WATER RESEARCH 73 (2015) 145–156

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/watres

Photogeneration of reactive transient species upon irradiation of natural water samples: Formation quantum yields in different spectral intervals, and implications for the photochemistry of surface waters

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ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form
9 January 2015
Accepted 10 January 2015
Available online 20 January 2015

Keywords:
Indirect photochemistry
Photogeneration quantum yields
Environmental photochemistry
Sensitised photolysis
Spectral intervals

ABSTRACT

Chromophoric dissolved organic matter (CDOM) in surface waters is a photochemical source of several transient species such as CDOM triplet states (^{3}CDOM*), singlet oxygen ($^1O_2$) and the hydroxyl radical (•OH). By irradiation of lake water samples, it is shown here that the quantum yields for the formation of these transients by CDOM vary depending on the irradiation wavelength range, in the order UVB > UVA > blue. A possible explanation is that radiation at longer wavelengths is preferentially absorbed by the larger CDOM fractions, which show lesser photoactivity compared to smaller CDOM moieties. The quantum yield variations in different spectral ranges were definitely more marked for ^{3}CDOM* and •OH compared to $^1O_2$. The decrease of the quantum yields with increasing wavelength has important implications for the photochemistry of surface waters, because long-wavelength radiation penetrates deeper in water columns compared to short-wavelength radiation. The average steady-state concentrations of the transients (^{3}CDOM*, $^1O_2$ and •OH) were modelled in water columns of different depths, based on the experimentally determined wavelength trends of the formation quantum yields. Important differences were found between such modelling results and those obtained in a wavelength-independent quantum yield scenario.

1. Introduction

Chromophoric dissolved organic matter (CDOM) is the main sunlight absorber in surface waters up to at least 500 nm (Loiselle et al., 2009; Bracchini et al., 2011). By absorbing sunlight, CDOM attenuates the penetration of UV and most notably UVB radiation in water columns and protects living organisms from the associated harmful effects (Rose et al., 2009; Ruiz-Gonzales et al., 2013). Radiation absorption by

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http://dx.doi.org/10.1016/j.watres.2015.01.016
0043-1354/

CDOM causes several modifications in the absorbing material, the most evident one being its photobleaching (loss of absorbance due to the transformation of chromophoric groups into non-chromophores) (Sulzberger and Durisch-Kaiser, 2009; Zhang et al., 2013). Some degree of photomineralisation has also been observed, most notably under acidic conditions (Anesio and Graneli, 2003, 2004; Vione et al., 2009). However, the most effective pathway leading to CDOM mineralisation is probably a combination of photochemical and microbial processes (Vahatalo and Wetzel, 2008), where irradiation enhances the bioavailability of the organic material (Vahatalo et al., 2003; Piccini et al., 2013).

Another important consequence of radiation absorption by CDOM is the generation of reactive transient species that are involved into the transformation of (C)DOM itself and of xenobiotics. In the latter case one speaks of indirect photolysis of pollutants (Canonica et al., 2006; Vione et al., 2014). The photogenerated transients are CDOM triplet states (^{3}CDOM*), singlet oxygen ($^1O_2$), the hydroxyl radical (•OH), superoxide (O_2^{-}•) and other still poorly characterised radical species arising from the photooxidation of organic matter (*e.g.* peroxy radicals, ROO•) (Hoigné, 1990; Canonica and Freiburghaus, 2001; Grebel et al., 2011). Of the above transients, ^{3}CDOM*, $^1O_2$ and •OH are well known to take part to the degradation of various biorefractory xenobiotics, including emerging pollutants (Boreen et al., 2003; Ruggeri et al., 2013), but secondary pollutants can also be formed in the relevant processes (Iesce et al., 2004; Méndez-Díaz et al., 2014). The production of $^1O_2$ directly stems from that of ^{3}CDOM* (reactions 1,2, where ISC = Inter-System Crossing) (Hoigné, 1990), while the pathways leading to •OH from irradiated CDOM are more controversial. Reactions (3–8) show possible H_2O_2-associated processes, where Fe^{III}-L is an organic ferric complex (a CDOM component as well; Xiao et al., 2013) and R is an easily oxidised organic compound. However, it is well known that part of the •OH production by CDOM does not depend on H_2O_2 (Page et al., 2011). In this case, possible pathways are either the fragmentation of oxygen-containing radical species or the oxidation of H_2O/OH^- by photoexcited CDOM. Some evidence of the latter pathway has been obtained with some triplet sensitisers as CDOM proxies (Sur et al., 2011), but the significance of these results for CDOM photochemistry is still highly uncertain.

