Assessing the potentiality of Romanian surface waters to produce hydroxyl and nitrite radicals

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ASSESSING THE POTENTIALITY OF SURFACE WATER TO PRODUCE $^\bullet$OH AND $^\bullet$NO$_2$ RADICALS.

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Abstract

The concentration of nitrate, nitrite, carbonate, bicarbonate, and the amount of dissolved organic matter were measured in the surface layer of a number of lakes in Romania. These data allowed the modelling of the steady-state concentration of the hydroxyl radical and of nitrogen dioxide under standardised irradiation conditions. The hydroxyl radical is involved in the oxidative degradation of biologically refractory pollutants in surface waters, while nitrogen dioxide has the potential to induce aromatic nitration with generation of toxic and genotoxic nitroaromatic compounds. It was found that the surface water of Lake Techirghiol, located near the Black Sea, has a potentially very elevated photochemical reactivity because of the high concentration of nitrate and nitrite.

Introduction

Photochemical reactions are important removal pathways for biologically refractory compounds in surface waters. They include the direct photolysis of sunlight-absorbing molecules and a number of indirect photochemical processes induced by the excited triplet states (^{3}DOM*) of Dissolved Organic Matter (DOM), and by other reactive transients such as $^\bullet$OH, CO$_3^{-\bullet}$, ^{1}O$_2$, $^\bullet$NO$_2$ and Cl$_2^{-\bullet}$.[1] Some radical species, and most notably CO$_3^{-\bullet}$ and $^\bullet$NO$_2$ can be produced as a consequence of the interaction between $^\bullet$OH and inorganic anions such as carbonate, bicarbonate and nitrite.[2] In the case of $^\bullet$NO$_2$, the direct photolysis of nitrate is also an additional source to the photo-oxidation of nitrite by $^\bullet$OH.[3,4]

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad \Phi_1 = 0.01 \qquad (1)$$

$$NO_2^- + {}^\bullet OH \rightarrow {}^\bullet NO_2 + OH^- \qquad k_2 = 1.0 \times 10^{10}\,L\,mol^{-1}s^{-1} \qquad (2)$$

The radical $^\bullet$OH is the most reactive species in surface waters and can be a significant sink for compounds that are refractory to the other degradation processes, including the photochemical ones.[5] The role of $^\bullet$OH in the more general degradation processes in surface waters is limited by its high reactivity, because it is consumed by major water components such as DOM. This fact limits the steady-state concentration [$^\bullet$OH] to quite low levels, but the hydroxyl radical can still be an important environmental factor when an elevated generation rate is coupled to a moderate or low consumption by DOM or other species.[5-7]

In the case of $^\bullet$NO$_2$, the formation in reactions 1, 2 is accompanied by the consumption upon hydrolysis in aqueous solution[13,14] (reactions 3, 4):

$$2\,^\bullet NO_2 \rightleftarrows N_2O_4 \qquad k_3 = 4.5\times10^8\,L\,mol^{-1}\,s^{-1} \qquad k_{-3} = 6.9\times10^3\,s^{-1} \qquad (3)$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2\,H^+ \qquad\qquad k_4 = 1\times10^3\,s^{-1} \qquad (4)$$

The radical $^\bullet$NO$_2$ can also be involved in the transformation of easy-to-oxidise compounds,[8] but the $^\bullet$NO$_2$-induced nitration of phenolic species to yield toxic and potentially genotoxic nitrophenols is much more important from an environmental point of view.[9,10]

Considering the above-mentioned processes, it has been possible to model the steady-state concentration of both $^\bullet$OH and $^\bullet$NO$_2$ under definite irradiation conditions, namely 22 W m^{-2} sunlight UV irradiance that can be found on 15 July at 45°N latitude at 9 a.m. or 15 p.m. solar time.[11] Under these conditions the steady-state values of [$^\bullet$OH] and [$^\bullet$NO$_2$] in the surface water layer would be[12,13]

$$[^\bullet OH] = \frac{1.7\cdot10^{-7}\,[NO_3^-] + 2.6\cdot10^{-5}\,[NO_2^-] + 5.7\cdot10^{-12}\,NPOC}{8.5\cdot10^6\,[HCO_3^-] + 3.9\cdot10^8\,[CO_3^{2-}] + 1.0\cdot10^{10}\,[NO_2^-] + 5.0\cdot10^4\,NPOC} \qquad (5)$$

$$[^\bullet NO_2] = \sqrt{2.0\cdot10^{-9}\cdot(10^{10}\cdot[^\bullet OH]\cdot[NO_2^-] + 1.7\cdot10^{-7}\cdot[NO_3^-])} \qquad (6)$$

