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Auto-remediation of surface waters by solar-light: Photolysis of 1-naphthol, and two herbicides in pure and synthetic waters

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Abstract

Solar-light reaching the earth surface is able to induce chemical reactions in absorbing chemicals. For many organic pollutants dispersed in surface waters, photolysis is an important transformation process. It results from absorption of light by the chemical itself or it is mediated by sensitizing or photoinducing chromophores contained in surface waters. Coloured dissolved organic matter (cDOM) and nitrate ions are among these. This paper gives a brief description of major photochemical processes that may occur in surface waters. It is illustrated by three examples of light induced pollutant transformation. The high volume chemical 1-naphthol and the herbicides methabenzthiazuron and mesotrione were chosen as substrates. Analytical and kinetic aspects of the reactions are reported.

Keywords: Phototransformation; Direct photolysis; Photosensitization; Natural organic matter; Nitrate ions; Organic pollutants

1. Introduction

Photolysis is a way of degradation of organic pollutants in the upper layer of surface waters. Indeed, solar-light reaching the earth surface shows a low limit in the UV at about 300 nm and radiations are energetic enough to induce chemical reactions in absorbing compounds. Chemicals that absorb at a wavelength longer than 300 nm may potentially undergo direct phototransformation. Transformation is effective when chemical reactions from excited states compete successfully with deactivation processes. In addition, absorbing as well as non-absorbing compounds can be degraded through indirect processes mediated by chromophoric constituents of surface waters. Due to the variety of species present in surface waters, there is a wide array of indirect or photosensitized possible degradation pathways of contaminants [1,2]. Coloured dissolved organic matter (cDOM) (see absorption spectrum in Fig. 1A) is in concentrations typically ranging from 1 to 30 mg/L in surface waters and is considered to be an important source of reactive species. The main reactive transients produced upon irradiation of cDOM are singlet oxygen [3], radical species [4] and probably excited triplet states [5–8]. Depending upon the chemical structure of the studied contaminant the relative contribution of these reactive species in the overall transformation reaction may vary significantly [9–11]. Nitrate (see absorption spectrum in Fig. 1A) present in concentrations up to several hundreds of micromolars could also be considered as an important component in surface waters. Under irradiation nitrate is a source of hydroxyl radical [1]. This non-selective and highly reactive intermediate is capable of degrading all types of organic contaminants [12]. However, its contribution in the overall transformation reactions is often small because it is mostly trapped by other constituents of natural waters such as cDOM or carbonate ions. The steady state concentration of hydroxyl radicals can be simply estimated from the DOC concentration of the water [13].

In this work, we focussed on three aquatic pollutants: 1-naphthol, mesotrione and methabenzthiazuron (Fig. 2). 1-Naphthol is a high volume chemical whose production is worth more than 1 million pounds annually. Given the high volume of production, it is expected to be released in all parts of the environment. It is also a breakdown product of naphthalene derivated pesticides. In particular, it is formed by hydrolysis or photolysis of the intensively used insecticide carbaryl [14]. Mesotrione is frequently used in replacement of atrazine since its registration in 2000 in EU and in 2001 in USA. Mesotrione belongs to a new class of triketone derivatives introduced by Zeneca Ag Products (now Syngenta) [14]. The interest in

