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UVA IRRADIATION INDUCES DIRECT PHOTOTRANSFORMATION OF 2,4-DINITROPHENOL IN SURFACE WATER SAMPLES

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Abstract

Lake water samples spiked with 2,4-dinitrophenol (24DNP) were irradiated under artificial UVA irradiance. It was found that the direct photolysis is the main photodegradation pathway of 24DNP in lake water. On the lake water samples it was also determined the formation and consumption rates of •OH, by means of the transformation reaction of benzene into phenol. It was found that the rate of direct photolysis prevails over the •OH phototransformation rate by one-two orders of magnitude. Moreover, the excited triplet states of chromophoric dissolved organic matter and singlet oxygen are expected to play a negligible role in the photodegradation of 24DNP. By modelling the direct photolysis of 24DNP in surface water bodies, one gets a half-life time of 2 to 10 summer sunny days for water column depths up to 10 m. This would make the direct photolysis a major pathway for the transformation of 24DNP in freshwaters.

Keywords: nitroaromatic compounds; direct and indirect photolysis; surface water photochemistry; UVA irradiation; environmental fate.

1. Introduction

Nitrophenols are environmentally harmful nitroaromatic compounds, with a potential to act as uncoupling agents in oxidative phosphorylation (Shea et al., 1983) and to form adducts with DNA bases, which could lead to oxidative damage to DNA itself (Chiron et al., 2007a). The occurrence of these compounds in surface waters is accounted for by atmospheric deposition, hydrolysis of parathion and similar products (Agarwal et al., 1994; Harrison et al., 2005), and photonitration of the corresponding phenols. The latter may be environmental transformation intermediates of phenolic herbicides (Chiron et al., 2007b; Chiron et al., 2009). Exposure to nitrophenols can cause harmful effects to algae (Uma maheswari and Venkateswarlu, 2004) and aquatic organisms (Howe et al., 1994).

Biodegradation of nitrophenols in soil and surface waters is thought to occur via transformation of the nitro group, which can be reduced to an amino one or released as nitrate
(McCormick et al., 1976). Interestingly, the biodegradation does not prevent accumulation of nitrophenols in soil and groundwater in the winter months, which can cause damage to plant development during springtime (Rippen et al., 1987). An alternative transformation pathway for nitrophenols in surface waters is represented by the photochemical processes, among which are the direct photolysis (Alif et al., 1987; Alif et al. 1991) and the reaction with photogenerated \( {\cdot}OH \) (Alif and Boule, 1991; Vione et al., 2009a). Moreover, very little is known of the role that the excited triplet states of chromophoric dissolved organic matter (\(^3\text{CDOM}*\)) play in nitrophenol transformation. \(^3\text{CDOM}^*\) is for instance responsible for the photodegradation of phenylurea herbicides in surface waters (Gerecke et al., 2001; Richard and Canonica, 2005). As far as the reaction with the radical \( \text{CO}_3^{\cdot-} \) is concerned, it is interesting to compare the reaction rate constants of the 4-nitrophenolate (the only nitrophenol for which the relevant data are available) with \( {\cdot}OH \) (7.6\( \times \)10\(^9\) M\(^{-1}\) s\(^{-1}\); Buxton et al., 1988) and \( \text{CO}_3^{\cdot-} \) (4.8\( \times \)10\(^7\) M\(^{-1}\) s\(^{-1}\); Neta et al., 1988). The relative importance of \( {\cdot}OH \) vs. \( \text{CO}_3^{\cdot-} \) as transformation pathways depends on ecosystem-related variables (which control the steady-state concentrations of the two radical species) at least as much as it depends on the reactivity of the relevant substrate. However, from a modelling approach to freshwater photochemistry (Vione et al., 2009b), it is possible to infer that the reaction of the 4-nitrophenolate with \( \text{CO}_3^{\cdot-} \) would be less important than that with \( {\cdot}OH \) in the vast majority of the freshwater environments.

24DNP is the most toxic nitrophenol that occurs in the environment to a significant extent, as it is a very powerful phosphorylation uncoupling agent (Haasio et al., 2002). The concentration of 24DNP in surface waters can reach some tens µg L\(^{-1}\) (Harrison et al., 2005). The transformation kinetics of 24DNP in surface waters, including the possible photoinduced pathways, is much less known than that of the mononitrophenols. Therefore, the purpose of the present paper is to study the photochemical lifetime of 24DNP and to assess the relative importance of the different phototransformation pathways. To do so, surface water samples spiked with 24DNP were irradiated; the kinetics of direct photolysis was compared with that of reaction with \( {\cdot}OH \), and it was studied the transformation of 24DNP by irradiated CDOM.

