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Original Citation:

Availability:

This version is available http://hdl.handle.net/2318/69358 since

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20 April 2024

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This is an author version of the contribution published on:
Questa è la versione dell'autore dell'opera:

D. Vione, M. Minella, C. Minero, V. Maurino, P. Picco, A. Marchetto, G. Tartari. Photodegradation of Nitrite in Lake Waters: Role of Dissolved Organic Matter. *Environ. Chem.* **2009**, *6*, 407-415. DOI: 10.1071/EN09050.

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PHOTODEGRADATION OF NITRITE IN LAKE WATERS: ROLE OF DISSOLVED ORGANIC MATTER.

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ENVIRONMENTAL CONTEXT

Nitrite is an important nutrient in surface waters, a key intermediate in the interconversion of nitrate to ammonium, and a considerable photochemical source of reactive species such as the hydroxyl radical. We have found that scavengers of hydroxyl radicals such as the dissolved organic matter, which are usually supposed to inhibit the photodegradation of dissolved compounds, are able on the contrary to enhance the phototransformation of nitrite. The three weeks' lifetime of nitrite in the surface layer of lakes, derived from the results of the present work, would make photochemistry an important issue in determining the concentration of nitrite in lake water.

ABSTRACT

Here we studied the degradation rate of nitrite (NO_2^-), added to lake water at sub-μM levels, upon ultraviolet (UV) irradiation. NO_2^- photodegradation was considerably faster in lake water compared to ultra-pure water. A key issue was the presence in lake water of hydroxyl radical ($^{\bullet}OH$) scavengers that inhibited the reaction between NO_2^- and $^{\bullet}OH$. Such a reaction, while causing additional NO_2^- transformation, produced nitrogen dioxide ($NO_2^{\bullet}$) that was subsequently involved into the regeneration of NO_2^- via dimerisation or the reaction with nitric oxide ($NO^{\bullet}$). The scavenging of $^{\bullet}OH$ by compounds different from NO_2^- (mainly dissolved organic matter, DOM) prevented the regeneration reactions to take place, and enhanced the phototransformation of NO_2^-. Model calculations for the direct photolysis of NO_2^-, applied to the lake water samples, yielded a NO_2^- half-life time of around three weeks in the mixing layer of the lakes because of photodegradation. Therefore, we conclude that photodegradation is a potentially important process

to control the concentration of NO_2^- in shallow lakes, or in deeper ones under stratification conditions.

KEYWORDS: environmental photochemistry, nitrite photodegradation, dissolved organic matter, nitrogen geochemistry, hydroxyl radical scavenging.

INTRODUCTION

The nitrogen cycle plays a key role in defining the availability of the main nutrients in surface waters, thereby affecting biological productivity and in some cases species distribution and biodiversity [1, 2]. Depending on the ecosystem conditions, nitrogen can enter into the water bodies *via* atmospheric depositions, surface runoff, or input from groundwater [3]. Among the main inorganic species of nitrogen (ammonium, NH_4^+, nitrite, NO_2^- and nitrate, NO_3^-), NO_2^- is an intermediate of the transformation of NH_4^+ to NO_3^- or of NO_3^- reduction, and its concentration in surface waters is often kept low by chemical and biological redox processes. Besides its biological cycle, NO_2^- can also be produced by the photochemical transformation of organic nitrogen present in dissolved organic matter (DOM) [4, 5]. The effect of irradiation is expected to change depending on the water composition, because NO_2^- can also undergo photolysis upon absorption of sunlight [6], and NO_2^- degradation has been observed in some surface water samples under irradiation [5].

Despite its low concentration, NO_2^- would play a significant role in surface-water photochemistry because of its ability to significantly absorb solar ultraviolet A (UVA) radiation and of its relatively elevated quantum yield of photolysis [7]. For instance, in sunlit surface waters NO_2^- gives on average a higher contribution to the photogeneration of reactive hydroxyl radicals ($^\bullet OH$) than NO_3^-, which is usually much more abundant than NO_2^- in the surface waters [5, 8, 9]. The $^\bullet OH$ radicals can play an important role in the degradation of biorecalcitrant and difficult-to-oxidise xenobiotic compounds [10]. Furthermore, NO_2^- also contributes to a significant extent to the photoinduced formation of toxic aromatic nitroderivatives in shallow waters [11]. The absorption of sunlight by NO_2^- yields the following reactions [6, 12, 13]:

$$NO_2^- + h\nu + H^+ \rightarrow {}^\bullet OH + NO^\bullet \qquad (1)$$

$${}^\bullet OH + NO_2^- \rightarrow OH^- + NO_2^\bullet \qquad [k_2 = 1.0\times10^{10}\ M^{-1}\ s^{-1}] \qquad (2)$$

$$NO^\bullet + NO_2^\bullet + H_2O \rightarrow 2\ NO_2^- + 2\ H^+ \qquad [k_3 = 1.6\times10^{8}\ M^{-1}\ s^{-1}] \qquad (3)$$

$$2\ NO_2^\bullet \rightleftarrows N_2O_4 \qquad [k_4 = 4.5\times10^{8}\ M^{-1}\ s^{-1};\ k_{-4} = 6.9\times10^{3}\ s^{-1}] \qquad (4)$$

$$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2\ H^+ \qquad [k_5 = 1.0\times10^{3}\ s^{-1}] \qquad (5)$$

The purpose of the present study is to assess the photodegradation rates of NO_2^- in several lake surface waters, considering the influence of different water biogeochemical components such as DOM and NO_3^-. We carried out irradiation experiments on both lake waters samples amended or

not with NO_2^-, and on ultrapure water amended with NO_2^-, humic acids, NO_3^- or ethanol. The target was to assess the possible formation of NO_2^- upon DOM degradation and the phototransformation of NO_2^-. Both raw and filtered lake water samples were irradiated to get insight into the possible role of the biological processes and of suspended solids.

EXPERIMENTAL

Lakes studied

The choice of the lakes to be studied was carried out to ensure that they were representative of different trophic conditions, according to the criteria of the Organisation for Economic Co-operation and Development (OECD) [14]. The sampled lakes cover a large trophic gradient from oligo-mesotrophy (Orta, Maggiore) to eutrophy (Candia, Varese). They are all located in the Po Plain, at the Southern margin of the Alps (N-W Italy). The Lakes Maggiore and Orta have been formed by fluvial and glacial excavation, and they are deeper (370 and 143 m, respectively) than Lake Candia and Varese (8 and 26 m, respectively), which are intra-morenic.

Because of the presence of carbonate rocks in the watershed, the water of the studied lakes is moderately buffered. The alkalinity values increase from about 0.26 meq L^{-1} in Lake Orta, to 0.82 meq L^{-1} in Lake Maggiore, 1.18 meq L^{-1} in Lake Candia, and 2.77 meq L^{-1} in Lake Varese. Total phosphorus in these lakes is mainly originating from urban and agricultural activities; its content varies from 5 µg P L^{-1} in Lake Orta, to 10 µg P L^{-1} in Lake Maggiore, 33 µg P L^{-1} in Lake Candia, and 105 µg P L^{-1} in Lake Varese. In Lakes Maggiore and Orta, relatively high nitrogen concentration (1.47 and 0.88 mg N L^{-1}, respectively) is mainly due to the atmospheric input of nitrogen compounds, [15] originating from agriculture (NH_4^+), industry and traffic (NO_3^-). In the case of Lake Orta, NO_3^- is partially originating from industrial pollution, although this contribution strongly decreased since the ‘90s. Details on the lakes under study can be found in [16 – 19].

