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PHOTOSTABILITY AND PHOTOLABILITY OF DISSOLVED ORGANIC MATTER UPON IRRADIATION OF NATURAL WATER SAMPLES UNDER SIMULATED SUNLIGHT

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Abstract. In this study the photostability/photolability of Dissolved Organic Matter (DOM) was assessed in both lake and groundwater. The latter could undergo significant photoprocessing when drawn to the surface for agricultural purposes. DOM was generally photostable in lake and photolabile in groundwater. In the latter case photolability would be linked with the amount and the nature of DOM in the studied groundwater samples. DOM in lake water became photolabile upon acidification. The parallel decrease of both Total Organic Carbon (TOC) and Non-Purgeable Organic Carbon (NPOC) suggests that actual photomineralisation took place in the samples. The $\bullet\text{OH}$ radicals play a secondary role into DOM photomineralisation in lake water, despite the fact that their generation rate considerably increases at acidic pH. The role of $\bullet\text{OH}$ is also minor in the photomineralisation of DOM contained in nitrate-rich groundwater.

Key words. Environmental photochemistry, DOM phototransformation, TOC, NPOC.

Introduction

Dissolved Organic Matter (DOM) is a major form in which organic carbon is present in natural waters. It consists of autochthonous (aquagenic) organic compounds such as proteins, peptides, polysaccharides, and of more biologically refractory (allochthonous) material (Oliveira et al., 2006). The latter is mainly made up of humic and fulvic acids, which are major radiation absorbers in the UV-Vis region (Richard et al., 2004). The transformation of DOM by micro-organisms, solar light, or both (Malouki et al., 2003) is an important process in surface waters as it influences DOM bio-availability and the penetration depth of solar radiation inside the water body, most notably as far as the UV component is concerned (Markager and Vincent, 2000).

The photochemical processing of DOM is known to yield readily bio-available fractions, among which low-molecular-weight organic acids, partially arising from the oxidation/depolymerisation of much larger molecules, but also more refractory compounds that undergo further biological processing with difficulty (Brinkmann et al., 2003a). It has also been found that the formation of reactive oxygen species upon irradiation of surface water inhibits the utilisation of DOM by micro-organisms (Kaiser and Sulzberger, 2004). Moreover, because the DOM fraction that absorbs radiation undergoes the fastest phototransformation, DOM photobleaching is observed under sunlight. Considering that coloured DOM is the main radiation absorber in surface waters, as a result of irradiation a consistent decrease of sample absorbance is usually observed (Brinkmann et al., 2003b). This finding could have important consequences on ecosystems because increased penetration of UVB radiation in surface water bodies could damage aquatic organisms (Gao and Zepp, 1998; Epp et al., 2007).

Along with photobleaching, irradiation of DOM by sunlight causes a variable degree of photomineralisation. Photochemical oxidation of DOM leads to oxygenated hydrocarbons, which are further transformed into CO₂ (Zuo and Hoigné, 1994). A parallel transformation route gives CO. A substantial fraction of photogenerated CO is released into the atmosphere before undergoing further oxidation in solution (Zou and Jones, 1997), which means that the final oxidation to CO₂ will take place in the gas phase (Finlayson-Pitts and Pitts, 1986).

The pathways involved in DOM photoprocessing have been the focus of various studies, but a general interpretation framework is not yet available. However, there is a general consensus that iron plays a major role in the photobleaching of DOM (Brinkmann et al., 2003b) and in the photochemical generation of short-chain fatty acids and of carbon monoxide (Zuo and Jones, 1997; Brinkmann et al., 2003a). Iron speciation is likely to deeply influence DOM photoprocessing, because correlation between phototransformation rate and total Fe content has not always been

detected (Bertilsson and Tranvik, 2000). Additionally, a Fe-independent pathway of DOM phototransformation is likely operational in surface waters (Brinkmann et al., 2003a).

Recently, in a work that has been focused on $\bullet\text{OH}$ quantification upon irradiation of natural water samples, we have found that DOM was photostable in surface lake water and photolabile in groundwater. In the latter case a 20-30% of organic carbon decrease has been observed upon 60 hour irradiation under simulated sunlight (Vione et al., 2006). The comparison between lake and groundwater was made problematic by the elevated amount of nitrate in the latter, over two orders of magnitude higher than in lake water. Nitrate is a well-known photochemical source of $\bullet\text{OH}$ radicals in solution (Brezonik and Fulkerson-Brekken, 1998), and DOM as the main $\bullet\text{OH}$ sink would be transformed at a certain extent. While nitrate at the typical lake water levels (often lower than 0.1 mM) has been reported to cause insignificant photochemical processing of DOM (Brinkmann et al., 2003a), the same might not be true of nitrate-rich groundwater that is characterised by an elevated formation rate of $\bullet\text{OH}$ upon irradiation. Indeed, hydroxyl radicals are extensively employed in Advanced Oxidation Processes aimed at the photochemical mineralisation of organic pollutants (Legrini et al., 1993). Accordingly, two alternative hypotheses could account for the observed photolability of DOM in groundwater: (i) photolability is caused by the elevated $\bullet\text{OH}$ photoproduction rate upon nitrate photolysis; (ii) photolability is due to a different nature of DOM in groundwater compared to lake water. Indeed, groundwater could contain a good amount of photolabile DOM that in the aquifers would be protected from photodegradation. In the surface lake water layer, photolabile DOM could be effectively photodegraded and therefore be present at very low concentration. For instance, the DOM of the deep ocean has been found to react with $\bullet\text{OH}$ much faster than that of the surface (Mopper and Zhou, 1990), and the same is true of groundwater compared to lake-water DOM (Vione et al., 2006).

The purpose of the present paper is to get further insight over the issue of DOM photostability and photolability in lake and groundwater. To account for the different nitrate levels, lake water was irradiated as it was and after spiking with nitrate, to reproduce the levels that can be found in nitrate-rich groundwater. In this way, possible differences in behaviour could be no longer attributed to nitrate, and its role toward DOM photomineralisation would be conclusively assessed.

Nitrate-rich groundwater was sampled in the rural village of Letcani, NE Romania. Here the aquifers are a major source of irrigation water, for which purpose groundwater is pumped to the surface and in many cases stored in open-top basins, where it can be illuminated by sunlight. Moreover, the village is partially placed on a small hill dominating the surrounding plain. A few springs in the lower part of the hill are fed by groundwater that can therefore reach the surface. This study assessed the possible consequences of the exposure to sunlight of groundwater DOM.

Experimental

Reagents and materials

Supplier and purity grade of the adopted reagents are reported in Vione et al. (2006) and in Minero et al. (2007a).

Sampling sites

Lake water samples were taken in Piedmont (NW Italy), with the single exception of Lake Moncenisio that is located in France, a few kilometres from the Italian border. Latitude was between 45° and 45°20' N, longitude in the 7-8° E range. Other details are reported in Table 1. Groundwater was sampled in the rural village of Letcani, near the town of Iasi (NE Romania), on 11 March 2006. Co-ordinates of the groundwater sampling sites were included between N47°10'-47°15' and E 27°22'-27°30'. Four sampling sites for groundwater were chosen out of a total of 15, which have been identified in the village and subjected to monitoring for the nitrate concentration. The criterion of choice was that of having a wide range of nitrate levels. The sampling sites chosen for the present study were within 1 km distance. The depth of the corresponding wells was around 10 m.

Sampling procedures and sample treatment

Lake water was sampled from the surface layer and kept refrigerated during transport to the laboratory. It was then vacuum filtered on 0.22 µm cellulose acetate membranes (Millipore) to achieve biological stabilisation, and kept refrigerated till subsequent use. Samples were taken in the morning and filtration completed within the same day. Whenever possible, sampling was carried out on Monday morning and irradiation experiments completed within the same week, with the exception of some remote high-mountain lakes that were reached in a single sampling campaign. In such cases the irradiation experiments were carried out within three weeks from sampling. Some water samples were acidified with HClO₄ before or after filtration. In the former case, to achieve dissolution of colloidal Fe(III) species that would otherwise be removed by filtration, the addition of HClO₄ took place on arrival of the sample to the laboratory; it followed overnight stirring and vacuum filtration.

In the case of groundwater, filtration was carried out at the University of Iasi. It followed air travel to Italy under refrigeration and fridge storage till irradiation (within one to four weeks).

Analytical procedures

The absorption spectra of the studied water samples were measured with a Varian Cary 100 Scan UV-Vis spectrophotometer. pH was measured with a Metrohm combined glass electrode connected to a Metrohm 713 pH meter.

Nitrate was determined by ion chromatography (detection limit 1 μM) using a Dionex DX 500 instrument equipped with Rheodyne injector (loop volume 20 μL), LC30 oven, GP40 gradient pump, Dionex Ion Pac AG4A-SC 4-mm (10-32) guard column, AS4A-SC 4-mm (10-32) column, ASRS-ULTRA 4-mm conductivity suppression unit and ED40 electrochemical detector. Isocratic eluent (1.0 mL min^{-1} flow rate, elution and detection at 30°C) was a mixture of 5 mM K_2CO_3 and 12 mM NaHCO_3 . Nitrate retention time was 2.50 min and column dead time 1.50 min. The nitrate values of the studied lake water samples are reported in Table 1.

