

The natural degradation of benzophenone at low concentration in aquatic environments

Dao-Yong Chen, Xiao-Feng Guo, Hong Wang and Hua-Shan Zhang

ABSTRACT

The natural degradation caused by sun irradiation and microbes in aquatic environments is of major significance in the elimination process of benzophenone (BP). In this study, the fate of BP in surface water at a low concentration of 10 µg/L was investigated, including both photodegradation and microbial degradation. The result showed that the photodegradation rate of BP was affected by several parameters such as the initial concentration, continuous input, and the presence of the analogue, ions and small molecules. Meanwhile, the rate of microbial degradation of BP was mainly influenced by the kind and amount of microbes in the environmental water.

Key words | benzophenone, microbial degradation, photodegradation

Dao-Yong Chen
Xiao-Feng Guo
Hong Wang
Hua-Shan Zhang (corresponding author)
Key Laboratory of Analytical Chemistry for Biology
and Medicine (Ministry of Education),
Department of Chemistry,
Wuhan University,
Wuhan 430072,
China
E-mail: hshzhang@whu.edu.cn

INTRODUCTION

Many UV filters, such as benzophenone (BP) and its analogues 2,4-dihydroxybenzophenone (BP-1) and 2-hydroxy-4-methoxybenzophenone (BP-3), were used as an ingredient of pharmaceuticals, insecticides, agricultural chemicals and fragrance in medicine and industry and as a UV light-absorber in plastic and polymers (FDA Department of Health & Human Services 1999). BPs are also widely used in cosmetic products such as photostabilizers to protect the skin and hair from UV irradiation. However, BPs are also known as an ubiquitous pollutant in the urban aquatic environment, found in both surface water and sediment in the order of parts per billion to parts per thousand (Balmer *et al.* 2005; Fent *et al.* 2008, 2010; Rodil & Moeder 2008a, b; Zenker *et al.* 2008; Moeder *et al.* 2010). In fact, hydrophobicity of BP and its partitioning in the sediments meant that the BP contamination mainly existed in sediments, but the removal of BP in sewage treatment plants (STPs) is often incomplete, so it is discharged into surface water and then into different aquatic compartments, such as groundwater and drinking water, which indicates that the degradation capabilities and removal efficiencies of the wastewater treatment process need to be improved. Furthermore, it was recently reported that BP has a certain estrogenic activity in mammals (Weisbrod *et al.* 2007; Fent *et al.* 2008; Kunisue *et al.* 2012), and it is also a toxin in aquatic systems and a contact allergen. Consequently, BP has been listed among endocrine-disrupter chemicals by the World Wildlife Fund and the Japanese Ministry of

Environment. Photodegradation of BP caused by sun irradiation and biodegradation caused by micro-organisms are the important steps in the natural elimination process. Therefore, it is of major significance to investigate the existence and natural transformation of BP.

To date, only a few studies have focused on the natural degradation of BP. For instance, BP-degrading microbes for potential bioremediation were screened and the degradation activity in the activated sludge of an STP in Hokkaido was found (Fujii & Kikuchi 2005), and BP biodegradability by 16 fungi from their stock culture was identified (Takita *et al.* 2005). Moreover, the ozonation and photostability of BPs in water were investigated (Legube & Leitner 1999; Hojerova *et al.* 2011; Gago-Ferrero *et al.* 2013), and some catalysts for the degradation BP in aqueous solution were reported, such as Mn-Fe-K modified ceramic honeycomb (Hou *et al.* 2006). However, in these studies, a high concentration of BP (mg/L) was used. In fact, UV filters exist in surface water at much lower concentrations (ppb to ppt) which may cause chronic poisoning, and the concentrations of coexisting organic compounds have an obvious impact on BP degradation. Thus, to evaluate the effect of BPs on the environment, it is necessary to study the natural degradation of BP at trace levels.

Usually, BP exists in the environment with continuous input and in the presence of coexisting compounds. The investigation of the photodegradation of BP with these conditions at real environmental concentrations under sunlight

will help to understand its fate in environment. However, to our best knowledge, few studies about this have been reported until now.