$$\mathrm{CDOM} + h\nu \rightarrow {}^1\mathrm{CDOM}^* \xrightarrow{ISC} {}^3\mathrm{CDOM}^* \quad (1)$$

$$^3\mathrm{CDOM}^* + O_2 \rightarrow \mathrm{CDOM} + {}^1O_2 \quad (2)$$

$$^3\mathrm{CDOM}^* + R \rightarrow \mathrm{CDOM}^{-\bullet} + R^{+\bullet} \quad (3)$$

$$\mathrm{CDOM}^{-\bullet} + O_2 \rightarrow \mathrm{CDOM} + O_2^{-\bullet} \quad (4)$$

$$2\, O_2^{-\bullet} + 2H^+ \rightarrow H_2O_2 + O_2 \quad (5)$$

$$Fe^{III}\text{-}L + h\nu \rightarrow Fe^{2+} + L^{+\bullet} \quad (6)$$

$$H_2O_2 + h\nu \rightarrow 2\ {}^\bullet OH \quad (7)$$

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^\bullet OH \quad (8)$$

CDOM is the only source of ^{3}CDOM* and $^1O_2$ and it is an important •OH source as well (Glover and Rosario-Ortiz, 2013; Lee et al., 2013). Significant CDOM absorption would still take place in deep waters, where the sunlight spectrum is depleted of UV radiation (which is absorbed in the upper water layers) (Loiselle et al., 2008). Some processes induced by irradiated CDOM (*e.g.* the reaction of pollutants with ^{3}CDOM* and $^1O_2$) are potentially more important in deep water bodies (De Laurentiis et al., 2013a), where the ability of CDOM photochemistry to be triggered by visible radiation is a major factor. In this context, the efficiency (quantum yield) by which irradiated CDOM produces different reactive transients as a function of the absorbed wavelength(s) has major importance.

Quantum yields of transient production by humic substances (HS) under UVC radiation have been determined in order to assess indirect photoreactions in UV water treatment. Comparison with results obtained under real or simulated sunlight suggests that HS quantum yields vary depending on the spectral range (Lester et al., 2013). It is also well known that the quantum yield of •OH photogeneration in natural waters is higher in the UVB than in the UVA region (Mopper and Zhou, 1990; Sharpless and Blough, 2014), and variations with wavelength have been reported for the quantum yield of $^1O_2$ generation by humic and fulvic substances (Sharpless, 2012). Unfortunately, very little is known about the wavelength trend under sunlight-relevant conditions of the formation quantum yields of ^{3}CDOM* (Sharpless and Blough, 2014), from which $^1O_2$ is directly formed and •OH might also arise (at least indirectly, see reactions 3–5,8). Moreover, few or no data are available on the photochemical generation of the main transients (^{3}CDOM* and $^1O_2$, in addition to •OH) upon irradiation of natural water samples (as opposed to CDOM isolates) in wavelength intervals of environmental significance. This is a knowledge gap when modelling photochemistry in whole columns of natural water bodies.

This paper undertakes the task of filling this gap, by measuring the formation quantum yields of ^{3}CDOM*, $^1O_2$ and •OH in different spectral intervals, in natural water samples taken from lakes that differ for trophic state and surrounding environment. The significance of the results for the modelling of the photochemistry of surface waters is assessed as well.

2. Experimental

2.1. Reagents and materials

$NaNO_3$ (purity grade 99%), $MgSO_4$ (99%), $CaCl_2 \cdot 2H_2O$ (98%), NH_4Cl (99.5%), HCl (37%), K_2CO_3 (99%), $NaHCO_3$ (99.5%), 2,4,6-trimethylphenol (97%), furfuryl alcohol (98%), phenol (99%), 2,4-dinitrophenylhydrazine (97%), methanol (gradient grade), tetrabutylammonium hydroxide (98%) and 2-nitrobenzaldehyde (98%) were purchased from Aldrich, $NaNO_2$ (97%) and H_3PO_4 (85%) from Carlo Erba, KNO_3 (99%), KCl