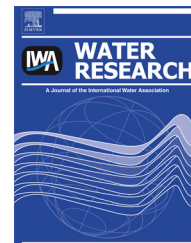


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Photoenhanced transformation of nicotine in aquatic environments: Involvement of naturally occurring radical sources

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ABSTRACT

This work investigated the fate of nicotine (Nico) in aqueous solution upon reaction with singlet oxygen (¹O₂) and hydroxyl radical (HO•). The second-order rate constants of Nico with ¹O₂ ($k_{\text{Nico},^1\text{O}_2} = (3.38 \pm 0.14) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and HO• ($k_{\text{Nico},\text{OH}} = (1.08 \pm 0.10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) were determined using competition kinetics. Photochemical modelling showed that the reaction of Nico with HO• would prevail over that with ¹O₂ in surface waters transformation pathway. The Nico photochemical half-life time could be accounted for by the two reactions. This value would vary in the month-year range depending on the environmental conditions: phototransformation would be favoured in shallow water poor in organic matter and rich in nitrate and nitrite. Irradiation experiments of Nico with nitrite suggested that transformation could not be accounted for by HO• reaction alone. Indeed, a variable fraction of Nico transformation (30–80% depending on the conditions) would take place upon reaction with additional transients, photogenerated NO_x being possible candidates. The chemical structures of the transformation intermediates were derived by means of HPLC-MS. The detection of nitroderivatives upon irradiation of Nico with nitrite suggests the involvement of nitrogen dioxide in the relevant photoprocesses.

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1. Introduction

The fate of pesticides, pharmaceuticals and personal care products (PPCPs) in surface waters is of interest due to their impact on human health and ecosystems (Edwards, 1993; U.S. Environmental Protection Agency). Numerous anthropogenic sources directly emit such compounds in the environment (i.e. water and air) and their presence has been extensively reported (Calamari et al., 2003; Garia de Llasera and Bernal-Gonzalez, 2001; Hernando et al., 2006; Kolpin et al., 2002; Schummer et al., 2010; Thomas, 2002).

Recently, particular attention has been devoted to the occurrence of nicotine (Nico) in the environmental compartments. From an atmospheric point of view, the possible formation of indoor aerosol from the heterogeneous chemistry of Nico has been reported (Petrick et al., 2011; Weschler and Fong, 1986). Furthermore, Nico can reach surface waters during tobacco processing and the manufacturing of tobacco products, and concentrations of a few ng L^{-1} have been measured in sewage treatment plants (Martinez Bueno et al., 2011) and in untreated and drinking waters (Illinois Environmental Protection Agency, 2008). Recently, Nico has been found in the main rivers of the Madrid Region in the range of $0.3\text{--}1.9\ \mu\text{g L}^{-1}$ (Huerta-Fontela et al., 2008; Valcarcel et al., 2011).

Xenobiotics can undergo a variety of abiotic and biological processes in surface waters, including most notably the photochemical reactions. An important issue is that environmental transformation yields products that are sometimes more stable and toxic than the parent compounds (DellaGrecia et al., 2003). In addition to direct photolysis, indirect photochemistry can be important and it does not require the relevant pollutants to absorb sunlight. Significant indirect photochemistry pathways involve reactive oxygen species (ROS) such as singlet oxygen ($^1\text{O}_2$) and hydroxyl radical (HO^\bullet). Singlet oxygen is mainly generated by energy transfer between the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$) and ground-state molecular oxygen ($^3\text{O}_2$) (Boreen et al., 2003). The HO^\bullet radical can be generated upon irradiation of naturally occurring compounds such as nitrite (NO_2^-), nitrate (NO_3^-) and CDOM. It is the most powerful

oxidant occurring in sunlit surface waters, although efficient scavenging by dissolved organic matter limits its steady-state concentrations (Brezonik and Fulkerson-Brekken, 1998). Moreover, the natural occurrence of inorganic nitrogen species such as NO_2^- and NO_3^- can accelerate transformation by photochemically producing nitrogen-centred radicals such as NO_2^\bullet , in addition to HO^\bullet (Passananti et al., 2013).