Sampling

Lake water was sampled at the centre of the lakes under study, reached by using motor boats, by means of Niskin bottles. The samples (5 L total) were taken from the surface layer (around 1 m depth) and transported under refrigeration to the laboratory. Half of the sampled volume underwent vacuum filtration (cellulose acetate filters, 47 mm diameter, 0.45 µm pore size). In some cases prefiltration on 3 mm or 1 mm pore-size filters was carried out to remove the larger particles and to make the subsequent 0.45 µm filtration easier. The filtered and unfiltered aliquots were then stored under refrigeration (4°C) and analyzed and irradiated within 2 days from sampling.

Irradiation experiments

Irradiation of all the studied water samples was carried out under magnetic stirring, adopting a 40 W Philips TLK 05 UVA lamp with emission maximum at 365 nm. The lamp irradiance was 110 W

m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter and corresponding to a photon flux of 1.39×10^{-6} einstein L^{-1} s^{-1} in the solution. The lamp was chosen because its emission maximum is relatively near to the absorption maximum of nitrite in the UVA region.

The samples for irradiation (300 mL each) were placed in Pyrex glass cells (10 cm diameter, 7 cm height). The Pyrex glass has a cut-off wavelength of 280 nm, thus it afforded a suitable transmittance (>80%) in the wavelength interval of interest (300 nm or higher). Some samples were placed in cells wrapped with aluminium foil, with the purpose of studying the dark reactivity under the same temperature conditions as for the irradiated samples. The temperature of the samples during the irradiation experiments was 28 ± 0.5 °C. By comparison, the *in situ* water temperature during sampling was in the range of 14 to 16 °C. Aliquots of 20 mL were withdrawn from the cells at regular times for the analysis of NO_2^-.

Figure 1 reports the emission spectrum of the lamp, together with the absorption spectra of NO_2^- and of the studied lake water samples. It is also reported a spectrum of sunlight, corresponding to UV irradiance of 22 W m^{-2} [20].

Irradiation was carried out of both raw and filtered lake water samples, with the purpose of highlighting the possible role of colloids and biological particles. The irradiation of samples not amended with NO_2^- was aimed at assessing the possible formation of NO_2^- upon phototransformation of DOM [4, 5]. Amended samples contained 0.61 µM NO_2^- as the sum of original and amended NO_2^-. Additional experiments were also carried out by irradiation of ultrapure water amended with NO_2^- + NO_3^-, NO_2^- + humic acids and NO_2^- + ethanol. In all the cases the initial concentration of NO_2^- was 0.61 µM.

The temporal evolution data of nitrite in the different experiments were fitted with pseudo-first order equations of the form $[NO_2^-] = C_o \exp(-k\,t)$, where $[NO_2^-]$ is the concentration at the time t, C_o the initial concentration (0.61 µM), and k the pseudo-first order degradation rate constant. The initial rate of NO_2^- degradation was $R_{NO2-} = k\,C_o$. The rate data are reported as $\mu\pm\sigma$, where σ was derived from the quality of the fit of the theoretical curve to the experimental data (intra-series variability). Some duplicate runs were carried out, which yielded a variability ≤ 5% in the determination of R_{NO2-}.

Analytical determinations

The measurements of conductivity and pH were carried out with a Radiometer ION 450 apparatus, equipped with a SAC 80 autosampler. The repeatability of the measurements, expressed as relative standard deviation (RSD), was around 1-2% for pH and < 5% for conductivity.

The measurement of the lake water absorption spectra and the determination of NO_2^- and NH_4^+ were carried out with a SAFAS UV mc^2 UV-Vis spectrophotometer. NO_2^- was determined with the Griess reaction [21], using sulphanilic acid and N-(1-naphthyl)ethylenediamine dichloride; the detection wavelength was 541 nm. NH_4^+ was determined with the indophenol method forming a blue colour compound, the detection wavelength was 695 nm. Cuvettes of 5 cm optical path length were used for both determinations. The limit of detection (LOD, three times the standard deviation

of the blank) was 0.3 µg N-NO_2 L^{-1} and 4 µg N-NH_4 L^{-1}. The limit of quantification (LOQ, ten times the standard deviation of the blank) was 0.9 µg N-NO_2 L^{-1} and 12 µg N-NH_4 L^{-1}. Repeatability (RSD) of the measurements was around 10% for NO_2^- and below 5% for NH_4^+.

Anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were determined by ion chromatography, with electrochemical eluent generation and suppression. For the anions the adopted apparatus was a Dionex DX320 chromatograph equipped with autosampler, 100 µL sample loop, AG19-AS19 columns with eluent 19 mM KOH at 1.0 mL min^{-1} flow rate, conductivity suppression unit, conductivity and UV 215 nm detector. The analytical parameters were as follows (LOD, LOQ): Cl^- (0.02 mg L^{-1}, 0.06 mg L^{-1}), NO_3^- (0.01 mg N L^{-1}, 0.04 mg N L^{-1}), SO_4^{2-} (0.06 mg L^{-1}, 0.19 mg L^{-1}), and in all the cases the repeatability was ~ 5%.

For the cations it was used a Dionex DX500 chromatograph equipped with autosampler, 100 µL sample loop, GC12A-CS12A columns with eluent 20 mM methanesulphonic acid at 1.0 mL min^{-1} flow rate, conductivity suppression unit and conductivity detector. The analytical parameters were as follows (LOD, LOQ): Na^+ (0.01 mg L^{-1}, 0.03 mg L^{-1}), K^+ (0.02 mg L^{-1}, 0.07 mg L^{-1}), Mg^{2+} (0.01 mg L^{-1}, 0.03 mg L^{-1}), Ca^{2+} (0.05 mg L^{-1}, 0.18 mg L^{-1}). In all the cases the repeatability was < 5%.

The determination of the dissolved organic carbon (DOC) was carried out with a Skalar FORMACS TC/TN Analyser, with LOD 0.23 mg C L^{-1}, LOQ 0.78 mg C L^{-1}, and repeatability was < 15%.

Alkalinity was determined with a Radiometer automatic titration unit connected to an autosampler, and the adopted Gran's method had < 3% repeatability.

All the reagents were of analytical grade, from Aldrich, VWR Int. or Fluka and were used as received, without further purification.

Quantum yield determination

The quantum yield of NO_2^- photodegradation was calculated as the ratio between the transformation rate of NO_2^- under irradiation (R_{NO2-}) and the photon flux absorbed by NO_2^- (P_a^{NO2-}). Note that R_{NO2-} and P_a^{NO2-} should be expressed in equivalent units. Accordingly, if R_{NO2-} is in mol L^{-1} s^{-1}, P_a^{NO2-} should be expressed in einstein L^{-1} s^{-1}, where 1 einstein = 1 mole of photons. The calculation of P_a^{NO2-} has to take into account the spectral distribution of both the emission spectrum of the lamp and the absorption spectrum of NO_2^-, and the fact that the radiation absorption by NO_2^- can be decreased by other dissolved components. They can compete for sunlight absorption, and mostly consist of coloured dissolved organic matter, CDOM [9].

