



Photochemical transformation of sunscreen agent benzophenone-3 and its metabolite in surface freshwater and seawater



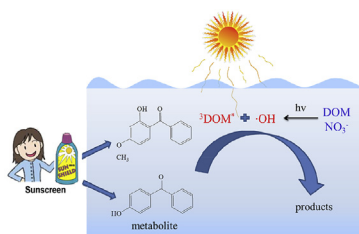
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HIGHLIGHTS

- Direct photolysis of benzophenone-3 and its metabolite exhibits pH dependence.
- Photolytic rates of both compounds are lower in seawater than those in freshwater.
- Triplet-excited DOM is largely responsible for indirect photolysis in seawater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 January 2016

Received in revised form

17 March 2016

Accepted 17 March 2016

Available online 29 March 2016

Handling Editor: Keith Maruya

Keywords:

Benzophenone-3

Metabolites

Photodegradation

Triplet-excited dissolved organic matter

Hydroxyl radical

ABSTRACT

The occurrence of sunscreen agents and their metabolites in surface waters gives rise to public concerns. However, little is known about the environmental fate of these pollutants at present, especially for their metabolites. In this study, we investigated the photochemical of sunscreen agents and their metabolites in natural waters, adopting benzophenone-3 (BP-3) and its human metabolite 4-hydroxybenzophenone (4-OH-BP3) as examples. Results show that only anionic forms of both BP-3 and 4-OH-BP3 can undergo direct photodegradation. The photolytic rates of both compounds in natural waters are faster as compared to those in pure water. Radical scavenging experiments revealed that triplet-excited dissolved organic matter ($^3\text{DOM}^*$) was responsible for the indirect photodegradation of BP-3 and 4-OH-BP3 in seawater, whereas in freshwater, the indirect photodegradation of these two compounds was attributed to $^3\text{DOM}^*$ and $\cdot\text{OH}$. $^1\text{O}_2$ plays a negligible role in their photodegradation because of the weak $^1\text{O}_2$ reactivity. Furthermore, we probed the contribution of $\cdot\text{OH}$ and $^3\text{DOM}^*$ to the photodegradation of both compounds in freshwater, and the results revealed that $\cdot\text{OH}$ accounted for 56% and 59% of the observed photodegradation for BP-3 and 4-OH-BP3, respectively, whereas $^3\text{DOM}^*$ accounted for 43% and 12% of the observed photodegradation for BP-3 and 4-OH-BP3, respectively. These results are helpful in assessing the ecological risk of BP-3 and its metabolite in the aquatic environment.

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1. Introduction

Benzophenone-3 (BP-3) is commonly used as sunscreen agent for personal care products to protect human skin and hair from

direct exposure to ultraviolet radiation (Jansen et al., 2013; Liao and Kannan, 2014). BP-3 has also been approved by the U.S. Food and Drug Administration as an indirect food additive (U.S. FDA Department of Health and Human Services, 2013), e.g., ultraviolet stabilizer in plastic surface coatings for food packaging (Kim and Choi, 2014). It was reported that approximately 4000 tons per year of BPs were produced in China (CCCC, 2012). Like many

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xenobiotics, BP-3 also undergoes phase I and phase II metabolism, and its metabolites are excreted from the body mainly through urine (Calafat et al., 2008; Kadry et al., 1995; Zhang et al., 2013a). Kunisue et al. (2012) observed that both BP-3 and its metabolites were detected in 83.8% of urine samples ($n = 625$). These compounds can enter the wastewater treatment plant through urban drainage network. Since complete removal of the compound in wastewater treatment plant is impossible, BP-3 and its metabolites are inevitably released into the aquatic environment, causing hazard to organisms (Kim and Choi, 2014). According to previous studies, BP-3 is capable of performing estrogenic and anti-androgenic activities (Calafat et al., 2008; Kim and Choi, 2014; Schlumpf et al., 2001). Some metabolites of BP-3 are even more toxic than BP-3 itself. For example, the estrogenic activities of 4-OH-BP3 are higher compared to those of BP-3 (Suzuki et al., 2005; Wang and Kannan, 2013). Thus, for full-scale risk assessment of sunscreens, special attentions should be paid to the environmental fate of their metabolites as well as the parent compounds.

Assessing the potential risks posed by aquatic pollutants requires an understanding of the processes influencing their transformation and fate. Photochemical degradation has been proved to be a major transformation pathway for organic pollutants in surface waters (Li et al., 2014; Pace and Barreca, 2013; Yan and Song, 2014). Some sunscreen agents have already been found to undergo phototransformation (Ji et al., 2013; Vione et al., 2013; Zhang et al., 2010, 2013b). In addition to the direct photodegradation, many sunscreens may also undergo indirect photodegradation, which is initiated through light absorption by photosensitizers. The photosensitizers, including dissolved organic matter (DOM), $\text{NO}_3^-/\text{NO}_2^-$, and Fe(III), are capable of generating reactive species, e.g., excited triplet state DOM ($^3\text{DOM}^*$), $^1\text{O}_2$, and $\cdot\text{OH}$ (Chen et al., 2013a, 2013b; Chowdhury et al., 2011; Ge et al., 2015; Niu et al., 2013; Sun et al., 2014).