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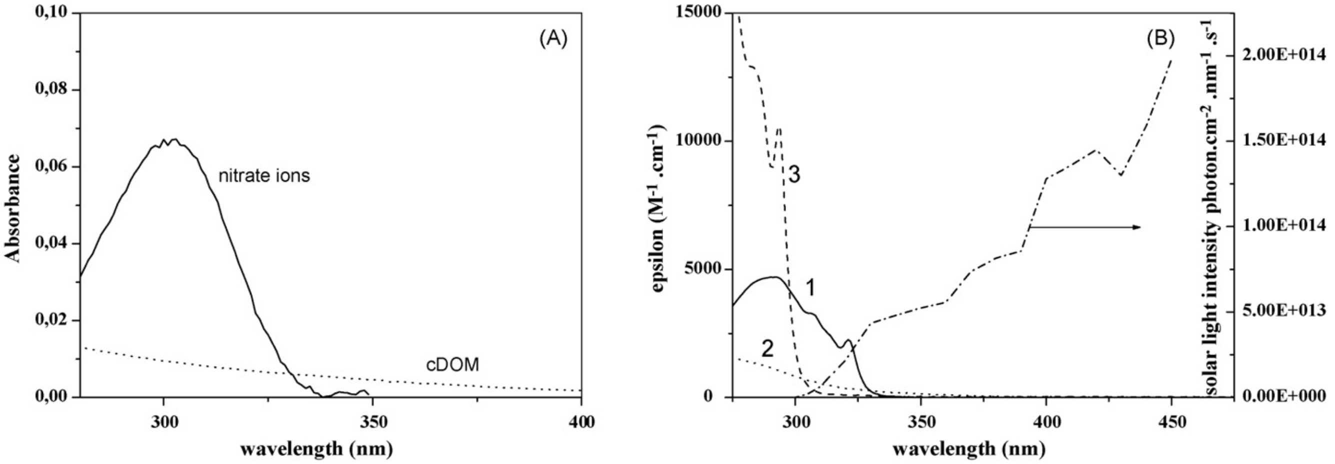
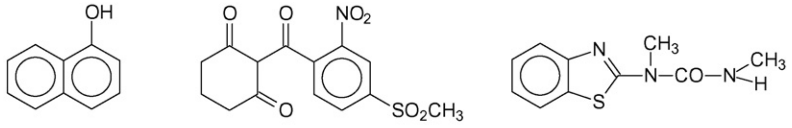


Fig. 1. Absorption spectra of (A) chromophoric constituents of water: nitrate (0.01 M) and cDOM (10 mg/L); (B) 1-naphthol (1), mesotrione (2) and MBTU (3). Spectral distribution of sunlight at sea level in summer and temperate region.



1-naphthol mesotrione methabenzthiazuron (MBTU)

Fig. 2. Chemical structure of pollutants.

mesotrione consists in the lately increase in its use in crops. The ecological fate of this compound in the environment is not completely elucidated and its photochemical behaviour in surface waters is not documented. Methabenzthiazuron (*N*-(2-benzothiazolyl)-*N*,*N*'-dimethylurea) (MBTU) is an active ingredient of Tribunil® (Bayer, France) and Ormet® (Phytorus S.A., France). MBTU belongs to the group of urea herbicides, which is used to control a broad spectrum of broad-leaved weeds and grasses in winter corn, spring wheat, grass seed and in nurseries. It is a toxic product that is bioaccumulated. MBTU is quite soluble in water (around 60 mg/L) and may be transferred into the aquatic environment by leaching.

The absorption spectra of the three selected compounds are shown in Fig. 1B. All of them absorb above 300 nm and have thus the potential to undergo direct photolysis when exposed to solar-light. However, MBTU was previously reported to be very slowly photolyzed in solutions when irradiated above 290 nm alone and in the presence of natural organic matter [15,16]. Thus, we only investigated the photolysis of MBTU in the presence of nitrate ions. For 1-naphthol and mesotrione we studied the photolysis in pure water. In the case it was slow, we also studied the influence of cDOM and nitrate ions. Experiments were conducted in order to approach environmental conditions.

2. Experimental

2.1. Materials

All chemicals were reagent grade and used as received. 1,2-Naphthoquinone (97%), 1,4-naphthoquinone hydrate (97%), 2-hydroxy-1,4-naphthoquinone (97%) and 5-hydroxy-1,4-naphthoquinone (97%) and 4-nitroanisole (97%) were obtained from Aldrich and pyridine from Lancaster. Suwannee River natural organic matter (cDOM) isolated by reverse osmosis (1R101N) was received from the International Humic Substances Society. Experiments were performed in water purified by a Millipore milli-Q device (Millipore αQ, resistivity 18 MΩ cm, DOC < 0.1 mg/L). Stock solutions were stored in the dark at 4 °C.