Non-Purgeable Organic Carbon (NPOC) was measured with a Shimadzu TOC-5000 analyser, acidifying the sample (10 mL) with two drops of concentrated (70%) HClO_4 and applying a 20-min sparge time with zero-grade air to drive out CO_2 . Unfortunately this procedure would also eliminate the volatile organic compounds, which implies that the Total Carbon analysis of the samples thus treated gives the total amount of non-volatile organic carbon or NPOC. These data are reported in Table 1. An alternative though time-consuming procedure was also applied to remove most of the inorganic carbon (IC) in a milder fashion, to maintain a higher fraction of volatile organic compounds inside the sample. In such a case the lake water samples were acidified with HClO_4 , and left for three days in closed containers under magnetic stirring in the dark. The Total Organic Carbon was then measured as $\text{TOC} = \text{TC} - \text{IC}$. Analyses indicated that the IC was not totally removed upon three-day stirring, but it was reduced at a sufficient extent to enable TOC measurement. This is usually not feasible in untreated surface-water samples where $\text{IC} \gg \text{TOC}$, and $\text{TC} \approx \text{IC}$ as a consequence.

Total Fe was measured in some samples with a Varian Liberty 100 Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES), equipped with a Czerny-Turner monochromator, Sturman-Masters spray chamber, V-groove nebuliser and a 40.68 MHz radio-frequency generator. Instrumental conditions were: plasma power 1.0 kW, nebuliser pressure 150 kPa, sample aspiration rate 2 mL min^{-1} , auxiliary argon flow 1.5 L min^{-1} . Detection wavelength was 259.94 nm.

Nitrite was measured in some samples adopting a pre-column derivatisation procedure with 2,4-dinitrophenylhydrazine in acidic solution by HCl (10 min contact time; Kieber and Seaton, 1996), yielding the corresponding azide by reaction with HNO_2 . It followed HPLC-UV analysis with a Merck-Hitachi chromatograph equipped with AS2000A autosampler (100 μL volume was chosen), L-6200 and L-6000 pumps for high-pressure gradients, L-4200 UV-Vis detector, and RP-C18 LiChrocart column (VWR Int., 125 \times 4 mm) packed with LiChrospher 100 RP-18 (particle diameter 5

µm). Isocratic elution was carried out with a 50:50 mixture of CH₃CN : aqueous H₃PO₄ (pH 2.8) at a flow rate of 1.0 mL min⁻¹. The retention time of the azide was 4.0 min, column dead time 0.9 min, and detection wavelength 307 nm. The main factor controlling the detection limit of nitrite (0.03 µM) under these circumstances is the formation of the azide upon reaction between ambient nitrogen dioxide and 2,4-dinitrophenylhydrazine in the stock solution. The azide peak was therefore detectable in the blanks. Exploiting the fact that 2,4-dinitrophenylhydrazine is positively charged under sufficiently acidic conditions (3 M HCl), but the azide is neutral, liquid-liquid extraction of the derivatisation reagent with CCl₄ before each analysis is strongly recommended to reduce the problem (Kieber and Seaton, 1996; Minero et al., 2007a).

Irradiation experiments

Irradiation was carried out in magnetically stirred, cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height) under a solar simulator (Solarbox, CO.FO.ME.GRA., Milan, Italy) equipped with a 1500 W Philips xenon lamp and a 315 nm cut-off filter. Irradiation intensity was 12 W m⁻² in the wavelength range 290-400 nm, measured with a CO.FO.ME.GRA. power meter. A summer sunny day such as 15 July at 45°N latitude would correspond to 17.5 h steady irradiation under the lamp. Typical irradiation experiments lasted 90-95 hours. The temperature of the irradiated samples was around 30-35°C. Dark experiments were also carried out in closed vials, wrapped with aluminium foil and placed under the same lamp.

To obtain the kinetics of DOM photoprocessing, the time trend of NPOC was fitted with equations of the form $NPOC_t = NPOC_0 \exp(-k_{NPOC} t)$, where NPOC_t (in mg C L⁻¹) is the measured value of NPOC after the irradiation time t (in h), NPOC₀ is the initial value (in mg C L⁻¹), and k_{NPOC} (in h⁻¹) is the pseudo-first order rate constant. In some cases it was useful to assess the rate of NPOC decrease in [mol C L⁻¹ s⁻¹]. This was obtained as $r_{NPOC} = 2.31 \times 10^{-8} k_{NPOC} NPOC_0$.

The measurement of the initial formation rate of •OH was carried out in some samples using the transformation reaction of benzene into phenol, induced by •OH and with 95% yield (Takeda et al., 2004). Samples were added with excess benzene (3 to 4 mM) and stirred overnight before irradiation to allow dissolution. The initial formation rate of phenol, r_{Phenol} [M s⁻¹] was measured as the initial slope of the time evolution curve of phenol with irradiation (concentration vs. time). Taking into account the 95% yield of the reaction, the formation rate of •OH under irradiation is $r_{\bullet OH} [M s^{-1}] = 1.05 r_{Phenol}$. Further details of the measurement principle are given in the Supporting Information to Vione et al. (2006).

Results and discussion

Time trend of NPOC upon irradiation of lake water.

As a general trend, DOM in lake water was photochemically stable under the adopted irradiation conditions and irradiation time. Little difference in the trend of NPOC could be observed between the irradiated samples and the dark controls. As an example, the time trend of NPOC in the samples taken from the lakes Candia (spring) and Viverone are reported in Figure 1. Figure 2 reports the trend of NPOC for the samples of Lake Grande in Avigliana and Candia (winter). In the latter two cases the lakes had an extensive ice cover, completely absent in the samples of Figure 1.

The NPOC showed a certain decrease under irradiation in some of the samples spiked with 0.01 M nitrate (see for instance Figures 1,2). Overall, a slight nitrate effect could be evidenced upon irradiation of samples from the lakes Candia (both samplings), Avigliana Grande (ice-covered, winter sampling), and Ciardonnet (covered with ice for most of the year 2006). By contrast, negligible nitrate effect was observed for the lake Avigliana Piccolo (covered with ice) and for the ice-free lakes Viverone, Avigliana Grande (spring sampling), Moncenisio and Laus.

The irradiation results suggest that 0.01 M nitrate is somewhat more likely to induce a limited NPOC decrease in samples from ice-covered lakes. A possible effect of the ice cover could be that of shielding sunlight, protecting photolabile organic compounds from degradation. These compounds could undergo transformation upon irradiation in the laboratory, in particular when nitrate was added to the samples. However, the spike with 0.01 M NO_3^- would represent an increase of over two orders of magnitude, compared to the natural nitrate levels of the studied samples (see Table 1). Typical $[\text{NO}_3^-]$ in the eutrophic Lake Greifensee (Switzerland) in the '80s was around 10^{-4} M (Zepp et al., 1987), which is also the upper level recently found in Piedmont lakes (Vione et al., 2006). Higher nitrate levels, up to 10^{-3} M, can be detected in river water draining urban or agricultural areas (Brezonik and Fulkerson-Brekken, 1998; Chiron et al., 2007). Considering the small or no effect of 0.01 M nitrate on NPOC decrease, it can be inferred that NO_3^- would play a minor role in DOM photoprocessing in most surface waters.

Figures 1,2 show a marked decrease of NPOC upon irradiation of the acidified lake water samples, and the decrease is significant compared to the dark controls. Figure 3 reports the absorption spectra of natural and acidified lake water in the environmental UV range, where DOM is the major radiation absorber (Brinkmann et al., 2003b), together with the emission spectrum of the adopted solar simulator. No difference between natural and acidified samples could be detected in the case of Lake Viverone and Lake Candia (February 2006 sample). Also for Lake Candia, May 2006, the spectral changes upon acidification were very limited. In contrast, the sample from Lake Avigliana Grande showed a significantly different spectrum when acidified. In the case of Lake

Avigliana Piccolo (data not shown), there was a significant NPOC decrease upon irradiation of the acidified sample, and no spectral changes upon acidification. Overall, variation of the absorption spectrum upon acidification seems not to be connected to the decrease of NPOC under irradiation.

The photolability of DOM in acidified lake water has already been reported (Anesio and Graneli, 2003). Comparison between irradiation experiments and dark controls suggests that the decrease of NPOC is not due to the precipitation of DOM on the photoreactor walls in acidic solution. Alternative explanations are actual DOM photomineralisation into CO₂ (and/or CO), and the generation of volatile compounds (e.g. short-chain carboxylic acids, Brinkmann et al., 2003a) that could be stripped off the acidic solution during the measurement of NPOC.

To get additional information about DOM in the studied samples, in addition to the standard NPOC measurements an alternative procedure was followed, consisting of sample acidification plus three-day stirring in the dark to drive out most of the CO₂ formed, and final TOC (TC-IC) analysis. Figure 4 shows the correlation between TOC₀ and NPOC₀; on average, TOC₀ = 1.33±0.07 NPOC₀ (μ±σ). This is a further confirmation that the loss of DOM by precipitation in acidic solution is not an important process. Moreover, the TOC₀/NPOC₀ ratio indicates that at least 25% of the DOM in the studied samples was made up of compounds that can be stripped off the acidic solution by the air flow adopted in the NPOC measures. The determination of TOC was also carried out as a function of the irradiation time of the acidified samples from Lake Avigliana Grande and Lake Candia. The time trend of TOC is reported in Figure 5A and 5B for each sample, and it is compared to the corresponding time trend of NPOC. A parallel decrease of TOC and NPOC could be observed in both samples. The adopted method for the measurement of TOC would limit the loss of volatile organic compounds. Accordingly, the decrease of TOC upon irradiation of the acidified samples could be attributed at least in part to actual mineralisation, and not only to the loss of volatile compounds (e.g. short-chain carboxylic acids) under acidic conditions.