2. Experimental

2.1. Chemicals

24DNP (purity grade 97 %), humic acids (HA, technical grade), \( \text{H}_3\text{PO}_4 \) (85 %), \( \text{HClO}_4 \) (70 %) and phenol (99%) were purchased from Aldrich, benzene (for gas chromatography), acetonitrile (HPLC gradient grade) and \( \text{NaOH} \) (99 %) from VWR Int. All reagents were used as received, without further purification. Note that Aldrich humic acids are reported to contain around 110 µmol Fe g\(^{-1}\) (Lovley and Blunt-Harris, 1999).
2.2. Experimental procedures

Lake water was sampled from the surface layer of the relevant water bodies listed in Table 1 in May-June 2008, and transported to the laboratory under refrigeration. Within a few hours from sampling, lake water was vacuum filtered on 0.22 µM membranes (47 mm diameter, cellulose acetate, Millipore) and stored in the dark under refrigeration (5 °C) till irradiation.

Irradiation of the aqueous samples (15 mL, containing 2 µM 24DNP and, where relevant, 0.1 mg L\(^{-1}\) HA) was carried out in magnetically stirred Pyrex glass cells (0.4 cm optical path length). Where relevant, the sample pH was adjusted by addition of NaOH. For the irradiation it was adopted a set of Philips TL K05 UVA lamps with emission maximum at 365 nm. The UV irradiance reaching the top of the cells, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter (290 – 400 nm), was 57 W m\(^{-2}\). The photon flux in solution (\(P_o\)) was \(1.1 \times 10^{-5}\) einstein L\(^{-1}\) s\(^{-1}\), measured by ferroxyalate actinometry (Kuhn et al., 2004).

To obtain the lamp spectra \(p(\lambda)\), measurements were initially carried out with an Ocean Optics SD2000 charge coupled device (CCD) spectrophotometer. Let \(q(\lambda)\) be the spectra thus derived. The transmittance \(T(\lambda)\) of the Pyrex-glass upper face of the irradiation cells was measured with a Varian Cary “100 Scan” UV-Vis spectrophotometer (see Figure A-SM in the Supplementary Material, hereafter SM). The spectrum of lamp radiation that passes the glass is \(p(\lambda) = T(\lambda) q(\lambda)\). It follows normalisation \((p(\lambda) \rightarrow p^o(\lambda))\) to the actinometrically determined photon flux \(P_o\), so that \(P_o = \int_{\lambda} p^o(\lambda) d\lambda\). Figure 1 reports the values of \(p^o(\lambda)\) for the adopted irradiation device, together with the absorption spectrum of 24DNP at pH 9 (chosen to ensure the almost exclusive presence of the anionic form). The Figure shows the very good overlap between the two spectra. The choice of the lamp was motivated by the fact that UVA radiation penetrates more deeply in surface waters than UVB (Bracchini et al., 2006). The 24DNP absorption spectrum was taken with the UV-Vis scan spectrophotometer, using a quartz cuvette of 1 cm optical path length. The same instrument was adopted to measure the absorption spectra of the lake water samples, which are reported in Figure 2. The solution pH was measured with a Metrohm 713 pH meter, equipped with a combined glass electrode. Water used was of Milli-Q quality.

Analyses were carried out by liquid chromatography, adopting a VWR-Hitachi Elite HPLC (Milan, Italy). The column used was a RP-C18 LichroCART (Merck, 125 mm × 4.6 mm × 5 µm). Isocratic elution (1 mL min\(^{-1}\) flow rate) was performed with a 40/60 (v/v) mixture of acetonitrile/aqueous phosphate buffer (0.050 M, pH 2.8). Injection volume was 60 µL using an autosampler system. The retention time of 24DNP was 5.1 min, the column dead time 0.9 min, the detection wavelength 258 nm. To confirm the peak purity of 24DNP, HPLC runs were also carried out at 210 nm, where the absorption coefficient of 24DNP is similar to that at 258 nm.

The transformation reaction of benzene into phenol (95 % yield; Takeda et al., 2004) was used to quantify the \(^*\)OH photoproduction by lake water under irradiation. The samples (spiked with benzene instead of 24DNP) were irradiated and the time trend of phenol and benzene was followed
by HPLC, under the same elution conditions as for 24DNP, adopting 210 nm as the detection wavelength. Retention times were 2.55 min for phenol and 8.10 min for benzene.