2.2. Irradiations

For quantum yield measurements, irradiations were performed in a quartz cuvette in a parallel beam at 313 nm using a high pressure mercury arc lamp equipped with a Bausch and Lomb monochromator or at 365 nm using a xenon lamp and a Schoeffel monochromator. Quantum yields were measured by dividing the initial rate of substrate loss by $I_0/l \times (1 - 10^{-A})$ where I_0 is the photon fluence rate expressed in einstein $\text{cm}^{-2}\,\text{s}^{-1}$, l the path length expressed in cm and A is the absorbance of the substrate solution at the irradiation wavelength. The photon fluence rates were measured using potassium ferrioxalate as a chemical actinometer. Irradiation times were adjusted in order to obtain a loss of substrate of around 10%. Substrates decays were monitored by HPLC. Quantum yields values were the average of three independent measurements.

Polychromatic irradiations were performed in two different devices. Device 1 was equipped with six fluorescent Duke sunlamp GL 20 tubes (SNEE, Aubervilliers, France) emitting within the wavelength range 275–350 nm with a maximum of emission at 313 nm. The reactor was cylindrical (internal diameter = 14 mm) and made in Pyrex glass in order to cut off the wavelengths shorter than 290 nm. In these conditions, samples received radiations in the range 290–350 nm only. A ventilator maintained room temperature inside the device.

Device 2 was a Suntest CPS photosimulator (Atlas) equipped with a Xe lamp and a special glass filter restricting the transmission of wavelengths below 290 nm. The lamp was set to an intensity of 750 W/m^2. Cold water flowed through the bottom of the photosimulator to maintain the internal temperature at approximately 27 °C. For irradiation, 10 mL of solutions were placed in dishes (40 mm diameter and 25 mm high) in a plexiglass box covered with a quartz plate to limit evaporation. Evaporation was monitored by weighting samples. In case of evaporation during irradiation due to the Suntest ventilation system, the evaporated water was compensated by addition of water. Each experiment was repeated twice (for a given irradiation time) and all the samples analyzed three times by HPLC. The chemical actinometer used in this study was a mixture of *p*-nitroanisole and pyridine [17]. Prior to kinetic experiments, actinometry was conducted for the 20 possible positions in the reactor to assess the uniformity of light distribution across the surface of the sunlight simulator. Relative error was low (≈5%) whatever the position was into the Suntest, indicating that the intensity of the light emitted from the Xe lamp was spatially homogeneous. Dark control experiments showed no loss of substrates within the timescale of irradiation experiments.

2.3. Analyses

UV–vis absorption spectra were recorded using a Carry 300 Varian spectrophotometer. HPLC-UV analyses were performed at room temperature using a photodiode array detector chromatograph fitted with a reverse phase column (C18 5 μm; 250 mm × 4.6 mm Nucleodur, Macherey-Nagel or Spherisorb S5 ODS2, Waters column). The mobile phase consisted of 40% MeOH and 60% water acidified at pH 2.5 with 3‰ of formic acid for mesotrione, 60% MeOH and 40% acidified water for MBTU and 1-naphthol. A flow rate of 1 mL/min was used for all analyses. For experiments with mesotrione at submicromolar concentrations an appropriate detector was used (Waters 2487). HPLC-ESI-MS analyses of mesotrione and MBTU photoproducts were performed using a Hewlett-Packard HP1100-MSD system working in positive and negative atmospheric pressure ionization. For the nebulization a capillary potential of 4000 V was applied under N_2 (11 L min^{-1}). The fragmentor was set either at 20 V and 120 V alternatively after optimization. The column was a Varian Omnispher C_{18} 100 mm × 3.5 mm (3 μm) for mesotrione and a Ultisphere HDO C_{18} (3 mm × 100 mm, 3 μm) for MBTU. Another set of analyses was performed on a Hewlett-Packard 5989 MS apparatus equipped with a HP G1075A APCI interface. Methanolic irradiated solutions were injected in the mobile phase using the flow injection technique. The following optimised conditions were used: APCI vaporiser temperature 350 °C; capillary temperature 150 °C; source voltage 6 kV; capillary voltage 25 V; source current 5 μA; sheath gas flow (N_2) 80 arbitrary units. Total organic carbon (TOC) measurements in the liquid phase were carried out with a TOC analyser Schimadzu model TOC-5O5OA. The calibration curves within the range 0–30 mg/L were obtained by using potassium hydrogen phthalate and sodium hydrogen carbonate for organic and inorganic carbon, respectively.

