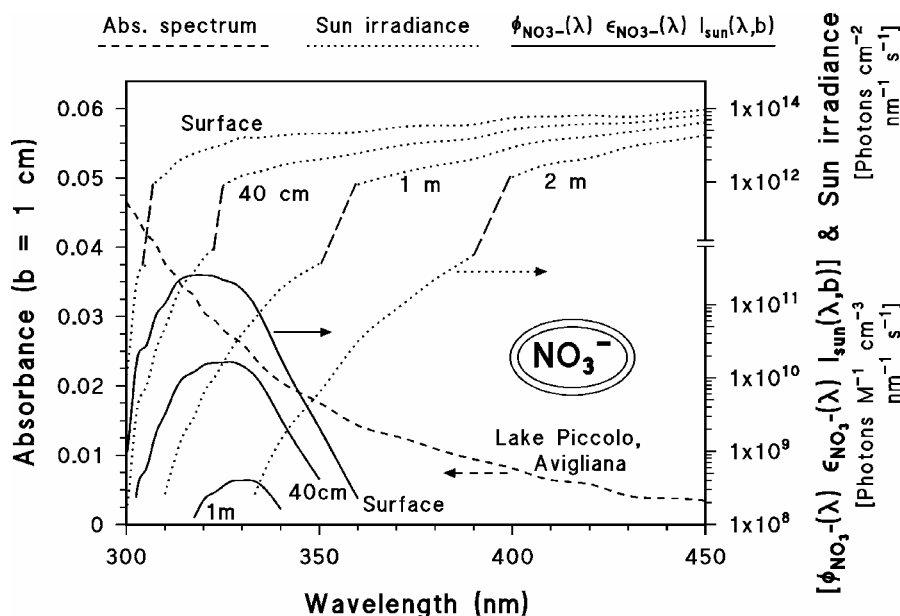

FIGURE 7. Dashed curve: absorption spectrum of unfiltered water from Lake Piccolo in Avigliana.[23] Dotted curves: October sunlight spectra at the ground and at different column depths, as expected in the Lake Piccolo water column based on equation (6). Solid curves: wavelength trend of the product $\phi_{NO3-}(\lambda)\ \varepsilon_{NO3-}(\lambda)\ I_{sun}(\lambda,b)$ at each depth b. The curve at 2 m depth is too low to be reported. Note the logarithmic scale and the break on the right Y-axis. The corresponding breaks in the sunlight spectra are shown as dashed lines.
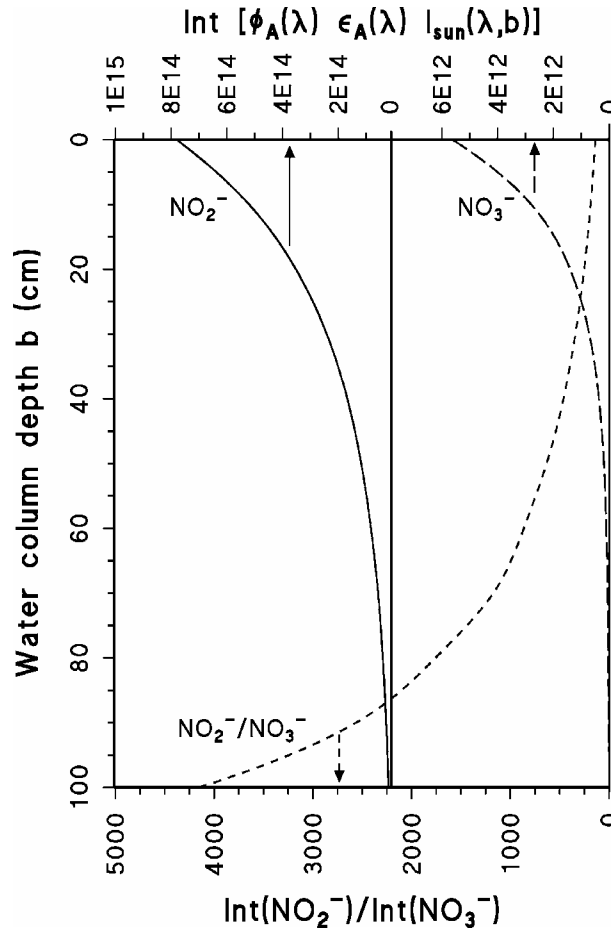
Figure 8. Water column trends, based on Lake Piccolo extinction and October sunlight emission spectra (see Figure 6,7), of the integrals $\int_\lambda \phi_A(\lambda) \, \varepsilon_A(\lambda) \, I_{sun}(\lambda,b) \, d\lambda$, with A = NO_2^- or NO_3^-. Note separate scales for nitrite and nitrate. The plot also shows the ratio of the integrals referred to nitrite and nitrate (NO_2^-/NO_3^- on the graph, as could be obtained from equation 8). This ratio is equal to the ratio of •OH photoformation rates by nitrite and nitrate, under the assumption of equal concentration values.