Although efforts have been made on the photochemical transformation of sunscreen agents (Mao et al., 2011; Sakkas et al., 2003; Zhang et al., 2012, 2013b; Zhou et al., 2013), studies on the environmental photochemical behavior of BP-3 are scant. Liu et al. (2011) reported that BP-3 was almost inert in pure water under simulated sunlight irradiation. Based on the second-order reaction rate constants of BP-3 with reactive species, Vione et al. (2013) predicted that besides direct photolysis, indirect phototransformation with $\cdot\text{OH}$ and $^3\text{DOM}^*$ were important pathways of BP-3 under conditions relevant to surface waters. Nevertheless, the contributions of the reactive species have not been experimentally verified in surface freshwater and seawater yet. Considering BP-3 is ionizable and has different dissociation forms under the aquatic environmental pH conditions (6–9), it may exhibit different photochemical behaviors as other ionizable compounds (Chen et al., 2013b; Maddigapu, et al., 2010; Wei et al., 2013). Therefore, it is necessary to investigate the photochemical behaviors of different dissociations of BP-3. Additionally, BP-3 was also detected in seawater and coastal water with a concentration as high as 577.5 ng/L (Tovar-Sánchez et al., 2013; Yu et al., 2011). Furthermore, metabolites of BP-3 have been found in natural waters, and some of them were observed to have stronger estrogenicity than the parent compound (Kim and Choi, 2014). So far, no any studies have been focused on the photochemical transformation of metabolites of BP-3 in natural waters, and the effects of reactive species on their photodegradation are unclear.

In this study, we investigated the photochemical behavior of BP-3 and 4-OH-BP3 in pure water, freshwater, and seawater. 4-OH-BP3, as an important metabolite of BP-3, which is frequently detected in human urine (Kunisue et al., 2012) with a concentration up to 61.4 $\mu\text{g/L}$ (Wang and Kannan, 2013). We determined the steady

state concentrations of reactive species in freshwater and seawater to clarify the contributions of reactive species on the photodegradation of 4-OH-BP3 and BP-3.

2. Materials and method

2.1. Chemicals

Benzophenone-3 (BP-3, 98% purity) and 4-hydroxybenzophenone (4-OH-BP3, 99%) were purchased from J&K Scientific (China). Sorbic acid (99%) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 99%) were obtained from Tokyo Chemical Industry (Japan). Rose Bengal (95%), acetophenone (99%), furfuryl alcohol (99%), and *p*-chlorobenzoic acid (*p*CBA, 99%) were provided by J&K Scientific (China). Acetonitrile and isopropanol were of the HPLC grade, and they were from Tedia. Aqueous solutions for the photolytic experiments were prepared with ultra pure water obtained from a system of Shanghai Lakecore Instrument (China). This water was also used as HPLC eluent. Other chemical reagents were of analytical grade and were used as received without further purification.

Freshwater and seawater samples (100 L) were collected from the Yellow River estuary, the second largest river in China. Emerging pollutants were frequently detected in this area (Wang et al., 2010; Xu et al., 2009). Water samples were filtered through 0.45 μm glass filters, and stored at -20°C until use. UV–vis absorption spectra of freshwater and seawater were shown in Fig. S1, and concentrations of inorganic ions, TOC, pH and conductivity were measured. Results are listed in Table 1 (detailed analytical processes see the Supplementary materials).

2.2. pK_a measurements

The pK_a values of BP-3 and 4-OH-BP3 were determined by a spectrophotometric titration method (Boreen et al., 2004). Stock solutions of BP-3 (1 mM) and 4-OH-BP3 (1 mM) were dissolved in pure water. Aqueous solutions containing 20 μM target compounds were obtained by diluting stock solutions with 5 mM phosphate buffers ($\text{pH} = 5\text{--}12$). Ultraviolet spectral of BP-3 and 4-OH-BP3 under different pH conditions were recorded by a Hitachi UV 2200 spectrophotometer. The absorbance at a single wavelength was plotted as a function of pH, and the resultant data curves were fitted using a non-linear sigmoidal regression to determine the pK_a values.

2.3. Photolytic experiments

Photolytic experiments were performed with an XPA-7 merry-go-round photoreactor (Xujiang Electromechanical Plant, China). A water-refrigerated 500 W medium-pressure Hg lamp surrounded by 290 nm cut-off filter was employed as light source. The light source irradiation spectrum was measured by optical sensors (RAMSES, TriOS) and the main irradiation wavelengths include 313, 334, 365, 405, and 436 nm (Fig. S2). The light intensity in the center of the tubes was 5.3 mW/cm. Photolytic solutions containing target compounds (5 μM) were prepared by diluting stock solutions (1 mM BP-3 and 1 mM 4-OH-BP3) with phosphate buffer (5 mM) or sampled water. Direct photolysis quantum yields (Φ) of the two compounds were obtained by the following equation:

$$\Phi_s = \frac{k_s}{k_{\text{PNA}}} \frac{\sum L_\lambda \epsilon_\lambda^{\text{PNA}}}{\sum L_\lambda \epsilon_\lambda^s} \Phi_{\text{PNA}} \quad (1)$$

where the subscripts “s” and “PNA” stand for the target compounds

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