The aim of this study was to investigate the natural degradation process of BP in environmental water at concentrations (ppb) close to those found in real environments. The effects of continuous input, the presence of a coexisting pharmaceutical and different initial concentrations on photodegradation of BP in aquatic solution were studied for the first time. In addition, kinetic parameters such as quantum yields and rate constants were also determined.

METHODS

Chemicals and materials

BP, ibuprofen, BP-3 and BP-1 with 99.5% purity were obtained from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Sodium nitrate, humic acid (HA), sodium azide, sodium chloride and ferric sulfate were all of analytical grade. Methanol and acetonitrile (high-performance liquid chromatography (HPLC) grade) were obtained from Tedia Company Inc. (Ohio, USA). Deionized water was prepared with a Milli-Q water purification system (Beijing, China).

Sample preparation

The stock standard solution of BP was prepared in methanol at a concentration of 1 mg/mL and stored at 4 °C in a refrigerator. Working standard solutions of BP were prepared by appropriate dilution of the stock solution using deionized water.

Water samples collected from the East Lake and the Changjiang River in Wuhan were filtered using 0.22 µm filters, and then stored at -20 °C. These water samples were free of BPs and ibuprofen.

Hydrolysis experiments

The solutions of BP in deionized water, East Lake water and Changjiang River water at the concentration of 10 µg/L were kept in test glass tubes covered by aluminum foil. About 5 mg of sodium azide was added to reach a concentration of 0.25 mg/mL, respectively. The temperature was maintained constantly at 25 °C by means of a water bath. Aliquots of each sample were withdrawn at appropriate

intervals (0, 1, 3, 6, 10, 20 and 30 days). The solutions were passed through a Whatman 0.45 µm fiber microfilter and analyzed by HPLC in order to monitor the substrate decay.

Photodegradation

Quartz tubes ($\varphi 1.8 \times 22$ cm) filled with 20 mL of solution with appropriate concentration of BP prepared by adding stock solution (about 5 mg of sodium azide was added) were exposed to solar irradiation on a building's terrace in Wuhan (30°58'N, 114°33'E) from March to April in 2013. Quartz tubes containing the solutions were held approximately 45° from the horizon, and exposed to clear sunshine from 9:00 to 16:00. Every 5 hours, aliquots of each sample solution were passed through a Whatman 0.45 µm fiber microfilter and analyzed by HPLC.

BP-1 and BP-3 as the analogue of BP and ibuprofen as the non-analogue were employed to investigate the competitive light degradation of the coexisting compounds. The pure solution of BP and a mixture of the analyte and its analogue and non-analogue were exposed to solar irradiation for a period, respectively. Then, the samples were analyzed immediately.

Quantum yields in pure water were measured by using potassium ferrioxalate as a chemical actinometer (Hatchard & Parker 1956). Dark controls shielded from light were performed simultaneously under the same conditions. Photodegradation experiments and the dark controls were carried out in triplicate.

Microbial degradation

Fifty milliliters of solution with 10 µg/L of BP was prepared by adding stock solution to East Lake water and Changjiang River water, respectively. The sample solutions were stored in cool, dark and anaerobic condition for 12 days. Aliquots of each sample were analyzed every 2 days by HPLC after being passed through a Whatman 0.45 µm fiber microfilter. At the same time, the same solutions received 5 mg sodium azide for the control experiments under the same conditions.

Analytical determinations

Initial and residual concentrations of BP were analyzed by a Dionex Summit U3000 HPLC system equipped with a manual injector and a photodiode array detector (Dionex Technologies, USA). Chromeleon ChemStation program

for LC was used to process chromatographic data. An amethyst-C18 column (4.6 mm × 250 mm, 5 μm) from Sepax Technologies Inc. (Newark, USA) was connected with a guard column (cartridge 2.1 mm × 12.5 mm, 5 μm, Agilent Technologies, Palo Alto, CA, USA) filled with the same packing material. The mobile phase was a mixture of methanol–water (80:20, v/v) and the flow rate was 1.0 mL/min. The column temperature was set at 30 °C. The UV detector was set at a wavelength of 256 nm for BP, 290 nm for BP-1 and BP-3 and 230 nm for ibuprofen. All injections were performed manually with a 20.0 μL sample loop. The absorption spectra of BP, BP-1, BP-3 and ibuprofen were measured by a UV and visible spectrophotometer.