The determination of the dissolved organic carbon (DOC) content of lake water was carried out with a Shimadzu TOC-V CSH Total Organic Carbon Analyser. The elimination of the inorganic carbon prior to DOC measurement was carried out by sample acidification with HCl, followed by 10 min sparge time with “zero grade” air (SIAD, Bergamo, Italy). The DOC data are reported in Table 1, and the associated error is referred to measurements made at least in triplicate.

2.3. Kinetic data treatment

The time evolution data of 24DNP were fitted with pseudo-first order decay equations of the form
\[ C_t = C_o \exp(-kt) \]
where \( C_t \) is the concentration of the substrate at the time \( t \), \( C_o \) the initial concentration, and \( k \) the pseudo-first order degradation rate constant. The initial transformation rate of 24DNP was calculated as \( \text{Rate}_{24\text{DNP}} = kC_o \). The errors associated to the rates (±σ) were derived from the scattering of the experimental data around the fitting curve (intra-series variability). The reproducibility of repeated runs (inter-series variability) was around 10 %.

The time evolution of phenol from benzene was fitted with
\[ C'_t = k_{f\text{Ph}} [\text{Benzene}] \left( k_{d\text{Ph}} - k_{d\text{B}} \right)^{-1} \left[ \exp(-k_{d\text{B}}t) - \exp(-k_{d\text{Ph}}t) \right], \]
where \( C'_t \) is the concentration of phenol at the time \( t \), [Benzene] the initial concentration of benzene, \( k_{d\text{Ph}} \) and \( k_{d\text{B}} \) the pseudo-first order rate constants for the transformation of phenol and benzene, respectively, and \( k_{f\text{Ph}} \) the pseudo-first order rate constant for the formation of phenol. The initial formation rate of phenol is
\[ \text{Rate}_{\text{Ph}} = k_{f\text{Ph}} [\text{Benzene}]. \]
Considering that the reaction between benzene and •OH yields phenol with 95 % yield, and that there is competition between added benzene and the natural scavengers for reaction with •OH, \( \text{Rate}_{\text{Ph}} \) would be expressed as follows (Takeda et al., 2004):

\[
\text{Rate}_{\text{Ph}} = \frac{0.95 R_{*\text{OH}} k_{B,*\text{OH}} [\text{Benzene}]}{k_{B,*\text{OH}} [\text{Benzene}] + \sum_i k_{Si} [S_i]} \tag{1}
\]

where \( R_{*\text{OH}} \) is the formation rate of •OH, \( \sum_i k_{Si} [S_i] \) (in s\(^{-1}\) units) the rate constant of the natural •OH scavengers, [Benzene] the initial concentration of benzene, and \( k_{B,*\text{OH}} = 7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) the second-order rate constant between •OH and benzene (Buxton et al., 1988). The value of 0.95 represents the phenol yield of the reaction between benzene and •OH. From equation (1) and the experimental data of \( \text{Rate}_{\text{Ph}} \) vs. [Benzene], it is possible to obtain \( R_{*\text{OH}} = (0.95)^{-1} \text{Rate}_{\text{Ph}} \) for \([\text{Benzene}] \gg \sum_i k_{Si} [S_i] \) (excess benzene), and \( \sum_i k_{Si} [S_i] = \lim_{[\text{Benzene}] \to 0} (0.95 R_{*\text{OH}} k_{B,*\text{OH}} [\text{Benzene}]/\text{Rate}_{\text{Ph}}) \) for low benzene concentration ([Benzene] » \( \sum_i k_{Si} [S_i] \)).
3. Results and Discussion

3.1. Transformation of 24DNP in surface water samples

Figure 3 shows the time evolution of 24DNP in the studied lake water samples, as well as in ultra-pure water at pH 9. The phenolate would always prevail over the undissociated phenol: 24DNP has pKa = 4.1 (Martell et al., 1997), and the pH values of the lake water samples were included in the range 6.2 – 8.6 (see Table 1). The photodegradation of 24DNP in ultra-pure water is accounted for by direct photolysis. In the case of lake water, both direct photolysis and photosensitised processes would contribute to 24DNP transformation. The initial transformation rates of 24DNP in the studied samples (Rate$_{24DNP}$) are reported in Table 1, which also reports the pH values and the DOC content of lake water.

It is apparent that the 24DNP phototransformation rate in lake water is comparable to the rate of direct photolysis. This finding suggests that the direct photolysis would be the main phototransformation pathway of 24DNP in the studied lake water samples. Interestingly, Rate$_{24DNP}$ was the lowest in the two samples with the highest absorbance (Candia and Meugliano, see Figure 2), possibly because of competition for irradiance between 24DNP and the natural absorbers, mostly CDOM.