RESULTS

Table 1 reports the chemical composition of the filtered and unfiltered lake water samples under study.

Photodegradation of NO_2^- in lake and pure waters

Irradiation experiments were carried out with both raw and filtered lake water samples. No formation of NO_2^- was observed upon irradiation of lake water alone, the NO_2^- content of which varied from 0.02 to 0.17 μM (LOQ = 0.02 μM). No evolution of NO_2^- was observed in the presence of lake water alone in the dark. Original and filtered samples were also amended with NO_2^-, so that the sum of original and added NO_2^- made up an initial concentration of 28 μg NO_2 L^{-1} (0.61 μM). Figure 2 shows the temporal evolution of 0.61 μM NO_2^- in the original and filtered samples of Lake Candia, as well as the trend of NO_2^- upon irradiation of ultrapure water. The figure also reports the results of the blank runs, without irradiation. In the latter case negligible evolution of NO_2^- was observed, in the presence of either ultrapure or lake water. Moreover, no difference was detected in the dark between the filtered and unfiltered lake water samples amended with NO_2^-.

A significant decrease of NO_2^- compared to the dark runs could be observed upon irradiation in ultrapure water, with a half-life time of around 60 hours. The photodegradation rate of NO_2^- in this system was $(1.8\pm0.2)\times10^{-12}$ M s^{-1}. In the presence of lake water the transformation rate of NO_2^- was considerably increased, and for lake Candia it was a bit faster for the original (unfiltered) compared to the filtered sample. This small difference could be attributed to the interaction between the radiation and the suspended particles larger than 0.45 μm, either biotic or abiotic. The NO_2^- trend for lake Candia (higher degradation rate in lake water compared to ultrapure water) was typical, and the same results were obtained with the other lake water samples. The degradation rates of NO_2^- are summarised in Figure 3. In the case of Lake Varese the transformation of NO_2^- was faster in the filtered sample, while in the other cases the original samples showed a faster NO_2^- degradation. The NO_2^- degradation rate in lake water compared to pure water was enhanced by 3.0-4.1 times in the raw samples, and by 2.4-3.2 times in the filtered ones, showing that the composition of lake waters had certainly an important effect on the NO_2^- photodegradation.

Photodegradation of NO_2^- in the presence of $^{\bullet}OH$ scavengers

Figure 4 reports the temporal evolution of 0.61 μM NO_2^- in the presence of ultrapure water amended with Aldrich humic acids (HUm, 10 mg L^{-1}), NO_3^- (1 mg L^{-1}) and ethanol (9.2 mg L^{-1}), both in the dark and under irradiation. Considerable degradation of NO_2^- was observed in the presence of HUm or ethanol under irradiation, in which cases the NO_2^- rates were significantly higher than the corresponding ones in the dark. In the presence of NO_3^- no transformation of NO_2^- was observed in the dark, and some formation of NO_2^- was operational under irradiation.

HUm are representative of the photoactive compounds of dissolved organic matter (DOM). The adopted Sigma-Aldrich humic acids have similar structure as soil humic acids, which in turn bear resemblance to the pedogenic fraction of lake water DOM. The pedogenic DOM is the fraction that absorbs most sunlight and shows the highest photoactivity [22]. HUm are able to absorb sunlight, and some of their components would undergo excitation to the first excited singlet state (^{1}HUm*),

which is followed by inter-system crossing (ISC) to the first excited triplet state (^{3}HUm*). The latter is chemically reactive and can induce the transformation of many dissolved compounds [23, 24].

$$\text{HUm} + h\nu \rightarrow {}^1\text{HUm}^* \xrightarrow{ISC} {}^3\text{HUm}^* \qquad (6)$$

Irradiated HUm are able to induce the degradation of many dissolved compounds by direct reaction of their excited triplet states, or *via* the intermediacy of reactive transients such as singlet oxygen ($^1O_2$) and $^\bullet$OH. The generation of $^1O_2$ takes place upon reaction between ground-state O_2 and ^{3}HUm*, that of $^\bullet$OH upon oxidation of water by ^{3}HUm* or via photo-Fenton reactions [13]. The initial concentration of HUm was 10 mg L^{-1}, which corresponds to 4.2 mg C L^{-1} [25]. Note that the DOC value of the studied samples was in the range 1-6 mg C L^{-1}, and only a fraction of the DOM in lake water is photoactive [26]. Accordingly, HUm at the adopted concentration are expected to show higher photoreactivity than the DOM in the lake water samples under study. Also note that the HUm are able to scavenge the hydroxyl radicals that are produced by NO_2^- photolysis. A reaction rate constant of 1.9×10^4 L (mg C)$^{-1}$ s^{-1} has been reported for humic acids [27], which at the concentration adopted in the present study would give an $^\bullet$OH scavenging rate constant of 8.0×10^4 s^{-1}. The reaction rate constant between NO_2^- and $^\bullet$OH is 1.0×10^{10} M^{-1} s^{-1} [12], which for 0.61 μM NO_2^- gives a scavenging rate constant of 6.1×10^3 s^{-1}. In the presence of 10 mg L^{-1} HUm, 0.61 μM NO_2^- would consume only 7% of the hydroxyl radicals generated by its photolysis, the remainder being scavenged by HUm. Figures 3 and 4 show that the degradation rate of NO_2^- in the presence of HUm was $(3.4\pm0.3)\times10^{-12}$ M s^{-1}, namely 1.9 times higher compared to NO_2^- alone. Some NO_2^- transformation was also operational in the presence of HUm in the dark, but its rate was less than 10% of that observed under irradiation.

The irradiation of NO_3^- can yield the hydroxyl radical $^\bullet$OH [28], a very reactive species that can oxidise NO_2^- at a diffusion-controlled rate (reaction (2); [12]).

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet\text{OH} + NO_2^\bullet \qquad (7)$$

The adopted NO_3^- concentration was 1 mg L^{-1}, corresponding to 1.6×10^{-5} M. By comparison, the NO_3^- levels in the lake water samples under study were in the range 10^{-3} – 1.3 mg L^{-1}. Figure 4 shows that NO_2^- increases with time in the presence of NO_3^-. This most likely means that the photogeneration of NO_2^- upon NO_3^- irradiation (from the hydrolysis of $NO_2^\bullet$, see reactions (7) and (4,5) [29]) is faster than the possible degradation of NO_2^-, induced by the hydroxyl radicals photogenerated by NO_3^-. Anyway, the observed degradation of NO_2^- in irradiated lake water cannot be accounted for by NO_3^- photochemistry, which would produce NO_2^- rather than degrade it.