3. Results and discussion

3.1. Photolysis of 1-naphthol

We first measured the quantum yield of photolysis of 1-naphthol. For this measurement, aerated solutions of 1-naphthol (0.1 mM, pH 6.5) were irradiated at 313 nm. We found a value of $(1.4 \pm 0.2) \times 10^{-2}$. Provided that this value is independent of 1-naphthol concentration, it can be used to estimate the half-life ($t_{1/2}$) of 1-naphthol in the aquatic environment where it is supposed to be dispersed in very small concentrations [18]. ECETOC proposed the following equation to evaluate the half-life of chemicals in very dilute solutions [19]:

$$t_{1/2} = \frac{\ln 2}{\phi \sum_{\lambda 1}^{\lambda 2} 2300 I_0(\lambda) \Delta\lambda\, \varepsilon(\lambda)}$$

in which ϕ is the quantum yield of direct photolysis in aerated solution, $I_0(\lambda)$ the value of available light intensity expressed in Einsteins cm^{-2} s^{-1} 10 nm^{-1}, λ_1–λ_2 the spectral range, $\Delta\lambda$ the waveband interval (10 nm) and $\varepsilon(\lambda)$ is the mean value of the molar extinction coefficient measured for every 10 nm spectral band expressed in M^{-1} cm^{-1}. The determination of $t_{1/2}$ requires the knowledge of the distribution of energy across the spectral solar emission. We used the sunlight intensities measured by Zepp and Cline [20] at midday, sea level, for latitude 40–50° North. Assuming that the quantum yield of 1-naphthol photolysis is constant over the range 290–350 nm, we finally get $t_{1/2}$ = 30 min. This value must be considered as a rough estimate because it is based on several assumptions. However, it demonstrates that the phototransformation of 1-naphthol through direct photolysis is very fast and should be the dominant degradation pathway in natural conditions.

To conduct the product identification, we irradiated 1-naphthol (0.1 mM) solutions using Device 1. The typical HPLC chromatogram of an aerated solution irradiated until a conversion extent of 30% is presented in Fig. 3. Photoproducts were characterized by reference to authentics. The first peak corresponded to a mixture of 1,2-naphthoquinone and 6-hydroxy-1,4-naphthoquinone. The second peak, which was eluted just after the first one, was assigned to 2-hydroxy-naphthoquinone. Then appeared 1,4-naphthoquinone and 1-naphthol. The fifth and last detected peak corresponded to 5-hydroxy-1,4-naphthoquinone. The formations of 1,4-naphthoquinone, 6-hydroxy-1,4-naphthoquinone and 2-hydroxy-1,4-naphthoquinone were monitored as a function of the irradiation time. 1,4-Naphthoquinone did not accumulate reaching a maximum concentration of 3.3 μM. In contrast to 1,4-naphthoquinone, 6-hydroxy-1,4-naphthoquinone accumulated

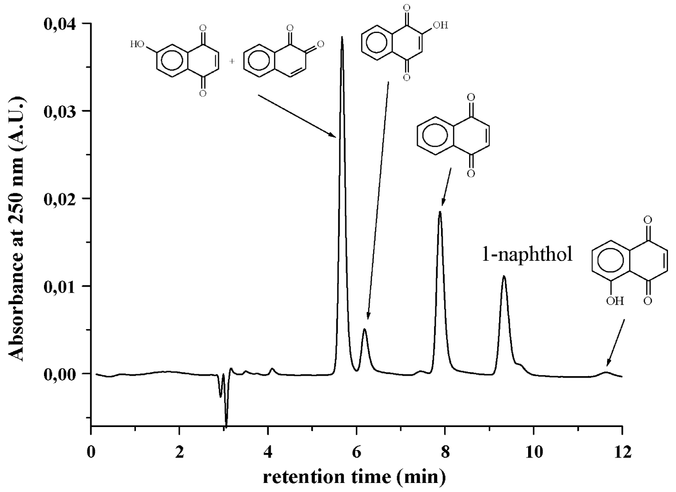


Fig. 3. HPLC chromatogram of an irradiated neutral solution of 1-naphthol (0.1 mM) until a conversion extent of 30%.

in the solution reaching a plateau value of 16 μM when the conversion extent of 1-naphthol was higher than 80%. 2-Hydroxy-1,4-naphthoquinone clearly showed secondary photoproduct kinetics. Thus, the analytical study showed that 1-naphthol is mainly converted into naphthoquinone derivatives.