Nico was found to be stable under simulated sunlight ($\lambda > 290\ \text{nm}$) (Boreen et al., 2003). For this reason, we focused on its possible indirect photochemical degradation upon reaction with ROS such as HO^\bullet and $^1\text{O}_2$. Particular attention was also focused on Nico phototransformation in the presence of nitrate and nitrite.

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (30%), sodium carbonate (99.5%) and sodium nitrate (99%) were purchased from Fluka; sodium sulphate anhydrous (99.5%) and sodium nitrite (98%) from Prolabo; nicotine ($\geq 99\%$), phosphoric acid (85% in water), sodium chloride (98%), terephthalic acid (98%), 2-hydroxyterephthalic acid (97%), Rose bengal (95%) and furfuryl alcohol ($\geq 98\%$) from Sigma Aldrich. All reagents were used as received, without additional purification. All solvents were of HPLC grade and were purchased from Sigma–Aldrich.

Fresh aqueous solutions of nitrate, nitrite or hydrogen peroxide were prepared before each experiment. The concentration of the stock solution of H_2O_2 in milli-Q water was determined using a molar absorption coefficient of $38.1 \pm 1.4\ \text{M}^{-1}\ \text{cm}^{-1}$ at 240 nm (Miller and Kester, 2002).

2.2. Steady-state irradiation experiments

Nico ($\text{pK}_{\text{a}1} = 3.37 \pm 0.02$, $\text{pK}_{\text{a}2} = 8.07 \pm 0.02$) (Nienow et al., 2009) in water may be present as neutral, monoprotonated or diprotonated form, depending on pH. In a broad pH range of environmental significance (4.0–7.5), monoprotonated Nico would be the main species. UV–visible spectra were recorded at different pH values to check for possible variations. Fig. 1 reports the absorption spectra of Nico in aqueous solution at pH 4.7 and 7.7 (showing no differences) and the emission spectrum of the used lamp (solar simulator). For these reasons photochemical experiments were performed at circumneutral pH values (6.5–7.0).

Aqueous solutions were irradiated in a 40 mL thermostated cylindrical reactor, cooled by water circulation at a temperature of $15 \pm 2\ ^\circ\text{C}$ to limit thermal reactions. The reactor was located at one focal point of the lamp to maintain a constant irradiation of the whole sample and it was equipped on top with a Pyrex filter to remove wavelengths lower than $\sim 285\ \text{nm}$. Samples were continuously stirred with a magnetic stirrer and a Teflon bar to ensure homogeneity.

The emission spectrum of the Xenon lamp (see Fig. 1) was recorded using a fiber optics coupled with a CCD spectrophotometer (Ocean Optics USD 2000 + UV-VIS). A reference lamp (DH-2000-CAL, Ocean Optics) was used for calibration. The irradiance reaching the reactor surface was calculated to

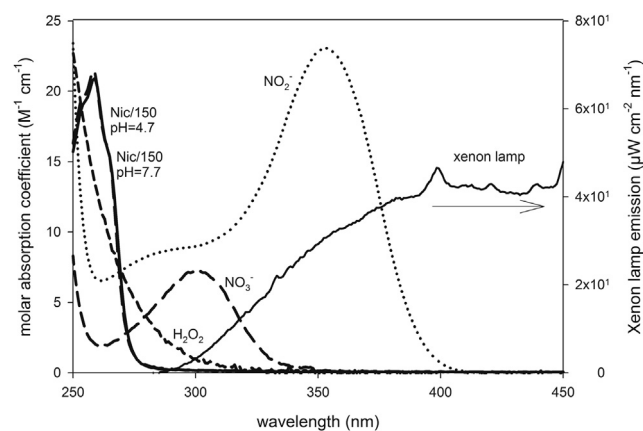


Fig. 1 – Emission spectrum reaching the solution and molar absorption coefficients of the aqueous Nico (at pH 4.7 and 7.7), nitrate, nitrite and H_2O_2 .

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