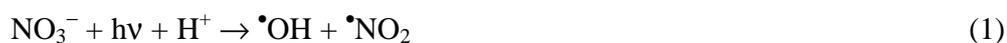
Figure 6 shows the time trend of NPOC upon irradiation of samples from Lake Candia and Lake Moncenisio. The samples have been acidified, either before filtration (abf) or after filtration (aaf). It is apparent from Figure 6 that the decrease of NPOC is mainly due to irradiation (by comparison with the dark controls) and is more marked in the abf compared to the aaf samples. An interesting difference is that the total Fe concentration was generally higher in the abf samples, which is reasonable because filtration in the aaf case would remove part of the colloidal Fe(III). Acidification before filtration would allow dissolution of Fe(III) colloids and prevent their loss by filtration. The total Fe level passed from 6.8×10⁻⁷ (aaf) to 1.5×10⁻⁶ M (abf) for Lake Candia, and from <1.8×10⁻⁷ to 3.2×10⁻⁶ M for Lake Moncenisio. Also note that the photoinduced decrease of NPOC was very limited in the aaf sample from Lake Moncenisio, where Fe was below detection limit. Iron could play a significant role in DOM photoprocessing, as reported in previous studies (Zuo and Jones,

1997; Brinkmann et al., 2003a/b), in particular under acidic conditions (Anesio and Graneli, 2004). Additionally note that NPOC₀ was very similar between abf and aaf samples, but significant differences were observed in the absorption spectra of the abf and aaf solutions as shown in Figure 7. DOM is known to take part to the redox cycling of Fe in sunlit surface waters (Emmenegger et al., 1998; Meunier et al., 2005). Such a process could potentially induce the phototransformation of DOM, although not all the relevant organic ligands are involved in charge-transfer photochemical reactions (Borer et al., 2005). Interestingly, DOM-induced dissolution of γ -FeOOH has been found to occur at a higher rate under acidic conditions, most likely because of higher concentration of Fe(III)-fulvate complexes under those circumstances (Voelker et al., 1997). Because Fe(III)-fulvate complexes are likely to undergo ligand-to-metal charge transfer reactions under irradiation (Gao and Zepp, 1998), enhanced Fe photoredox cycling at acidic pH could lead to a corresponding higher extent of phototransformation of some organic compounds.

Formation rate of \bullet OH upon irradiation of lake water.

The initial formation rate of \bullet OH was measured upon irradiation of water taken from Lake Avigliana Grande and Lake Candia (winter samplings). The samples that underwent irradiation were either natural (just filtered) or acidified after filtration (pH 2 by HClO₄). The radical \bullet OH was quantified with the reaction that transforms benzene (3 mM) into phenol. In both cases a substantial increase of \bullet OH generation rate was observed upon sample acidification. Figure 8A shows the time evolution of phenol upon irradiation of the samples from Lake Avigliana Grande (natural and acidified).

The initial formation rates of \bullet OH in the four irradiated samples ($r_{\bullet\text{OH}}$) are reported in Table 2. Possible sources of \bullet OH upon irradiation are nitrate, nitrite, nitrous acid, DOM, and Fe. The following reactions are involved (Hoigné, 1990; Benkelberg and Warneck, 1995; Vaughan and Blough, 1998; Mack and Bolton, 1999).



The contribution of NO_3^- , NO_2^- , HNO_2 , and FeOH^{2+} to \bullet OH photoproduction under the adopted irradiation device was quantified with dedicated experiments. The initial formation rate of phenol was measured upon irradiation of mixtures of benzene and the compound under study at variable

concentration. Considering that the phenol yield of the reaction between benzene and $\bullet\text{OH}$ is 95%, it is $r_{\bullet\text{OH}} = 1.05 r_{\text{phenol}}$. The results of the relevant irradiation experiments are reported in Figure 8B, from which one obtains the following equations for the formation rates of $\bullet\text{OH}$ by the studied compounds under the adopted irradiation conditions (concentration values are in molarity):

$$r_{\bullet\text{OH}}^{\text{NO}_3^-} [\text{M s}^{-1}] = 3.7 \times 10^{-8} [\text{NO}_3^-] \quad (7)$$

$$r_{\bullet\text{OH}}^{\text{NO}_2^-} [\text{M s}^{-1}] = 1.4 \times 10^{-5} [\text{NO}_2^-] \quad (8)$$

$$r_{\bullet\text{OH}}^{\text{HNO}_2} [\text{M s}^{-1}] = 1.9 \times 10^{-4} [\text{HNO}_2] \quad (\text{pH } 2) \quad (9)$$

$$r_{\bullet\text{OH}}^{\text{Fe(III)}} [\text{M s}^{-1}] = 1.7 \times 10^{-5} [\text{Fe(III)}] \quad (\text{pH } 2) \quad (10)$$

From equations (7-10) and the concentration values of the relevant species (see Table 2) it is possible to calculate the contribution of each compound to $\bullet\text{OH}$ photoproduction in lake water. An important issue is that equation (10) is suitable to calculate the Fe(III) contribution to $\bullet\text{OH}$ at pH 2, but the photogeneration of $\bullet\text{OH}$ by Fe(III) is strongly dependent on pH. It has been demonstrated that the rate of $\bullet\text{OH}$ photogeneration by Fe(III) is directly proportional to $\alpha_{\text{FeOH}^{2+}} = [\text{FeOH}^{2+}] [\text{Fe(III)}]^{-1}$ (King et al., 1993), thus it is possible to derive the pH dependence of $r_{\bullet\text{OH}}^{\text{Fe(III)}}$ from that of $\alpha_{\text{FeOH}^{2+}}$. Considering the equilibria between the different Fe(III) species (Fe^{3+} , FeOH^{2+} , Fe(OH)_2^+ , Fe(OH)_3), and assuming that $[\text{Fe}_2(\text{OH})_2^{4+}]$ would be negligible below 0.1 mM Fe(III), from the reported stability constants (Martell et al., 1997) one gets $\alpha_{\text{FeOH}^{2+}} \approx 0.1$ at pH 2 and, as a consequence:

$$r_{\bullet\text{OH}}^{\text{Fe(III)}} [\text{M s}^{-1}] \approx 1.7 \times 10^{-4} \cdot \alpha_{\text{FeOH}^{2+}} \cdot [\text{Fe(III)}] \quad (11)$$

In the natural lake water samples under study the pH values were 8.3 (Avigliana Grande) and 8.0 (Candia), which would correspond to $\alpha_{\text{FeOH}^{2+}} = 1.3 \times 10^{-5}$ and 2.9×10^{-5} , respectively (Martell et al., 1997). In the calculation of the Fe(III) contribution to $\bullet\text{OH}$ photogeneration it was additionally hypothesised that, in all the samples, $[\text{Fe}_{\text{TOT}}] \approx [\text{Fe(III)}]$.

Table 2 shows that NO_2^- and HNO_2 are important sources of $\bullet\text{OH}$ in the natural and acidified samples from Lake Avigliana Grande. For Lake Candia there is some contribution to $\bullet\text{OH}$ generation from nitrite in the natural sample and from FeOH^{2+} in the acidified one. Nitrate photolysis always plays a minor role, and also the role of Fe(III) in the natural samples is very low. The percentage of $\bullet\text{OH}$ photogeneration unaccounted for by nitrate, nitrite and Fe(III) might derive from water oxidation by photoexcited DOM (reactions 4,5) and from the photo-Fenton process

(White et al., 2003), which could be important under acidic conditions (Southworth and Voelker, 2003).

The time trend of NPOC upon irradiation of the acidified samples from Lake Avigliana Grande and Lake Candia is reported in Figure 2. Fitting of the experimental data yielded the initial transformation rate of NPOC (r_{NPOC}), expressed in $[\text{mol C L}^{-1} \text{ s}^{-1}]$. The r_{NPOC} values of the relevant samples are reported in the last row of Table 2. Comparison between $r_{\bullet\text{OH}}$ and r_{NPOC} shows that $r_{\bullet\text{OH}} < r_{\text{NPOC}}$ in both cases, indicating that organic matter disappears faster than $\bullet\text{OH}$ is formed. Note that reaction of more than one $\bullet\text{OH}$ with DOM would be required to mineralise organic carbon, or at least to make it sufficiently volatile to be lost in NPOC measurements. In the latter case the production of CO or of short-chain carboxylic acids would be required (Zuo and Jones, 1997; Brinkmann et al., 2003a). Under the hypothesis of an average oxidation number of -2 for C in DOM, the number n of $\bullet\text{OH}$ radicals to be added to DOM to produce the target compounds would be CO_2 (~ 6) $>$ CO (~ 4) $>$ carboxylic acids. Accordingly, it should be $r_{\bullet\text{OH}} = n r_{\text{NPOC}}$ for $\bullet\text{OH}$ to play a substantial role in DOM photomineralisation or volatilisation. The experimentally measured rates suggest that, in spite of the elevated hydroxyl photogeneration rate in acidic solution, the reaction between DOM and $\bullet\text{OH}$ cannot account for the NPOC decrease. The role of $\bullet\text{OH}$ in DOM photoprocessing, although not negligible, would be a secondary one. This finding is consistent with the limited effect of the nitrate spike on the phototransformation of lake-water DOM.

Time trend of NPOC upon irradiation of groundwater.