3.2. Photolysis of mesotrione

The quantum yield of mesotrione photolysis (0.1 mM, pH 6.5) was measured at 365 nm. It was evaluated as to be $(7 \pm 2) \times 10^{-5}$ which is a very small value. Based on this data and using the equation of ECETOC, one can estimate that mesotrione diluted in pure water and exposed to solar-light would show a half-life higher than 1 month. As direct photolysis appears to be a very slow process of mesotrione degradation in real conditions, we also assessed photoinduced reactions. The phototransformation of mesotrione in the presence of cDOM and/or nitrate ions under conditions approaching those prevailing in natural waters was investigated. Typical contaminant concentrations in natural waters are in the ng/L range. At these very low concentrations contaminants do not change the steady state concentrations of transient species they react with. However, it is difficult to conduct kinetic studies at such low concentrations. We chose the concentration of 0.1 μM for mesotrione that should be low enough to not alter quasi-stationary transient concentrations [21], but still allow the monitoring of mesotrione concentration evolution directly from irradiated solutions. Mesotrione was irradiated in Device 2 in the presence of cDOM at concentrations that fall within the range of concentrations encountered in natural waters (15 and 30 mg/L). Rates of mesotrione loss followed pseudo-first-order kinetics ($-d[\text{Mesotrione}]/dt = k \times [\text{Mesotrione}]$). While the reaction rate coefficient (k) for mesotrione alone was $3.3 \times 10^{-7}\ \text{s}^{-1}$, the addition of cDOM (30 mg/L) increased it by a factor of 10. Similarly, cDOM (15 mg/L) enhanced the reaction rate coefficient by a factor of 4.

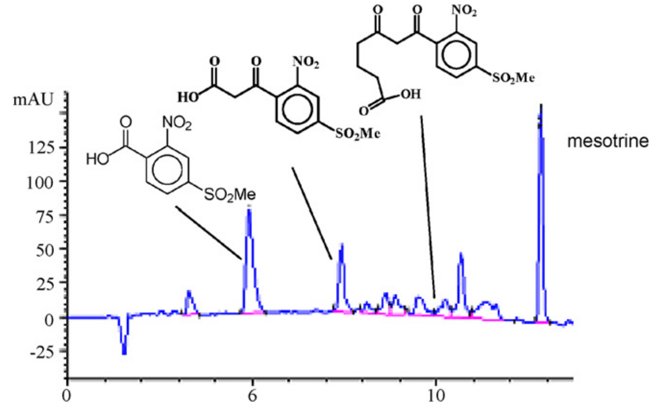


Fig. 4. HPLC-ESI-MS chromatogram of an irradiated neutral solution of mesotrione (0.1 mM).

The effect of nitrates on the reaction was also investigated. The addition of nitrates (50 μM) to mesotrione solutions increased the rate of mesotrione transformation by a factor of 10. At last, mesotrione (0.1 μM) was irradiated in the presence of both cDOM (30 mg/L) and nitrate (50 μM). The rate coefficient was the same as in the presence of cDOM alone.

For products identification, mesotrione was irradiated in Device 1 at a concentration of 0.1 mM. Among all the detected photoproducts, only three compounds were identified by HPLC-ESI-MS analysis (Fig. 4). They were produced by photohydrolysis. The first eluted product was 4-(methylsulfonyl)-2-nitrobenzoic acid as confirmed by the molecular ion at $m/z = 244$ corresponding to $[M - H]^-$ ion observed in ES(−) and a daughter ion at $m/z = 200$ corresponding to the loss of CO_2. The second photoproduct is proposed to be 1,3-diketo-3-(2-nitro-4-methylsulfonylphenyl)-butanoic acid. For this peak the expected parent ion at $m/z = 286$ in ES(−) mode was not detected but instead the supposed decarboxylated daughter ion at $m/z = 242$ in ES(−) mode was observed. The last photoproduct was identified as being 5,7-diketo-7-(2-nitro-4-methylsulfonylphenyl) heptanoic acid on the basis of the parent ion at $m/z = 356$ in ES(−) mode and of the daughter ion at $m/z = 312$ after decarboxylation.