Ethanol was used at 0.2 mM concentration. It was chosen as an easily available scavenger of $^\bullet$OH and because it is otherwise inactive under photochemical conditions [13]. The reaction between ethanol and $^\bullet$OH takes place upon H-atom abstraction and has a second-order rate constant of

1.9×10^9 M^{-1} s^{-1} [12]. The rate constant, multiplied by the concentration, gives a $^{\bullet}OH$ scavenging rate constant of 3.8×10^5 s^{-1}. In the presence of 0.61 μM NO_2^- and 0.2 mM ethanol, NO_2^- would consume just 1.6% of the $^{\bullet}OH$ radicals generated by its photolysis, the remainder being scavenged by ethanol. By comparison, note that the studied lake water samples had DOC values in the range 1-6 mg C L^{-1}. With a reaction rate constant of 5×10^4 L (mg C)$^{-1}$ s^{-1} for lake-water DOM [30], the scavenging rate constant of DOM in the studied samples would be in the range 0.5-3×10^5 s^{-1}. In all these cases NO_2^- would scavenge just a minor fraction of the $^{\bullet}OH$ radicals it produces. Figures 3 and 4 show that NO_2^- in the presence of ethanol undergoes transformation to a substantial rate ($(5.8\pm0.6)\times10^{-12}$ M s^{-1}), which is over three times faster compared to the degradation of NO_2^- alone. The degradation rate of NO_2^- with ethanol is also comparable to that observed for NO_2^- in the lake water samples (see Figure 3). Note that some transformation of NO_2^- was observed with ethanol in the dark, but it was less than 10% compared to the irradiated system. Considering that ethanol would mainly be a consumer of $^{\bullet}OH$, the data suggest that the scavenging of hydroxyl radicals plays an important role in the enhancement of NO_2^- degradation. Also HUm at the adopted levels (10 mg L^{-1}) would be able to scavenge the majority of $^{\bullet}OH$ produced by NO_2^- photolysis, and also in this case a considerable enhancement of the photodegradation of NO_2^- was observed compared to NO_2^- alone. Given the NO_2^- trend with ethanol, it is much more likely that HUm enhanced NO_2^- degradation through $^{\bullet}OH$ scavenging, rather than upon photooxidation of NO_2^- by ^{3}HUm*. In the case of lake water, the increase of NO_2^- degradation rate compared to ultrapure water can therefore be attributed to the scavenging of $^{\bullet}OH$ carried out by DOM.

Quantum yields for NO_2^- photodegradation in lake water

The quantum yield of NO_2^- photodegradation can be obtained from the ratio of the NO_2^- transformation rate $Rate_{NO2-}$ (see Figure 3) to the photon flux absorbed by NO_2^- ($P_{a,NO2-}$, to be calculated). Such an approach yields an average quantum yield for NO_2^- photodegradation, in the wavelength interval in which the spectra of NO_2^- and of the lamp overlap (300-410 nm). Such an interval is environmentally significant because it also represents the overlap between the spectrum of NO_2^- and that of sunlight (see Figure 1).

At a given wavelength λ the absorbance of NO_2^- would be the same, at equal concentration, when it is alone in ultra pure water and when it is added to lake water. In contrast, the photon flux density absorbed by NO_2^- would be lower in the lake water, because of interference for absorption by the dissolved species, mainly DOM. However, the ratio between the absorbance of NO_2^- and that of the other dissolved species would be equal to the ratio of the corresponding absorbed photon fluxes [31], which enables the calculation of radiation absorption. Let $A_1(\lambda)$ be the absorbance of the original lake water, for an optical path length of 1 cm ([cm^{-1}] units, see Figure 1); $A_{lake}(\lambda) = b\ A_1(\lambda)$ is the corresponding absorbance of the lake water samples under the lamp (optical path length b = 5 cm); $\varepsilon_{NO2-}(\lambda)$ is the molar absorption coefficient of NO_2^- (Figure 1); $A_{NO2-}(\lambda) = \varepsilon_{NO2-}(\lambda)\ b\ [NO_2^-]$ is the absorbance of 0.61 μM NO_2^-; $A_{tot}(\lambda) = A_{lake}(\lambda) + A_{NO2-}(\lambda) \approx A_{lake}(\lambda) = A_1(\lambda)\cdot b$ is the total absorbance of the NO_2^--amended lake water; $p°(\lambda)$ is the spectral photon flux density emitted by

the lamp (Figure 1); $p_{a,NO2-}(\lambda)$ is the spectral photon flux density absorbed by 0.61 μM NO_2^-; $p_{a,tot}(\lambda)$ is the spectral photon flux density absorbed by the lake water sample; and $P_{a,NO2-}$ is the photon flux absorbed by 0.61 μM NO_2^-. The following relationships hold [31]:

$$p_{a,tot}(\lambda) = p^{\circ}(\lambda) \cdot \left[1 - 10^{-A_1(\lambda) \cdot b}\right] \quad (8)$$

$$p_{a,NO2-}(\lambda) = p_{a,tot}(\lambda) \cdot \frac{A_{NO2-}(\lambda)}{A_{tot}(\lambda)} \cong p_{a,tot}(\lambda) \cdot \frac{\varepsilon_{NO2-}(\lambda) \cdot [NO_2^-]}{A_1(\lambda)} \quad (9)$$

$$P_{a,NO2-} = \int_{\lambda} p_{a,NO2-}(\lambda)\, d\lambda \quad (10)$$

Considering the studied lake water samples, after numerical integration one gets that $P_{a,NO2-}$ = 1.0×10^{-10} einstein L^{-1} s^{-1} for the unfiltered samples from the lakes Orta and Maggiore, 9.4×10^{-11} einstein L^{-1} s^{-1} for Varese, and 9.6×10^{-11} einstein L^{-1} s^{-1} for Candia. The quantum yields of NO_2^- photodegradation in the raw (unfiltered) samples, which would be more representative of the actual environmental case, are Φ_{NO2-} = $Rate_{NO2-}$ $(P_{a,NO2-})^{-1}$ = 7.6×10^{-2} for Candia, 5.2×10^{-2} for Orta, 5.4×10^{-2} for Maggiore, and 5.6×10^{-2} for Varese.

DISCUSSION

Enhancement of NO_2^- photodegradation by scavengers of hydroxyl radicals

The experimental data suggest that the photodegradation of nitrite in lake water is enhanced compared to ultrapure water, because of the scavenging of $^{\bullet}OH$ by DOM. This result is intriguing because $^{\bullet}OH$ is usually involved into the degradation of the dissolved species with which it reacts (and NO_2^- reacts with $^{\bullet}OH$ at a diffusion-controlled rate), thus the scavenging of $^{\bullet}OH$ by DOM would be expected to inhibit rather than enhance the degradation processes.