Figure 9 shows the time trend of NPOC upon irradiation of the four groundwater samples, just following filtration or upon addition of nitrate to obtain an initial concentration of 0.01 M, which includes both original and added nitrate. The natural nitrate concentration in the different samples is reported in Table 3. Nitrate spiking was not carried out for sample A because in that case the original concentration of nitrate was already 0.02 M. Sample A was instead acidified with HClO_4 till pH 2, in a similar way as lake water.

Significant NPOC decrease upon irradiation could be observed for the samples A and B (compare with the dark controls), while for sample C and even more for D the decrease was considerably lower. It is noteworthy that practically no difference in the NPOC trend could be observed between the natural and the nitrate-spiked samples, and between the natural and the acidified one. The lack of an effect of acidification might be connected with the low levels of Fe, which was under detection limit in the studied groundwater samples. The similarity of the trends of natural and nitrate-spiked samples suggests that the $\bullet\text{OH}$ radicals produced upon nitrate photolysis would play a minor role in DOM decrease. This is confirmed by the fact that, for sample A, $r_{\bullet\text{OH}} = 7.5 \times 10^{-10} \text{ M s}^{-1}$ (natural sample) was significantly lower than $r_{\text{NPOC}} = 2.6 \times 10^{-9} \text{ M s}^{-1}$. Similarly, for sample B the respective

values were $r_{\bullet\text{OH}} = 1.7 \times 10^{-10}$ and $r_{\text{NPOC}} = 5.2 \times 10^{-10} \text{ M s}^{-1}$. Table 3 additionally shows that the values of k_{NPOC} do not follow those of $[\text{NO}_3^-]$ in the groundwater samples.

From Table 3 it is possible to see that the samples with higher NPOC_0 have also higher k_{NPOC} , which suggests a connection between the kinetics of NPOC decrease and the initial amount of DOM. The quantity and possibly also the nature of DOM could play an important role in its photolabilisation in the studied samples. DOM in water samples can be characterised by use of the spectrophotometric indexes, such as the specific absorbance at 254 nm (A_{254}/NPOC_0), that at 285 nm (A_{285}/NPOC_0), and the E_2/E_3 index (A_{250}/A_{365}) (Oliveira et al., 2006). A_{254} is the absorbance of a water sample at the wavelength of 254 nm, with an optical path length of 1 cm, and the meaning of A_{250} , A_{285} , and A_{365} is analogous. The indexes A_{254}/NPOC_0 and A_{285}/NPOC_0 are able to differentiate between aquagenic organic matter, consisting of peptides, proteins, polysaccharides and complex carbohydrates, and the pedogenic one that is mainly composed of humic and fulvic substances. The differentiation is based on the fact that aquagenic organic matter is mainly made up of aliphatic chains that poorly absorb UV radiation, and thus contribute to NPOC_0 but not or very little to A_λ . In contrast, humic and fulvic substances contain many UV-absorbing aromatic groups (Zumstein and Buffle, 1989).

Reference values for A_{254}/NPOC_0 are $12 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ for purely aquagenic DOM, and $44 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ for fulvic acids (Oliveira et al., 2006). The values of the studied groundwater samples were in the range $25\text{-}30 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ (Table 3), to be compared with an average of $14.4 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ for lake water in the Piedmont region (Minero et al., 2007b).

In the case of A_{285}/NPOC_0 , reference values are $<10 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ for aquagenic DOM and $20 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ for fulvic acids (Oliveira et al., 2006). Groundwater samples had $A_{285}/\text{NPOC}_0 \approx 20 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ (Table 3), to be compared with an average value of $9 \text{ L (gC)}^{-1} \text{ cm}^{-1}$ for lake water (Minero et al., 2007b). Data from A_{254}/NPOC_0 and A_{285}/NPOC_0 suggest that DOM in the studied groundwater samples could be richer of fulvic acids compared to lake water.

The E_2/E_3 index is inversely related to the molecular weight and aromaticity degree of the organic matter that absorbs UV radiation (Oliveira et al., 2006). E_2/E_3 is a different index compared to the specific absorbance because, not including NPOC_0 , it completely neglects the contribution of the DOM fraction made up of non-absorbing aliphatic groups. Reference values for E_2/E_3 are <3.5 for humic and >3.5 for fulvic acids (Oliveira et al., 2006). Lake water has $E_2/E_3 \approx 7$ on average (Minero et al., 2007b), while for the studied groundwater samples E_2/E_3 was in the range 11-26. The difference suggests that UV-absorbing DOM in groundwater could have smaller molecular size and lower aromaticity degree compared to lake water. Also note that the E_2/E_3 index was significantly lower for the samples A and B (in the range 11-15) compared to C and D (22-26). Interestingly, samples A and B were also those showing the fastest kinetics of NPOC decrease. This finding

suggests that the decrease of NPOC upon irradiation of the studied groundwater samples depended on DOM features, such as its amount and nature, and not on external factors such as the concentration of nitrate.

Conclusions

In this study the photostability/photolability of DOM was assessed in both lake and groundwater. The latter could undergo significant photoprocessing when drawn to the surface and stored in basins for agricultural purposes (mainly irrigation).

DOM in natural lake water was generally photostable. Spiking with elevated amounts of nitrate, typical of nitrate-rich groundwater, induced only a slight decrease of DOM. In contrast, significant decrease of organic carbon was observed upon irradiation of acidified lake water. The comparison with dark controls and the parallel time trend of both TOC and NPOC indicates that some photomineralisation was actually occurring in the samples. It was possible to exclude that the decrease of DOM in acidic solution was due to its precipitation on the photoreactor walls, and insignificant spectral differences could be seen in the majority of cases between the natural samples and those acidified after filtration. Fe could play some role in the decrease of NPOC in acidified lake water samples.

The hydroxyl radical had a secondary role in the decrease of NPOC, although the photogeneration rate of $\bullet\text{OH}$ was considerably higher in acidified compared to natural lake water samples. The photolysis of HNO_2 and/or Fe species could contribute to the observed increase of $\bullet\text{OH}$ photoproduction under acidic conditions. Interestingly, elevated $\bullet\text{OH}$ photogeneration has been previously observed in acidic mine drainage water (Allen et al., 1996).

Differently from lake water, DOM in natural groundwater was significantly photolabile. Nitrate spiking or acidification of groundwater had negligible effect on the kinetics of NPOC decrease, which was faster in the samples where NPOC_0 was more elevated. The spectrophotometric indexes A_{254}/NPOC_0 , A_{285}/NPOC_0 , and E_2/E_3 suggested that DOM in groundwater could be significantly different than in lake water, probably due to the presence of a higher fraction of humic and fulvic compounds.

A possible reason for the difference in the nature and the photostability of DOM between lake and groundwater is that, in the former case, sunlight exposure would cause degradation of photolabile organic compounds and thus keep their concentration very low. In contrast, groundwater could contain a significant amount of photolabile DOM that would be protected from photodegradation in the aquifer. Under this hypothesis one would expect lake-water DOM to show

some photobleaching compared to groundwater, because the DOM component that absorbs UV radiation would undergo selective degradation (Brinkmann et al., 2003b). The removal of compounds that absorb radiation in the UVA or UVB region would likely decrease the sample absorbance in the UVC as well. Coherently, the spectral indexes $A_{\lambda}/NPOC_0$ were about twice higher in groundwater compared to lake water.

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Table 1. Data concerning the studied lake water samples. The data concerning area and average depth have been provided by the Regione Piemonte. Whenever applicable, data and error bounds represent the average and standard deviation values of runs made at least in triplicate. The values of k_{NPOC} are referred to the lake water samples that were acidified to pH 2 after filtration (aaf). " : same as above; n/a: not available.

Lake	Date	Area, km ²	Avg. depth, m	Temp., °C	pH	Nitrate, μM	NPOC ₀ , mgC L ⁻¹	k_{NPOC} (aaf), h ⁻¹
Viverone (229 m a.s.l.)	16Jan06	5.72	22.5	3.8	8.1	9.78±0.19	3.80±0.13	2.9×10 ⁻²
Avigliana Grande (ice-covered)	24Jan06	0.89	19.5	0.7	8.3	9.63±1.02	5.05±0.61	1.1×10 ⁻²
Avigliana Grande (346 m a.s.l.)	27Feb06	"	"	4.1	8.4	14.2±1.0	3.86±0.21	—
Avigliana Grande	02May06	"	"	17.5	8.5	11.0±0.1	4.16±0.06	—
Avigliana Piccolo (ice-covered) (356 m a.s.l.)	31Jan06	0.58	7.7	0.3	7.7	19.1±0.9	5.08±0.17	1.3×10 ⁻²
Candia (ice-covered)	07Feb06	1.35	5.9	3.7	8.0	1.65±0.48	5.43±0.25	1.4×10 ⁻²
Candia (227 m a.s.l.)	15May06	"	"	15.0	8.1	2.01±0.29	6.08±0.29	1.3×10 ⁻²
Moncenisio	28May06	n/a	n/a	8.0	8.0	10.5±0.6	0.60±0.04	7.1×10 ⁻⁴
Laus (2270 m a.s.l.)	05Jun06	0.012	<5	11.0	8.0	7.28±2.08	1.32±0.12	—
Ciardonnet (ice-covered, 2558 m a.s.l.)	12Jun06	0.03	<5	0.6	7.0	7.98±0.26	0.99±0.01	—
Rouen (2391 m a.s.l.)	18Jun06	0.018	<10	7.0	6.3	14.0±0.2	0.54±0.03	2.5×10 ⁻³

Table 2. Initial formation rates of $\bullet\text{OH}$ ($r_{\bullet\text{OH}}$) and concentration values of nitrate, nitrite and Fe_{TOT} in the relevant lake water samples under study. The percentage contribution of NO_3^- , NO_2^- , HNO_2 and Fe(III) to $\bullet\text{OH}$ photoproduction is also reported, together with the disappearance rate of organic carbon (r_{NPOC}). n/a: not applicable.