In the case of $^\bullet$OH it was taken into account that it is produced by irradiation of nitrate, nitrite and DOM (quantified as NPOC, Non-Purgeable Organic Carbon, in mg C L^{-1}) and consumed by bicarbonate, carbonate, nitrite and DOM.[12]

It is thus possible to assess the steady-state [$^\bullet$OH] and [$^\bullet$NO$_2$] in the surface water layer from the values of nitrate, nitrite, carbonate, bicarbonate, and NPOC as a measure of DOM. In this paper such an approach was applied to a number of Romanian lakes with the purpose of making a survey of the expected photochemical reactivity of lake water. To our knowledge, this is the first time that the photochemistry of lake water has been considered in Romania. The purpose was the identification of photochemically interesting ecosystems to be subjected to further study.

Results and discussion

Water was sampled from the lake surface layer, and the location of the sampling sites is reported in Figure 1. Table 1 reports the analytical data of the lakes under study, and in particular the values relative to the components of photochemical significance (nitrite, nitrate, DOM, carbonate, bicarbonate). From these values it is possible to derive the steady-state [$^\bullet$OH] and [$^\bullet$NO$_2$] from equations (5) and (6), respectively. These values are also reported in Table 1. As far as [$^\bullet$OH] is concerned, it can be seen that many values are in the 10^{-16} M range. This is due to the fact that the model foresees [$^\bullet$OH] $\approx 10^{-16}$ M if DOM is both the main source and the main sink of the hydroxyl radicals.
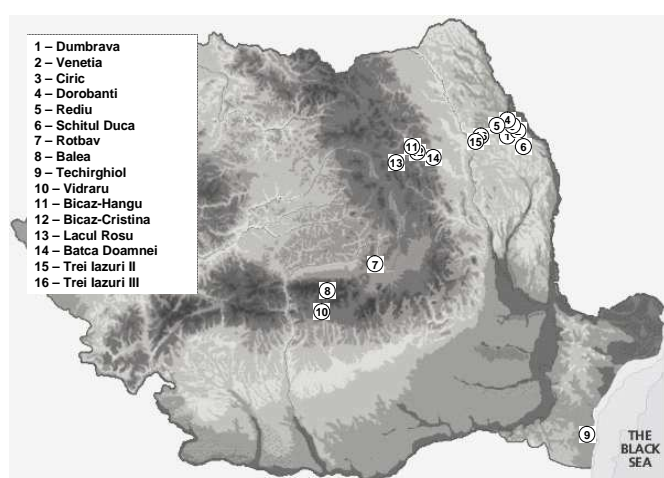

1 – Dumbrava
2 – Venetia
3 – Ciric
4 – Dorobanti
5 – Rediu
6 – Schitul Duca
7 – Rotbav
8 – Balea
9 – Techirghiol
10 – Vidraru
11 – Bicaz-Hangu
12 – Bicaz-Cristina
13 – Lacul Rosu
14 – Batca Doamnei
15 – Trei Iazuri II
16 – Trei Iazuri III

Figure 1. Map of the sampling sites.