The possible explanation of this apparent contradiction could come from a closer look at the main processes that involve NO_2^- after the primary photolysis step. In the presence of NO_2^- alone, let consider the absorption of a photon that is able to induce photolysis (the probability of such an event is given by the quantum yield Φ_1 of reaction (1), which varies between 0.065 and 0.025 depending on the wavelength [7]). The cited photon would cause the transformation of a NO_2^- ion, and a second NO_2^- would be transformed in reaction (2) by the $^{\bullet}OH$ radical that is produced upon NO_2^- photolysis (reaction (1)). Note that if NO_2^- is alone in the solution, it would also be the only species to scavenge $^{\bullet}OH$, and a single photon would therefore cause the transformation of two NO_2^-. However, NO_2^- is partially reformed in the reactions (3-5) that involve the nitrogen oxides $NO^{\bullet}$ and $NO_2^{\bullet}$. The effect of these reactions is to reduce the degradation rate of NO_2^-. Indeed if reactions (1-3) only were operational, a null cycle would result in which NO_2^- is transformed and reformed at the same rate, with no resulting degradation. Under such circumstances no transformation of NO_2^- upon irradiation would be observed. The actual degradation of NO_2^- when

it is irradiated alone is accounted for by its partial transformation into NO_3^- in reactions (4,5). As a consequence, the transformation of NO_2^- is linked to the branching ratio between reaction (3) on one side, and (4,5) on the other. Reaction (4) yields N_2O_4, which can either give back $NO_2^\bullet$ in the reverse reaction (4), or produce $NO_2^- + NO_3^-$ in reaction (5). Upon application of the steady-state approximation to N_2O_4, one obtains the combined rate constant of reactions (4,5) as $k_{45} = k_4\, k_5\, (k_5 + k_{-4})^{-1}$. The branching ratio would therefore be $\eta = k_3\, k_{45}^{-1} = k_3\, (k_4\, k_5)^{-1}\, (k_5 + k_{-4}) \approx 3$. Reaction (3) would therefore be about 3 times faster than reactions (4,5). Around three quarters of the nitrogen involved in the NO_2^- photolysis process would thus follow reaction (3), and yield back NO_2^- in a null cycle. Of the remaining one-quarter of nitrogen that would be involved in reactions (4,5), half would yield back NO_2^- and half NO_3^- (see reaction (5)). Accordingly, in total only one-eight of the NO_2^- originally transformed would undergo actual degradation. If one comes back to the absorption of the photon by NO_2^- that causes the photolysis, and induces transformation of two NO_2^- ions in reactions (1,2), in the end only 0.25 ions will be transformed in the full reaction sequence (1-5), in the presence of NO_2^- alone.

The opposite case to NO_2^- alone (100% of $^\bullet$OH scavenging by NO_2^-) is the scenario in which other scavengers consume all of the hydroxyl radicals (negligible $^\bullet$OH scavenging by NO_2^-). Such a scenario is relatively near to the case of the lake water amended with NO_2^-, and to the NO_2^-/ethanol or the NO_2^-/HUm systems. In this case, if the absorption of a photon causes NO_2^- photolysis in reaction (1), the result would be the transformation of one NO_2^-. Moreover, the scavenging of $^\bullet$OH by other molecules would prevent reactions (2-5) to take place. As a consequence one usefully absorbed photon would consume one NO_2^- ion, with no further transformation/regeneration processes, and the degradation rate of NO_2^- would therefore be increased by four times compared to NO_2^- alone. The increase could be lower if the additional compounds do not scavenge all of the hydroxyl radicals, or if they absorb radiation: it is the case of lake water DOM and of HUm. Radiation absorption would decrease the initial rate of NO_2^- photolysis. This is compatible with the results of the irradiation experiments in the presence of $^\bullet$OH scavengers, which yielded an increase of 2.4 - 4.1 times of NO_2^- degradation rate compared to NO_2^- alone.

Assessment of NO_2^- photodegradation in lake water

From the quantum yield data it is possible to calculate the expected kinetics of NO_2^- phototransformation in the mixing layer of lake water. To this purpose it is possible to consider the radiation absorption and transformation rates within a definite volume V, e.g. a cylinder of standard surface area S and height equal to the depth d of the mixing layer of the lake. For shallow, thoroughly mixed lakes it is possible to adopt the average depth [32-34]. Because of the choice of the volume V = S d, the units for radiation absorption ($\mathscr{P}_{a,NO2-}$) and NO_2^- degradation (R_{NO2-}) will be einstein s^{-1} and mol s^{-1}, respectively. As standard surface area it can be assumed S = 12.6 cm^2 as done in previous work [32], but the results are independent of the choice of S. For the sunlight spectrum [20] we used a UV irradiance (290-400 nm) of 22 W m^{-2}, which corresponds to the irradiance that can be observed in a clear summer day in mid latitude (15 July, 45°N, at 10 a.m. [5]).

Generally, solar radiation spectrum is reported in units of [einstein s^{-1} nm^{-1} cm^{-2}] [20]. The main issue is that here the sunlight spectrum i°(λ) should be referred to the standard surface area S = 12.6 cm^2, in order to be consistent with the approach outlined above. Such a spectrum is presented in Figure 1; note that the units of i°(λ) are [einstein s^{-1} nm^{-1}], not [einstein L^{-1} s^{-1} nm^{-1}], nor [einstein s^{-1} nm^{-1} cm^{-2}]. The intensity of radiation absorption by NO_2^- ($\mathscr{P}_{a,NO2-}$, in einstein s^{-1} given the units of i°(λ)) can be calculated from equations (8-10), by replacing p°(λ) [einstein L^{-1} s^{-1} nm^{-1}] with i°(λ) [einstein s^{-1} nm^{-1}]. In this way one obtains equations (11-13):

$$\wp_{a,tot}(\lambda) = i°(\lambda)\cdot\left[1-10^{-A_1(\lambda)\cdot d}\right] \tag{11}$$

$$\wp_{a,NO2-}(\lambda) \cong \wp_{a,tot}(\lambda)\cdot\frac{\varepsilon_{NO2-}(\lambda)\cdot[NO_2^-]}{A_1(\lambda)} \tag{12}$$

$$\mathscr{P}_{a,NO2-} = \int_\lambda \wp_{a,NO2-}(\lambda)\, d\lambda \tag{13}$$

The optical path length should be equal to the water column depth d, referred to the mixing layer or the average depth of the water body (the latter in the case of thoroughly mixed lakes). The calculation results are independent of $[NO_2^-]$, provided that $A_{NO2-} \ll A_{lake}$, but for the calculations it was initially considered $[NO_2^-]$ = 0.1 μM. In the case of Lake Maggiore (d = 30 m = 3×10^3 cm for the mixing layer, and $\Phi_{NO2-} = 5.4\times10^{-2}$) one gets $\mathscr{P}_{a,NO2-} = 5.9\times10^{-11}$ einstein s^{-1} and $R_{NO2-} = \Phi_{NO2-}\,\mathscr{P}_{a,NO2-} = 3.2\times10^{-12}$ mol s^{-1} in the volume V = 38 L, which corresponds to $-d[NO_2^-]/dt = R_{NO2-}\,V^{-1} = 8.4\times10^{-14}$ M s^{-1}. The corresponding first-order degradation rate constant is $k_{NO2-} = (-d[NO_2^-]/dt)\,[NO_2^-]^{-1} = 8.4\times10^{-7}$ s^{-1}. From k_{NO2-} one can get the half-life time of NO_2^-, $t_{1/2} = \ln 2\,(k_{NO2-})^{-1} = 8.2\times10^5$ s. Such a value of $t_{1/2}$ is valid for continuous illumination at 22 W m^{-2} irradiance, which is not the case for the actual environment. If one takes the clear-sky 15 July at 45°N as standard summer day (SSD), the sunlight energy reaching the ground over the whole day would be equivalent to 10 hour (3.6×10^4 s) illumination at 22 W m^{-2} UV irradiance [5]. The half-life time of NO_2^- in SSD units would therefore be $t_{1/2}^{SSD} = t_{1/2}\,(3.6\times10^4\ s\ SSD^{-1})^{-1} = 23$ SSD. Note that $t_{1/2}^{SSD}$ is referred to the whole mixing layer (up to 30 m from the surface) of Lake Maggiore. The same results would be obtained by considering $[NO_2^-]$ = 1 or 0.01 μM, because $\mathscr{P}_{a,NO2-}$ and R_{NO2-} are directly proportional to $[NO_2^-]$, and k_{NO2-} and $t_{1/2}^{SSD}$ are therefore independent of it. Based on the previous discussion, the half-life time of NO_2^- in SSD units can be expressed as follows:

$$t_{1/2}^{SSD} = \frac{\ln 2\ V\,[NO_2^-]}{3.6\cdot10^4\,\Phi_{NO2-}\,\mathscr{P}_{a,NO2-}} = \frac{1.9\cdot10^{-5}\ S\cdot d}{\Phi_{NO2-}\displaystyle\int_\lambda\left[i°(\lambda)\cdot\left[1-10^{-A_1(\lambda)\cdot d}\right]\frac{\varepsilon_{NO2-}(\lambda)}{A_1(\lambda)}\right]d\lambda} \tag{14}$$

In the case of the shallower Lake Candia (3.8 m average depth, $\Phi_{NO2-} = 7.6\times10^{-2}$) one gets $t_{1/2}^{SSD}$ = 18 days. The similarity of the results with Lake Maggiore can be explained by the compensation

between the higher absorbance of Candia (which yields lower $\mathscr{P}_{a,NO2-}$, and lower R_{NO2-} as a consequence) and its lower depth (lower V, which gives similar $-d[NO_2^-]/dt$ and k_{NO2-} for lower R_{NO2-}).

CONCLUSIONS

No formation of NO_2^- was observed from UVA irradiation of lake water samples, excluding thus the NO_2^- photoproduction upon photolysis of DOM. As far as the NO_2^--amended samples are concerned, the degradation rate of NO_2^- upon UV irradiation was considerably faster in lake compared to ultra-pure water. The results of further irradiation experiments in the presence of NO_2^- + NO_3^-, NO_2^- + humic acids, and NO_2^- + ethanol indicated that a key issue was the presence of $^{\bullet}OH$ scavengers (humic acids and ethanol) that inhibited the further reaction between NO_2^- and $^{\bullet}OH$ itself. Interestingly the latter reaction, while causing additional NO_2^- transformation, produced $NO_2^{\bullet}$ that was subsequently involved in the regeneration of NO_2^- via dimerisation or reaction with $NO^{\bullet}$. Accordingly, in the presence of NO_2^- alone the transformation was faster in the first steps because of the reaction with $^{\bullet}OH$, but around 7/8 of the initially transformed NO_2^- was subsequently reformed. In the presence of the $^{\bullet}OH$ scavengers, the photodegradation rate of NO_2^- was lower but no (or limited) regeneration was operational afterwards. The $^{\bullet}OH$ scavengers could potentially be able to increase the degradation rate by four times compared to NO_2^- alone, but in many actual cases they could also inhibit the primary event of NO_2^- photolysis by absorbing UV radiation: it is the case of HUm, and of DOM in lake water. The result would be a less than four-fold increase of NO_2^- degradation rate. A further confounding factor could be the possible photosensitised oxidation of NO_2^- by HUm and DOM, but the more important effect of $^{\bullet}OH$ scavenging precluded the demonstration of the possibility of such a process.

A quantum yield of 0.05-0.07 was calculated for NO_2^- photodegradation in the lake water samples under study. Model calculations for the direct photolysis of NO_2^-, applied to Lake Maggiore and Lake Candia, yielded a half-life time of around three weeks for NO_2^- in the mixing layer of the lakes because of photodegradation. It could therefore be inferred that photodegradation is a potentially important process to control the concentration of NO_2^- in shallow lakes, or in deeper ones under stratification conditions.

ACKNOWLEDGEMENTS

Financial support by Università di Torino – Ricerca Locale and the Italian Inter-University Consortium of Chemistry and the Environment (INCA) is gratefully acknowledged.

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Table 1. Chemical composition of the studied filtered and unfiltered samples. NF = unfiltered sample; F = filtered sample.

	Candia		**Maggiore**		**Orta**		**Varese**	
	NF	*F*	*NF*	*F*	*NF*	*F*	*NF*	*F*
Sampling date	26 Aug 2008		23 Sep 2008		11 Nov 2008		19 Nov 2008	
Alk, meq L^{-1}	0.97	0.98	0.77	0.74	0.26	0.26	2.61	2.66
Cond., µS cm^{-1}	110	111	128	128	102	100	272	271
pH	7.8	7.7	7.8	7.7	7.4	7.6	8.1	8.2
N-NO_2^-, µg L^{-1}	1	1	6	6	8	8	2	2
N-NO_3^-, µg L^{-1}	4	1	627	609	1324	1323	180	192
N-NH_4^+, µg L^{-1}	3	4	14	15	50	45	271	209
DOC, mg C L^{-1}	6.2	6.2	1.1	2.4	0.8	0.8	4.0	4.0
SO_4^{2-}, mg L^{-1}	3.2	3.6	25	24	23	23	9.9	9.9
Cl^-, mg L^{-1}	4.7	4.8	2.8	2.6	4.4	4.4	8.8	8.7
Ca^{2+}, mg L^{-1}	15	15	19	19	13	13	44	44
Mg^{2+}, mg L^{-1}	4.1	4.1	3.1	3.2	1.6	1.6	7.7	7.7
Na^+, mg L^{-1}	2.1	2.2	2.8	2.7	4.6	4.5	8.3	8.4
K^+, mg L^{-1}	1.5	1.6	1.4	1.4	1.0	0.9	1.8	1.8