	Avigliana Grande	Av. Grande, pH 2	Candia	Candia, pH 2
Sampling date	24 Jan 2006	24 Jan 2006	7 Feb 2006	7 Feb 2006
$r_{\bullet\text{OH}}$, M s^{-1}	7.3×10^{-11}	3.0×10^{-10}	2.5×10^{-11}	9.6×10^{-10}
Nitrate, M	$(9.6 \pm 1.0) \times 10^{-6}$	$(9.6 \pm 1.0) \times 10^{-6}$	$(1.6 \pm 0.5) \times 10^{-6}$	$(1.6 \pm 0.5) \times 10^{-6}$
Nitrite, M	$(1.4 \pm 0.1) \times 10^{-6}$	$(1.4 \pm 0.1) \times 10^{-6}$, as HNO_2	$(1.5 \pm 0.4) \times 10^{-7}$	$(1.5 \pm 0.4) \times 10^{-7}$, as HNO_2
Fe_{TOT}, M	$(7.9 \pm 1.4) \times 10^{-7}$	$(7.9 \pm 1.4) \times 10^{-7}$	$(5.7 \pm 0.6) \times 10^{-6}$	$(5.7 \pm 0.6) \times 10^{-6}$
% $\bullet\text{OH}$, Nitrate	0.5%	0.1%	0.2%	0.01%
% $\bullet\text{OH}$, Nitrite	27%	n/a	8.4%	n/a
% $\bullet\text{OH}$, HNO_2	n/a	89%	n/a	3.0%
% $\bullet\text{OH}$, Fe(III)	0.002%	4.5%	0.1%	10%
r_{NPOC}, M s^{-1}	Low	2.0×10^{-9}	Low	1.3×10^{-9}

Table 3. Data concerning the studied groundwater samples.

	Well A	Well B	Well C	Well D
Nitrate, M	$(2.03 \pm 0.02) \times 10^{-2}$	$(4.64 \pm 0.01) \times 10^{-3}$	$(7.13 \pm 0.01) \times 10^{-3}$	$(5.75 \pm 0.02) \times 10^{-3}$
NPOC₀, mg C L⁻¹	13.31 ± 0.15	4.59 ± 0.09	3.29 ± 0.13	2.06 ± 0.08
k_{NPOC}, h⁻¹	7.2×10^{-3}	4.2×10^{-3}	3.4×10^{-3}	1.0×10^{-3}
A₂₅₄/NPOC₀, L [gC]⁻¹ cm⁻¹	29.0	24.8	26.5	29.4
A₂₈₅/NPOC₀, L [gC]⁻¹ cm⁻¹	22.2	18.6	22.4	26.0
E₂/E₃ (250 vs. 365 nm)	15.2	11.2	26.3	22.2

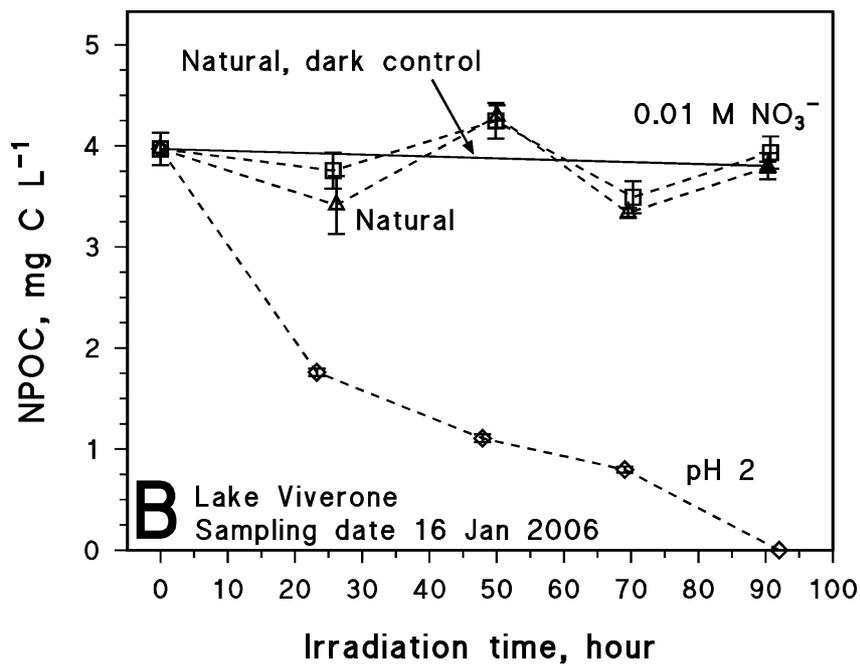
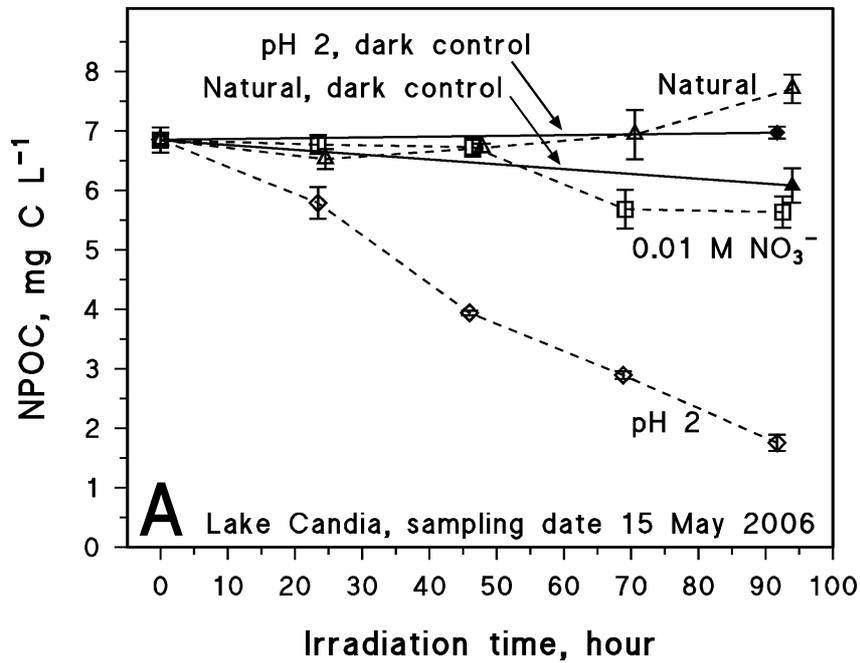


Figure 1. Time trend of NPOC upon irradiation of the samples from Lake Candia (1A, spring sampling) and Lake Viverone (1B, winter sampling). It is reported the trend of the natural samples (just filtered) and of the samples spiked with 0.01 M nitrate and with HClO₄ to pH 2, as well as the dark controls. Irradiation under simulated sunlight (12 W m⁻² UV intensity).

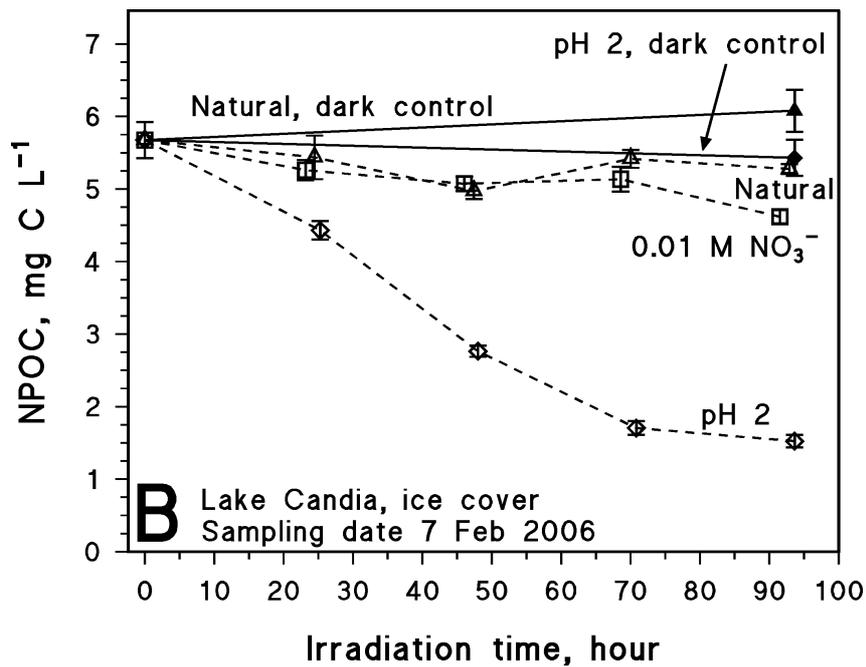
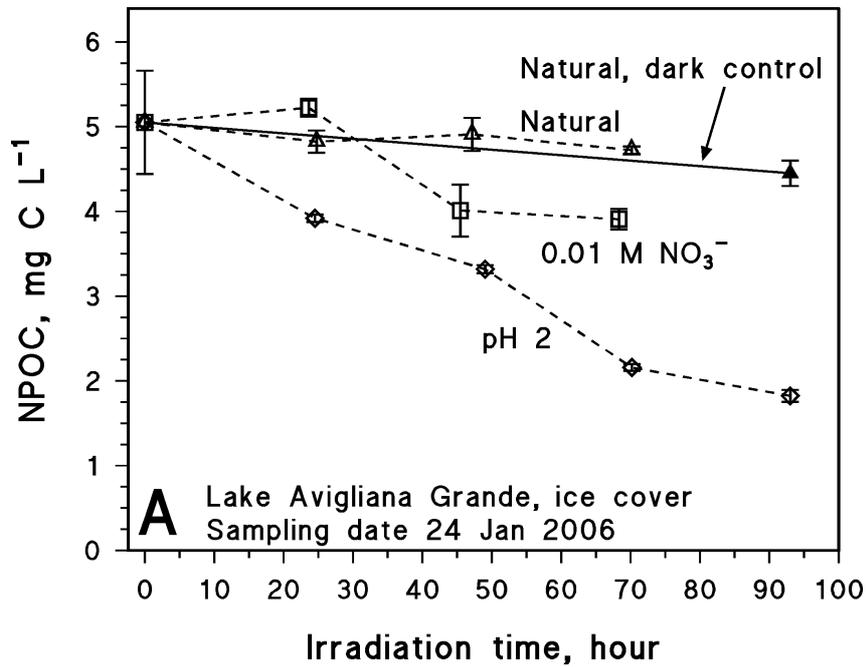