This fact can be seen graphically upon adoption of a simplified model, in which [$^\bullet$OH] is approximately expressed as a function of only nitrate (adopting a reasonable correlation between [NO$_3^-$] and [NO$_2^-$]), NPOC, and IC [mg C L^{-1}] = 12000 ([H$_2$CO$_3$] + [HCO$_3^-$] + [CO$_3^{2-}$]):[12]

$$
\begin{cases}
[^\bullet\text{OH}] = \dfrac{3.1\cdot10^{-7}\cdot[\text{NO}_3^-]+5.7\cdot10^{-12}\cdot\text{NPOC}}{\xi(\text{IC})+5.0\cdot10^4\cdot\text{NPOC}+5.2\cdot10^7\cdot[\text{NO}_3^-]} \\[2mm]
\xi(\text{IC}) = \dfrac{\text{IC}}{12000\cdot(10^{-10.2}+10^{-\text{pH}})}\cdot\left(8.5\cdot10^6\cdot10^{-\text{pH}}+0.025\right) \\[2mm]
\text{pH} = 1.95\cdot\left(1-10^{-0.075\cdot\text{ IC}}\right)+6.32
\end{cases}
\qquad (7)
$$

Table 1. Concentration values of the photoactive components in the lake water samples under study. The steady-state concentrations [$^{\bullet}$OH] and [$^{\bullet}$NO$_2$] have been calculated with equations (5) and (6), respectively. They are valid for 22 W m^{-2} sunlight irradiance in the UV (e.g. 15 July at 45°N latitude, at 9 a.m. or 15 p.m.). In the case of Rotbav and Trei lazuri III the concentration of carbonate was negligible because of the low pH values (6.74 and 6.37, respectively).

Lake	Date (dd mmm yy)	[NO$_2^-$], μM	[NO$_3^-$], μM	A$_{285}$, cm^{-1}	NPOC, mg C L^{-1}	[CO$_3^{2-}$], mM	[HCO$_3^-$], mM	[$^{\bullet}$OH], M	[$^{\bullet}$NO$_2$], M
Dumbrava	01 Jul 07	0.98	14.5	0.24	24	1.19	2.63	9.7×10^{-17}	8.2×10^{-11}
Dumbrava	08 Jul 07	0.64	7.9	0.24	24	0.69	3.63	1.0×10^{-16}	6.3×10^{-11}
Dumbrava	15 Jul 07	1.02	11.4	0.22	22	0.44	3.88	1.2×10^{-16}	7.8×10^{-11}
Venetia	01 Jul 07	0.70	1.8	0.23	23	1.19	7.13	8.9×10^{-17}	4.3×10^{-11}
Venetia	06 Jul 07	0.84	6.7	0.19	19	0.81	8.63	9.7×10^{-17}	6.2×10^{-11}
Venetia	08 Jul 07	0.59	11.0	0.18	18	0.95	7.88	8.9×10^{-17}	6.9×10^{-11}
Venetia	26 Sep 07	0.69	6.2	0.15	15	0.94	11.1	8.6×10^{-17}	5.7×10^{-11}
Ciric	06 Jul 07	0.44	9.4	0.12	12	0.56	8.38	9.2×10^{-17}	6.3×10^{-11}
Ciric	08 Jul 07	0.32	18.9	0.19	19	0.69	8.88	9.3×10^{-17}	8.3×10^{-11}
Ciric	26 Sep 07	1.15	6.7	0.16	16	0.23	11.6	1.2×10^{-16}	7.1×10^{-11}
Dorobanti	01 Jul 07	0.75	1.3	0.24	24	0.94	8.63	9.5×10^{-17}	4.3×10^{-11}
Dorobanti	26 Sep 07	3.20	23.6	0.23	23	0.81	13.6	1.4×10^{-16}	1.3×10^{-10}
Rediu	12 Jul 07	1.30	1.6	0.24	24	0.64	7.21	1.1×10^{-16}	5.8×10^{-11}
Schitul Duca	26 Sep 07	7.53	0.6	0.21	21	0.63	2.63	2.2×10^{-16}	1.8×10^{-10}
Rotbav	10 Aug 07	0.97	3.1	0.10	10	< DL	1.64	1.6×10^{-16}	6.4×10^{-11}
Techirghiol	10 Aug 07	17.8	984	0.05	5	0.69	6.63	9.0×10^{-16}	8.0×10^{-10}
Bicaz-Hangu	06 Oct 07	0.52	41.4	0.05	5	0.06	2.88	1.6×10^{-16}	1.2×10^{-10}
Bicaz-Cristina	06 Oct 07	0.34	30.9	0.02	2	0.06	1.88	1.8×10^{-16}	1.1×10^{-10}
Lacul-Rosu	06 Oct 07	1.21	31.7	0.02	2	0.07	2.95	3.0×10^{-16}	1.3×10^{-10}
Batca-Doamnei	07 Oct 07	0.66	25.5	0.02	2	0.07	1.85	2.2×10^{-16}	1.1×10^{-10}
Trei lazuri III	07 Oct 07	0.50	1.0	0.06	6	< DL	3.65	1.4×10^{-16}	4.2×10^{-11}