RESULTS AND DISCUSSION

Photodegradation of BP

Photodegradation in natural waters and quantum yields of BP

At room temperature, upon preserving the control solutions in the dark for up to 30 days, the BP concentrations decreased by only 0.8, 4.2 and 4.7% in pure water, East Lake water and Changjiang River water, respectively. This result indicated that the decay by hydrolytic microbiological or thermal means was negligible during the photodegradation experiments. The wavelength-averaged (250–350 nm) quantum yields of BP were determined to be 0.0013 ± 0.001 using potassium ferric oxalate as the chemical actinometer.

To assess the sunlight capability to promote the direct photolysis of the target compounds, photodegradation experiments with the use of solar radiation were carried out. The kinetic parameters were calculated choosing first-order kinetics as the mathematical models. The detection limit of the analytical method was 0.3 μg/L. As shown in Table 1, photodegradation rates of BP in natural water were faster than those in pure water under solar irradiation. Meanwhile, the photodegradation rate of BP in Changjiang River water was faster than that in East Lake water. The similar or different photodegradable potential in natural water compared with pure water can be attributed to the integrative effects of different constituents (e.g. Cl⁻, Fe³⁺, NO₃⁻ and HA) on the photodegradation (Lam *et al.* 2003). The photolysis of BP in the presence of common water constituents such as Cl⁻, Fe³⁺, NO₃⁻ and HA was investigated

Table 1 | Kinetic parameters for the photolytic degradation of BP. Initial concentration 10 μg/L

Matrix	k , h ⁻¹	R ²	$t_{1/2}$, h
Pure water	0.0427 ± 0.0011	0.9631	16.23
East Lake water	0.0671 ± 0.0053	0.9134	10.62
Changjiang River water	0.0852 ± 0.0108	0.9541	8.672
0.5 mmol/L NaCl	0.0460 ± 0.0094	0.9630	15.03
10 mg/L NaNO ₃	0.0542 ± 0.0047	0.9598	16.25
5 mg/L HA	0.0677 ± 0.0240	0.9335	10.24
5 mg/L Fe ₂ (SO ₄) ₃	0.0512 ± 0.0066	0.9599	13.54

by adding them to pure water with BP to understand the different degradation of BP in nature water and pure water. The corresponding values of degradation rate constant k (h⁻¹) and half-life $t_{1/2}$ (h) are listed in Table 1. The removal of BP was faster obviously in the presence of Cl⁻, Fe(III) and HA, which should explain the different photodegradable potential in natural water and pure water.

Effects of initial concentration on photodegradation

The change of concentration of micropollutants in water could cause the change of degradation of micropollutants. So, the effect of different initial concentration of BP on photodegradation efficiency by solar radiation was studied. As shown in Figure 1, the photodegradation rate k of BP decreased obviously as the initial concentration c_0 rose from 10 to 100 μg/L, and then, the photodegradation rate decreased slowly as the initial concentration rose from 100 to 500 μg/L. There was a relation approximating to the exponential function between the photodegradation rate k and

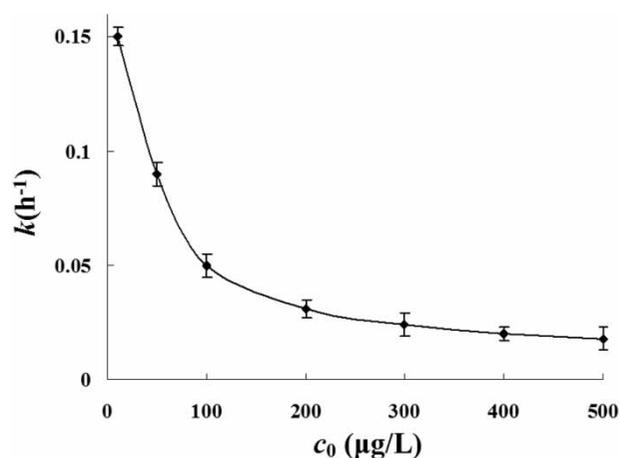


Figure 1 | Effect of initial concentration on the photodegradation of BP in pure water under solar irradiation.

the initial concentration c_0 of BP. The effect could be ascribed to the effect of self-sensitization (Werner *et al.* 2006). And the same tendency for photodegradation of the pharmaceuticals was observed by Doll & Frimmel (2003) and Neamtu & Frimmel (2006). So, a realistic low concentration of compounds should be used when their photodegradation in natural environment was studied.