Figure 2. Time trend of NPOC upon irradiation of the samples from Lake Avigliana Grande (2A) and Lake Candia (2B). In both cases the samples were taken in winter, when the lakes were extensively covered with ice. It is reported the trend of the natural samples (just filtered) and of the samples spiked with 0.01 M nitrate and with HClO₄ to pH 2, as well as the dark controls. Irradiation under simulated sunlight (12 W m⁻² UV intensity).

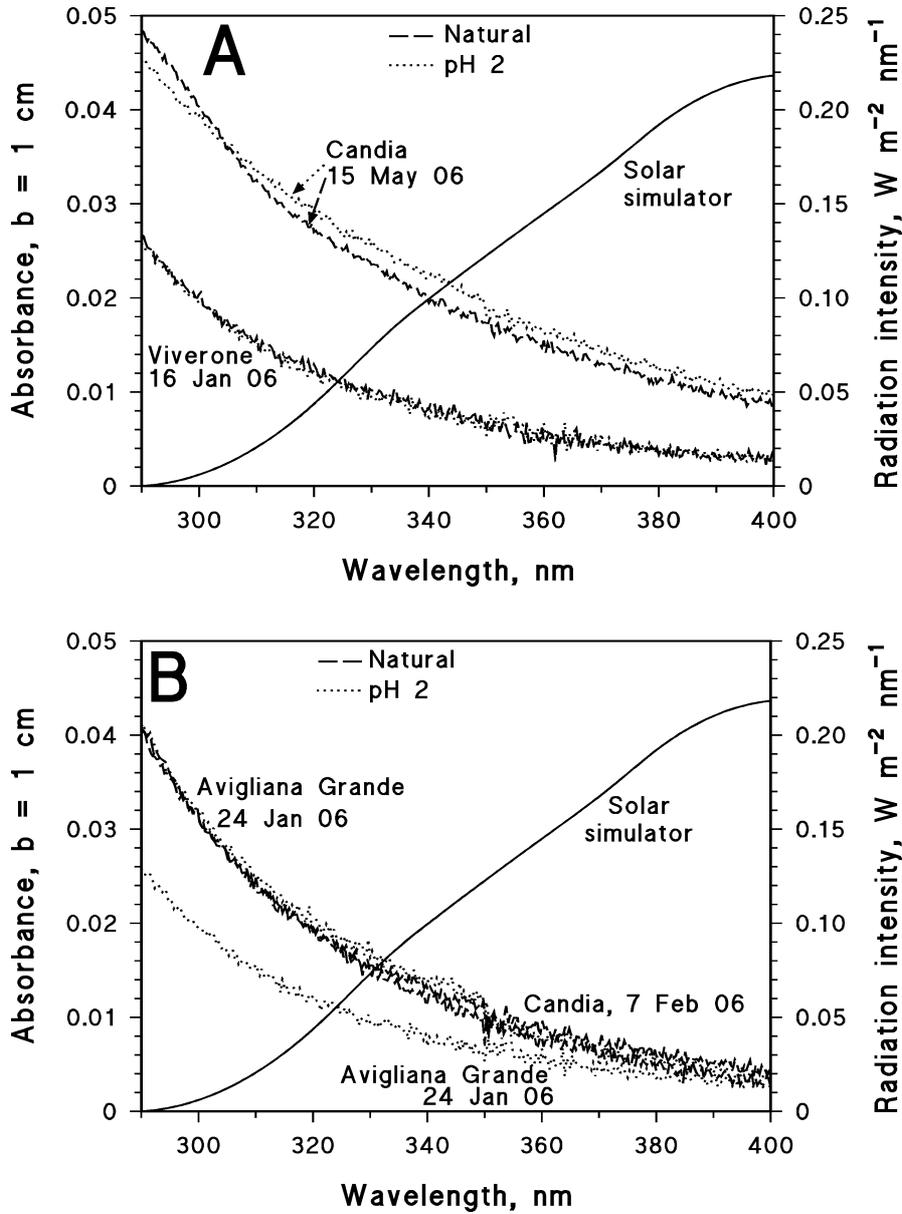


Figure 3. Absorption spectra (optical path length $b = 1$ cm) of the samples, for which the irradiation results are reported in Figures 1, 2. The spectra of Lake Viverone (natural and acidified, 3A) overlapped almost perfectly. The same happened for the natural and acidified spectra of Lake Candia in the winter sampling (3B), which were by chance also very similar to the absorption spectrum of the natural sample from Lake Avigliana Grande. The emission spectrum of the adopted solar simulator is also reported (data provided by the manufacturer).

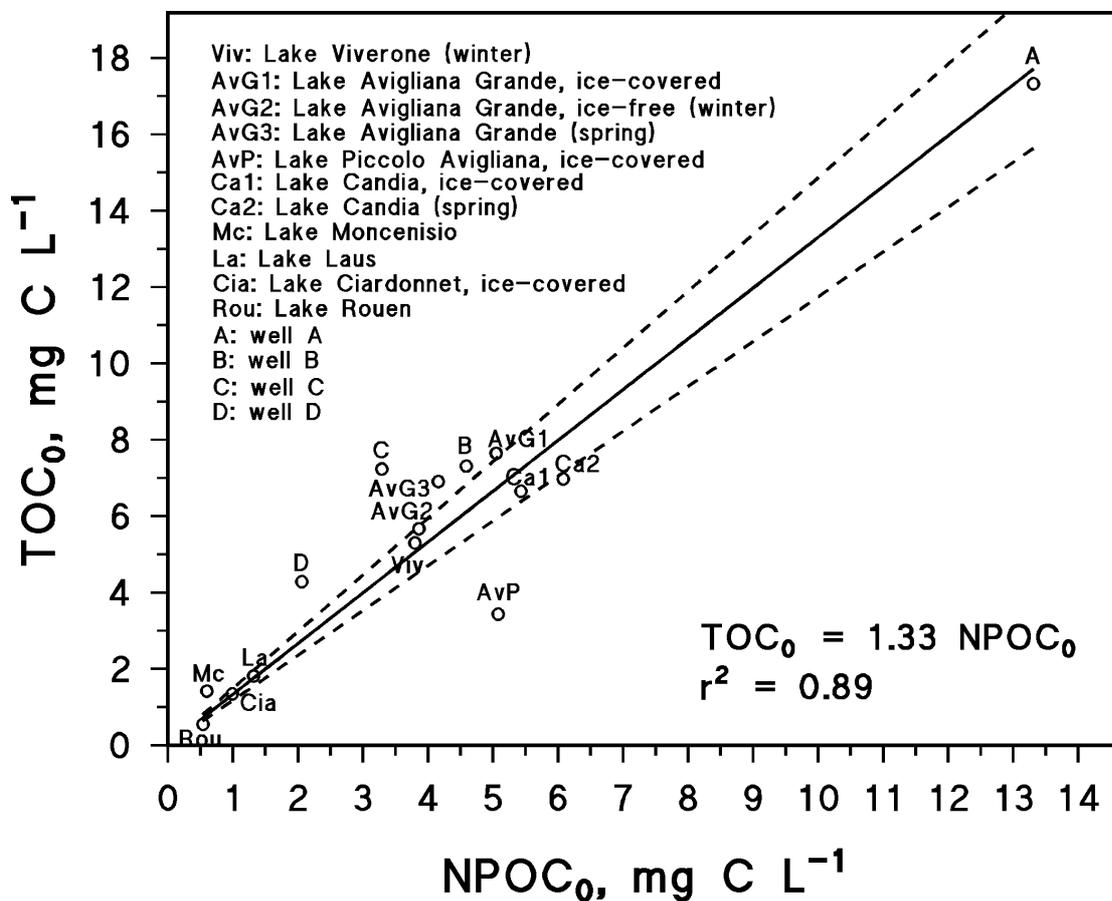


Figure 4. Correlation between initial NPOC (NPOC₀) and initial TOC (TOC₀) in the samples under study (identified as legend on the graph). TOC was measured as described in the Experimental section. The 95% confidence limits of the regression line are reported as dashed curves.