The importance of the reaction with $^{•}\text{OH}$ was also assessed from the transformation of benzene into phenol (Takeda et al., 2004), by which it was possible to determine $R^{•}\text{OH}$ and $\Sigma k_S[S_i]$. The corresponding plots of Rate$_{\text{Ph}}$ vs. [Benzene], with the relevant data fits according to equation (1), are reported in Figure B-SM. Table 1 reports the values of $R^{•}\text{OH}$ and $\Sigma k_S[S_i]$ obtained from the fit. From these values it is possible to derive the expected rate of 24DNP degradation that is accounted for by $^{•}\text{OH}$, Rate$_{^{•}\text{OH},24DNP}$. In the irradiated samples, there would be competition between 24DNP and the natural scavengers for reaction with $^{•}\text{OH}$, and the hydroxyl radical would reach a steady-state concentration. From these considerations one gets:

$$Rate_{^{•}\text{OH},24DNP} = \frac{R^{•}\text{OH} k^{•}\text{OH},24DNP [24DNP]}{k^{•}\text{OH},24DNP [24DNP] + \sum i k_{Si} [S_i]}$$

The lake water samples spiked with 24DNP had pH > 6 (see Table 1), thus $k^{•}\text{OH},24DNP$ should be referred to the phenolate ($2.3\times10^9 \text{ M}^{-1} \text{s}^{-1}$; Albinet et al., submitted). The values of Rate$_{^{•}\text{OH},24DNP}$ are reported in Table 1 for each lake water sample. The percentage contribution of $^{•}\text{OH}$ to the overall 24DNP degradation was 3.5-10 %, which indicates that the reaction with $^{•}\text{OH}$ plays a minor role into the degradation of 24DNP in lake water.

The transformation of the substrate was also studied upon irradiation of Aldrich humic acids (HA). This material could show some resemblance with the pedogenic fraction of organic matter in surface waters. The latter constitutes the DOM fraction that is most responsible for the absorption of solar irradiance and for photochemical reactivity (Zumstein and Buffle, 1989; Loiselle et al.,
Accordingly, the adopted HA should be more reactive than the organic matter in the studied samples, which is mainly of autochthonous origin and, therefore, shows a relatively low specific absorbance (Minero et al., 2007). The irradiation of HA produces the excited triplet states ($^3$HA*), •OH radicals and singlet oxygen ($^1$O$_2$) as the main reactive transients (Richard and Canonica, 2005).

The trend with pH of the initial degradation rate of 2 µM 24DNP, upon UVA irradiation of 0.1 mg L$^{-1}$ HA, is reported in Figure 4. The rate is maximum in the pH range of 2 to 4 and, for instance, the degradation rate at pH 8 is around 60% that at pH 4. The rates observed in the presence of HA (5.5×10$^{-11}$ – 1.0×10$^{-10}$ M s$^{-1}$) are significantly higher compared to the direct photolysis of 24DNP under the same lamp (1–3×10$^{-11}$ M s$^{-1}$). Interestingly, the addition of 30 mM 2-propanol as •OH scavenger was able to quench the degradation of 24DNP. This effect suggests that the transformation of 24DNP upon irradiation of HA is mainly due to •OH, with $^3$HA* and $^1$O$_2$ playing little to negligible role. The pH trend of 24DNP degradation by irradiated HA is consistent with a photo-Fenton process as source of •OH in the system, which would be most effective around pH 3 (Vermilyea and Voelker, 2009). The data obtained here with humic acids suggest that, under the adopted UVA irradiation conditions, excited triplet states and $^1$O$_2$ would be less important than •OH toward the degradation of 24DNP. In turn, lake water irradiation suggested that the direct photolysis would be more important than the reaction with •OH. Finally, the electron-withdrawing character of the two nitro groups of 24DNP should ensure limited to negligible reactivity toward CO$_3$• (Neta et al., 1988).