Figure 2 reports the trend of [$^\bullet$OH], according to equation (7) and as a function of nitrate and NPOC, for IC = 100 mg C L^{-1} that is a representative condition for the lakes Venetia, Ciric, Dorobanti and Rediu. It is apparent from Figure 2 that [$^\bullet$OH] approaches 10^{-16} M at elevated NPOC. It should be considered that, although the model equations (5) and (7) reproduce an average behaviour of DOM,[11,12] the features of DOM itself can vary at a significant extent in different water bodies. An index of the nature of light-absorbing DOM is given by E_2/E_3, namely the ratio between the absorbance values at 250 and 365 nm.
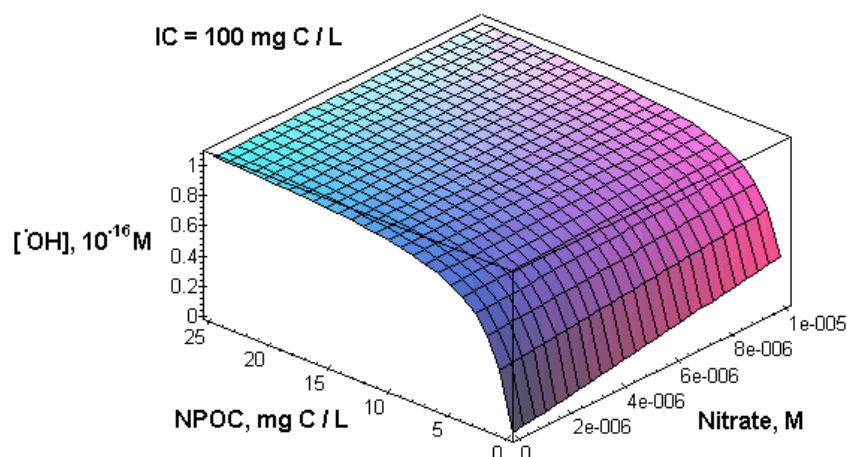

Figure 2. Trend of the steady-state [$^\bullet$OH] as a function of nitrate and NPOC, for IC = 100 mg C L^{-1}, under 22 W m^{-2} sunlight UV irradiance.

E_2/E_3 is inversely proportional to the size and the degree of aromaticity of the DOM molecules, and for instance it would be lower than 3.5 for humic and > 3.5 for fulvic acids.[15] Figure 3 reports the trend of A_{250nm} vs. A_{365nm} for the lake water samples under study. There is very reasonable correlation (r^2 = 0.91), suggesting that the distribution of the E_2/E_3 values is not very wide as shown in the Figure inset. This could imply that the variability of DOM is not excessive in the samples, which justifies the use of the model equations (5) and (7).