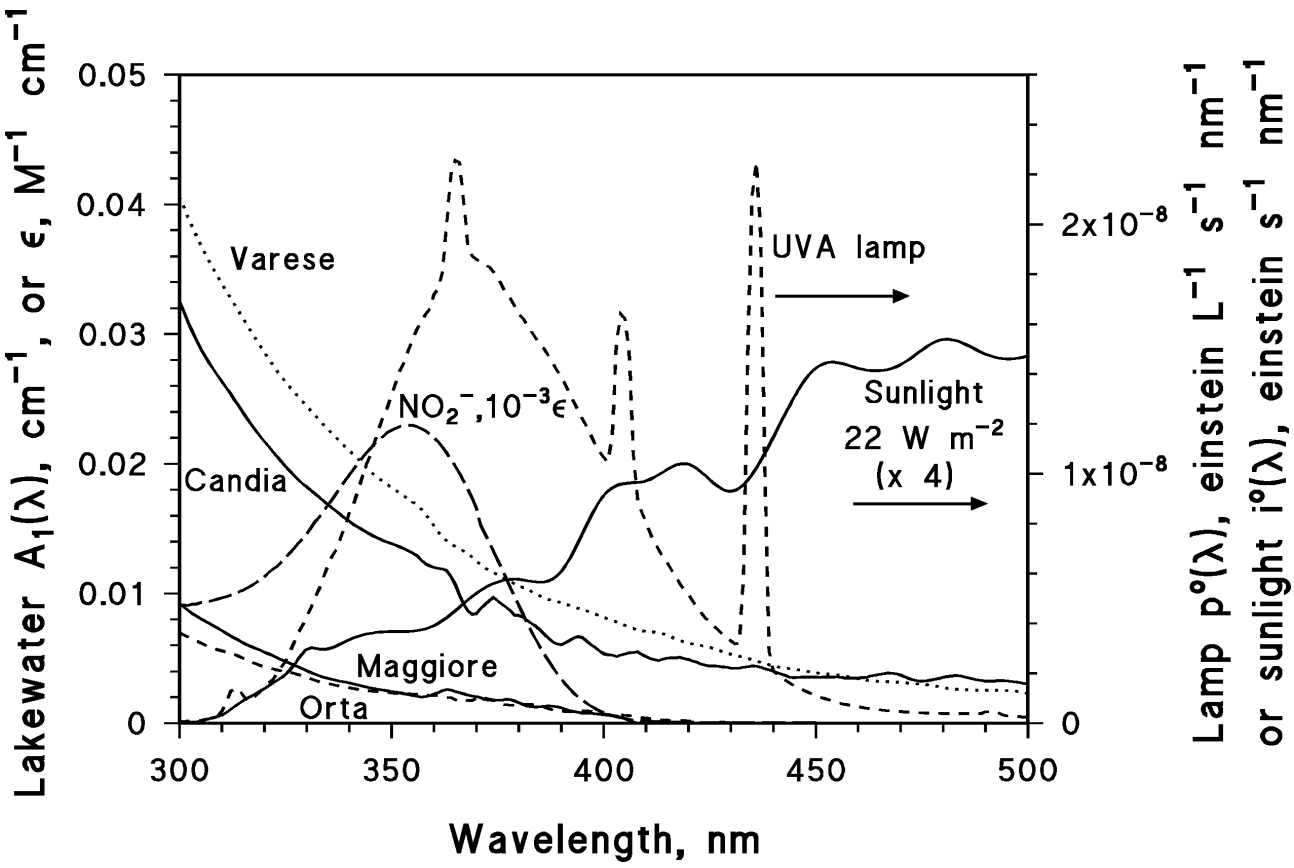

Figure 1. Emission spectrum of the Philips TLK 05 lamp used for the irradiation experiments. Absorption spectra of the studied, original lake water samples ($A_1(\lambda)$, lakewater absorbance for an optical path length b = 1 cm) and of NO_2^- (molar absorption coefficient ε, in M^{-1} cm^{-1}). It is also reported the spectrum of sunlight (i°(λ)), corresponding to a UV irradiance (290-400 nm) of 22 W m^{-2} [20].

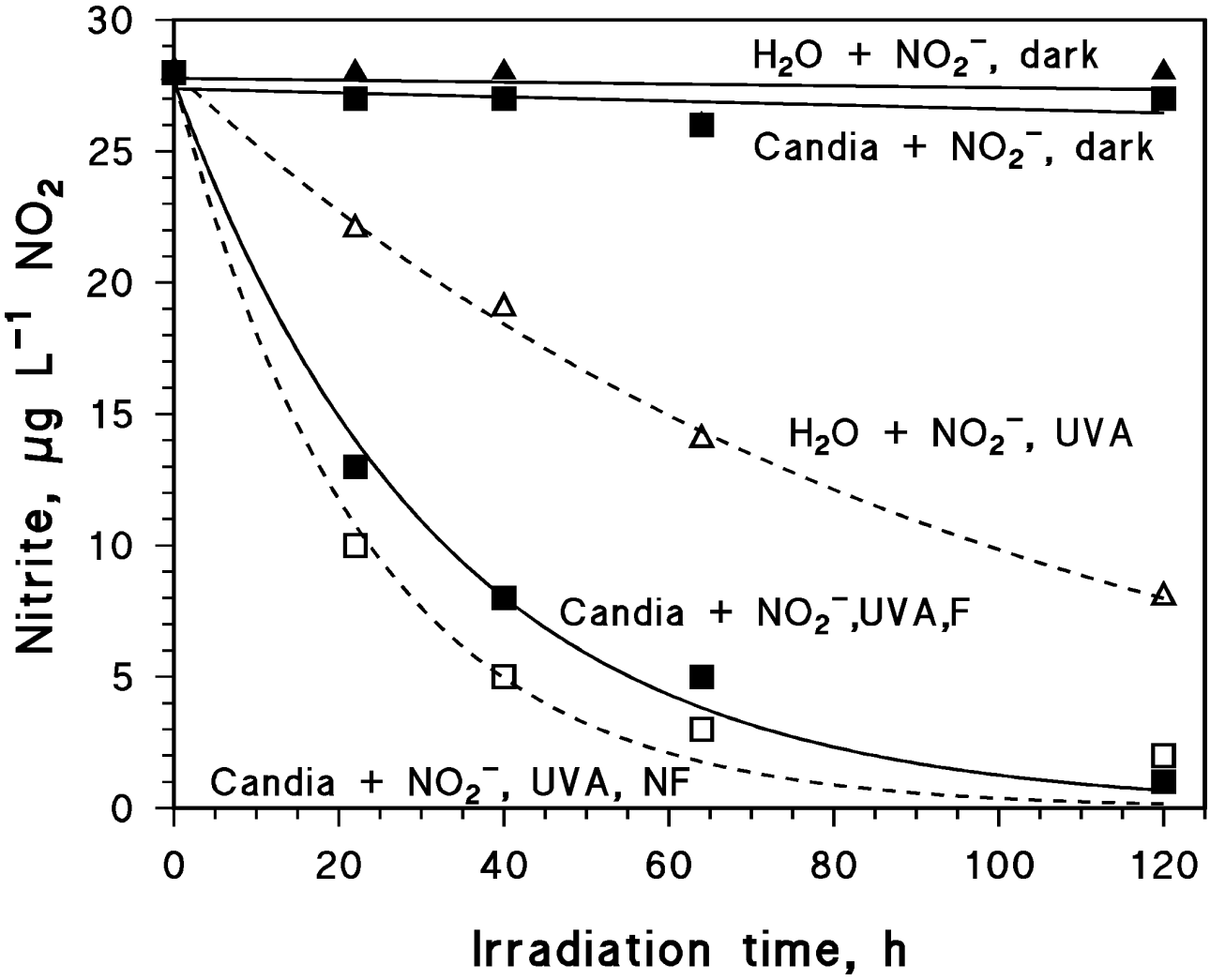

Figure 2. Temporal evolution of 28 μg L^{-1} NO_2^- (0.61 μM), in the dark and under UVA irradiation, in ultra pure water and in the presence of the Lake Candia samples, raw (NF) and filtered (F). Note that there was no difference in the dark runs between the raw and filtered Candia samples.