The result showed that the photodegradation of BP was not a first-order reaction. However, for the convenience of data analysis, the experimental data obtained in this study were calculated by using a pseudo-first-order kinetic model.

Effects of continuous input

Like other micropollutants, BP exists in the environment with continuous input. And it has been found that many micropollutants were not removed or degraded completely during the wastewater treatment process (Heberer *et al.* 2000). So, the concentration of micropollutants in surface waters will probably rise with the passing of time, which would affect the degradation of BP with continuous input. To investigate the effect of continuous input on the photodegradation of the pharmaceuticals, a definite concentration of BP solution with calculated volume was added repetitively after the reaction solution was irradiated under solar for a period, to keep the BP concentration equal to the initial concentration. Figure 2 shows the effect of continuous input on the photodegradation of BP in pure water. Linear regression of $\ln(c/c_0)$ on time (t) indicated that the photodegradation of BP after adding followed the pseudo-first-order kinetics ($r^2 > 0.98$). Continuous input resulted in an obvious decrease in the degradation rate of BP. Comparing to the solution without continuous input of BP during the process, the $t_{1/2}$ for BP

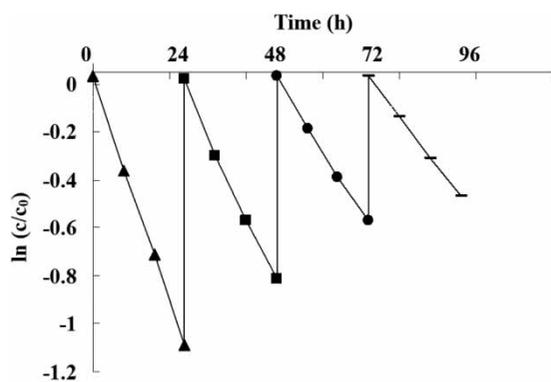


Figure 2 | The photodegradation of BP under solar irradiation after four times of continuous input. Initial conditions: conc. = 10 $\mu\text{g/L}$. Symbols: \blacktriangle , \blacksquare , \bullet and \times represent the first to the fourth time continuous input of BP.

increased 16.23 h to 36.46 h after four times of concentration recovery. The result indicated that continuous input of BP would cause its accumulation in the natural water environment. This is the first report about the influence of continuous input on BP, which was important for assessing the fate and pollution of BP.

Effects of the presence of coexisting compound

To simulate the natural conditions, the effect of the coexisting compounds on the photodegradation of BP was investigated. BP-1 and BP-3 as the analogue of BP and ibuprofen as the non-analogue of BP were employed to assess the influence of the coexisting compounds in this study. Their structures are shown in Figure 3, and the results are shown in Figure 4.

The results showed that the existence of both BP-1 and BP-3 could reduce the photodegradation rate of BP in pure water. Conversely, the effect could be negligible when ibuprofen was present. This could be explained by the fact that BP-1 and BP-3 have an obvious absorption at 356 nm, which was the maximum absorption wavelength of BP, while no obvious overlap in the UV absorption spectrum between BP and ibuprofen was observed (Figure 5). Wagner *et al.* have reported that the overlap in the UV absorption spectrum could result in a reduction of the rate of hydroxyl radical production (Wagner *et al.* 1980). The self-sensitized photodegradation was due to the similar structures among BP-1, BP-3 and BP.

