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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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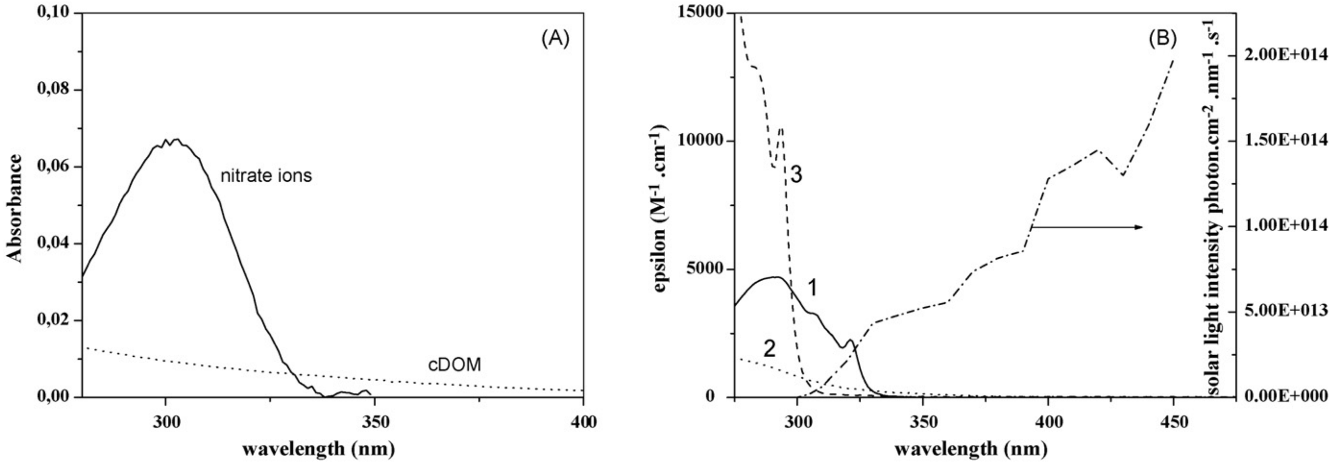
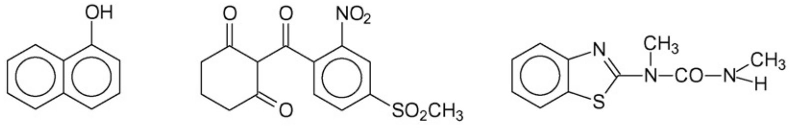


Fig. 1. Absorption spectra of (A) chromophoric constituents of water: nitrate (0.01 M) and cDOM (10 mg/L); (B) 1-naphthol (1), mesotrione (2) and MBTU (3). Spectral distribution of sunlight at sea level in summer and temperate region.



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 $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, 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