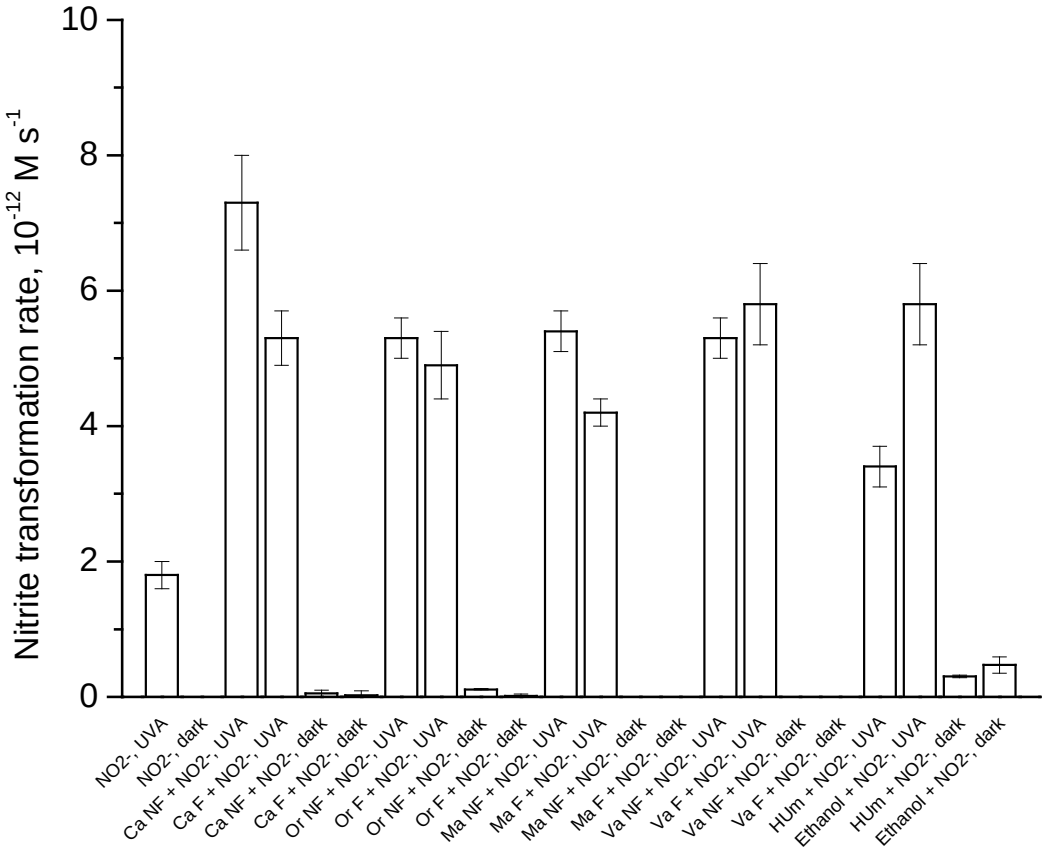

Figure 3. Photodegradation rates of NO_2^- in the samples under study (UVA irradiation and dark controls). The error bounds represent ±σ. NF = unfiltered (raw) sample; F = filtered sample; Ca = Lake Candia; Or = Lake Orta; Ma = Lake Maggiore; Va = Lake Varese.

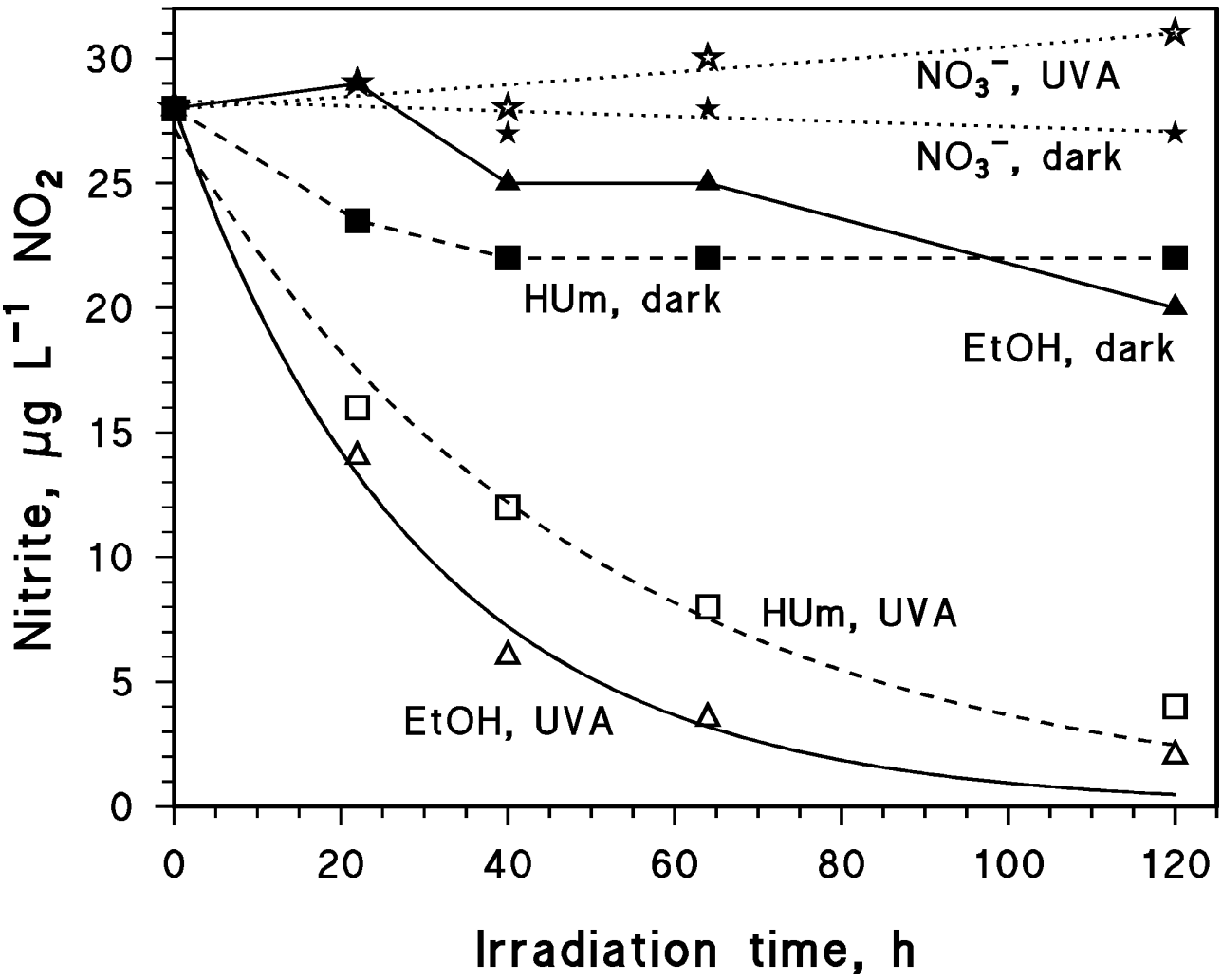

Figure 4. Temporal evolution of 28 μg L^{-1} NO_2^- (0.61 μM), in the dark and under UVA irradiation, in the presence of 10 mg L^{-1} HUm, $1.6 \cdot 10^{-5}$ M NO_3^-, and of $2.0 \cdot 10^{-4}$ M ethanol.