Microbial degradation

The microbial degradation of BP in aquatic environment is also an important part of the BP natural degradation. In the study, Changjiang River water with good flowability and East Lake water with bad flowability were used to

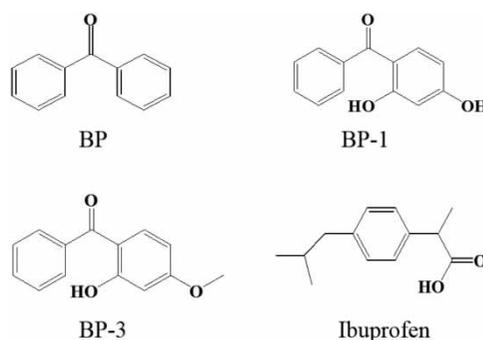


Figure 3 | Structures of BP, BP-1, BP-3 and ibuprofen.

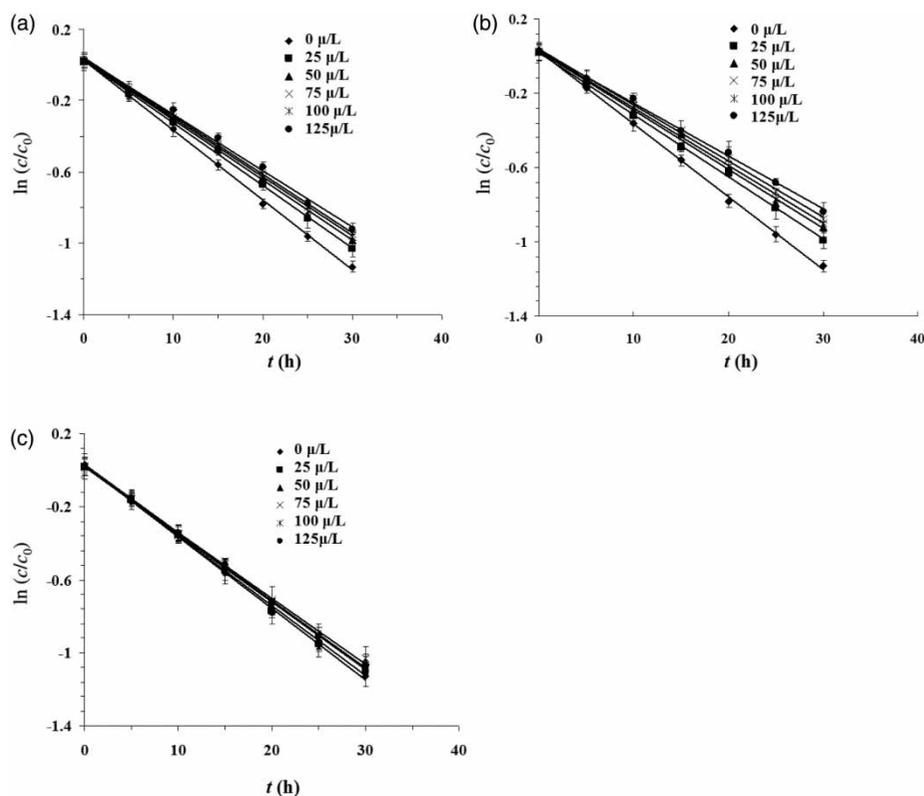


Figure 4 | Effect of different concentrations of BP-1 (a), BP-3 (b) and ibuprofen (c) on the photodegradation of BP in pure water under solar irradiation.

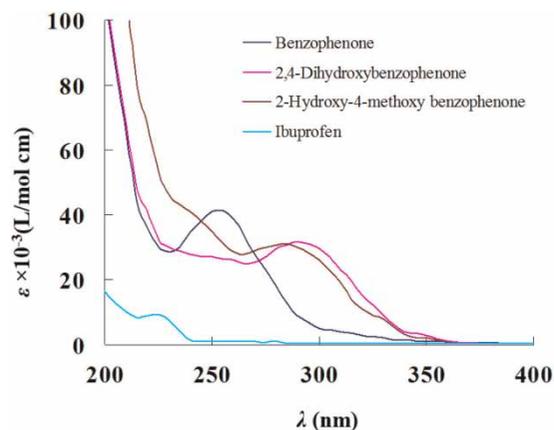


Figure 5 | Ultraviolet absorption spectra of BP, BP-1, BP-3 and ibuprofen.

investigate the microbial degradation of BP at low concentrations of 10 $\mu\text{g/L}$, respectively. The organic and solids contents of East Lake water were 0.37 and 0.2 mg/L and those of Changjiang River water were 139.2 and 256.5 mg/L, respectively, determined by permanganate titration and gravimetric analysis. The results are shown in Figure 6. The physical and chemical properties of the Changjiang River water and East Lake water are showed in Table 2.