Interestingly, [$^\bullet$OH] would reach relatively elevated values in the samples from Lacul-Rosu (around 3×10^{-16} M) and lake Techirghiol (around 9×10^{-16} M). To have an idea of the meaning of such values, Figure 4 reports the lifetime of some water pollutants (in summer sunny days equivalent to 15 July at 45°N latitude) as a function of the steady-state [$^\bullet$OH] under 22 W m^{-2} sunlight UV irradiance (for the rationale of this approach see [12]). The [$^\bullet$OH] levels expected for representative lake water samples are also reported (the lakes are identified as numbers as of Figure 1).
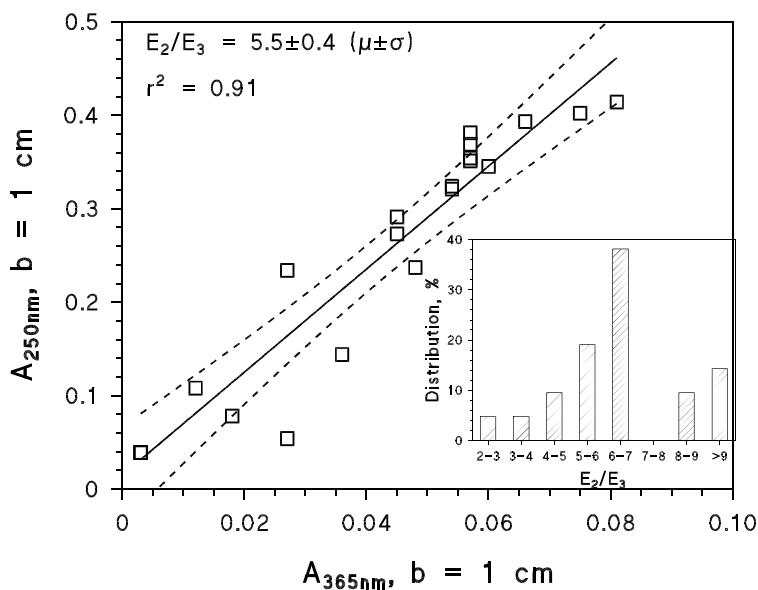
Figure 3. Trend of the values of A_{250nm} vs. A_{365nm} for the studied lake water samples. The solid line represents the regression line, the dashed curves the corresponding 95% confidence limits. Note the good correlation ($r^2 = 0.91$). The inset shows the distribution plot of E_2/E_3 for the samples. Note that around 60% of the data is included in the interval of 5 to 7.
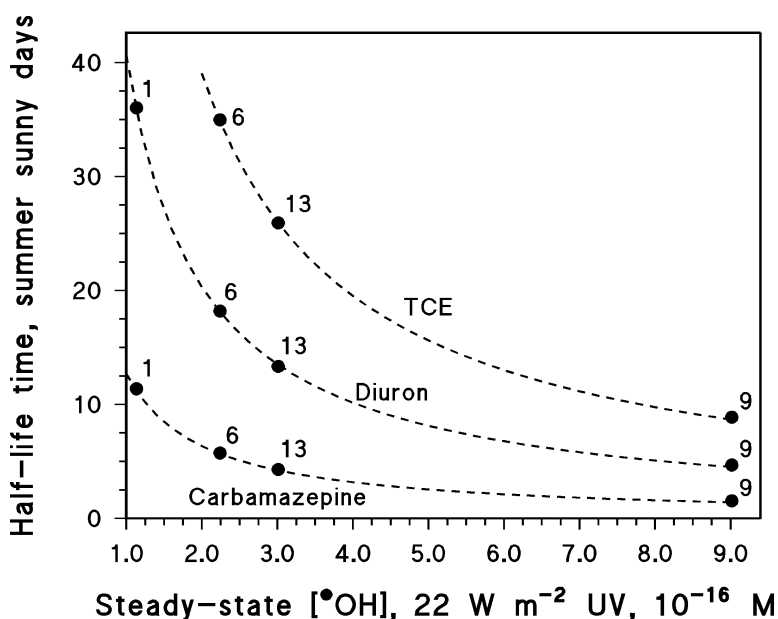

Figure 4. Half-life time (in summer sunny days equivalent to 15 July at 45°N) as a function of the steady-state [$^{\bullet}$OH] under 22 W m^{-2} sunlight UV irradiance, for carbamazepine, diuron and tetrachloroethylene (TCE). The second-order rate constants for the reaction of these compounds with $^{\bullet}$OH are 1.6×10^{10}, 5×10^9, and 2.6×10^9 M^{-1} s^{-1}, respectively.[2,16] The steady-state [$^{\bullet}$OH] calculated for some lake water samples is also reported (the numbers referring to the lakes are the same as in Figure 1).