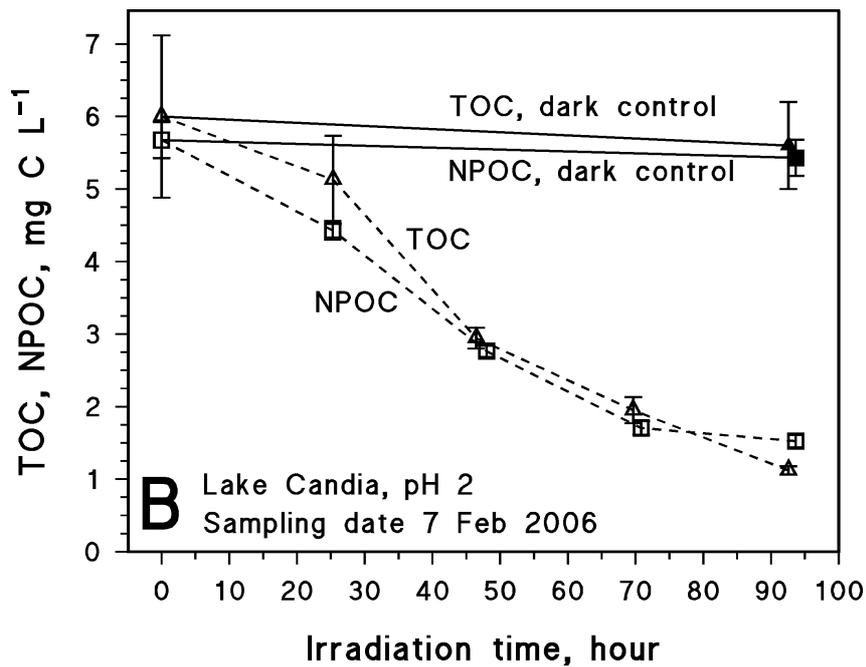
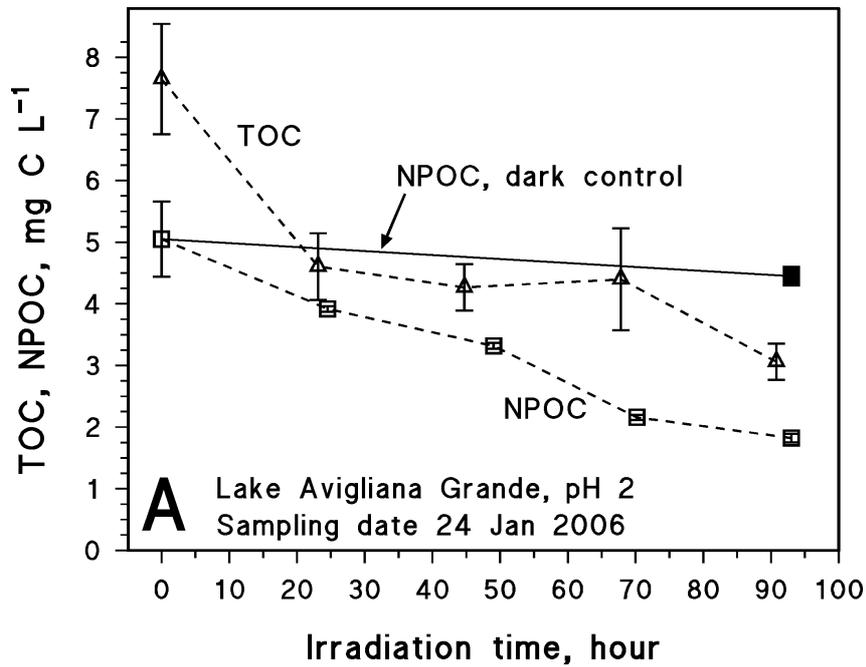


Figure 5. Time trend of NPOC and TOC upon irradiation of the acidified samples (HClO_4 , pH 2) from Lake Avigliana Grande (5A) and Lake Candia (5B). The dark controls are also reported. Irradiation under simulated sunlight (12 W m^{-2} UV intensity).

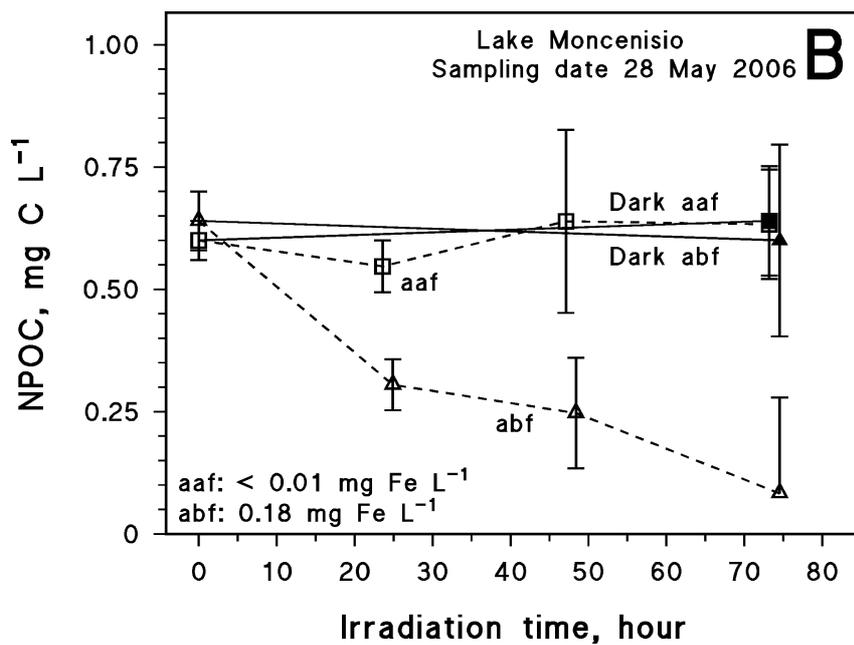
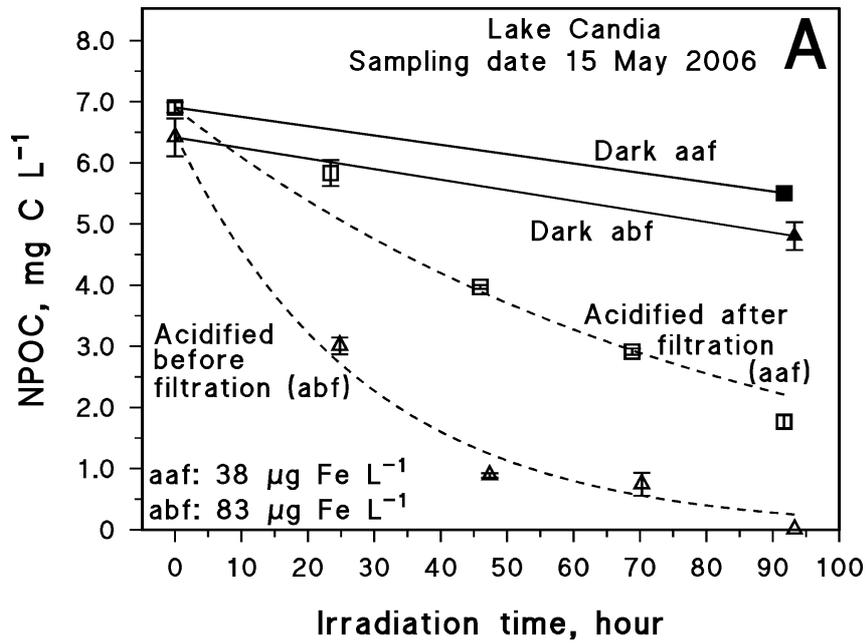


Figure 6. Time trend of NPOC upon irradiation of the samples from Lake Candia (6A, spring sampling) and Lake Moncenisio (6B). It is reported the trend of the samples acidified with HClO_4 to pH 2, after filtration (aaf) and before filtration (abf), as well as the dark controls. In both cases the total Fe content was higher in the samples acidified before filtration. Irradiation under simulated sunlight (12 W m^{-2} UV intensity).