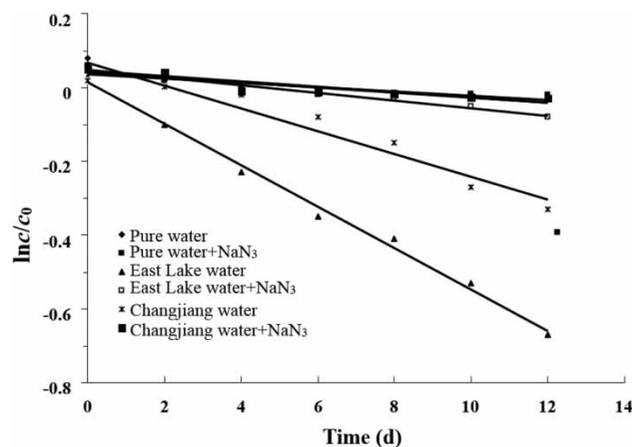


Figure 6 | Microbial degradation of BP in different water samples.

The results indicated that the microbial degradation of BP in East Lake water was faster than that in Changjiang River water. The degradations were very weak in the control experiments when sodium azide was added to the water. These results illustrated that the microbial degradation of BP in real water samples does exist. And the rates of microbial degradation of BP were different, which may be because of different kinds and amounts of microbes. The

Table 2 | The physical and chemical properties of the Changjiang River water and East Lake water (passed through a Whatman 0.22 µm fiber microfilter)

Property/specification	Changjiang River	East Lake
pH at 25 °C	7.30	7.21
Electrical conductivity (µs/cm)	296	291
COD (mg/L) ^a	20.7	26.2
Chloride (mg/L)	13.8	20.1
Bicarbonate (mg/L)	126.0	130.7
Sulfate (mg/L)	20.4	20.1
Fe (µg/L)	421.8	457.8
Ca (mg/L)	69.0	64.2
Mg (mg/L)	6.42	7.08

^aChemical oxygen demand.

cell numbers, microbial type, chemical oxygen demand, nitrogen content and carbon content of the natural water influenced the natural transformation of target compounds directly.

Implications for humans

As some BP compounds have been found in the human body (Asimakopoulos *et al.* 2013), 0.5–1120 ng/mL of BPs were found in human urine from Athens, Greece (Asimakopoulos *et al.* 2014). BPs have been shown to elicit estrogenic activities, and may be a contact allergen. Thus, complete removal of BPs is significant. Most of the BPs could be removed in STPs, but BPs at ppb level still exist. From the results of this study, the natural degradation of BPs at ppb level is possible including both photo- and microbial degradation, and some points can be summarized. First, the continuous input is unfavorable for photodegradation. After four times of continuous input, the $t_{1/2}$ for BP increased obviously under solar irradiation. Second, BPs degrades in East Lake water more efficiently than in Changjiang River water, which indicated that the microbial degradation should be related to kind or amount of microbe, and some typical microbes could be selected to accelerate the degradation process of BPs.

CONCLUSIONS

This study focused on the natural degradation of BP including both photo- and microbial degradation in environmental water at low concentration of about 10 µg/L, which is the real level of BP in environmental water. Regarding

photodegradation, some parameters influence the degradation rate obviously, such as the coexisting compounds which have overlap in the UV absorption spectrum and similar structure, the initial concentration and continuous input. The rates of microbial degradation of BP in different natural water indicated that the type and amount of microbes should be important for the degradation rate of BP. Interestingly, the continuous input is unfavorable for photodegradation of BP at ppb level, which should be avoided in the wastewater treatment procedure.

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First received 12 February 2015; accepted in revised form 23 April 2015. Available online 15 May 2015