The lifetime is referred to the water surface layer and it would vary from about 80 days for tetrachloroethylene (TCE) in lake Dumbrava to about one day and a half for carbamazepine in lake Techirghiol. The latter seems to be characterised by an elevated photochemical reactivity, most likely caused by the very elevated concentration of both nitrate and nitrite. Such a water system deserves further studies as far as photochemistry is concerned. Interestingly, Lake Techirghiol is also characterised by an elevated salinity. This fact could be important for photochemical processes because the interaction between Fe(III) oxides and Cl^- yields the reactive radical species $Cl_2^{-\bullet}$,[13] a powerful monoelectronic oxidant.[8]

Lake Techirghiol is also interesting because the calculated $[^\bullet NO_2]$ is much higher compared to the other lakes. This fact points to a significant potential to induce aromatic photonitration processes. When considering the nitration reaction (8) of phenol by $^\bullet NO_2$ in the aqueous solution,[17] one finds that the time required to transform 10^{-8} M phenol into 10^{-9} M of 2- and 4-nitrophenol is (in seconds of irradiation under 22 W m^{-2} sunlight UV): $t_N = 3.1 \times 10^{-5} [^\bullet NO_2]^{-1}$.
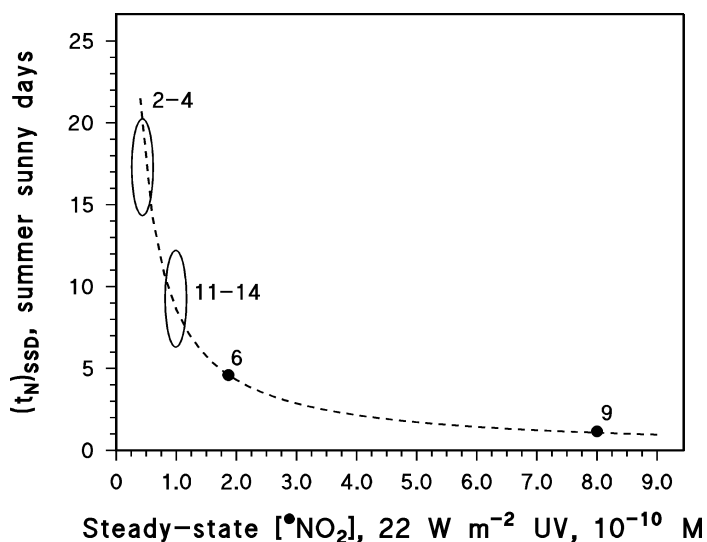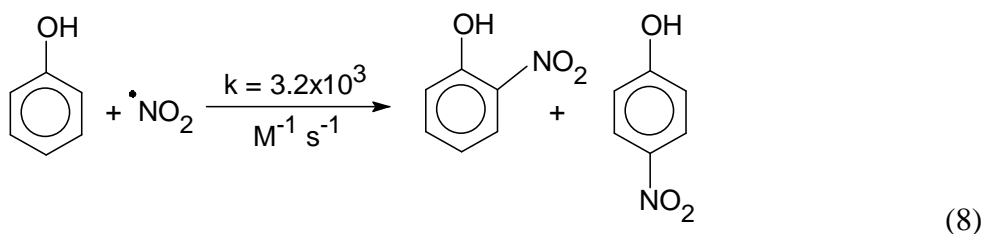

$$(8)$$

Figure 5. Time (in summer sunny days equivalent to 15 July at 45°N) required to transform 10^{-8} M phenol into 10^{-9} M of 2- and 4-nitrophenol, as a function of the steady-state $[^\bullet NO_2]$ under 22 W m^{-2} sunlight UV. The $[^\bullet NO_2]$ values calculated for some lake water samples are also reported (see Figure 1 for the correspondence between lakes and numbers).