3.3. Phototransformation of methabenzthiazuron

We investigated the phototransformation of MBTU in the presence of nitrate ions only, because MBTU was shown to be photostable when irradiated alone or in the presence of cDOM (quantum yield of photolysis less than 2×10^{-4}) [16]. For kinetic studies, MBTU (1 μM) was irradiated in Device 1 in the presence of NO_3^- (0.1 mM). The rates could be treated in first-order form. The rate coefficient was 10-fold higher in the presence than in the absence of nitrate ions ($k = 0.012 \pm 0.001\ \text{h}^{-1}$ with $R^2 = 0.977$ in pure water, against $0.12 \pm 0.01\ \text{h}^{-1}$ with $R^2 = 0.998$ in the presence of nitrate).

The typical HPLC chromatogram of a solution of MBTU (0.1 mM) and NO_3^- (1 mM) irradiated until a conversion extent of 70% is given in Fig. 5. Numerous photoproducts are present. Several could be identified with the help of LC–MS

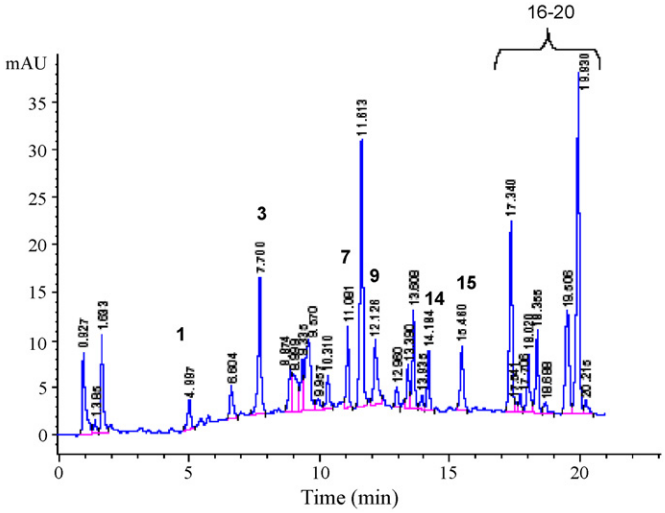


Fig. 5. HPLC chromatogram of a solution containing MBTU (0.1 mM) and NO_3^- (1 mM) irradiated in polychromatic light until a conversion extent of 70%.

using ES interface and of MS using APCI interface and the flow injection technique. Structure of some of them are given in Fig. 5. Photoproducts resulted from oxidation of the ring and of the terminal urea chain. In a first step, hydroxylation of the ring occurs (products 16–20) then the ring is opened (products 1, 3 and 7). Oxidation of the methyl of urea chain leads to demethylation (products 1, 3 and 15). Nitration of the ring was also observed.

3.4. Discussion

This study showed different types of photolysis behaviours of three organic chemicals.

The relative contributions of direct photolysis and photo-induced or photosensitized reactions to the overall transformations vary drastically from one compound to the other. In the case of 1-naphthol, direct photolysis is a quite efficient reaction and the degradation in pure water is fast. In accordance, 1-naphthol was reported to be rapidly photodegraded ($t_{1/2}$ less than 2 h) in artificial sunlight in sea water or in pH 7 buffered water [22,23]. In sea water containing mud, $t_{1/2}$ was reported to be longer (around 5 days) but in these conditions adsorption of 1-naphthol to the sediments should occur, slowing down the photodegradation process [24].

In contrast to 1-naphthol, mesotrione and MBTU are very slowly photolysed in pure water. But, photoinduced and/or photosensitized processes constitute an alternative pathway of degradation. Dissolved organic matter significantly increases the rate of mesotrione degradation but not that of MBTU. It means that mesotrione is reactive towards singlet oxygen, triplet excited states and/or oxygenated radicals photogenerated by cDOM but not MBTU. Only nitrate is able to photoinduce its oxidation. Screening surveys in France showed that concentrations of MBTU up to 1 μM may be reached in surface waters close to agriculture areas. The measurement of a so high concentration is an evidence for methabenzthiazuron build-up due to a slow degradation in the aquatic medium.