$$\left(\frac{\text{Rate}_{\text{phot,NO2-}}}{\text{Rate}_{\text{phot,NO3-}}} \right)_{\substack{\text{Water} \\ \text{column} \\ \text{average}}} = \frac{\displaystyle\int_{b=0}^{100\,cm} \left[\int_\lambda \phi_{NO2-}(\lambda) \cdot \varepsilon_{NO2-}(\lambda) \cdot I_{sun}(\lambda) \, d\lambda \right] db}{\displaystyle\int_{b=0}^{100\,cm} \left[\int_\lambda \phi_{NO3-}(\lambda) \cdot \varepsilon_{NO3-}(\lambda) \cdot I_{sun}(\lambda) \, d\lambda \right] db} = 240 \tag{9}$$

Note that a ratio of 240 was obtained under the hypothesis of equal concentration values of nitrate and nitrite. In an actual water body the value calculated according to equation (9) should be further multiplied by the concentration ratio $[NO_2^-]/[NO_3^-]$. The sample from Lake Piccolo in Avigliana, based on which the water column effect was computed, had $[NO_2^-]/[NO_3^-]$ = 1.04 × 10^{-2},[23] thus one obtains Rate$_{•OH}(NO_2^-)$/Rate$_{•OH}(NO_3^-)$ = 2.5 for the whole water column.

CONCLUSIONS

The relative contributions of nitrate and nitrite to $^\bullet$OH photogeneration in surface water samples could be calculated given the absorption spectra, the sunlight spectrum at the ground and the photolysis quantum yields. On an equimolar basis nitrite would be over 100 times more effective than nitrate toward $^\bullet$OH photogenerations under illumination conditions relevant to temperate latitudes during summertime at solar noon, in the surface layer of water bodies. This ratio would often more than compensate the higher concentration values of nitrate compared to nitrite in natural waters. Additionally, the fact that the wavelength where $^\bullet$OH photoproduction is most effective under sunlight is around 320 nm for nitrate and 340 nm for nitrite has important consequences. Definitely, any decrease in the sunlight intensity departing from the noon, summertime, surface layer scenario, due to either lower sun height over the horizon or to radiation extinction by the water column, would affect more heavily the shorter wavelengths. Accordingly, the relative role of nitrite as $^\bullet$OH source compared to nitrate would further increase during wintertime, with increasing depth in the water body, and presumably also at dawn and sunset. For this reason, nitrite can be expected to produce $^\bullet$OH at a higher rate than nitrate in many surface water bodies.

The reported calculation procedure (equation 7) will easily allow the assessment of the relative role of nitrate and nitrite as $^\bullet$OH sources in the surface layer of natural waters at temperate latitudes, given the $[NO_2^-]/[NO_3^-]$ ratio and the month of the sampling. An approximate procedure to quantitatively account for the water column effects is also reported (equations 8,9).

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