Moreover, considering that the UV energy emitted in the whole sunny day of 15 July at 45°N is equivalent to 10 h irradiation at 22 W m^{-2} UV, the corresponding nitration time in summer sunny day equivalents (SSD) is: $(t_N)_{SSD} = 8.6 \times 10^{-10}$ [$^{\bullet}NO_2$]$^{-1}$. Figure 5 reports $(t_N)_{SSD}$ as a function of the steady-state [$^{\bullet}NO_2$] under 22 W m^{-2} sunlight UV. In the photoactive surface layer of lake Terchighiol the described photonitration reaction would take place in less than 2 days, therefore pointing to a considerable potential for aromatic photonitration processes.

Conclusions

From the analytical data of nitrite, nitrate, NPOC, carbonate and bicarbonate of a series of Romanian lakes it was possible to carry out an assessment of the expected photochemical reactivity of the surface water layers. The sample from Lake Techirghiol appeared very different from the others because of a peculiarly elevated [$^{\bullet}OH$] and [$^{\bullet}NO_2$]. The water chemical composition suggests that the photochemistry of this lake would be dominated by nitrate and nitrite as $^{\bullet}OH$ and $^{\bullet}NO_2$ sources. In such an environment both the $^{\bullet}OH$-induced transformation of organic molecules (including pollutants) and aromatic photonitration processes yielding toxic nitrated compounds are expected to play an important role. It is clear that additional studies would be required to better characterise such a water system, and to see at what extent the generation of harmful species and their expected fast degradation would compensate for each other.

Experimental

Lake water was sampled from the surface layer by means of a Teflon bottle, and transported refrigerated to the laboratory where it was vacuum filtered on cellulose acetate filters (0.45 μm pore diameter) before any other processing. Filtration was motivated by the sake of biological stabilisation and to avoid damage to the analytical apparatus. Some samples were transported to Italy under refrigeration and promptly analysed upon delivery.

Carbonate and bicarbonate were determined by potentiometric titration with a Meter Lab ION 450 (Ion analyser, Radiometer analytical) and a PHC 4001-9 type glass electrode. Most of the analysed samples were characterised by pH values above 8.3, which suggest the presence of both carbonate and bicarbonate species in the investigated systems. For each run a 100 mL sample of the natural water under investigation was titrated with 0.1 N HCl to the second end point of the titration curve. The estimation of the carbonate-bicarbonate system was performed on the basis of the

equivalent volume for the first and second titration stage. Based on triplicate measurements, the equivalent volumes were characterised by a dispersion of V_{eI} ±0.144 mL and V_{eII} ±0.144 mL (± standard deviation of triplicate measurements).

Nitrate was determined by three-wavelength photometry, measuring the absorbance of the lake water over a 1 cm path length at the wavelengths of 210, 220 and 230 nm. The molar concentration of nitrate was then determined as: $[NO_3^-] = (A_{210nm} - 1.60 \, A_{220nm} + 0.26 \, A_{230nm})/2396$.[18] This approach has been proved suitable for the determination of nitrate in lake water from the Piedmont region.[19] The three-wavelength photometry accounts for the possible spectral interference by dissolved organic matter (DOM), and the results obtained for NO_3^- were comparable with the quantification of nitrate by ion chromatography. For the analysis it was used a CINTRA 10e UV-Vis spectrophotometer, and for an appropriate spectra recording the samples were diluted three times.

Nitrite was quantified by pre-column derivatisation with 2,4-dinitrophenylhydrazine in HCl, followed by analysis in High Performance Liquid Chromatography with UV detection (HPLC-UV). The reaction yields an azide that can be eluted over a reverse-phase column and detected at 307 nm. The instrument used during the investigation was an Agilent High Performance Liquid Chromatograph (Agilent 1100 Series) equipped with a G1312 Bin HPLC pump, a UV-Vis (Agilent G1365B MWD) spectrophotometer detector, and a Rheodyne 7725i injection valve with a loop volume of 20 µL. An Agilent ZORBAX SB-C18 reverse-phase column (150 mm × 4.60 mm i.d., 5 µm particle size) was used for the analysis. The standard deviation of repeated runs was around 1-2%, and the DL was about 5 mg NO_2^- L^{-1}. Elution was carried out with a 50:50 mixture of acetonitrile: phosphate buffer (pH 3) at 1.0 mL min^{-1} flow rate, with detection at 307 nm. Under these conditions the retention time of the azide was 4.87 min, and the column dead time was 1.31 min.