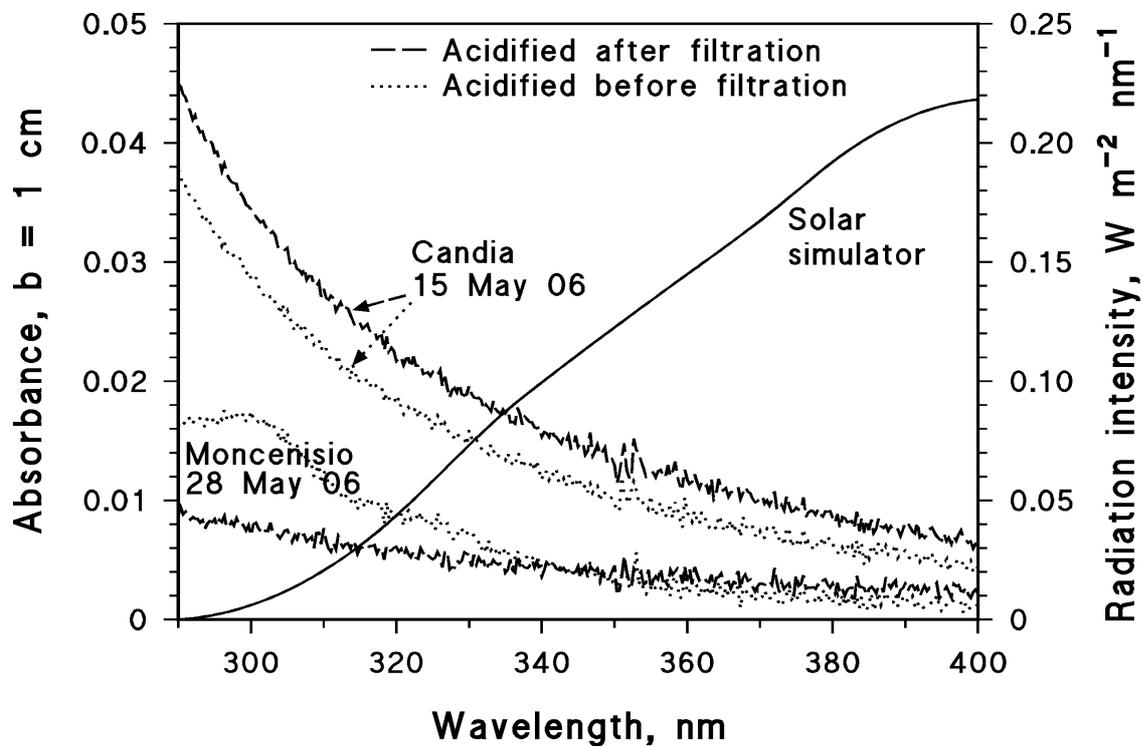


Figure 7. Absorption spectra (optical path length $b = 1$ cm) of the samples from Lake Candia (spring sampling) and Lake Moncenisio. The respective irradiation results are reported in Figure 6A/B. The emission spectrum of the adopted solar simulator is also reported.

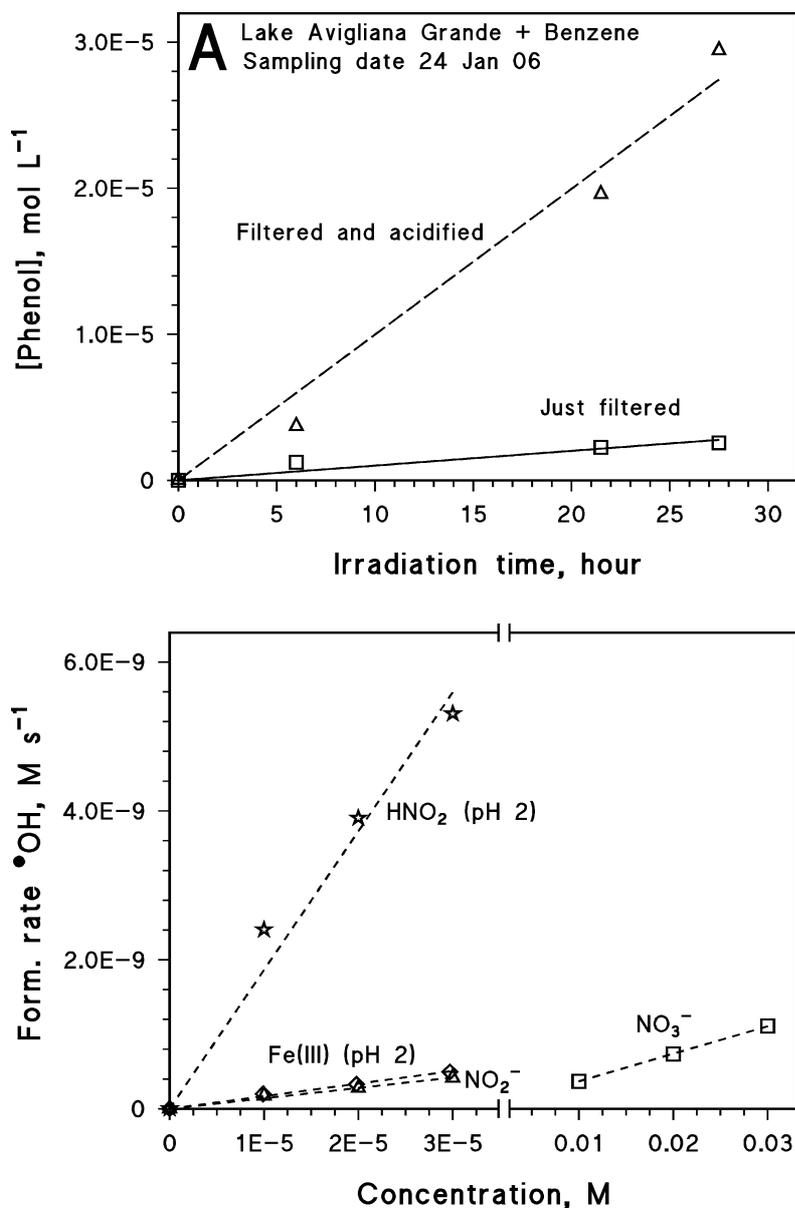


Figure 8. A) Time evolution of phenol upon irradiation of the sample from Lake Avigliana Grande (natural and acidified to pH 2 with HClO₄), spiked with 3.3 mM benzene. Irradiation under simulated sunlight (12 W m⁻² UV intensity).
 B) Formation rate of [•]OH, quantified by the initial formation rate of phenol from benzene (95% yield), in the presence of NO₃⁻, NO₂⁻, HNO₂ (pH 2), and Fe(III) (pH 2). Irradiation under simulated sunlight (12 W m⁻² UV intensity).
 Note that 1.0E-5 means 1.0 × 10⁻⁵, and so on.

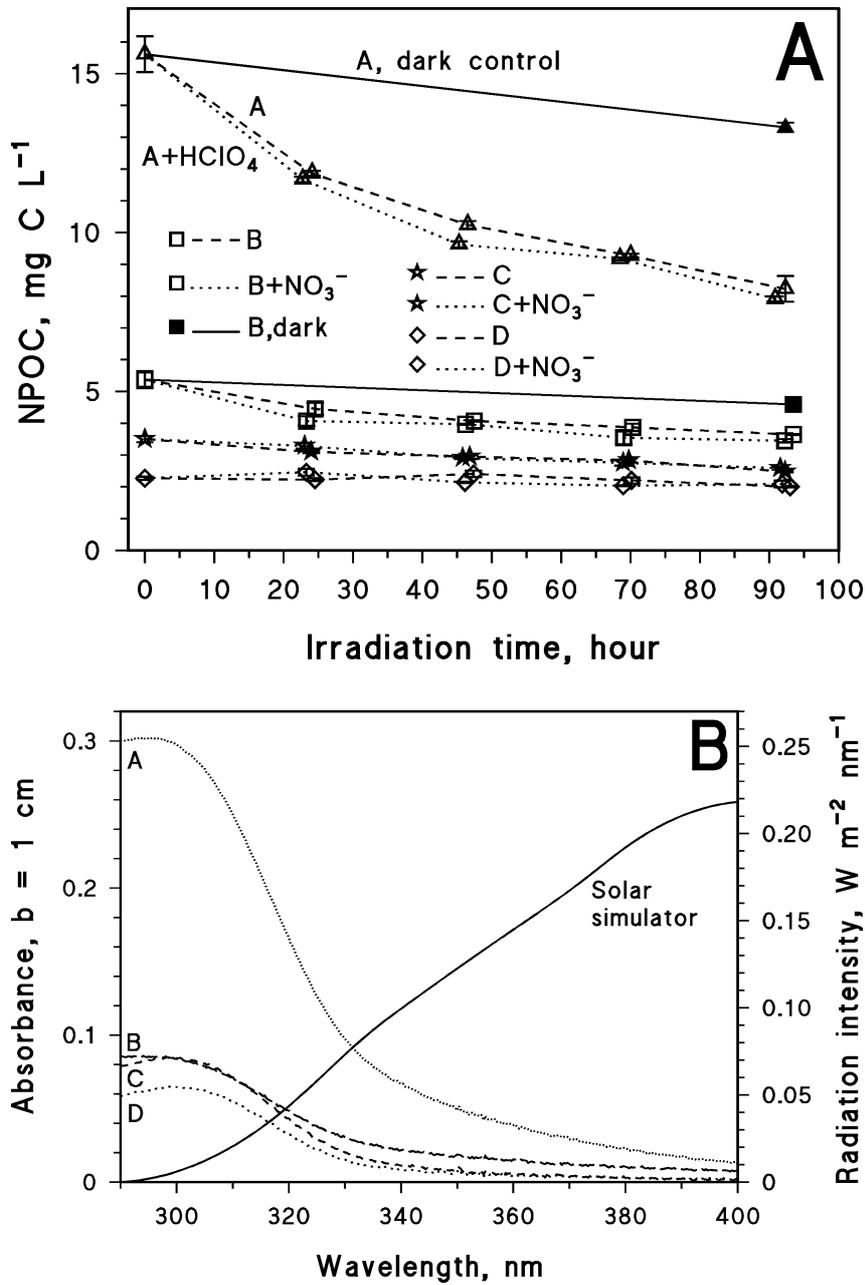


Figure 9. A) Time trend of NPOC upon irradiation of the studied groundwater samples, natural (just filtered), spiked with nitrate up to 0.01 M total concentration, or acidified with HClO₄. Addition of nitrate was not carried out for sample A because the initial [NO₃⁻] was already 0.02 M. Irradiation under simulated sunlight (12 W m⁻² UV intensity). B) Absorption spectra of the groundwater samples. The emission spectrum of the adopted solar simulator is also reported.