Nitrate ions are known to generate hydroxyl radicals under light absorption (1 and references therein). Although nitrate ions absorb solar-light poorly ($\varepsilon \approx 7\ M^{-1}\ cm^{-1}$ at 305 nm) and produces hydroxyl radicals with a rather small quantum yield ($\phi \approx 0.01$), the rate enhancements of mesotrione and MBTU measured in the presence of nitrate seem to be attributable to hydroxyl radicals. To demonstrate this one has to evaluate the rates of mesotrione and MBTU consumption through direct photolysis and compare them to the rate of hydroxyl radical formation in the first stages of the reactions. At 305 nm, the rates of mesotrione and MBTU direct photolysis (0.1 μM and 1 μM, respectively) are equal to $I_0 \times \varepsilon_{305} \times [\text{substrate}] \times l \times \phi \times 2.3$, that is to say around $I_0 \times l \times 8 \times 10^{-9}$ and $I_0 \times l \times 7 \times 10^{-7}$ $M\ s^{-1}$, respectively. The rate of hydroxyl radical formation is equal to $I_0 \times \varepsilon_{305} \times [\text{nitrate}] \times l \times \phi \times 2.3$, that is to say $I_0 \times l \times 8 \times 10^{-6}\ M\ s^{-1}$ for the experiment with mesotrione and $I_0 \times l \times 1.6 \times 10^{-5}\ M\ s^{-1}$ for the experiment with MBTU. As mesotrione absorbs in a much larger wavelength range than nitrate, its rate of direct photolysis has to multiplied by about 10 to largely take into account possible underestimation. On the one hand, we measured that the rate of mesotrione consumption was 10-fold higher in the presence than in the absence of nitrate. On the other hand, the rate of hydroxyl radical formation is 100-fold higher than the rate of mesotrione direct photolysis. Thus, our results are consistent with an oxidation of mesotrione by hydroxyl radicals provided that mesotrione is able to trap one tenth of produced hydroxyl radicals. Similarly, the rate of MBTU consumption was 10-fold higher in the presence than in the absence of nitrate. Based on the rate of MBTU direct photolysis and on the rate of hydroxyl radicals formation, our result would indicate that MBTU is able to trap around one twentieth of produced hydroxyl radicals.

In the case of mesotrione, we added nitrate and cDOM simultaneously and observed the same degradation rate as in the presence of cDOM alone. Using the average value of 2.3×10^4 $(\text{mg C/L})^{-1}\ s^{-1}$ for k_{DOM} [13], the rate constant of reaction of hydroxyl radicals with cDOM, one computes k_{DOM} $[\text{cDOM}] = 2.3 \times 10^5\ s^{-1}$ against $k_{\text{Mesotrione}}$ $[\text{mesotrione}] = 10^3\ s^{-1}$ if one takes for $k_{\text{Mesotrione}}$ a value of $10^{10}\ M^{-1}\ s^{-1}$ close to the diffusional limit. As mesotrione traps one-tenth of hydroxyl radicals, the value of $2.3 \times 10^5\ s^{-1}$ has to be compared with $10^4\ s^{-1}$ corresponding of the sum of hydroxyl radical monomolecular disappearance rates in the absence of cDOM. The addition of cDOM is thus expected to reduce by a factor of 20 the stationary concentration of hydroxyl radicals and also the rate of mesotrione degradation through hydroxyl radicals reaction.

In conclusion, a lot of photochemical reactions take place in the upper layer of the surface waters exposed to solar-light. They lead to the generation of reactive species that can in turn degrade organic contaminants. We assessed the photodegradability of three absorbing organic contaminants in pure and synthetic waters in order to predict their fate in environmental conditions. 1-Naphthol rapidly disappears in pure water. The degradation of mesotrione will be greatly influenced by the level of cDOM of the surface waters. Lastly, methabenzthiazuron is expected to photodegrade in waters containing hydroxyl radicals producers such as nitrate ions. The contribution of photoinduced or photosensitized reactions to the whole transformation reaction is however quite difficult to evaluate because it strongly depends on the presence of potential reactive species scavengers.

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