The analysis of NPOC was carried out on some samples with a Hitachi TOC 5000 analyser, upon sample acidification to pH 2 by $HClO_4$ and 20 min sparge time with zero-grade air (SIAD, Bergamo, Italy) to drive out the CO_2 formed from inorganic carbon. It followed the analysis of the non-volatile organic carbon by catalytic combustion and non-dispersive infra-red photometry. The standard deviation of repeated runs was around 1-2%, and the DL was about 0.1 mg C L^{-1}. It was found that the NPOC values of the samples correlated well with their absorbance at 285 nm, over a path length of 1 cm (A_{285}). The ratio between A_{285} and NPOC depends on the nature of the DOM,[15] and for the samples under study it was found that A_{285} $[cm^{-1}]$ = 0.01 NPOC [mg C L^{-1}]. Such a ratio is comparable with that previously measured in lake water from Piedmont,[19] and was used for an assessment of the DOM content in the samples.

References

1. J. Hoigné, "Aquatic Chemical Kinetics", ed. W. Stumm, Wiley, NY, 1990, p. 43-70.
2. G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, **1988**, *17*, 1027-1284.
3. J. Mack and J. R. Bolton, J. Photochem. Photobiol. A: Chem., 1999, 128, 1-13.
4. C. Minero, V. Maurino, E. Pelizzetti and D. Vione, *Environ. Sci. Pollut. Res.*, **2007**, *14*, 241-243.
5. P. L. Brezonik and J. Fulkerson-Brekken, *Environ. Sci. Technol.*, **1998**, *32*, 3004-3010.
6. K. Takeda, H. Takedoi, S. Yamaji, K. Ohta and H. Sakugawa, *Anal. Sci.*, **2004**, *20*, 153-158.
7. J. M. Allen, S. Lucas and S. K. Allen, *Environ. Toxicol. Chem.*, **1996**, *15*, 107-113.
8. C. Minero, V. Maurino, E. Pelizzetti and D. Vione, *Environ. Sci. Pollut. Res.*, **2006**, *13*, 212-214.
9. D. Vione, V. Maurino, C. Minero and E. Pelizzetti, *Environ. Sci. Technol.*, **2005**, *39*, 7921-7931.
10. D. Vione, V. Maurino, C. Minero and E. Pelizzetti, *Ann. Chim. (Rome)*, **2002**, *92*, 919-929.
11. D. Vione, G. Falletti, V. Maurino, C. Minero, E. Pelizzetti, M. Malandrino, R. Ajassa, R. I. Olariu and C. Arsene, *Environ. Sci. Technol.*, **2006**, *40*, 3775-3781.
12. C. Minero, V. Lauri, V. Maurino, E. Pelizzetti and D. Vione, *Ann. Chim. (Rome)*, **2007**, *97*, 685-698.
13. S. Chiron, C. Minero and D. Vione, *Environ. Sci. Technol.*, **2007**, *41*, 3127-3133.
14. M. Fischer and P. Warneck, *J. Phys. Chem.*, **1996**, *100*, 18749-18756.
15. J. L. Oliveira, M. Boroski, J. C. R. Azevedo and J. Nozaki, *Acta Hydrochim. Hybrobiol.*, **2006**, *34*, 608-617.
16. S. Canonica, B. Hellrung, P. Müller and J. Wirz, *Environ. Sci. Technol.*, **2006**, *40*, 6636-6641.
17. C. Minero, S. Chiron, G. Falletti, V. Maurino, E. Pelizzetti, R. Ajassa, M. E. Carlotti and D. Vione, *Aquat. Sci.*, **2007**, *69*, 71-85.
18. I. E. Kalinichenko and L. NH. Demutskaya, *J. Analyt. Chem.*, **2004**, *59*, 211-214.
19. C. Minero, V. Lauri, G. Falletti, V. Maurino, E. Pelizzetti and D. Vione, *Ann. Chim (Rome)*, **2007**, *97*, 1107-1116.