### 3.2. Modelling the lifetime of 24DNP in surface water samples

A model has been developed to foresee the direct photolysis half-life time of a compound dissolved in a water body of column depth $d$ (Vione et al., 2009c,d). This model takes into account the rates of radiation absorption and of reaction inside a cylindrical volume of surface $S$ and depth $d$ (however, the adopted value of $S$ does not influence the results). The depth $d$ (expressed in cm) can be the average depth of a thoroughly mixed water body, or the mixing layer depth of a large, stratified lake. Within the volume under consideration, a simplified Lambert-Beer approach was adopted to take into account the competition for radiation absorption between the substrate (24DNP) and the other light-absorbing compounds (mostly CDOM; Bracchini et al., 2004 and 2006). A more detailed description of the model is reported as SM. In the case of 24DNP, the half-life time in summer sunny days (SSD) units would be:

$$\tau_{24\text{DNP}}^{\text{SSD}} = \frac{1.9 \cdot 10^{-8} \ d}{\Phi_{24\text{DNP}} \int_{\lambda} \rho^\circ(\lambda) \cdot \left\{ 1 - 10^{-A_{\lambda}(\lambda) \ d} \right\} \ \frac{E_{24\text{DNP}}(\lambda)}{A_{\lambda}(\lambda)} \ d\lambda}$$

(3)
The standard summer sunny day (SSD) adopted here is equivalent to 15 July at 45°N latitude. Moreover, \( d \) is the column depth (in cm), \( p^0(\lambda) \) the spectrum of sunlight (units of einstein cm\(^{-2}\) s\(^{-1}\) nm\(^{-1}\) and corresponding to 22 W m\(^{-2}\) UV irradiance, which can be observed in a sunny day at 45°N latitude, on 15 July, at 10 am or 2 pm solar time), \( \varepsilon_{24\text{DNP}}(\lambda) \) (in M\(^{-2}\) cm\(^{-1}\)) the molar absorption coefficient of the phenolate, which is the prevailing form of 24DNP in surface waters, and \( \Phi_{24\text{DNP}} \) its polychromatic, average photolysis quantum yield between 300 and 500 nm (3.45×10\(^{-5}\); Albinet et al., submitted). \( A_1(\lambda) \) (in cm\(^{-1}\)) is the specific absorbance of the surface water layer, where most of the photochemical reactivity of a water body would take place. \( A_1(\lambda) \) is here referred to an organic matter content of 2 mg C L\(^{-1}\) (Vione et al., 2009d). Figure C-SM shows the overlap between \( p^0(\lambda) \) and \( A_1(\lambda) \).

Figure 5 reports \( \tau_{24\text{DNP}}^{\text{SSD}} \) as a function of the water-column depth, up to 10 m. The half-life time varies from 2 to 10 days, and increases with increasing the depth. This is reasonable because most of the photochemical activity is going to take place in the top layer, which is a decreasing fraction of the water body by increasing the column depth.

4. Conclusions

The irradiation of 24DNP in lake water samples suggested that the direct photolysis is the main phototransformation pathway under the adopted UVA irradiation conditions. This finding was confirmed by the determination of the rates of \(^{1}\text{OH} \) formation and scavenging in the samples. It is found that the reaction between 24DNP and \(^{1}\text{OH} \) contributes some 3.5-10 % to the overall phototransformation rate of 24DNP. Moreover, reaction between 24DNP and \(^{3}\text{CDOM}^* \) or \(^{1}\text{O}_2 \) is expected to be even less important than that with \(^{1}\text{OH} \).

Modelling of the half-life time of 24DNP in freshwater suggests that the direct photolysis could be a major pathway for the removal of 24DNP from these environments.

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References


Chiron, S., Barbati, S., De Méo, M., Botta, A., 2007a. In vitro synthesis of 1,N\(^{6}\)-etheno-2'-deoxyadenosine and 1,N\(^{2}\)-etheno-2'-deoxyguanosine by 2,4-dinitrophenol and 1,3-dinitropyrene in presence of a bacterial nitroreductase. Environ. Toxicol. 22, 222-227.


Figure 1. Emission spectrum of the adopted irradiation device. Absorption spectrum of 24DNP at pH 9, adjusted with NaOH.
**Figure 2.** Absorption spectra of the studied lake water samples.
Figure 3. Time evolution upon irradiation of 24DNP in the lake water samples under study and in pure water solution at pH 9 (adjusted with NaOH).
Figure 4. Initial degradation rates of 2 µM 24DNP, as a function of pH, upon irradiation of 0.1 mg L$^{-1}$ humic acids under the TL K05 lamp. The error associated to a repeated run is also reported.
Figure 5. Half-life time of 24DNP ($\tau_{24\text{DNP}}^{\text{SSD}}$) by direct photolysis, as a function of the column depth of a surface water body with 2 mg C L$^{-1}$ dissolved organic carbon. $\tau_{24\text{DNP}}^{\text{SSD}}$ was calculated by means of equation (3). SSD = summer sunny day, equivalent to 15 July at 45°N latitude.